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Reactions of 1-Triptycyl Carbinol and Bis-(1-Triptycyl)-Carbinol

Bryce Arthur Milleville
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REACTIONS OF 1-TRIPTCYL CARBINOL AND
BIS-(1-TRIPTCYL)-CARBINOL

by

Bryce Arthur Milleville

A Thesis Submitted to the Faculty of the Graduate School
of Loyola University of Chicago in Partial Fulfillment
of the Requirements for the Degree of
Master of Science

January

1993

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In every endeavor there are individuals involved that contribute to it's completion, I would like to particularly thank and acknowledge the following persons: Dr. David Crumrine, without whose guidance, assistance, helpfulness, and understanding this investigation would not have been consummated; my wife Maryann, and, my parents, for instilling the necessary perseverance to complete this thesis; and AKZO Chemicals for providing the necessary resources and time required for this investigation.

VITA

The author, Bryce Arthur Milleville, is the son of Arthur William Milleville and Myra Elizabeth Milleville. He was born, and educated in Niagara Falls, New York.

In September, 1978, Mr. Milleville entered Niagara University, receiving the degree of Bachelor of Science in biochemistry in May, 1981. Mr. Milleville entered Loyola University of Chicago in January, 1985.

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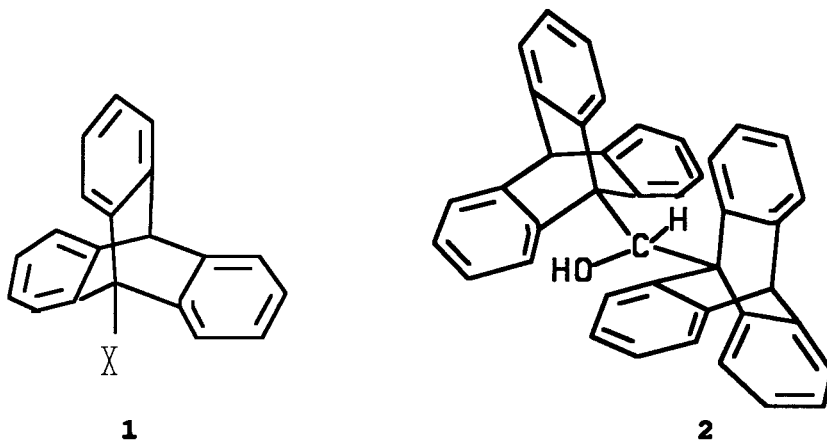
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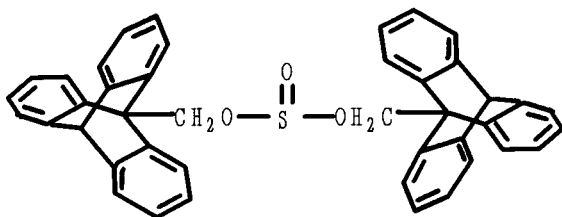
STATEMENT OF THE PROBLEM

The hydroxy triptycene derivatives; 1-triptycyl carbinol **1** ($X=CH_2OH$) and bis(1-triptycyl)carbinol **2** were subjected to chlorination reactions using thionyl chloride or phosphorous trichloride with and without DMF, in an attempt to prepare the corresponding triptycyl chlorides directly from the alcohols. These chlorides have not previously been prepared in a direct manner.

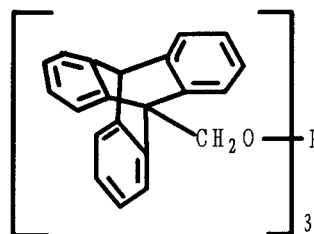


The triptycyl carbinols shown above can give rise to many possible products, under these reaction conditions of which three include: the alkyl chloride resulting from substitution of the hydroxy group by chloride, the sulfite or phosphate esters **3**, **4**, resulting from the nucleophilic

attack of the hydroxyl group on the sulfur or phosphorous atoms.

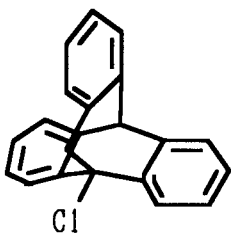


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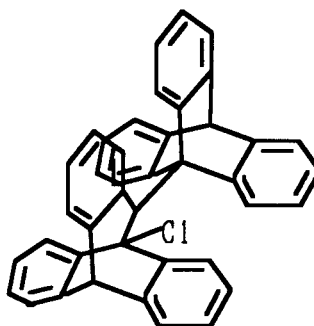


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The third possible product from each alcohol is the result of the rearrangement of the intermediate carbocation to the homotriptycene analogues **5**, **6**, respectively.



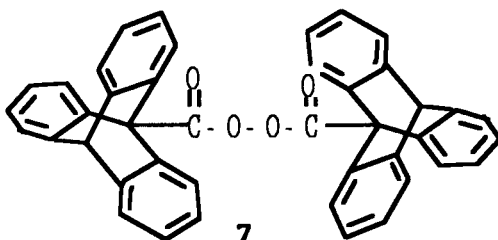
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HISTORICAL REVIEW

TRIPTYCENE^a AND BIS(1-TRIPTYCENES) : The first synthesis of triptycene **1** (**X=H**) was reported by Bartlett¹ in 1942. As shown in Scheme I, the basis for the synthesis was the cycloaddition of quinone to anthracene to form a triptycenehydroquinone-type intermediate. Subsequent reduction, dehydrobromination, formation of the dioxime, and deamination yielded triptycene. Bartlett *et al.*² continued analogous preparations with 1- Bromotriptycene **1** (**X=Br**) in 1950, and the carboxylic acid **1** (**X=CO₂H**) as well as the di-triptycyl peroxide **7** in 1953.³ In the preparation of 1-bromotriptycene, Bartlett also reported the first reactions of triptycene derivatives. In these studies the unreactivity of the 1-bromotriptycene towards nucleophilic displacement was reported.



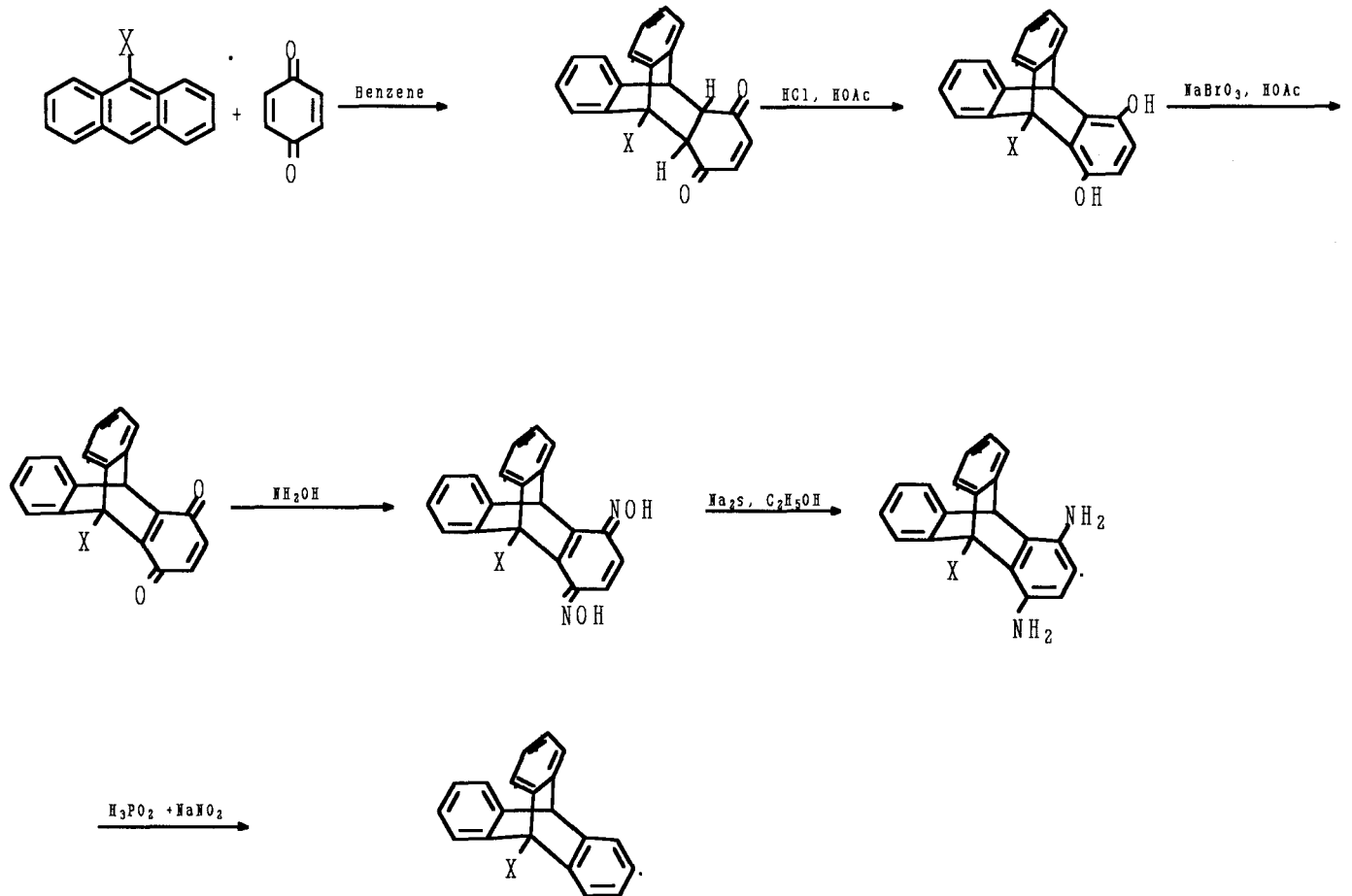
^a The Chemical Abstracts name for triptycene is: 9,10[1',2']benzeno-anthracene-(9,10H). For simplicity the common name triptycene will be used in this study.

Triptycene also was prepared *via* benzyne addition to anthracene by Wittig and Ludwig in 1956.⁴ This route was investigated further with the synthesis of various triptycene derivatives by Stiles *et al.*^{5a} and Friedman *et al.*^{6a,b} in 1963. In this reaction sequence, Scheme II, diazotization of anthranillic acid, with isoamyl nitrite, led to the benzyne precursor that adds directly to anthracene to form triptycene in relatively high yields. Friedman followed this approach and used the associated anthracene derivatives to prepare 1-triptycyl aldehyde **1** ($X=CHO$), and 1-carbomethoxytriptycene **1** ($X=CO_2CH_3$).

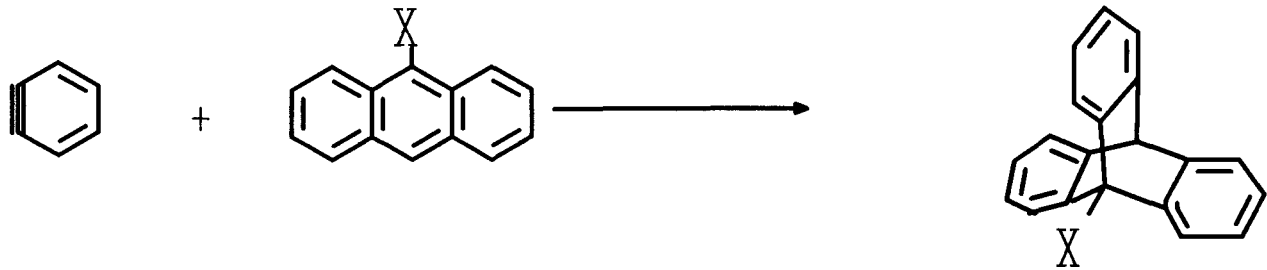
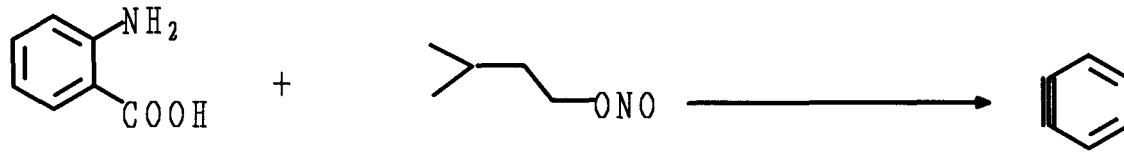
The relative selectivity of the benzyne addition reaction was investigated by Klanderman and Criswell⁷ and Klanderman⁸. In these studies it was shown that benzyne adds in a Diels-Alder fashion at both the center (1,8) ring and the terminal (3,6) ring of anthracene. The substituents on anthracene strongly determine the ratio of addition at the 1,8 and 3,6 ring positions. This was demonstrated using 1,8-diphenyl anthracene in which the first disubstituted triptycene; 1,8-diphenyl-triptycene was prepared.

Cycloaddition products from the benzyne addition to anthracene closely paralleled that found with maleic anhydride. This study showed the limits

Scheme I



Scheme II

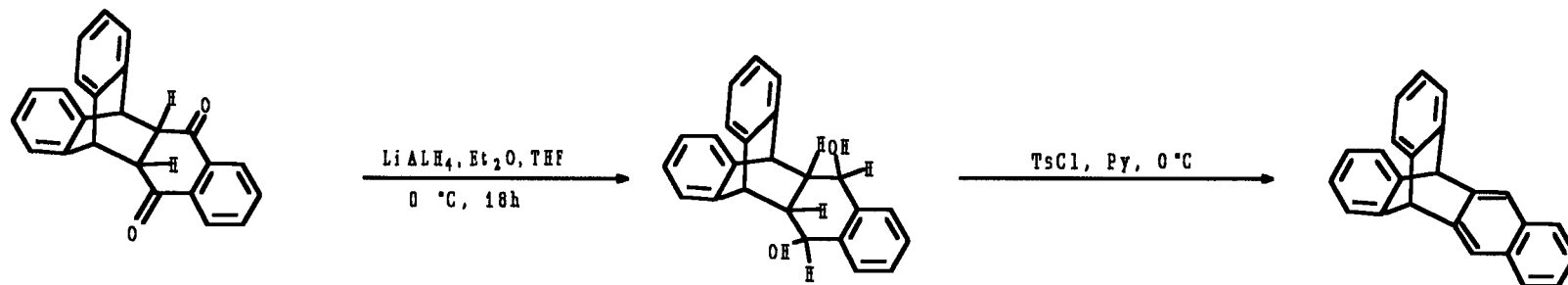
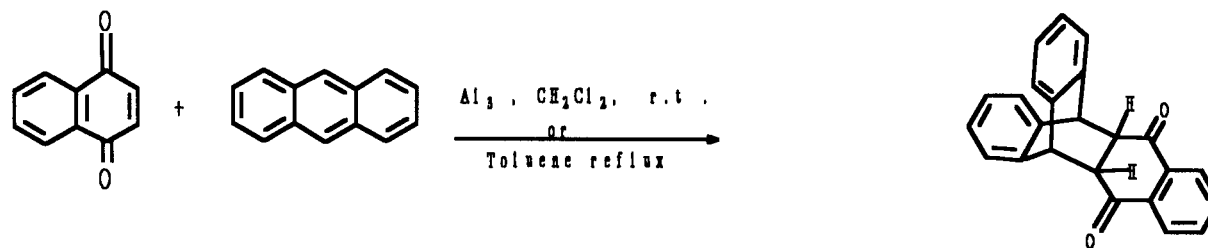


of Friedman's benzyne route in that electron donating substituents in the 1 or 8 position of anthracene favored the addition of benzyne, while electron withdrawing groups limited the addition. This follows the reactivity demonstrated in Diels Alder type additions.

The most comprehensive study on the preparation of triptycene derivatives was performed by Kornfeld *et al.*⁹ in 1965. Through the addition of benzyne to selected anthracene derivatives, and by subsequent reaction of these resulting triptycene derivatives, a total of 58 different 1-substituted triptycene derivatives were reported. These derivatives were evaluated as medicinal agents with the idea that the nonplanar aromatic triptycene group would act as an ideal blocking group in suppressing biochemical reactions. A large number of these derivatives did indeed display both stimulant and depressive CNS activity as well as anti-inflammatory reactivity.

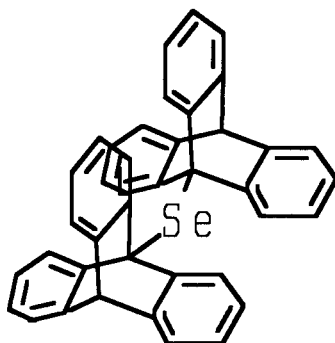
In a most recent investigation by Patney,¹⁰ a simple route to triptycene derivatives was reported that is very similar to the original synthesis of Barlett. The cycloaddition of substituted quinone derivatives to anthracene is followed by treatment of the resulting dione with lithium aluminum hydride. This is followed by reaction with *p*-toluenesulfonyl chloride in pyridine resulting in high yields of triptycene and triptycene derivatives. (Scheme III)

Scheme III



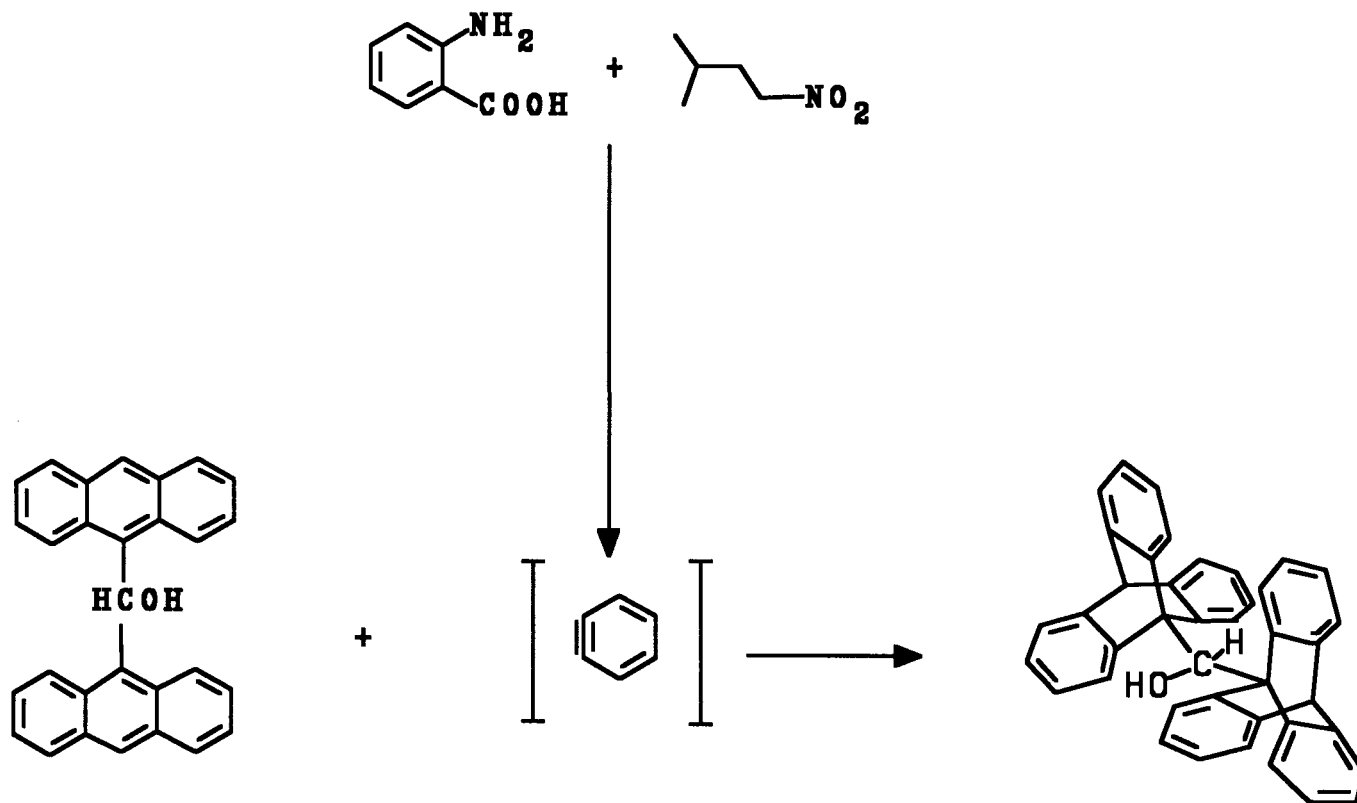
The first investigations of bis-triptycyl derivatives was in 1962 by Wittig and Tochtermann¹¹ who synthesised the bis (1-triptycyl) selenide **8**. In 1973, 1,1'- ditriptycyl tetraacetylene was reported by Akiyama *et al.*¹² The first reported syntheses of bis (1-triptycyl) carbinol **2** were in 1980 by Mislow *et al.*¹³ and Iwamura,¹⁴ in which benzyne was added to the bis(9-anthryl) carbinol. (Scheme IV)

Bis-(triptycyl) carbinol as well as bis-(triptycyl)-methane were prepared to serve as models in the investigation of empirical force field calculations.¹⁵ These calculations predicted that the meshed aromatic groups in

**8**

molecules such as bis(1-triptycyl)carbinol paralleled the behavior of meshed gear systems. The calculations predicted a 1 kcal/mol activation energy from the ground state for the meshed triptycyl groups to undergo cogwheel rotation about

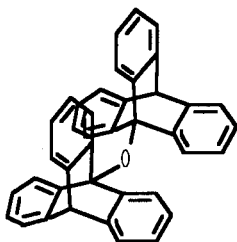
Scheme IV



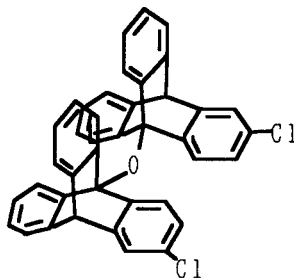
the central carbon. Additionally, for gear slippage to take place, the activation energy was 20 kcal mol⁻¹ above the ground state. These calculations were supported by NMR studies that showed that the triptycyl groups are securely meshed and that free rotation around the central carbon is unhindered on the nuclear magnetic resonance time scale. Further investigations provided additional support of these findings. Substituted bis(9-triptycyl)methanes such as bis(2,3-dimethyl-9-triptycyl) methane were prepared by Mislow^{16a-c} and Iwamura^{17a,b} in 1981. By investigating substituted derivatives, residual stereoisomerism under the constraint of dynamic gearing was demonstrated. Two diastereomers were isolated from bis(2,3-dimethyltriptycyl) methane which were readily differentiated using their respective ¹³C and ¹H NMR spectra. These were given the assignments as the residual meso isomer and the residual DL pair. Through the isolation of these two diastereomeric pairs, further evidence was obtained confirming the slow gear slippage in these compound at ambient temperatures.

Investigations on the effect that the central atom has on the gear rotation was performed by Iwamura^{18a-c} through the synthesis and characterization of bis(1-triptycyl)ether **9**, bis(4-chloro-1-triptycyl)ether **10**, and, bis(2-chloro-1-triptycyl)amine **11**. Crystal structure data on bis(1-triptycyl)methane and bis(1-triptycyl)ketone were reported by Mislow *et al.*¹⁹, while Iwamura²⁰ reported the data for the

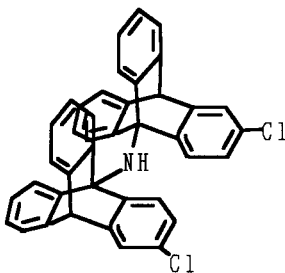
bis(triptycyl)ethers. These results further substantiated the results of the dynamic gearing studies.



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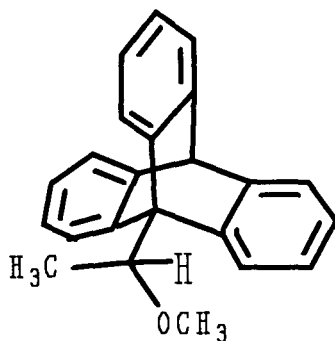
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11

Studies on the restricted rotation on the triptycyl bridgehead also show the influence on the planar aromatic rings in triptycenes. In a study on the rotational energy barrier in mono and di-bridgehead substituted chloromethyl triptycenes, Sergeveyev *et al.*²¹ reported a 16 kcal mol⁻¹ barrier to rotation. This was unexpectedly high compared to

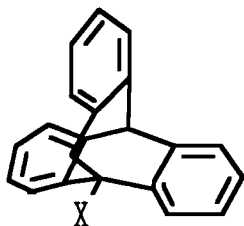
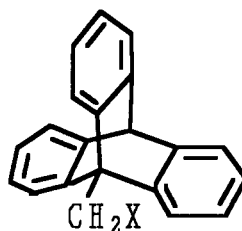
a molecule with normal C-C bonds, such as ethane, where the barriers are usually below 5 kcal mol⁻¹, while steric crowding increases this to 10 kcal mol⁻¹. As reported by Tanaka *et al.*²² and Suzuki *et al.*²³ the rotational barriers about the bridgehead to substituent bond in substituted 9-(1-methoxyethyl) triptycenes **12** were 21-23 kcal mol⁻¹. A number of studies^{24a,b} have reported the results of investigations involving the restricted rotation at tetrahedral carbon using triptycene derivatives as model compounds.

**12**

REACTIONS OF TRIPTYCENES: The influence of the aromatic groups on the reactions of triptycyl compounds has generated much interest. The question of transannular π - π thru space interaction between the nonconjugated benzene rings and intermediates in triptycene reactions is still under

investigation.^{25a-d} Evidence supporting this interaction has been reported by Nakayama *et al.*²⁶ and also by Iwamura and Mikima.²⁷

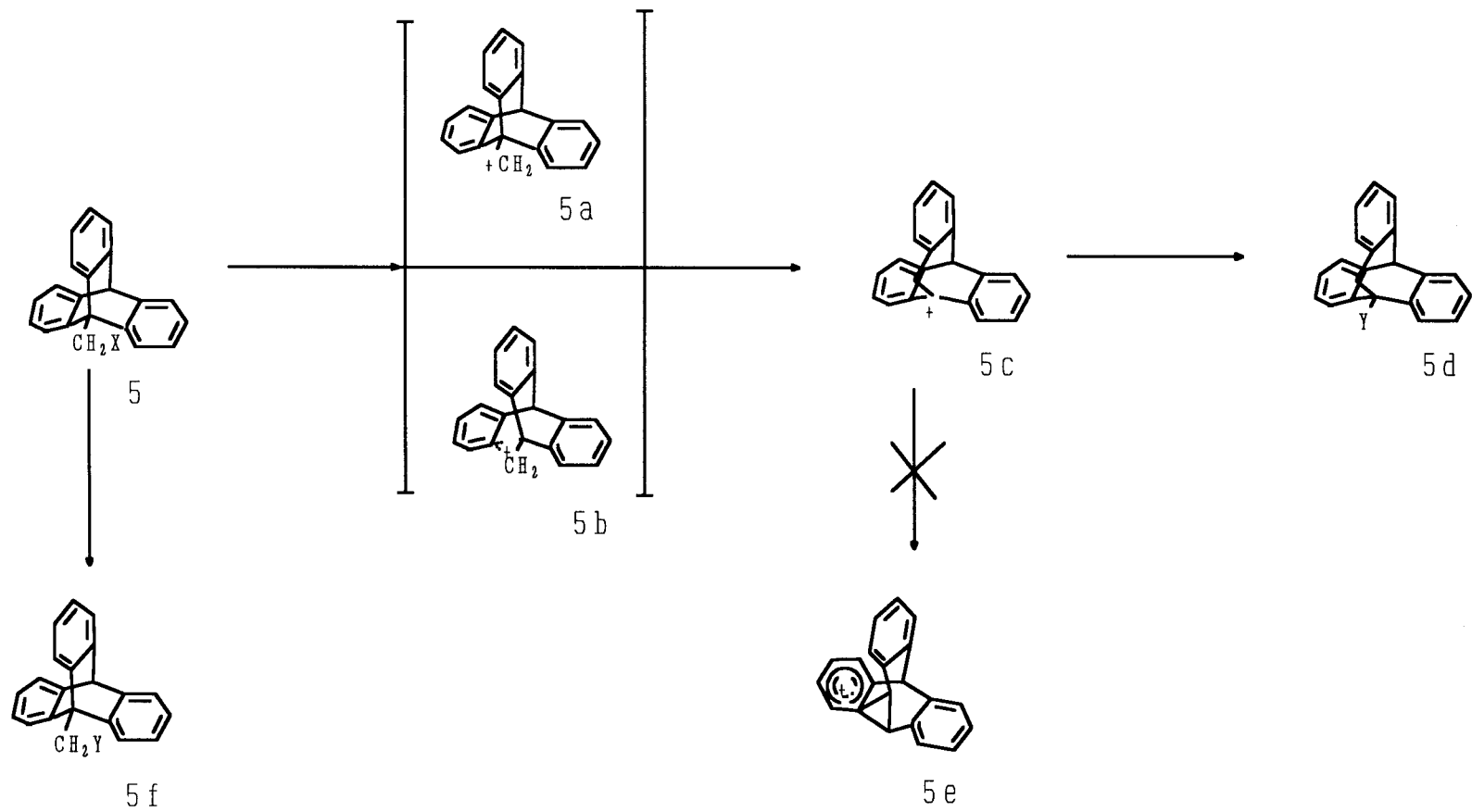
The first extensive investigation on the reaction of substituted 1-triptycenes was by Cristol and Pennelle²⁸ in 1970. The investigation focused on the synthesis of "homotriptycene" (tribenzobicyclo[3.2.2] nonatriene) **13** ($X=H$) through deamination of 1-aminomethyltriptycene **14** ($X=NH_2$).

**13****14**

Reaction of **14** with nitrous acid/acetic acid yielded a mixture of 1-homotriptycyl alcohol **13** ($X=OH$) and the 1-homotriptycyl acetate **14** ($X=OAc$).²⁸ The isolation of rearranged products indicated that a "Demjanov" type ring expansion was involved. Reaction of **14** with nitrosyl chloride/methylene chloride produced a mixture of both 1-homotriptycyl chloride **13** ($X=Cl$) and 1-triptycyl methlychloride **14** ($X=Cl$).

From these results, it is apparent that the intermediate in these reactions is a highly reactive

Scheme V



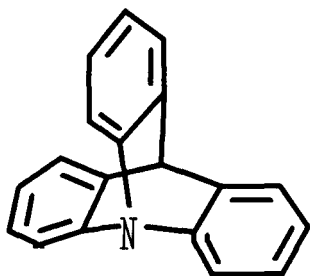
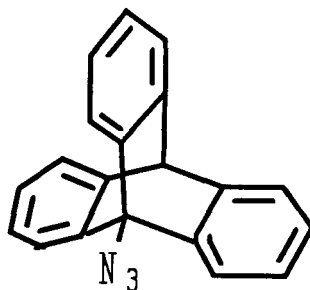
carbocation. Shown in Scheme V, are a number of possible reaction pathways and the carbocations that could be involved. The presence of unrearranged product when nitrosyl chloride was used indicated that chloride ion was trapping a precursor to **14**(X=Cl) before the rearrangement to **13**(X=Cl) took place. Of the various possibilities shown in Scheme V, the phenonium ion **5e** was eliminated as no scrambled products were found when labeled studies were performed. The presence of 1-chloromethyltriptycene indicated that chloride ion was trapping ion **5b** or **5a** before ion **5c** could be generated. In 1975, Wilt and Malloy²⁹ reported the solvolysis of 1-bromomethyl triptycene **1** (X=CH₂,Br). The solvolysis yielded only 1-methyltriptycene, further indicating that if a carbocation such as **5a** exists it is highly reactive and is formed only with great difficulty.

In 1973, Skvarchenko and Abdula³⁰ reported the chlorination of 4-hydroxymethyltriptycene using thionyl chloride and further reactions of the corresponding chloride. The complicated behavior of the bridgehead carbon of triptycyl compounds also is displayed by the 1-triptycyl radical. Magnetic resonance experiments on the decomposition of di-triptycyl peroxide have shown that this species differs in geometry from that of a tert-butyl radical which is tetrahedral.³¹ The results indicated that, in the triptycyl radical, the singly occupied orbital is a sp^{8.6} hybrid on the bridgehead carbon with the bonds of the

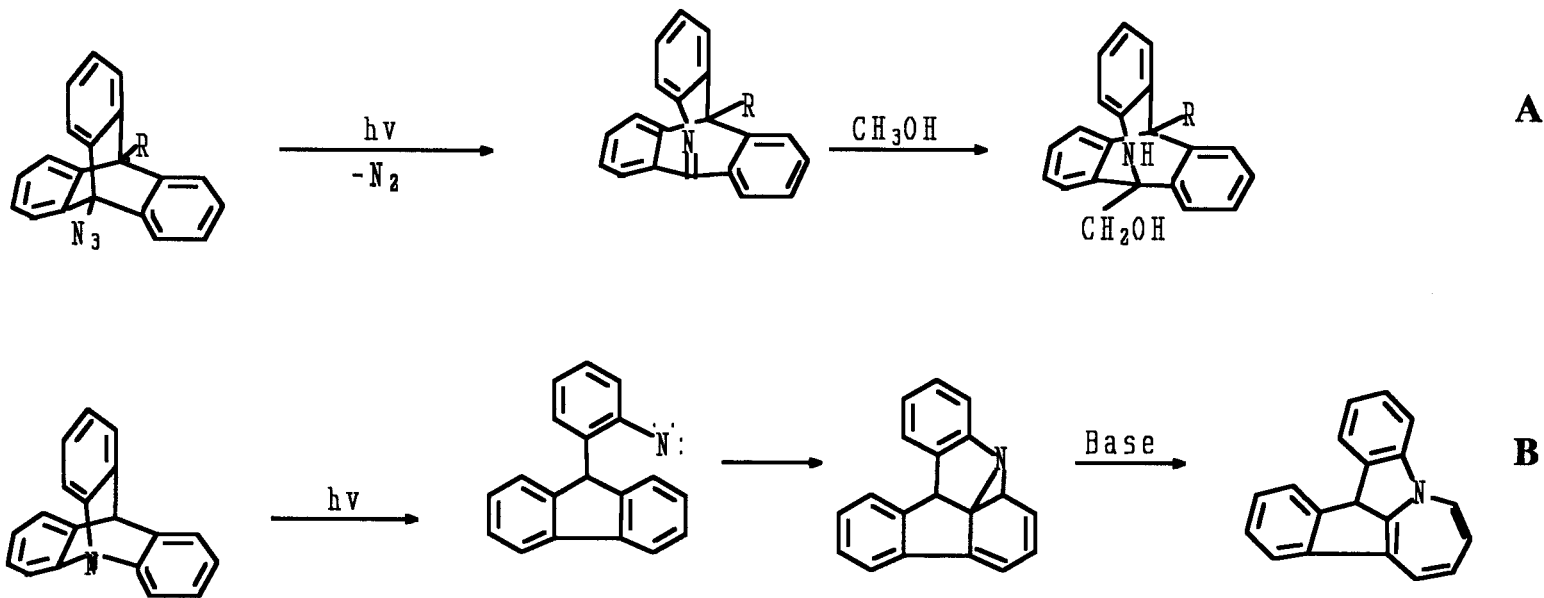
trivalent carbon strongly bent from the normal. This radical would be considered to be highly reactive.

In 1981, Iwamura³² showed that 1-triptycyl-lithium could be easily prepared from the 1-bromotriptycene using n-butyl lithium. The stability of triptycyl lithium was shown in an investigation by Molle and Bauer³³ in which the reaction of triptycyl lithium with highly hindered ketones was reported. Reaction of 1-triptycyl lithium with carbon dioxide yielded 1-triptycyl acid as a major product. Other products obtained; triptycene and 1-(1-triptycyl)ethanol, could only be explained if the reaction proceeded via a free radical intermediate involving electron transfer, a reaction pathway common in metal alkyl reactions.³⁴

In two concurrent studies, one by (Iwamura and Sugawara)³⁵ and one by Quast *et al.*³⁶ the synthesis and photochemistry of 1-azatriptycenes **18** and 1-azidotriptycenes **19** were reported.

**18****19**

Scheme VI (A&B)



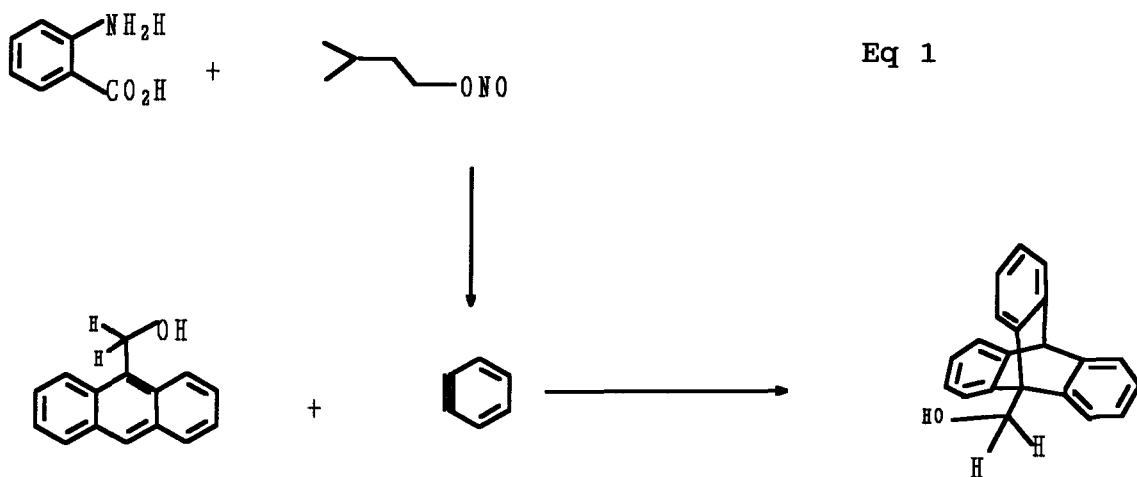
Photolysis of 1-azatriptycene **18** in methanol undergoes a rearrangement via 2-(9-florenyl)phenyl nitrene, Scheme VIB, to afford 4H-azepine derivatives. The photolysis of 1-azidotriptycene **19** in methanol produced the azahomotriptycene via the severely strained imine, Scheme VIA, which was trapped by the solvent.

Recent investigations by Crumrine³⁷ have shown that 1-triptycyl carbinol reacts with Vilsmeier reagents³⁸ to afford the bis(1-methyltriptycyl)sulfite ester **3**. The same reaction conditions with bis(1-triptycyl)carbinol **2**, yielded the 1-chloro-2-(1-triptycyl)tribenzobicyclo [3.2.2]nonatriene **6** via the ring expansion of one of the triptycyl rings in bis(1-triptycyl)carbinol.

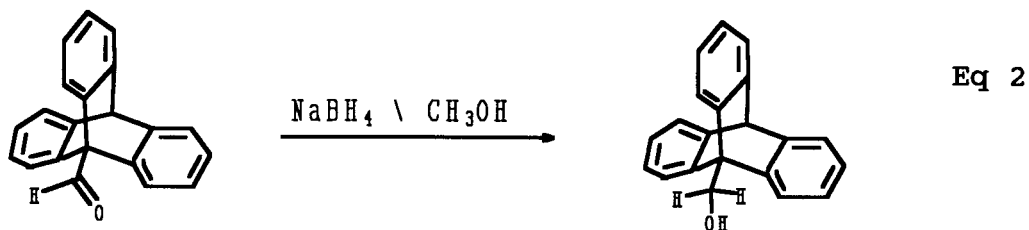
This work is a continuation of the investigations into the scope of chlorination reactions of 1-triptycyl carbinol and bis(1-triptycyl) carbinol. The possibility of synthesizing the bis(1-triptycyl)chloromethane using various modifications to the previously used Vilsmeier reaction conditions will be discussed.

RESULTS

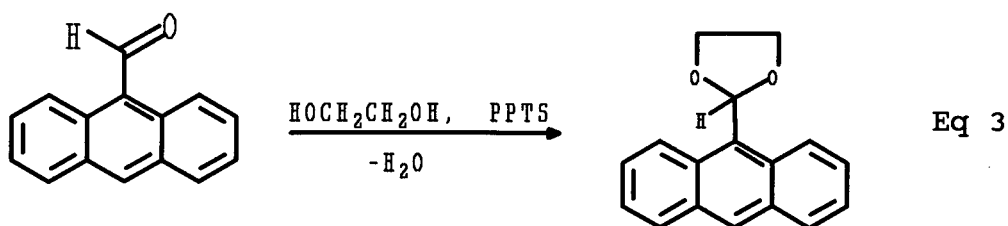
SYNTHESIS: 1-Triptycyl carbinol (method 1): Anthranilic acid and isoamyl nitrite, both dissolved in diglyme were added simultaneously to a refluxing solution of 9-anthracene-methanol in 1,2-dichloroethane. Following the addition of maleic anhydride, KOH, methanol and water the mixture was filtered to yield, 1-triptycyl carbinol as a light yellow powder. Washing with methanol/water yielded 1-triptycyl carbinol, 31%, (mp 240-242°C; lit⁹ 238-240°C), as a white powder. (Equation 1)



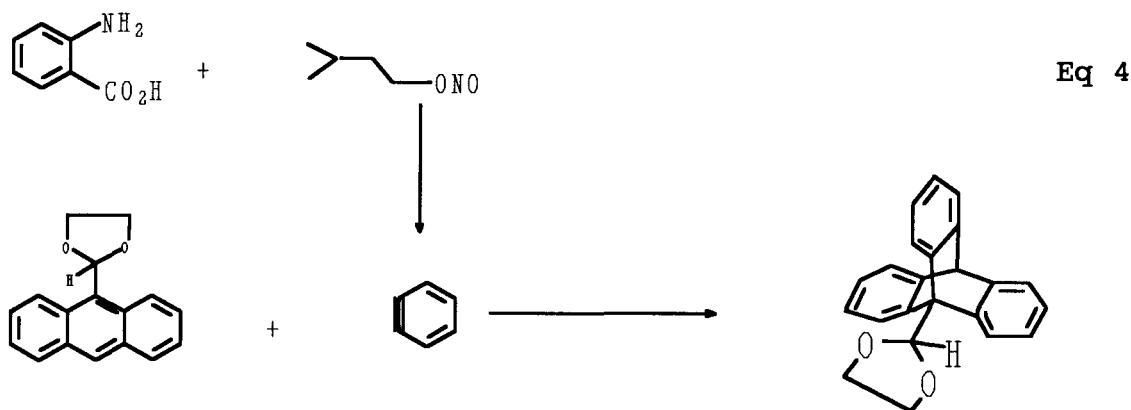
1-Triptycyl carbinol (method 2): 1-Triptycyl aldehyde(see below) was added to warm methanol followed by addition of sodium borohydride. Recrystallization from methanol and drying at 100 C, yielded 1-triptycyl carbinol as a white crystalline powder, 97 % (mp 238-239; lit⁹ 239-240°C) . (Equation 2)



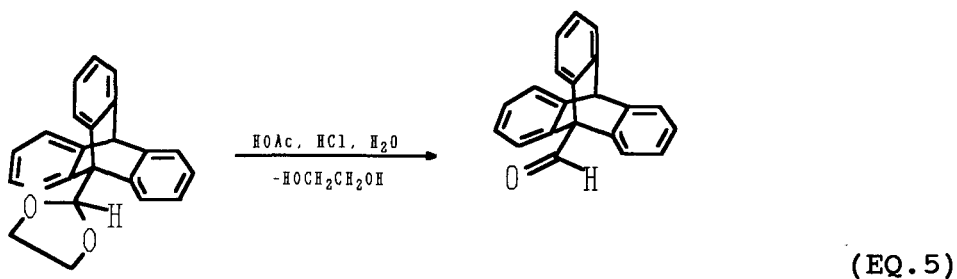
9-Anthracene-1,3-dioxolane: 9-Anthraldehyde was reacted with ethanediol and pyridinium p-toluenesulfonate in refluxing benzene under nitrogen for 3 h. (Equation 3) After removal of the benzene, the product was taken up in diethyl ether and washed with sodium hydrogen carbonate solution and saturated sodium chloride solution. 9-Anthracene-1,3-dioxolane was obtained as a yellow crystalline powder, 98.5%, (mp 183-185°C; lit⁴³ 181-185°C).



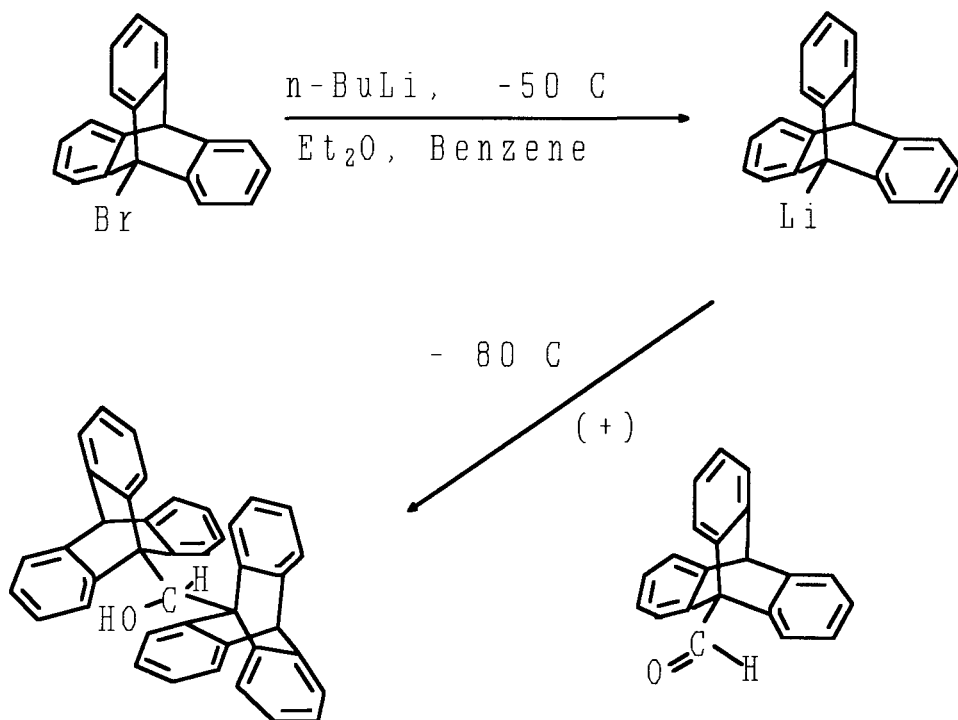
Preparation of 1-Triptycyl-1,3-dioxolane: Anthranilic acid, and isoamyl nitrite, both dissolved in diglyme, were added simultaneously via pulse pumps, to a refluxing solution of 9-Anthracene-1,3-dioxolane in ethylene dichloride under nitrogen. Following the addition of maleic anhydride, KOH, methanol and water the mixture was cooled and, filtered to yield, 1-triptycyl-1,3-dioxolane as light yellow powder, 74.2% (mp 282-285°C; lit⁹ 284-285°C). (Equation 4)



Preparation of 1-Triptycyl aldehyde: 1-triptycyl-1,3-dioxolane was refluxed with glacial acetic acid, hydrochloric acid, and water for 3 h. After cooling, filtering, and washing; HOAc/H₂O, 1-Triptycyl aldehyde was obtained, 91%, (mp 233-235°C; lit⁹ 235-238°C). (Equation 5)



Preparation bis-(1-triptycyl) carbinol: n-Butyl lithium was added to 1-bromotriptycene dissolved in benzene/diethyl ether (1:5) at -50°C under nitrogen. After 60 min a white precipitate of 1-triptycyl lithium was observed, after which the reaction was cooled to -80°C . 1-Triptycyl aldehyde in benzene was added via syringe and stirred for 60 min, at -80°C and 3h, at ambient temperature. Separation via column chromatography afforded bis-(1-triptycyl)carbinol as an off white crystalline material, 73% (mp: $355\text{--}358^{\circ}\text{C}$; lit³⁷ $355\text{--}357^{\circ}\text{C}$). (Equation 6)



Eq 6

REACTIONS: 1-Triptycyl-carbinol and triphenylphosphine /CCl₄
1-Triptycylcarbinol and triphenylphosphine were dissolved in carbon tetrachloride and heated to reflux for 8 h, after which the solid precipitate was filtered off and the carbon tetrachloride removed in *vacuo*. After evaporation of the pentane, a white crystalline material was recovered, and identified as unreacted 1-triptycyl carbinol, 91% (mp 237-240; lit⁹238-240).

1-Triptycyl carbinol and polystyryl-diphenylphosphine:

1-Triptycyl-carbinol was refluxed with polystyryldiphenylphosphine in carbon tetrachloride for 8 h. After filtration of the polymer and removal of the solvent, unreacted 1-triptycyl-carbinol 89%, (mp 355-358; lit³⁷355-357) was obtained. No evidence of chloride formation was found.

1-Triptycyl carbinol and thionyl halides:

1-Triptycylcarbinol was dissolved in solvent with equal molar amounts of thionyl halide and dimethyl formamide or pyridine. After refluxing for 24 h the solvents were removed and the off white solid chromatographed on silica gel to yield as the major product bis-(1-triptycyl)sulfite ester. (Equation 7) In the the case of thionyl chloride and pyridine an additional product, identified as 1-chloromethyl triptycene (mp 230-233°C; lit⁹ 233-235°C) was obtained. The results obtained are summarized in Table 1.

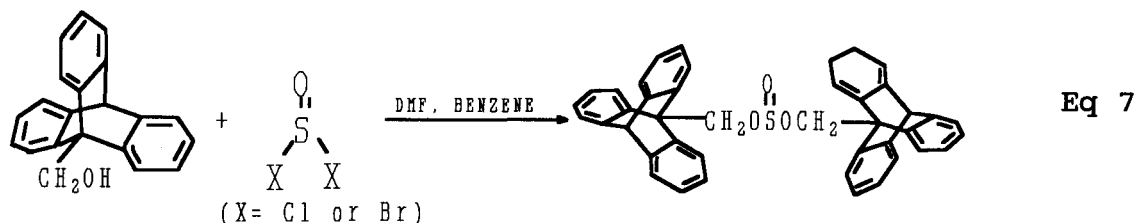


TABLE 1

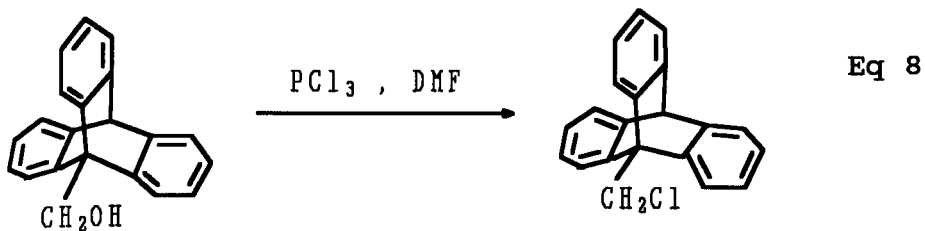
% YIELD OF BIS-(1-TRIPTYCYL)METHYL SULFITE ESTER

THIONYL HALIDE/BASE	CHLOROFORM	BENZENE
THIONYL CHLORIDE/DMF	97%	83 %
THIONYLCHLORIDE/PYRIDINE	51% ^(a)	-----
THIONYL BROMIDE/DMF	64 %	0

(a) 1-chloromethyl triptycene isolated, 32%.

1-Triptycyl carbinol and phosphorous trichloride/DMF

To a mixture of dimethyl formamide in chloroform was added phosphorous trichloride and the mixture allowed to react for 1 h. 1-Triptycylcarbinol was added and the mixture refluxed for 24 hours, the benzene was removed to afford 1-chlorormethyl triptycene derivative, 62%, (mp 231-234°C; lit⁹ 232-235°C) as a white solid. (Equation 8)



Bis (1-triptycyl) carbinol and phosphorous trichloride/DMF:

Phosphorous trichloride and DMF were mixed in chloroform and allowed to react at ambient temperature for 1 h. Bis-(1-triptycyl)carbinol was added and the mixture refluxed for 24 h. After removal of the solvent, the off white solid was identified as unreacted bis-(1-triptycyl) carbinol, 81%, (mp 354-356°C; lit³⁷ 355-357°C).

DISCUSSION

SYNTHESIS: The synthesis of both 1-triptycyl carbinol and bis(1-triptycyl) carbinol although previously reported³⁸, were not optimized. Previous results afforded the carbinols in both low yield and low purity resulting in lengthy purification procedures. As both carbinols were the starting materials in the investigation to prepare the corresponding chloro derivatives, there existed much area of improvement in the yield and purity of the previously used procedures. The 1-triptycyl aldehyde, being a precursor to both the mono and the bis triptycyl carbinol was an obvious starting point.

The synthesis of triptycene derivatives is routinely performed by benzyne addition to substituted anthracenes.³⁹ The nature and position of the substituents in the anthracene ring system has been shown to strongly influence the course of the addition.^{40,41} Typically, when anthracene is substituted in the 9 position by electron donating groups, benzyne addition to the center ring is favored, due to the electrophilic nature of benzyne. Electron withdrawing groups show the opposite effect as would be expected.

The most logical route to 1-triptycyl aldehyde, was the benzyne addition to 9-anthraldehyde. Alternatively the addition of benzyne to 9-anthracene methanol, followed by oxidation to the aldehyde could be used. As a one step, direct route, was of interest, the second choice was less interesting.

Previous investigations by Kornfeld *et al.*⁴² showed that the direct addition of benzyne to 9-anthraldehyde yielded 1-triptycyl aldehyde only in moderate yield. As previously stated, this would be expected as the addition of benzyne to 9-anthraldehyde is not highly favored due to the strong electron withdrawing effect of the aldehyde on the 9 carbon position of anthracene. With this in mind, the approach used by Kornfeld, the conversion of the 9-anthraldehyde to cyclic ethylene acetal was chosen. Using *p*-toluene-pyridinium sulfonate as the catalyst, 9-anthracene-1,3-dioxolane was obtained quantitatively from 9-anthraldehyde. Using this material as the substrate, the addition of benzyne yielded 1-triptycyl-1,3-dioxolane in excellent yield and purity. Hydrolysis of the dioxolane yielded 1-triptycyl aldehyde quantitatively and also in high purity. The overall yield of 1-triptycyl aldehyde starting from 9-anthraldehyde was 71%, an increase of 26% over the direct addition route. In addition the product was obtained in excellent purity, 96% as determined via DSC melting point thus eliminating lengthy chromatographic purification procedures.

It should be pointed out that the key to improving this reaction was in the use of the pyridinium p-toluene sulfonate in the preparation of the cyclic acetal.⁴³ The previous synthesis of 9-anthracene-1,3-dioxolane by Rio yielded the product in only moderate amounts, due to poor cyclization of the aldehyde with ethanediol.⁴⁴

With an acceptable synthesis of the aldehyde, the synthesis of 1-triptycyl carbinol via the reduction of 1-triptycyl aldehyde was investigated. It was found that using sodium borohydride in methanol, quantitative reduction of the aldehyde was obtained.

The synthesis of 1-triptycylcarbinol through the benzyne addition to 9-anthracenemethanol was attempted. The isolated 1-triptycylcarbinol was obtained in moderate yield but was contaminated with both unreacted starting material as well as unidentified by products. Compared to the benzyne addition to 9-anthracene methanol route, the reduction of the aldehyde, obtained from the benzyne addition to the cyclic ketal of 9-anthraldehyde, followed by hydrolysis, affords the carbinol in high yield, (97% vs 31%). Based on 9-anthraldehyde the yield of 1-triptycyl carbinol was 69%.

The synthesis of bis(1-triptycyl)carbinol in the past has followed two methods, The first, benzyne addition to bis(9-anthryl)carbinol did not give high yields and was contaminated with side reaction products due to additions of

benzyne to multiple site on the anthracene rings.⁴⁵ The second route as reported by Curtin and the one chosen here, was the nucleophilic addition of 1-triptycyl lithium to 1-triptycyl aldehyde. In the initial investigation by Curtin a yield of 43% of the bis(1-triptycyl)carbinol was obtained along with significant reduction of 1-triptycyl aldehyde to the carbinol. This resulted in lengthy chromatographic purification procedure to obtain the bis(1-triptycyl) carbinol.⁴⁶

In an attempt to decrease the reduction of the 1-triptycyl aldehyde, two significant changes to the reaction conditions were performed. First, there was proof that the reduction of aldehydes in addition reactions with lithium alkyls could be minimized by performing the reaction at temperatures no higher than -78°C .⁴⁷

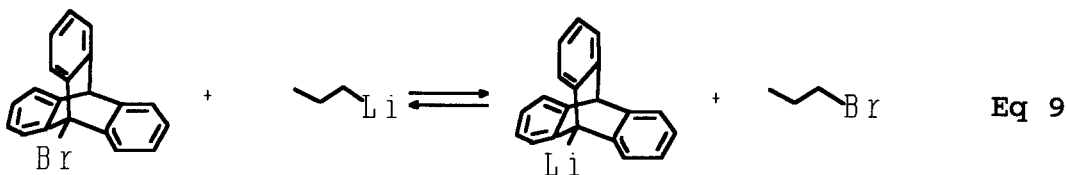
Secondly, we found that the solvent system originally used, benzene/ethyl ether, (1:2), had to be changed due to the freezing and precipitation of benzene at these temperatures. A ratio of benzene to ethyl ether of 1:5 was found to work effectively in this reaction at the lower temperature.

We have now been able to synthesize bis(1-triptycyl) carbinol in 69% yield via the addition of 1-triptycyl lithium, (generated from 1-bromotriptycene), to 1-triptycyl aldehyde. In addition, no significant reduction of the 1-triptycyl aldehyde to 1-triptycyl carbinol was observed.

The only isolated byproducts recovered were the starting materials 1-bromotriptycene and 1-triptycyl aldehyde.

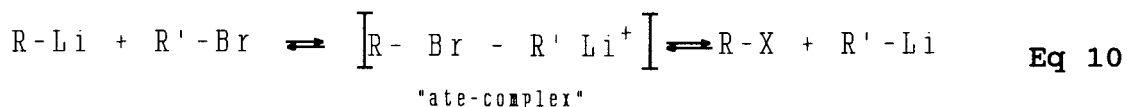
It is interesting to note that of the 1-bromotriptycene used only 61% was converted to the bis(1-triptycyl)carbinol, the other 31% was recovered. This indicated that either the metal-halogen exchange between 1-bromotriptycene and n-butyl lithium was not complete or that during the addition of the aldehyde, the equilibrium between 1-bromotriptycene and its lithium dervative was shifted so as to regenerate the 1-bromotriptycene.

The conversion of 1-bromotriptycene to 1-triptycyl lithium has been shown to be quantitative and to exhibit high stability.⁴⁸ The metal halogen exchange reaction has been shown to be an equilibrium process (as depicted in equation 9) and is influenced by both solvent basicity and temperature.⁴⁹



Wittig in 1958, investigated the reaction of n-butyl lithium with 1-bromotriptycene and proposed that the reaction proceeded via a reversible nucleophilic mechanism with the formation of an intermediate "ate-complex" as shown in equation 10.^{50a,b} Recently, investigators have isolated and

characterized intermediates having the structure of the "ate complex".^{51a,b} The stability and rate of formation of the



"ate-complex" formed originally, can be influenced by both temperature and solvent composition. Evidence has been reported that lithium-halogen exchange equilibrium constants are not affected by solvent and temperature but that the rate constants are.⁵² More basic solvents increase the rate of formation. In addition solvent composition has been shown to strongly affect the degree of association of alkyl lithiums, as these species exist in polymeric forms in solution, also affecting reaction rate.⁵³ Again here, the more basic the solvent the higher degree of association and increased stability of the alkyl lithium.

This "ate-complex" formation can explain the presence of 1-bromotriptycene isolated from the preparation of the bis-(1-triptycyl) carbinol. When the aldehyde (in solvent) is added to the 1-triptycyl lithium, the addition of the alkyl lithium to the aldehyde is a slow reaction due to the steric hinderance of both the aldehyde and alkyl lithium. The change in the solvent composition may affect now the

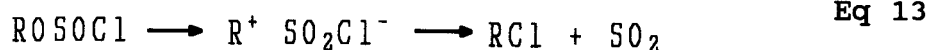
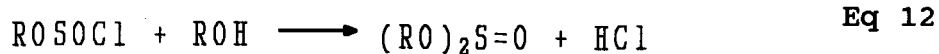
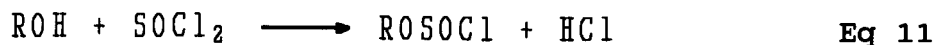
stability of the "ate-complex" and over time may decompose to form the original 1-bromotriptycene. The choice between incomplete formation of the 1-triptycyl lithium or decomposition of an intermediate "ate-complex" can not be made based on our limited investigation of the reaction. It was significant that the reaction was optimized in both percent yield and product purity.

REACTIONS: The reaction of 1-triptycyl carbinol with thionyl chloride in the presence of DMF, as previously reported³⁷, yields the bis(1-triptycylmethyl)sulfite ester. It was not surprising to find that thionyl bromide in DMF also affords the sulfite ester. It was observed that the reaction of both thionyl halides though with 1-triptycyl carbinol was influenced by the solvent. Highest yields of the sulfite ester were obtained using chloroform as the solvent instead of benzene. In the case of thionyl bromide and DMF, when chloroform was used as the solvent no reaction occurred. No previous report of this type of solvent dependency for this type of reaction could be found.

If pyridine is substituted for DMF as the base, not only was the sulfite ester formed but also 1-chloromethyl-triptycene. This was not formed in the presence of DMF.

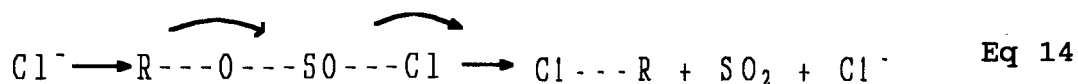
The reaction of thionyl halides, alone or in the presence of tertiary bases, with alcohols to yield the corresponding chlorides was first reported in 1911.⁵⁴

The reaction of thionyl halides and alcohols is thought to proceed according to the sequence shown in equations 11-13.⁵⁵

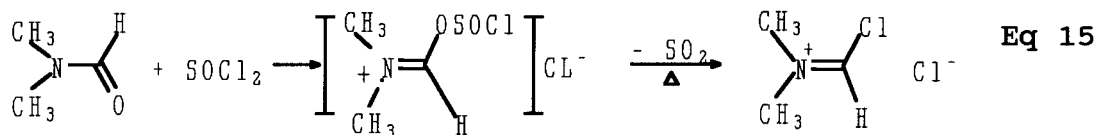


Initial reaction of the alcohol with thionyl chloride yields the chlorosulfinate which in turn can form the sulfite ester upon reaction again with alcohol. It has been shown that the formation of the sulfite ester is dependent on both reaction temperature and thionyl chloride concentration. Excess alcohol favors sulfite formation.⁵⁶ Formation of the chlorosulfite can be formed from the attack of the thionyl chloride on the sulfite ester. This reaction has been shown to be first order in sulfite ester.^{57a-b}

In presence of pyridine, the HCl generated during the reaction reacts with pyridine to form pyridinium hydrochloride, the presence of which catalyzes the decomposition of the chlorosulfinate to the corresponding chloride.⁵⁸ The mechanism proposed, (equation 14) shows an Sn2 type bimolecular displacement between chloride ion and chlorosulfite, in the absence of base, the decomposition of the chlorosulfite follows equation 13.



The use of DMF as a catalyst in the chlorination of hydroxylic compounds was first reported in 1963.^{59a-b} The actual reactive species, chloromethylenedimethyl ammonium chloride is formed by the reaction of DMF and thionyl chloride as shown in equation 15. From the intermediate, $[\text{Me}_2\text{N}^+\text{CHCl}^-][\text{OSOCl}^-]$, SO_2 is readily lost upon heating, generating chloromethylenedimethyl ammonium chloride.

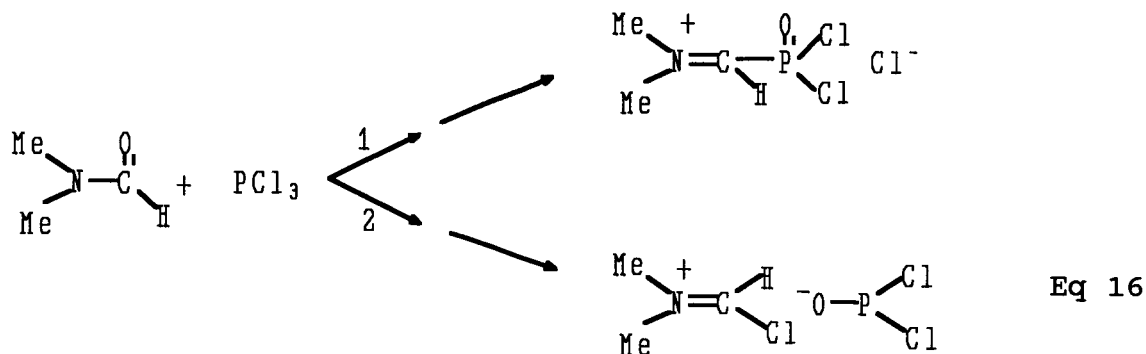


The reaction of DMF with thionyl chloride can be considered an acid-base association (nucleophilic attack on sulfur by the enol of the amide) and is the rate determining step in this reaction.⁶⁰ Solvent effects on this association have shown that the reaction rate increases as proton donating ability of the solvent increases. The association is also favored by high concentrations of both DMF and thionyl chloride.

The formation of only sulfite ester in the reaction of 1-triptycyl carbinol with thionyl chloride (bromide) and DMF can be related to this DMF/ SOCl_2 association reaction. The formation of the 1-triptycyl chlorosulfinate proceeds at a rate higher than the DMF/thionyl chloride association. This reduces the concentration of the thionyl chloride available

and the association being the slower reaction, would favor the formation of the sulfite ester. The DMF present in this case acts solely as a chloride scavenger, preventing the reverse of the reaction in equation 12 by attack of HCl.

The reaction of phosphorous halides in the presence of DMF as a method to prepare alkyl chlorides directly from alcohols has been well documented^{61a-c}. The proposed reactive species formed from PCl_3 / DMF has two halogens bonded to phosphorous, a clear differentiation was not made between structures 1 and 2 as shown in equation 16.⁶²



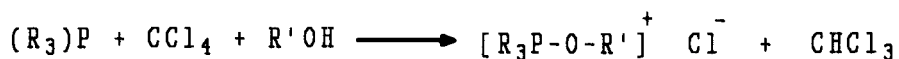
The reaction of 1-triptycyl carbinol, with PCl_3 / DMF yielded 1-chloromethyltriptycene in moderate yields, without the formation of other phosphorous ester byproducts. It was first thought that possibly a trialkylphosphite derivative of triptycene might be formed, as this is the standard reaction expected in the reaction of phosphorous trihalides with alcohols.^{63a-b} During the investigation it was found that the order of addition played a large role on the

reaction. If the 1-triptycyl carbinol was added before the DMF no formation of the chloride was observed. Allowing a pre-reaction or induction period between PCl_3 / DMF, afforded 1-chloromethyl-triptycene upon addition of the 1-triptycyl carbinol. These results would seem to favor reactive intermediate 2 shown in equation 8, as the active chlorinating species, which is very similar to Vilsmeier type reagents.

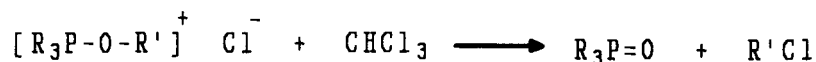
The use of triphenylphosphine reagents in combination with carbon tetrachloride to prepare chloride derivatives of primary and secondary alcohols is well known.^{64a-c} It was felt that this type of reagent would possibly yield the chloride derivative from 1-triptycyl carbinol as highly hindered 1° and 2° alcohols were reported to give the corresponding chlorides in high yields.⁶⁵ The reaction of 1-triptycylcarbinol with polystyryldiphenylphosphine / carbon tetrachloride or triphenylphosphine / carbon tetrachloride failed to produce 1-chloromethyl-triptycene. The 1-triptycylcarbinol was fully recovered (97%) in both cases.

The reactions of alcohols with these reagents has been shown to proceed through the formation of a phosphorylated intermediate as shown in equation 17.

The formation of the phosphorylated intermediate in the case of highly hindered primary and secondary alcohols, proceeds at a rate faster than its decomposition, while for



Eq 17



unhindered primary and benzylic alcohols the reverse is true.⁶⁶ In fact, it was shown that in the case of neopentyl alcohol (hindered primary), intermediate formation was fast and the intermediate easily isolated. Only after heating, did the intermediate decompose to the neopentyl chloride.

In the case of 1-triptycyl-carbinol, being a highly hindered primary alcohol, the decomposition of the phosphorylated intermediate if formed, to the corresponding chloride would be sterically controlled.

Based on the results of the reactions with 1-triptycyl carbinol, we attempted to prepare the corresponding chloride from the bis-(1-triptycyl) carbinol using the DMF / PCl₃ system. We did not find any indication that the bis-carbinol reacted with this system. In all probability, the large steric crowding present in the bis-(1-triptycyl) carbinol prevents attack from this type of Vilsmeier reagent.

CONCLUSION

The evidence presented here demonstrates that while 1-chloromethyl triptycene can be prepared directly from the 1-triptycyl carbinol using "Vilsmeier" type reagents, the bis(1-triptycyl)carbinol fails to react under the same conditions. The direct synthesis of the 1-chloromethyl-triptycene from the carbinol has not been reported before. In addition, the type of "Vilsmeier complex"⁵⁷ used, has a profound effect on the course of the desired chlorination reaction. This observation was not found to be presented elsewhere in the literature.

Specifically, whereas the use of the thionyl chloride/DMF type complex predominantly yields the sulfite ester, substituting pyridine as the base, also yields the corresponding chloride. Keeping the base the same (DMF), and then changing the halogen source to phosphorous trichloride, only the chloride derivative is obtained. Although no direct determination of the reactive intermediates was made in this investigation, it may be concluded that; the reactivity of the "Vilsmeier complex" is inherently determined by both the type of halogen source and base used to generate the complex. Additional

investigations are needed to fully support this conclusion.

The other major accomplishment, was the large improvement in yield, during the synthesis of both the 1-triptycyl aldehyde and the bis(1-triptycyl) carbinol. The use of the dioxolane derivative of 9-anthraldehyde as a protecting group strongly favored the benzyne addition to form the 1-triptycyl aldehyde.

To further elucidate the scope of these observations and conclusions several possibilities exist for additional research. Examination of the reactive intermediates involved in the 1-triptycyl carbinol/Vilsmeier complex reaction needs to take place. Further substitutions of both the base employed (alkyl, aryl substituted formamides) as well as the halogen source, would provide information as to the limits of the reaction. In addition the use of chloromethylene-dimethylammonium chloride, (commercial from Aldrich Chemicals) the proposed Vilsmeier intermediate⁵⁹, should be performed as this would eliminate the base during the reaction.

Also, the type of alcohol that is reacted with the Vilsmeier complex; formed from different chloride sources and DMF, should be varied to determine the extent of this reaction. Other highly hindered alcohols as well as cage structure alcohols such as 1-adamantanol, might be useful in explaining the reactivity differences in the Vilsmeier complexes.

Lastly, the addition of benzyne to bis(9-anthracene) derivatives, should be reinvestigated with the idea of employing the use of a protecting group to facilitate the formation of the bis(1-triptycyl) chloride. Thus preventing any rearrangement of the bis(1-triptycyl) structure.

EXPERIMENTAL

General: Melting points were determined using a Mettler 3000 differential scanning calorimeter, calibrated to Indium . Infrared spectra were recorded using a BIO-RAD 200 FTIR as thin films from chloroform on salt plates. Spectra were recorded in the transmission mode under nitrogen atmosphere. Peaks are assigned respective transmissions in wavenumbers (cm^{-1}). Unless otherwise indicated ^1H and ^{13}C magnetic resonance spectra were recorded on a Varian Gemini FT200 multinuclear NMR spectrometer. Deuterated chloroform was used as the solvent with 0.1% tetramethylsilane (TMS) as the internal standard. The chemical shifts are reported in parts per million (ppm) with mutiplicity designated as: s = singlet, d = doublet, t=triplet, m= multiplet. Flash column chromatography was performed following the method of Still *et al.*⁶⁷ using silica gel, 40 micron, ex Baker Chemicals. Preparative layer chromatography(PLC) was performed using pre-coated PLC plates, (Silica gel 60 F-254) from Baker. TLC anaysis was performed using pre-coated flexible TLC sheets (13181 silica gel) from Eastman Kodak.

Solvents (benzene, diethyl ether, THF), were obtained

from commercial sources, dried following standard procedures⁶⁷, and stored over 4Å molecular sieves to maintain anhydrous conditions. Reagents were obtained from Aldrich Chemicals and used as received.

9-Anthracene-1,3-dioxolane: Anthraldehyde, 3.0 g (14.5 mmol) was dissolved in 145 ml benzene. To this was added 4.5 g (72.6 mmol), 1,2-ethanediol, 1.1 g (4.4 mmol), pyridinium p-toluene sulfonate, "PPTS", and the mixture refluxed for 3 h with water separation by a Dean-Stark trap. Solvent was removed *in vacuo*, diethyl ether 250 ml added, and the mixture extracted with NaHCO₃ solution and 25% NaCl solution. The organic phase was dried with MgSO₄ and Na₂SO₄. Removal of the diethyl ether afforded 9-anthracene-1,3-dioxolan, 3.6 g, (14.3 mmol, 98.5%), mp 182-184°C, (lit³⁸ 181-185°C). ¹H NMR (90 MHz: DMSO): 3.39 (s, 4H), 4.25 (m, 2H), 4.55 (m, 2H), 7.52, (s, 1H ArH), 7.64, (m, 4H, ArH), 8.20, (m, 2H, ArH), 8.64, (m, 3H, ArH). ¹³C NMR; 130.08, 130.1, 129.7, 128.7, 125.9, 124.8, and 124.3 (protonated Ar C's), 100.3 (ether carbon), 64.6 (methylene). IR (Neat); 3049, 2857, 2772, 1668, 1553, 1249, 1048, 899, 731 cm⁻¹.

1-Triptycy-1,3-dioxolane: Anthranilic acid, 4.5 g (32.6 mmol) in 25 ml diglyme and isoamyl nitrite 4.2 g (35.6 mmol) in 25 ml diglyme were added simultaneously using pulse

addition pumps to a refluxing solution of 3.5 g (14.0 mmol) 9-anthracene-1,3-dioxolane in 30 ml ethylene dichloride over a 3 h period, under nitrogen. After refluxing for an additional hour, the mixture was distilled to a head temperature of 145-150°C. Maleic anhydride 3 g was added and refluxed an additional 20 min. After cooling to 20°C, MeOH (30 g), KOH (7.5 g), and 15 ml H₂O was added and the mixture was cooled to 0-5°C. The precipitate was collected on a filter, washed with MeOH/H₂O, 1/3, and dried overnight to afford 1-triptycyl-1,3-dioxolane, as a yellow crystalline powder, 3.4 g, (10.4 mmol, 76.5%), mp 284-286°C, (lit.⁹ 284-285°C). ¹H NMR (90 MHz; DMSO): 3.35(4Hs, CH₂), 4.40(4Hm, CH₂O), 5.62(1Hs, CH), 6.35(1Hs, ArH), 7.15(5Hm, ArH), 7.55(7Hm, ArH). ¹³C NMR (26 MHz); 146.32 (quat. Ar C's), 124.67, 124.16, 123.16 (protonated Ar C's) 102.93(C-O), 64.32 (CH₂O), 55.60 (quat. bridgehead), 53.05 (protonated bridgehead).

1-Triptycyl-aldehyde: To a refluxing solution of 2.8 g (8.6 mmol) of 1-triptycyl-1,3-dioxolane was added 165 ml glacial HOAc, 43 ml H₂O and 33 ml conc. HCl. After refluxing 3 hours, the mixture was cooled to 5-10 °C and the product filtered. This material was washed with 50% HOAc, H₂O, and MeOH to afford 1-triptycyl aldehyde, as an off white fine crystalline powder, 2.2g, (7.8 mmol, 91%), mp 233-235°C (lit⁹ 225-238°C). ¹H NMR (200 MHz; CDCl₃) 11.39 (1Hs, CHO),

7.70 (3H, m, protonated ArH), 7.50 (3H, m, protonated ArH), 7.10 (6H, m, protonated ArH), 5.50 (2H, s, bridgehead); ^{13}C NMR 50 MHz; 201.19 (CHO), 145.94, 142.76, (Ar, quat), 125.97, 125.35, 124.23, 122.57 (protonated Ar C's), 54.30 (bridgehead C's); IR (neat) 3020, 2736, 1732, 1453, 908, 750, 626 cm^{-1} .

1-Triptycyl carbinol (from the aldehyde): Methanol, 50 ml, was heated to reflux followed by addition of 515 mg (1.83 mmol) of 1-triptycyl aldehyde. After stirring for 10 min, 564 mg (14.9 mmol) sodium borohydride was added in small portions relative to the foaming upon addition. After 2h, 25 ml water was added and the mixture was filtered. The methanol was removed under vacuum and the resulting solid filtered to yield 1-triptycylcarbinol as a white crystalline powder, 503 mg (1.77 mmol) after drying. (97.0 % yield). The melting peak was observed at 238–239°C (lit⁹ 238–240°C). ^1H NMR (200 MHz); 7.46 (6Hm, ArH), 7.10 (6Hm, ArH), 5.40 (1Hs, bridgehead), 5.25 (2Hs, CH_2), 2.65 (1Hs, OH); ^{13}C NMR (50 MHz) 146.70, 144.50 (Ar quat. C's), 125.20, 125.10, 124.00, 122.60 (protonated Ar C's), 61.50 (CH_2OH), 54.20 (bridgehead C's); IR (neat) 3295, 2870, 1723, 1456, 1282, 1071, 750 cm^{-1} .

1-Triptycyl carbinol- Benzyne route: Anthranilic acid, 10.3 g (75.2 mmol) in 30 ml diglyme and 9.6 g (82.1 mmol) isoamyl nitrite in 30 ml diglyme were added simultaneously to 6.6 g

(31.8 mmol) 9-anthracenemethanol in 30 ml 1,2-dichloroethane while refluxing under nitrogen over a 4 h period. After an additional 1 h reflux, the mixture was distilled to a head temperature of 145-150°C. Maleic anhydride, 7 g was added and the mixture refluxed 20 min. After cooling to 20°C; 13 g KOH, 52 g MeOH, 30 ml H₂O were added and further cooled to 0-5°C. The precipitate was collected by filtration, washed with MeOH/H₂O and dried overnight to afford 1-triptycyl carbinol, as a yellow powder 3.7 g, (13.0 mmol, 31%) mp 240-242°C (lit⁹ 238-240°C).

Bis-(1-triptycyl)-Carbinol: A flask containing 153 mg 1-bromotriptycene (0.46 mmol), was evacuated twice and filled with nitrogen. The bromotriptycene was dissolved in 30 ml of THF and cooled to -50° C. N-butyl lithium (1.0 ml, 1.6 M) in hexanes (0.96 mmole) was added via syringe and the reaction stirred at -50°C for 30 min. The mixture was allowed to warm to room temperature and stirred an additional 60 min. After cooling to -78°C, 194 mg (0.69 mmole) of 1-triptycyl aldehyde in 15 ml THF was added via syringe over 5 min. The mixture was stirred at -78°C for 30 min, and at room temperature for 3 h. The reaction was judged complete when the presence of the aldehyde could no longer be detected (TLC). The mixture was hydrolyzed with 20 ml saturated NH₄Cl, filtered, and extracted with chloroform (3 x 25 ml). The extracts were dried with MgSO₄ /

Na_2SO_4 , filtered, and the chloroform removed, to yield the crude bis-(1-triptycyl)carbinol as a yellow-brown solid material. TLC analysis (benzene) indicated the presence of four components. These were identified as; (1) unreacted 1-bromotriptycene (2) 1-triptycyl carbinol (3) bis-(1-triptycyl)carbinol and 1-triptycylaldehyde. The crude bis-triptycyl carbinol was dissolved in benzene, then suspended on 5 g silica gel. After removal of the benzene the crude bistriptycyl carbinol was obtained as a fine powder on silica gel. This material was chromatographed on a 3.5 cm by 36 cm column packed with Florosil in hexanes. Fractions, solvents, and products are listed in Table II. Fractions 5-7 yielded bis-(1-triptycyl) carbinol as a fine light yellow crystalline powder, 112.8 mg (0.2 mmol, 45.6%), mp 350-356°C, (lit¹³ 355-357°C). ¹H NMR (200 MHz); δ 8.00 (1Hm, CHOH), 7.85 (6Hd, ArH), 7.45 (6hd, ArH), 7.00 (6Ht, ArH), 6.78 (6Ht, ArH), 5.42, (2Hs, bridgehead), 2.88 (1Hs, OH); ¹³C NMR (50 MHz); 146.71, 145.29 (quat. Ar C's), 127.11, 125.38, 124.45, 123.71 (protonated Ar C's), 72.71, (CHOC), 62.68, (quat aliphatic), 56.05 (bridgehead); IR (neat); 3580, 2956, 1717, 1456, 1286, 1135, 748 cm^{-1} .

Table 2

<u>FRACTION</u>	<u>DILUENT</u>	<u>PRODUCT</u>
1.	Benzene	Bromotryp
2.	Benzene	Bromotryp/Unkn
3.	1/1 Benz ene-Ether	Brmotryp/Unkn
4.	1/1 Benzene-Ether	None
5.	1/1 Benzene-Ether	Bis-tryp-OH
6.	2/1 Benzene-Ether	Bis-tryp-OH
7.	4/1 Benzene-Ether	Bis-tryp-OH
8.	Ether	None
9.	Ether	Tryp-OH
10.	Ether	Tryp-OH

REACTIONS

1-Triptycyl carbinol and thionyl chloride / DMF: 1-Triptycyl carbinol 123 mg (0.43 mmol), was dissolved in 10 ml of chloroform. Thionyl chloride. 31.5 ul (0.43 mmol) and dimethylformamide 33.4 ul (0.43 mmol), were added, and the mixture placed in a wax bath at 79°C under reflux for 24 h. After removal of the solvent, the crude material 191 mg was dissolved in benzene and chromatographed on a 0.5 in by 12 inch flash column packed with silica gel in benzene. A total of 24 fractions, 3-4 ml, were collected. The product, bis-(1-methyltriptycyl)sulfite ester was recovered from fractions 1-11 yielding 126 mg (0.21 mmol, 97.0%) mp 390-

395°C, as fine crystalline powder. Repeating the same reaction with benzene as the solvent afforded 110 mg (0.18 mmol, 83.4%) of the sulfite ester. ^1H NMR (300 MHz); δ 7.42 (6Hm, ArH), 7.34 (6Hm, ArH), 6.95 (12Hm, ArH), 5.85 (2Hd, $J=8.5\text{Hz}$), 5.60 (2Hd, $J=8.5\text{Hz}$), 5.35 (2Hs, bridgehead H). ^{13}C NMR (75 MHz); δ 146.31, 143.64 (Ar quats. C's), 124.44, 125.11, 123.67, 121.93 (protonated Ar C's), 61.00 (CH_2O), 54.31 (protonated bridgehead), 52.45 (quat. bridgehead); IR (neat) 3063, 1456, 1192, 997, 919, 739, 703, 626 cm^{-1} .

Thionyl Bromide/DMF: Thionyl bromide, 31.5 ul (0.43 mmol) and dimethylformamide 33.4 ul (0.43 mmol) were added to 1-triptycyl carbinol 123 mg (0.4 mmol) in 10ml of chloroform. After refluxing for 24 h and work up, 83.8 mg (0.13 mmol, 63.8%) of the bis-(1-methyltriptycyl) sulfite ester was obtained. Similar reaction with benzene as the solvent yielded no sulfite ester after 72 h at reflux.

Thionyl chloride/pyridine: Thionyl chloride, 33.4 ul (0.43 mmol) and pyridine 34.94 ul (0.43 mmol) were added to 1-triptycyl-carbinol 123 mg (0.43 mmol) in 10 ml of chloroform. After refluxing for 24 h, and work up, 67.6 mg (0.11 mmol, 51.1%) of the bis-(1-methyltriptycyl)sulfite ester was obtained. In addition 40.7 mg (0.13 mmol, 31.0%) of the 1-chloromethyltriptycene, mp 232-234°C, (lit²⁸ 231-233°C) was obtained. (See spectral data below)

Phosphorous trichloride/DMF: To dimethylformamide, 100 μ l, (0.28 mmol) in 1.0 ml chloroform, was added phosphorous trichloride, 10 μ l, (0.28 mmol) under a nitrogen atmosphere. After standing for 1 h, 80mg, (0.28 mmol), 1-triptycyl carbinol dissolved in 500 μ l benzene was added and the mixture refluxed for 24 h. After removal of the solvents, the crude product, 82 mg was chromatographed on TLC/sila gel plates eluting with pet. ether (30-70)/CHCl₃, (10:1), to yield 1-chloromethyltriptycene, 51.42 mg (0.17 mmol, 62.1%), mp 230-232°C, (lit⁹ 231-234). ¹H NMR (200 MHz); 7.80 (3Hm, ArH), 7.40 (3Hm, ArH), 7.08 (6Hm, ArH), 5.44 (1hs, bridgehead), 5.29 (2Hs, CH₂CCl); ¹³C NMR (50 MHz); 125.43, 124.96, 123.68, (protonated ArH C's), 52.50(bridgehead), 53.80, (bridgehead), 42.50(CH₂CL), IR(neat); 3068, 1457, 1439, 1278, 1189, 752, 627 cm⁻¹.

Triphenylphosphine / CCl₄: 1-Triptycyl carbinol, 99.2 mg (0.35 mmol) and triphenylphosphine 91.2 mg (0.36 mmol), were suspended in 5 ml dry carbon tetrachloride and heated at reflux under nitrogen for 8 h. The solid salt (190 mg), was filtered off, and the carbon tetrachloride was removed by evaporation leaving 30 mg of a white crystalline material identified as unreacted 1-triptycyl carbinol, 91% (mp 239-241; lit⁹ 238-240°C).

Polystyryl-diphenylphosphine / CCl₄: A mixture of 250 mg

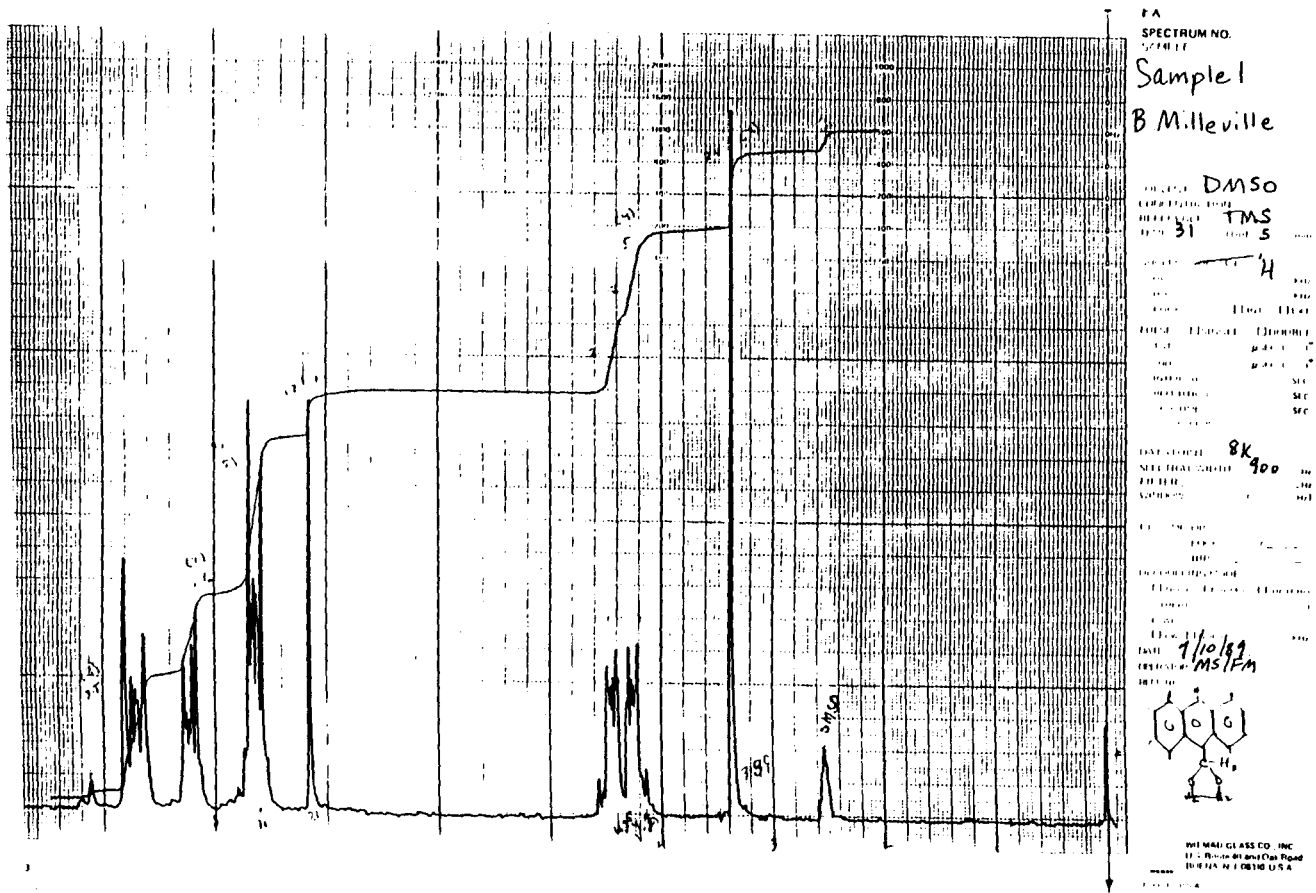
(0.88 mmol) of 1-triptycyl carbinol, 350 mg of polystyryl-diphenylphosine (3 mmol $P(Ph)_3$ / g resin and 3 ml CCl_4 were placed in a 25 ml flask flushed with nitrogen, and heated to reflux for 8 h. After cooling, the polymer was filtered off, washed with 15 ml carbon tetrachloride, and the combined filtrate was evaporated leaving a white crystalline solid, which was identified as unreacted 1-triptycyl-carbinol, 94% (mp 239-241; lit⁹ 238-240°C).

Bis-(1-triptycyl) carbinol and PCl_3 / DMF: To dimethylformamide, 15.5 μ l, (0.20 mmol) in 1.0 ml chloroform, was added phosphorous trichloride, 20 μ l, (0.20 mmol) under a nitrogen atmosphere. After standing for 1 h, 82 mg, (0.15 mmol), bis-(1-triptycyl)carbinol dissolved in 500 μ l benzene was added and the mixture refluxed for 24 h. After removal of the solvents, the crude product, 82 mg was chromatographed on PLC/silca gel plates eluting with pet. ether (30-70) / $CHCl_3$, (10:1). Only unreacted bis-(1-triptycyl) carbinol was found, 89%, (mp 354-356; lit³⁷355-357).

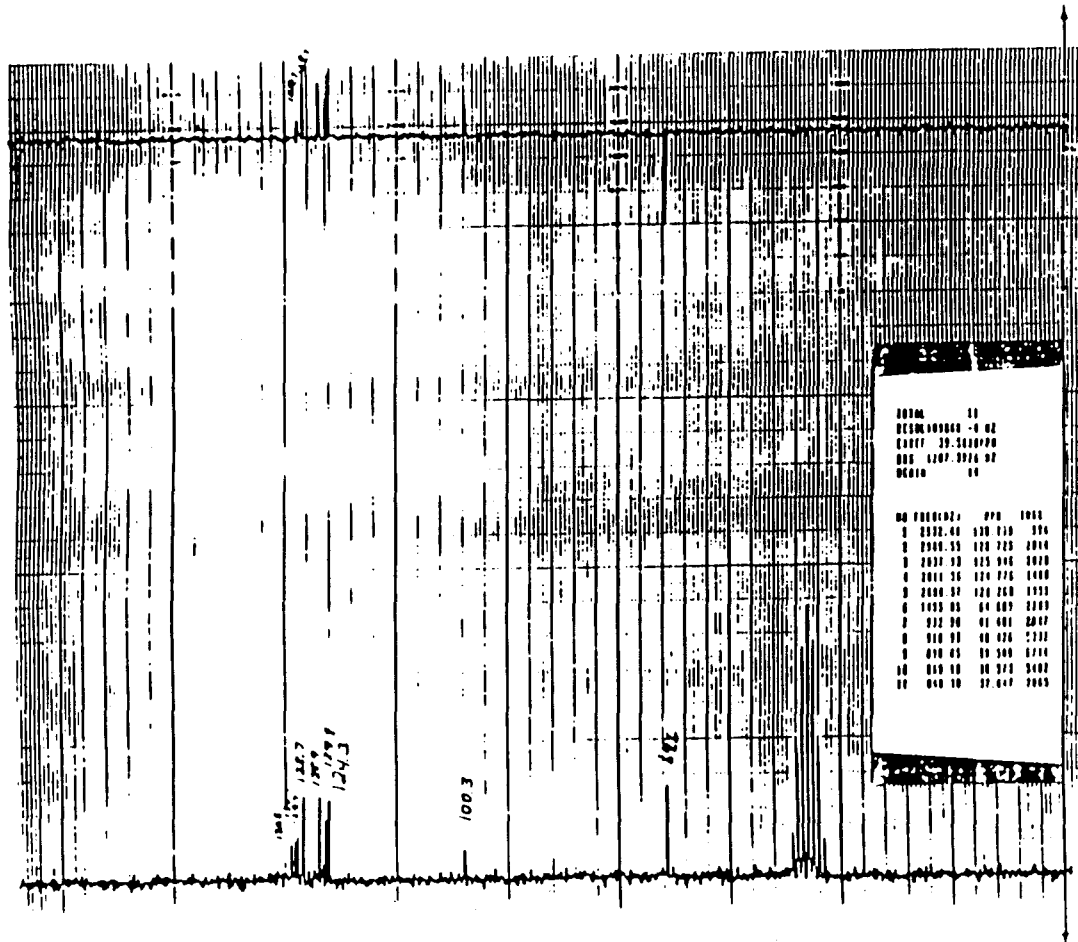
TABLE 3

The following R_f values were determined using commercially available precoated, silica gel-thin layer chromatography sheets, (Eastman) with benzene as the solvent.

<u>Compound</u>	<u>R_f Values</u>
9-Anthracene-1,3-dioxolane	0.57
1-Triptycyl-1,3-dioxolane	0.49
1-Triptycyl aldehyde	0.83
1-Bromotriptycene	0.91
1-Chloromethyltriptycene	0.60
1-Triptycyl carbinol	0.32
Bis(1-triptycyl)carbinol	0.24
Bis(1-methyltriptycyl)sulfite ester	0.66



9-(ANTHRACENE)1,3-DIOXOLANE



NO	FREQ(CZ)	PPM	INTEG
1	2032.46	8.70	1.00
2	2044.35	8.95	2.00
3	2037.33	8.85	1.00
4	2041.35	8.94	1.00
5	2040.37	8.94	1.00
6	1935.85	8.4	1.00
7	1932.86	8.4	1.00
8	1940.85	8.6	1.00
9	1939.86	8.6	1.00
10	1947.85	8.8	1.00
11	1946.86	8.8	1.00

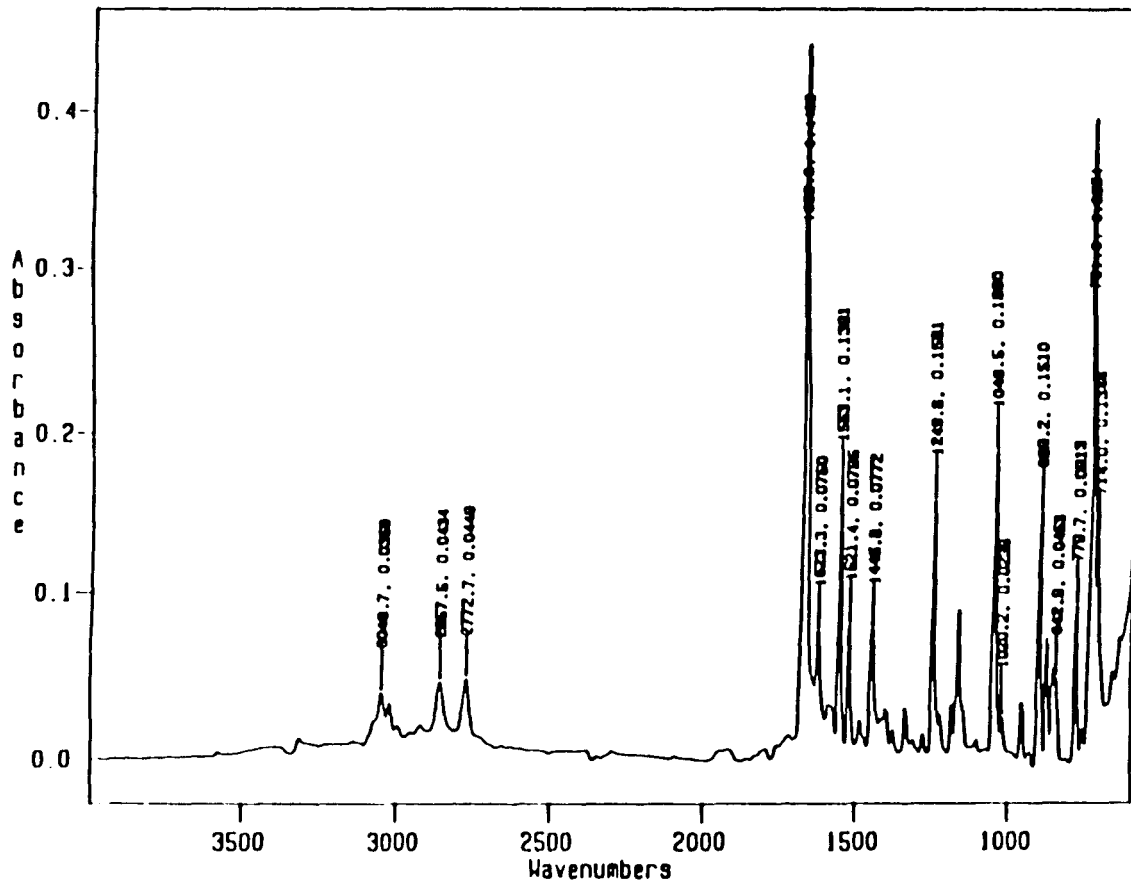
FX
SPECTRUM NO
SAMPLE
Sample 1
B Milleville

CONC. 1.00
SOLVENT DMSO
PULSE PROGRAM
PULSE 91
2700

8KDP
4502

7/10/81
MSIFM

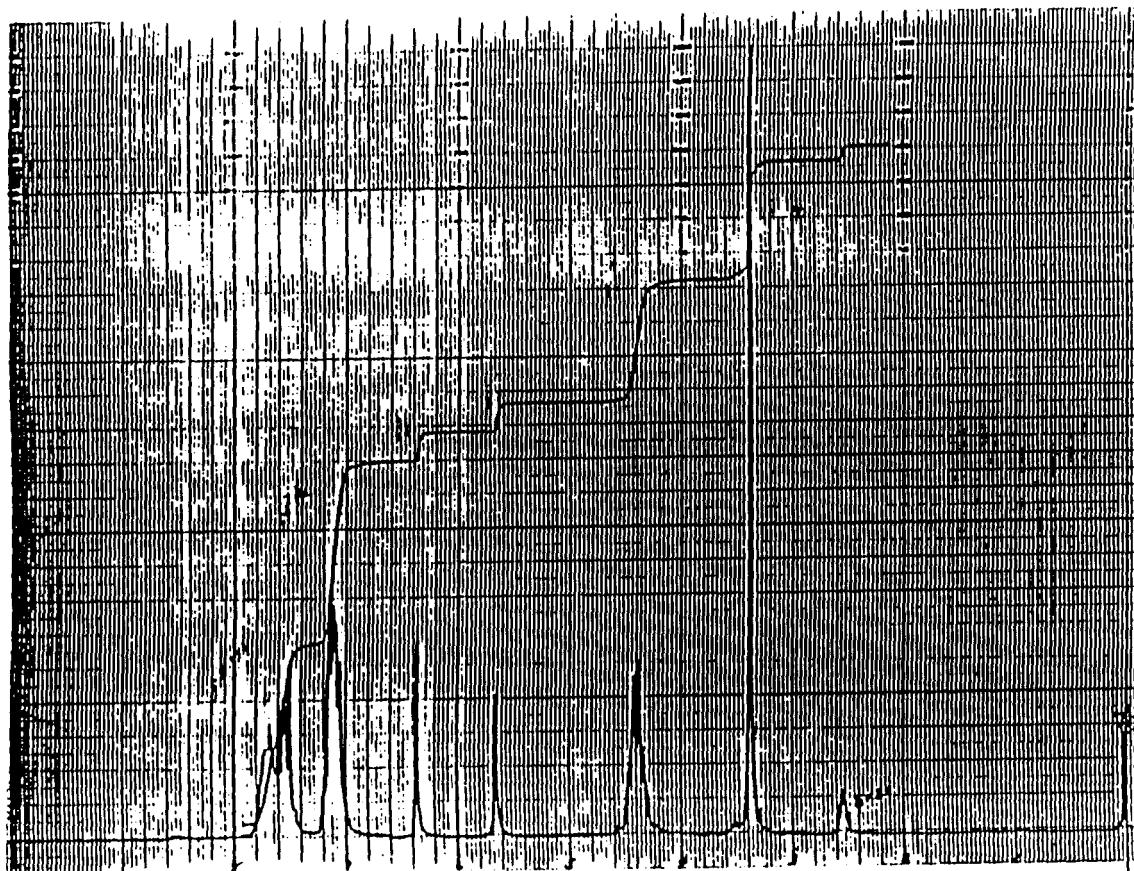
9-(ANTHRACENE)1,3-DIOXOLANE



Res=8

Scans=16

9-(ANTHRACENE)1,3-DIOXOLANE



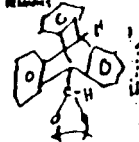
Sample 2
B. Milleville

SOLVENT DMSO
 CONCENTRATION _____
 REFERENCE TMS
 TEMP 31 °C

PROB 1H
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 INT 1 SEC
 PHO _____
 INTERVAL _____ SEC
 RESOLUTION _____ SEC
 ACQ TIME _____ SEC
 NO. OF ACQUIS _____

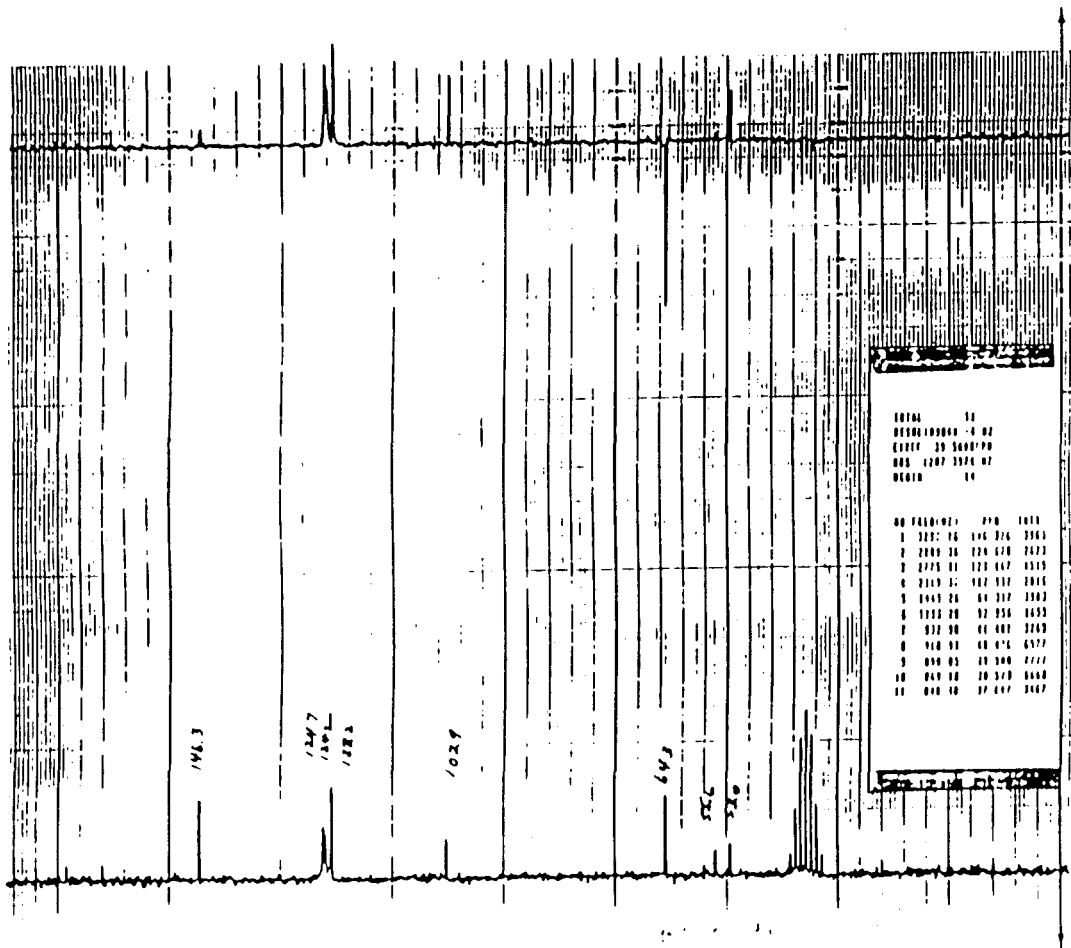
DATA POINTS 8K
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 FILTER _____
 WINDOW _____

RF AMP 0dB
 LOCK _____
 ERR _____
 DECOUPLING MODE
 NONE WALTZ HETERO
 PHASE _____
 F1 110.4 MHz
 F2 MSIEM MHz



VII
 U.S. Patent and Trademark Office
 U.S. Patent 3,800,000

1-TRIPTCYL-1,3-DIOXOLANE



FX
SPECTRIMNO

Sample 2

B.Milleville

DMSO

91 5

8K

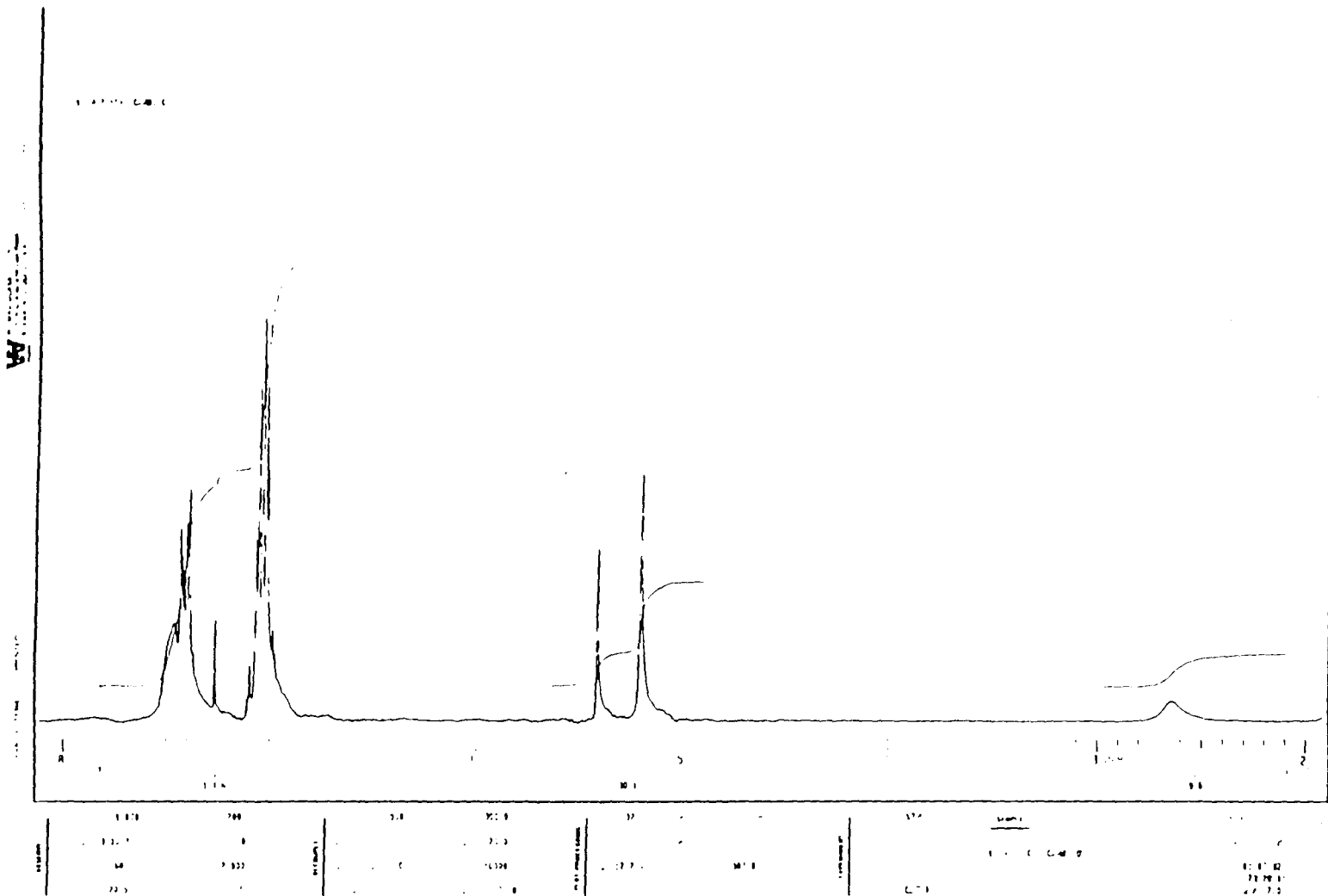
4500

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11	00000000	00	0000

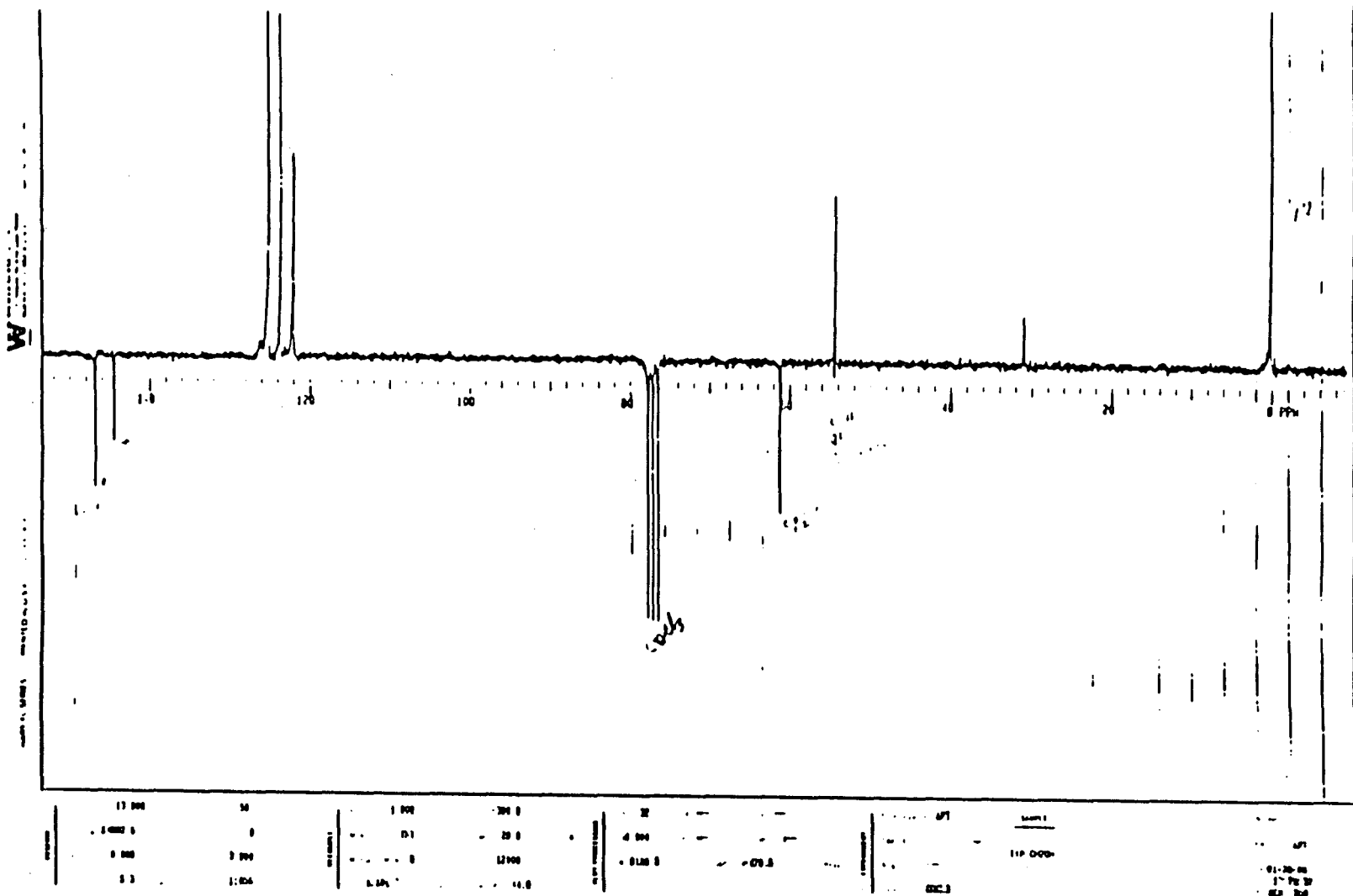
7/1/99
MSLEM

10
11

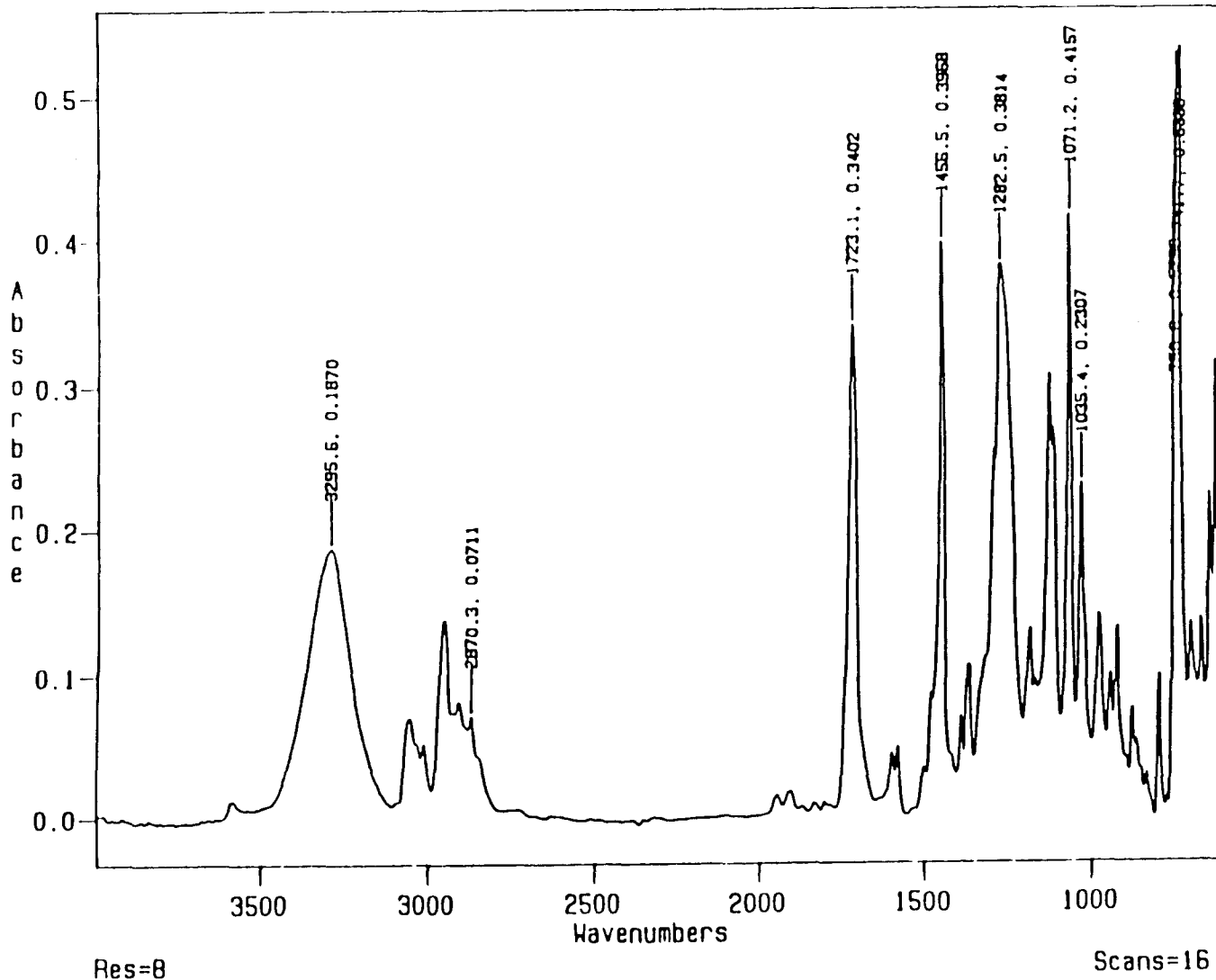
1-TRIPTYCYL-1,3-DIOXOLANE



1-TRIPTYCYL CARBINOL



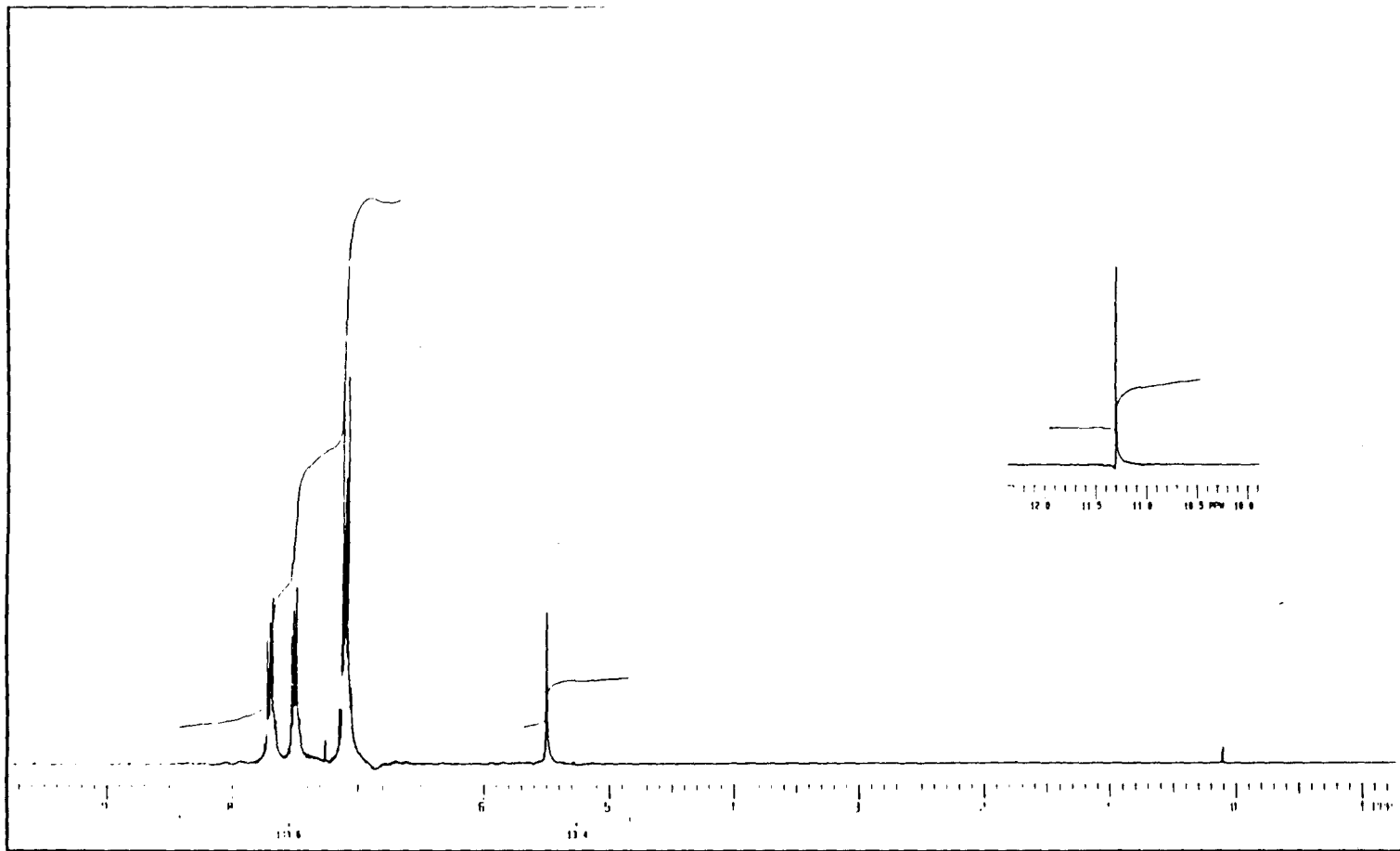
1-TRIPTCYL CARBINOL



1-TRIPTYCYL CARBINOL

WILMINGTON, DE. 19806
WILMINGTON, DE. 19806
WILMINGTON, DE. 19806

445 445 445

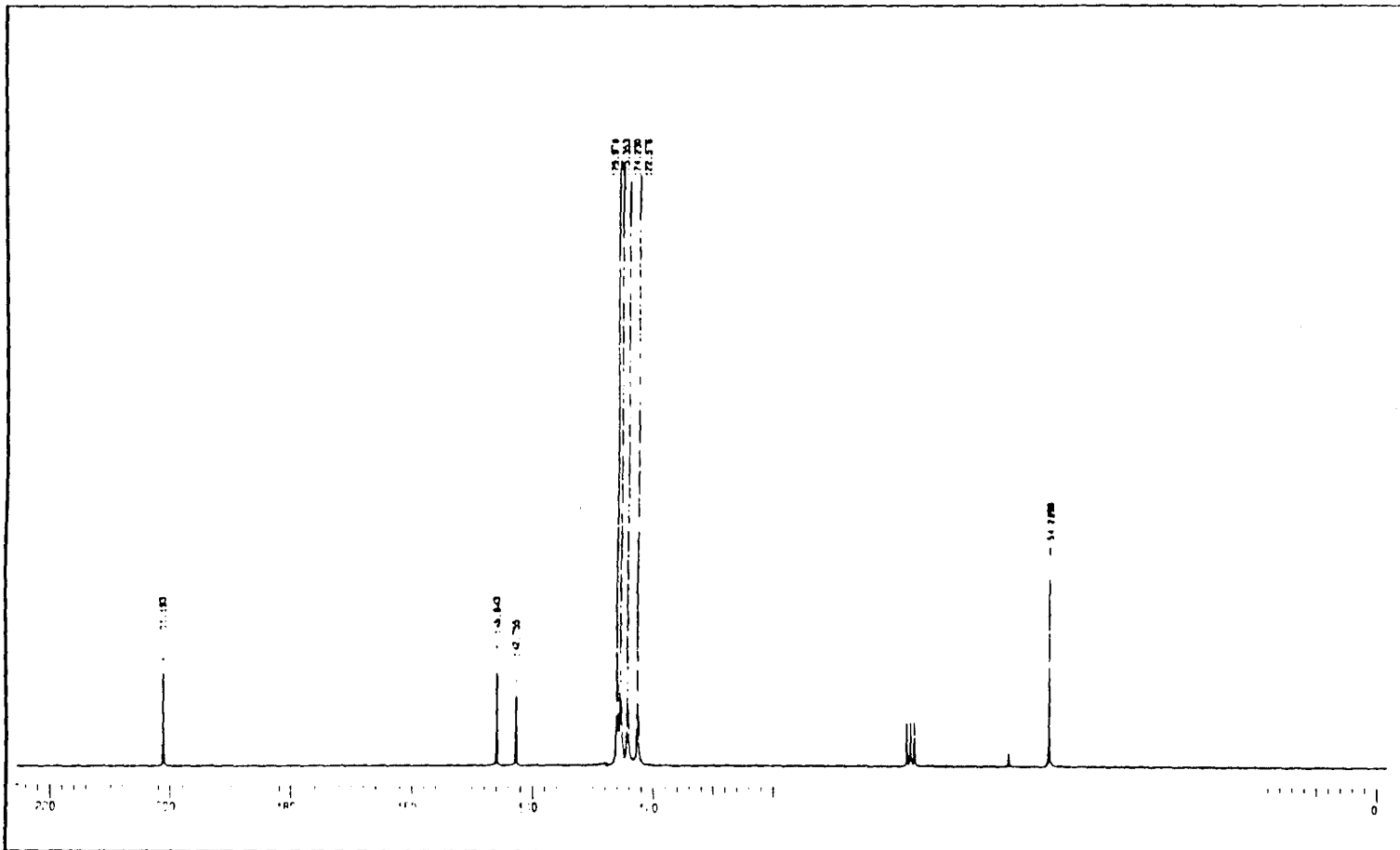


Chemical Shift (ppm)	Integration	Assignment
11.8	1.00	CHO
11.4	0.20	CH
10.5-11.0	1.00	CH

1-TRIPTYCYL ALDEHYDE

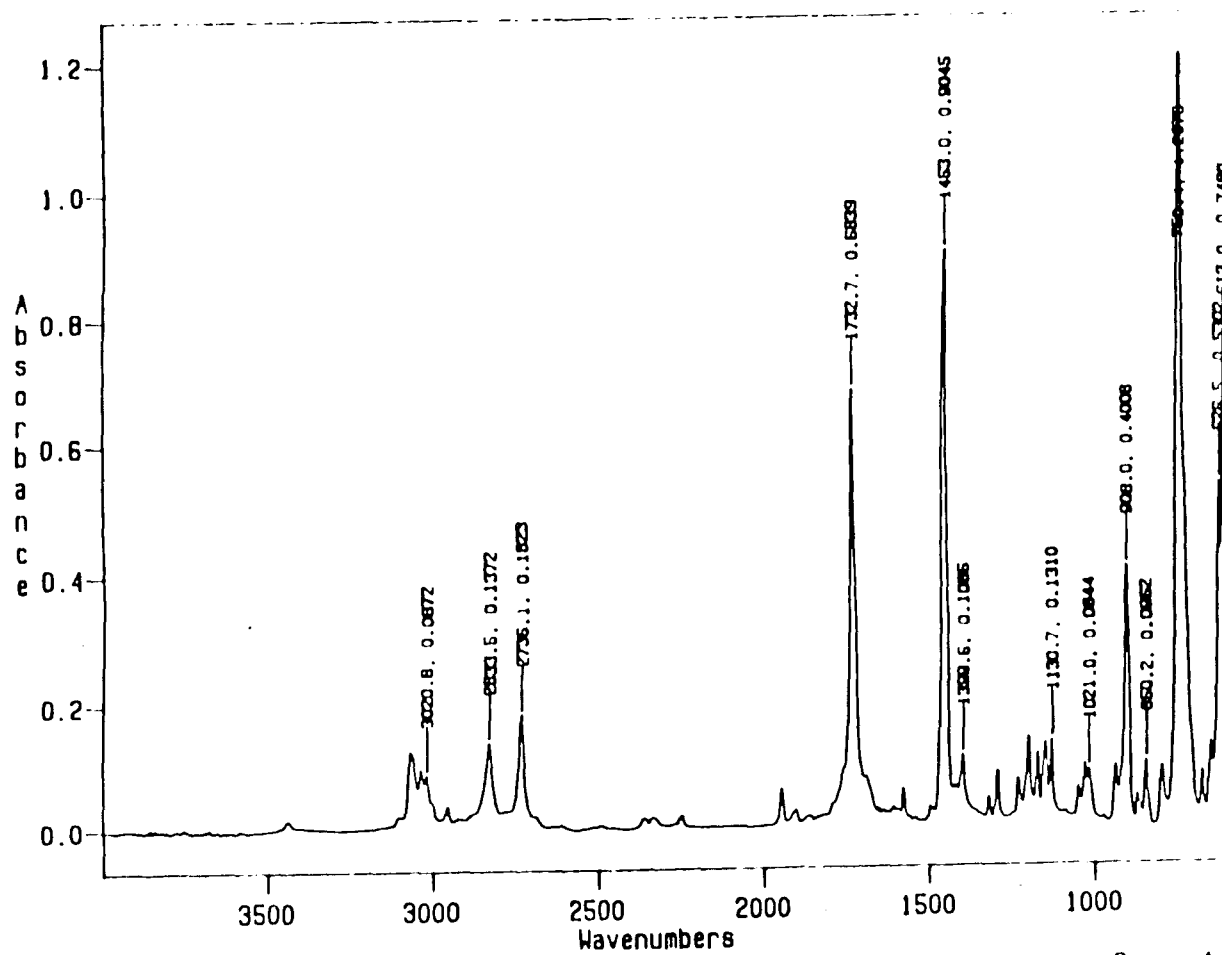
W
 1111
 1111

1111 1111 1111



Retention Time	Area	Height	Width	Resolution	Integration	Sample	Conc.	Time	Date	Operator
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11.95
12.05

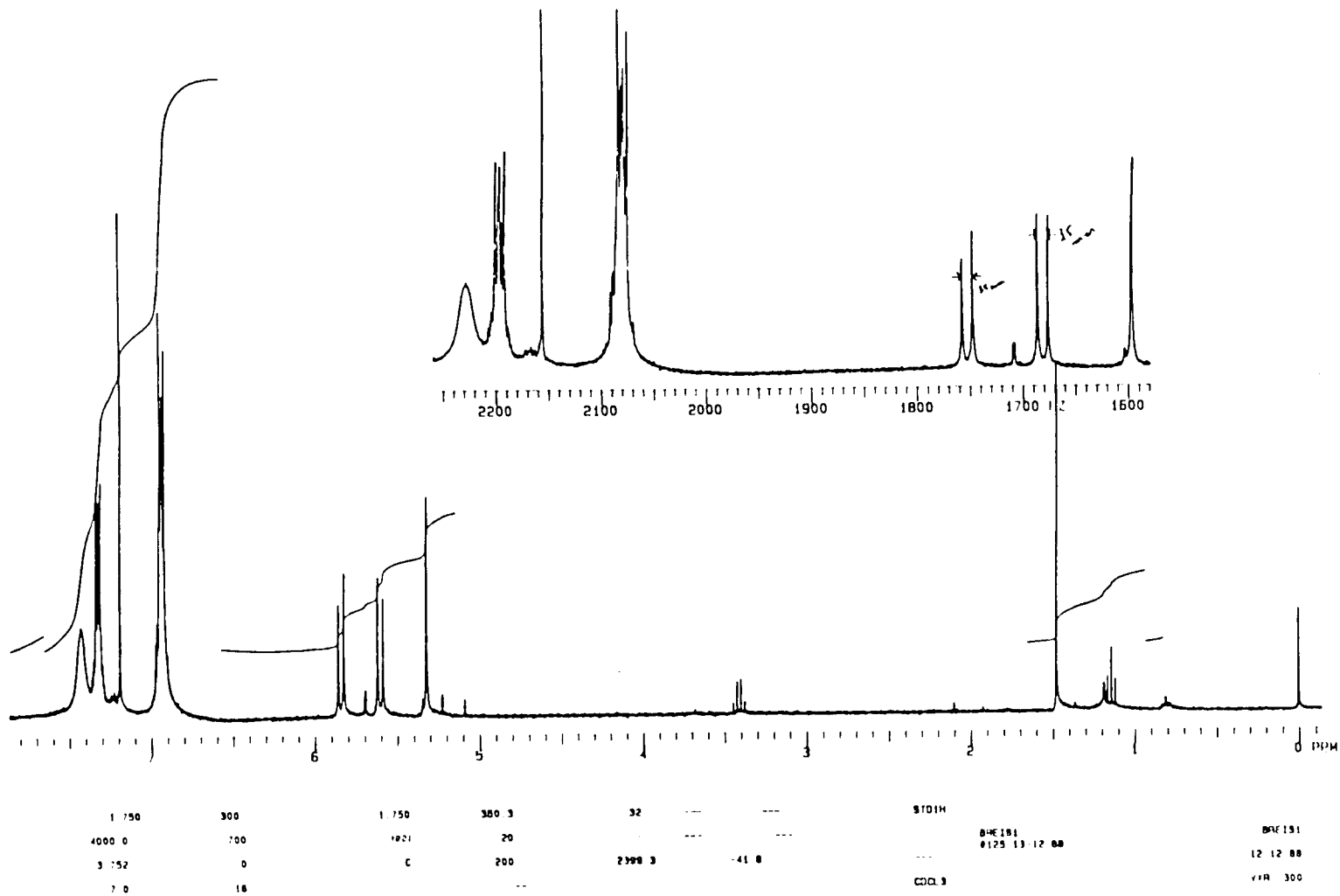
1-TRIPTCYL ALDEHYDE



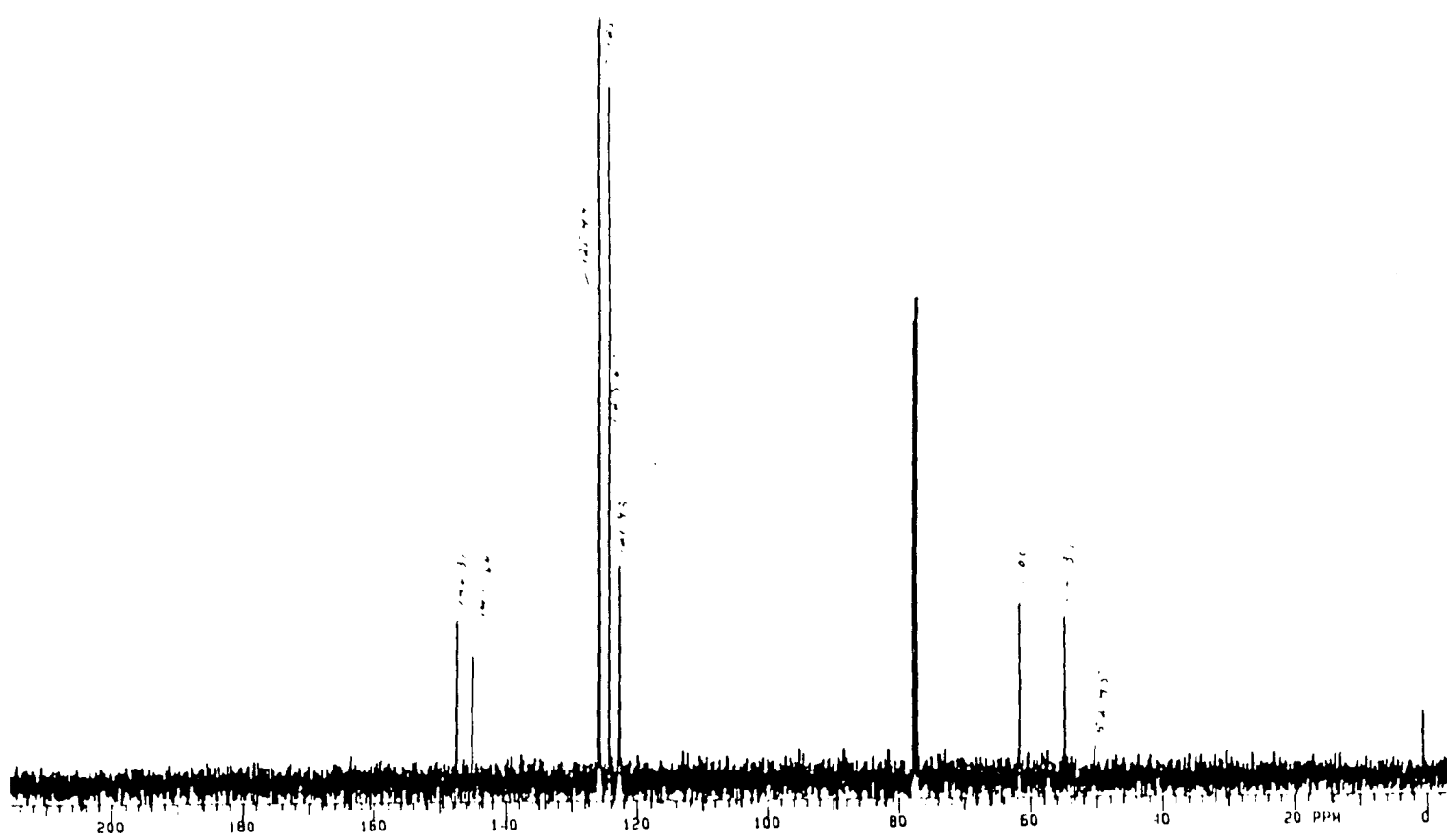
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1-TRIPTYCYL ALDEHYDE

Scans=4

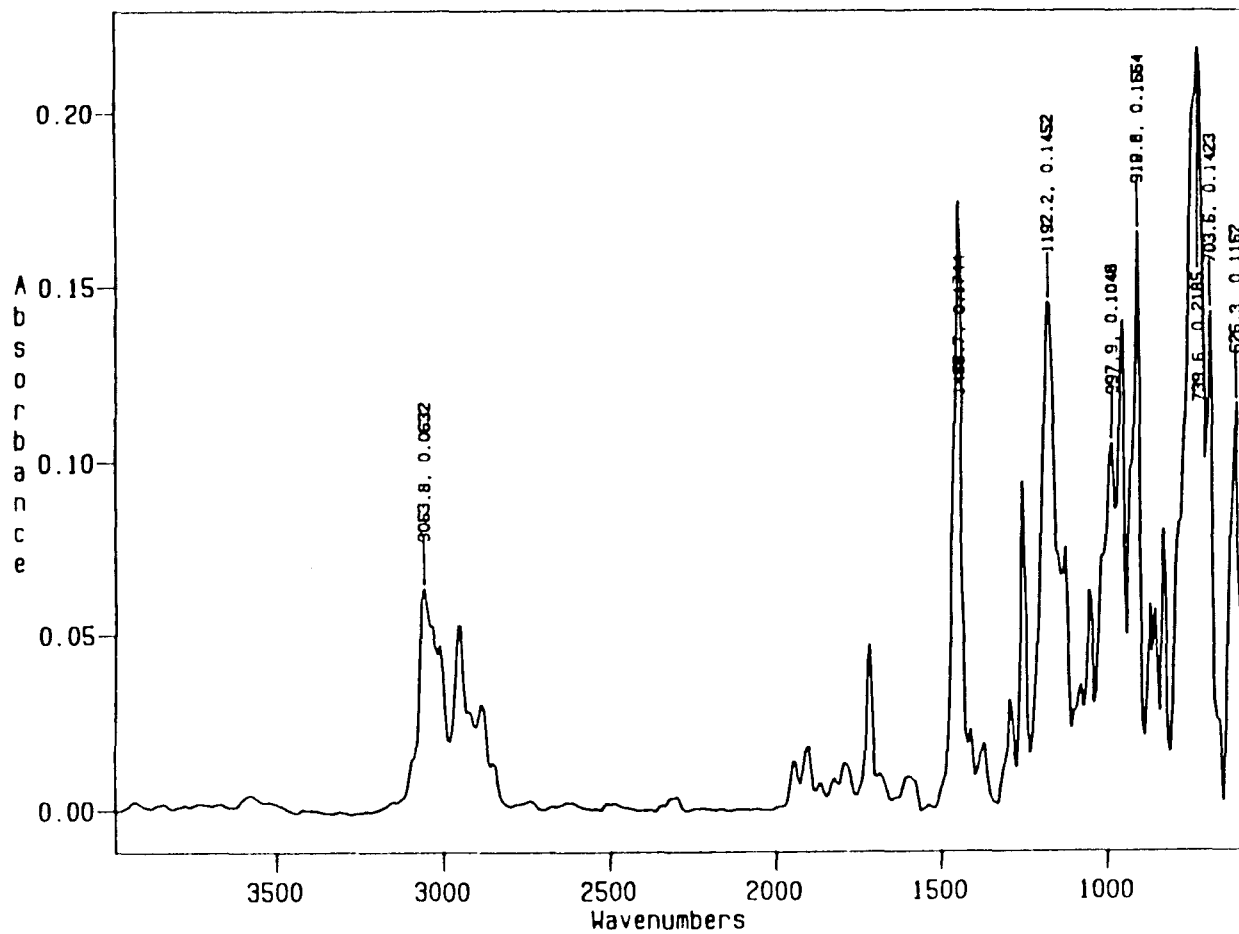


BIS(1-TRIPTCYL)METHYL SULFITE ESTER



13	50	5	1	50	350	3	84	573	30	
1850	:	00	11	:	5	:	1	000		C
1	839	0	5	9900	:	6001	211	:		0 03 89
8		95								1 300

BIS(1-TRIPTYCYL)METHYL SULFITE ESTER



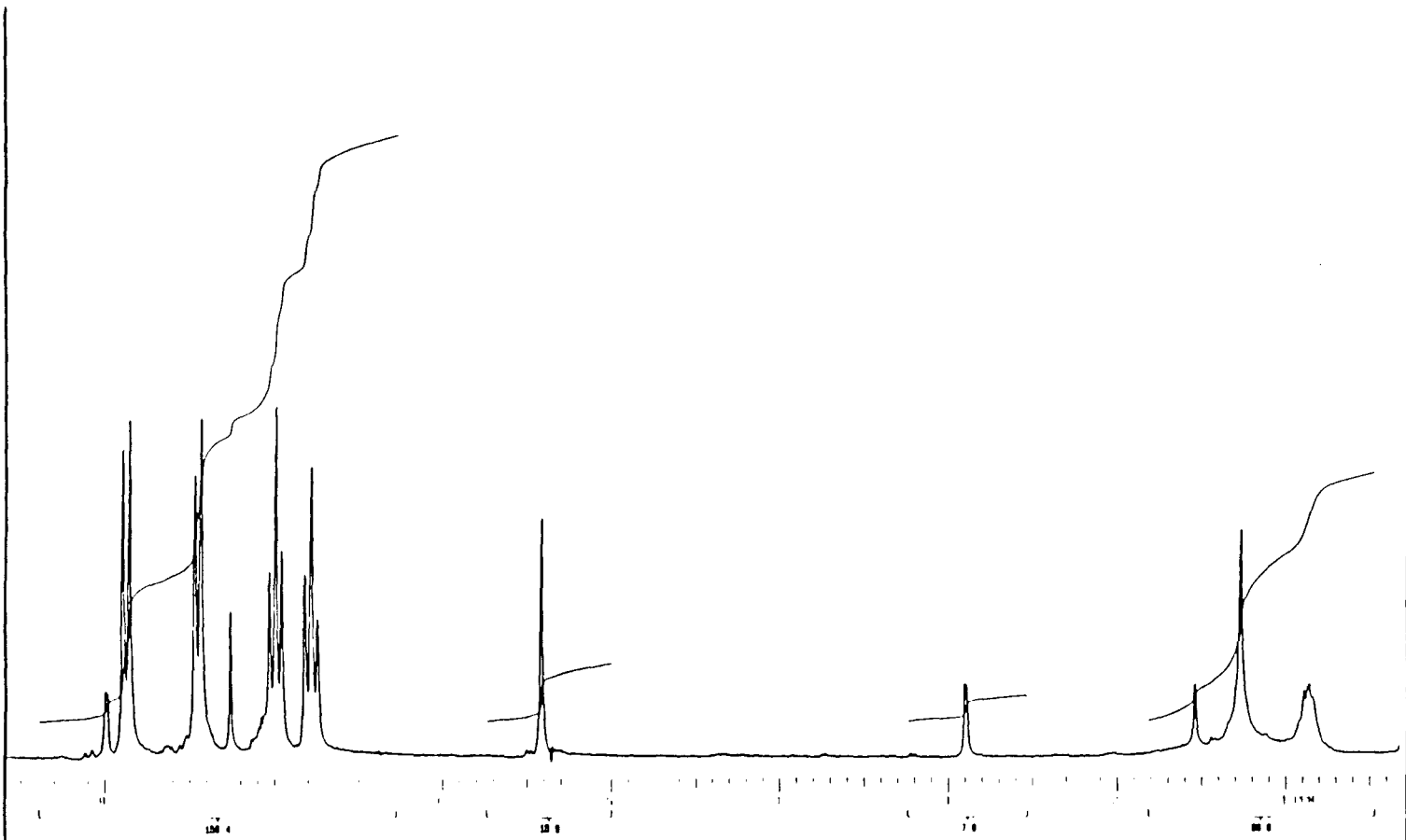
Res=16

Scans=16

BIS(1-TRIPTYCYL)METHYL SULFITE ESTER

W
WILSON
UNIVERSITY OF CALIFORNIA
LABORATORY

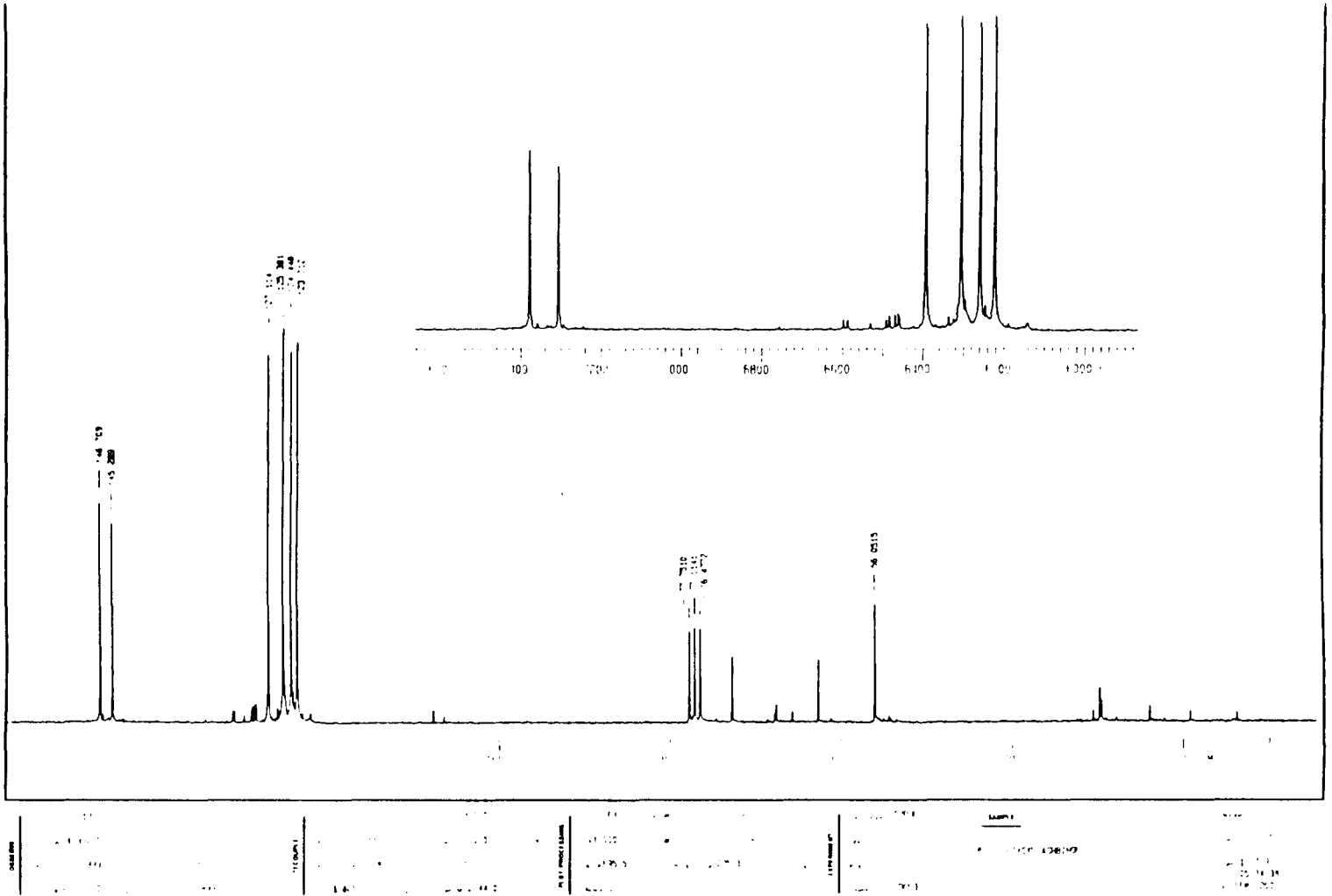
100% SEPIUMS LIMITED IN U.S.A.



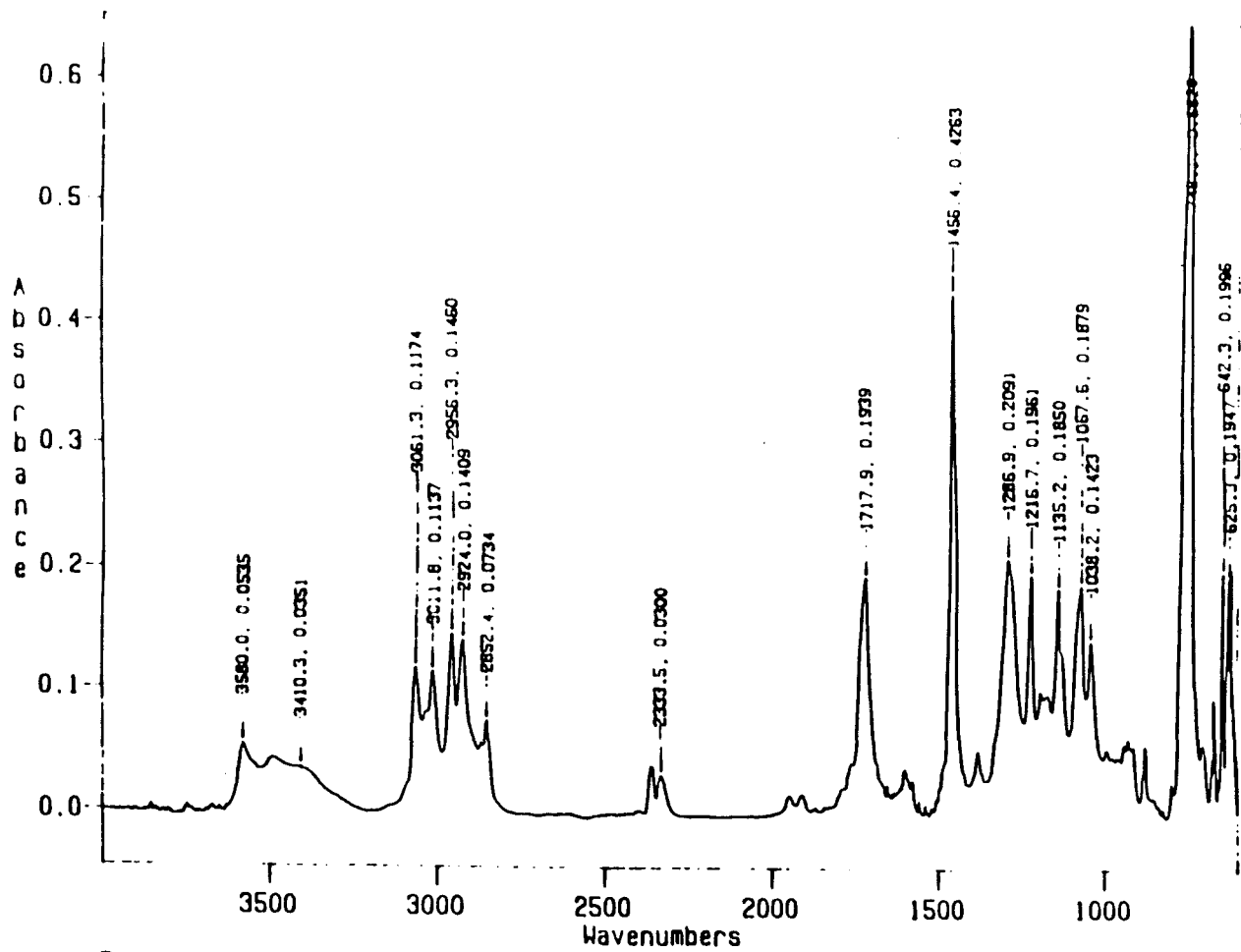
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7.0	1.000
6.5	1.000
6.0	1.000
5.5	1.000
5.0	1.000
4.5	1.000
4.0	1.000
3.5	1.000
3.0	1.000
2.5	1.000
2.0	1.000
1.5	1.000

BIS(1-TRIPTCYL) CARBINOL

WALSH LABORATORIES, INC.
1000 W. 15th St., Des Moines, IA 50319
515-281-1111



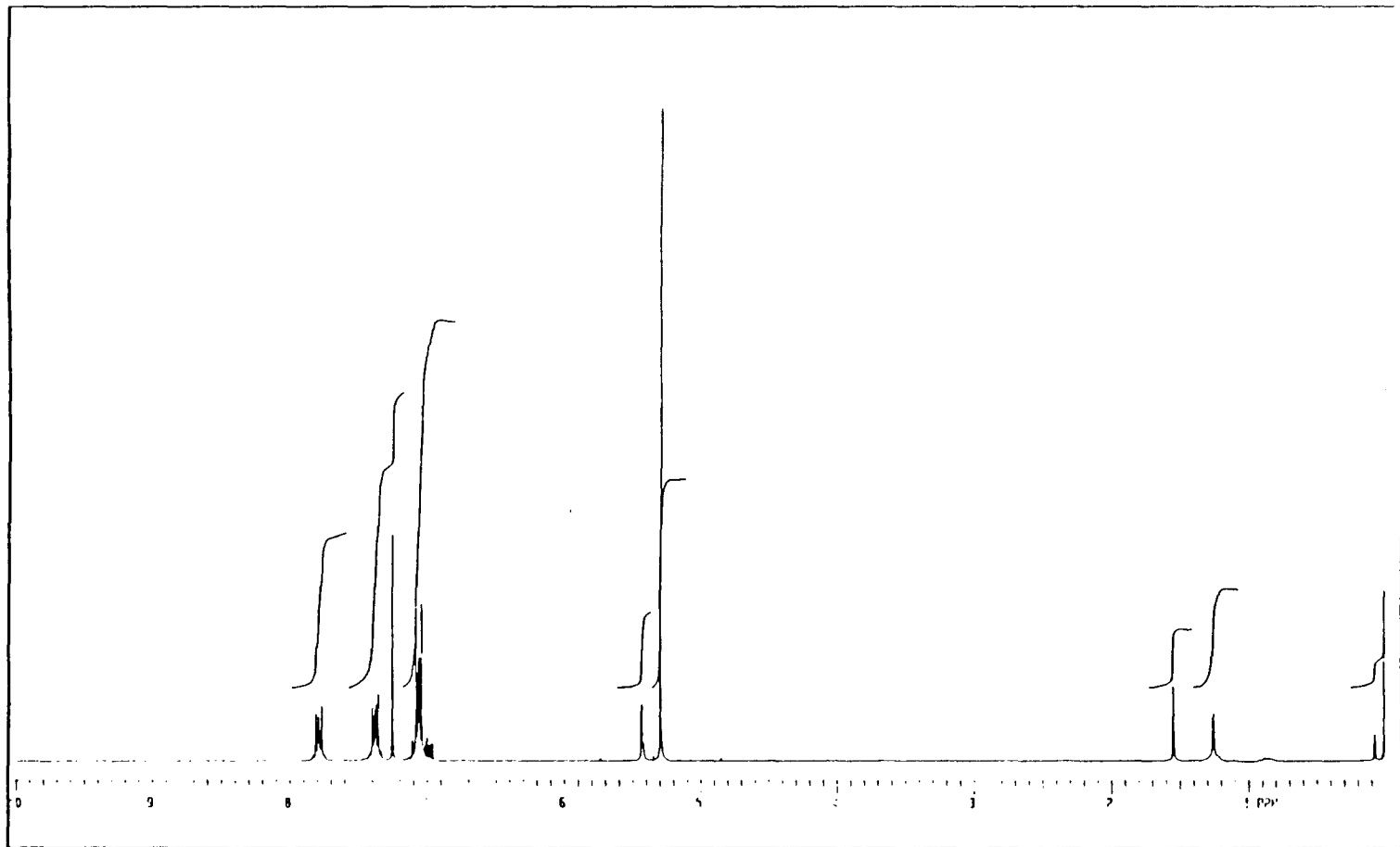
BIS(1-TRIPTYCYL) CARBINOL



BIS(1-TRIPTYCYL) CARBINOL

WALTON LABORATORIES, INC.
ANN ARBOR, MICHIGAN, U.S.A.

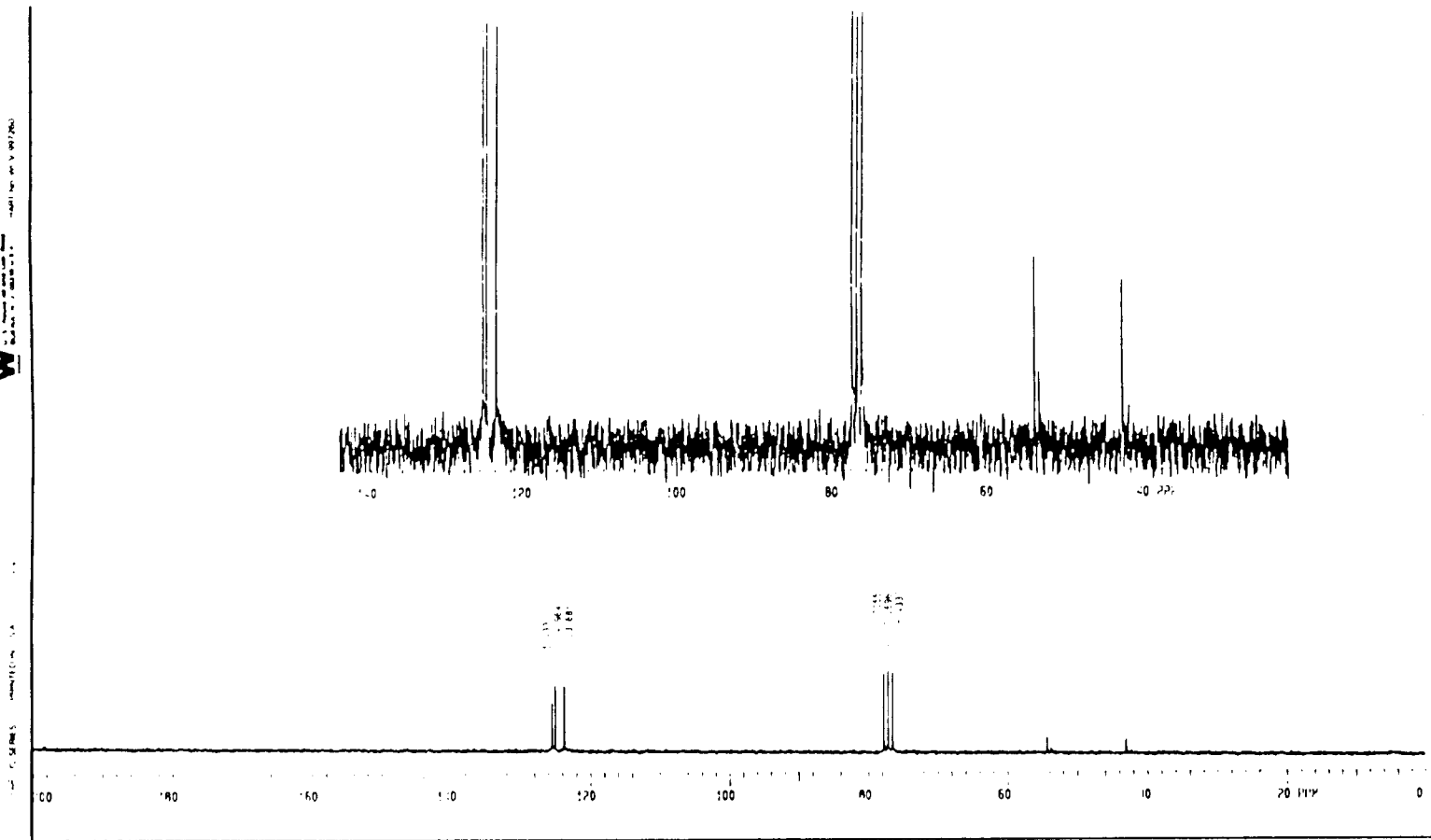
100 MHz 100 MHz



Chemical Shift (ppm)	Integration	Assignment
7.5 - 8.0	1.000	Aromatic protons
6.8 - 7.2	1.000	Aromatic protons
5.2	1.000	CH ₂ Cl
0.8 - 1.5	1.000	Aliphatic protons

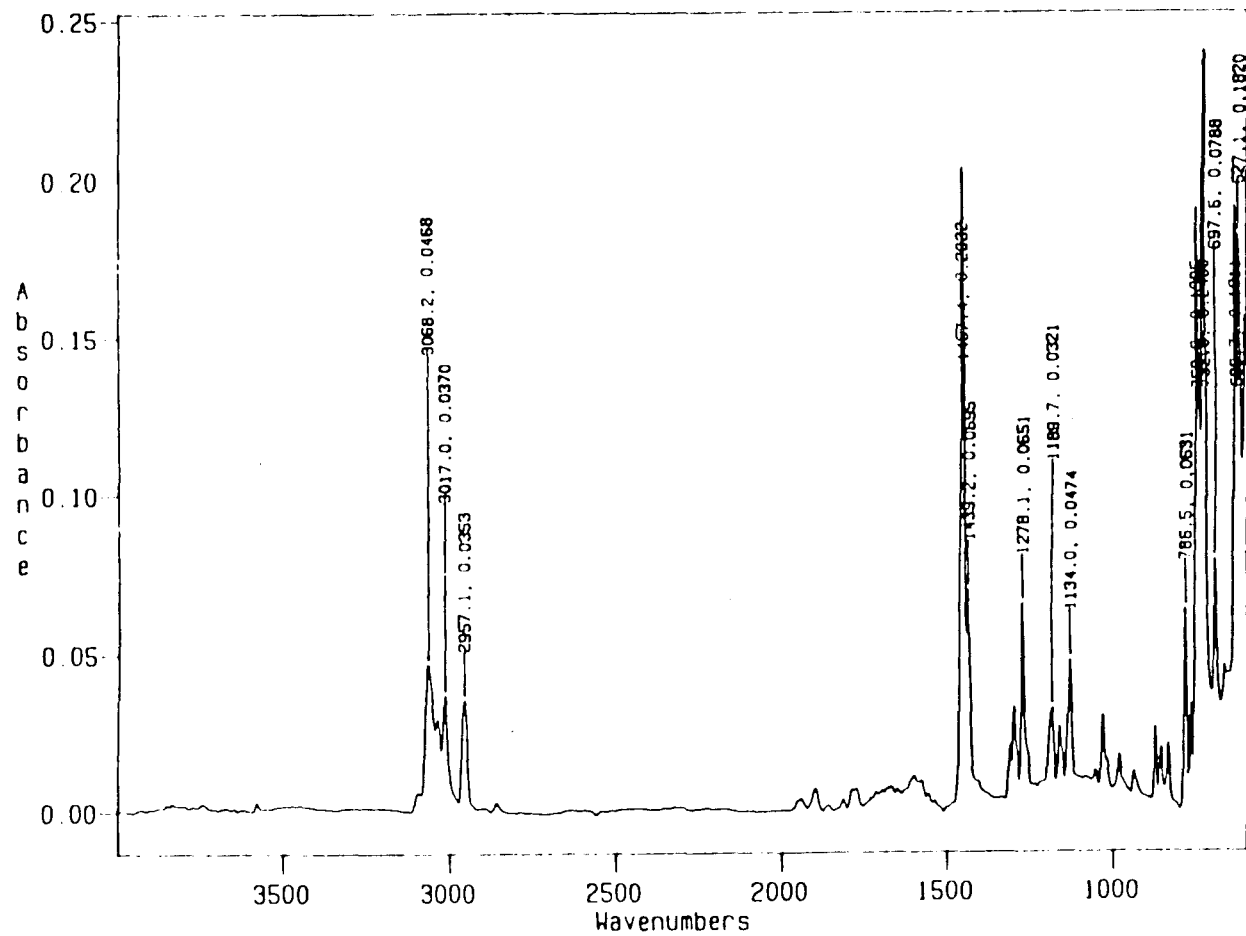
1-CHLOROMETHYL TRIPTYCENE

W
 1000 MHz (1H) NMR
 1000 MHz (13C) NMR
 1000 MHz (1H) NMR



Chemical Shift (ppm)	Integration	Assignment
7.2	1.000	Aromatic H
7.1	1.000	Aromatic H
4.5	1.000	-CH ₂ -Cl
3.4	1.000	Aromatic H
133	1.000	Aromatic C
131	1.000	Aromatic C
78	1.000	CH ₂ -Cl
76	1.000	Aromatic C

1-CHLOROMETHYL TRIPTYCENE



Res=8

Scans=64

1-CHLOROMETHYL TRIPTYCENE

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APPROVAL SHEET

The thesis submitted by **Bryce A. Milleville** has been read and approved by the following committee:

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The final copies have been examined by the director of the thesis, and the signature which appears below verifies the fact that any necessary changes have been incorporated and that the thesis is now given final approval by the Committee with reference to content and form.

The thesis is, therefore, accepted in partial fulfillment of the requirements for the degree of Masters of Science.

12/17/92
Date

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