[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Stevens 1,2-Shift of Certain Substituted Dibenzyldimethylammonium Ions by Sodium Amide. Influence of Structure on Courses of Rearrangement[1]

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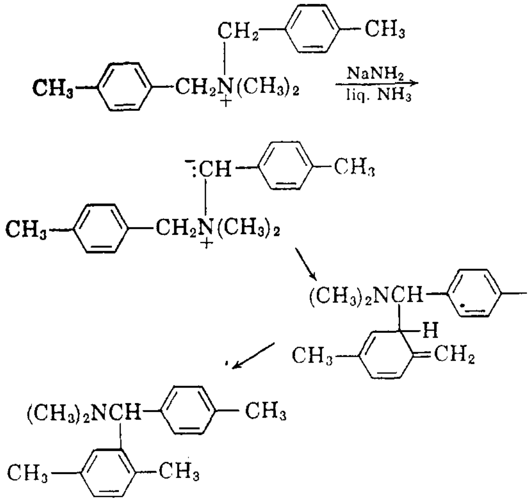
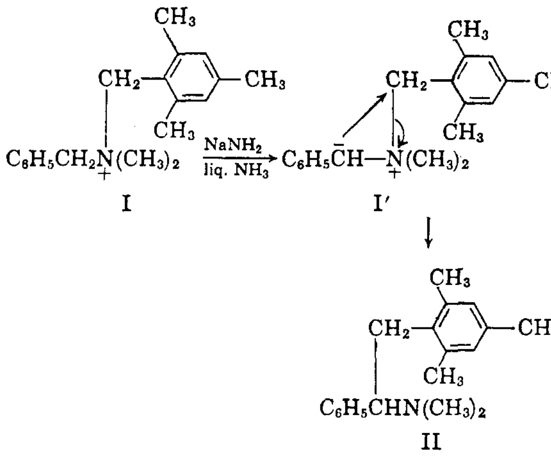
In contrast to the 2- or 4-substituted and 4,4′-disubstituted dibenzyldimethylammonium ions which undergo the *ortho* substitution rearrangement, the dibenzyldimethylammonium ions having 2,4,6-trimethyl substituents in one or both of the aromatic rings underwent the Stevens type of 1,2-shift with sodium amide in liquid ammonia. Besides good yields of the rearranged amines, there were also isolated small amounts of neutral products. The influence of structure on the *ortho* substitution rearrangement versus the 1,2-shift is considered.

Recently[2] one 2-substituted, two 4-substituted, and four 4,4′-disubstituted dibenzyldimethylammonium ions were shown to undergo the *ortho* substitution rearrangement with sodium amide in liquid ammonia. The reaction may be illustrated with the bis(4-methylbenzyl)dimethylammonium ion (Equation 1).



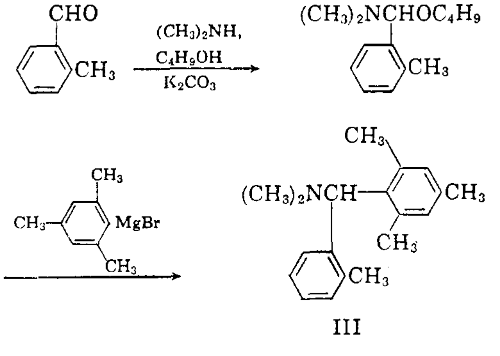
(1)

In the present investigation the substituted dibenzyldimethylammonium ions having methyl groups in the 2-, 4-, and 6-positions of one or of both of the aromatic rings were found to undergo under similar conditions the Stevens 1,2-shift instead of the *ortho* substitution rearrangement. Thus, the unsymmetrical quaternary ion I rearranged to form tertiary amine II in 83% yield (Equation 2).



(2)

Little if any other amine appeared to be formed, since the crude product melted only a few degrees low. The infrared spectrum of this amine showed bands at 755 cm.$^{-1}$ and 702 cm.$^{-1}$ for the monosubstituted benzene ring[3] found in a Stevens 1,2-shift product such as II rather than a single band in the 770–730 cm.$^{-1}$ region for four adjacent aromatic ring hydrogen atoms. The latter absorption would have been observed had the amine been the possible *ortho* substitution rearrangement product III, which was synthesized according to Equation 3 and shown to exhibit this absorption.



(3)

The amine from the rearrangement of I was definitely shown not to be III by comparison of infrared spectra and by the mixed melting point method.

Besides II, there were six other possible Stevens 1,2-shift products.[4] The formation of these seven amines would involve ionizations of the three types of active hydrogens and the migrations of the three types of groups. Amine II seemed the most likely

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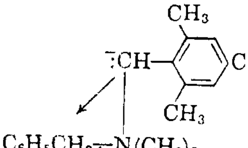
[1] Supported by the National Science Foundation.

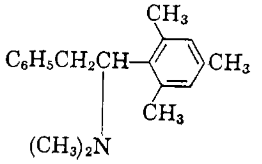
[2] W. Q. Beard and C. R. Hauser, *J. Org. Chem.*, **26**, 371 (1961).

[3] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., John Wiley & Sons, New York, N. Y., 1958, p. 76.

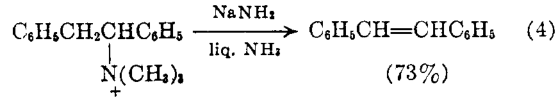
[4] See ref. 3, page 77.

of such products, since not only should the benzyl hydrogen be ionized more readily than the 2,4,6-trimethylbenzyl or the methyl hydrogen, but also the 2,4,6-trimethylbenzyl group in the resulting carbanion I′ should then undergo the 1,2-shift rather than a methyl group (see Equation 2). There was a definite possibility, however, that the 2,4,6-trimethylbenzyl hydrogen would be ionized to form carbanion I″, which should then undergo the 1,2-shift of the benzyl group to give amine IV.


I″

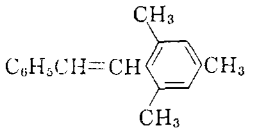

IV

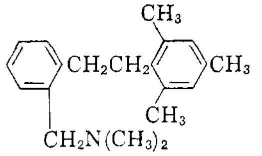
Fortunately, of the seven possible Stevens products only amines II and IV could produce stilbene derivatives on treatment of their methiodides with sodium amide in liquid ammonia, a type of elimination reaction observed in this laboratory[5] with the methiodide of α,β-diphenylethyldimethylamine (Equation 4).



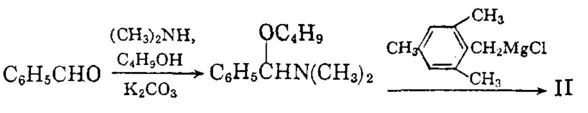
$$C_6H_5CH_2\underset{\overset{+}{N}(CH_3)_3}{\underset{|}{C}}HC_6H_5 \xrightarrow[\text{liq. } NH_3]{NaNH_2} \underset{(73\%)}{C_6H_5CH{=}CHC_6H_5} \quad (4)$$

Actually the methiodide of the amine product from the rearrangement of quaternary ion I did give the known stilbene derivative V (30%). In addition, there was obtained an amine that appeared to have structure VI (31%).


V


VI

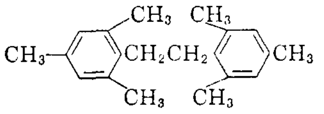
That the amine was the *ortho* substitution rearrangement product VI and not a possible Stevens 1,2-shift product was supported by its infrared spectrum, which exhibited a single band at 753 cm.$^{-1}$, indicating the presence of only four adjacent aromatic hydrogen atoms as in VI, and no band in the 710-680 cm.$^{-1}$ region which would indicate five adjacent hydrogens as would be expected in the latter type of product. Since the methiodide of II but not that of IV[6] could rearrange to amine VI, II was indicated to be the rearranged amine from quaternary ion I. This was confirmed by an independent synthesis (Equation 5).

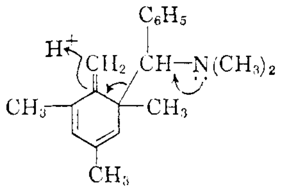


(5)

The product obtained in this synthesis was shown to be identical with that produced in the rearrangement of quaternary ion I by their infrared spectra and by the mixed melting point method.

Besides amine II (see Equation 2), the reaction of quaternary ion I with sodium amide in liquid ammonia produced small amounts of the neutral products 1,2-dimesitylethane (VII) (4-5%), isodurene (1%) and benzaldehyde (2-3%), which was isolated as its 2,4-dinitrophenylhydrazone. The benzaldehyde and isodurene might have arisen through the first stage of the *ortho* substitution rearrangement of the benzyl carbanion I′ into the mesityl ring to form the *exo*-methyleneamine VIII, which should have been decomposed readily by the acid employed in working up the reaction mixture to form the methylene-imine IX and isodurene. The acid should also decompose IX to give the aldehyde. Such a course of reaction has been observed previously with the 2,4,6-trimethylbenzylmethylammonium ion.[7] The dimesitylethane (VII) is unaccounted for at the present time.

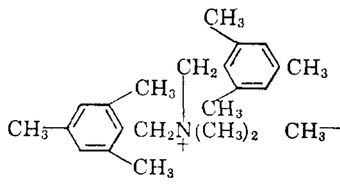

VII

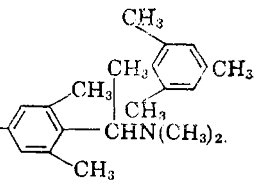

VIII

$C_6H_5CH{=}\overset{+}{N}(CH_3)_2$

IX

Similarly the symmetrical quaternary ion X underwent the Stevens 1,2-shift with sodium amide in liquid ammonia to form amine XI in 58% yield. This rearrangement occurred more slowly than that of quaternary ion I.


X


XI

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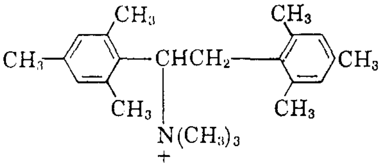
[5] Unpublished result of T. G. Ledford and C. R. Hauser. Besides stilbene there was obtained a small amount of a rearranged amine that may have been the *ortho* substitution rearrangement product.

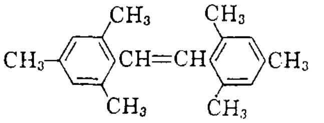
[6] The methiodide of amine IV might undergo the first stage of the *ortho* substitution rearrangement but if so, the resulting *exo*-methyleneamine should be unstable toward acid; see ref. 7.

[7] C. R. Hauser and D. N. Van Eenam, *J. Am. Chem. Soc.*, 76, 1264 (1954).

The structure of the product was established as XI by effecting the elimination reaction of its methiodide XII with sodium amide in liquid ammonia to form the known stilbene derivative XIII in 51% yield. This reaction corresponds to that represented by Equation 4. Olefin XIII was reduced by means of sodium in liquid ammonia to give the known dimesitylethane (VII) in 91% yield.

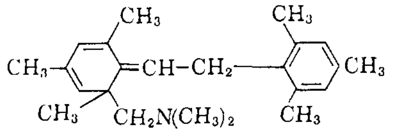


XII

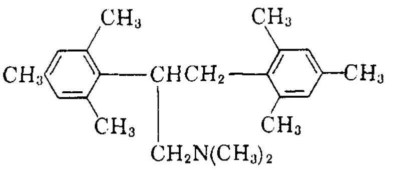


XIII

Since the elimination reaction of XII with sodium amide was expected to be accompanied by the formation of the acid unstable *exo*-methyleneamine XIV, the reaction mixture was heated before adding acid to convert XIV to the stable amine XV. Actually an amine that gave a satisfactory analysis for XV was isolated in 11% yield. The intermediate *exo*-methyleneamine XIV would presumably have been decomposed by acid to form dimesitylethane (VII), which would have been difficult to separate from olefin XIII.



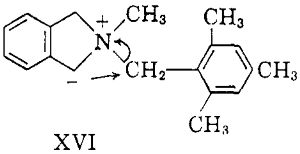
XIV



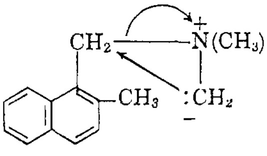
XV

Besides amine XI, the reaction of quaternary ion X with sodium amide produced small amounts of dimesitylethane (VII) (0.5%) and 2,4,6-trimethylbenzaldehyde, which was isolated as its 2,4-dinitrophenylhydrazone (0.2%). This aldehyde might be accounted for by a mechanism analogous to that indicated above for benzaldehyde.

Previously the Stevens 1,2-shift has been observed with the related quaternary ions XVI[8,9] and XVII,[10,11] whereas the corresponding quaternary ions having no methyl group in the *ortho* position exhibited the *ortho* substitution rearrangement.



XVI



XVII

Also, whereas the dibenzyldimethylammonium ion undergoes the *ortho* substitution rearrangement,[12] the more complex benzylbenzohydryl- and benzylfluorenyl-dimethylammonium ions exhibit the 1,2-shift.[13]

All of these results are in line with the earlier conclusion[13] that an increase in the size or complexity of a benzyl type quaternary ammonium ion may favor the 1,2-shift over the *ortho* substitution rearrangement with sodium amide in liquid ammonia.[14]

EXPERIMENTAL[15]

Benzyl-2,4,6-trimethylbenzyldimethylammonium chloride (I). To 27.0 g. (0.16 mole) of 2,4,6-trimethylbenzyl chloride[16] in 100 ml. of acetonitrile was added all at once 27.0 g. (0.20 mole of benzyldimethylamine. The mixture was warmed on a steam bath, the salt precipitating after several minutes. After 30 min. at steam bath temperature the mixture was cooled and 500 ml. of ether slowly added to complete the precipitation. The product was collected, washed with ether, and recrystallized from absolute ethanol. A yield of 48.1 g. (99%) of benzyl-2,4,6-trimethylbenzyldimethylammonium chloride (I), m.p. 197–198°, was obtained.

Anal. Calcd. for $C_{19}H_{26}ClN$: C, 75.09; H, 8.62; N, 4.61. Found: C, 74.82; H, 8.57; N, 4.79.

Rearrangement of I to α-(2,4,6-trimethylbenzyl)-N,N-dimethylbenzylamine (II). To a suspension of 0.381 mole of sodium amide in 700 ml. of liquid ammonia[17] was added 38.7 g. (0.128 mole) of benzyl-2,4,6-trimethylbenzyldimethyl-

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(8) G. Wittig and H. Streib, *Ann.*, **584**, 1 (1953).

(9) Like quaternary ions I and X, ion XVI also produced products that may be accounted for by the acid decomposition of an *exo*-methyleneamine arising through the first stage of the ortho substitution rearrangement.

(10) C. R. Hauser, D. N. Van Eenam, and P. L. Bayless, *J. Org. Chem.*, **23**, 354 (1958).

(11) This is one of the few known 1,2-shifts in which the methyl carbanion is the reactive intermediate, another one occurring is the ferrocene series; C. R. Hauser, J. K. Lindsay, and D. Lednicer, *J. Org. Chem.*, **23**, 358 (1958). A similar 1,2-shift in which an aliphatic methylene carbanion serves partly as the reactive intermediate has been observed by L. P. A. Ferry and L. van Hove, *Bull. soc. chim. belg.*, **68**, 65 (1959).

(12) S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **73**, 4122 (1951).

(13) C. R. Hauser, R. M. Manyik, W. R. Brasen, and P. L. Bayless, *J. Org. Chem.*, **20**, 1119 (1955).

(14) For consideration of the influence of temperature and of the use of certain other reagents, see ref. 13.

(15) Analyses are by Galbraith Microanalytical Laboratory, Knoxville, Tenn. All melting points and boiling points are uncorrected.

(16) G. Vavon, J. Bolle, and J. Calin, *Bull. soc. chim. France*, [5] **6**, 1025 (1939).

(17) See C. R. Hauser, F. W. Swamer, and J. T. Adams, *Org. Reactions*, 122 (1954).

ammonium chloride (I). After 2.5 hr. the mixture was treated with 20 g. (0.384 mole) of ammonium chloride, and the ammonia was replaced with ether. The salts were filtered from the ethereal solution and triturated with 100 ml. of water. A small amount (0.17 g.) of a bright yellow material which was somewhat soluble in water but not in ether was filtered out. After one recrystallization from ethanol it melted at 156–157°. It was not characterized. No attempt was made to recover unchanged starting material, which was water soluble.

The ethereal solution from the reaction mixture was treated with 400 ml. of 6*N* hydrochloric acid, which caused an immediate precipitate of amine hydrochloride. After 5 min. of vigorous stirring, the mixture was filtered, and the solid hydrochloride was washed several times with small portions of ether. The ether solution was separated from the aqueous phase, washed with water, and extracted twice with saturated sodium bisulfite solution. The sodium bisulfite extracts were made slightly basic with sodium hydroxide and extracted with ether. The ether extract was dried over magnesium sulfate and evaporated, and the 2,4-dinitrophenylhydrazone of the benzaldehyde residue was prepared. The yield was 0.51 g., corresponding to a 2% yield of benzaldehyde, and after two recrystallizations from ethyl acetate and ethanol the melting point was 242–243°, lit.,[18] m.p. 241°. Admixture with an authentic sample produced no depression of the melting point.

The ether layer from the sodium bisulfite extraction was evaporated and steam distilled. Extraction of the steam distillate with ether and subsequent evaporation yielded 0.18 g. (1%) of isodurene, whose dinitro derivative melted at 179–180° after two recrystallizations from ethanol, lit.,[19] m.p. 181°.

The pot mixture from the steam distillation was cooled and extracted with ether. The ether extract was dried and evaporated, leaving 0.64 g. (4%) of 1,2-dimesitylethane, m.p. 116–117°, after one recrystallization from methanol, lit.,[20] m.p. 117–118°. An additional recrystallization raised the melting point to 118–118.5°. Admixture with an authentic sample produced no depression of the melting point.

The solid amine hydrochloride was added to the original acid layer and the mixture made strongly basic by the careful addition of solid sodium hydroxide. The mixture was cooled and stirred with 200 ml. of ether until all solid had dissolved. The layers were separated and the aqueous phase was extracted again with ether. After the combined ether extractions were dried evaporation yielded 26.2 g. (79%)[21] of crude amine, m.p. 54–56°. After two recrystallizations from petroleum ether (b.p. 30–60°) at −70° there was obtained 22 g. of α-(2,4,6-trimethylbenzyl)benzyldimethylamine, m.p. 62–63°.

Anal. Calcd. for $C_{19}H_{25}N$: C, 85.34; H, 9.42; N, 5.24. Found: C, 85.56; H, 9.55; N, 5.28.

The picrate, recrystallized three times from a mixture of ethanol and acetone, melted at 175–176°.

Anal. Calcd. for $C_{25}H_{28}N_4O_7$: C, 60.47; H, 5.68; N, 11.29. Found: C, 60.61; H, 5.51; N, 11.43.

Preparation of 2,2′,4,6-tetramethylbenzohydryldimethylamine (III). (A) *o-Methyl-α-dimethylaminobenzyl n-butyl ether.* This amino ether was prepared by method A of Stewart and Hauser[22] from 22.0 g. (0.183 mole) of *o*-tolualdehyde, 74.0 g. (1.0 mole) of *n*-butyl alcohol, 8.6 g. (0.20 mole) of dimethylamine, and 25.0 g. (0.183 mole) of anhydrous potassium carbonate. The yield was 18.33 g. (45%), b.p. 92–93° at 1.5 mm.

Anal. Calcd. for $C_{14}H_{23}NO$: C, 75.97; H, 10.47; N, 6.33. Found: C, 75.97; H, 10.64; N, 6.53.

(B) *Reaction of amino ether with mesitylmagnesium bromide.* The general method of Stewart and Hauser[22] for the addition of Grignard reagents to α-amino ethers was employed, using 18.30 g. (0.083 mole) of the above *o*-methyl-α-dimethylaminobenzyl *n*-butyl ether, 25.0 g. (0.125 mole) of 2-bromomesitylene and 3.65 g. (0.15-g.-atom) of magnesium. An additional 2.43 g. (0.1 mole) of magnesium and 18.8 g. (0.1 mole) of 1,2-dibromoethene were added to activate the formation of the Grignard reagent. The yield of 2,2′-4,6-tetramethylbenzohydryldimethylamine (III) was 17.0 g. (77%), m.p. 58–59°, after one recrystallization from hexane at −70°. A mixed melting point with amine II was depressed strongly. The infrared spectrum of amine III had one strong band at 750 cm.,$^{-1}$ but no band in the 710–690 cm.$^{-1}$ region.

The methiodide of II was prepared from 15.2 g. (0.057 mole) of amine II and excess methyl iodide in 75 ml. of acetonitrile. The reaction mixture was allowed to stand overnight, at which time much of the salt had crystallized. The remainder was precipitated by the addition of 200 ml. of anhydrous ether. The crystals were collected, washed with ether and dried. A yield of 23.4 g. (99%) of the methiodide of II, m.p. 216–217°, was obtained.

Anal. Calcd. for $C_{20}H_{28}IN$: C, 58.70; H, 6.90; N, 3.42. Found: C, 58.80; H, 6.73; N, 3.32.

Reaction of the methiodide of II *with sodium amide in liquid ammonia.* To a suspension of 0.10 mole of sodium amide in 200 ml. of liquid ammonia was added 20.4 g. (0.05 mole) of the methiodide of amine II. The color remained a deep purple throughout the 1.5-hr. reaction period, after which the mixture was neutralized with excess ammonium chloride and the ammonia replaced by ether. After filtration of the mixture the ethereal filtrate was extracted with two 100-ml. portions of 2*N* hydrochloric acid. The ether solution was then dried over magnesium sulfate and evaporated. The residue was recrystallized once from methanol, yielding 3.31 g. (30%) of 2,4,6-trimethylstilbene (V), m.p. 55–55.5°, lit.,[23] m.p. 55–56°.

The acid extract from above was made strongly basic with solid sodium hydroxide, cooled and extracted with ether. The ethereal solution was dried and distilled yielding 4.32 g. (31%) of somewhat viscous 2-(2-mesitylethyl)benzyldimethylamine (VI), b.p. 153–158° at 0.75 mm. Redistillation gave a boiling range of 153–157° at 0.70 mm.

Anal. Calcd. for $C_{20}H_{27}N$: C, 85.35; H, 9.67; N, 4.98. Found: C, 85.49; H, 9.72; N, 5.09.

The picrate, after two recrystallizations from ethanol, melted at 165°.

Anal. Calcd. for $C_{26}H_{30}N_4O_7$: C, 61.16; H, 5.92; N, 10.98. Found: C, 61.24; H, 5.79; N, 10.99.

Independent synthesis of II. This amine was prepared by the general method of Stewart and Hauser[22] from 11.4 g. (0.0685 mole) of 2,4,6-trimethylbenzyl chloride, 10.35 g. (0.05 mole) of α-dimethylaminobenzyl *n*-butyl ether[22] and 1.82 g. (0.075 g.-atom) of magnesium. The yield of II after one recrystallization from hexane was 3.12 g. (23%), m.p. 63–64°. A mixed melting point with the product from the rearrangement was not depressed. The infrared spectra of the two samples of amine were superimposable.

Bis(2,4,6-trimethylbenzyl)dimethylammonium chloride (X). A mixture of 13.16 g. (0.074 mole) of 2,4,6-trimethylbenzyldimethylamine, 16.85 g. (0.10mole) of 2,4,6-trimethylbenzyl chloride and 100 ml. of acetonitrile was refluxed for 24 hr. Two volumes of ether were added to the cooled mixture to precipitate the product. The salt was collected, washed with ether, and dried. A yield of 23.2 g. (91%) of bis(2,4,6-trimethylbenzyl)dimethylammonium chloride, m.p. 202–203°, was obtained.

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(18) C. H. Hassall and A. E. Lippman, *J. Chem. Soc.*, **1953**, 1062.

(19) L. I. Smith and C. L. Moyle, *J. Am. Chem. Soc.*, **55**, 1680 (1933).

(20) F. Wenzel, *Monatsh.*, **35**, 961 (1914).

(21) An 83% yield was obtained in a 3-hr. reaction. Also a 3% yield of benzaldehyde and a 5% yield of dimesitylethane were obtained.

(22) A. T. Stewart and C. R. Hauser, *J. Am. Chem. Soc.*, **77**, 1098 (1955).

(23) R. C. Fuson, J. J. Denton, and C. E. Best, *J. Org. Chem.*, **8**, 64 (1943).

Anal. Calcd. for $C_{22}H_{32}ClN$: C, 76.37; H, 9.34; N, 4.05. Found: C, 76.38; H, 9.21; N, 3.98.

Rearrangement of X to form α-(2,4,6-trimethylbenzyl)-2,4,6-trimethylbenzyldimethylamine (XI). This rearrangement was carried out with 24.7 g. (0.0715 mole) of bis(2,4,6-trimethylbenzyl)-dimethylammonium chloride (X) and 0.2 mole of sodium amide in 300 ml. of liquid ammonia essentially as described for the rearrangement of I. The reaction period was 6 hr. The ether insoluble salts were triturated with 100 ml. of water acidified with hydrochloric acid. Removed from this mixture by filtration was 9.2 g. (37% recovery) of quaternary salt X, m.p. 196–197°, mixed m.p. 200–201°.

The neutral fraction was not steam distilled. After evaporation of the ether the solid residue was recrystallized from methanol yielding 0.05 g. (0.5%) of crudel, 2-dimesitylethane, m.p. 100–105°. Two more recrystallizations from methanol raised the melting point to 112–114°, mixed m.p. 114–115°, lit.,[20] m.p. 117–118°.

The mother liquor from the first recrystallization of the dimesitylethane was treated with 2,4-dinitrophenylhydrazine solution and a yield of 0.05 g. (0.2%) of 2,4,6-trimethylbenzaldehyde-2,4-dinitrophenylhydrazone was precipitated, which after one recrystallization from ethanol melted at 246–248°, mixed m.p. 249–250°, lit.,[24] m.p. 250–251°.

From the amine fraction was obtained 12.90 g. (58%) of crude amine, which after one recrystallization from methanol yielded 11.1 g. (50%) of pure α-(2,4,6-trimethylbenzyl)-2,4,6-trimethylbenzyldimethylamine (XI), m.p. 100.5–101°.

Anal. Calcd. for $C_{22}H_{31}N$: C, 85.38; H, 10.10; N, 4.53. Found: C, 85.42; H, 10.30; N, 4.37.

Reaction of the methiodide of XI *with sodium amide in liquid ammonia.* The methiodide of 6.08 g. (0.0195 mole) of amine XI was prepared by refluxing with excess methyl iodide in 100 ml. of acetonitrile for 8 hr. The salt was precipitated with ether. The yield of the crude, dry methiodide was 11.32 g. (70%).

This methiodide, 6.3 g. (0.014 mole), was added to 0.03 mole of sodium amide in 200 ml. of liquid ammonia. After 2 hr. the reaction was quenched with 1.6 g. (0.03 mole) of solid ammonium chloride and the ammonia replaced by ether. The mixture was filtered and the ethereal filtrate was evaporated on a steam bath. After the residue was heated on the steam bath for 0.5 hr. to thermally rearrange any *exo*-methyleneamine present, the residue was cooled, taken up in ether and filtered, and gaseous hydrogen chloride was bubbled through until no more amine hydrochloride precipitated. The mixture was filtered and evaporated, yielding after one recrystallization from a mixture of methanol and ethanol 1.9 g. (51%) of 1,2-dimesitylethylene (XIII), m.p. 131–132°, lit.,[25] m.p. 132–133°. A second recrystallization raised its melting point to 132–132.5°. Admixture with only 5% of 1,2-dimesitylethane, which would have been formed by acidic decomposition of *exo*-methyleneamine XIV, produced a melting point of 126–128°.

The solid amine hydrochloride was stirred with 50 ml. of 3*M* sodium hydroxide and 50 ml. of ether until all solid was dissolved. The ether layer was separated, dried, and evaporated, leaving 0.50 g. (11%) of crude amine, m.p. 60–63°. Three recrystallizations from methanol raised the m.p. to 68–69°. The structure of the amine is assumed to be 2,3-dimesitylpropyldimethylamine (XV).

Anal. Calcd. for $C_{23}H_{33}N$: C, 85.39; H, 10.28; N, 4.33. Found: C, 85.12; H, 9.77; N, 4.04.

Reduction of 1,2-dimesitylethylene (XIII) *to 1,2-dimesitylethane* (VII) *with sodium in liquid ammonia.* A 0.55-g. portion of 1,2-dimesitylethylene was dissolved in 30 ml. of anhydrous ether. A solution of 0.5 g. of sodium in 100 ml. of liquid ammonia was slowly dropped into the stirred solution of hydrocarbon until the blue color of the sodium remained for 10 seconds. The reaction mixture was then quickly treated with 1.0 g. of solid ammonium chloride, the ammonia replaced by ether and the mixture filtered. Evaporation of the filtrate and recrystallization of the residue from methanol yielded 0.50 g. (91%) of 1,2-dimesitylethane, m.p. 117–117.5°, mixed m.p. 117–117.5°, lit.,[22] m.p. 117–118°.

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[CONTRIBUTION FROM THE HOOKER CHEMICAL CORPORATION RESEARCH LABORATORIES]

A Study of the Acid and Base Hydrolysis of Bridged Ketones Derived from Diels-Alder Adducts of 1,2,3,4-Tetrachloro-5,5-dimethoxycyclopentadiene

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A series of new Diels-Alder adducts of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene have been prepared. The adducts derived from vinyl chloride, ethyl acrylate, ethylene, propylene, and cyclohexene yield the expected bicyclic ketones upon treatment with concentrated sulfuric acid. The 1,2-dichloroethene adduct with sulfuric acid yields pentachlorobenzene. A diene obtained by dehydrohalogenation of the 1,4-dichloro-2-butene adduct undergoes a hydrolytic acid cleavage with sulfuric acid to give 2,3,4-trichloro-5-methylphthalid. Treatment of the bicyclic ketones with alcoholic base results in hydrolytic cleavage of the carbonyl bridge and dehydrohalogenation of the bridge head halogens to yield chlorine containing aromatic acids. An intermediate 2,3,4-trichloro-4a,5,6,7,8,8a-hexahydronaphthoic acid was isolated from the alcoholic base treatment of the bicyclic ketone derived from the cyclohexene adduct.

The Diels-Alder adducts of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene with olefinic dienophiles yield bicyclic bridged ketals of the general structure indicated in Fig. 1. Many such adducts have been reported in the literature.[1,2]

The Diels-Alder adducts of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene prepared for this investigation are all new compounds. Physical properties and analysis of these adducts are listed in Table I.

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