60–68°). Recovered sulfur (19 mg., 56%)[12] was eluted with petroleum ether (b.p. 60–68°). Recovered III (0.09 g., 67%, m.p. 127–145°) was eluted with a 30% solution of methylene chloride in petroleum ether (b.p. 60–68°). The purest fraction of III, m.p. 142–145°, gave a mixed m.p. of 140–143° with authentic III (m.p. 144.5–145.5°). Subsequent fractions were eluted with solutions containing up to 100% methylene chloride, but the yellow oils and semi-solids obtained bore no resemblance to the by-product X.

Infrared Analysis of Mixtures of I, II and III.—The infrared spectra were recorded on the Perkin–Elmer Model 21 double beam spectrophotometer equipped with sodium chloride optics. The analysis was based on the following characteristic maxima: 2-*p*-methoxyphenyl-4-phenylthiophene (III), 731 cm.$^{-1}$; 2-*p*-methoxyphenyl-5-phenyl-1,4-dithiadiene (I), 746 cm.$^{-1}$; 2-phenyl-4-*p*-methoxyphenylthiophene (II), 762 cm.$^{-1}$. All three maxima were strong sharp peaks and, in mixtures, were neatly resolved. The intensities of the maxima were measured relative to an absorbance minimum which appeared in all the spectra at 677 cm.$^{-1}$. Three other minima, and three lines drawn among the four minima, were also examined as prospective base lines.[13] But absorptivity, tabulated as a function of base line in a series of reference spectra, varied much less among different base lines in a single spectrum than among different spectra at the same base line, indicating that any of the seven base lines considered was suitable within the experimental error. It was convenient to use the absorption minimum at 677 cm.$^{-1}$.[14]

Reference spectra for the analysis were prepared from samples of the pure compounds (I, II, III) and from mixtures of I, II and III. Calibration curves constructed from these spectra showed that the intensities measured at the three wave lengths varied linearly with concentration.

(12) Sulfur was determined by the ultraviolet spectroscopic method of J. K. Bartlett and D. A. Skoog, *Anal. Chem.*, **26**, 1008 (1954).

(13) For a discussion of the base line technique see R. P. Bauman in "Advanced Analytical Chemistry," by L. Meites and H. C. Thomas, McGraw–Hill Book Co., Inc., New York, N. Y., 1958, Chap. 9.

(14) Good results were also obtained with a single minimum for a base line by G. S. Hammond and K. J. Douglas, THIS JOURNAL, **81**, 1184 (1959).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY, DURHAM, N. C.]

Some Reactions of 2-Aza-1,2-dihydrodicyclopentadiene[1,2]

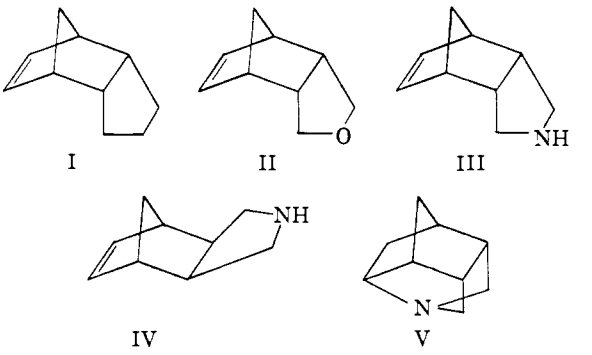
BY CHICITA F. CULBERSON AND PELHAM WILDER, JR.

RECEIVED MARCH 10, 1960

Both the *exo* and the *endo* isomers of 2-aza-1,2-dihydrodicyclopentadiene react with halogen acids to give unrearranged 9-halo derivatives and in the *endo* compound the stereochemical configuration of the halogen substituent permits facile intramolecular cyclization. The lack of rearrangement in the 2-oxa- and 2-aza-1,2-dihydrodicyclopentadiene systems is discussed briefly.

While 1,2-dihydro-*endo*-dicyclopentadiene (I), *endo*-dicyclopentadiene and similar systems are known to rearrange to their less hindered *exo* forms by addition of acids to the norbornylene double bond,[3–5] 2-oxa-1,2-dihydro-*endo*-dicyclopentadiene (II) undergoes many of the same reactions with little or no rearrangement.[6] The synthesis of the *endo* and *exo* isomers of 2-aza-1,2-dihydrodicyclopentadiene (III and IV)[7] now leads to a study of the reactions of these amines with acids. Neither isomer undergoes rearrangement, but the stereochemistry of the addition of halogen acids to the *endo* compound allows intramolecular cyclization leading to a novel tertiary amine.[8]

The tertiary amine V was originally isolated upon addition of hydrobromic acid to 2-aza-1,2-dihydro-*endo*-dicyclopentadiene (III). After the publication of a brief statement of these results, it was found that the tertiary amine V can be more easily obtained in pure form by the reaction of



I II III IV V

hydrochloric acid with the secondary amine III. The present paper concerns the addition of hydrobromic and hydrochloric acids to 2-aza-1,2-dihydro-*endo*-dicyclopentadiene (III), the addition of hydrobromic acid to 2-aza-1,2-dihydro-*exo*-dicyclopentadiene (IV) and the proof of the structure of the tertiary amine V.

The *endo*-amine III, cooled in an ice-bath and treated with concentrated hydrobromic acid, yields the hydrobromide VI. After heating the amine III for five hours in excess hydrobromic acid, it is converted to a bromoamine hydrobromide VIII. This salt, difficult to isolate and purify, was removed in one run to determine the nature of the product before neutralization. Addition of base to the reaction mixture precipitates the tertiary amine V contaminated with starting material. Both these amines are subliming solids. Although a pure sample of the tertiary amine V can be obtained by repeated vacuum sublimations of the mixture, such purification is both tedious and

(1) Presented in part before the Division of Organic Chemistry, 135th National Meeting, American Chemical Society, Boston, Mass., April 5–10, 1959.

(2) Taken in part from a dissertation submitted by Chicita F. Culberson to the Graduate School of Duke University in partial fulfillment of the requirements for the Ph.D. degree, 1959.

(3) P. D. Bartlett and A. Schneider, THIS JOURNAL, **68**, 6 (1946).

(4) H. A. Bruson and T. W. Riener, *ibid.*, **67**, 723, 1178 (1945); **68**, 8 (1946).

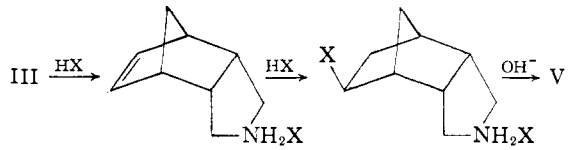
(5) P. Wilder, Jr., Chicita F. Culberson and G. T. Youngblood, *ibid.*, **81**, 655 (1959).

(6) Chicita F. Culberson, J. H. Seward and P. Wilder, Jr., *ibid.* **82**, 2541 (1960).

(7) Chicita F. Culberson and P. Wilder, Jr., *J. Org. Chem.*, **25**, 1358 (1960).

(8) P. Wilder, Jr., and Chicita F. Culberson, THIS JOURNAL, **81**, 2027 (1959).

unreliable. The Hinsburg method for separations of secondary and tertiary amines is not applicable here because the tertiary amine V is cleaved yielding a chloroamine benzenesulfonamide. Attempted separations with acetic anhydride and with 3-nitrophthalic anhydride[9] were also unsuccessful.

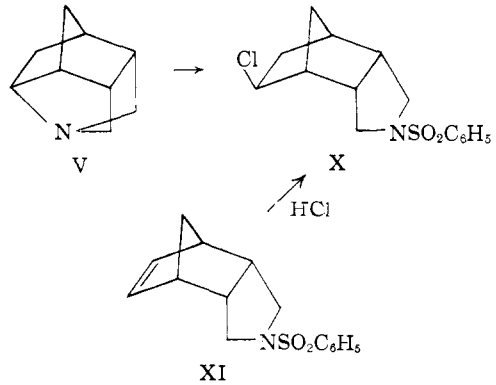


VI, X = Br VIII, X = Br
VII, X = Cl IX, X = Cl

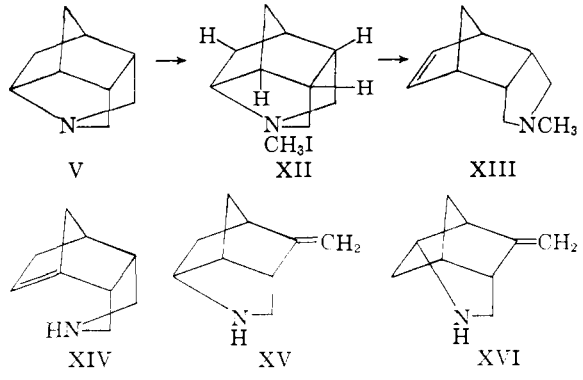
Addition of hydrochloric acid to the secondary amine III proceeds with less decomposition and the chloroamine hydrochloride formed can be separated and purified more easily and in higher yield than the corresponding bromoamine hydrobromide. With base such a haloamine salt should yield the tertiary amine V free of secondary amine starting material; therefore previous reactions involving hydrobromic acid and the *endo*-amine III were repeated using hydrochloric acid.

When the *endo*-amine III is cooled in an ice-bath and concentrated hydrochloric acid is added slowly, the amine hydrochloride VII precipitates. This salt is identical to that obtained by bubbling hydrogen chloride gas through a solution of the amine III in anhydrous ether and is converted, by addition of aqueous picric acid, to the same picrate obtained from the free amine III. When excess hydrochloric acid is added to the amine III and the solution is heated and stirred for several hours, the chloroamine hydrochloride IX is isolated upon cooling the reaction mixture. This salt yields a chloroamine picrate by addition of aqueous picric acid, but all attempts to isolate the free chloramine failed. Instead when a solution of the chloroamine hydrochloride IX is made basic, the halogen-free tertiary amine V is liberated in high yield. The purity of this product with respect to the starting amine III was proved by gas chromatography: one peak was clearly distinguishable by retention time from the possible contaminant.

The tertiary amine V forms a high melting picrate, a hydrochloride, a methiodide and as previously noted a chloroamine benzenesulfonamide. This chloroamine benzenesulfonamide is also obtained by the addition of hydrochloric acid to the benzenesulfonamide XI of the *endo*-amine. In structure X the chloroamine benzenesulfonamide is shown to have the *endo* configuration. There is no direct proof for this formulation and it is possible that both reactions leading to this product proceeded with rearrangement yielding 9-*exo*-chloro-2-azatetrahydro-*exo*-dicyclopentadiene. Since the tertiary amine V reacts with hydrochloric acid without rearrangement (*vide infra*), the unrearranged *exo*-chloro structure for the benzenesulfonamide seems more probable. The tertiary amine V probably complexes with the benzenesulfonyl chloride and then chloride ion attacks at C_9.



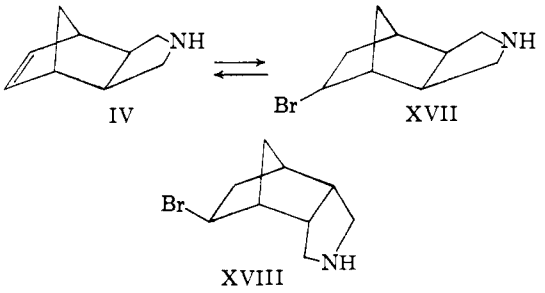
The tertiary amine V could not be reduced over Adams catalyst at one atmosphere pressure although both the *endo* and the *exo* secondary amines are reduced quickly under these conditions.[7] Molecular weight determination and elemental analysis show that the tertiary amine V is isomeric with the *endo*-amine and the structure of the tertiary amine finally was proved by a Hofmann degradation. The major product of the decomposition of the hydroxide obtained from the tertiary amine methiodide XII was proved to be N-methyl-2-aza-1,2-dihydro-*endo*-dicyclopentadiene, previously obtained by two other routes.[7] The gas chromatograph of the crude Hofmann product has a single large peak and a very small peak at a slightly lower retention time. N-Methylamine XIII causes the large peak but the product responsible for the small peak was not determinable. In analyzing the possible products of this Hofmann degradation it is seen that there are four β-hydrogens, one at each of the carbons C_4, C_5, C_6 and C_9. Elimination of the C_6-hydrogen would give an olefin violating Bredt's rule (see structure XIV). Only elimination at C_9 can give a product having an *endo*-cyclic rather than an *exo*-cyclic (XV and XVI) double bond. The small peak observed in the chromatograph of the Hofmann degradation product may be due to one of the other possible products, both of which are unknown.



Addition of hydrobromic acid to 2-aza-1,2-dihydro-*exo*-dicyclopentadiene (IV) yields a bromoamine (XVII). If rearrangement had occurred during this addition, the product would have been 9-*exo*-bromo-2-aza-1,2-dihydro-*endo*-dicyclopentadiene (XVIII) which would cyclize to the tertiary

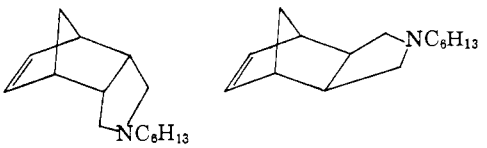
(9) J. W. Alexander and S. M. McElvain, THIS JOURNAL, **60**, 2285 (1938).

amine V upon the addition of base. No tertiary amine was observed and dehydrohalogenation of the haloamine yielding the starting *exo*-amine IV.



IV XVII XVIII

The course of the addition of hydrobromic acid to an N-alkylated 2-aza-1,2-dihydrodicyclopentadiene was studied briefly. The N-hexyl *endo* and *exo* compounds (XIX and XX) yield different bromoamine hydrobromides upon treatment with concentrated hydrobromic acid. That rearrangement did not occur is indicated but certainly not proved since the compounds could differ by the configuration of the 9-bromo substituent, in which case the halogen would have had to add *endo* to the amine which reacted without rearrangement. Further studies of N-alkylated cases are necessary to determine the course of these reactions. Cyclization in the *endo* compounds is complicated because the product would be a salt.



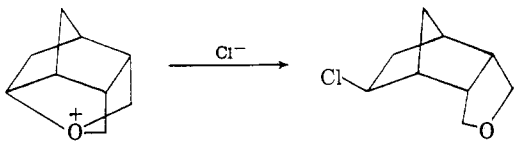
XIX XX

It was thought that alkyl halides might add to the tertiary amine V to give haloamine quaternary salts by opening the N–C_9 bond in a manner similar to that observed with benzenesulfonyl chloride. Cleavage with methyl iodide occurs with N-methylethyleneimine.[10] Such a reaction would complicate the results of the Hofmann degradation, but the methiodide of the tertiary amine V gives correct analysis for the addition of just one methyl iodide. Reaction of the tertiary amine V with hexyl bromide yields a quaternary salt isolated as the perchlorate which has the correct analysis for the tertiary amine hexyl perchlorate.

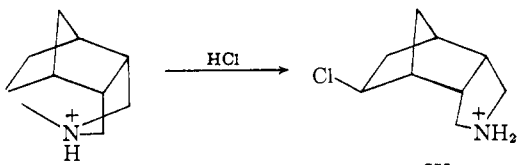
Discussion

Skeletal rearrangements observed upon addition of acids to norbornylene double bonds have been attributed to steric factors[11]: for example the highly hindered 1,2-dihydro-*endo*-dicyclopentadiene (I) gives 9-substituted derivatives of tetrahydro-*exo*-dicyclopentadiene, in which the cyclopentyl ring occupies a much less crowded position. When an oxygen is substituted for the methylene group at the 2-position of 1,2-dihydro-*endo*-dicyclopentadiene, the addition of acids to the double bond proceeds with little or no rearrangement. This must be explained by an electronic effect of the 2-oxa atom, since steric factors are almost identical to those in the hydrocarbon analog. In the 2-aza system no *endo* to *exo* rearrangement is observed upon treatment with strong acids.

An initially appealing explanation of the lack of *endo* to *exo* rearrangement in the 2-oxa and 2-aza systems involves reaction of the C_9-carbonium ion with an electron pair of the oxygen or nitrogen, yielding intermediates of the type XXI and XXII. Attack of halide ion at C_9 displacing the electron pair to the heteroatom would yield unrearranged derivatives. This route now has been tested in the 2-aza system where the intermediate XXII is identical to the salt of the tertiary amine V. Two



XXI



XXII IX

experiments to determine the ease with which hydrochloric acid reacts with the tertiary amine V to open the C_9–N bond show that although cleavage can occur, no reaction is observed when the tertiary amine is treated with hydrochloric acid under the mildest conditions used to prepare the chloroamine hydrochloride IX from the secondary amine III. Also no salts of the tertiary amine V have been obtained from the reaction mixtures of the secondary amine III with either hydrochloric or hydrobromic acids. Therefore, the tertiary amine V is not an intermediate in the reaction of the secondary amine III with hydrochloric acid.

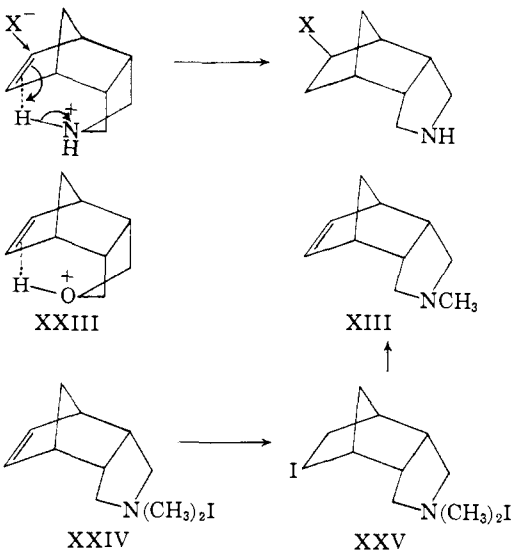
Acid addition without rearrangement might involve donation of a proton from the amine salt or secondary oxonium ion XXIII with concerted attack by halide ion. Such a route to unrearranged derivatives would not require the free C_9-carbonium ion, which could rearrange, or the C_9-heteroatom cyclic intermediate rejected above. To test this mechanism, hydriodic acid was added to the methiodide XXIV. Dehydrohalogenation and Hofmann degradation of the addition product yields unrearranged N-methylamine XIII. Thus, at least in this case, intramolecular attack is not required for retention of the stereochemical configuration of the pyrrolidyl ring during addition of strong acid to the norbornylene double bond.

Bromination of the cyclopentadiene–maleic anhydride adduct is known to yield an unrearranged *exo-cis*-dibromide. Kwart and Kaplan[12] propose that an inductive effect of the carbonyl substituent inhibits contribution of a nortricyclinium ion and in this way prevents rearrangement. It has been

(10) W. Marckwald and O. Frobenius, *Ber.*, **34**, 3544 (1901).

(11) See for example D. H. R. Barton, *J. Chem. Soc.*, 1027 (1953).

(12) H. Kwart and L. Kaplan, THIS JOURNAL, **76**, 4078 (1954).



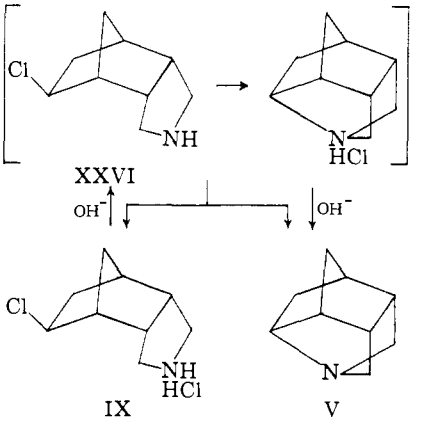
suggested[13] that the protonated heteroatoms in the 2-oxa and 2-aza systems may inhibit rearrangement through inductive or field effects in a manner similar to that described by Kwart and Kaplan.

Such an inductive effect should be greatest at C_1 and C_3 and diminished at C_4 and C_5, although field effects at the latter positions may be significant. We cannot but think it surprising, however, that inductive and field effects may have greater steric control over the reaction than the combined driving forces for rearrangement presented by steric strain in the *endo* configuration and the electrostatic repulsion of the C_9-carbonium ion and the quaternary nitrogen.

Cyclization of the chloroamine hydrochloride by addition of base is an example of a haloamine ring closure. Three-, five- and six-membered rings are formed by the action of base on haloamines of the type $X(CH_2)_nNH_2$. The kinetics of this cyclization as a function of n and the entropy effect retarding cyclizations where n is from six to ten are reviewed by Streitwieser.[14] Rate studies have shown that for straight chain haloamines, the five-membered ring, $n = 4$, is the most rapidly formed. Transannular interaction of nitrogen and carbonyl groups in rings of medium size is reviewed by Leonard.[15] In simple monocyclic compounds interactions are observed between groups diametrically substituted on eight-, nine- and ten-membered rings, reaction in these instances yielding pentalane, indane and decalin systems.

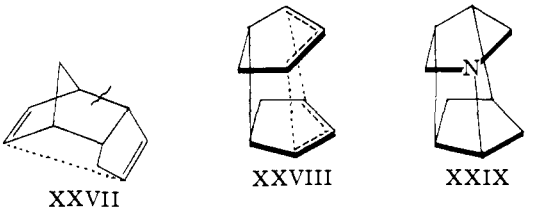
In the synthesis of the tertiary amine V a five-membered ring is formed. Counting the number of atoms in each of the rings which include nitrogen there are two each with five, six, seven and nine and three with eight. Of those a five, an eight- and a nine-membered ring are already present before cyclization. Therefore, the cyclization stop creates eight new nitrogen-containing rings, five of which have more than six members. The large entropy change contributing to the lessened rate of formation of nitrogen cycles of 7–11 members would not apply to the present system since the members of these cycles are already highly restrained.

In neutral solution, a haloamine capable of ring closure is in equilibrium with the cyclized amine salt. Although the hydrochloride and picrate salts are stable, the free haloamine, 9-*exo*-chloro-2-aza-1,2-dihydro-*endo*-dicyclopentadiene (XXVI), could not be isolated. No measurements of basic strength have been made, but if the tertiary amine V is a weaker base than the chloroamine XXVI then the free chloroamine always would revert to a mixture of the tertiary amine V and the chloroamine hydrochloride IX.



The facile displacement of halogen by nitrogen in the present system suggests that the halide ion has the *exo* configuration. In this geometry the amine can displace from the rear, while if the halogen were *endo* the angle between the departing halide ion and the attacking nitrogen would be greatly reduced.

Recently Woodward and Katz[16] have presented evidence for a two-step mechanism for the Diels–Alder reaction on the basis of studies of the thermal rearrangements of α- and β-1-hydroxydicyclopentadienes. Using dicyclopentadiene (XXVII) as a model, Woodward illustrates the isomerization as passing through the structure XXVIII during formation of a C_2–C_9 bond and cleavage of a C_5–C_6 bond. When rewritten in the form XXIX, the tertiary amine V is geometrically similar to the structure proposed by Woodward and Katz.



Experimental[17]

Addition of Hydrobromic Acid to the *endo*-Amine III.—A solution of 15.0 g. (0.11 mole) of *endo*-amine[7] was refluxed

(13) Private communication from Dr. Paul von R. Schleyer.
(14) A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956).
(15) N. J. Leonard, *Rec. Chem. Prog.*, **17**, 243 (1956).
(16) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).
(17) Melting points and boiling points are uncorrected. Analyses are by Galbraith Microanalytical Laboratories, Knoxville, Tenn.; Drs. Weiler and Strauss, Oxford, Eng.; Dr. Ing. A. Schoeller Microanalytisches Laboratorium, West Germany; and Spang Microanalytical Laboratory, Ann Arbor, Mich. Gas chromatographs were run

for 5 hours in 26 ml. (0.23 mole) of 48% hydrobromic acid. The mixture was made basic with 25% sodium hydroxide and extracted with ether. The extract was dried over magnesium sulfate and removal of the solvent yielded 10.5 g. (70%) of crude product which could not be distilled effectively due to solidification in the condenser tube; initial boiling point 88° (0.8 mm.). The amine V was purified by repeated sublimation, m.p. 126–128° with sublimation at about 70°.

Anal. Calcd. for $C_9H_{13}N$: C, 79.95; H, 9.69; mol. wt., 135. Found: C, 79.58; H, 9.89; mol. wt., 149.

A picrate was prepared and recrystallized three times from ethanol–water, m.p. 273–275° dec.

Anal. Calcd. for $C_{15}H_{16}N_4O_7$: C, 49.45; H, 4.43. Found: C, 49.30; H, 4.32.

During the original addition of hydrobromic acid to the *endo*-amine cooled in an ice-bath, a solid formed which was soluble in excess acid. In one run a small sample of the salt VI was removed and purified by recrystallization from absolute ethanol, m.p. 246.5–248°.

Anal. Calcd. for $C_9H_{14}BrN$: C, 50.01; H, 6.53. Found: C, 50.29; H, 6.41.

This salt was proved to be the hydrobromide VI of the *endo*-amine by adding alkali and benzenesulfonyl chloride. The solid derivative which formed was recrystallized from ethanol, m.p. 107–108°; a mixed melting point with a sample of the benzenesulfonamide of the *endo*-amine III was not depressed.

In one preparation of the tertiary amine V the reaction mixture was cooled in an ice-bath prior to neutralization and a precipitate formed which was removed by filtration. The salt VIII was purified by recrystallization from absolute ethanol, m.p. 189.5–190.5°.

Anal. Calcd. for $C_9H_{15}Br_2N$: C, 36.39; H, 5.09. Found: C, 36.14; H, 5.21.

Addition of Hydrochloric Acid to the *endo*-Amine III.—Concentrated hydrochloric acid (38 ml., 0.46 mole) was added dropwise to 25 g. (0.19 mole) of the *endo*-amine III cooled in an ice-bath. A precipitate formed which redissolved in excess acid and the solution was warmed on a steam-bath with stirring for 24 hours. The reaction mixture was cooled in an ice-bath and the dark precipitate, collected by filtration, was recrystallized from absolute ethanol. The yield of chloroamine hydrochloride IX obtained, after one recrystallization and thorough washing with small portions of cold absolute ethanol to remove most of the color, was 9.5 g. (24%).[18] This solid was recrystallized several times for an analytical sample, m.p. 210–211°.

Anal. Calcd. for $C_9H_{15}Cl_2N$: C, 51.93; H, 7.26. Found: C, 51.78; H, 7.34.

The chloroamine picrate was obtained by adding a warm aqueous solution of picric acid to an aqueous solution of the chloroamine hydrochloride. The product was recrystallized from 95% ethanol, m.p. 184–185° (melts and resolidifies, then decomposes slowly over a large temperature range).

Anal. Calcd. for $C_{15}H_{17}ClN_4O_7$: C, 44.95; H, 4.28. Found: C, 45.15; H, 4.14.

The initial precipitate formed upon addition of hydrochloric acid to the cold amine was identified as the amine hydrochloride VII. The salt was separated after mixing equivalent amounts of amine and hydrochloric acid. The solid, purified by several recrystallizations from absolute ethanol–ether, was identical to that obtained by bubbling hydrogen chloride gas through a solution of the amine in anhydrous ether, m.p. 226–228° dec.

Anal. Calcd. for $C_9H_{14}ClN$: C, 62.96; H, 8.22. Found: C, 62.70; H, 7.99.

The hydrochloride, dissolved in water and treated with aqueous picric acid, yielded the picrate of the *endo*-amine III, m.p. 195–196° dec., a mixed melting point with a sample of the picrate obtained from the free amine was not depressed.

Preparation of the Tertiary Amine V from the Chloroamine Hydrochloride IX.—A suspension of 5.2 g. (0.025 mole) of the amine salt in 5 ml. of water was stirred and 20 ml. of 5 *N* sodium hydroxide was added dropwise. The mixture was covered with a layer of ether and stirred slowly with gentle warming for 1 hour. After the solution was cooled, the amine was removed by ether extraction. The ether solution was dried over magnesium sulfate and the solvent removed under diminished pressure. After one sublimation of the residue, 2.83 g. (84%) of the tertiary amine V was obtained. A sample of this product subjected to gas chromatography, gave a single peak after 21.4 min. at 190° and about 40 ml./min. helium flow. Under the same conditions and when admixed with a sample of the tertiary amine, the *endo*-amine III had a retention time of 18.2 min.

A sample of this tertiary amine known to be free of starting material was purified for analysis by two additional sublimations, m.p. 164–166.5° in a sealed tube.

Anal. Calcd. for $C_9H_{13}N$: C, 79.95; H, 9.69; mol. wt., 135. Found: C, 80.12; H, 9.76; mol. wt., 146, 149.

The hydrochloride salt was prepared by bubbling hydrogen chloride through a solution of the amine and anhydrous ether. The salt was recrystallized from absolute ethanol–anhydrous ether, m.p. 248.5–249° dec.

Anal. Calcd. for $C_9H_{14}ClN$: C, 62.96; H, 8.22. Found: C, 63.01; H, 8.38.

Reaction of the Tertiary Amine V with Benzenesulfonyl Chloride.—Four hundred milligrams (0.0030 mole) of the tertiary amine V in 5 ml. of 10% sodium hydroxide was treated with benzenesulfonyl chloride and stirred vigorously. A solid product was obtained from the alkaline solution which was recrystallized three times from absolute ethanol to give a pure sample, m.p. 176–177.5°; a Beilstein test was positive.

Anal. Calcd. for $C_{15}H_{15}ClNO_2S$: C, 57.77; H, 5.82. Found: C, 57.56; H, 5.83.

Reaction of 2-Aza-1,2-dihydro-*endo*-dicyclopentadiene Benzenesulfonamide (XI) with Hydrochloric Acid.—Six grams (0.022 mole) of the sulfonamide,[7] 20 ml. of 90–120° ligroin and 5.7 ml. (0.066 mole) of concentrated hydrochloric acid were stirred under reflux for 2 hours. First the solid dissolved on heating and then a precipitate formed which was removed by filtration; recrystallization from 95% ethanol yielded 4.3 g. (63%) of a crude solid, m.p. 165–170°. The product was recrystallized again, m.p. 171–172°, mixed melting point with the product of the tertiary amine and benzenesulfonyl chloride, 172–175°. The infrared spectra of the two derivatives were identical.

Attempted Reduction of the Tertiary Amine V.—A mixture of 100 ml. of absolute ethanol and Adams catalyst was saturated with hydrogen at one atmosphere of pressure for 30 min. When hydrogen uptake ceased, 0.0633 g. (0.00047 mole) of the tertiary amine was added. No hydrogen was absorbed in 4 hours. The activity of the catalyst then was confirmed by adding a small quantity of cyclohexene whereupon hydrogen was immediately absorbed. The solvent was removed under diminished pressure and 2.5 ml. of 10% sodium hydroxide and 0.15 g. of benzenesulfonyl chloride were added. The solid which formed during vigorous stirring of the mixture was recrystallized from ethanol–water and identified as the chloroamine benzenesulfonamide, m.p. 174–176°.

Tertiary Amine Methiodide XII.—Two grams (0.015 mole) of the amine in 4 ml. of absolute ethanol was treated dropwise with 1.5 ml. of methyl iodide. Heat was evolved and the methiodide precipitated. After 15 min., 0.5 ml. of methyl iodide was added and the reaction allowed to stand at room temperature for 30 min. The solid was removed by filtration and additional product was precipitated from the mother liquor by addition of anhydrous ether. The combined solids were washed with ether and dried in a desiccator yielding 4.0 g. (98%) of the methiodide, m.p. 279–280°. A small sample was purified by recrystallization from absolute ethanol, m.p. 282.5–283° dec.

Anal. Calcd. for $C_{10}H_{16}IN$: C, 43.33; H, 5.82. Found: C, 43.54; H, 5.85.

Hofmann Degradation of the Methiodide XII.—A solution of 3.28 g. (0.118 mole) of the methiodide in 10 ml. of water was added to a mixture of 0.47 g. (0.012 mole) of sodium hydroxide and 2.01 g. (0.012 mole) of silver nitrate in 20 ml. of water. The mixture was distilled almost to

with a Perkin–Elmer model 154-C vapor fractometer and a 2 m. × 6 mm. column packed with one part Union Carbide polypropylene glycol-1025 to four parts Johns–Manville Chromosorb W (30/60 mesh).

(18) Similar yields are obtained by refluxing the amine III and concentrated hydrochloric acid for 4 hours, but the salt is darker and not so easily purified.

dryness and then, as decomposition began, water was added dropwise while the distillation was continued. When reaction stopped, the distillate was extracted four times with ether. The ether was dried over magnesium sulfate and removed under diminished pressure.

A gas chromatograph of this product with 65 ml./min. helium flow and at 150°, showed a large peak at 9.0 min. The retention time was identical to that of N-methyl-2-aza-1,2-dihydro-*endo*-dicyclopentadiene from another source and different from that of the *exo* isomer (7.6 min.) of the N-methylamine. A small second peak was observed at 8.0 min. but the identity of this compound was not determined.

The remaining product of the degradation was distilled under reduced pressure, b.p. 77–79° (14 mm.), $n^{23}D$ 1.5065 (reported[7] b.p. 80–81° (15 mm.), $n^{23}D$ 1.5050) yielding 0.45 g. (20%) of the N-methylamine.

A picrate was prepared, m.p. 222–223.5° (reported[7] m.p. 222–223° dec.); mixed melting point with the picrate of the N-methyl-*endo*-amine, 222.5–224°; mixed melting point with the *exo* isomer, 221–227°.

Comparison of the infrared spectra of the Hofmann product and its picrate with those of the N-methylamine and its picrate definitely establish the identity of these compounds.

Reaction of Hydrochloric Acid and the Tertiary Amine. (1) Under Reflux Conditions.—To 0.50 g. (0.0037 mole) of the tertiary amine, cooled in an ice-bath, was added 0.70 ml. (0.0084 mole) of concentrated hydrochloric acid. The solution was heated under reflux, but an additional 0.20 ml. (0.0024 mole) of concentrated hydrochloric acid had to be added to keep the mixture from going dry. After 4 hours the reaction mixture was cooled and the solid which precipitated was removed by filtration. After one recrystallization from absolute ethanol a total of 0.5 g. of a mixture of hydrochloride salts was obtained. The first salt to precipitate from the aqueous reaction mixture was identified by infrared traces as the chloroamine hydrochloride, but the total product after recrystallization was a mixture. The hydrochlorides were converted to the picrates by treating an aqueous solution of the salts with aqueous picric acid. Fractional recrystallization of the mixed picrates from 95% ethanol yielded 0.07 g. (5.2%) of the tertiary amine picrate and 0.11 g. (7.3%) of the chloroamine picrate, identified by melting points, mixed melting points and infrared spectra.

(2) On the Steam-bath.—Concentrated hydrochloric acid (1.40 ml., 0.0168 mole) was added to 1.0 g. (0.0074 mole) of the tertiary amine cooled in an ice-bath. The solution was heated on a steam-bath for 24 hours. After this time there was only slight darkening of the solution and cooling in an ice-bath gave no precipitate. The aqueous solution was diluted with acetone and then ether was added. The solution was decanted from a precipitate, the process being repeated several times until the total volume of solution had reached about 500 ml. and no further precipitation of oil or solid was observed. The combined residues were taken up in absolute ethanol and the salts precipitated in fractions by adding ether to the warmed solution just to the cloudy point, cooling slowly, filtering and repeating the process until no more solid was obtained. Six fractions were obtained, but the last two were so small that they were combined. Each fraction was then identified as the tertiary amine hydrochloride by melting point and mixed melting point. Finally, infrared spectra were obtained for all fractions and these were compared with the curves of the tertiary amine hydrochloride and the chloroamine hydrochloride. The latter salt has a strong peak at 6.2 μ and several smaller peaks not present in the absorption curve of the tertiary amine hydrochloride. Peaks characteristic of the chloroamine hydrochloride were totally absent in the spectra of the reaction product and these spectra were all identical with that of the tertiary amine hydrochloride. The total yield of salt obtained was 1.05 g. (82%).

9-Bromo-2-aza-tetrahydro-*exo*-dicyclopentadiene (XVIII).—By the usual method 6.8 g. (0.05 mole) of the *exo*-amine IV[7] was refluxed with stirring in 17 ml. (0.15 mole) of 48% hydrobromic acid for 5 hours. The reaction mixture was cooled, poured into water, made basic with 25% sodium hydroxide and extracted with ether. The extract was washed with water and dried over magnesium sulfate. Removal of ether yielded 8.0 g. (73%) of crude bromoamine of which 2.0 g. was used to prepare derivatives and the remaining material was twice distilled to obtain a pure sample, b.p. 94–95° (0.2 mm.).

Anal. Calcd. for $C_9H_{14}BrN$: C, 50.01; H, 6.53. Found: C, 50.01; H, 6.74.

A picrate was prepared, m.p. 193–194° dec.

Anal. Calcd. for $C_{15}H_{17}BrN_4O_7$: C, 40.46; H, 3.85. Found: C, 40.64; H, 3.89.

A benzenesulfonamide was prepared and recrystallized from absolute ethanol, m.p. 174.5–176.5°.

Anal. Calcd. for $C_{15}H_{18}BrNO_2S$: C, 50.56; H, 5.09. Found: C, 50.39; H, 5.02.

Dehydrohalogenation of 9-Bromo-2-azatetrahydro-*exo*-dicyclopentadiene (XVIII).—A solution of 2.16 g. (0.010 mole) of the bromoamine XVIII and 2.24 g. (0.04 mole) of potassium hydroxide in 10 ml. of absolute ethanol was refluxed with stirring for 12 hours. The reaction mixture was diluted with water and extracted with ether. The extract was washed with water and dried over magnesium sulfate. Removal of the ether yielded a crude residue which was distilled under reduced pressure to give 0.72 g. (54%) of the *exo*-amine IV, b.p. 73–74° (7.5 mm.) (reported[7] b.p. 73–74° (7.5 mm.)).

A benzenesulfonamide was prepared and recrystallized from 95% ethanol; m.p. 112–113° (reported[7] m.p. 113–113.5°); a mixed melting point with an authentic sample was not depressed.

Reaction of the N-Hexyl-*endo*-amine XIX with Hydrobromic Acid. Preparation of the Hydrobromide of 9-Bromo-N-hexyl-2-aza-1,2-dihydro-*endo*-dicyclopentadiene.—To 4.4 g. (0.020 mole) of the N-hexylamine[7] cooled in an ice-bath was added with stirring 6.9 ml. of hydrobromic acid. The solution then was refluxed with stirring for 3 hours and, upon cooling the darkened reaction mixture in an ice-bath, 3.6 g. (47%) of crystalline product was obtained. A sample was purified by dissolving the solid in ethanol, treating the solution with Norite and precipitating the salt with anhydrous ether. The product was not hygroscopic and was insoluble in cold water, m.p. 210–211.5°.

Anal. Calcd. for $C_{15}H_{27}Br_2N$: C, 47.26; H, 7.14. Found: C, 47.10; H, 6.96.

Addition of Hydrobromic Acid to the N-Hexyl-*exo*-amine XX.—A solution of 2.8 g. (0.013 mole) of the N-hexylamine XX[7] in 4.4 ml. (0.04 mole) of 48% hydrobromic acid was refluxed with stirring. The mixture did not turn as dark as the reaction of the *endo*-N-hexylamine with hydrobromic acid. After 4 hours the brownish-red solution which was homogeneous at the temperature of the reaction was cooled to room temperature and a solid precipitated. The yield of crude salt XXXI dried in a vacuum desiccator overnight was 4.2 g. (85%). A sample was purified by precipitation from absolute ethanol by addition of anhydrous ether, m.p. 256–257°.

Anal. Calcd. for $C_{15}H_{27}Br_2N$: C, 47.26; H, 7.14. Found: C, 47.00; H, 6.97.

Treatment of the Tertiary Amine V with Hexyl Bromide and Preparation of the Quaternary Hexyl Perchlorate.—A solution of 2.0 g. (0.012 mole) of hexyl bromide and 1.35 g. (0.010 mole) of the tertiary amine V was allowed to stand for 2 hours. An oil formed which was dissolved in absolute ethanol. Precipitation by addition of anhydrous ether yielded a solid which readily liquified and darkened upon exposure to the air. All attempts to purify this salt were unsuccessful. The crude product was converted to the perchlorate which was recrystallized readily from water, m.p. 177–178°.

Anal. Calcd. for $C_{18}H_{26}ClNO_4$: C, 56.32; H, 8.19. Found: C, 56.38; H, 8.21.

Addition of Hydriodic Acid to the Methiodide XXIV.—Ten grams (0.034 mole) of the methiodide XXIV, 5.4 ml. (0.04 mole) of 55% hydriodic acid and 2 ml. of water were combined and heated under reflux for 3.5 hours during which time a precipitate formed in the hot solution. The mixture was cooled and the yellow solid collected by filtration. Most of the color was removed by repeated washing with cold absolute ethanol, in which the product was only slightly soluble, yielding 8.2 g. (57%) of crude product. A sample was purified for analysis by recrystallization from absolute ethanol, m.p. 212–214° dec.

Anal. Calcd. for $C_{11}H_{19}I_2N$: C, 31.52; H, 4.57. Found: C, 31.44; H, 4.80.

Dehydrohalogenation and Hofmann Degradation of the Iodoamine Methiodide XXV.—A suspension of 8.0 g. (0.019 mole) of the methiodide in a solution of 4.3 g. (0.077 mole) of potassium hydroxide and 25 ml. of absolute ethanol was heated under reflux with vigorous stirring for 15 hours. The mixture was filtered and diluted with water. An oily precipitate formed which was insoluble in ether, soluble in water and could be recrystallized from a mixture of absolute ethanol and ether. The identity of this product, of which 1.6 g. was obtained, is still under investigation. The ether extract was dried over magnesium sulfate and removal of ether left a very small residue which was not investigated further. The aqueous solution after ether extraction was evaporated to dryness and the solid was heated to cause decomposition. Water was added to aid in the distillation of the product. Heating followed by addition of water was continued until no further product could be observed. The ether extract of the distillate was dried over magnesium sulfate and evaporation of the ether left a small residue which was distilled under reduced pressure, b.p. about 75° (14 mm.) (reported[7] for the N-methylamine XIII, b.p. 80–81° (15 mm.)). The product was obviously contaminated, being dark in color and having a more pungent odor than that of the N-methylamine XIII. The yield of this crude product was 0.80 g. (36%). A methiodide was prepared, m.p. 254–256°; a mixed melting point with the methiodide of the N-methylamine was not depressed and the infrared spectra of the two samples were identical. A gas chromatograph of the once-distilled amine product showed a large peak at 11.1 min. caused by the N-methylamine and three very small peaks at 9.0, 10.6 and 15.0 min. The chromatograph was run at 149°, with a helium flow of about 60 cc./min. and the retention time of N-methyl-2-aza-1,2-dihydro-*exo*-dicyclopentadiene[7] under these conditions was 9.3 min.

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Reactions of Active Methylene Compounds in Pyridine Solution.[1] II. Aldol-type Reactions of Indene and Fluorene[2]

BY EUGENE GHERA AND YAIR SPRINZAK

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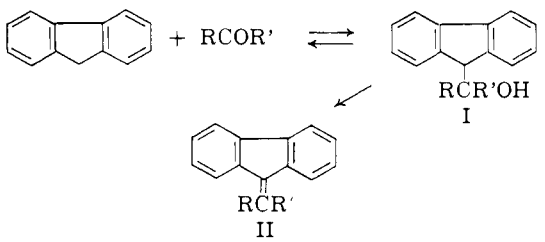
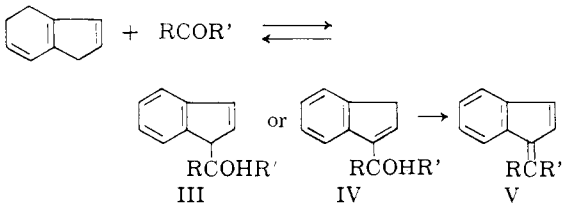
Indene and fluorene condense with aldehydes in pyridine containing benzyltrimethylammonium hydroxide to give secondary carbinols and the fluorenylcarbinols react further to give β-glycols. Under similar conditions some ketones react reversibly with indene and fluorene to afford tertiary carbinols. Dibenzofulvenes, including alkylidenefluorenes, are ordinarily the major products in the reaction of fluorene with aldehydes at room tempreature. They are also obtainable by dehydration of carbinols, prepared as above, with ethanolic KOH. This dehydration method is also used for the preparation of alkylideneindenes, as the direct preparation from indene and aldehydes has proved unsatisfactory. Under the present conditions two dimers of propylidenefluorene and two trimers of ethylidenefluorene can also be obtained. Structure and mode of formation of these compounds are discussed.

It has long been known that fluorene condenses with aldehydes in the presence of basic catalysts to form dibenzofulvenes (II). While it is generally agreed that reactions of active methylene compounds with carbonyl compounds invariably proceed through an "aldol" stage, no carbinols of structure I have so far been isolated from condensations of fluorene. Carbinols of this type, few of which are known, have been prepared from Grignard derivatives of the hydrocarbon[3] and by other



indirect methods.[4] It may further be noted that while the formation of dibenzofulvenes from aromatic aldehydes is relatively easy, difficulties are encountered in the case of aliphatic aldehydes, as these usually undergo self-condensation under the influence of the basic catalyst. No aldol-type reaction of fluorene with ketones has been reported. Similarly, no carbinols of structure III (or IV) have been isolated from the reaction of indene with aldehydes and ketones.



It has now been found that fluorene and indene react readily with aldehydes in pyridine solution and in the presence of benzyltrimethylammonium hydroxide (Triton B). The high reactivity, presumably due to the presence of appreciable concentrations of carbanions under these conditions,[5] allows low enough temperatures to be employed in order to avoid dehydration of the carbinols formed (I and IV, respectively; R′ = H), which can thus be isolated in substantial yields. The above hydrocarbons react similarly with certain ketones to give the corresponding tertiary carbinols. Unlike the reaction with aldehydes, the reversible formation of these carbinols is ordinarily uncomplicated by side-reactions (see below).

(1) Part I, Y. Sprinzak, THIS JOURNAL, **80**, 5449 (1958).

(2) Taken in part from the Ph.D. Thesis submitted to the Hebrew University of Jerusalem by E. Ghera.

(3) C. Courtot, (a) *Ann. chim.*, **4**, 58 (1915); (b) p. 157.

(4) (a) E. J. Greenhow, D. McNeil and F. N. White, *J. Chem. Soc.*, 986 (1952); (b) W. G. Brown and B. Bluestein, THIS JOURNAL, **62**, 3256 (1940); (c) A. Kliegl, F. Weng and G. Wiest, *Ber.*, **63**, 1262 (1930).

(5) See following article, p. 4953.