AN IMPROVED ROUTE FOR THE SYNTHESIS OF PLANAR DERIVATIVES OF TRIARYLMETHANE

by

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To

my best friend,

Gerry

ACKNOWLEDGEMENT

I wish to express my gratitude to Dr. Joseph V. Paukstelis for his guidance and suggestions throughout my graduate studies, and to Rosh Chandraratna for his friendship and for the help he has given me with my research.

My special thanks goes to my wife, Gerry, for her loving support during our time here in Kansas.

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INTRODUCTION

Triarylmethane dyes have been used for many purposes: as textile dyes, pH indicators[1], reagents for the trace determination of halides,[2] H_2S,[3] Ga,[4] Ge,[5] In,[6] etc., and have been used even for such diverse purposes as ballpoint pen inks[7] and corrosion inhibitors[8]. We are especially interested in their use as redox indicators. Several triarylmethane dyes are good indicators for the titration of Fe(II), Ti(III), Cr(II), and Cu(I) with Ce(IV); and for the titration of Fe(II), $Fe(CN)_6^{4-}$, U(IV), Mo(V) and hydroquinone with dichromate. Some of the problems with these indicators are that they are not all reversible, and they are often not stable in oxidizing solutions. In spite of this, they are often the indicator of choice.[9,10] These useful redox indicators were found by testing commercially available triarylmethane dyes. There have apparently been no specific attempts to design and synthesize new structures that contain the elements of a triarylmethane but would be more useful as redox indicators.

There has been much chemical interest in traiarylmethanes because of the unique properties of the central carbon atom. A free radical, a positive charge or a negative charge on the atom is stabilized by delocalization onto the aromiatic rings. This stabilization is dependent on the angle of twist of each ring, and would be at a maximum when the rings are coplanar. This is normally not possible because of steric interactions at the ortho positions, resulting in a propeller-shaped molecule, as has been documented in the organic literature.[11,12]

Stablization at the central carbon atom, and thus the properties of triarylmethanes, is dependent on the ring substitutents. For

example, under sufficently basic conditions, a proton is removed from triarylmethanes. The acidity is increased greatly by electron withdrawing substituents on the aromatic rings. Thus, tris(p-nitrophenyl) methane is quite acidic, having a pK_a of 14.3[13] compared to 32 for triphenylmethane.[14]

When triphenylcarbinol is in a sufficiently acidic solution it is protonated and loses water.

$$H^+ + Ar_3C\text{-}OH \rightleftarrows \left[Ar_3C^{\pm}\text{-}O^{H}_{H}\right] \rightleftarrows Ar_3C^+ + H_2O$$

This type of compound is called a "secondary base" and the equilibrium constant is expressed in terms of K_{R+}.[15] The carbenium ion formed owes its stability to delocalization of the positive charge onto the ring. The amount of stabilization depends on the ring substituents, the angle of twist, ring twist, and solvation.

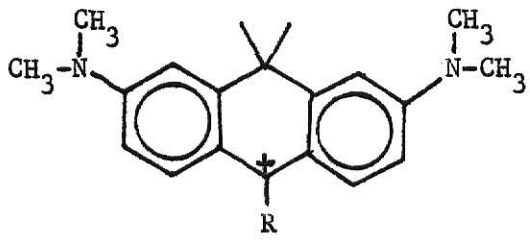
The parent compound, triphenylcarbinol, has a pK_{R+} of -6.63. Adding a para methyl group increases this to -3.40. When three para methoxy groups are added, the pK_{R+} increases to 0.82. Three para dimethylamino groups have a very large stabilizing effect on the carbenium ion, resulting in a pK_{R+} of 9.63. Electron withdrawing groups destabilize the carbenium ion as shown by tris(p-nitrophenyl) carbinol which has a pK_{R+} of -16.27.[16]

The degree of ring twist will increase when substituents are placed in the ortho positions. This increased twist is expected to decrease stabilization of the carbenium ion, but the situation is complicated by the electronic effects of the substituents. In addition,

the introduction of bulky substituents can decrease the carbenium ion stability by hindering solvation.[17]

We wish to take advantage of the unique properties of this central carbon atom to design better analytical indicators with increased stability, reversibility, and selectivity. By varying the structure we hope to develop new indicators with increased stability, reversibility, and selectivity.

In designing new triarylmethane reagents and indicators, one needs to know not only what effect substitution has on the pK_{R+}, but also how substitution affects the λ_{max} and ε. Barker and co-workers have investigated the UV-visible spectra of a wide variety of triarylmethane dyes and have attempted to explain and predict the effect of various substituents.[18,19,20] Much of this work was with derivatives of Malachite Green, Crystal Violet, and Michler's Hydrol Blue.



Michler's Hydrol Blue

R = H

Malachite Green

R = Phenyl

Crystal Violet

R = p-dimethylaminophenyl

In general, electron donating groups should produce a hypsochromic shift (longer λ), whereas electron withdrawing groups should give a bathochromic shift. This can be explained by considering the

molecular orbitals of these dyes. The major peak is due to the $n \rightarrow \pi^*$ transition. Electron donating substituents stabilize the π^* orbital and destablize the π orbitals, decreasing the $n \rightarrow \pi^*$ transition energy and producing a hypochromic shift. With electron withdrawing substituents the opposite situation results, and a bathochromic shift occurs. When substituents are placed in the ortho positions, there is a steric effect on λ_{max} in addition to the electronic effect. The increased ortho interactions cause the rings to twist out of plane even more. This decreases the resonance among the π orbitals, and thus decreases the energy for the $n \rightarrow \pi^*$ transition, resulting in a bathochromic shift.

It is not known exactly what effects the various ortho substituents have on configuration of a molecule. Thus, it is difficult to correlate the angle of twist with λ_{max} and ε. It is possible to overcome the problem of not knowing the configuration by joining the rings with isopropylidene bridges. This holds the rings in a planar or near-planar conformation, so that the conformation is more accurately known, as well as increasing the resonance stabilization at the central carbon atom. These bridged compounds are of interest to us because the may make good analytical indicators. The flat structure may give higher ε's, and the bulky isopropylidine bridges may increase stability by hindering attack of electrophiles on the ring.

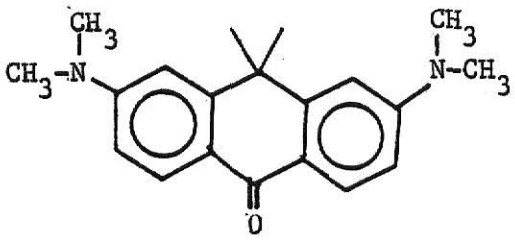
Barker and co-workers made derivatives of Malachite Green and Crystal Violet with one and two isopropylidine bridges, but were unsuccessful in making the derivatives with three bridges.[18] To make the monobridged derivatives of Malachite Green and Crystal Violet, the appropriate lithium reagent (2d or 2e) was reacted with

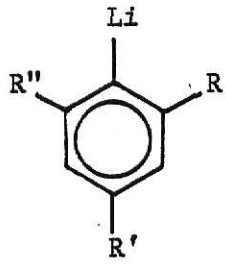
the anthrone (1) to give the product (3d or 3e). To make the dibridged derivatives, the appropriate lithium reagent (2a or 2b) was added to the anthrone (1) to give the intermediate triarylcarbinol (3a or 3b). This was reduced (zinc and HCl in acetic acid), cyclized (CH_2Cl_2 and liquid HF), and oxidized (chloranil) to give the product (4a or 4b).

Attempts by Barker and co-workers to prepare the tri-isopropylidene bridged derivative of Malachite Green proved fruitless. They reacted 2,6-di-isopropenyl lithium (2c) with the anthrone (1). The product (3c) was reduced, but the attempted cyclization in liquid HF or polyphosphoric acid gave only polymers.[18]

There is still a considerable amount of twist present in these dibridged molecules (4a and 4b). Barker and co-workers reported that the aromatic rings in these compounds may be distorted. One would expect that the introduction of electron donating isopropylidene bridges and the increased coplanarity of the rings would result in a hypsochromic shift of the electornic absorption bands, whereas a bathochromic shift was observed. Barker and co-workers attributed this bathochromic shift to distortion of the aromatic rings.[18,21]

Hellwinkle, Melan and Aulmich have made the hexacyclic triphenylmethane with three isopropylidene bridges, 12,12c-dihydro,4,4,8,8,12,12-hexamethyl-4H,8H-dibenzo[cd,mn]pyrene (6).[22] We have given this compound the trivial name CTAM (for cyclic-triarylmethane). They used two routes to make this compound. In the first they reacted o-isopropenylbenzoate to give 2,2',2"-triisopropenyltriphenylcarbinol (5). They then formed the ether which resulted from the attack of the oxygen on an isopropylene group (HCl, ether; 70% yield). The ether was reduced and one isopropylidene bridge was formdd (1i, THF; 45% yield). The





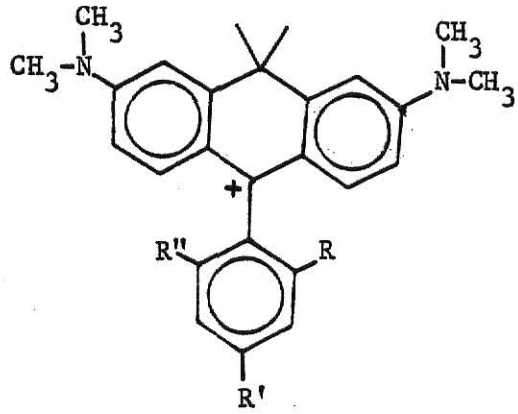
2a R = isopropenyl, R' = R" = H

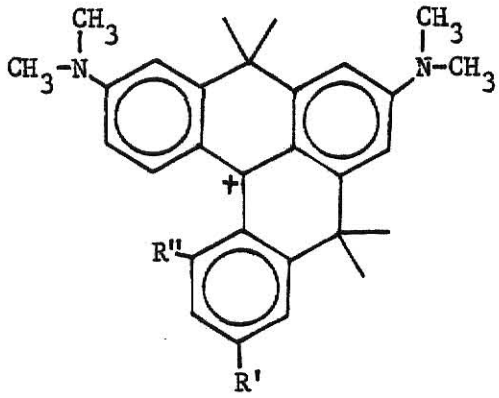
2b R = isopropenyl,
R' = $N(CH_3)_2$, R" = H

2c R = R" = isopropenyl,
R' =

2d R = R' = R" = H

2e R = R" = H, R' = $N(CH_3)_2$





3a R = isopropenyl, R' = R" = H

3b R = isopropenyl,
R' = $N(CH_3)_2$, R" = H

3c R = R" = isopropenyl, R' = H

3d R = R' = R" = H

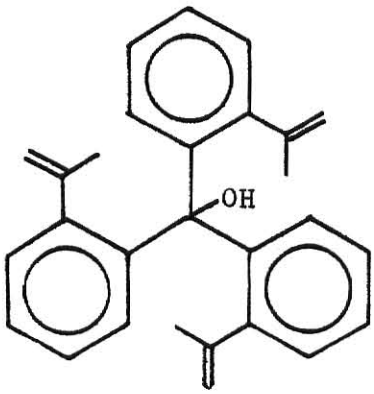
3e R = R" = H, R' = $N(CH_3)_2$

4a R' = R" = H

4b R' = $N(CH_3)_2$, R" = H

Figure 1

cyclization was then completed by closing the other two bridges ($ZnCl_2$, HCl and ether; 14% yield) to give CTAM (6). In the second method, they reacted 2,6-diisopropenylphenyl lithium (2c) with 9,9-dimethylanthrone. The product was treated with AcBr in ether to form the cyclic ether, which was reduced and cyclized as in the first method (overall yield 6.4%).



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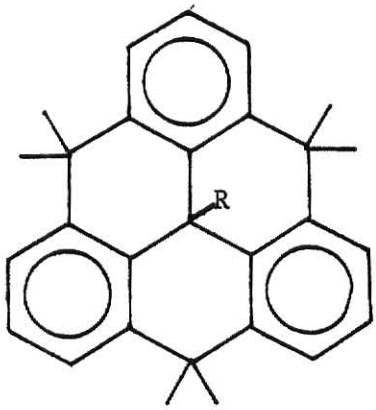


6a R = H

6b R = OH

6c R = +

We undertook this investigation to lay the ground work for further investigations into the synthesis of substituted CTAMs and their testing as analytical indicators. In the past, there has been little work done in using triarylmethanes as redox indicators and there has been no systematic attempt to synthesize them for this purpose. We undertook this project because further investigation into this area appeared very promising.

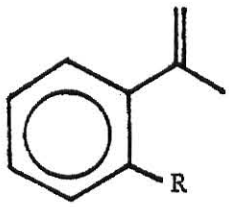
DISCUSSION OF RESULTS

Hellwinkel, Milan and Aulmich prepared CTAM only as a curiousity, and their yield was only 2.4 to 6.4%. The only property that was studied was the e.s.r. of the radical.[23] We needed to prepare large amounts of CTAM so that derivatives could be made and tested as analytical indicators, thus we attempted to devise a route that would give higher yields.

Our initial approach was to make 2,2',2"-triisopropenyltriphenylcarbinol via the intermediate trimethyl ester of triphenyl-2.2',2"-tricarboxylic acid, but we were unable to repeat Weisse and Korczyn's synthesis of the triacid.[24] The preparation of o-tolyphthalide proceeded well. Attempts to repeat the oxidation step of Weisse and Korczyn failed. It appeared that the alkaline permanganate would not wet the phthalide, thus no reaction occurred. Attmpted oxidations with acetic acid solutions of Na_2CrO_7 and $KMnO_4$ also failed. Our experience indicated that a different route might give better results.

Adding o-isopropenylphenylmagnesium chloride (7b) to 3,3-dimethylphthalide (8) was expected to give a triarylcarbinol which could be reduced and cyclized to give CTAM. 3,3-Dimethylphthalide was prepared from phthalic anhydride and CH_3MgI.[25] o-Chlorobenzoic acid was esterified (CH_3OH, H_2SO_4) and reacted with CH_3MgI. The alcohol produced was dehydrated to give o-chloro-α-methylstyrene (7a).[26] Initial attempts to prepare the Grignard (7b) and lithium (7f) reagents from o-chloro-α-methylstyrene proved unsuccessful, so the corresponding bromo Grignard reagent (7d) was made. o-Bromo-α-methylstyrene (7c) was prepared from o-bromo-benzoic acid using the method used for the corresponding chloro compounds. The bromo Grignard reagent (7d) was

prepared and reacted with 3,3-dimethylcarbonate (8). Even with an excess of the Grignard (7d), it only added to the phthalide once, forming a stable hemiketal (9). This hemiketal showed no tendency to form the ketone as was shown by the lack of a carbonyl absorption peak in its IR spectrum.



7a R = Cl

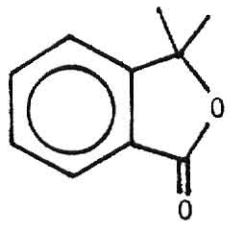
7b R = MgCl

7c R = Br

7d R = MgBr

7e R = CO_2CH_3

7f R = Li



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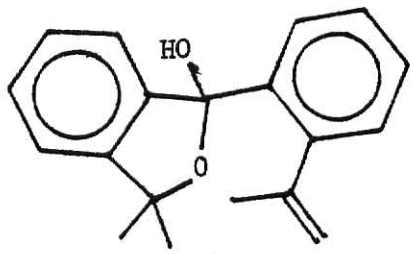

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In order to aviod formation of an unreactive hemiketal, we attampted to prepare 2-isopropenylbenzoic acid, the methyl ester of which (7e) would be reacted with two moles of the Grignard reagent. The preparation of the acid yielded a dark oil. The proton NMR showed that it contained only about 20% of the desired product. Since the yield was low and the separation of the pure compound may

have been difficult, another route was tried.

An attempt was made to react the bromo Grignard (7d) with dimethylcarbonate, but no reaction occurred. Because the Grignard reagents were not giving the desired products, the lithium reagent (7f) was prepared and reacted with dimethylcarbonate to give the desired compound (5) in 100% yield.

The lithium reagent was originally prepared by reacting o-bromo-α-methylstyrene with metallic lithium in ether. A more convenient way to form the lithium reagent is to use a lithium exchange reaction between o-bromo-α-methylstyrene and n-butyl lithium to give the lithium reagent and 1-bromobutane.[27,28] This method was easier to perform in the lab and gave a product of higher purity.

The CTAM carbenium ion (CTAM+), (6c) which resulted from the oxidation of CTAM at the 12c carbon atom was very interesting, as it was completely stable in aqueous HCl. When made basic, the carbinol (6b) formed.

To determine the pK_{R+} of the cation (6c), a solution of the cation in 1:1 ethanol-water was prepared and the absorbance determined at various pH's on a Spectronic 20 at 405 nm. The pK_{R+} was calculated from the relationship $pK_{R+} = pH + \log A/(A_{max}-A)$ where A is the absorbance of the solution and A_{max} is the absorbance of an acidic solution. The average pK_{R+} of eight determinations at pH's from 7.10 to 6.21 was determined to be 6.72 with a standard deviation of 0.03.

The $\log A/(A_{max}-A)$ vs. pH was plotted and a least squares linear regression done to give a pK_{R+} of 6.72, with a correlation coefficient of 0.97.

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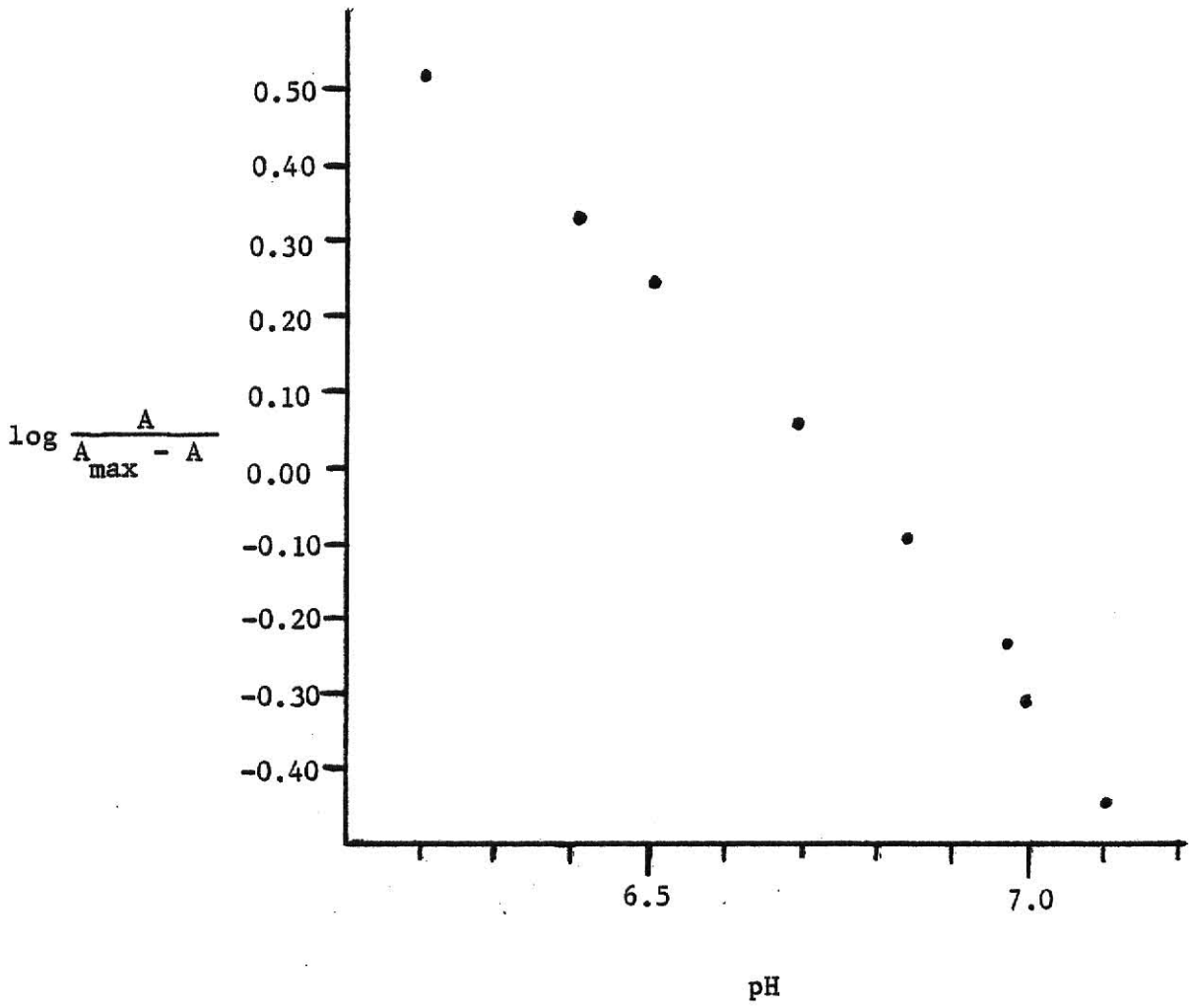
0.50
0.40
0.30
0.20
0.10
0.00
-0.10
-0.20
-0.30
-0.40
log A / (A max - A)
6.5
7.0
pH

This is very unusual, since most carbenium ions are stable only in very acidic solutions. In other "carbenium" ions with a pK_{R+} in this range, the positive charge is mostly on substituent heteroatoms.

If CTAM and its derivatives are to be useful indicators, they should have a λ_{max} in the visible range and have a large ε so that only a minute amount of the indicator is required. The λ_{max} of the carbenium ion was determined to be 405 nm. This is just into the visible range, and any electron donating substituents should produce a hypsochromic shift, giving good colors for analytical indicators. In addition, the introduction of substituents with lone pairs of electrons will make possible a lower energy $n \rightarrow \pi^*$ and give another absorption band at longer wavelength. The $E_1^{1\%}$ cm was determined to be 697. The ε could not be determined because it was not known what anion was associated with the carbenium ion. If the anion was chloride, the ε would be 27,000.

After CTAM had been prepared in good yield, we needed to derivatize it. It would be desirable to develop a route by which we could make a large number of derivatives so that they could be tested as analytical reagents. There are two ways to make derivatives of CTAM. One is to start with o-bromoisopropenylbenzene, and the other is to derivatize CTAM itself.

We first tried to carry out substitutions on the aromatic rings of CTAM. Substitution should occur in the 2, 6, and 10 positions, as attack at the other positions (1, 3, 5, 7, 9, and 11) is sterically hindered by the isopropylidene bridges, although these positions may be favored by electronic effects.[29] Nitration to give the 2,6,10-trintro derivative was attempted. We chose this compound because it could be reduced to give the amine which could be converted to many

other derivatives via the diazonium ion. Several nitration methods were tried without success, including HNO_3, HNO_3-H_2SO_4 and nitronium fluoroborate in sulfolane.[31] The product isolated from these reactions was the carbenium ion CTAM+ (6c) or the carbinol (6b) resulting from the oxidation of the central carbon atom. Apparently the nitrating agent oxidized CTAM before substitution could take place, with the resulting positive charge deactivating the rings so that an electrophilic reaction could not take place.[32] We also tried without success, direct dimethylamination with dimethylchloroamine and $AlCl_3$,[33] bromination with Br_2 and with pyridinium bromide perbromide.

The electrophilic substitution of CTAM was not proceeding well so we attempted to make derivatives by starting with substituted o-bromo-α-methylstyrene. 2-Bromo-5-methoxy-α-methylstyrene was prepared from m-methoxybenzoic acid and reacted with n-butyl lithium to give the corresponding lithium reagent. This lithium reagent was added to dimethylcarbonate to give 4,4',4"-trimethoxy-2,2',2"-triisopropenyltriphenylcarbinol, but attempted cyclization of this compound was not successful.

It appeared that the carbinol was reacting with the acid before cyclization and reduction could occur. When HCl was added to a solution of the carbinol, the solution initially turned purple, then the color slowly faded. Removal of the solvent from the resulting colorless solutions yielded an unidentified white solid. Attempting reduction and cyclization in the absence of HCl yielded only starting material.

This method of making derivatives of CTAM by starting with substituted o-bromo-α-methylstyrenes should work with substituents which do not change the reactivity as much as does the methoxy group.

5-Methyl or 5-chloro derivatives of 2-bromo-α-methylstyrene should give carbinols which can be cyclized to give substituted CTAMs. From these many other derivatives can be made.

CONCLUSION

We have succeeded in synthesizing 12,12c-dihydro-4,4,8,8,12,12-hexamethyl-4H,8H-dibenzo[cd,mn]pyrene in greatly improved yield while simplifying the reaction sequence. Using our synthetic route it should be possible to derivatize CTAM. The use of these CTAM derivatives as analytical indicators appears very promising. Even without substituents CTAM+ has a λ_{max} in the visible range (405 nm) and an $E^{1\%}_{1\ cm}$ of 696.

EXPERIMENTAL

3,3-di-o-tolylphthalide.[34,35] To a stirred, refluxing suspension of 36.5 g (1.5 mol) of magnesium turnings in 100 mL of tetrahydrofuran (THF) under nitrogen was added dropwise over 2½ hours a solution of 126.6 g (1.00 mol) of o-chlorotoluene and 47.0 g (0.25 mol) of 1,2-dibromoethane in 300 mL of THF. To this mixture was added in small portions over 5½ hours a solution of 47.0 g (0.25 mol) of 1,2-dibromoethane in 100 mL of THF. To the resulting Grignard reagent was added dropwise a solution of 59.0 g (0.40 mol) of phthalic anhydride in 380 mL of THF. After standing overnight dilute HCl was added until the mixture was acidic, and the layers were separated. The solvent was removed from the organic layer under vacuum. To the residue was added 200 mL of ether. The resulting crystals were filtered, washed with ether and dried to give 45.5 g (36%) of the product as a tan solid. Crystallization from hexanes gave yellow crystals; mp 171-172°C; lit mp 128-131°C;[34] NMR δ 8.1-6.9 (m,12), 2.12 (s,6); IR 2930, 1730, 1430, 1160, 1105 cm^{-1}.

3,3-Dimethylphthalide (8).[25] To a stirred solution of 29.6 g (0.200 mol) of phthalic anhydride in 1 L of ether under nitrogen was added 160 mL of 2.8 $\pm$ 0.3 M CH_3MgI in ether dropwise with cooling. After stirring at room temperature for two hours. 6N HCl was added dropwise until the white precipitate dissolved. The layers were separated and the ether layer was washed with dilute HCl then with several portions of 5% $NaHCO_3$. The ether layer was filtered through Na_2SO_4 and the solvent was removed under vacuum. Crystallization of the residue from a mixture of hexanes gave 11.4 g (35%) of the product as white crystals; mp 67.5-68°C; lit mp 67-68°C;[25] NMR δ 8.0-7.3 (m,4), 2.07 (s,6); IR 2950,

1720, 1270, 1230, 1110, 1080, 1030, 940, 845, 755 cm^{-1}. A second crop from the mother liquid gave 5.8 g (18%) of the product as yellow crystals.

Methyl o-chlorobenzoate. A solution of 31.2 g (0.20 mol) of o-chlorobenzoic acid, 12 mL of concentrated H_2SO_4 and 150 mL of methanol was heated under reflux for 5 hours. The solution was cooled and poured into 500 mL of 10% Na_2CO_3. The layers were separated and the aqueous layer extracted with ether. The combined organic solutions were washed with saturated NaCl, dried (Na_2SO_4) and the solvent was removed under vacuum. The residue was distilled to give 28.6 g (84%) of the product as a colorless liquid; bp 81-82°C (1.8 mm); lit bp 234-235°C, (762.4 mm); NMR δ 7.9-7.6 (m,1), 7.4-7.0 (m,3), 3.85 (s,3); IR 2950, 1710, 1410, 1270, 1230, 1100, 1040, 740 cm^{-1}.

1-(o-Chlorophenyl)-1-methylethanol.[26] To a stirred solution of 25.1 g (0.16 mol) of methyl o-chlorobenzoate in 500 mL of ether under nitrogen was added with cooling 135 mL of 2.8 $\pm$ 0.3N CH_3MgI in ether. After 2 hours at room temperature, dilute HCl was added to dissolve the precipitate and the layers were separated. The aqueous layer was extracted twice with ether. The combined ether solutions were washed with saturated NaCl, dried (Na_2SO_4) and the solvent removed under vacuum to give 23.2 g (92%) of the product as a yellow liquid, which was used in subsequent reactions without further purification. Distillation of a small portion gave the product as a colorless liquid; bp 80-85°C (2.2 mm); lit bp 126-130°C (30 mm);[26] NMR δ 7.8-7.5 (m,1), 7.4-6.9 (m,3), 2.88 (s,1), 1.67 (s,6); IR 3350, 2970, 1425, 1355, 1270, 1170, 1030, 950, 850, 750 cm^{-1}.

o-Chloro-α-methylstyrene (7a).[26] To a refluxing solution of 10.2 g (0.060 mol) of 1-(o-chlorophenyl)-1-methylethanol and 0.35 mL of concentrated H_2SO_4 in 60 mL of acetic acid was added in small portions over a 4 hour period 16 g of zinc dust. The mixture was poured into 450 mL of 20% NaOH and steam distilled. The distillate was extracted with ether. The ether extract was washed with saturated NaCl, dried (Na_2SO_4) and the solvent removed under vacuum to give 7.9 g (87%) of the product as a colorless liquid; bp 97-102°C (45 mm); lit bp 182-184°C,[26] NMR δ 7.5-7.0 (m,4), 5.20 (m,1), 4.95 (m,1), 2.05 (m,3); IR 2980, 1640, 1465, 1420, 1040, 900, 755, 732 cm^{-1}.

Methyl o-bromobenzoate. The general procedure for esterification (page 17), with the reflux period increased to 22 hours, was used with 160.7 g (0.799 mol) of o-bromobenzoic acid to give 163.1 g (95%) of the product as a colorless liquid; bp 104-106°C (3.4 mm), lit. bp 114°C (15 mm);[37] NMR δ 7.8-7.1 (m,4), 3.87 (s,3); IR 2980, 1735, 1600, 1290, 1250, 740 cm^{-1}.

1-(o-Bromophenyl)-1-methylethanol. The general procedure for the addition of a Grignard reagent to an ester (page 17), using CH_3MgBr rather than CH_3MgI/ was used with 81.7 g (0.40 mol) of methyl o-bromobenzoate to give 80,1 g of a dark oil. This was used in subsequent reactions without further purification. Distillation of a small portion gave the product as a colorless liquid; bp 97-101°C (3.0 mm), lit. bp 112°C (5.2 mm);[38] NMR δ 7.8-6.8 (m,4), 3.21 (s,1), 1.71 (s,6); IR 3400, 2950, 1455, 1425, 1360, 1270, 1170, 1020, 950, 850, 755, 720 cm^{-1}.

o-Bromo-α-methylstyrene (7c). The general procedure for the dehydration of a tertiary alcohol (page 18) was used with 50.0 g of unpurified 10(o-bromophenyl)-1-methylethanol to give 35.4 g (72% from methyl o-bromobenzoate) of the product as a colorless liquid; bp 80-84°C (12 mm), lit. bp 80°C (1 mm);[37] NMR δ 7.7-7.0 (m,4), 5.20 (m,1), 4.92 (m,1), 2.07 (m,3); IR 3115, 3010, 1640, 1460, 1016, 897, 753 cm^{-1}.

2,5-Dihydro-5,5-dimethyl-2-(2-isopropenylphenyl)-benzo[c]furan (9). To 0.7 g (0.029 mol) of magnesium, 5 mL of THF and three drops of 1,2-dibromoethane was added with stirring under N_2 a solution of 5.4 g (0.027 mol) of o-bromo-α-methylstryene in 40 mL of ether. After most of the magnesium had been consumed, 2.3 g (0.014 mol) of 3,3-dimethylphthalide in 25 mL of ether was added dropwise with cooling. After heating under reflux for 2 hours, 15 mL of water was added dropwise with cooling and the layers were separated. The ether layer was washed with saturated NaCl, dried (Na_2SO_4) and the solvent removed under vacuum. The residue was crystallized from hexanes to give 3.1 g (79%) of the product as yellow crystals; mp 69.5-70.0°C; NMR δ 7.5-6.9 (m,9), 5.12 (m,1), 4.87 (m,1), 4.41 (s,1), 2.22 (m,3), 1.61 (s,3) 1.51 (s,3); IR 3350, 2950, 1350, 1255, 1215, 1180, 1145, 1080, 1025, 970, 940, 894, 837, 747 cm^{-1}; Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.42; H, 7.40.

Attempted preparation of 2-isopropenylbenzoic acid (39). To 14.8 g (0.10 mol) of phthalic anhydride in 500 mL of ether was added under N_2 with stirring 75 mL (0.225 mol) of 3N CH_3MgI in ether. The ether was removed by distillation and the residue heated to 190-210°C under vacuum (1.4 mm) for 2 hours. To the residue was added 400 mL of water and this dark slurry was extracted with ether. The ether

extract was washed with 20% NaOH, dried (Na_2SO_4) and the solvent removed under vacuum to give 6.8 g of a dark oil which was shown by NMR to be mostly 3,3-diemthylphthalide. The aqueous solution remaining after extraction was made acidic and extracted with ether. The ether extract was washed with saturated NaCl, dried (Na_2SO_4) and the solvent removed under vacuum to give 6 g of a dark oil. Proton NMR showed it to contain only about 20% of the desired product.

Attempted reaction of o-isopropenylphenyl magnesium bromide with dimethylcarbonate (preparation of α-methylstyrene). To 0.75 g (0.030 mol) of magnesium turnings was added under N_2 with stirring a solution of 5.7 g (0.029 mol) of o-bromo-α-methylstyrene and three drops of 1,2-dibromoethane in 40 mL of tetrahydrofuran. After nearly all of the magnesium had been consumed 0.65 g (0.0073 mol) of dimethylcarbonate in 20 mL of THF was added dropwise and the mixture heated under reflux for four hours. 50 mL of water was added dropwise with cooling and the mixture extracted twice with ether. The ether extract was washed with saturated NaCl, dried (Na_2SO_4) and the solvent removed under vacuum. Distillation of the residue gave 1.7 g (51%) of α-methylstyrene; bp 50-60°C (15 mm), lit. bp 60-61°C (17 mm);[40] NMR δ 7.6-7.0 (m,5), 5.32 (s,1), 5.03 (m,1), 2.12 (m,3); IR 3070, 1630, 1485, 1430, 1370, 1020, 880, 770, 724, 695 cm^{-1}.

2,2',2"-Triisopropenyltriphenylcarbinol (5). Method A: To a stirred suspension of 0.75 g (0.11 mol) of lithium in 10 mL of ether under argon was added dropwise 7.88 g (0.040 mol) of o-bromo-α-methylstryene in 40 mL of ether. After formation of the lithium reagent was complete, 1.0 g (0.012 mol) of dimethylcarbonate in 20 mL of ether was added dropwise. 30 mL of water was added and the layers were separated.

The ether layer was washed with saturated NaCl, dried (Na_2SO_4) and the solvent removed under vacuum to give 5.1 g (100%) of the product as yellow crystals; mp 99-104°C. Method B: To a solution of 8 mL (0.040 mol) of 5N n-butyl lithium in hexane and 200 mL of ether under argon was added 7.88 g (0.040 mol) of o-bromo-α-methylstyrene in 30 mL of ether. After 45 seconds, 1.0 g (0.012 mol) of dimethylcarbonate in 20 mL of ether was added and the mixture was stirred at room temperature for 20 minutes. 200 mL of water was added and the layers were separated. The ether layer was washed with saturated NaCl, dried (Na_2SO_4) and the solvent and n-butyl bromide were removed under vacuum. Crystallization of the residue from methanol gave 3.1 g (61%) of the product as white crystals. A second crop from the mother liquod gave 0.9 g (18%) of the product as yellow crystals; mp 111-113°C; NMR δ 7.3-6.6 (m,9), 4.77 (m,3), 4.33 (s,1), 4.10 (m,3), 1.90 (m,9); IR 3500, 2970, 1630, 1430, 1025, 895, 758 cm^{-1}.

12,12c-Dihydro-4,4,8,8,12,12-hexamethyl-4H,8H-dibenzo[cd,mn]pyrene (6a). To a refluxing solution of 1.0 g (0.0026 mol) of 2,2',2"-tri-isopropenyltriphenylcarbinol and 9 ml of 6N HCl in 200 mL of acetic acid was added in small portions over a four hour period 1.0 g (0.015 mol) of zinc dust, 6 mL of 50% NaOH was added and most of the acetic acid was removed by distillation. The residue was made basic with 180 mL of 14% NaOH and extracted with ether. The ether extract was washed with saturated NaCl, dried (Na_2SO_4) and the solvent removed under vacuum. The residue was purified by column chromatography (activity 1 alumina, petroleum ether; CH_2CI_2, 9:1) to give 0.96 g (100% the yield may be reduced to 80% with the impurities being removed during the column chromatography); mp 174-177°C on rapid heating, liq. mp darkens at

180°C and forms a black melt at 200°C;[22] NMR δ ($CDCl_3$) 7.6-7.1 (m,9), 5.00 (s,1), 1.97 (s,9), 1.38 (s,9), (CS_2) 7.5-7.0, 4.80, 1.88, 1.30, lit. NMR δ ----, 4.85, 1.88, 1.31;[22] IR 3000, 1590, 1450, 1060, 770, 718 cm^{-1}.

Determination of the pK_{R+} of the 12,12c-dihydro-4,4,8,8,12,12-hexamethyl-4H,8H-dibenzo[cd,mn]pyrenyl cation (6c). A solution of the cation in 1:1 ethanol water was prepared and the absorbance determined at various pHs on a Spectronic 20 at 405 nm. The pK_{R+} was calculated from the relationship $pK_{R+} = pH + \log A/(A_{max} - A)$ where A is the absorbance of the solution and A_{max} is the absorbance of an acidic solution. The average pK_{R+} of eight determinations of pHs from 7.10 to 6.21 was determined to be 6.72 with a standard deviation of 0.03.

A	pH	pK_{R+}
0.114	7.10	6.656
0.142	6.99	6.682
0.160	6.97	6.741
0.193	6.83	6.739
0.230	6.69	6.749
0.274	6.50	6.641
0.293	6.40	6.727
0.330	6.21	6.724
0.431	<4.60	

Attempted Nitration of CTAM. Method A: To a solution of 0.2 g of CTAM in 100 mL of acetic acid and 6 mL of concentrated H_2SO_4 was added 20 drops of 70% HNO_3 with stirring and cooling. After 15 minutes the solution was poured over ice and partially neutralized with 250 mL or 20% NaOH, and extracted with ether. The ether extract was washed

with 5% $NaHCO_3$, dried (Na_2SO_4), and the solvent removed under vacuum. The only product isolated was 12c-hydroxy-CTAM. Method B: To a solution of 0.83 g (0.0025 mol) of CTAM in 70 g of sulfolane was added, under N_2, 1.0 g (0.0075 mol) of $NO_2^+BF_4^-$ in 30 mL of sulfolane. After 30 minutes at room temperature, 200 mL of water was added. Extraction of the sulfolane-water solution with hexane and ether yielded only sulfolane. The sulfolane-water solution was concentrated by vacuum distillation of the water and solfolane and the residue was crystallized from chloroform-ethylacetate to give 0.7 g of the carbenium ion CTAM+; NMR δ 8.17 (s,9), 1.93 (s,18); IR 1580, 1475, 1390, 1300, 1050 cm^{-1}.

Attempted dimethylamination of CTAM.[33] To 0.5 g of CTAM in 15 mL of nitrobenzene was added a solution of 0.7 g (0.005 mol) of $AlCl_3$ and 0.4 g (0.005 mol) of dimethylchloroamine in 15 mL of nitrobenzene and the mixture heated under N_2 to 60-70°C for 3 hours. The solution was extracted with acidic water. This extract was made basic and extracted with ether. The ether extract was dried (Na_2SO_4) and the solvent removed under vacuum to give 0.1 g of 12c-hydroxy-CTAM.

Attempted bromination of CTAM. To a solution of 0.2 g (0.0005 mol) of CTAM in 30 mL of CCl_4 was added with stirring a solution of 0.24 g (0.0015 mol) of Br_2 in 10 mL of CCl_4 and 1.0 g of reduced iron. After the solution became clear and a brown precipitate had formed the iron was removed and the solvent was removed under vacuum to give 0.1 g of 12c-hydroxy CTAM (6b).

2-Bromo-5-methoxybenzoic acid (42). To a stirred solution of 88.0 g (0.58 mol) of m-methoxybenzoic acid in 550 mL of acetic acid was added 94.3 g (0.59 mol) of bromine in 260 mL of acetic acid. To this, 550 of water was added and the solution was heated to boiling,

then slowly cooled. The crystals which precipitated were filtered (vacuum), washed (acetic acid-water, 1:1), and dried to give 105 g of the product as light tan crystals; mp 154-156°C; lit mp 158-160°C.[41] NMR δ 12.5 (S,1), 7.53 (d,1, J = 8.4 Hz), 7.30 (d,1, J = 3.2 Hz), 6.93 (d of d,1, J = 8.4, 3.2 Hz); IR 2985, 2675, 1690, 1275, 1040 cm^{-1}.

Methyl 2-bromo-5-methoxybenzoate.[42] The general procedure for esterification (page 17), with the reflux period increased to 17 hours, was used with 100.0 g (0.433 mol) of 2-bromo-5-methoxybenzoic acid to give 105.7 g (100%) of the product as a colorless liquid; bp 104-106°C (3.4 mm), lit. bp 114° (15 mm); NMR δ 7.49 (d,1, J = 8.0 Hz), 7.27 (d,1, J= 3.4 Hz), 6.83 (d of d,1, J = 8.0, 3.4 Hz), 4.89 (s,3), 4.78 (s,3); IR 2950, 1730, 1465, 1430, 1320, 1280, 1245, 1225, 1105, 1050, 1020 cm^{-1}.

1-(2-Bromo-5-methoxyphenyl)-1-methylethanol. The general procedure for the addition of a Grignard reagent to an ester (page 17), using CH_3MgBr rather than CH_3MgI, was used with 105.7 g (0.422 mol) of methyl 2-bromo-5-methoxybenzoate to give 103.4 g (98%) of the product as a green solid. This was used in subsequent reactions without further purification. Crystallization of a small portion gave the product as white crystals; mp 95.5-96.0°C; NMR δ 7.43 (d,1, J = 8.8 Hz), 7.24 (d,1, J = 3.4), 6.61 (d of d,1, J = 8.8, 3.4 Hz), 3.77 (s,3), 2.53 (s,1), 1.72 (s,6); IR 3350, 2950, 1550, 1445, 1280, 1230, 1050, 1035, 1005, 878, 796 cm^{-1}. Anal. Calcd. for $C_{10}H_{13}BrO_2$: C, 49.00; H, 5.35; Br, 32.60. Found: C, 49.09; H, 5.46; Br, 32.44.

2-Bromo-5-methoxy-α-methylstyrene. The general procedure for the dehydration of a tertiary alcohol (page 18) was used with 50.0 g (0.204 mol) of unpurified 1-(2-bromo-5-methoxyphenyl)-1-methanolethanol to give 37.6 g (81%) of the product as a colorless liquid; bp 97-99°C

(4.4 mm); NMR δ 7.6-6.4 (m,3), 5.17 (m,1), 4.92 (m,1), 3.74 (s,3), 2.05 (m,3); IR 2990, 1600, 1570, 1460, 1220, 1040, 1015 cm^{-1}: Anal. Calcd. for $C_{10}H_{11}BrO$: C, 52.89; H, 4.88; Br, 35.18. Found: C, 53.07; H, 5.03; Br, 34.92.

4,4',4"-Trimethoxy-2,2',2"-triisopropenyltriphenylcarbinol. The general method for the synthesis of a traiaryl carbinol (page , method B) was used with 7.6 g (0.033 mol) of 2-bromo-5-methoxy-α-methylstyrene to give 2.9 g (56%) of the product as white crystals; mp 170-172°C; NMR δ 6.8-6.4 (m,9), 4.77 (m,3), 4.13 (m,3), 3.75 (s,9), 1.88 (s,9); IR 3630, 3000, 1600, 1550, 1470, 1205, 1060, 1020, 893 cm^{-1}; Anal. Calcd. for $C_{31}H_{34}O_4$: C, 79.12; H, 7.28. Found: C, 79.12; H, 7.23.

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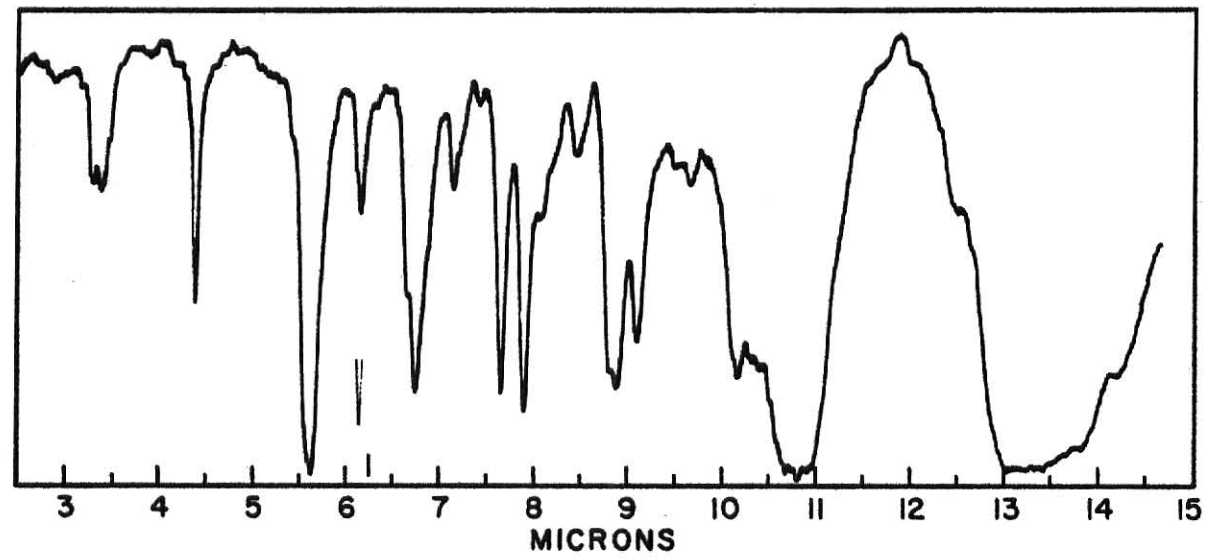
INFRARED SPECTRA

3,3-Ditolylphthalide

(Thin film in $CDCl_3$)

3,3-Dimethylphthalide

(KBr)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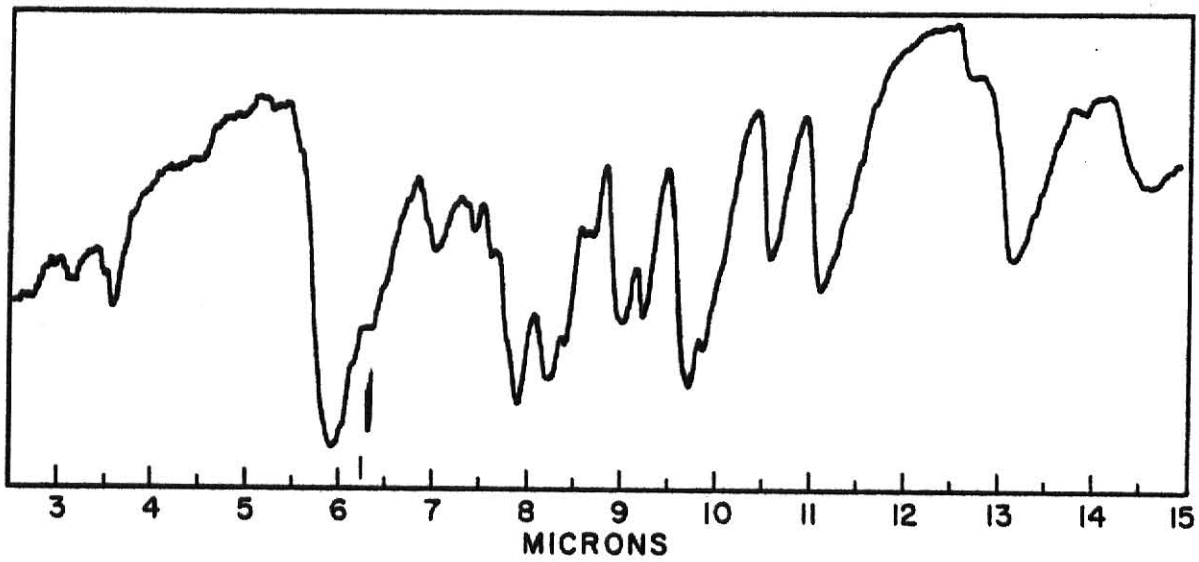
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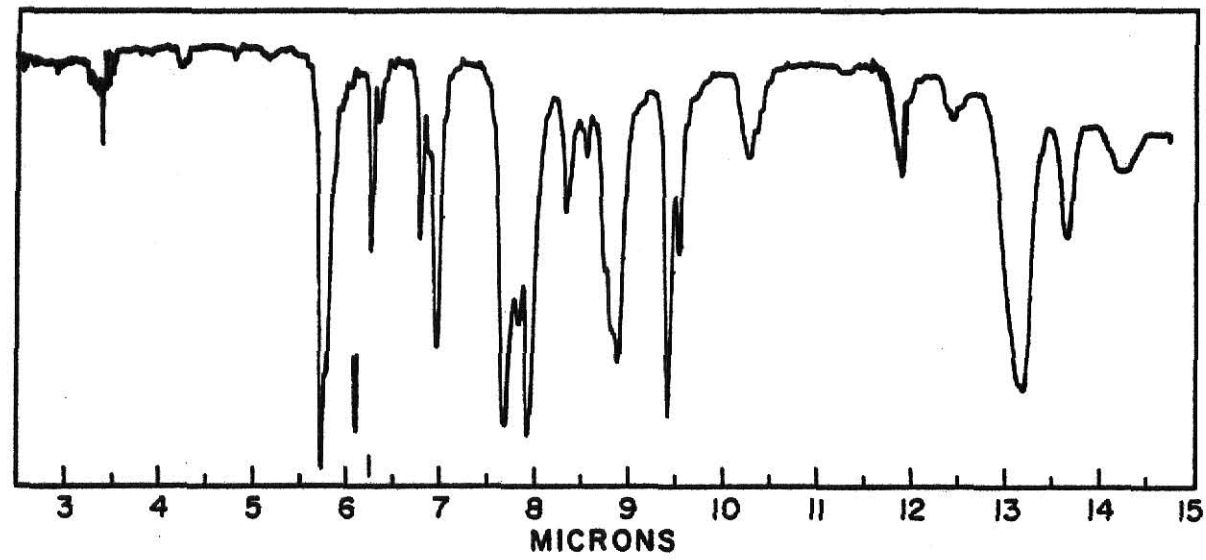
INFRARED SPECTRA

Methyl o-chlorobenzoate

(Thin film)

1-(o-Chlorophenyl)-1-methylethanol

(Thin film)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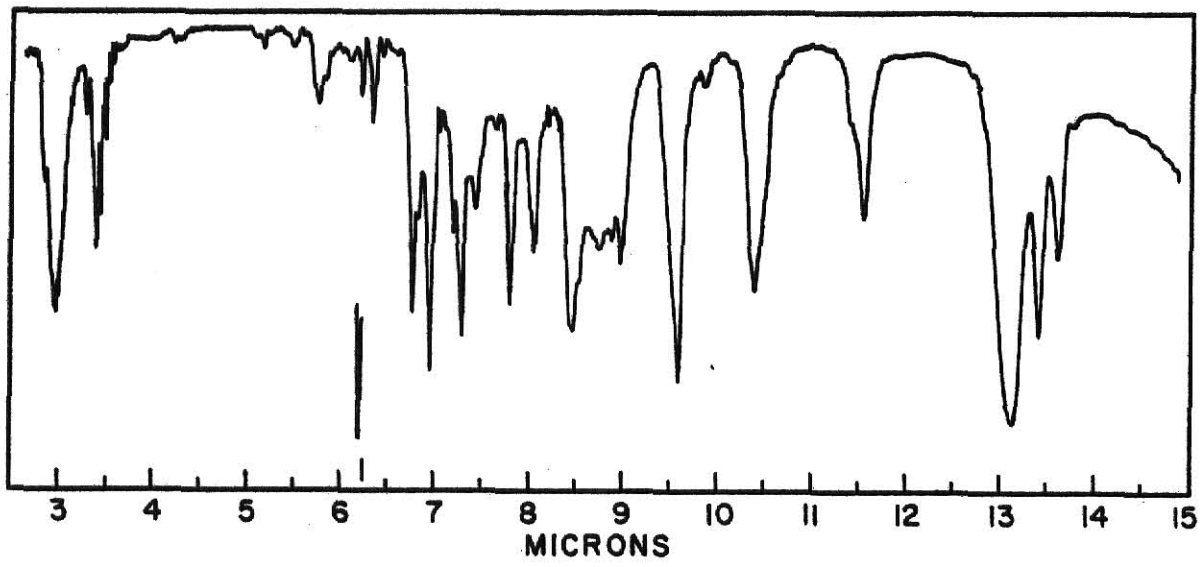
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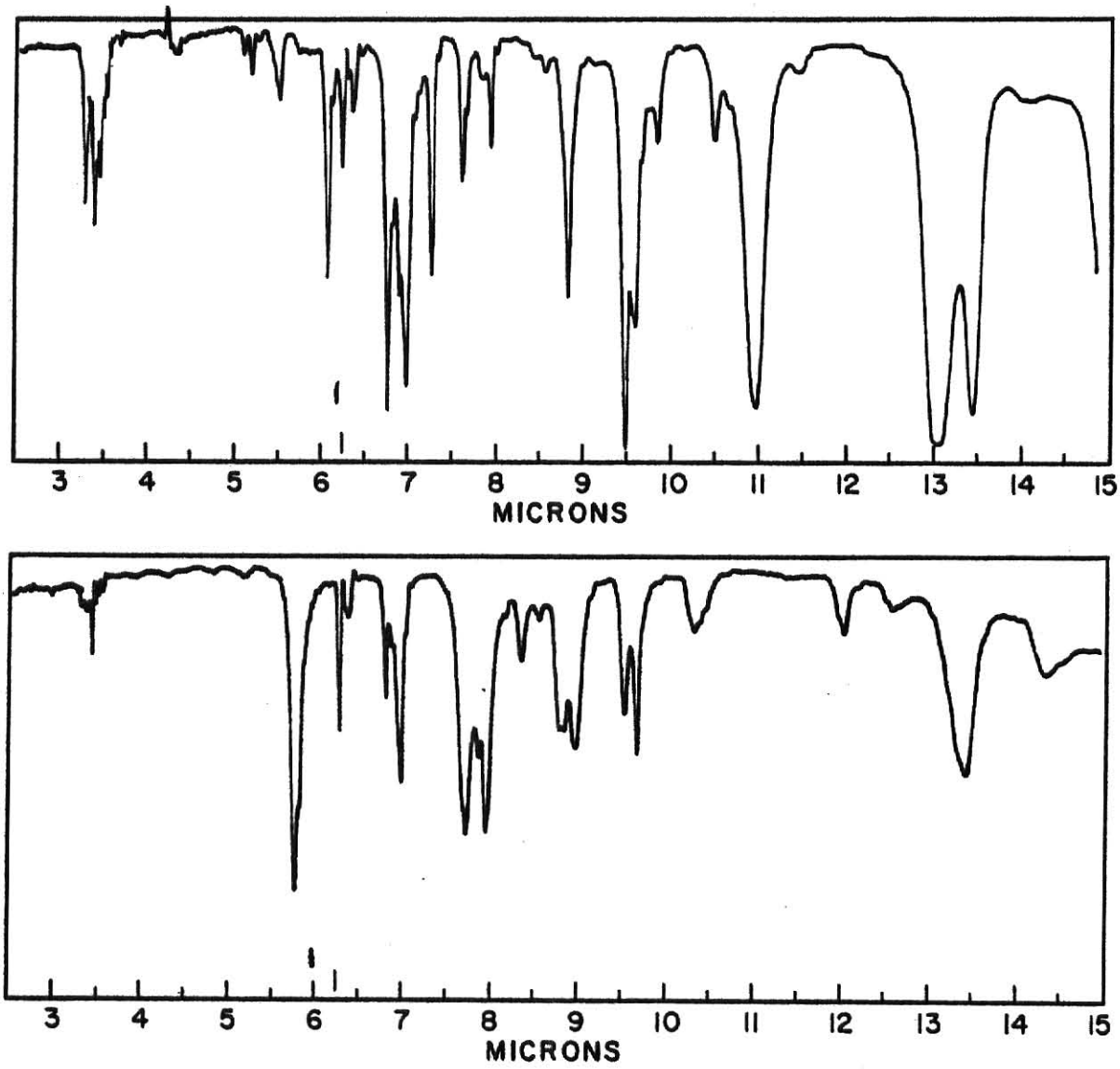
INFRARED SPECTRA

o-Chloro-α-methylstyrene

(Thin film)

Methyl o-bromobenzoate

(Thin film)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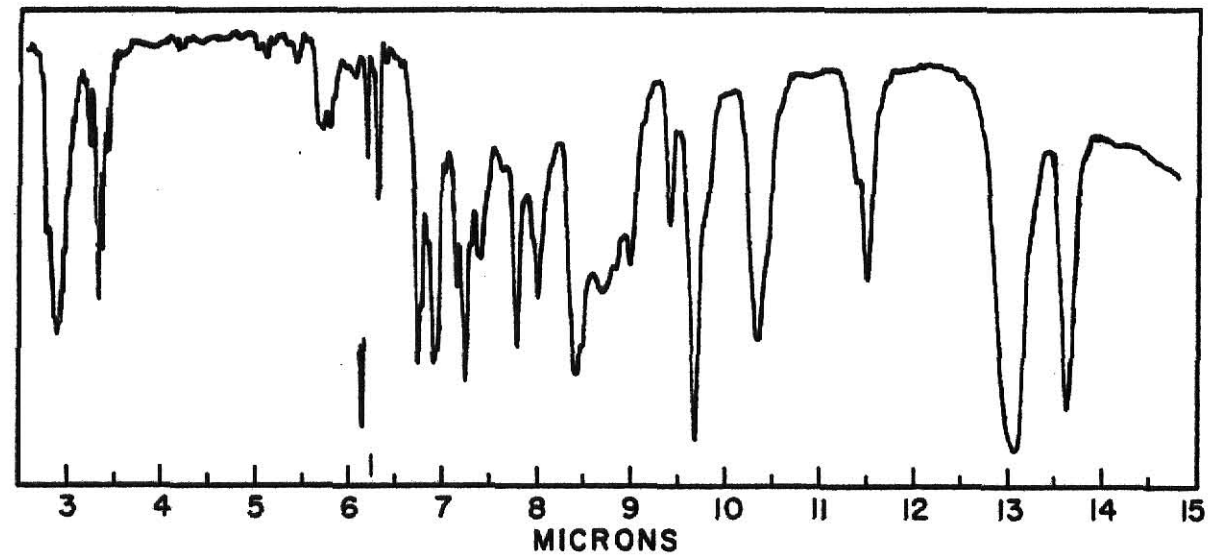
INFRARED SPECTRA

1-(o-Bromophenyl)-1-methylethanol

(Thin film)

o-Bromoα-methylstyrene

(Thin film)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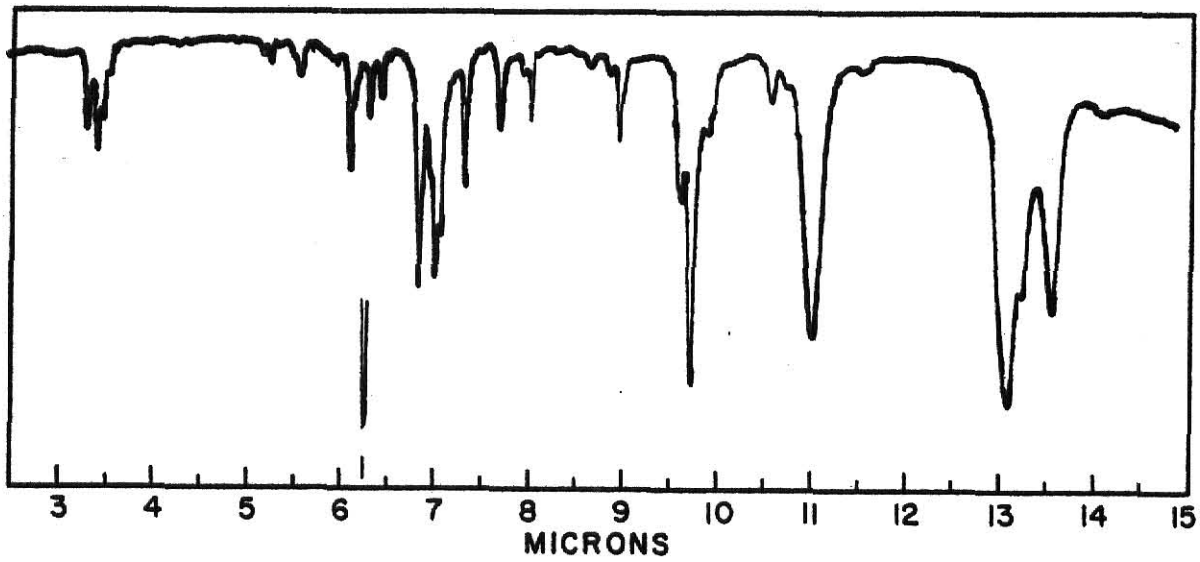
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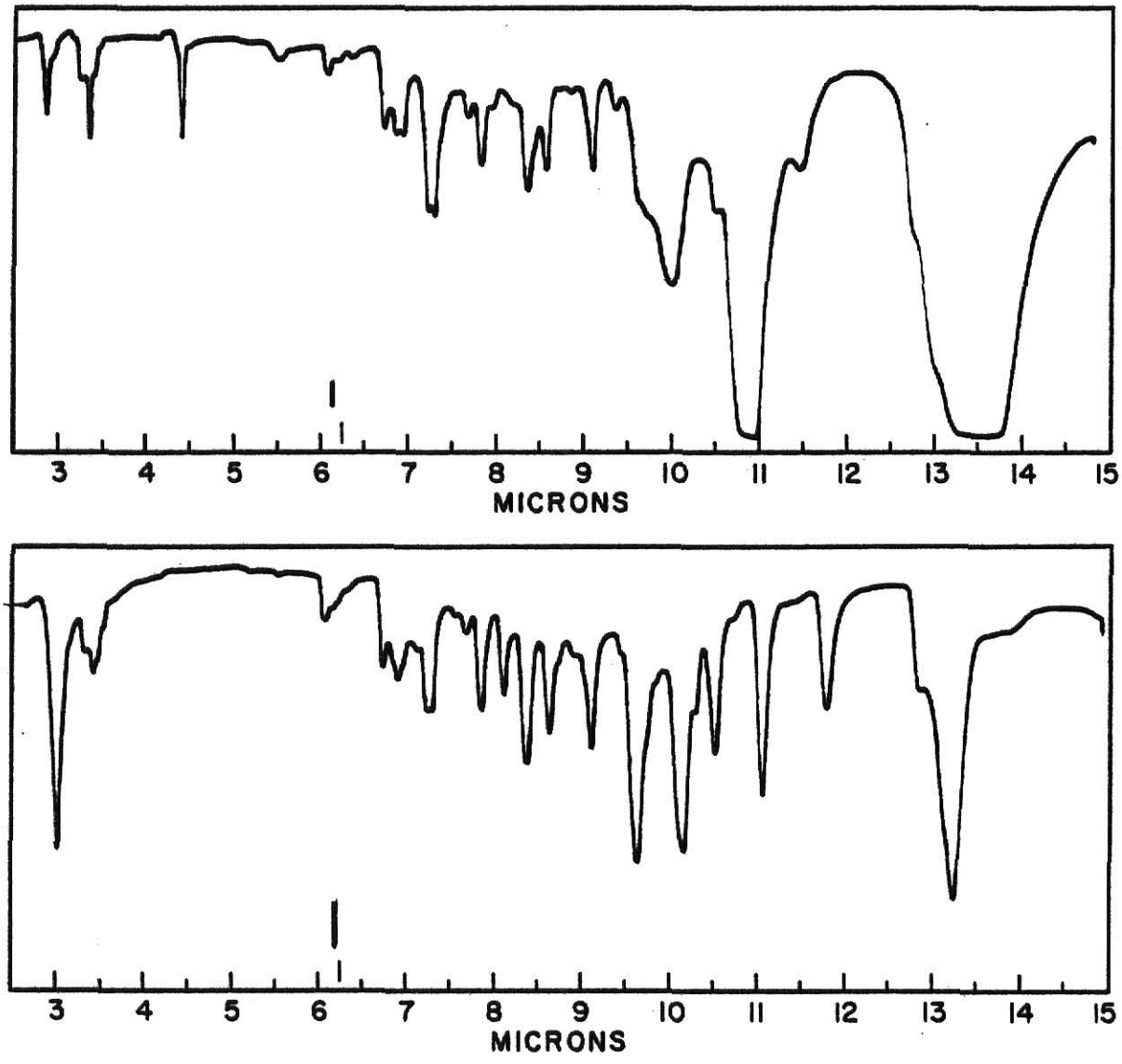
INFRARED SPECTRA

2,5-Dihydro-5,5-dimethyl-2-hydroxy-2-(2-iso-propenylphenyl)-benzo[c]furan

(Thin film in $CDCl_3$)

2,5-Dihydro-5,5-dimethyl-2-hydroxy-2-(2-iso-propenylphenyl)-benzo[c]furan

(KBr)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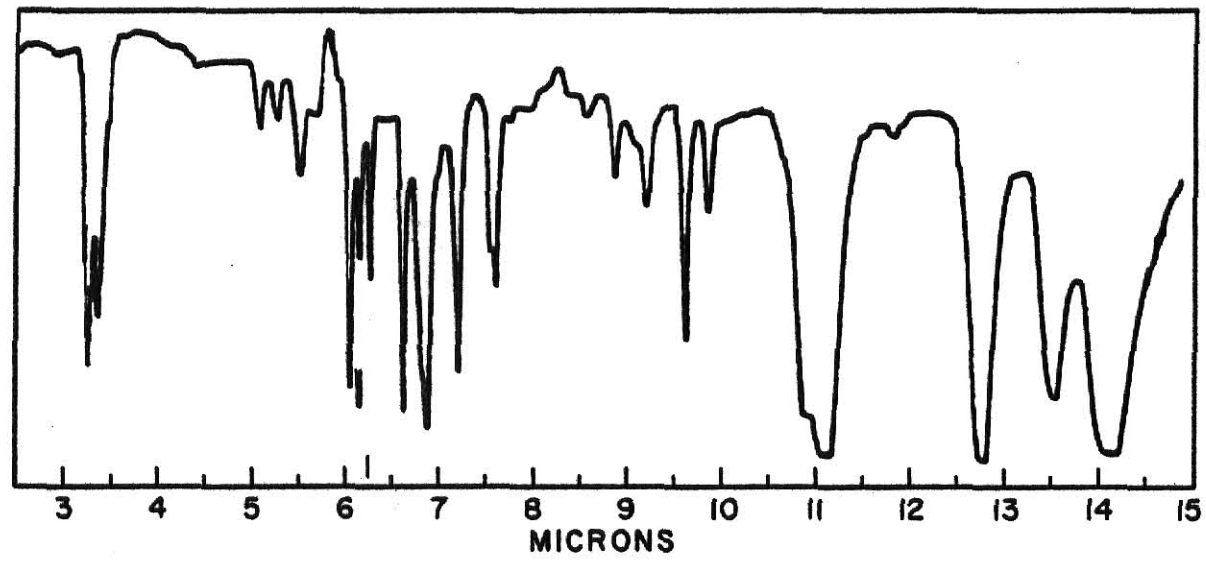
INFRARED SPECTRA

α-Methylstyrene

(Thin film)

2,2',2"-Triisopropenyltriphenylcarbinol

(KBr)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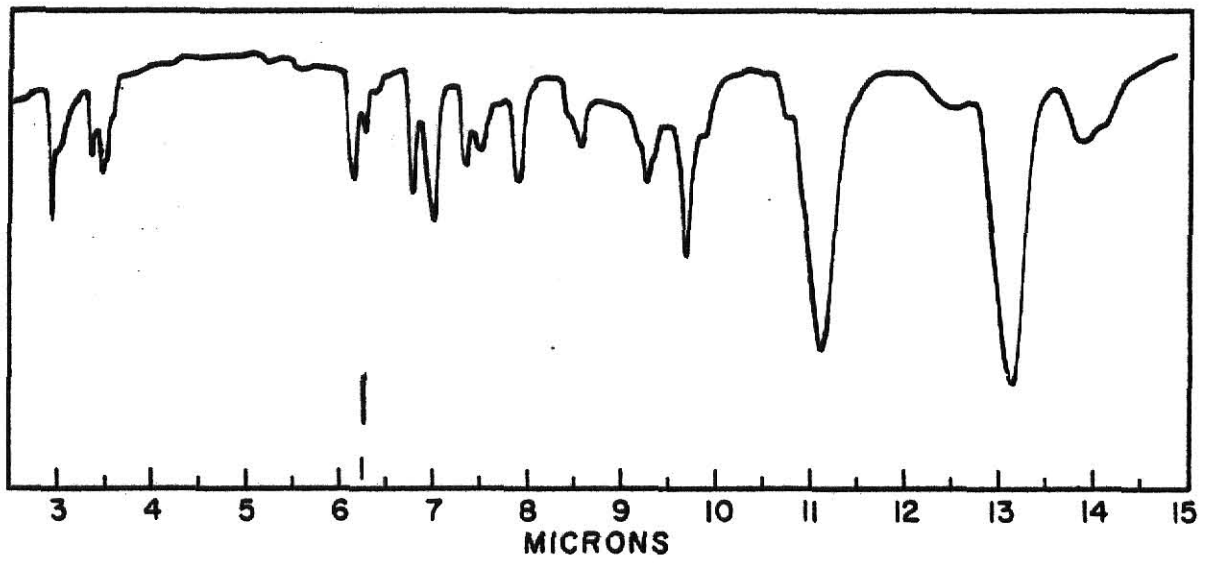
14
15
MICRONS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14
15
MICRONS

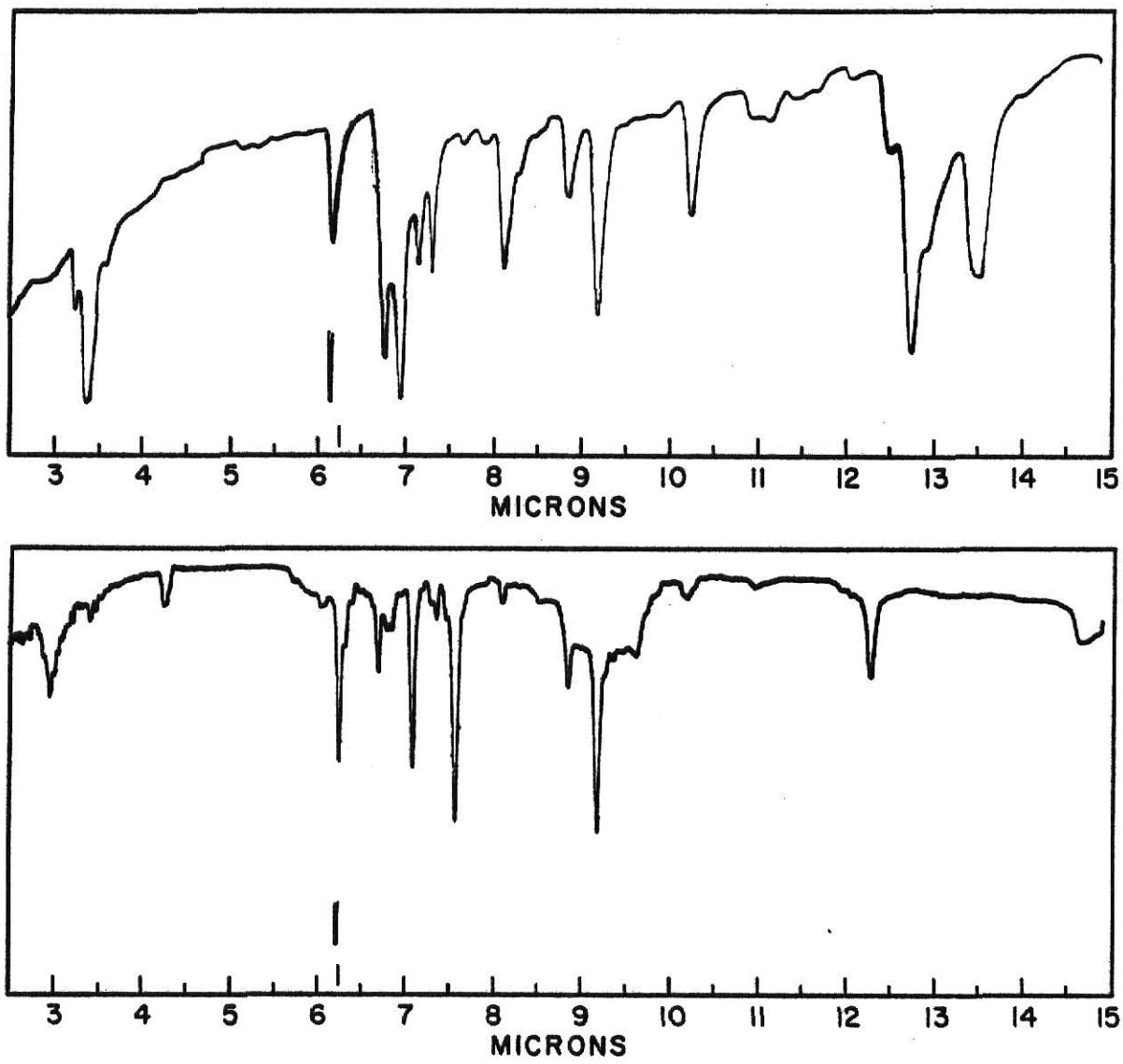
INFRARED SPECTRA

12,12c-Dihydro-4,4,8,8,12,12-hexamethyl-4H,8H-dibenzo[cd,mn]pyrene

(KBr)

12,12c-Dihydro-4,4,8,8,12,12-hexamethyl-4H,8H,-dibenzo[cd,mn]pyrenyl cation

(KBr)


3
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12
13
14
15
MICRONS
3
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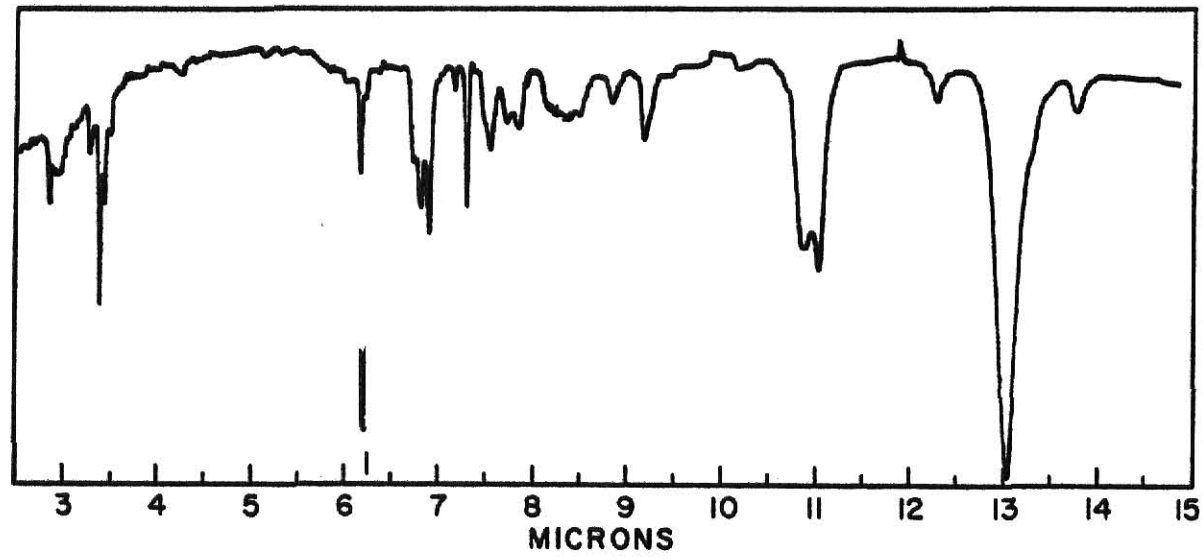
11
12
13
14
15
MICRONS

INFRARED SPECTRA

12c-Hydroxy-12,12c-dihdro-4,4,8,8,12,12-hexa-
methyl-4H,8H-dibenzo cd,mn pyrene
(KBr)

2-Bromo-5-methoxybenzoic acid
(KBr)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12
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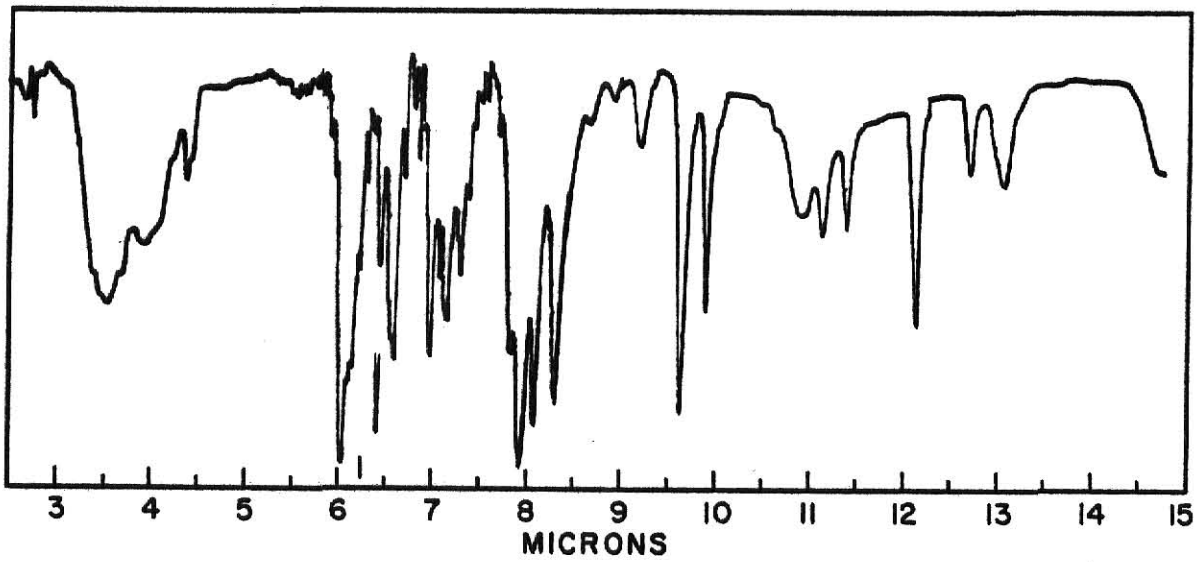
MICRONS


3
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11
12
13
14
15
MICRONS

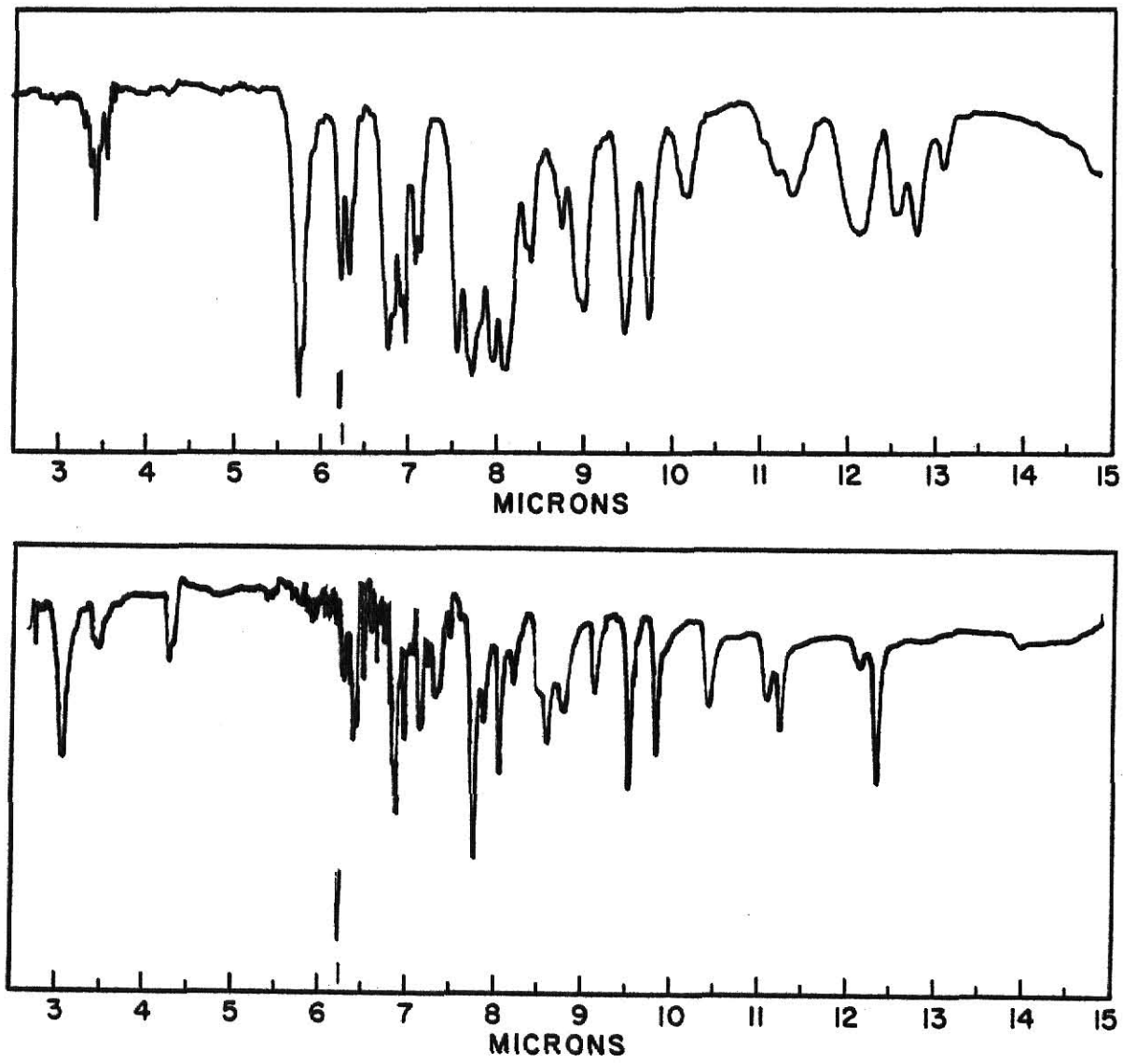
INFRARED SPECTRA

Methyl 2-bromo-5-methoxybenzoate

(Thin film)

1-(2-Bromo-5-methoxyphenyl)-1-methylethanol

(KBr)


3
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11
12
13
14
15
MICRONS
3
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6
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8
9
10
11
12
13
14
15
MICRONS

INFRARED SPECTRA

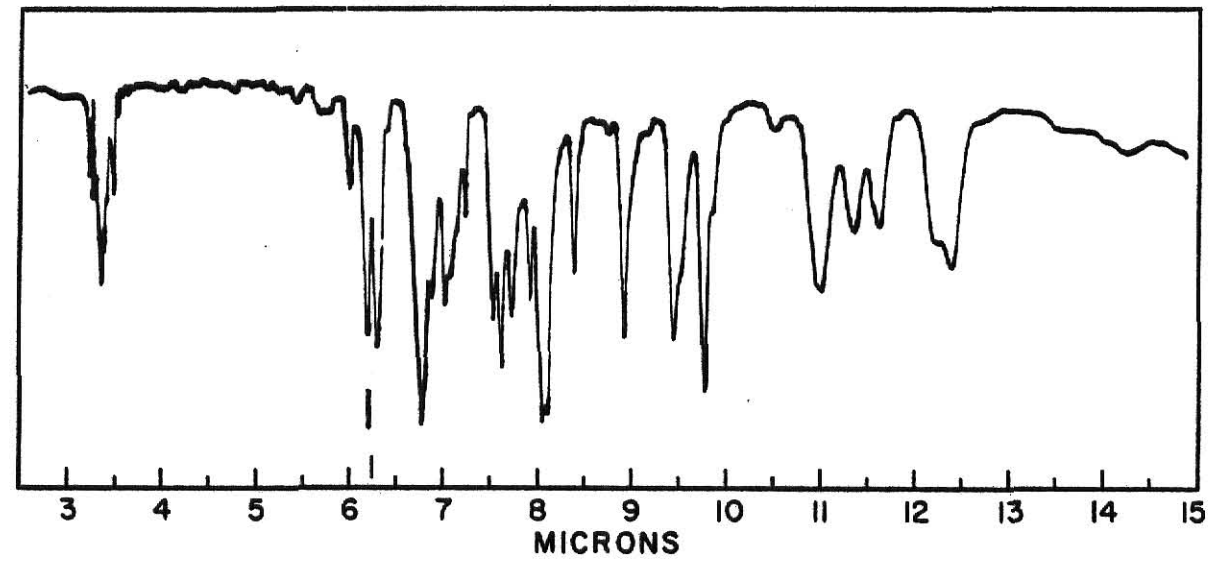
2-Bromo-5-methoxyα-methylstyrene

(Thin film)

Start

2,2',2"-Triisopropenyl-4,4',4"-trimethoxytriphenylcarbinol

(KBr)


3
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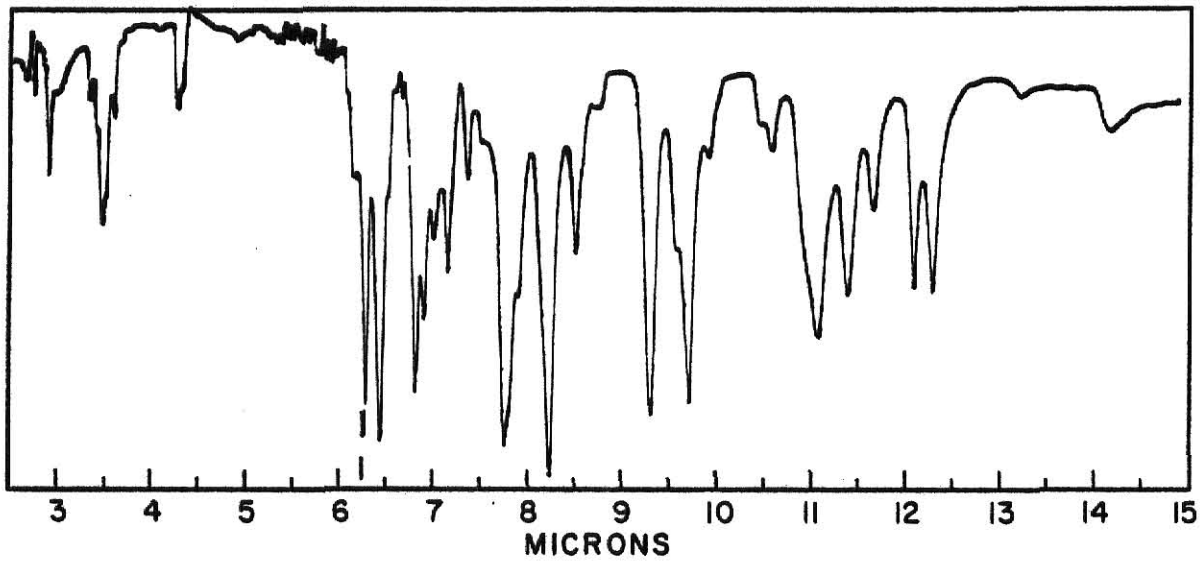
11
12
13
14
15
MICRONS


3
4
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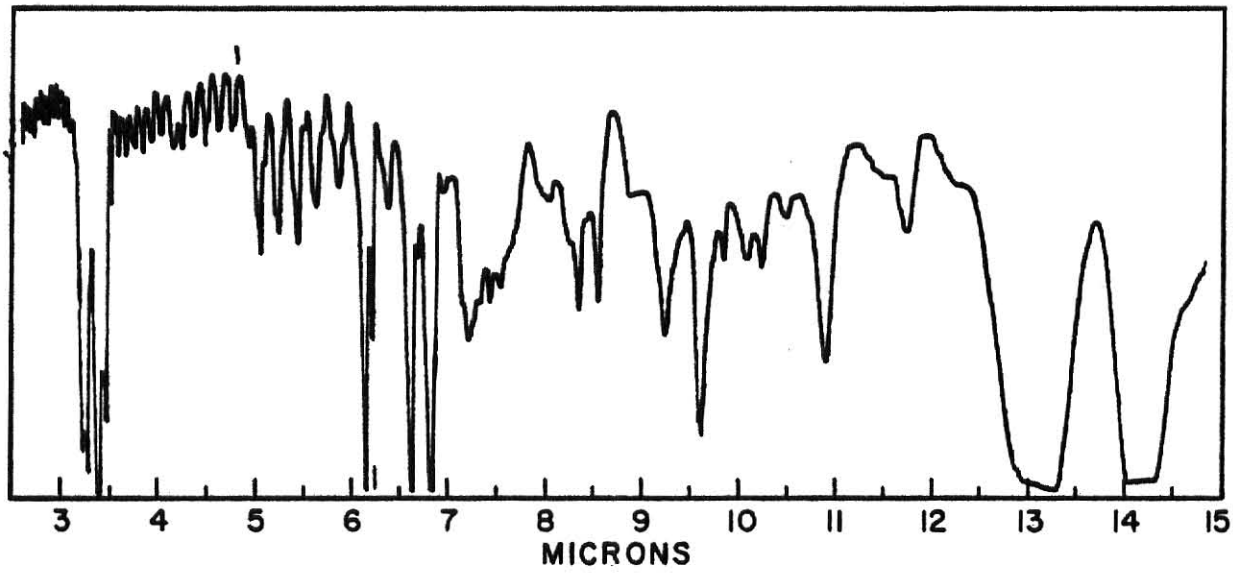
7
8
9
10
11
12
13
14
15
MICRONS

INFARED SPECTRA

Calibration Spectra, Polystyrene


3
4
5
6
7
8
9
10
11
12
13
14
15
MICRONS

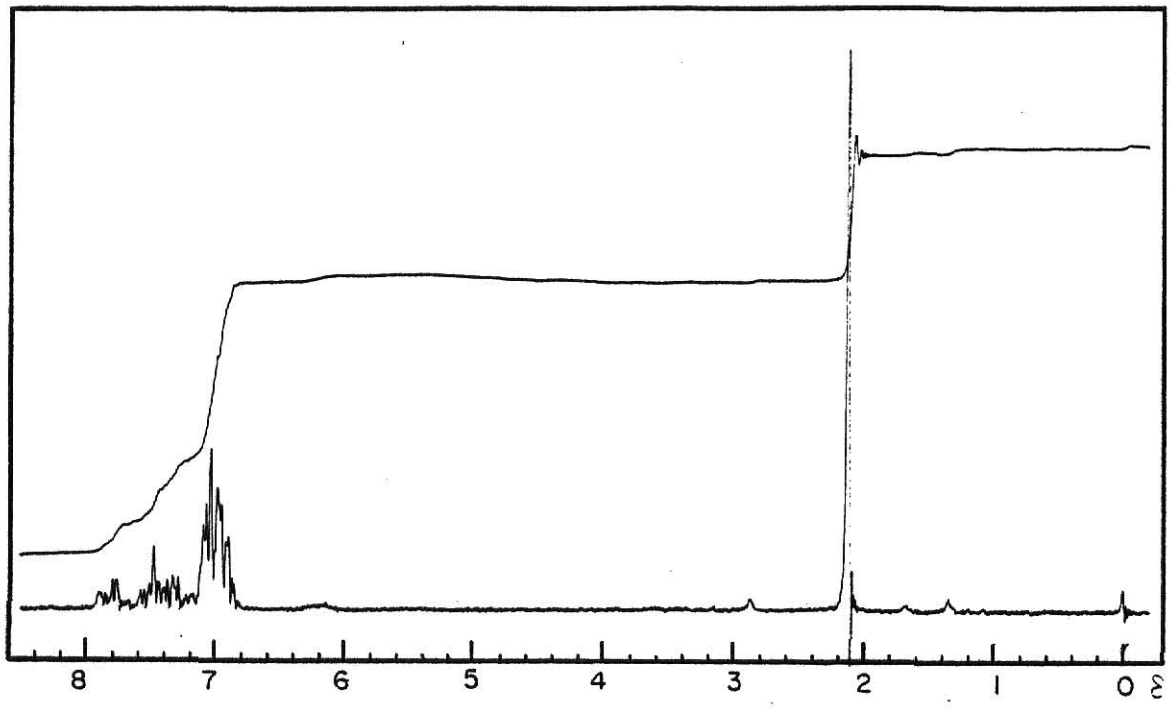
NMR SPECTRA

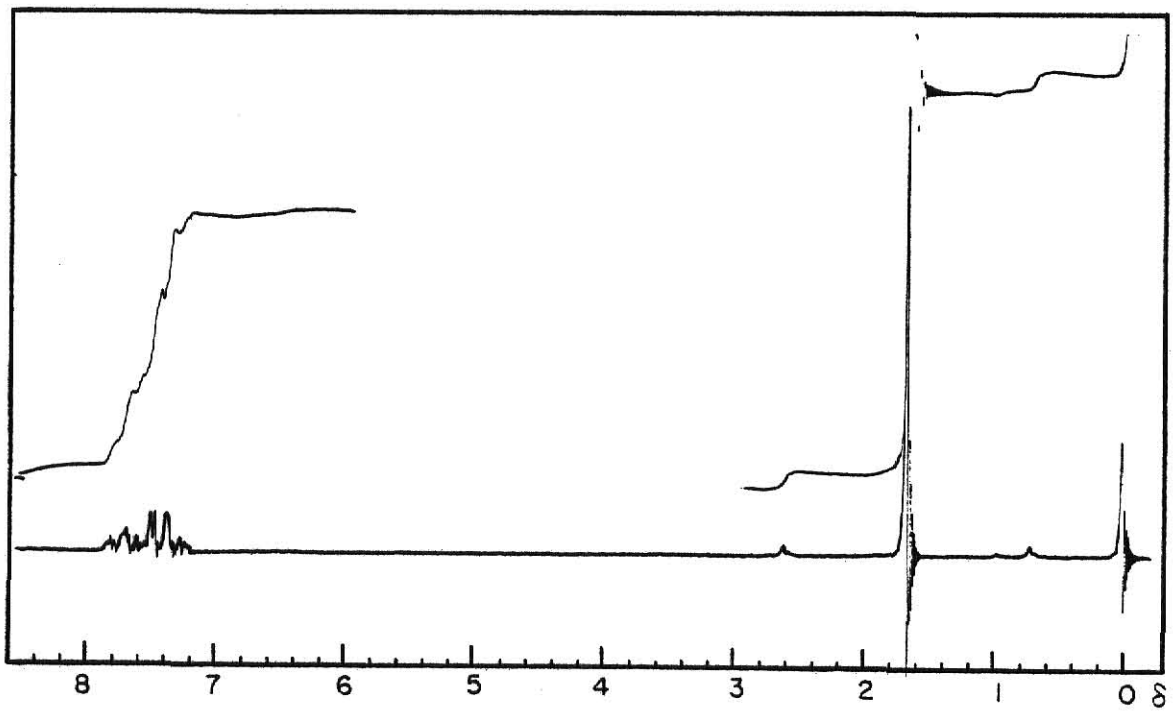
3,3-Ditolylphthalide

($CDCl_3$, Internal TMS)

3,3-Dimethylphthalide

($CDCl_3$, Internal TMS)


8
7
6
5
4
3
2
1
0
δ


8
7
6
5
4
3
2
1
0
δ

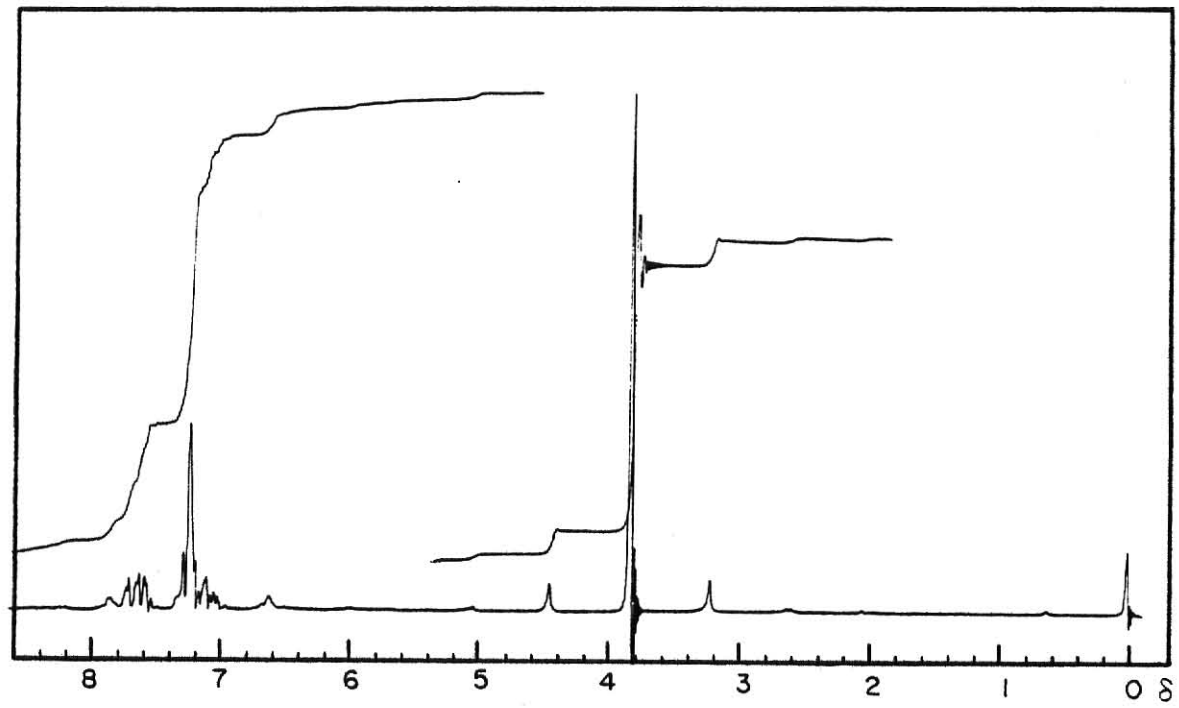
NMR SPECTRA

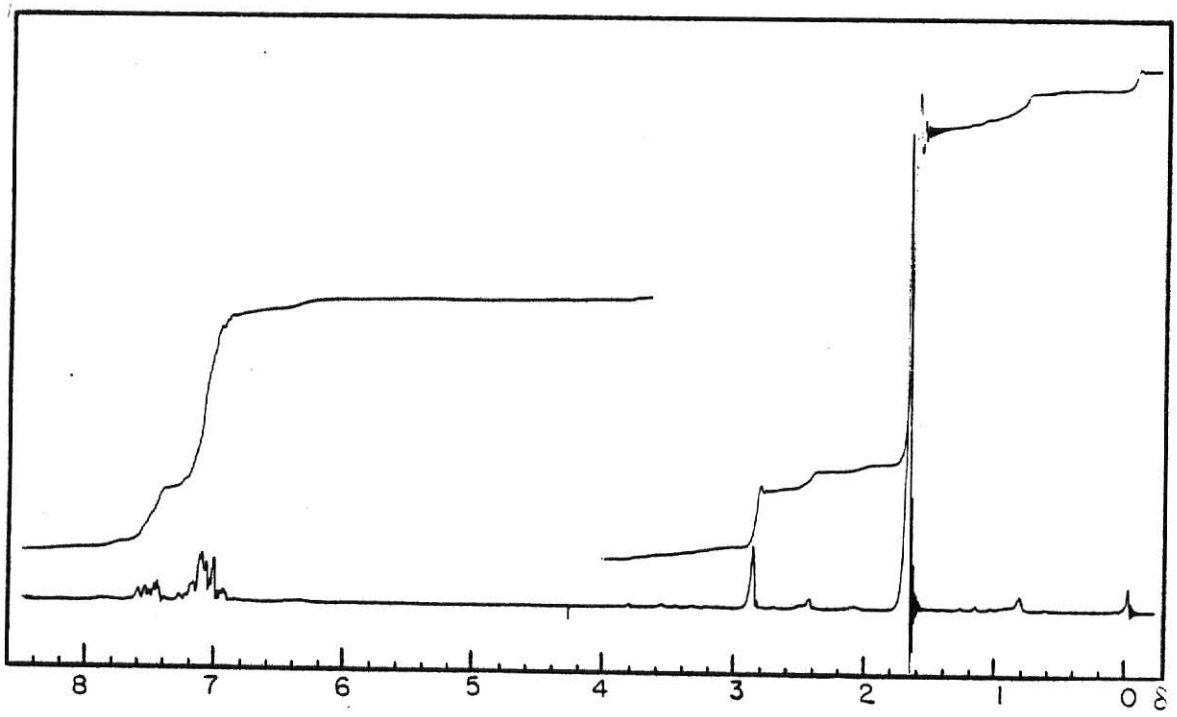
Methyl o-chlorobenzoate

($CDCl_3$, Internal TMS)

1-(o-Chlorophenyl)-1-methylethanol

($CDCl_3$, Internal TMS)


8
7
6
5
4
3
2
1
0 δ


8
7
6
5
4
3
2
1
0 δ

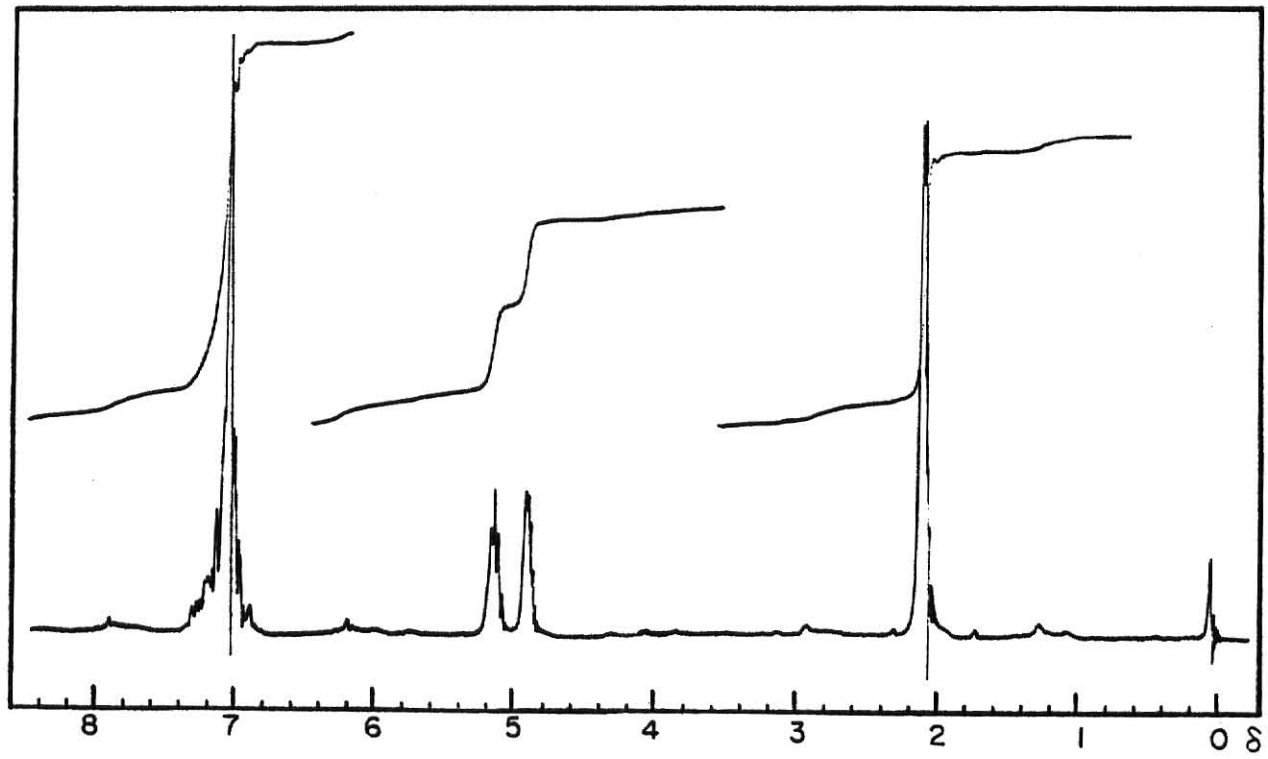
NMR SPECTRA

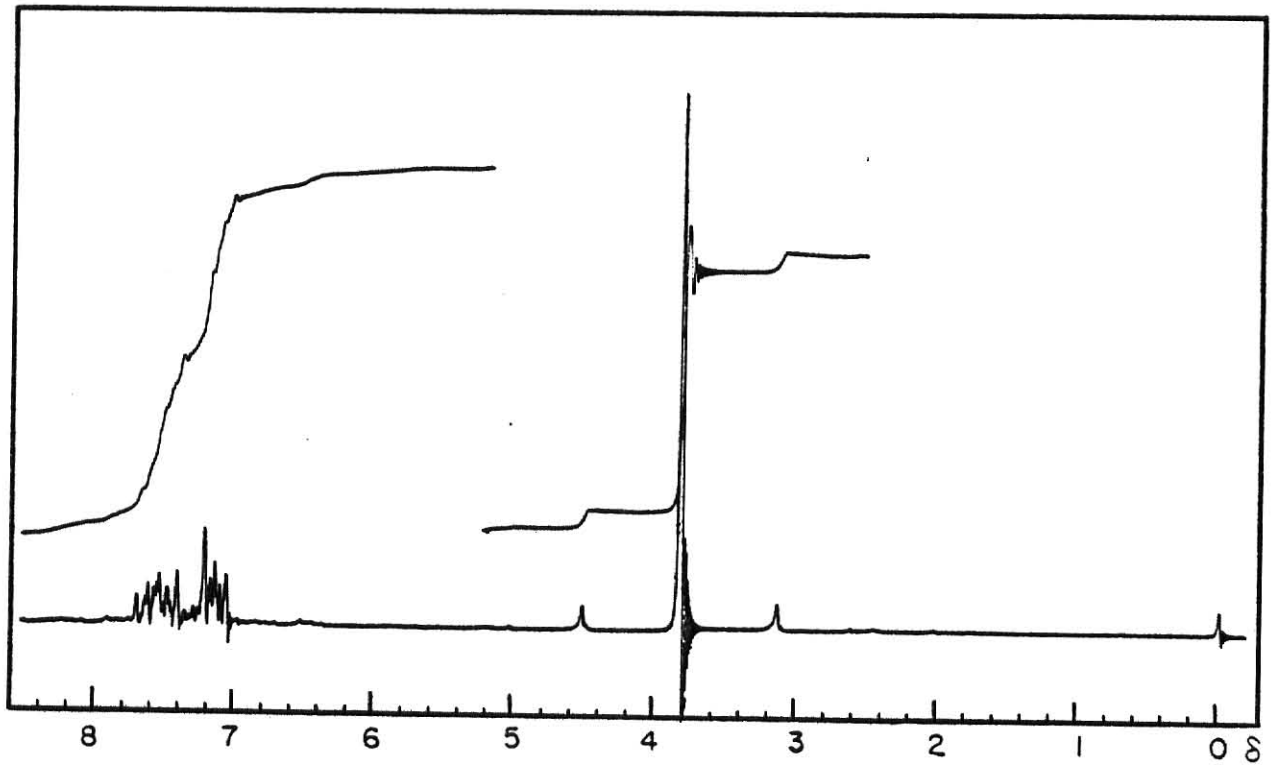
o-Chloro-α-methylstyrene

($CDCl_3$, Internal TMS)

Methyl o-bromobenzoate

($CDCl_3$, Internal TMS)


8
7
6
5
4
3
2
1
0 δ


8
7
6
5
4
3
2
1
0 δ

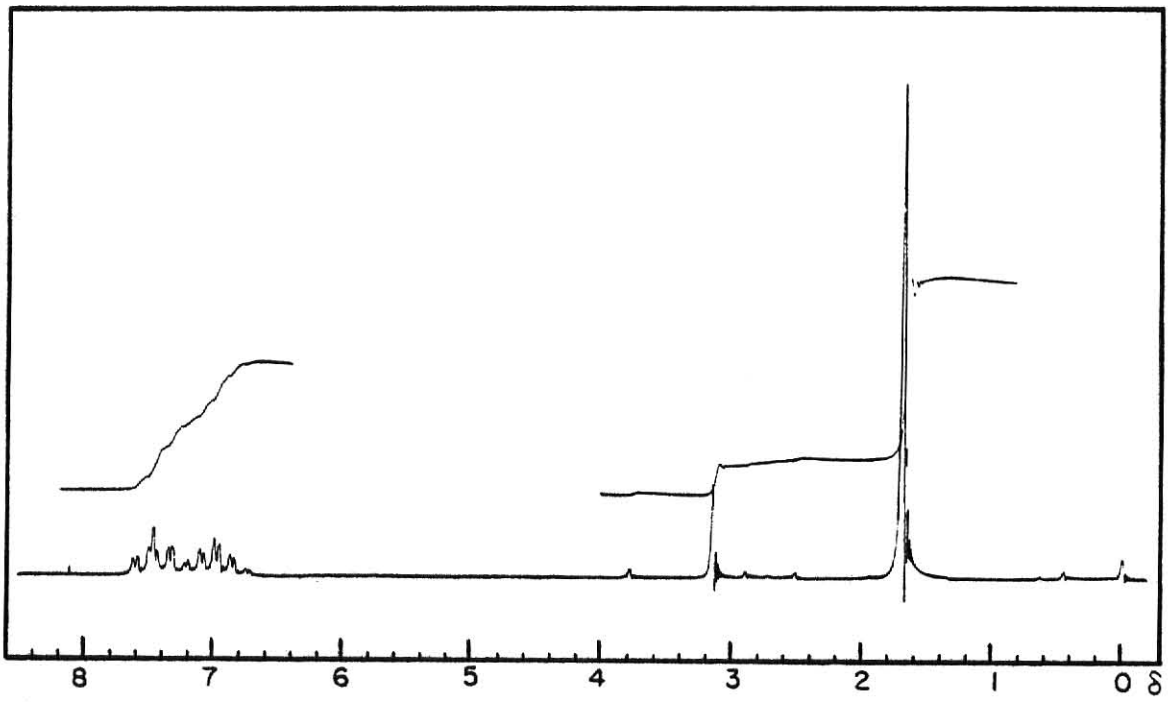
NMR SPECTRA

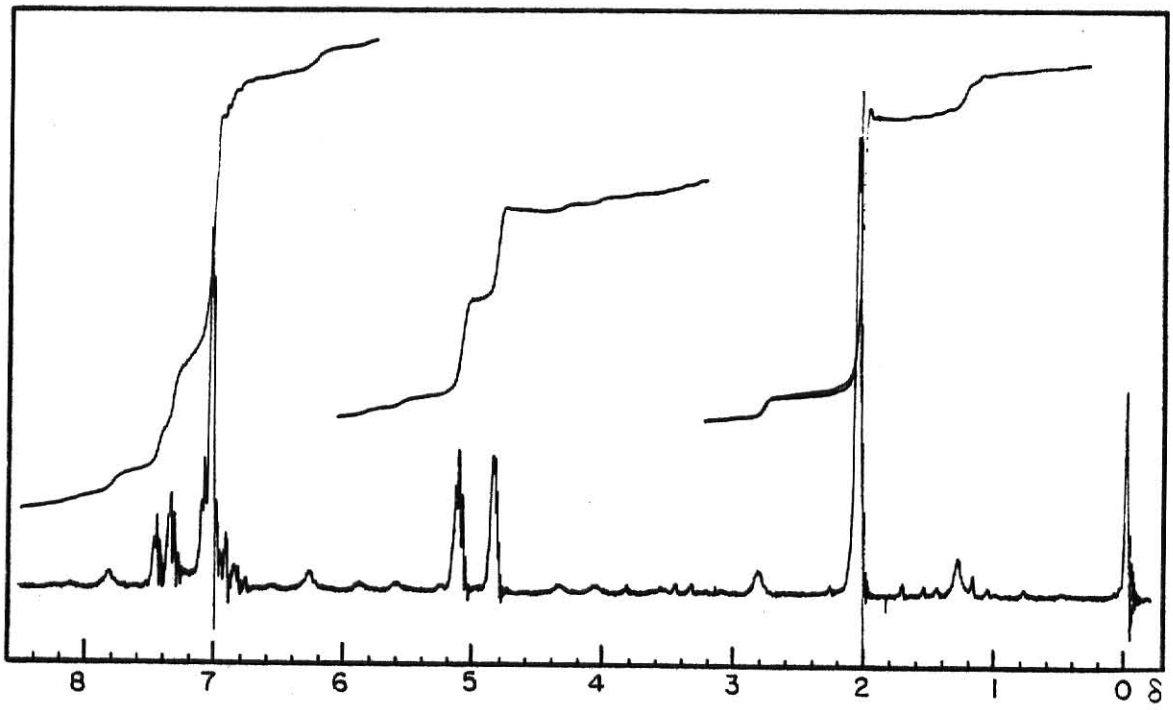
1-(o-Bromophenyl)-1-methylethanol

($CDCl_3$, Internal TMS)

o-Bromo-α-methylstyrene

($CDCl_3$, Internal TMS)


8
7
6
5
4
3
2
1
0 δ


8
7
6
5
4
3
2
1
0 δ

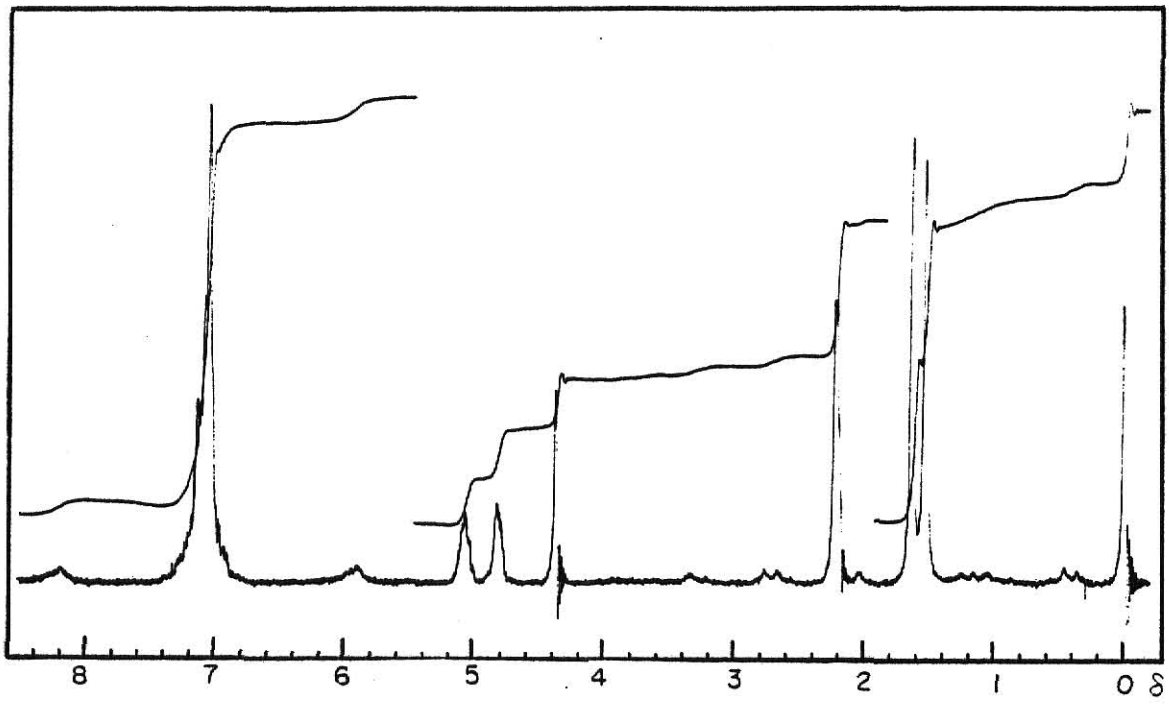
NMR SPECTRA

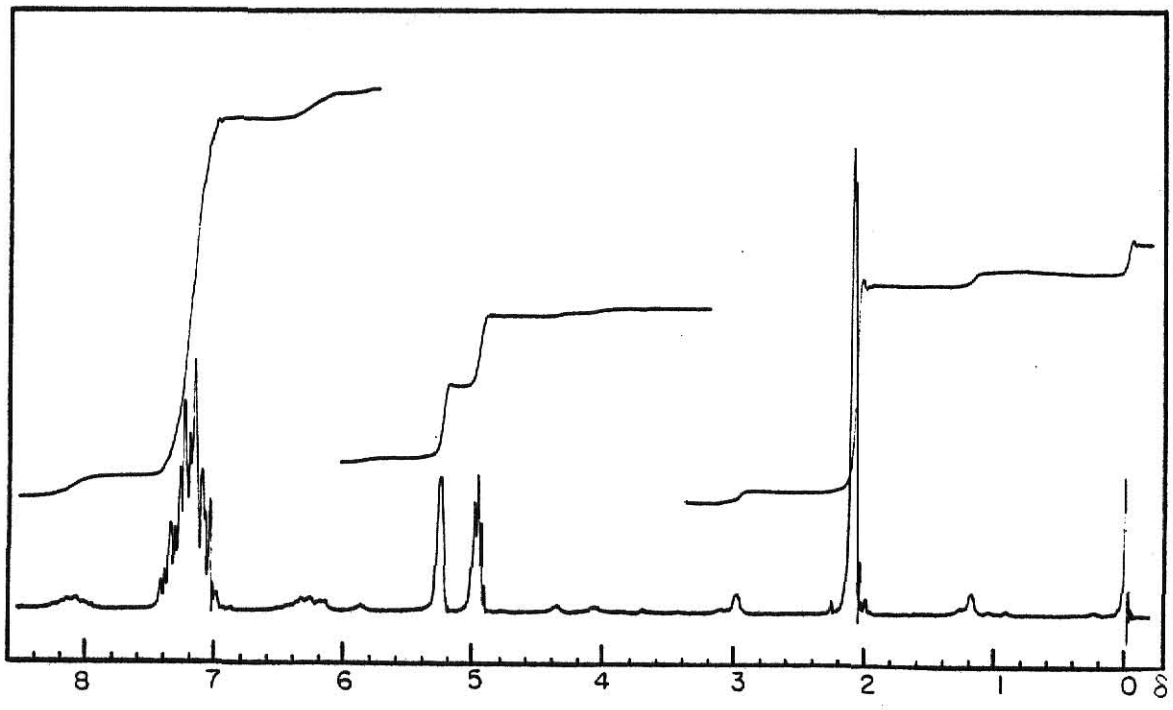
2,5-Dihydro-5,5-dimethyl-2-hydroxy-2-(2-iso-propenylphenyl)-benzo[c]furan

($CDCl_3$, Internal TMS)

α-Methylstyrene

($CDCl_3$, Internal TMS)


8
7
6
5
4
3
2
1
0 δ


8
7
6
5
4
3
2
1
0 δ

NMR SPECTRA

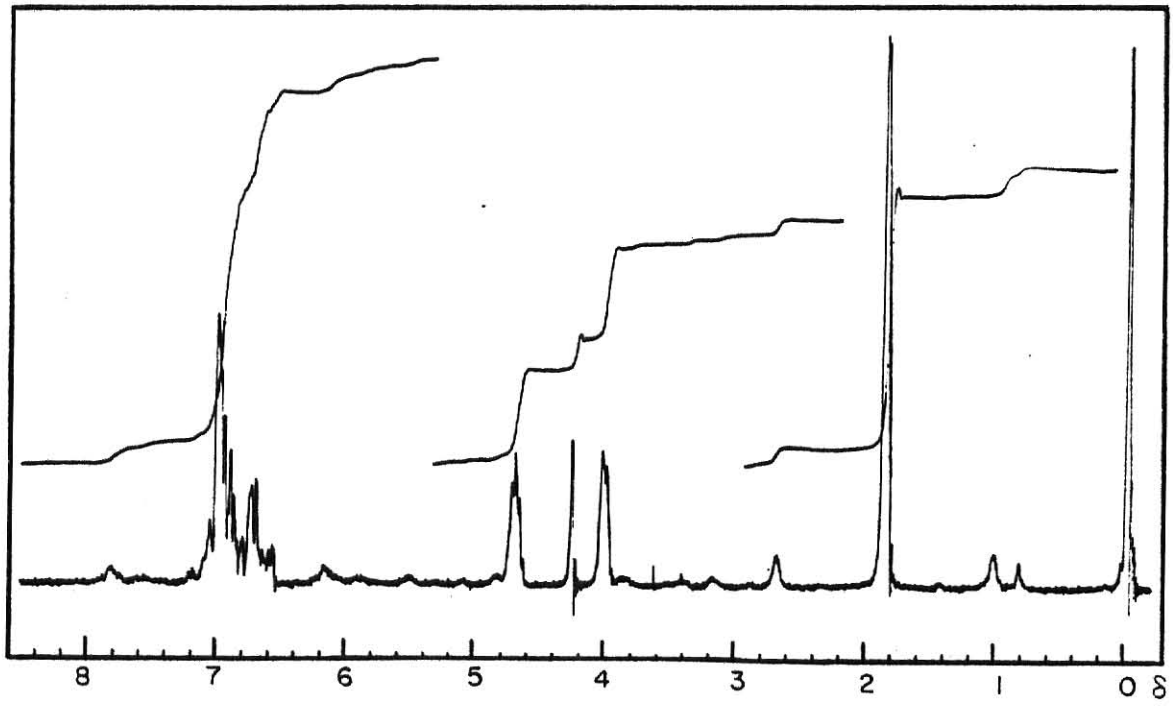
2,2',2"-Triisopropenyltriphenylcarbinol

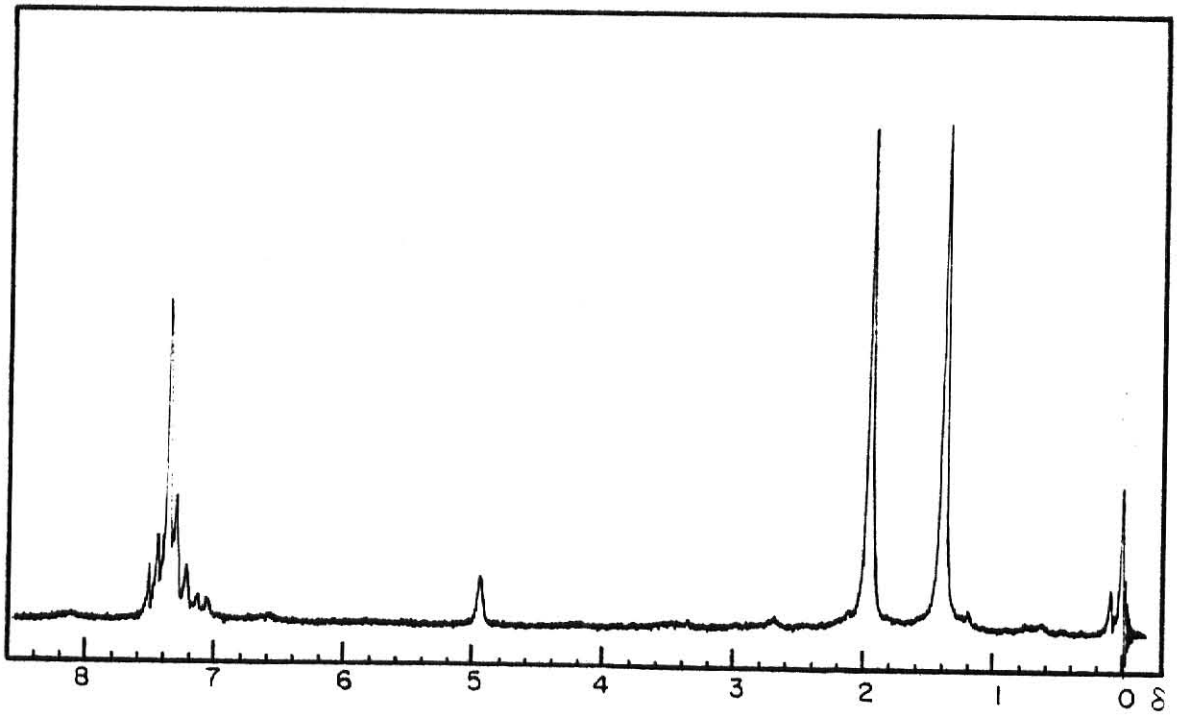
($CDCl_3$, Internal TMS)

12,12c-Dihydro-4,4,8,8,12,12-hexa-

methyl-4H,8H-dibenzo[cd,mn]pyrene

($CDCl_3$, Internal TMS)


8
7
6
5
4
3
2
1
0 δ


8
7
6
5
4
3
2
1
0 δ

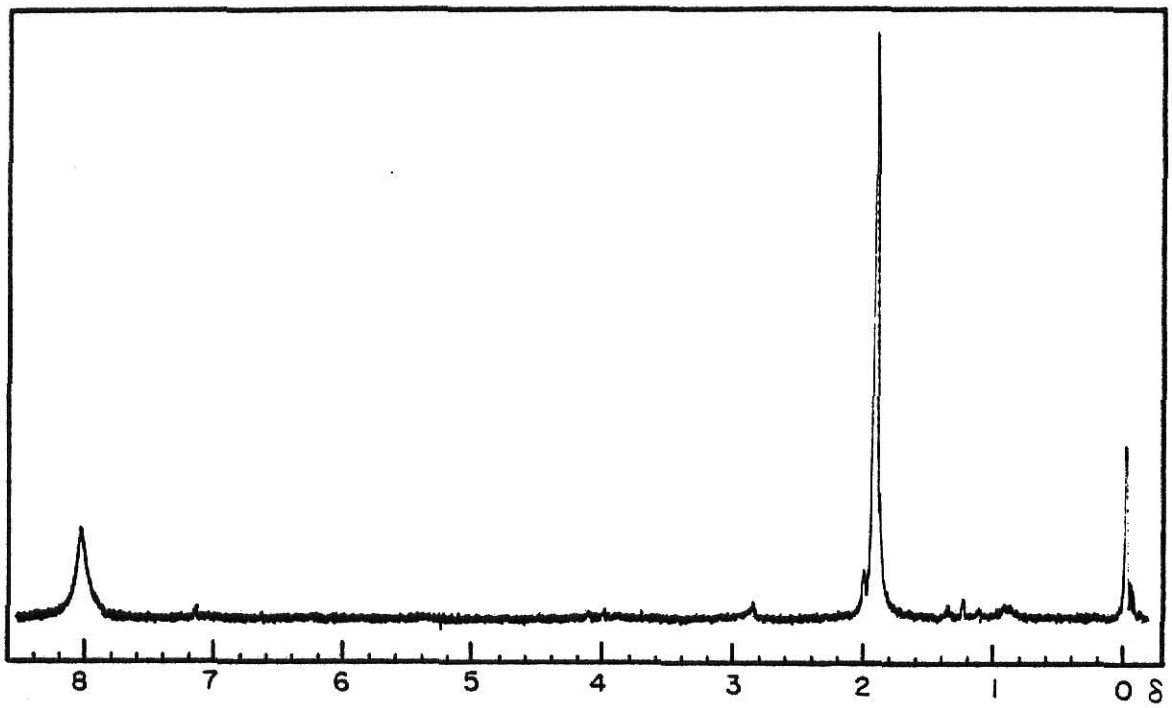
NMR SPECTRA

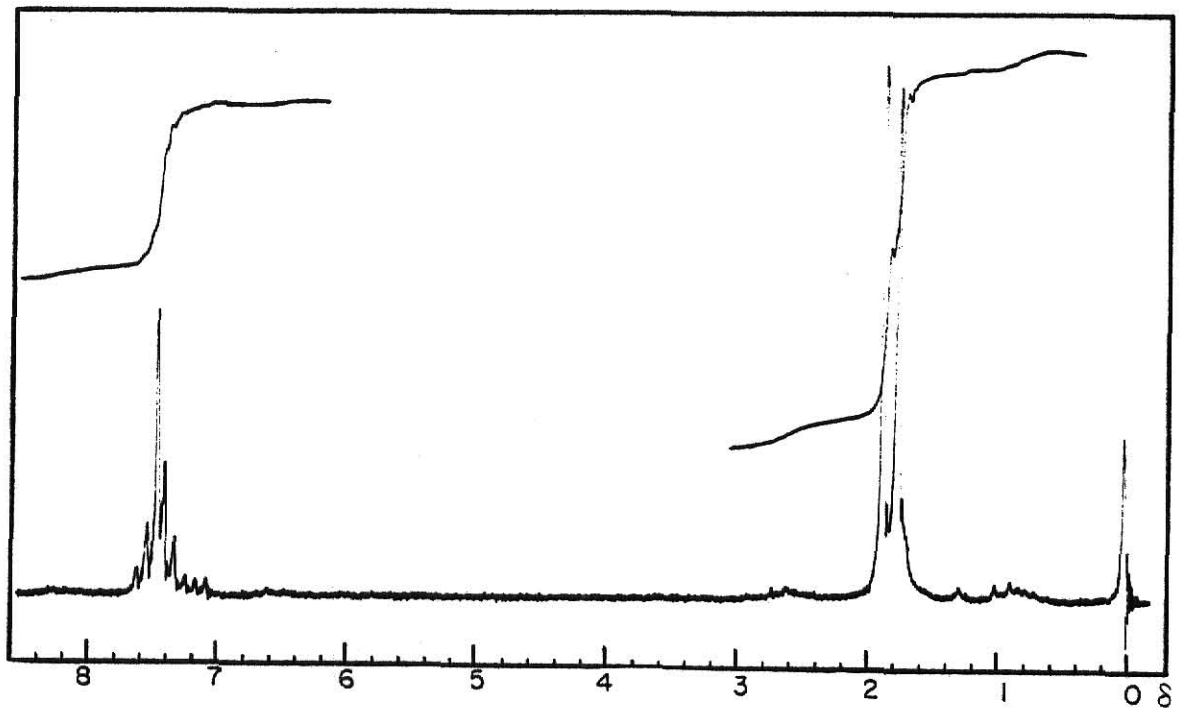
12,12c-Dihydro-4,4,8,8,12,12-hexamethyl-4H,8H-dibenzo[cd,mn]pyrenyl cation

($CDCl_3$, Internal TMS)

12c-hydroxy-12,12c-dihydro-4,4,8,8,12,12-hexamethyl-4H,8H-dibenzo[cd,mn]pyrene

($CDCl_3$, Internal TMS)


8
7
6
5
4
3
2
1
0 δ


8
7
6
5
4
3
2
1
0 δ

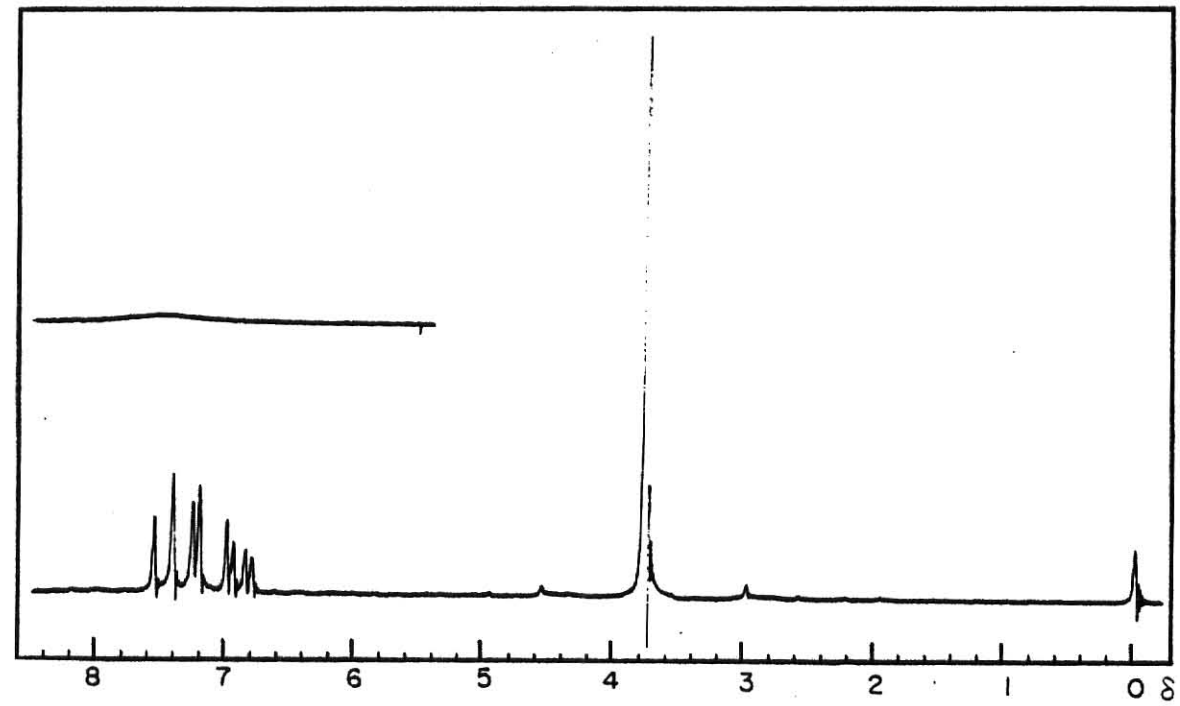
NMR SPECTRA

2-Bromo-5-methoxybenzoic acid

($CDCl_3$, Internal TMS)

Methyl 2-bromo-5-methoxybenzoate

($CDCl_3$, Internal TMS)


8
7
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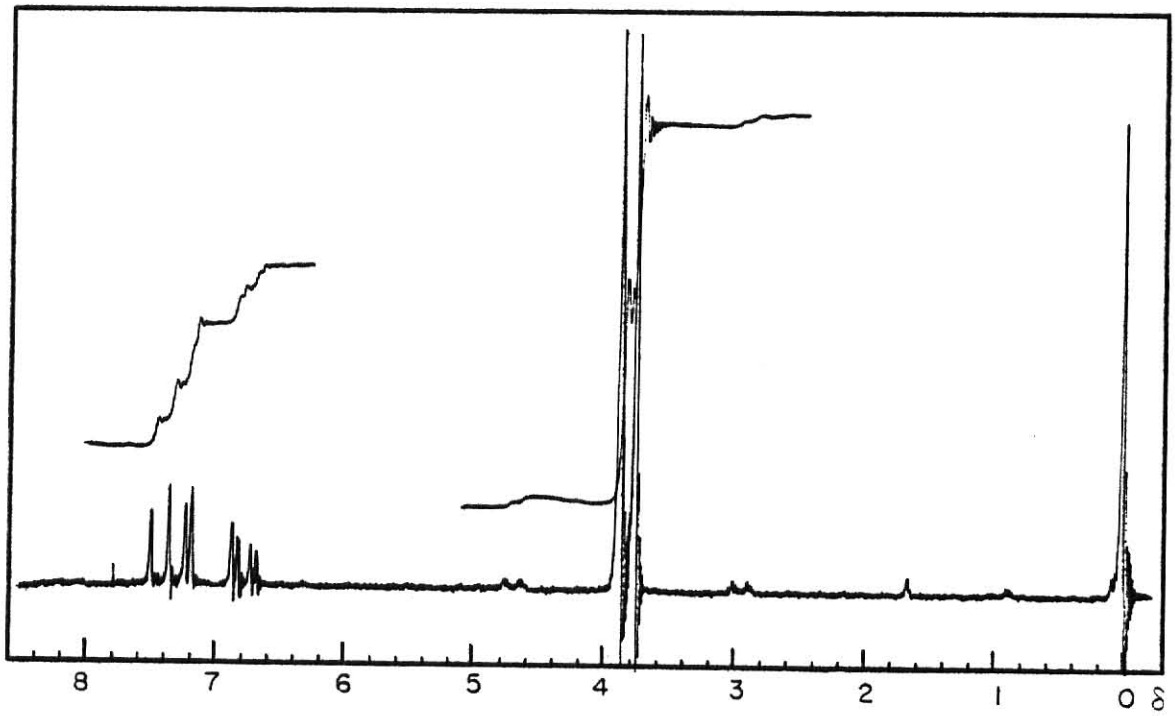
4
3
2
1
0 δ


8
7
6
5
4
3
2
1
0 δ

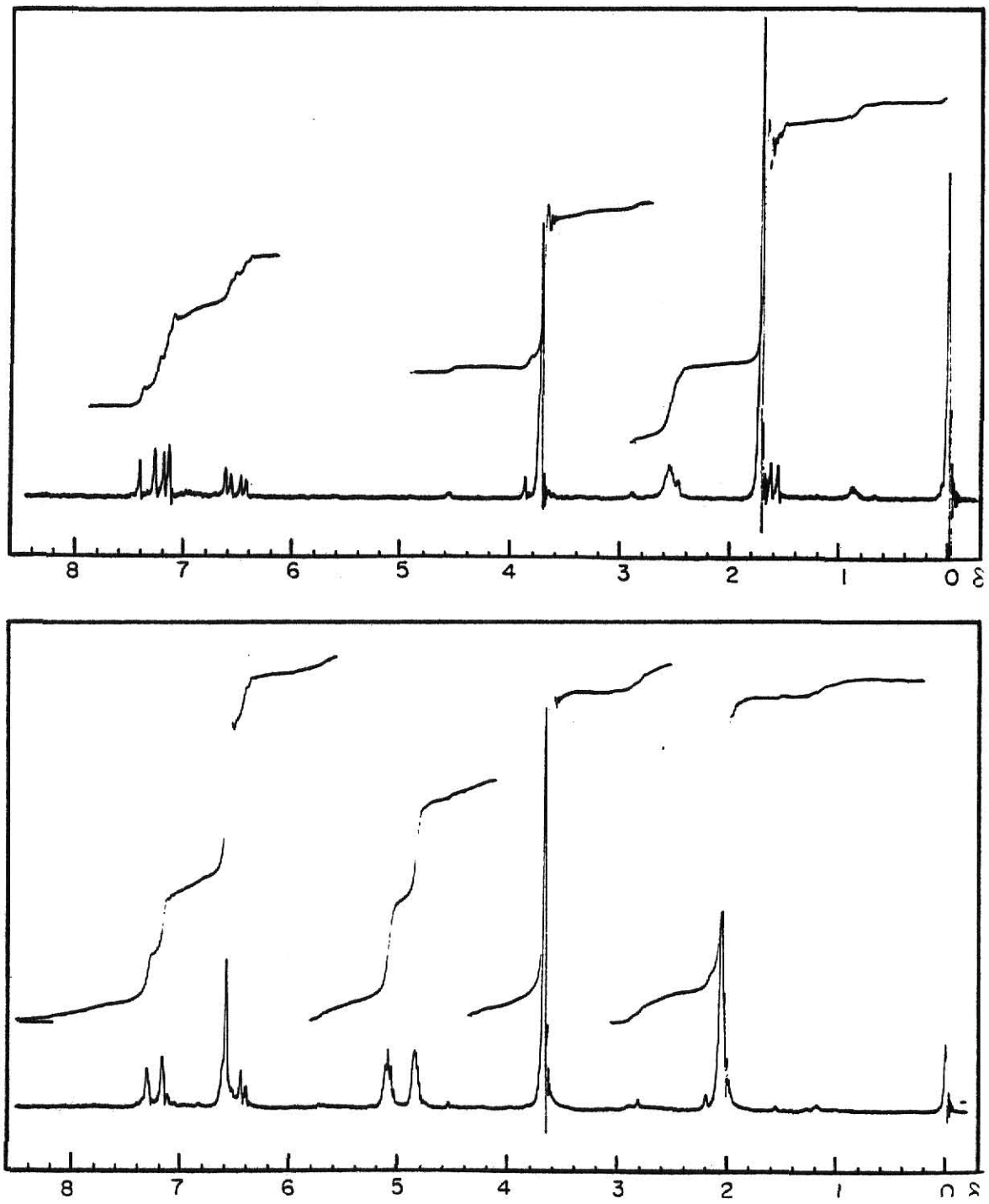
NMR SPECTRA

1-(2-Bromo-5-methoxyphenyl)-1-methylethanol

($CDCl_3$, Internal TMS)

2-Bromo-5-methoxy-α-methylstyrene

($CDCl_3$, Internal TMS)

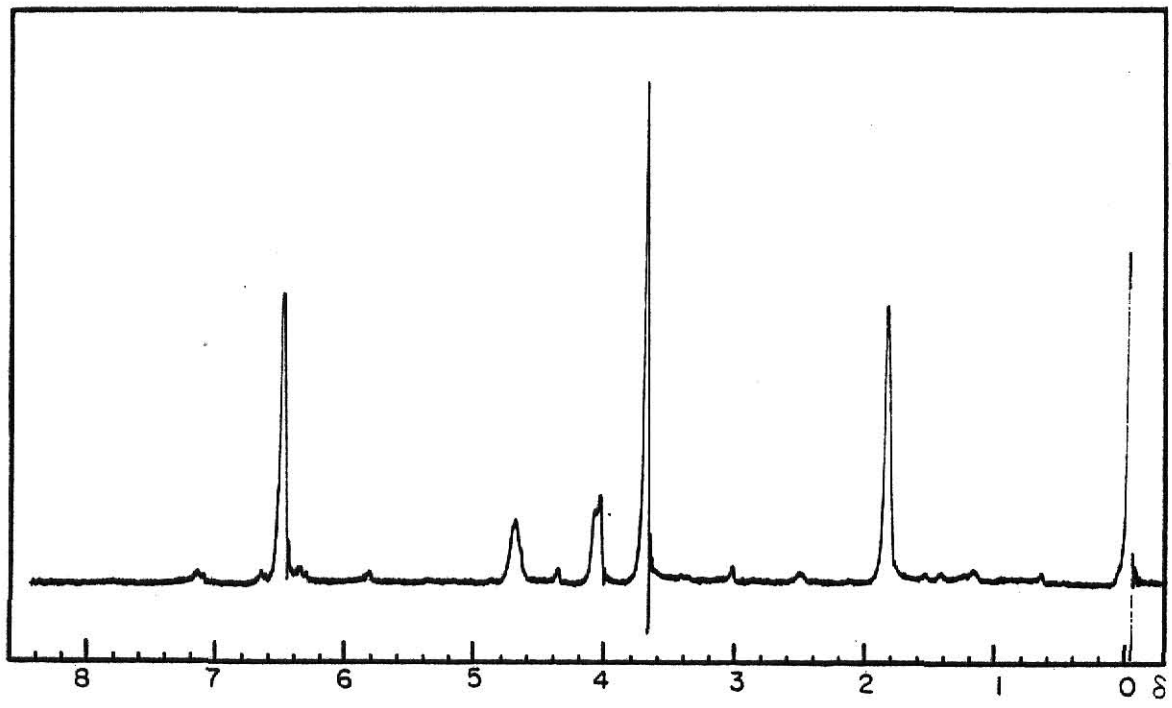

8
7
6
5
4
3
2
1
0
δ
8
7
6
5
4
3
2
1
0
δ

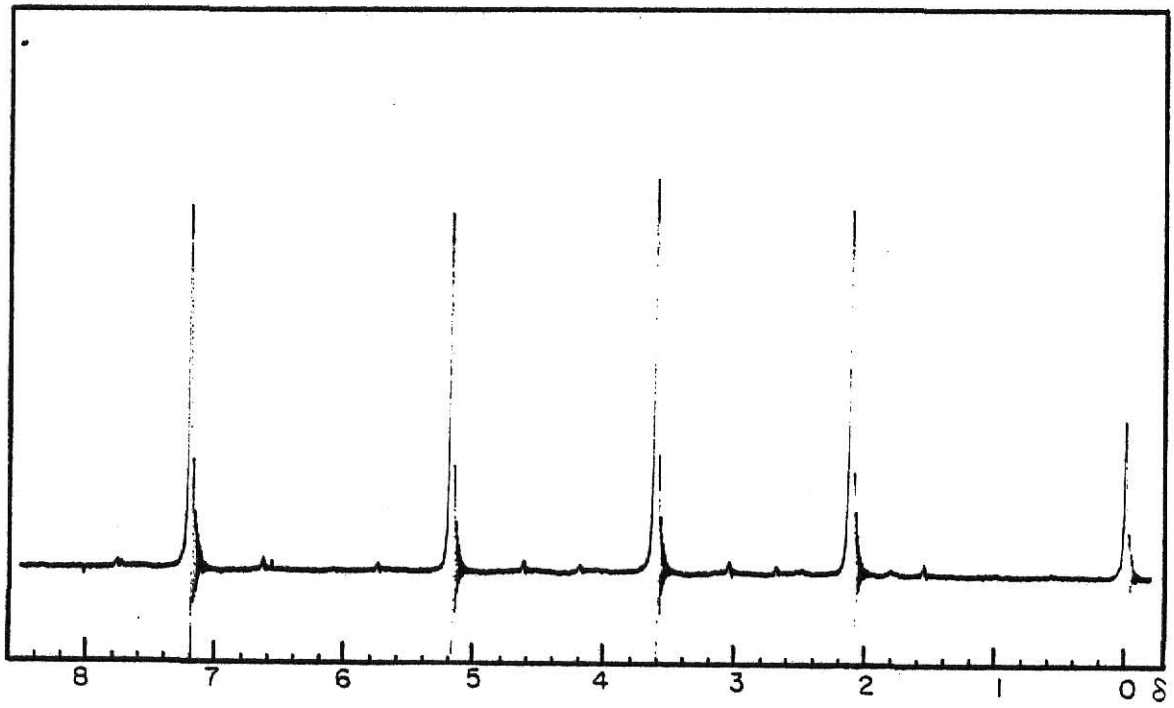
NMR SPECTRA

2,2',2"-Triisopropenyl-4,4',4"-trimethoxytriphenylcarbinol

($CDCl_3$, Internal TMS)

Calibration Spectra	ppm
Benzene	7.37
Dichloromethane	5.30
p-Dioxane	3.70
Acetone	2.17
TMS	0.00


8
7
6
5
4
3
2
1
0 δ


8
7
6
5
4
3
2
1
0 δ

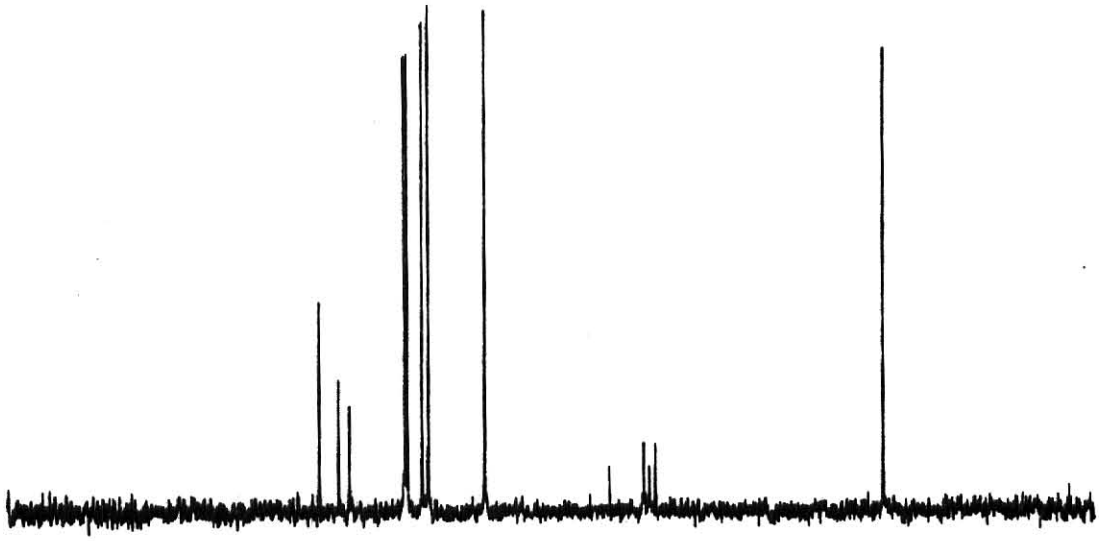
^{13}C NMR SPECTRA

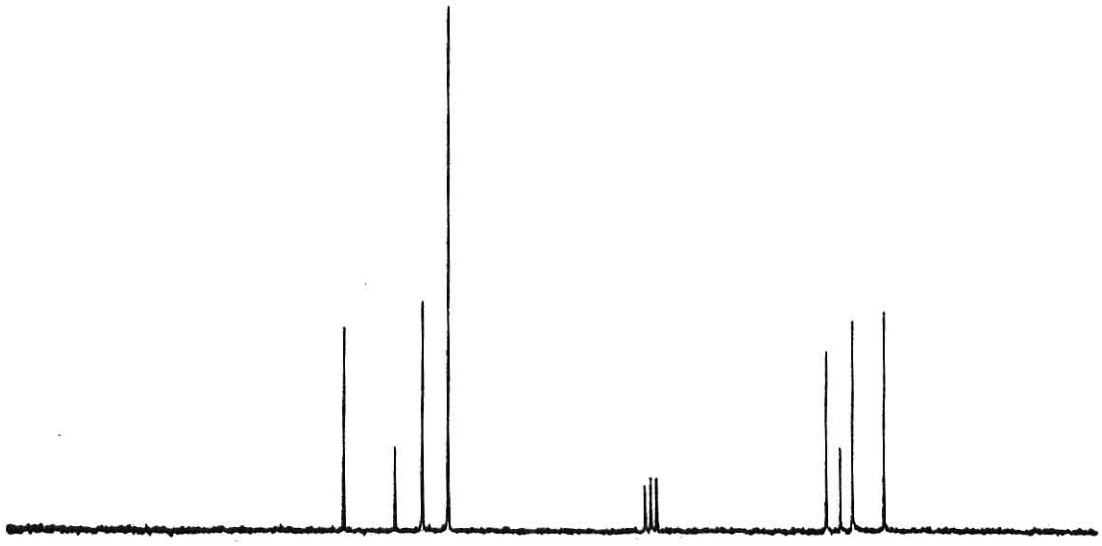
2,2',2"-Triisopropenyltriphenylcarbinol

149.3 ppm	126.7 ppm
145.0	125.3
142.6	112.9
130.6	85.7
130.0	25.8

12,12c-Dihydro-4,4,8,8,12,12-hexamethyl-4H,8H-dibenzo-[cd,mn]pyrene

144.1 ppm	(s)	38.6 ppm	(s)
132.8	(s)	35.5	(d)
126.8	(d)	32.9	(q)
121.2	(d)	26.0	(q)





^{13}C NMR SPECTRA

12,12c-Dihydro-4,4,8,8,12,12-hexamethyl-4H,8H-dibenzo[cd,mn] pyrenyl cation

156.9 ppm

140.5

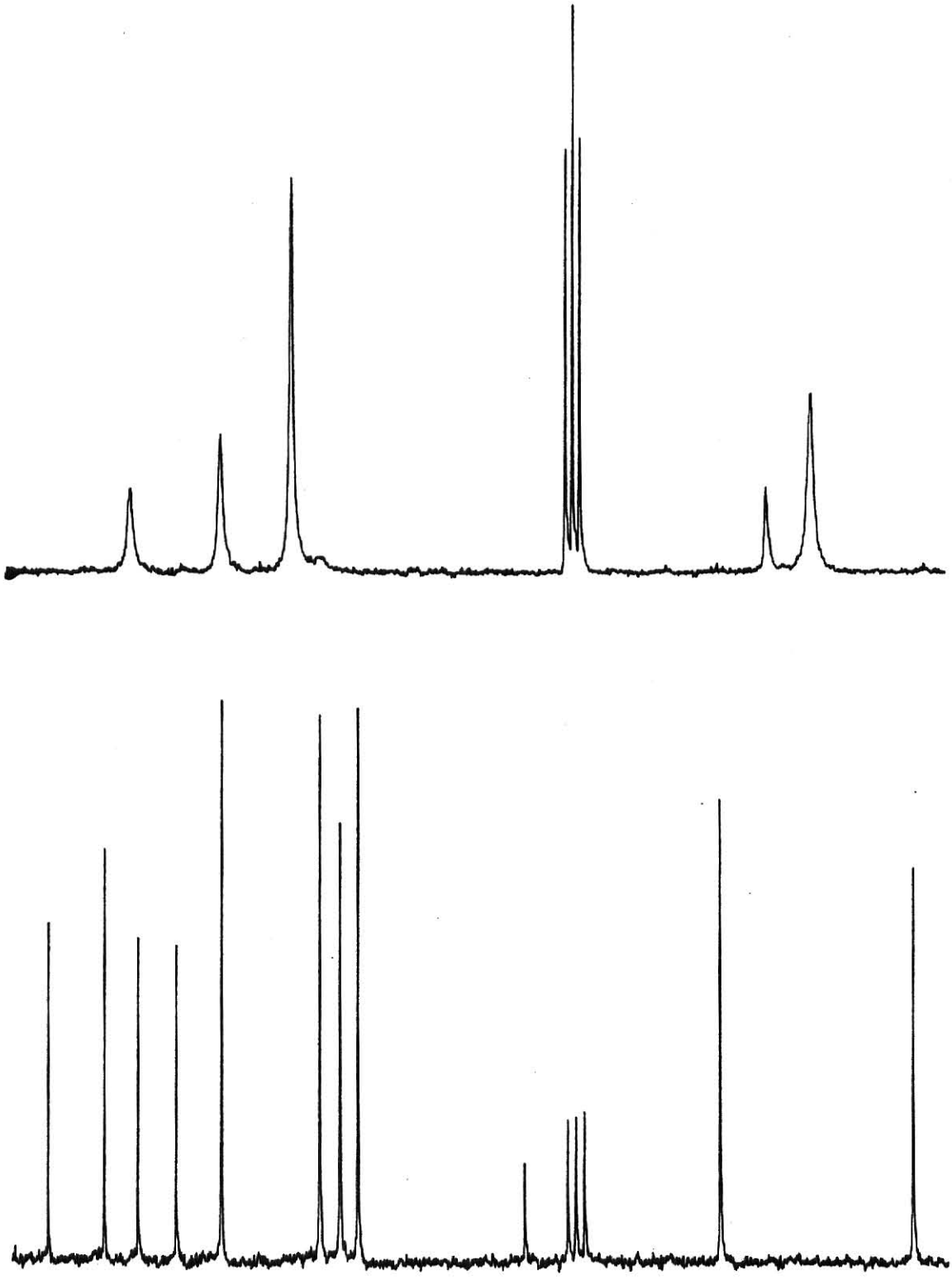
127.6

42.2

34.4

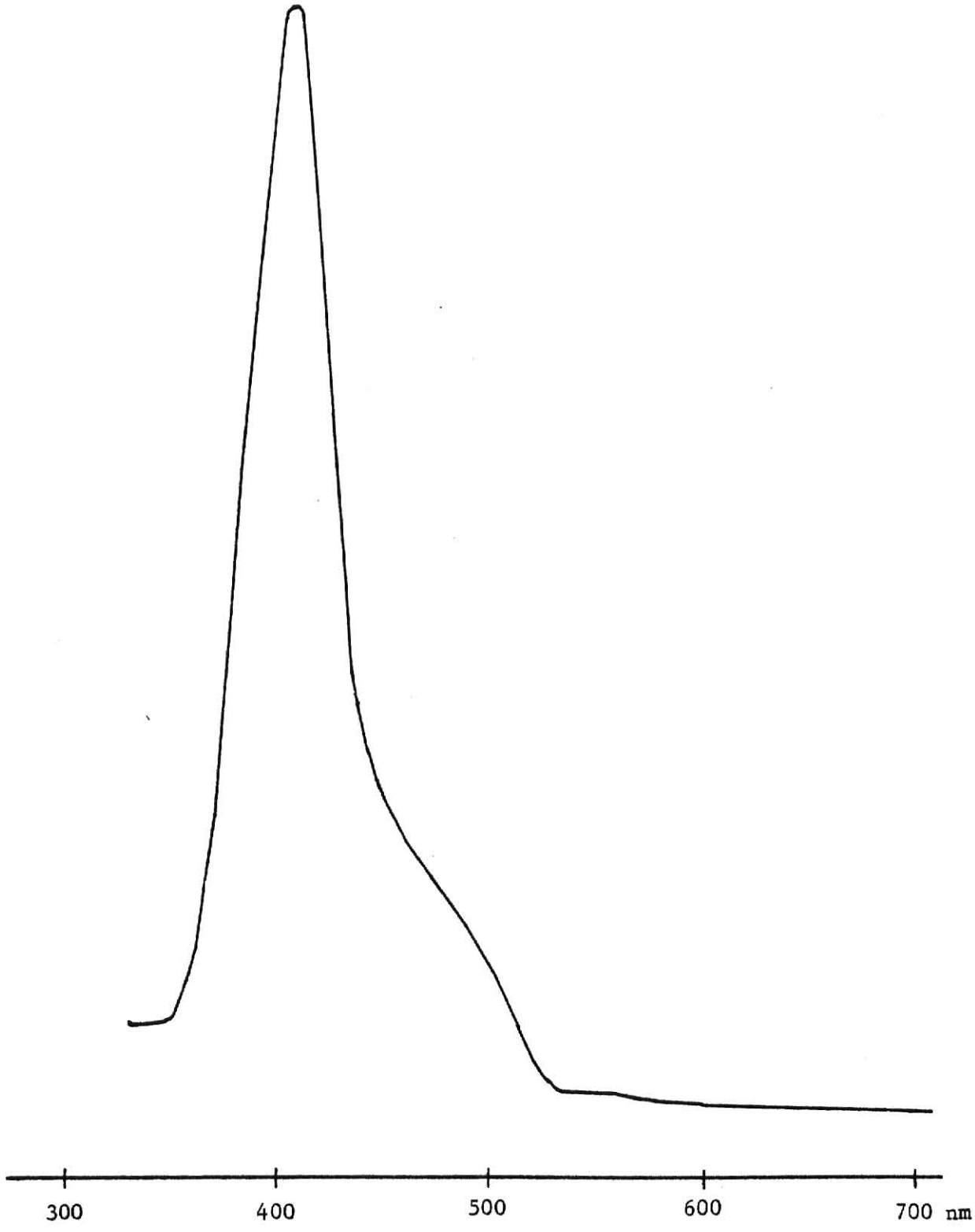
12c-hydroxy-12,12c-dihydro-4,4,8,8,12,12-hexamethyl-4H,8H-dibenzo [cd,mn] pyrene

157.8 ppm	112.8 ppm
149.2	110.1
143.9	84.7
138.0	55.0
131.0	25.7
115.9	



UV-VISIBLE SPECTRA

12,12c-Dihydro-4,4,8,8,12,12-hexamethyl-
4H,8H-dibenzo[cd,mn]pyrenyl cation


300
400
500
600
700 nm

AN IMPROVED ROUTE FOR THE SYNTHESIS OF PLANAR DERIVATIVES OF TRIARYLMETHANE

by

MICHAEL DAVID ROGERS

B. S., Northwest Missouri State University, 1976

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1980

ABSTRACT

We have synthesized the unique planar triarylmethane, 12,12c-dihydro-4,4,8,8,12,12-hexamethyl-4H,8H,dibenzo[cd,mn]pyrene in 80% yield. Our synthetic route, which results in more than a ten fold increase in yield over the previous route, uses more readily available starting materials and reduces the number of synthetic steps required. This has allowed us to study its properties and reactivity.

It should be possible to take advantage of the properties induced by the unique shape of this compound to design derivatives which are useful as anlytical indicators. Deriviatives can be synthesized either by using appropriately substituted starting materials or by reaction of the parent compound. Attempted electrophilic substitution on the aromatic rings proved unsuccessful, yielding the product of oxidation at the 12c position, 12c-hydroxy-12,12c-dihydro-4,4,8,7,12,12-hexamethyl-4H-8H-dibenzo[cd,mn]pyrene, or the corresponding carbenium ion. This carbenium ion was exceptionally stable in acidic aqueous solutions as shown by its pK_R+ which was determined to be 6.72 $\pm$0.03 in 1:1 ethanol-water. Its λ_{max} was 405 nm with an $E^{1\%}_{1\ cm}$ of 696.