was hydrolyzed with iced hydrochloric acid, and the ethereal layer, after being combined with several ether extractions of the aqueous layer, was dried over Drierite. The solvent was removed and the residue washed with ether to give 18.5 g. (48%) of lactone-ester IX, m.p. 150–153°. One recrystallization from ether raised the melting point to 155–156°.

Anal. Calcd. for $C_{25}H_{22}O_4$: C, 77.70; H, 5.74. Found: C, 77.56; H, 5.80.

Cyanoethylation of 3-phenylphthalide (I) *to form* X. To a stirred solution of the sodium derivative of 3-phenylphthalide prepared from 0.1 mole each of sodium amide and the lactone I in 500 ml. of liquid ammonia, there was added 5.3 g. (0.1 mole) of freshly distilled acrylonitrile in an equal volume of anhydrous ether. After stirring for 30 min., a few drops of excess acrylonitrile was added, causing the color to change from red to a deep, greenish black. After stirring for an hour longer, the liquid ammonia was replaced by ether during 15 min. on the steam bath. Some of the acrylonitrile appeared to polymerize. The reaction mixture was decomposed with iced hydrochloric acid, and the ethereal layer carefully separated and combined with several ether extracts of the aqueous layer. After drying over Drierite, the solvent was removed to leave 14.5 g. (56%) of lactone-nitrile X, m.p. 176–180°. After two recrystallizations from ethanol, the product melted at 177–178°.

Anal. Calcd. for $C_{17}H_{13}O_2N$: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.78; H, 4.80; N, 5.26.

Carbonation of phthalide (XI) *to form lactone acid* XII. This reaction was carried out as described above for 3-phenylphthalide (I), employing sodium amide. The intermediate sodium derivative which formed was deep orange. There was obtained, after recrystallization of the product from a mixture of chloroform and ligroin (b.p. 90–120°) and finally washing with cold ether, a 46% yield of 3-carboxyphthalide (XII) m.p. 152–153° (reported m.p. 150–151°).[14]

In an attempt to determine whether the amide ion was attacking the lactone ring, the phthalide was allowed to stir for 5 hr. with an equimolar portion of sodium amide before carbonation. Once again, an approximately 46% yield of acid XII was obtained along with considerable tar.

DURHAM, N. C.

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[14] S. Ruhemann, *J. Chem. Soc.*, 2030 (1910).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Rearrangements of 2,6-Dimethyl- and 2,3,4,6-Tetramethylbenzyltrimethylammonium Ions with Sodium Amide and Reactions of the Products[1]

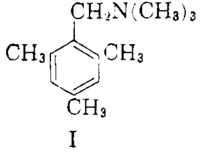
CHARLES R. HAUSER AND DONALD N. VAN EENAM

Received November 22, 1957

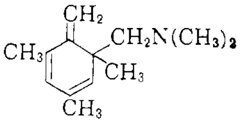
2,6-Dimethyl- and 2,3,4,6-tetramethylbenzyltrimethylammonium ions were rearranged by sodium amide in liquid ammonia to form corresponding *exo*-methylenecyclohexadieneamines which exhibited characteristic reactions of such compounds. The methiodide of each of these *exo*-methyleneamines was converted by sodium amide in liquid ammonia to another *exo*-methyleneamine which also exhibited certain of the characteristic reactions. Evidence is presented that the unsymmetrical 2,3,4,6-tetramethyl quaternary ion underwent only one of the two possible courses of rearrangement.

The 2,4,6-trimethylbenzyltrimethylammonium ion (I) has previously[2] been rearranged by sodium amide in liquid ammonia to *exo*-methyleneamine II,[2] the methiodide of which was converted to another *exo*-methyleneamine (III)[3] on further treatment with this reagent.

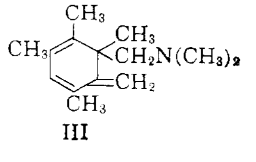
The corresponding reactions have now been carried out with the 2,6-dimethyl- and 2,3,4,6-tetramethylbenzyltrimethylammonium ions. The former quaternary ion (IV) was rearranged by sodium amide in liquid ammonia to give *exo*-methyleneamine V, the mechanism being indicated in Equation 1. The ultraviolet absorption wave length maximum of the product agreed with the value calculated[4] for structure V.



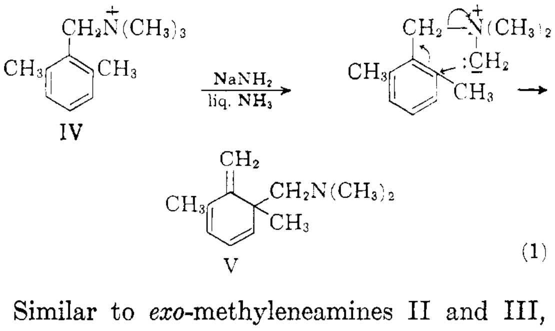
I



II



III



(1)

Similar to *exo*-methyleneamines II and III, V

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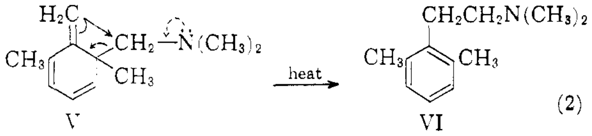
[1] Supported by the National Science Foundation.

[2] C. R. Hauser and D. N. Van Eenam, *J. Am. Chem. Soc.*, **79**, 5512 (1957).

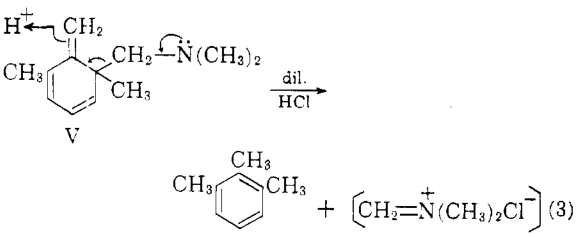
[3] C. R. Hauser and D. N. Van Eenam, *J. Am. Chem. Soc.*, **79**, 6280 (1957).

[4] For calculations of absorption maxima by Woodward's rules, see L. F. Fieser and M. Fieser, *Natural Products Related to Phenanthrene*, third ed., Reinhold Publishing Corp., New York, N. Y., 1949, pp. 185–188.

readily underwent thermal isomerization to form β-arylethylamine VI (Equation 2). In fact some of this aromatic compound was generally produced in the distillation of *exo*-methyleneamine V which was isolated in yields ranging from 55 to 75%, depending on the distillation temperature.

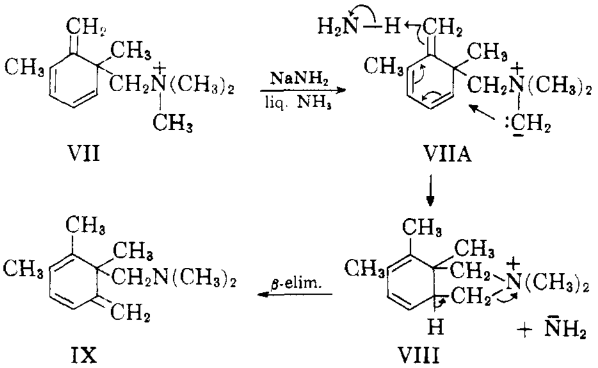

V VI (2)

Also, similar to *exo*-methyleneamines II and III, V underwent an acid-induced decomposition to form an aromatic hydrocarbon, hemimellitene, and dimethylmethyleneiminium chloride (Equation 3).


V (3)

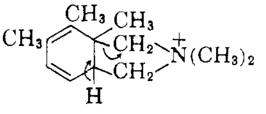
It should be mentioned that the starting quaternary ammonium ion undoubtedly had structure IV since it was synthesized by unequivocal reactions from 2,6-dimethylaniline (see Experimental).

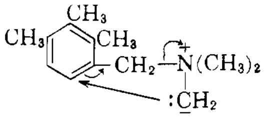
The methiodide of *exo*-methyleneamine V, (Formula VII) was converted by sodium amide in liquid ammonia to another *exo*-methyleneamine (IX), the probable mechanism being indicated in Scheme A.

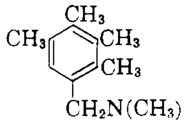

VII VIIA VIII IX

Scheme A

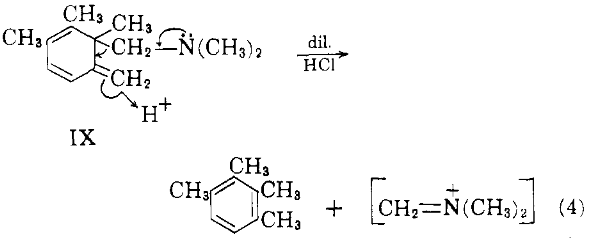
Evidence supporting this type of mechanism for the analogous conversion of the methiodide of *exo*-methyleneamine II to III has previously been discussed.[3] The conversion of VII to IX, like that of II to III, was accompanied by deep coloration. This might indicate the intermediate formation of carbanions in addition to carbanion VIIA. The present results show that the possible aromatization of intermediate quaternary ion VIII (indicated in X) does not occur since this would have formed quaternary ion XI which would have undergone the normal ortho substitution rearrangement to give tertiary amine XII. No such aromatic product was obtained.


X≅VIII


XI

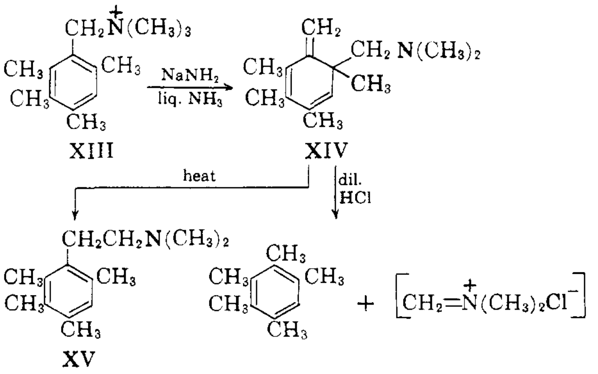

XII

The structure of *exo*-methyleneamine IX was established not only by its ultraviolet absorption maximum but also by its conversion to prehnitene by dilute acid (equation 4).


IX (4)

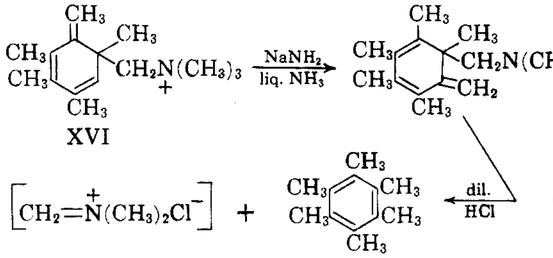
Although this acid-induced decomposition did not occur as readily as that of *exo*-methyleneamines II, III, and V, the aromatic hydrocarbon was obtained in high yield (85%). *exo*-Methyleneamine IX was also more stable toward heat than the other *exo*-methyleneamines, being largely recovered after heating to 150° for 5 min. At 200°, *exo*-methyleneamine IX was slowly converted to a mixture of products.

The other benzyl type quaternary ion studied in this investigation, the 2,3,4,6-tetramethylbenzyltrimethylammonium ion (XIII), was of interest because its unsymmetrical structure made possible two modes of rearrangement with sodium amide in liquid ammonia. Actually only one mode of rearrangement, that indicated in Scheme B to form *exo*-methyleneamine XIV, was realized, the methiodide of the product isolated melting sharply. The polyene structure of the product was established as usual by its ultraviolet absorption maximum and by the reactions represented in Scheme B.


XIII XIV XV

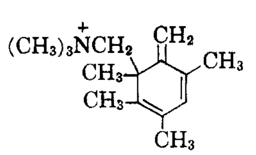
Scheme B

As might be expected, the methiodide of *exo*-methyleneamine XIV (formula XVI), on treatment with sodium amide in liquid ammonia followed by acid, produced hexamethylbenzene (Equation 5).



(5)

The second possible mode of rearrangement of quaternary ion XIII would have formed *exo*-methyleneamine III which has previously been prepared from the methiodide of II.[3] Like *exo*-methyleneamine XIV, III undergoes thermal isomerization to β-arylethylamine XV and acid-induced decomposition to form pentamethylbenzene.[3] However, the product obtained from quaternary ion XIII was shown not to be *exo*-methyleneamine III by the refractive indices of the two amines and especially by the melting points of their methiodides. Moreover, whereas the product obtained from XIII was converted through its methiodide to hexamethylbenzene (Equation 5), the methiodide of *exo*-methyleneamine III (Formula XVII) failed to produce this aromatic hydrocarbon on similar treatment.[3]



XVII
(Methiodide of III)

It should be mentioned that the starting quaternary ammonium ion undoubtedly had structure XIII since it was synthesized by the chloromethylation of isodurene.

EXPERIMENTAL[5]

2,6-Dimethylbenzyltrimethylammonium iodide (IV). This quaternary ammonium salt was synthesized in four steps from 2,6-dimethylaniline.

Conversion of this amine (300 g., 2.48 moles) into 2,6-dimethylbenzonitrile was effected in 46% yield according to the general directions of Clarke and Read[6] for the synthesis of tolunitriles from the corresponding toluidines *via* the Sandmeyer reaction. The diazotized aniline was added with vigorous stirring to the cold cuprous cyanide solution with a layer of benzene on the surface. After the ensuing reaction, the solvent was removed, and the dark reddish brown solid was crystallized several times from ligroin (b.p. 60–90°) to afford 2,6-dimethylbenzonitrile (as white needles), m.p. 89–90° (reported m.p. 89–89.5°).[7]

This nitrile (1.13 moles) was reduced with 1.50 moles of lithium aluminum hydride in 2 l. of ether employing the procedure of Nystrom and Brown[8] for the reduction of *o*-tolunitrile. After stirring under reflux for 6 hr., the reaction mixture was decomposed by the addition of a 20% solution of sodium potassium tartrate. Distillation of the product *in vacuo* gave 99.7 g. (65%) of slightly impure 2,6-dimethylbenzylamine, b.p. 111–114° at 15 mm., n_{D}^{25} 1.5223, which was used without further purification for the following reaction.

Methylation of 2,6-dimethylbenzylamine was effected by the Eschweiler-Clarke procedure, employing the directions of Icke and Wisegarver[9] for the alkylation of β-phenylethylamine. From 98.0 g. (0.725 mole) of the amine, 190 g. of 88% formic acid, and 140 g. of 37% formalin solution (24-hr. reflux), there was isolated (second distillation) 96.1 g. (81%) of 2,6-dimethylbenzyldimethylamine, b.p. 104–106° at 15 mm., n_{D}^{25} 1.5087.

Anal. Calcd. for $C_{11}H_{17}N$: C, 80.92; H, 10.50; N, 8.58. Found: C, 80.80; H, 10.72; N, 8.31.

The picrate, crystallized three times from 95% ethanol, melted at 164–165°.

Anal. Calcd. for $C_{17}H_{20}N_4O_7$: C, 54.04; H, 5.14; N, 14.28. Found: C, 54.23; H, 5.20; N, 14.00.

To a solution of 86.8 g. (0.532 mole) of this tertiary amine in 100 ml. of acetonitrile was added with swirling 100 g. (0.70 mole) of methyl iodide, the flask being cooled occasionally by immersion in an ice bath. After standing at room temperature for 2 hr. (some crystalline product separated), 1 l. of ether was added to precipitate the quaternary ammonium salt, which (after a second crystallization) was collected on a funnel, washed with ether, and dried *in vacuo*. There was obtained 156.7 g. (97%) of 2,6-dimethylbenzyltrimethylammonium iodide (IV), m.p. 156–157.5° (dec.), with darkening at 140°. Its picrate, following three crystallizations from water, melted at 131–132°.

Anal. Calcd. for $C_{18}H_{22}N_4O_7$: C, 53.20; H, 5.46; N, 13.79. Found: C, 53.32; H, 5.61; N, 13.67.

Rearrangement of IV *to 6-methylene-1,5-dimethyl-1-dimethylaminomethylcyclohexadiene-2,4* (V). This reaction was carried out with 30.5 g. (0.10 mole) of 2,6-dimethylbenzyltrimethylammonium iodide (IV) and 0.30 mole of sodium amide in 500 ml. of liquid ammonia essentially as described[2] for the corresponding rearrangement of 2,4,6-trimethylbenzyltrimethylammonium chloride (I), omitting steam distillation[10] of the crude reaction product. Ammonium chloride (10.7 g., 0.20 mole) was added to the purple colored reaction mixture after 3 hr. stirring, followed by the addition of 600 g. of Reagent Grade ether during the careful evaporation of the liquid ammonia on the steam bath. As soon as the ether began to reflux in the cold condenser the reaction mixture was cooled, filtered, and the solvent carefully distilled on the steam bath, the last traces being removed *in vacuo* at 35°. Distillation of the residual oil through a 40-cm. Podbielniak type column at a relatively low temperature afforded 10.3 g. (58%) of *exo*-methyleneamine V, b.p. 43–44° at 0.4 mm., n_{D}^{25} 1.5128.

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(5) Melting and boiling points are uncorrected. Microanalyses are by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Ultraviolet absorption spectra were measured in 95% ethanol solution using a Warren Spectracord Model 3000 automatic-recording spectrophotometer.

(6) H. T. Clarke and R. R. Read, *Org. Syntheses*, **4**, 69 (1925).

(7) R. C. Fuson and co-workers, *J. Am. Chem. Soc.*, **62**, 2092 (1940).

(8) R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **70**, 3740 (1948).

(9) R. N. Icke and B. B. Wisegarver, *Org. Syntheses*, **Coll. Vol. 3**, 723 (1955).

(10) In the isolation of *exo*-methyleneamine II, steam distillation was desirable in removing the product from polymeric material (see Ref. 2, note 26). However, in the present case the low content of high boiling polymer in the crude reaction mixture rendered steam distillation unnecessary.

Anal. Calcd. for $C_{12}H_{19}N$: C, 81.30; H, 10.80; N, 7.90. Found: C, 81.13; H, 10.80; N, 7.82. Ultraviolet absorption spectrum, calcd.[4] λ_{max} 308 mμ. Found: λ_{max} 309 mμ (3.8).

Also there was obtained from the above distillation 5.1 g. (29%) of the thermal isomerization product, aromatic amine VI, b.p. 63–65° at 0.4 mm., and 1.5 g. (9%) of polymeric residue.

In similar experiments the yield of *exo*-methyleneamine V varied from 55–75%, depending for the most part on the size of the run and the distillation temperature. Amine V, like other *exo*-methyleneamines, had a reasonably strong camphoric odor.

Thermal isomerization of V *to form β-(2,6-dimethylphenyl)-ethyldimethylamine* (VI). Crude *exo*-methyleneamine V, prepared from 21.4 g. (0.07 mole) of 2,6-dimethylbenzyltrimethylammonium iodide (IV) and 0.21 mole of sodium amide in 400 ml. of liquid ammonia, was thermally rearranged by distillation *in vacuo* at a higher temperature than employed above to yield 7.8 g. (63%) of β-(2,6-dimethylphenyl)ethyldimethylamine (VI), b.p. 116–118° at 10 mm., n_D^{25} 1.5077 (leaving a distillation residue of 4.0 g.).

Anal. Calcd. for $C_{12}H_{19}N$: C, 81.30; H, 10.80; N, 7.90. Found: C, 81.31; H, 10.78; N, 7.84.

The picrate, recrystallized three times from 95% ethanol, melted at 135–136°.

Anal. Calcd. for $C_{18}H_{22}N_4O_7$: C, 53.20; H, 5.46; N, 13.79. Found: C, 53.39; H, 5.45; N, 13.86.

Reaction of exo-methyleneamine V *with hydrochloric acid to form hemimellitene.* To an ethereal solution of crude *exo*-methyleneamine V, obtained from the rearrangement of 0.10 mole of 2,6-dimethylbenzyltrimethylammonium iodide (IV) with 0.30 mole of sodium amide, was added all at once with vigorous shaking 250 ml. of cold 6*N* hydrochloric acid. After standing for 5 min., the ethereal layer was drawn off, washed with water, and dried, and the solvent was removed. The residue was distilled to give 8.9 g. (74%) of hemimellitene, b.p. 80–80.5° at 30 mm., n_D^{25} 1.5117 (reported b.p. 176° at 760 mm., n_D^{25} 1.5116).[11] The picrate of this hydrocarbon melted at 88.5–89.5° (from 95% ethanol) (reported m.p. 89.5°).[12]

When the aqueous acidified layer (containing dimethylmethyleneiminium chloride and basic products) was made alkaline with sodium hydroxide solution, strong fumes of formaldehyde and dimethylamine were detected,[2] and 2.1 g. of an oil (presumably aromatic amine VI, 12%) was isolated from the reaction mixture.

Rearrangement of exo-methyleneamine methiodide VII *to exo-methyleneamine* IX. Conversion of tertiary amine V into *exo*-methyleneamine methiodide VII was effected in 96% yield by the action of methyl iodide on V in acetonitrile solution. After crystallization from dry acetonitrile-ether and drying *in vacuo*, this salt[13] melted with decomposition at 128.5–130°.

To a stirred suspension of 0.26 mole of sodium amide in 500 ml. of liquid ammonia was added rapidly 27.3 g. (0.086 mole) of finely powdered methiodide VII, essentially as described[3] for the amide ion rearrangement of the methiodide of *exo*-methyleneamine II. After stirring for 1 hr. the deep, bright red reaction mixture was decomposed with excess ammonium chloride (color faded) and the ammonia replaced by Reagent Grade ether, followed by the addition of 25 ml. of 5*N* sodium hydroxide solution. The resulting mixture was rapidly steam distilled[10] and the distillate, after saturation with solid sodium carbonate and extraction with reagent grade ether, was worked up to give 10.9 g. (67%) of *exo*-methyleneamine IX, b.p. 52.5–54° at 0.5 mm., n_D^{25} 1.5108.

Anal. Calcd. for $C_{13}H_{21}N$: C, 81.62; H, 11.07; N, 7.31. Found: C, 81.66; H, 11.17; N, 7.35. Ultraviolet absorption spectrum, calcd.[4] λ_{max} 313 mμ. Found: λ_{max} 316 mμ (3.8).

The residue remaining after the steam distillation mentioned above consisted of 3.3 g. (20%) of polymeric material.

Also there was isolated 2.1 g. (12%) of what appeared to be the thermally isomerized amine. However, *exo*-methyleneamine IX was largely recovered after heating to 150° for 5 min. On heating 15.3 g. (0.09 mole) of IX at 200° for 2 hr. (Wood's metal bath, electrically controlled), there was obtained on distillation *in vacuo* 10.1 g. of a mixture of amines, b.p. 83–110° at 5 mm., and 3.5 g. of undistillable residue. This mixture was shown not to contain unreacted starting material by its failure to liberate prehnitene on treatment with hydrochloric acid (see below).

Reaction of exo-methyleneamine IX *with hydrochloric acid to form prehnitene.* To 5.74 g. (0.03 mole) of *exo*-methyleneamine IX was added all at once with stirring 25 ml. of 12*N* hydrochloric acid. The amine dissolved immediately with slight warming and within several minutes the solution became turbid. After standing at room temperature for 24 hr. (when an oily layer had separated on the surface) the reaction mixture was diluted with 100 ml. of water and extracted with ether. The ethereal extract was dried, the solvent removed, and the residue distilled to give 3.4 g. (85%) of prehnitene, b.p. 97–98° at 25 mm., n_D^{25} 1.5183 (reported b.p. 96.5° at 25 mm., n_D^{20} 1.5202.[14] The dinitro derivative of this hydrocarbon, after two recrystallizations from 95% ethanol, melted at 175–176° (reported m.p. 176–177°).[15] Formaldehyde was detected during the workup procedure.

2,3,4,6-Tetramethylbenzyltrimethylammonium chloride (XIII). α^2-Chloropentamethylbenzene, b.p. 114–117° at 5 mm. (reported b.p. 113–115° at 5 mm.),[16] was prepared in 83% yield from isodurene and monochloromethyl ether according to the directions of Varon and Bolle[17] for the chloromethylation of mesitylene.

Into a solution of 52.0 g. (0.284 mole) of this halide in 300 ml. of dry acetonitrile was slowly bubbled anhydrous trimethylamine for 1 hr. (some crystalline product separated). After standing at room temperature for an additional hour, 500 ml. of dry ether was added with swirling; the precipitated salt was collected on a funnel, washed with dry ether, and dried *in vacuo*. There was obtained 70.1 g. (quantitative) of 2,3,4,6-tetramethylbenzyltrimethylammonium chloride (XIII), m.p. 209–210° (dec.). The picrate of this hygroscopic compound melted at 164–165° after 3 crystallizations from water.

Anal. Calcd. for $C_{20}H_{26}N_4O_7$: C, 55.29; H, 6.03; N, 12.90. Found: C, 55.29; H, 6.13; N, 12.93.

Rearrangement of XIII *to 6-methylene-1,3,4,5-tetramethyl-1-dimethylaminomethylcyclohexadiene-2,4* (XIV). This reaction was carried out with 36.3 g. (0.15 mole) of 2,3,4,6-tetramethylbenzyltrimethylammonium chloride (XIII) and 0.45 mole of sodium amide in 500 ml. of liquid ammonia essentially as described[2] for the corresponding rearrangement of II. The lavender colored reaction mixture initially formed gradually changed to deep violet during 1 hr., this color persisting until ammonium chloride was added to the mixture after stirring for 3 hr. After replacing the ammonia with ether and steam-distilling the crude reaction product (see isolation of IX above), the distillate was processed to give, on distillation through a 40-cm. Podbielniak type column, 13.6 g. (44%) of *exo*-methyleneamine XIV, b.p. 62–62.5° at 0.4 mm., n_D^{25} 1.5240. (Compare *exo*-methyleneamine III,

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(11) B. J. Mair and S. T. Schicktanz, *J. Research Nat. Bur. Standards*, **11**, 665 (1933).

(12) O. L. Baril and E. S. Hauber, *J. Am. Chem. Soc.*, **53**, 1087 (1931).

(13) Methiodide VII, which gradually darkened and partially decomposed on exposure to air, was used immediately for further reaction.

(14) L. I. Smith and O. W. Cass, *J. Am. Chem. Soc.*, **54**, 1609 (1932).

(15) L. I. Smith and S. A. Harris, *J. Am. Chem. Soc.*, **57**, 1289 (1935).

(16) R. C. Fuson and C. A. Sperati, *J. Am. Chem. Soc.*, **63**, 2643 (1941).

(17) G. Varon and J. Bolle, *Compt. rend.*, **204**, 1826 (1937).

n_D^{25} 1.5232[3]; see below for comparison of melting points of methiodides of XIV and III).

Anal. Calcd. for $C_{14}H_{23}N$: C, 81.89; H, 11.29; N, 6.82. Found: C, 81.95; H, 11.39; N, 6.63. Ultraviolet absorption spectrum, calcd.[4] λ_{max} 318 mμ. Found: λ_{max} 321 mμ (3.9).

Also there was obtained from the above distillation 2.3 g. (8%) of the thermally rearranged product, aromatic amine XV, b.p. 88–89.5° at 0.4 mm., and 1.2 g. (4%) of undistillable residue. Considerable polymeric material (12.2 g., approximately 39%) remained from the steam distillation of XIV.

Thermal isomerization of XIV *to form β-(2,3,4,6-tetramethylphenyl)ethyldimethylamine* (XV). Crude *exo*-methyleneamine XIV, prepared from 19.3 g. (0.08 mole) of XIII and 0.24 mole of sodium amide, was thermally isomerized at 150° for 1 hr. to produce 7.4 g. (45%) of β-(2,3,4,6-tetramethylphenyl)ethyldimethylamine (XV), b.p. 90–90.5° at 0.5 mm., n_D^{25} 1.5163 (reported b.p. 88.5–89° at 0.45 mm., n_D^{25} 1.5162).[3] The picrate, recrystallized three times from 95% ethanol, melted at 178–179° (reported m.p. 179.5–180°).[3] Its melting point was not depressed on admixture with an authentic sample of the compound.

Reaction of exo-methyleneamine XIV *with hydrochloric acid to form pentamethylbenzene.* This reaction was carried out with an ethereal solution of crude *exo*-methyleneamine XIV (obtained from 0.07 mole of quaternary salt XIII and 0.21 mole of sodium amide) and 200 ml. of 6*N* hydrochloric acid as described for the acidic decomposition of V. The ethereal extract (containing neutral products) was steam-distilled, and the distillate worked up to yield 5.3 g. (51%) of pentamethylbenzene, m.p. 51–52°, after crystallization from absolute methanol (cooled to −78°). A mixed melting point determination with an authentic sample of this hydrocarbon, m.p. 52–53°, gave no depression in the melting point.

When the aqueous acidified extract (containing dimethylmethyleneiminium chloride) was made alkaline with sodium hydroxide solution, pungent fumes of formaldehyde were detected.

Rearrangement of the methiodide of exo-methyleneamine XIV *(Formula* XVI*) and acidic decomposition of its exo-methyleneamine product to form hexamethylbenzene.* Tertiary amine XIV (13.0 g., 0.063 mole), b.p. 62–62.5° at 0.4 mm., was converted into *exo*-methyleneamine methiodide XVI, m.p. 176–177° (dec.), in 98% yield by the action of 0.10 mole of methyl iodide on XIV in acetonitrile solution. The dissimilarity of this methiodide with that from *exo*-methyleneamine III [Formula XVII, m.p. 188–189° (dec.)][2] was demonstrated by the depression in melting point to 140–152° on admixture of these two quaternary ammonium salts.

To a stirred suspension of 0.19 mole of sodium amide in 300 ml. of liquid ammonia was added rapidly 21.2 g. (0.062 mole) of methiodide XVI, the resulting reddish violet colored reaction mixture being decomposed by the addition of ammonium chloride after 1 hr. The ammonia was replaced by ether, the suspension filtered, and the ethereal solution shaken with 200 ml. of 6*N* hydrochloric acid for 5 min. The two layers were separated. From the ether layer there was obtained 4.8 g. of impure hexamethylbenzene, m.p. 142–149°, which, after two crystallizations from ethanol afforded 4.2 g. (42%) of colorless hexamethylbenzene, m.p. 162–163°. This melting point was not depressed on admixture with an authentic sample of hexamethylbenzene, m.p. 162.5–164°.

From the aqueous hydrochloric acid layer (see above) there was obtained, on neutralization with sodium hydroxide and extraction with ether, 1.3 g. of unidentified material, b.p. 89–110° at 0.5 mm. (having a slight camphoric odor), and 2.7 g. of dark undistillable residue.

DURHAM, N. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT BERKELEY]

Unsaturated Four-Membered Ring Compounds. I. *cis-* and *trans-*1,2-Diiodobenzocyclobutene and Their Interconversion

FREDERICK R. JENSEN AND WILLIAM E. COLEMAN

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The reaction of α,α,α′,α′-tetrabromo-*o*-xylene with excess sodium iodide in ethanol gives two isomeric $C_8H_6I_2$ compounds. Evidence is presented which indicates these compounds are *cis-* and *trans*-1,2-diiodobenzocyclobutene. The stereochemical relationship of the isomers was assigned by dipole moment measurements. The *cis*-isomer (m.p. 150°) melts 87° higher than the *trans*-isomer (m.p. 63°). These compounds are readily interconverted by light in the presence of iodine in a free radical reaction, and by sodium iodide in ethanol in a reaction which is postulated to involve benzocyclobutadiene as an intermediate. At 30°, the equilibrium mixture contains 6% of the *cis*-isomer.

In his Inaugural Dissertation, Finkelstein reported the preparation of 1,2-dibromobenzocyclobutene (I) by refluxing sodium iodide with α,α,α′,-α′-tetrabromo-*o*-xylene in ethanol solution.[1] Except for a brief reference to these results in connection with other work,[2] the details of this interesting reaction were not reported further until recently when Cava and Napier[3] reinvestigated and confirmed this preparation.

In this reaction an iodine-containing side product is produced which has been shown to be 1,2-diiodobenzocyclobutene (II). The same compound was also prepared in 70% yield by refluxing 1,2-dibromocyclobutene with ethanolic sodium iodide containing some iodine for eight days. As a side product in these reactions, a compound, $C_{16}H_{12}BrI_3$ (m.p. 135–136°), has been reported. The parent hydrocarbon, benzocyclobutene (III) was prepared by hydrogenolysis of (I) or (II).[3]

In attempting to prepare 1,2-diiodobenzocyclobutene directly by treating α,α,α′,α′-tetrabromo-*o*-xylene with a large excess of sodium iodide we obtained two isomeric $C_8H_6I_2$ compounds. This re-

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(1) H. Finkelstein, Inaugural Dissertation, Strassbourg, 1910, carried out with J. Thiele.

(2) H. Finkelstein, *Ber.*, **43**, 1532 (1910).

(3) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **78**, 500 (1956); M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **79**, 1701 (1957).