4,5-Dihydroisojervone Diacetate.—To 77 mg. of platinum oxide prereduced in 20 ml. of ethanol was added 231 mg. (0.44 mmole) of Δ^4-isojervone diacetate in 20 ml. of ethanol and the mixture was hydrogenated until one mole equivalent of hydrogen had been adsorbed (10 min.). The catalyst was removed by filtration, the solvent evaporated under reduced pressure, and the yellow oil crystallized from dilute methanol. The material was recrystallized first from the same solvent and then from dilute acetone; yield 150 mg. (67%), m.p. 202.5–204.0°, $[\alpha]_D$ +71° (*c* 2.25).

Anal. Calcd. for $C_{31}H_{43}O_5N$ (509.66): C, 73.05; H, 8.50. Found: C, 73.25; H, 8.51.

Stereospecific Protonation of 4a-Methyl-1,3,9-triphenyl-4a*H*-fluorene[1]

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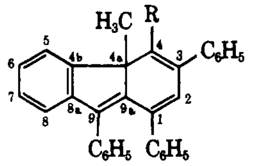
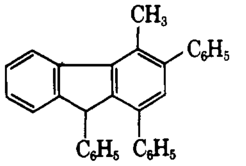
It is shown that 4a-methyl-1,3,9-triphenyl-4a*H*-fluorene (Ia) forms a carbonium ion in acid media. The protonation is stereospecific and takes place at the 4-position.

In earlier papers of this series[2,3] it was shown that the lower-melting hydrocarbon obtained from the polyphosphoric acid-catalyzed condensation of acetophenone is 4a-methyl-1,3,9-triphenyl-4a*H*-fluorene (Ia). It was also established that this hydrocarbon, Ia, is isomerized by hydrogen bromide in glacial acetic acid to 4-methyl-1,3,9-triphenylfluorene (II).



Ia. R = H
b. R = D
c. R = Br



II

Compound Ia is very soluble in strong acids, such as sulfuric acid, trifluoroacetic acid and fluoroboric–acetic acid, giving intense blue-green solutions. The color is due to the presence of a carbonium ion. The hydrocarbon, Ia, can be quantitatively regenerated by the addition of water to solutions of the carbonium ion. The perchlorate, fluoroborate, and bromide have been isolated. The possibility that the color is due to the presence of a free radical was eliminated by the electron-spin resonance spectrum of Ia in concentrated sulfuric acid; no paramagnetism was detected.[4]

With the aid of proton magnetic resonance spectroscopy it was shown that protonation of Ia is a stereospecific process and that attack takes place at the 4-position. The proton magnetic resonance spectrum of Ia in deuteriochloroform (Figure 1) shows an *AB* pattern at τ, 3.33, J = 1.5 c.p.s. and $\delta\nu$ = 3.0 c.p.s. which is due to the vinyl protons at the 2- and 4-positions. The methyl group gives a singlet at τ, 8.31. The aromatic region of the spectrum is very complex, covering a range of 48 c.p.s. (τ, 2.37 to τ, 3.18). The spectrum (Figure 2) of Ia in trifluoroacetic acid, which gives the same spectrum as does the perchlorate salt of Ia in trifluoroacetic acid, shows an *AB* pattern centered at τ, 6.40, J = 18 c.p.s., $\delta\nu$ = 78 c.p.s. This pattern can only be explained in terms of non-equivalent methylene protons.[5] A singlet due to the protons of the methyl group appears at τ, 8.27. The relative intensity of the *AB* pattern to the methyl group absorption is 2:3. The aromatic absorption is shifted to lower field relative to the hydrocarbon, Ia, and it covers a range of 65 c.p.s. (τ, 1.67 to τ, 2.75).

The methylene group formed by the protonation of Ia has been assigned to the 4-position. A methylene group at the 4-position is adjacent to an asymmetric center which causes the methylene protons to be in different chemical environments. These protons are nonequivalent and will appear as an *AB* pattern in the proton magnetic resonance spectrum. If protonation took place at the 2-position, the nonequivalency of the resulting methylene protons in the carbonium ion (IV) would be caused by the asymmetric center three carbon atoms away. It does not seem likely that in such a case the effect would be as great as was observed—*i.e.*, J = 18 c.p.s. and $\delta\nu$ = 78 c.p.s. The absence of any absorption in the vinyl proton region of the proton magnetic resonance spectrum of the carbonium ion is also sig-

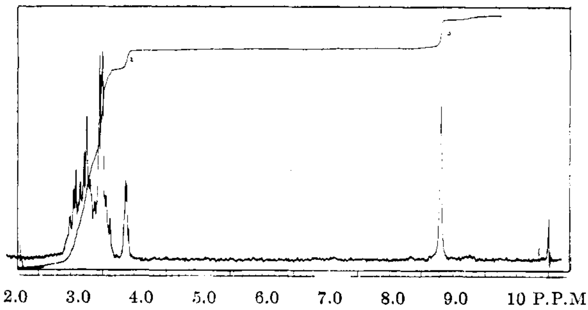


Figure 1

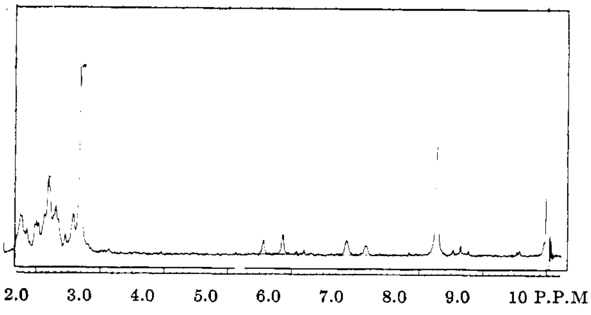


Figure 2

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[1] Grateful acknowledgment is made of partial support of this work by a grant from the National Science Foundation (G-6223) and of a Fellowship (1960–1962) to H. W. M. provided by the Phillips Petroleum Company.

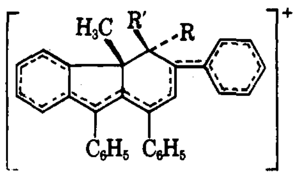
[2] H. W. Moore and H. R. Snyder, *J. Org. Chem.*, in press.

[3] R. W. Roeske, D. B. Bright, R. L. Johnson, W. J. DeJarlais, R. W. Bush, and H. R. Snyder, *J. Am. Chem. Soc.*, **82**, 3128 (1960).

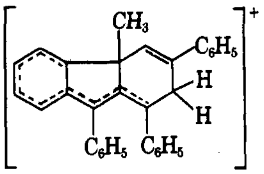
[4] R. W. Bush, thesis, Doctor of Philosophy, University of Illinois, 1960.

[5] L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1959, p. 85.

nificant. Protons bonded to carbon atoms which carry a partial positive charge, as in conjugated aromatic carbonium ions, show a significant shift to lower field (relative to the neutral hydrocarbon) in the proton magnetic resonance spectrum.[6-10] Protonation at the 4-position would result in a highly conjugated carbonium ion (IIIa) in which the carbon atom at the 2-position would carry some of the positive charge. This would shift the absorption due to the proton at position 2 to lower field; it would appear near or under the aromatic absorption. On the other hand, protonation at the 2-position would result in a carbonium ion (IV) in which no charge can be carried on the 3, 4, and 4a positions. Therefore, the proton at the 4-position would be expected to show absorption in the vinyl proton region—*i.e.*, τ, 3 to τ, 5.[11] As stated above, the proton magnetic resonance spectrum of the carbonium ion formed by the protonation of Ia shows only aromatic, methylene, and methyl absorption. Therefore, position 4 is favored as the site of protonation. Ground state resonance stabilization of the carbonium ion also favors the carbonium ion formed by protonation of the 4-position; nine resonance structures can be drawn for IIIa while only five can be drawn of IV (the phenyl groups at the 1- and 9-positions cannot be coplanar with the rest of the molecule, and their resonance contribution to the carbonium ion therefore is probably negligible).



IIIa. R = R' = H
b. R = D, R' = H
c. R = H, R' = D



IV

Unequivocal evidence that the site of protonation is position 4 and that attack at position 4 is stereospecific was obtained in the following manner. The hydrocarbon was brominated with dimethyl sulfoxide–ethyl bromide according to the method of Fletcher and Pan.[12] This reaction, which is the first reported example of a bromination of a hydrocarbon under these conditions, led to a 66% yield of 4-bromo-4a-methyl-1,3,9-triphenyl-4a*H*-fluorene (Ic). The n.m.r. spectrum of compound Ic showed the absorption of only one vinyl proton, as a singlet, at τ, 3.70. Therefore, the bromine atom could either be in the 4- or the 2-position. The bromine atom was replaced with a deuterium atom by treatment of an ether solution of Ic with butyllithium followed by the addition of 99.5% deuterium oxide to the intense blue-green solution, giving a 61% yield of 4a-methyl-1,3,9-triphenyl-4a*H*-fluorene-4d (Ib). The n.m.r. spectrum of the deuterated hydrocarbon showed the absorption of only one vinyl proton at τ, 3.40. A deuterium analysis of the deuterated hydrocarbon showed that one molecule of the hydrocarbon contained 1.57 atoms of deuterium (6.55 atom per cent). The deuterated compound, Ib, was treated with 48% hydrobromic acid in acetic acid under the same conditions[2,3] used to rearrange the hydrocarbon, Ia, to 4-methyl-1,3,9-triphenylfluorene, II. If the deuterium is in the 4-position of Ib, rearrangement would lead to the isomeric fluorene, II, with the loss of one atom of deuterium. If the deuterium was in the 2-position, no deuterium would be lost upon rearrangement. Rearrangement of the deuterated hydrocarbon, Ib, resulted in 4-methyl-1,3,9-triphenylfluorene, II, whose analysis showed 0.62 atom of deuterium per molecule (2.59 atom per cent). Therefore, the rearrangement involves the loss of one atom of deuterium and thereby proves that the deuterium was in the 4-position of Ib and that the bromine was in the 4-position of Ic. It will be shown that protonation occurs at the carbon bearing the deuterium in Ib—*i.e.*, position 4, thereby confirming the site of protonation.

The asymmetric center at 4a has a great directional influence on the protonation of 4a-methyl-1,3,9-triphenyl-4a*H*-fluorene, Ia. The carbonium ion is formed by a stereospecific attack at position 4. This was shown by the lack of deuterium exchange and by the investigation of the proton magnetic resonance spectra of carbonium ions IIIa, IIIb and IIIc. It was impossible to bring about exchange of the proton at position 4 for deuterium by allowing Ia to react with various deuterated acids. No deuterium was incorporated in Ia when it was allowed to stand at room temperature in deuteriotrifluoroacetic acid for one and a half hours, refluxed in deuterioacetic acid–catalytic amount of sulfuric acid for two hours, or refluxed in 50% (by weight) deuteriotrifluoroacetic acid–deuterium oxide for four days. Under each of these acid conditions the carbonium ion was formed. The hydrocarbon, Ia, was regenerated by the addition of deuterium oxide to the acid solutions. The lack of substitution of a deuterium for a proton at position 4 is due to a stereospecific attack of Ia from the least hindered side of the molecule. This results in forcing the original proton at the 4 position into a sterically protected environment. Exchange, under the conditions we employed, takes place only with the proton (or deuteron) which attacks the molecule. Stuart and Breglieb models show that attack of a proton from the side opposite the methyl group pushes the original proton into a position which is protected by the proton at position 5, the methyl group, and the phenyl ring at position 3. The attacking proton is left in a position which would provide very little steric hindrance to the base which promotes the exchange. In the proton magnetic resonance spectrum (Figure 2) of IIIa (Ia in trifluoroacetic acid) the high field doublet of the *AB* pattern is slightly broadened, which may be an indication that the proton causing this absorption is undergoing exchange. However, the possibility that the broadening is caused by long-range coupling between one of the non-equivalent methylene protons and the methyl protons cannot be eliminated. Long-range coupling of this nature has recently been reported,[13] and

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[6] C. MacLean and E. L. Mackor, *Mol. Phys.*, **4**, 241 (1961).

[7] C. MacLean, J. H. van Der Waals, and E. L. Mackor, *ibid.*, **1**, 247 (1958).

[8] *Arch. Sci. Physiol.*, **13**, Special no. 553–554 (1960).

[9] G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960).

[10] J. R. Leto, F. D. Cotton, and J. S. Waugh, *Nature*, **180**, 978 (1957).

[11] The proton *cis* to the phenyl ring in α-methylstyrene absorbs at τ, 4.64. N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "High Resolution NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, spectrum no. 232.

[12] T. L. Fletcher and H. L. Pan, *J. Am. Chem. Soc.*, **78**, 4812 (1956); *Chem. Ind.*, (London) 660 (1957).

[13] H. Finegold, *Proc. Chem. Soc.*, 213 (1962).

could cause coupling of as much as 0.15 c.p.s. Each peak of the high-field doublet would be split into a quartet and unless very good resolution was obtained the doublet would have a broadened appearance. The proton magnetic resonance spectrum (Figure 3) of IIIb (Ia in deuteriotrifluoroacetic acid) shows that the high-field doublet of the *AB* pattern in the spectrum of IIIa is due to the attacking proton. The spectrum of IIIb shows a collapse of the *AB* pattern. The high-field doublet now disappears, since the carbonium ion, IIIb, is formed by the attack of a deuteron. The low-field doublet of the *AB* pattern coalesces to a singlet. The chemical shift of this singlet comes at τ, 5.47 which corresponds to the position of the center of gravity of the low-field doublet in the *AB* pattern of IIIa. The proton magnetic resonance spectrum (Figure 4) of IIIc (Ib in trifluoroacetic acid) again shows a collapse of the *AB* pattern of IIIa. The low-field doublet disappears as a result of the substitution of a deuterium for the proton which gave rise to the low-field doublet. The high-field doublet, which is due to the attacking proton, has now coalesced into a singlet at τ, 7.02. The chemical shift of this singlet (τ, 7.02) comes at the position corresponding to the center of gravity of the high-field doublet of the *AB* pattern of IIIa. These data can only be explained in terms of a stereospecific protonation of Ia at the 4-position.

Experimental[14]

Preparation of the Perchlorate of the Conjugate Acid of 4a-Methyl-1,3,9-triphenyl-4a*H*-fluorene.—Two grams (0.005 mole) of 4a-methyl-1,3,9-triphenyl-4a*H*-fluorene, Ia, was added to 60 ml. of glacial acetic acid in a 250-ml. Erlenmeyer flask. To this mixture was added 10 ml. of 70% perchloric acid. The mixture immediately became deep blue-green and the hydrocarbon dissolved completely. The flask was stoppered and allowed to stand at room temperature for 48 hr. At the end of this time the solution was concentrated by removal of 20 ml. of solvent by distillation at reduced pressure. The resulting blue-green solution was allowed to stand in the refrigerator at 8° for 48 hr. Filtration through a sintered glass funnel gave 2.2 g. (88%) of bronze crystals, m.p. 185–205° (decomp.).

Anal. Calcd. for $C_{32}H_{25}ClO_4$: C, 75.51; H, 4.91. Found: C, 75.66; H, 5.19.

The perchlorate appears to be very stable. When a few milligrams of the salt was placed in a flame, it burned with a yellow flame and gave off very dark smoke. No explosive decomposition took place. No decomposition was observed when the salt was scratched or hammered.

Preparation of the Fluoroborate of the Conjugate Acid of 4a-Methyl-1,3,9-triphenyl-4a*H*-fluorene.—One gram (0.0025 mole) of Ia was added to 30 ml. of glacial acetic acid in a 125-ml. Erlenmeyer flask. To this mixture was added 10 ml. of a 30% (by weight) solution of fluoroboric acid in tetramethylene sulfone.[15] An intense blue-green solution was immediately obtained upon addition of the acid. The flask was stoppered and allowed to stand at room temperature for 48 hr. Filtration of the reaction mixture gave 0.7 g. (56%) of the bronze crystalline fluoroborate. The salt gave a positive flame test for boron. The infrared spectrum (KBr disk) was nearly identical to that of the perchlorate. The fluoroborate is rather unstable. It loses hydrogen fluoride and boron trifluoride upon standing at room temperature. It can be stored much more conveniently when kept at 0°. Upon heating it loses its bronze color and becomes a rather dull yellow. This solid melts with decomposition, evolution of a gas, from 180 to 225°. The salt is soluble in organic solvents such as acetone and acetic acid. Addition of water to solutions of the salt results in almost quantitative conversion to the hydrocarbon, Ia.

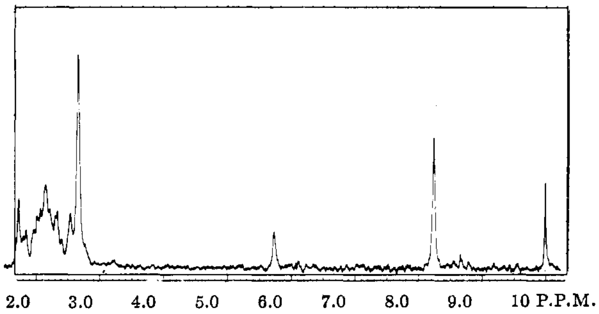

Figure 3

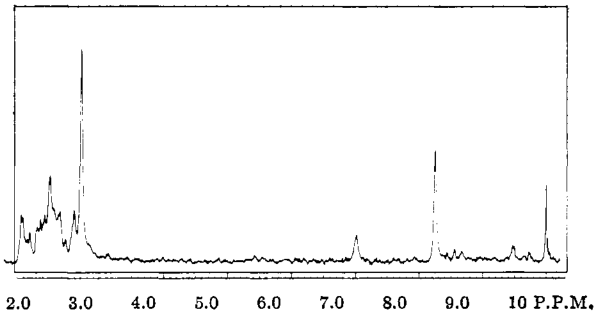

Figure 4

Preparation of the Bromide of the Conjugate Acid of 4a-Methyl-1,3,9-triphenyl-4a*H*-fluorene.—Two grams (0.005 mole) of Ia was dissolved in 100 ml. of dry benzene in a 250-ml. three-necked, round-bottom flask equipped with a gas inlet tube and a condenser. The solution was cooled to 0° by means of an ice bath and gaseous anhydrous hydrogen bromide was bubbled through the solution for 35 min. Immediately upon introduction of the hydrogen bromide the solution became deep blue-green in color. At the end of 35 min. a bronze crystalline solid formed in the bottom of the flask. The reaction mixture was allowed to warm to room temperature and stand for 12 hr. The crystalline solid was then removed by filtration, giving 2.0 g. (80%) of the bronze colored salt. The salt can be stored for indefinite periods of time at 0° in a tightly stoppered container. Upon heating the salt loses hydrogen bromide, giving Ia, m.p. 177–180° (lit. m.p., 180–181°[2,3]).

Reaction of the Perchlorate with Water.—To 100 ml. of dry reagent-grade acetone was added 0.3683 g. (0.000721 mole) of the perchlorate of the conjugate acid of 4a-methyl-1,3,9-triphenyl-4a*H*-fluorene. The solution had a deep blue-green coloration. Ten milliliters of water was added to the acetone solution. The blue-green color immediately disappeared and a yellow solid precipitated. This solid was filtered and dried, giving 0.2921 g. (0.000716 mole) of 4a-methyl-1,3,9-triphenyl-4a*H*-fluorene, Ia, m.p., 177–179°. A mixed melting point with an authentic sample of Ia showed no depression. The infrared spectrum was also identical to that of an authentic sample of Ia.

Preparation of Deuterioacetic Acid.—A mixture of 12 g. (0.60 mole) of 99.5% deuterium oxide and 70 g. (0.68 mole) of freshly distilled acetic anhydride was refluxed for 1 hr. The solution was fractionated and yielded 80 g. of deuterioacetic acid.

Attempted Deuteration of 4a-Methyl-1,3,9-triphenyl-4a*H*-fluorene, Ia, in Deuteriotrifluoroacetic Acid.—Three grams (0.0075 mole) of Ia was dissolved in 34 g. (0.16 mole) of trifluoroacetic anhydride in a 250-ml. three-necked, round-bottomed flask equipped with a dropping funnel, calcium chloride protected condenser and an automatic stirrer. The solution was cooled to 0° by means of an ice water bath. Four grams (0.20 moles) of 99.5% deuterium oxide was dropped into the stirred solution over a period of 20 min. Hydrolysis of the anhydride took place instantaneously giving a deep blue-green solution. This solution was stirred at room temperature for 1.5 hr. Thirty-five grams of deuterium oxide was then added, resulting in the precipitation of Ia. The mixture was stirred for 30 min. The yellow solid, Ia, was recovered by filtration. No deuterium could be detected by infrared and n.m.r. spectra (estimated sensitivity of these tests, 5%).

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(14) Melting points are uncorrected. Microanalyses were carried out by Mr. Josef Nemeth and his associates, University of Illinois.

(15) J. W. Powell and M. C. Whiting, *Proc. Chem. Soc.*, 412 (1960).

Attempted Deuteration of 4a-Methyl-1,3,9-triphenyl-4a*H*-fluorene in Deuterioacetic Acid–Concentrated Sulfuric Acid.—Two grams (0.005 mole) of Ia was added to a solution of 50 g. of deuterioacetic acid and 100 mg. of concentrated sulfuric acid (0.001 mole). Immediately upon addition of the hydrocarbon the solution became deep blue-green in color. The solution was refluxed with stirring for 2 hr. and then allowed to stand at room temperature for 12 hr. Twelve grams of 99.5% deuterium oxide was then added to bring about precipitation of Ia. The solid was collected by filtration. The infrared and nuclear magnetic resonance spectra showed no incorporation of deuterium.

Attempted Deuteration of 4a-Methyl-1,3,9-triphenyl-4a*H*-fluorene, Ia, in 50% Deuteriotrifluoroacetic Acid–Deuterium Oxide.—Two grams (0.005 moles) of Ia was added to 70 g. of 50% (by weight) deuteriotrifluoroacetic acid–99.5% deuterium oxide. This blue-green heterogeneous mixture was refluxed for 4 days. The reaction mixture was then cooled and the solid, Ia, collected by filtration. The infrared and n.m.r. spectra showed no incorporation of deuterium.

Bromination of 4a-Methyl-1,3,9-triphenyl-4a*H*-fluorene with Ethyl Bromide in Dimethyl Sulfoxide. Preparation of 4-Bromo-4a-methyl-1,3,9-triphenyl-4a*H*-fluorene, Ic.—Two grams (0.005 moles) of Ia was added to 100 ml. of dry dimethyl sulfoxide in a 250-ml. three-necked, round-bottom flask equipped with a thermometer, calcium chloride protected condenser and an automatic stirrer. Ten milliliters of ethyl bromide was then added to the reaction mixture. The mixture was vigorously stirred while it was slowly heated. At a temperature of 50° the color of the reaction mixture became deep blue-green and at 60° complete solution occurred. The solution was heated to 70°. Approximately 15 min. after the color change to blue-green there was another color change from blue-green to yellow. The solution was allowed to cool to room temperature after the second color change. Two hundred milliliters of water was added to the reaction solution, causing the precipitation of a bright yellow solid. This solid was collected by filtration, giving 2.3 g. Recrystallization twice from a 1:1 mixture of ethanol and chloroform gave 1.6 g. (66%) of yellow crystalline 4-bromo-4a-methyl-1,3,9-triphenyl-4a*H*-fluorene, Ic, m.p., 212–214°.

Anal. Calcd. for $C_{32}H_{23}Br$: C, 78.85; H, 4.72. Found: C, 78.66; H, 4.73.

Bromine was detected by sodium fusion and by the Beilstein test. The infrared spectrum of Ic was very similar to that of Ia. The n.m.r. spectrum of Ic in chloroform showed, in addition to aromatic and methyl absorption, only one vinyl proton at τ, 3.70. The n.m.r. spectrum of the starting material, Ia, showed absorption of two vinyl protons at τ, 3.33.

Reaction of 4-Bromo-4a-methyl-1,3,9-triphenyl-4a*H*-fluorene with Butyllithium Followed by Deuterium Oxide. Preparation of 4a-Methyl-1,3,9-triphenyl-4a*H*-fluorene-4d.—One and one half grams (0.0031 mole) of Ia was dissolved in 200 ml. of anhydrous diethyl ether in a 500-ml. three-necked, round-bottom flask equipped with a dropping funnel and a calcium chloride drying tube. Twenty milliliters of a butyllithium solution (15% by weight in one third pentane and two thirds heptane, Foote Mineral Company) was added in one portion. Immediately upon addition of the butyllithium, the solution became deep blue-green. This solution was allowed to stand at room temperature for 15 min. Four grams of 99.5% deuterium oxide was then slowly added causing an immediate vigorous reaction. The color changed from deep blue-green to yellow. The solvent was removed by distillation under reduced pressure leaving a yellow solid. This material was recrystallized from a 1:1 mixture of ethanol and ether, giving 0.8 g. (0.0019 mole, 61%) of 4a-methyl-1,3,9-triphenyl-4a*H*-fluorene-4d, m.p. 179–180°.

The infrared spectrum was identical to that of Ia except for a small peak at 2250 cm.$^{-1}$ due to the C—D stretching frequency. The n.m.r. spectrum showed absorption of only one vinyl proton at τ, 3.40. The n.mr. spectrum of Ia showed absorption of two vinyl protons at τ, 3.33.

N.m.r. Spectroscopy.—The n.m.r. spectra were recorded by Mr. D. Johnson and his associates with a Varian Associates high resolution spectrometer (A-60) at a frequency of 60 Mc. per second. Spectra were obtained in 30% solutions with tetramethylsilane as an internal standard. Chemical shifts are expressed as shielding values, τ, as defined by G. V. D. Tiers.[16]

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[16] G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

The Chemistry of Actinamine[1]

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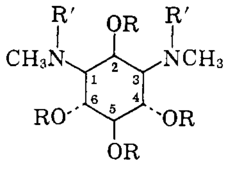
Received September 10, 1962

Chemical evidence is presented for the structure and stereochemistry of actinamine, I, a degradation product of the antibiotic actinospectacin.

Actinospectacin,[3] a broad spectrum antibiotic produced by the actinomycete *Streptomyces spectabilis* has the composition $C_{14}H_{24}N_2O_7 \cdot 2HCl \cdot 5H_2O$. Hydrolysis of actinospectacin with hot 6 *N* hydrochloric acid gives a crystalline fragment, actinamine dihydrochloride $C_8H_{18}N_2O_4 \cdot 2HCl$. The free base, actinamine $C_8H_{18}N_2O_4 \cdot 1/2H_2O$, is readily obtained from its dihydrochloride by ion exchange. In the following discussion we present chemical evidence for the structure and stereochemistry of actinamine (I).



I. R = R′ = H
II. R = R′ = CH_3CO
III. R = H, R′ = CH_3CO
VI. R = H, R′ = CH_3
VII. R = CH_3CO, R′ = CH_3
XI. R = H, R′ = $COOCH_3$
XII. R = CH_3CO, R′ = $COOCH_3$

Functional Groups and Carbon Skeleton of Actinamine.—The infrared absorption spectrum of actinamine shows no evidence of unsaturation. Strong absorption at 3300 cm.$^{-1}$ shows the presence of hydroxyl and/or amino groups. The basic nature of both nitrogen atoms is obvious from the formation of a dihydrochloride. Potentiometric titration of the dihydrochloride against sodium hydroxide gave two breaks in the curve and the neutralization equivalent obtained agreed with that expected for I. Titration of actinamine against aqueous hydrochloric acid gave pK_a values 7.2

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[1] (a) Research supported by grant E-1138 of the U. S. Public Health Service; (b) A. L. Johnson, Union Carbide Predoctoral Fellow at the University of Rochester, 1962–1963.

[2] To whom inquiries should be addressed.

[3] (a) D. J. Mason, A. Dietz, and R. M. Smith, *Antibiot. Chemotherapy*, **11**, 118 (1961); (b) M. E. Bergy, T. E. Eble, and R. R. Herr, *ibid.*, **11**, 661 (1961); (c) P. F. Wiley, *J. Am. Chem. Soc.*, **84**, 1514 (1962); (d) D. D. Chapman, R. L. Autrey, R. H. Gourlay, A. L. Johnson, J. Souto, and D. S. Tarbell, *Proc. Natl. Acad. Sci., U.S.*, **48**, 1108 (1962); (e) After the preparation of this manuscript a communication by H. Hoeksema, A. D. Argoudelis, and P. F. Wiley describing the complete structure of actinospectacin appeared in *J. Am. Chem. Soc.*, **84**, 3212 (1962).