

neutral products afforded, on distillation *in vacuo*, 2.6 g. (19%) of isodurene,<sup>40</sup> b.p. 84–87° at 18 mm., dinitro derivative m.p. 179–180.5°, and 1.5 g. (8%) of *n*-amylmesitylene (XVII), b.p. 101–104° at 3 mm.,  $n_D^{20}$  1.4984.

**Hydrogenation of *exo*-Methyleneamine II.**—*exo*-Methyleneamine II (38.2 g., 0.20 mole) in ethanol was hydrogenated over Raney nickel at 55° under 400 p.s.i. of hydrogen.<sup>18</sup> Hydrogenation at lower temperatures was ineffective at this pressure. After removal of the solvent *in vacuo*, the residual oil was taken up in ether and extracted with dilute acid. A small amount (1.5 g.) of neutral products, mainly isodurene, was obtained from the ethereal solution. The aqueous acid extract was made alkaline with 50% sodium hydroxide, and the liberated basic material distilled *in vacuo* to give 24.7 g. of an amine, b.p. 86–88.5° at 5 mm.,  $n_D^{20}$  1.4828.

(40) This product arose from the acidic decomposition of unreacted starting material.

*Anal.* Calcd.<sup>41</sup> for C<sub>13</sub>H<sub>25</sub>N: C, 79.93; H, 12.90; N, 7.17. Found: C, 80.07; H, 13.27; N, 7.36.

The picrate, crystallized three times from 95% ethanol, melted at 177–178° dec.

*Anal.* Calcd.<sup>41</sup> for C<sub>19</sub>H<sub>23</sub>N<sub>4</sub>O<sub>7</sub>: C, 53.76; H, 6.65; N, 13.20. Found: C, 54.00; H, 6.51; N, 13.20.

A second, higher boiling fraction (5.4 g., 14%), b.p. 108–112°,  $n_D^{20}$  1.5076, consisted mainly of  $\beta$ -mesitylethyl-dimethylamine (III). A mixed melting point of the picrate of this product with an authentic sample of the picrate of III was not depressed.

(41) These calculated values are those for the singly unsaturated amine and its picrate. The corresponding data for the fully saturated amine are C<sub>13</sub>H<sub>27</sub>N: C, 79.11; H, 13.70; N, 7.10; and those for the picrate, C<sub>19</sub>H<sub>23</sub>N<sub>4</sub>O<sub>7</sub>: C, 53.51; H, 7.09; N, 13.14.

DURHAM, NORTH CAROLINA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

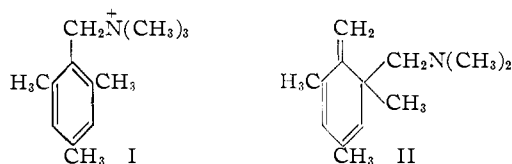
## Rearrangement of 2,4,6-Triisopropylbenzyltrimethylammonium Ion by Sodium Amide to Form an *exo*-Methylenecyclohexadieneamine and its Reactions<sup>1</sup>

BY DONALD N. VAN EENAM<sup>2</sup> AND CHARLES R. HAUSER

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The 2,4,6-triisopropylbenzyltrimethylammonium ion was rearranged by sodium amide in liquid ammonia to form an *exo*-methylenecyclohexadieneamine that was rearranged thermally to a  $\beta$ -arylethylamine. The *exo*-methyleneamine was decomposed by acid to form an aromatic hydrocarbon and an aromatic amine, the relative yields of these products depending upon the strength of the acid. The methiodide of the *exo*-methyleneamine and also that of the corresponding 2,4,6-trimethyl compound were aromatized similarly with acid. Some of the factors influencing these reactions are considered.

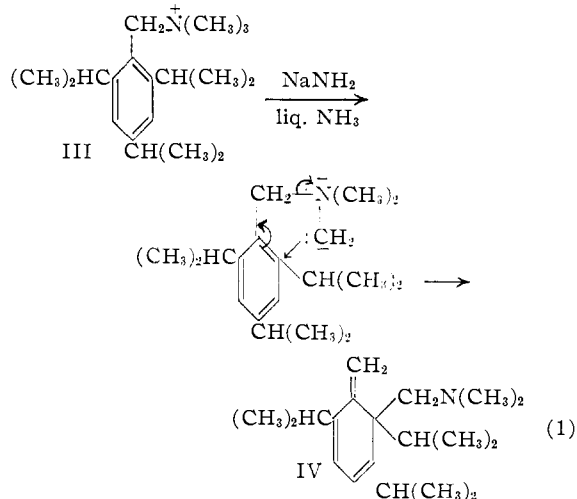
A previous paper<sup>3</sup> described the rearrangement of the 2,4,6-trimethylbenzyltrimethylammonium ion (I) by sodium amide in liquid ammonia to form *exo*-methyleneamine II and the thermal isomerization and reactions with electrophilic and nucleophilic reagents of this interesting alicyclic product.



The present paper describes a similar study of the rearrangement of the 2,4,6-triisopropylbenzyltrimethylammonium ion (III) and of the reactions of its rearrangement product IV. This product was obtained in practically quantitative yield in accordance with equation 1. The undistilled compound was analytically pure,<sup>4</sup> and its ultraviolet absorption spectrum agreed satisfactorily with that calculated<sup>5</sup> for structure IV.

The quantitative yield of IV was not anticipated since *exo*-methyleneamine II was obtained from quaternary ammonium ion I in only 70% yield ac-

companied by polymeric material. Evidently the relatively large isopropyl groups in quaternary ion III favor intramolecular rearrangement over the



possible intermolecular self-alkylation which is assumed to be responsible for the polymeric material from I.

*exo*-Methyleneamine IV readily underwent isomerization to form aromatic tertiary amine V (92%), whose structure was established by an independent synthesis from 2,4,6-triisopropylbenzyl chloride (equation 2).

This thermal isomerization occurred more readily than that of *exo*-methyleneamine II. Thus, whereas II was steam distilled without appreciable change, *exo*-methyleneamine IV underwent spontaneous isomerization at 90–100°. The greater

(1) Supported in part by the Office of Ordnance Research, U. S. Army.

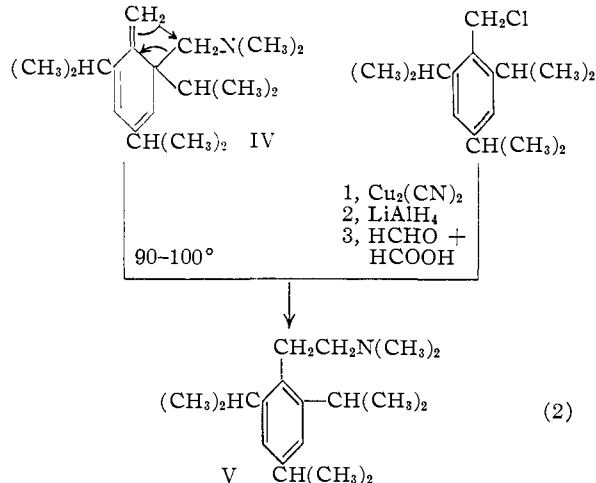
(2) Monsanto Chemical Co. Fellow, 1955–1956.

(3) C. R. Hauser and D. N. Van Eenam, *This Journal*, **79**, 5512 (1957).

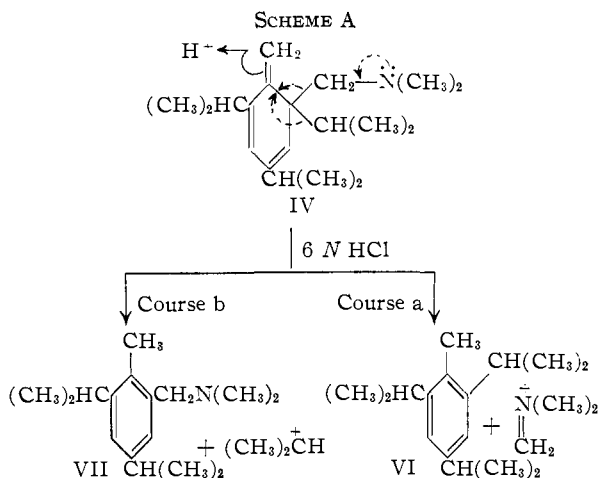
(4) This was fortunate since *exo*-methyleneamine IV undergoes thermal isomerization so readily that the method of purification of *exo*-methyleneamine II, involving steam distillation, does not appear feasible with IV.

(5) For calculations of absorption maxima by Woodward's rules, see L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1949, pp. 185–188.

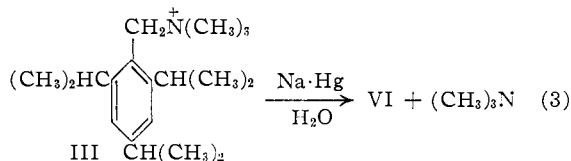
reactivity of IV apparently is associated with the relief of more steric strain around the quaternary carbon of this compound having the isopropyl group than around that of II having the smaller methyl group.



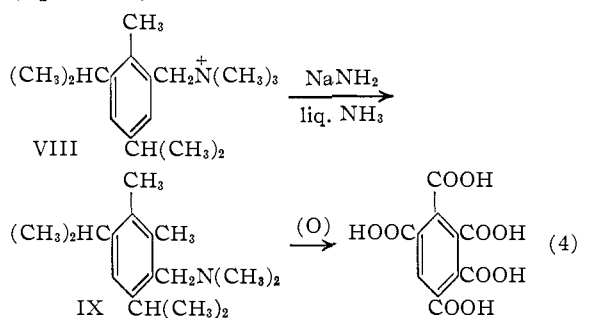
*exo*-Methyleneamine IV underwent two courses of reaction with dilute hydrochloric acid at room temperature as represented in Scheme A.



In course a, the dimethylmethylene iminium ion was eliminated to form aromatic hydrocarbon VI, the structure of which was established by an independent synthesis involving an Emde reduction of quaternary ammonium ion III (equation 3). The dimethylmethylene iminium ion was hydrolyzed by alkali to form formaldehyde and dimethylamine; the latter product was isolated as its phenyl isothiocyanate derivative in 79% yield.



In course b of Scheme A, the isopropylcarbonium ion was eliminated to form aromatic amine VII, whose structure was established by effecting the normal *ortho* substitution rearrangement with its methiodide VIII and oxidizing the resulting aromatic amine IX to benzenepentacarboxylic acid (equation 4).



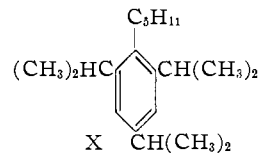
The mechanism indicated in Scheme A suggested that the relative extents of the two courses of reaction should be dependent on the hydronium ion concentration, since coordination of the proton with the free pair of electrons on the nitrogen atom of IV in salt formation<sup>6</sup> should retard course a and thereby favor course b. In agreement with this, the yields of aromatic hydrocarbon VI decreased while those of aromatic amine VII increased as the normality of hydrochloric acid was increased as shown in Table I.

TABLE I  
REACTIONS OF *exo*-METHYLENEAMINE IV WITH HYDROCHLORIC ACID

Hydrochloric acid, <i>N</i>	Hydrocarbon VI yield, %	Amine VII yield, %
0.15	74	19
6	26	59
12	13	68

It should be mentioned that *exo*-methyleneamine II has been observed<sup>8</sup> to undergo with 6 *N* hydrochloric acid only the course corresponding to a to form isodurene, although course b might be realized with more concentrated acid. This is not surprising since the methyl group should be less prone to eliminate as a carbonium ion than the isopropyl group.

*exo*-Methyleneamine IV reacted readily with butyllithium in ether to form a colored lithio derivative which apparently simultaneously eliminated trimethylamine as a carbanion to give aromatic hydrocarbon X (as indicated by ultraviolet absorption analysis) and considerable polymeric material. However, satisfactory analysis for this product was not obtained. On the other hand, the



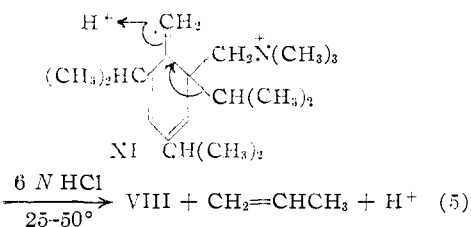
analogous reaction of *exo*-methyleneamine II with butyllithium produced a lithio derivative that decomposed to *n*-amylmesitylene with little polymeric material.<sup>8</sup> Moreover, the intermediate lithio derivative was more stable<sup>7</sup> and gave on hydrolysis a

(6) The preferential protonation of nitrogen over direct proton attack on the *exo*-methylene group of II was demonstrated in ref. 3.

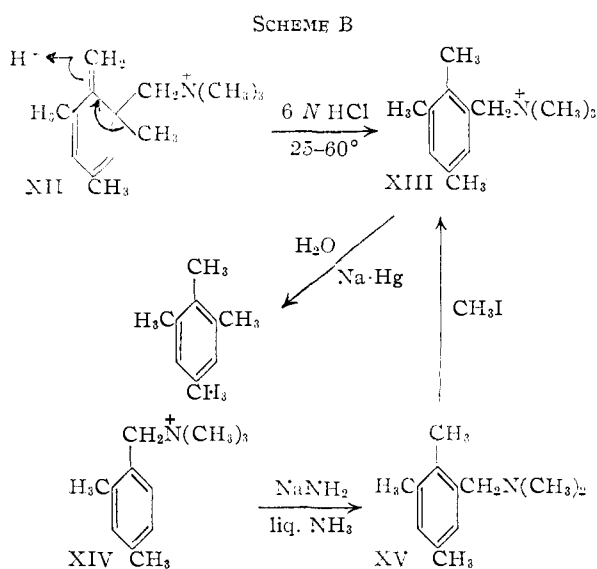
(7) The greater stability of the lithio derivative from II appears to be due to less steric hindrance and buttressing effect.

good yield of the corresponding *n*-amylcyclohexadieneamine product.<sup>8</sup>

**Aromatization of the Methiodide of *exo*-Methyleneamine IV.**—The above observation that *exo*-methyleneamine IV eliminated mainly the isopropylcarbonium ion with concentrated hydrochloric acid (course b, Scheme A) suggested that the methiodide of IV in which the nitrogen atom has no free pair of electrons might eliminate exclusively this carbonium ion even with dilute acid. In agreement with this, quaternary ammonium ion XI readily underwent aromatization with 6 *N* hydrochloric acid to form quaternary ion VIII (91%) and propylene which was isolated as its dibromide (77%) (equation 5). Presumably the olefin arose by loss of a proton from the isopropylcarbonium ion.

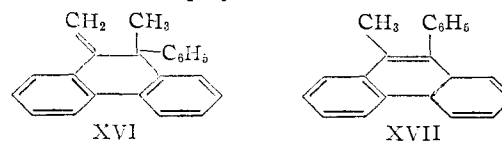


Similarly, the methiodide of *exo*-methyleneamine II (cation XII) underwent aromatization with 6 *N* hydrochloric acid to form quaternary ammonium ion XIII (85%). Presumably the methyl group was eliminated as a carbonium ion (or as methanol). The structure of quaternary ion XIII was determined by an Emde reduction to isodurene (96%) and by an independent synthesis from quaternary ion XIV. The latter reaction involved a normal *ortho* substitution rearrangement to form tertiary amine XV which was realized in 68% yield. These results are summarized in Scheme B.



It seems rather remarkable that the elimination of the methylcarbonium ion occurred readily at relatively low reaction temperatures (25–60°). A somewhat similar aromatization involving the elimination of a methyl group has been observed

by Bradsher and co-workers<sup>8</sup> with *exo*-methylene compound XVI to form XVII, but more drastic conditions were employed.



### Experimental<sup>9</sup>

**2,4,6-Triisopropylbenzyltrimethylammonium Chloride (III).**—2,4,6-Triisopropylbenzyl chloride, b.p. 126–128° at 3.5 mm.,  $n_D^{25}$  1.5158 (reported<sup>10</sup> b.p. 129–130° at 4 mm.,  $n_D^{25}$  1.5151), was prepared<sup>10</sup> in 73% yield by the chloromethylation of 1,3,5-triisopropylbenzene.<sup>11</sup>

Into a solution of 91.8 g. (0.363 mole) of this halide in 400 ml. of dry acetonitrile was bubbled slowly anhydrous trimethylamine for 1 hr., following which 500 ml. of dry ether was added with swirling to precipitate the quaternary ammonium salt. The product was collected on a funnel, washed with ether, recrystallized from acetonitrile-ether and dried *in vacuo* in a desiccator. There was obtained 108.2 g. (96%) of 2,4,6-triisopropylbenzyltrimethylammonium chloride (III), m.p. 229–230° dec. Its picrate, after three recrystallizations from ethanol-ether, melted at 160–161.5°.

*Anal.* Calcd. for  $\text{C}_{25}\text{H}_{36}\text{N}_4\text{O}_7$ : C, 59.51; H, 7.19; N, 11.10. Found: C, 59.76; H, 7.32; N, 11.13.

**Rearrangement of III to 6-Methylene-1,3,5-triisopropyl-1-dimethylaminomethylcyclohexadiene-2,4 (IV).**—This reaction was carried out with 15.6 g. (0.05 mole)<sup>12</sup> of 2,4,6-triisopropylbenzyltrimethylammonium chloride (III) and 0.15 mole of sodium amide in 400 ml. of liquid ammonia essentially as described for the corresponding rearrangement of I.<sup>8</sup> Ammonium chloride (5.4 g., 0.10 mole) was added to the light gray reaction mixture after 2 hr. stirring, followed by the addition of 500 ml. of reagent grade ether during the careful evaporation of the liquid ammonia on the steam-bath. After refluxing for 15–30 seconds,<sup>13</sup> the ether suspension was filtered and the solvent evaporated from the filtrate *in vacuo* at room temperature, first on a water aspirator and finally on a high-vacuum pump to remove the last traces of ether. The yield of colorless *exo*-methylene-cyclohexadieneamine IV,  $n_D^{25}$  1.4997, was 13.8 g. (quantitative).

*Anal.* Calcd. for  $\text{C}_{19}\text{H}_{33}\text{N}$ : C, 82.84; H, 12.08; N, 5.09. Found: C, 82.65; H, 12.25; N, 5.12; ultraviolet absorption spectrum calcd.<sup>5</sup>  $\lambda_{\text{max}}$  313  $\mu$ , found  $\lambda_{\text{max}}$  315  $\mu$  (3.9).

*exo*-Methyleneamine IV reacted with methyl iodide in acetonitrile to form a quaternary ammonium iodide XI, m.p. 150–151.5° dec., which darkened rapidly and partially decomposed on standing.

**Thermal Isomerization of IV to form  $\beta$ -(2,4,6-Triisopropylphenyl)-ethyl-dimethylamine (V).**—An ether solution of *exo*-methyleneamine IV (prepared from 0.15 mole of III and 0.45 mole of sodium amide) was evaporated on the steam bath. When most of the solvent had been removed and the temperature reached approximately 90°, the residual oil underwent a vigorous exothermic reaction (resulting in boiling). The pale yellow product was distilled *in vacuo* to give 38.0 g. (92%) of  $\beta$ -(2,4,6-triisopropylphenyl)-ethyl-dimethylamine (V), b.p. 96–97° at 0.3 mm.,  $n_D^{25}$  1.4964 (and 2.7 g. of undistillable residue).

(8) C. K. Bradsher, L. Rapoport and P. Anderson, *THIS JOURNAL*, **68**, 2153 (1946); see also, R. L. Shriner and L. Geipel, *ibid.*, **79**, 227 (1957).

(9) 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.

(10) K. C. Fuson, *et al.*, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 68.

(11) We are indebted to the Dow Chemical Co. for a generous sample of their product Alkazene-13 which was used in this experiment.

(12) Larger scale runs of 0.15 mole and 0.20 mole were without adverse effect on the yield or purity of IV.

(13) Prolonged refluxing of the ether is to be avoided because of the facile thermal isomerization of the alicyclic product.

*Anal.* Calcd. for  $C_{19}H_{33}N$ : C, 82.84; H, 12.08; N, 5.09. Found: C, 82.92; H, 12.29; N, 4.88.

The methiodide,<sup>14</sup> after three recrystallizations from 95% ethanol, melted at 255–256° dec.

*Anal.* Calcd. for  $C_{20}H_{35}NI$ : C, 57.54; H, 8.69; N, 3.36. Found: C, 56.97; H, 8.53; N, 3.11.

**Independent Synthesis of  $\beta$ -(2,4,6-Triisopropylphenyl)-ethyl-dimethylamine (V).**—This product was synthesized in three steps in an over-all yield of 44% from 2,4,6-triisopropylbenzyl chloride.

2,4,6-Triisopropylphenylacetonitrile was prepared<sup>15</sup> in 67% yield from the halide and cuprous cyanide in pyridine. The product distilled at 125–128° at 2 mm., m.p. 79–80.5° (reported<sup>15</sup> b.p. 129–130° at 4 mm., m.p. 81–82°).

To 7.60 g. (0.20 mole) of lithium aluminum hydride in 300 ml. of ether was added dropwise with stirring a solution of 34.2 g. (0.133 mole) of the nitrile in 250 ml. of ether. The resulting reaction mixture was stirred and heated under reflux for 12 hr., cooled and the excess hydride destroyed by the addition of ethyl acetate. Following hydrolysis with 500 ml. of 20% sodium potassium tartrate, the ethereal layer was worked-up to give 28.8 g. (87%) of crude  $\beta$ -(2,4,6-triisopropylphenyl)-ethylamine. This primary amine, which readily absorbed carbon dioxide from the air, was used without purification for the following reaction.

Methylation of  $\beta$ -(2,4,6-triisopropylphenyl)-ethylamine was effected by the Eschweiler-Clarke procedure, employing the directions of Icke and Wisegarver<sup>16</sup> for the alkylation of  $\beta$ -phenylethylamine with formic acid and formaldehyde. From 28.8 g. (0.116 mole) of amine and 40 ml. each of 88% formic acid and 37% formalin solution there was isolated (second distillation) 24.3 g. (76%) of  $\beta$ -(2,4,6-triisopropylphenyl)-ethyl-dimethylamine (V), b.p. 96–97° at 0.3 mm.,  $n_D^{25}$  1.4965. Its methiodide melted at 255–256° dec. The identity of this methiodide and that of the amine resulting from the thermal isomerization of *exo*-methyleneamine IV was established by a mixed melting point determination.

**Reactions of *exo*-Methyleneamine IV with Hydrochloric Acid to Form 2,4,6-Triisopropyltoluene (VI) and 2-Methyl-3,5-diisopropylbenzyl-dimethylamine (VII).**—In Table I are summarized the results of the reactions of *exo*-methyleneamine IV with 0.15, 6 and 12 *N* hydrochloric acid. The procedure with 6 *N* hydrochloric acid is described below.<sup>17</sup>

To 600 ml. (3.6 moles) of vigorously stirred 6 *N* hydrochloric acid was added dropwise a solution of 55.1 g. (0.20 mole) of *exo*-methyleneamine IV in 100 ml. of 95% ethanol,<sup>18</sup> the temperature of the reaction mixture being maintained at 25°. The reaction mixture immediately became turbid, and near the end of the addition globules of hydrocarbon became visible. The resulting mixture was shaken with ether and the aqueous layer drawn off and worked-up as described below. The ethereal layer afforded, on distillation *in vacuo*, 11.5 g. (26%) of triisopropyltoluene (VI), b.p. 105–106° at 5 mm.,  $n_D^{20}$  1.4994 (reported<sup>19</sup> b.p. 252–253° at 757 mm.,  $n_D^{20}$  1.4995).

This hydrocarbon was converted to a sulfonamide derivative by the general procedure of Huntress and Autenrieth<sup>20</sup> for highly hindered compounds, employing the sulfonyl chloride and gaseous ammonia in ether. After 3 crystallizations from hexane–benzene the product melted at 138.5–139.5°.<sup>21</sup>

*Anal.* Calcd. for  $C_{13}H_{21}O_2NS$ : C, 61.15; H, 8.29; N, 5.49. Found: C, 61.70; H, 8.37; N, 5.39.

(14) Attempts to prepare the picrate of this and other polyisopropyl-substituted amines failed. The most convenient derivative for these amines was the corresponding methiodide.

(15) R. C. Fuson, L. J. Armstrong and W. J. Shenk, *THIS JOURNAL*, **66**, 964 (1944).

(16) R. N. Icke and B. B. Wisegarver, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 723.

(17) The reactions with the other two normalities were carried out similarly employing molecular equivalents of IV and 0.15 *N* acid and an 80-fold excess of 12 *N* hydrochloric acid over IV.

(18) Ethanol was used as solvent to emulsify the reactants in the reaction mixture, thereby lowering local excesses of either reactant.

(19) G. Desseigne, *Bull. soc. chim. France*, [5] **2**, 617 (1935).

(20) See E. H. Huntress and J. S. Autenrieth, *THIS JOURNAL*, **63**, 2446 (1941).

(21) This sulfonamide analyzed for a methyl-diisopropylbenzene-sulfonamide instead of the expected triisopropyl derivative. The apparent loss of an isopropyl group appears to have occurred in the reaction of the hydrocarbon with chlorosulfonic acid.

The aqueous layer mentioned above was made alkaline (pH 9–10) with 50% sodium hydroxide. The resulting oily layer of amine VII, which gradually separated, was drawn off, leaving the aqueous solution of the alkaline hydrolysis products of dimethylmethylene iminium chloride (see below). The oily amine VII was taken up in ether, washed with water and dried over anhydrous magnesium sulfate. After filtering and removing the solvent by evaporation, the residue was distilled *in vacuo* to give (second distillation) 27.7 g. (59%) of 2-methyl-3,5-diisopropylbenzyl-dimethylamine (VII), b.p. 85–86° at 0.5 mm.,  $n_D^{25}$  1.4993, ultraviolet absorption analysis  $\lambda_{max}$  278 m $\mu$  (2.8). The residue (4.2 g., 9%) melted at 65–66° after 3 crystallizations from methanol cooled to –78°. This appeared to consist of a dimeric amine.

A sample of amine VII was converted to its methiodide VIII with methyl iodide in acetonitrile. After several crystallizations from acetonitrile–ether, it melted at 240–241.5° dec.

*Anal.* Calcd. for  $C_{17}H_{30}NI$ : C, 54.40; H, 8.06; N, 3.73. Found: C, 54.55; H, 8.33; N, 3.57.

The aqueous alkaline solution mentioned above smelled strongly of pungent formaldehyde. The presence of dimethylamine in this solution was established by the addition of 8.1 g. (0.06 mole) of phenyl isocyanate to the solution with vigorous shaking. There was isolated 7.4 g. (79%, based on triisopropyltoluene) of *N,N*-dimethylphenylthiourea, m.p. and mixed m.p. 134–135° (reported<sup>22</sup> m.p. 135°) after crystallization from a minimum of refluxing ethanol.

**Independent Synthesis of 2,4,6-Triisopropyltoluene (VI).**—The synthesis of this hydrocarbon was effected by an adaptation of the general procedure of Emde<sup>23</sup> for the reduction of quaternary salts to hydrocarbons. From a solution of 18.7 g. (0.06 mole) of 2,4,6-triisopropylbenzyl-trimethylammonium chloride (III) in 400 ml. of water and 250 g. of 5% sodium amalgam (0.54 mole), after a reaction period of 12 hr. on the steam-bath, was isolated 12.9 g. (98%) of 2,4,6-triisopropyltoluene (VI), b.p. 105–105.2° at 5 mm.,  $n_D^{20}$  1.4993. This hydrocarbon was converted to its sulfonamide, m.p. 138.5–139.5°,<sup>22</sup> which did not depress the melting point of the sulfonamide prepared as described above from the hydrocarbon obtained in the acidic decomposition of *exo*-methyleneamine IV.

**ortho Substitution Rearrangement of Methiodide VIII to Form 2,3-Dimethyl-4,6-diisopropylbenzyl-dimethylamine (IX).**—Quaternary ammonium salt 2-methyl-3,5-diisopropylbenzyl-trimethylammonium iodide (VIII), m.p. 240–241° dec., was prepared in 96% yield from tertiary amine VII and methyl iodide in acetonitrile.

To a stirred suspension of 0.40 mole of sodium amide in 700 ml. of liquid ammonia was added rapidly 51.4 g. (0.137 mole) of the salt. The resulting reddish-tan colored reaction mixture gradually changed to rose during 1 hr., this color persisting up to 2 hr. Ammonium chloride (16 g., 0.30 mole) was added, the ammonia evaporated and replaced by ether, the suspended salts filtered off and the ethereal filtrate shaken with 500 ml. of 6 *N* hydrochloric acid. The two layers were separated, the ethereal extract of neutral products yielding 2.9 g. of a dark colored, viscous oil, which was discarded. From the aqueous acidified solution there was isolated 26.6 g. (78%) of 2,3-dimethyl-4,6-diisopropylbenzyl-dimethylamine (IX), b.p. 95–95.5° at 0.5 mm.,  $n_D^{20}$  1.5086.

*Anal.* Calcd. for  $C_{17}H_{30}N$ : C, 82.52; H, 11.82; N, 5.66. Found: C, 82.58; H, 11.83; N, 5.46.

The methiodide of tertiary amine IX, after two recrystallizations from a mixture of acetonitrile–ether, melted with decomposition at 217–218° with prior darkening at 180°.

*Anal.* Calcd. for  $C_{18}H_{32}NI$ : C, 55.52; H, 8.29; N, 3.59. Found: C, 55.18; H, 8.68; N, 3.52.

**Oxidation of Amine IX to Form Benzenepentacarboxylic Acid.**—This reaction was carried out essentially as described previously<sup>24</sup> for the oxidations of polyalkylbenzyl-dimethyl-

(22) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 4th ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 288.

(23) H. Emde, *Ber.*, **42**, 2590 (1909).

(24) C. R. Hauser and A. J. Weinheimer, *THIS JOURNAL*, **76**, 1264 (1954).

amines with alkaline potassium permanganate. From 5 g. of amine IX, 300 ml. of water and 80 g. of potassium permanganate (added during 20 hr.), there was obtained through the barium salt (12.0 g.) 3.1 g. (40%) of benzene-pentacarboxylic acid pentahydrate, m.p. 229–231° (reported m.p. 230°).<sup>25</sup> The melting point was not depressed by admixture with an authentic sample of this acid pentahydrate, m.p. 228–231°, prepared by the oxidation of pentamethylbenzene.

**Reaction of *exo*-Methyleneamine IV with Butyllithium.**—This reaction was carried out essentially as described<sup>3</sup> for the condensation of *exo*-methyleneamine II with butyllithium. The initial greenish-brown reaction mixture, resulting from the rapid addition of a solution of 41.3 g. (0.15 mole) of *exo*-methyleneamine IV in 300 ml. of ether to a solution of butyllithium (prepared from 1.25 g. atoms of lithium and 0.50 mole of *n*-butyl bromide in 200 ml. of ether), became reddish-brown during the 10-minute reaction period. On working up the reaction mixture there was isolated (third distillation) 12.8 g. (31%) of what appeared to be 2,4,6-trisopropyl-*n*-amylbenzene (X), b.p. 104–105° at 0.4 mm.,  $n_D^{25}$  1.4928, ultraviolet absorption analysis,  $\lambda_{max}$  278 m $\mu$  (2.8). Also there was obtained 27.3 g. (approximately 67%) of a very viscous, neutral liquid, b.p. 180–192° at 7 mm., which apparently consisted of a polymeric hydrocarbon.

**Decomposition of Methiodide XI with Acid to Form 2-Methyl-3,5-diisopropylbenzyltrimethylammonium Iodide (VIII) and Propylene.**—*exo*-Methyleneamine methiodide XI, m.p. 150–151.5° dec., was prepared in 98% yield from IV and methyl iodide in acetonitrile.

Forty-two grams (0.10 mole) of this salt was placed in a 500-ml. 3-necked flask equipped with a sealed stirrer, condenser and a Y-shaped tube fitted with an additional funnel and a gas inlet tube (connected to a tank of compressed nitrogen) extending to the bottom of the flask. The condenser was jointed by tubing to a 20-cm. tall gas-drying tower containing a solution of 48.0 g. (0.30 mole) of bromine in 250 ml. of carbon tetrachloride.

While nitrogen was introduced slowly into the flask containing the methiodide (to transfer the propylene evolved during the reaction to the bromine-carbon tetrachloride reagent), 165 ml. (1 equivalent) of 6 *N* hydrochloric acid was added dropwise to the reaction mixture with stirring over 15 minutes. During the ensuing reaction, which brought about solution of the quaternary salt and caused a temperature rise to about 50°, considerable foaming occurred. Nitrogen was bubbled through the resulting orange mixture for 15 minutes with stirring, the evolved propylene being readily absorbed from the exit gases. The reaction mixture was then cooled to 0° to produce a thick precipitate which was collected on a funnel and air-dried. The crude quaternary ammonium salt was dissolved in hot acetonitrile and triturated with a minimum of 95% hydrazine.<sup>26</sup> Following filtration, the colorless filtrate was cooled and the quaternary salt precipitated by the addition of anhydrous ether. The filtered product, after two recrystallizations from acetonitrile-ether, was dried *in vacuo* in a desiccator. There was obtained 34.2 g. (91%) of 2-methyl-3,5-diisopropylbenzyltrimethylammonium iodide (VIII), m.p. 240–241° dec., whose melting point was not depressed by admixture with a sample prepared previously from amine VII (resulting from the acidic decomposition of *exo*-methyleneamine IV; see above).

The solution contained in the gas-drying tower was treated with a saturated solution of sodium bisulfite to remove the bromine. The organic layer was shaken with aqueous sodium bicarbonate, washed with water and dried over magnesium sulfate. After removal of the solvent on the steam-bath, the residue was distilled to give 15.6 g. (77%) of 1,2-dibromopropane, b.p. 140–140.5°,  $n_D^{20}$  1.5205 (reported<sup>27</sup> b.p. 141°,  $n_D^{20}$  1.5203). An authentic sample of the dibromide prepared from propylene and bromine in carbon tetrachloride solution had identical physical properties.

**Decomposition of Methiodide XII with Acid to Form 2,3,5-Trimethylbenzyltrimethylammonium Iodide (XIII).**—

(25) H. Schrötter and R. Weitzenböck, *Monatsh. Chem.*, **29**, 396 (1908).

(26) This reagent neutralized hydrogen chloride (which tenaciously clung to the quaternary ammonium salt) and removed colored impurities.

(27) Reference 22, p. 312.

This reaction was carried out similarly to that described above for the acidic decomposition of quaternary ammonium iodide XI. The orange reaction mixture, resulting from the addition of 250 ml. (1.5 equivalents) of 6 *N* hydrochloric acid to 66.7 g. (0.20 mole) of *exo*-methyleneamine methiodide (XII), m.p. 153–154° dec.<sup>3</sup> (temperature rose to approximately 60°), after several minutes began to precipitate quaternary salt XIII from solution.<sup>28</sup> The resulting reaction mixture was cooled and allowed to stand at 0° for several hours, when the thick precipitate was collected on a funnel and air-dried. The filtrate was evaporated *in vacuo* to near dryness and again cooled to 0°, a second crop of quaternary salt being obtained on filtration. The combined crops were worked-up (as described above) to afford 54.1 g. (85%) of 2,3,5-trimethylbenzyltrimethylammonium iodide (XIII), m.p. 227–229°, with darkening at 185°. A small sample, recrystallized twice more from acetonitrile-ether, melted at 229–230°, with previous darkening at 190°.

*Anal.* Calcd. for C<sub>13</sub>H<sub>22</sub>N<sub>1</sub>I: C, 48.91; H, 6.95; N, 4.39. Found: C, 48.79; H, 7.19; N, 4.22.

**Reduction of Methiodide XIII to Form Isodurene.**—A solution of 31.9 g. (0.10 mole) of 2,3,5-trimethylbenzyltrimethylammonium iodide (XIII) in 500 ml. of hot water was reduced with 400 g. of 5% sodium amalgam by the general method of Emde<sup>23</sup> to give 12.9 g. (96%) of isodurene, b.p. 85–86.5° at 18 mm.,  $n_D^{25}$  1.5108 (reported<sup>29</sup> b.p. 84.6–84.7° at 17 mm.,  $n_D^{25}$  1.5107). The dinitro derivative, after two recrystallizations from 95% ethanol, melted at 180–181° (reported<sup>30</sup> m.p. 181°). The melting point of this compound was not depressed by admixture with an authentic sample of dinitroisodurene, m.p. 179.5–181°.

**2,4-Dimethylbenzyltrimethylammonium Chloride (XIV)**—A slight modification of the method of Vavon and Bolle<sup>31</sup> for the chloromethylation of aromatic hydrocarbons was used for the preparation of 2,4-dimethylbenzyl chloride. The reaction mixture, composed of 53.1 g. (0.50 mole) of *m*-xylene, 44 g. (0.55 mole) of chloromethyl methyl ether, 200 ml. of glacial acetic acid and 25 ml. of concentrated hydrochloric acid, was stirred for 15 hr. at 70° and worked up to give 56.8 g. (73%) of 2,4-dimethylbenzyl chloride, b.p. 95–96° at 10 mm. (reported<sup>32</sup> b.p. 116–118° at 16 mm.).

The quaternary ammonium chloride XIV was obtained in 97% yield from gaseous trimethylamine and 0.367 mole of this halide in 200 ml. of dry acetonitrile essentially as described for the preparation of 2,4,6-trisopropylbenzyltrimethylammonium chloride (III) (see above). After two crystallizations from acetonitrile-ether, the hygroscopic salt XIV melted at 230–231° dec. Its picrate, crystallized twice from water, melted at 180–181°.

*Anal.* Calcd. for C<sub>13</sub>H<sub>22</sub>N<sub>4</sub>O<sub>7</sub>: C, 53.20; H, 5.46; N, 13.79. Found: C, 53.12; H, 5.64; N, 13.64.

**ortho Substitution Rearrangement of XIV to Form Amine XV and its Conversion to Methiodide XIII.**—This reaction was carried out with 64.1 g. (0.30 mole) of 2,4-dimethylbenzyltrimethylammonium chloride (XIV) and 0.60 mole of sodium amide in 1 l. of liquid ammonia as described for VIII. The deep, bright blue-purple reaction mixture was stirred for 2 hr. and worked-up to give 36.2 g. (68%) of colorless 2,3,5-trimethylbenzyltrimethylamine (XV), b.p. 107–108° at 10 mm.,  $n_D^{25}$  1.5105, leaving a basic residue of 2.2 g. and a neutral one of 10.2 g. (mainly polymeric material).

*Anal.* Calcd. for C<sub>12</sub>H<sub>19</sub>N: C, 81.30; H, 10.80; N, 7.90. Found: C, 81.17; H, 10.95; N, 7.94.

The methiodide of this amine was obtained in 98% yield from XV and methyl iodide in acetonitrile. After two recrystallizations from acetonitrile-ether it melted at 231–233° dec., with shrinking at 229° and prior darkening at 190°. It did not depress the melting point of 2,3,5-trimethylbenzyltrimethylammonium iodide (XIII) prepared previously from the acidic decomposition of *exo*-methyleneamine methiodide XII.

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(28) The benzyl quaternary ammonium iodides VIII and XIII are much less water soluble than the corresponding alicyclic reactants XI and XII, respectively.

(29) L. I. Smith and F. H. MacDougall, *THIS JOURNAL*, **51**, 3004 (1929).

(30) L. I. Smith and L. C. Moyle, *ibid.*, **55**, 1680 (1933).

(31) G. Vavon and J. Bolle, *Compt. rend.*, **204**, 1826 (1937).

(32) R. B. Akin, G. S. Stamatoff and M. T. Bogert, *THIS JOURNAL*, **59**, 1271 (1937).