ture was maintained below 10°. The precipitated potassium bromide was filtered and 100 cc. of dry ether was added to the filtrate. After the mixture had been cooled, the water-soluble precipitate XI (7.3 g., 80%) melted at 127–128° dec. after recrystallization from isopropyl alcohol.

Anal. Calcd. for $C_8H_{17}ONBr_2$: N, 4.62; (total) Br, 52.75; Br^-, 26.38; mol. wt., 303. Found: N, 4.56; (total) Br, 52.70; Br^-, 26.05; mol. wt., (water) 301.

A solution prepared from 19.2 g. of X′ and 30 cc. of water was made strongly alkaline with potassium carbonate and the precipitated oily base was extracted with ether. The extract was dried over magnesium sulfate and the solvent was removed at room temperature under reduced pressure. The water-insoluble oil, after about 12 hours, became semisolid and completely water soluble. The product XI′ turned crystalline when rubbed under acetone and melted at 104–106° after recrystallization from isopropyl alcohol–ether, yield 7.0 g.

Anal. Calcd. for $C_8H_{17}ONBr_2$: (total) Br, 52.75; Br^-, 26.38; mol. wt., 303. Found: (total) Br, 52.40; Br^-, 26.41; mol. wt. (water), 301.

Derivatives of the basic alcohols (Table I) were prepared by the following procedures.

Hydrobromides were obtained by addition of 37 cc. of 1.35 *M* alcoholic hydrogen bromide to 0.05 mole of the required alcohol. The solvent was removed under reduced pressure and the residue was rubbed under dry ether.

Methochlorides were formed when a mixture of 0.24 mole of the alcohol, 0.24 mole of methyl chloride and 200 cc. of chloroform was heated for 12 hours on a steam-bath. The solvent was removed and the residue was triturated with ether.

Methiodides were prepared from 0.025 mole of the alcohol, 0.25 mole of methyl iodide and 30 cc. of dry ether. After 2 days at room temperature, the precipitate was recrystallized.

In order to obtain the acetates, 0.60 mole of acetyl chloride was added (through a condenser), during a 30-minute period, to a solution of 0.30 mole of the alcohol in 75 cc. of chloroform at such a rate that the mixture just boiled. The chloroform was removed by distillation and the residue was dissolved in water. The aqueous solution was made alkaline with potassium carbonate, extracted with ether and the extract was dried with anhydrous potassium carbonate. The solution was then fractionated.

Acetate methochlorides were synthesized by heating a mixture of 0.12 mole of the acetate, 0.20 mole of methyl chloride and 200 cc. of chloroform in a pressure bottle for 12 hours on a steam-bath. The solvent was removed and the residue recrystallized. Compound 1d was obtained also by heating 3.9 g. of compound 1b and 18 g. of acetic anhydride at 100° for 8 hours. The reaction mixture was poured into dry ether and the oily precipitate was triturated with ether; m.p. 164–166°.

Compound 1e precipitated when 7.9 g. of 1c, 30.0 g. of benzyl chloride and 25 cc. of dry ether were refluxed for 12 hours.

Diphenylacetate hydrochlorides were obtained when a mixture of 0.05 mole of the alcohol, 0.05 mole of diphenylacetyl chloride and 50 cc. of reagent acetone was refluxed for 12 hours. After removal of the solvent, the ester salt was recrystallized.

A mixture of 14.5 g. of the required alcohol, 18.6 g. of *p*-nitrobenzoyl chloride and 50 cc. of reagent acetone was refluxed for 2 hours and the precipitated *p*-nitrobenzoate hydrochloride (4c) was filtered and recrystallized.

When 16.5 g. of the hydrochloride (4c) was hydrogenated under an initial pressure of 45 pounds in the presence of 100 cc. of absolute ethanol and 0.5 g. of platinum oxide catalyst, the *p*-aminobenzoate salt (4d) was obtained after filtration and removal of the ethanol.

The benzhydryl ether hydrochloride (8c) was obtained by refluxing a mixture of 7.1 g. of the alcohol, 12.3 g. of benzhydryl bromide and 25 cc. of pyridine for 5 hours. Water and then potassium carbonate were added, the mixture was extracted with ether and the extract was dried with anhydrous potassium carbonate. The ether and pyridine were removed by distillation and the residue was fractionated; b.p. 185–188° (3 mm.). When the base was dissolved in ether and the calculated amount of alcoholic hydrogen bromide was added, the crystalline hydrobromide precipitated.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Rearrangement of 2,4,6-Trimethylbenzyltrimethylammonium Ion by Sodium Amide to Form an *exo*-Methylenecyclohexadieneamine and its Reactions[1]

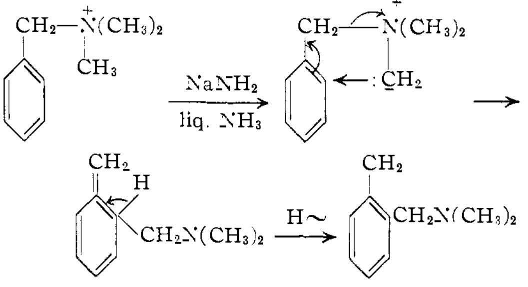
BY CHARLES R. HAUSER AND DONALD N. VAN EENAM[2]

RECEIVED MAY 22, 1957

The 2,4,6-trimethylbenzyltrimethylammonium ion was found to undergo with sodium amide in liquid ammonia the first phase of the *ortho* substitution rearrangement to give an *exo*-methylenecyclohexadieneamine. This alicyclic compound underwent thermal isomerization to form β-mesitylethyldimethylamine, and reacted with electrophilic and nucleophilic reagents to produce certain aromatic compounds and by-products. The latter reagents formed an intermediate alicyclic product. Mechanisms for these reactions are discussed. The *exo*-methyleneamine also was hydrogenated.

The *ortho* substitution rearrangement of benzyl type quaternary ammonium ions by sodium amide in liquid ammonia to form tertiary amines[3] has been assumed to involve the intermediate formation of not only a carbanion but also an *exo*-methylenecyclohexadieneamine. The latter intermediate undergoes a prototropic change resulting in the aromatic product. The reaction may be illustrated by the rearrangement of the benzyltrimethylammonium ion to *o*-methylbenzyldimethylamine (equation 1).[3,4]

Although this reaction would be difficult to stop at the *exo*-methylene stage, the corresponding reac-



(1)

tion of the 2,4,6-trimethylbenzyltrimethylammonium ion (I) was found in the present investigation[5]

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[1] Supported in part by the National Science Foundation.

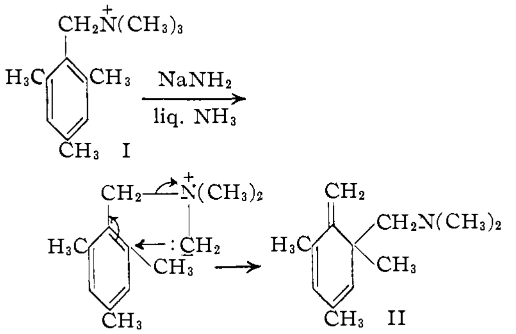
[2] Monsanto Chemical Co. Fellow, 1955–1956.

[3] S. W. Kantor and C. R. Hauser, THIS JOURNAL, **73**, 4122 (1951).

[4] The ionization of a methyl hydrogen shown in this equation may be preceded by that of the more reactive benzyl hydrogen; see ref. 3.

[5] For a preliminary report on this reaction see C. R. Hauser and D. N. Van Eenam, THIS JOURNAL, **78**, 5698 (1956).

to produce *exo*-methylenecyclohexadieneamine II which cannot undergo such a prototropic change. The conversion of the intermediate carbanion to this product may be considered to involve an SNi′ type of displacement (equation 2).



(2)

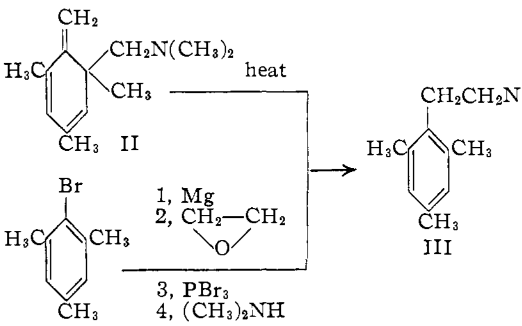
Calcd. λ_{max} 313 mμ
Found λ_{max} 313 mμ (log ε 3.8)

Because of its sensitivity to aqueous acids and heat, *exo*-methyleneamine II was isolated by rapid steam distillation from alkaline medium. This gave a 70% yield of an essentially pure product (see Experimental).

The polyene structure of this compound was established by an ultraviolet absorption spectrum which gave a single maximum at 313 mμ (Fig. 1, curve A). In fact, this value agrees with that calculated for structure II[6] of the basis of Woodward's rules.[7] No absorption maxima were observed in the region of 260–280 mμ, which is characteristic of aromatic compounds such as β-mesitylethyldimethylamine (Fig. 1, curve B).

exo-Methyleneamine II underwent several types of reaction that appear explicable only on the basis of structure II. These types include thermal isomerization and reactions with electrophilic and nucleophilic reagents as discussed below. In each of these interesting reactions the *exo*-methylene group of II is one of the reactive centers, and an aromatic system is regenerated directly or through another intermediate.

Thermal Isomerization of *exo*-Methyleneamine II.—On heating at 150° for one hour, this compound underwent isomerization to form β-mesitylethyldimethylamine (III, 83%), the structure of which was established by an independent synthesis from bromomesitylene (equation 3).



(3)

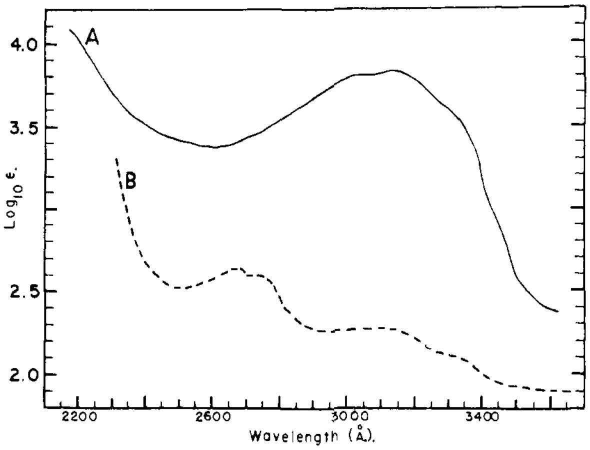


Fig. 1.—Ultraviolet absorption spectrum of 6-methylene-1,3,5-trimethyl-1-dimethylaminomethylcyclohexadiene-2,4 (curve A) (———) and β-mesitylethyldimethylamine (curve B) (---------) in 95% ethanol.

This isomerization occurred slowly even at relatively low temperatures. Actually, some 5–10% of aromatic product III was obtained when II was fractionated through a distilling column at 50° (see Experimental). In Table I are summarized the results of isomerization of II to III at various temperatures with and without solvent. In these experiments unreacted II was recovered as isodurene, which was produced on adding dilute hydrochloric acid (see next section).

TABLE I

ISOMERIZATION OF *exo*-METHYLENEAMINE II TO FORM III

Solvent	Temp., °C.	Time, hr.	Yield, %	Recov.,[a] %
None	150	1	83	..
Benzene	80	6	62	28
Ether	36	36	39	53
Ether	Room	720	48	37
Petr. ether	Room	720	32	59
None	Room	720	21	76

[a] Recovered as isodurene after treatment with acid.

It can be seen from Table I that the ease of isomerization is dependent not only on the temperature but apparently also on the solvent. Thus, at room temperature for the same period, more isomerization occurred in ethyl ether than in petroleum ether, and more in the latter solvent than in no solvent (other than liquid amine II itself). However, such an influence of solvent is not considered established.

The mechanism of conversion of II to III appears to involve a 1,3-shift of the dimethylaminomethyl group as indicated in IVa, although this electronic movement may lose its significance in passing to the four-carbon transition state represented in IVb. Because of the relatively low temperatures at which the isomerization occurs, the driving force seems to be expressed partly in lowering the energy of the transition state.[8]

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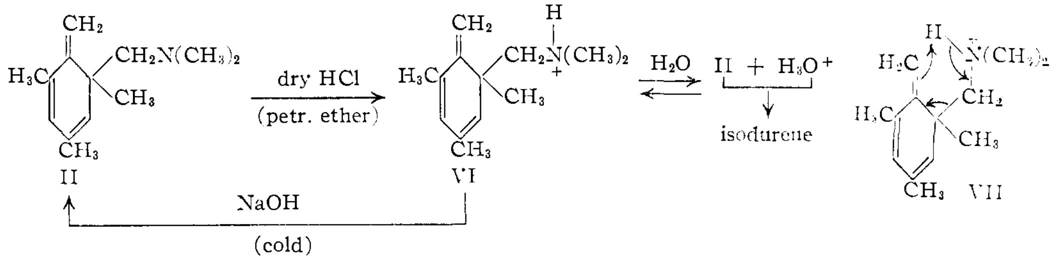
[6] The calculated value for the corresponding *p*-*exo*-methyleneamine derivative was 252 mμ, which is much lower than the value found.

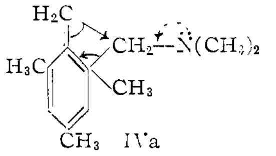
[7] See L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," third ed., Reinhold Publ. Corp., New York, N. Y., 1949, pp. 185–188.

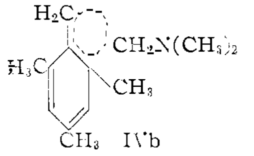
[8] Since all the bonds broken and formed are carbon-to-carbon, the significant free energy decrease evidently is furnished by the formation of the aromatic system. Also, the relief of steric strain around the quaternary carbon may be a contributing factor.

SCHEME A

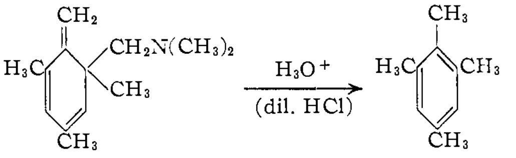


It should be mentioned that, although a number of 1,3-shifts are known, the transition states in at least most of them involve one or more atoms other than carbon. Moreover, they appear to require relatively high temperatures. For example, the isomerization of isopropenyl acetate to acetylacetone[9] and that of α-ethoxystyrene to n-butyrophenone[10] have been effected at 500 and 250–270°, respectively.

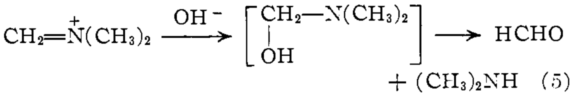

IVa


IVb

Reactions of *exo*-Methyleneamine II with Electrophilic Reagents.—This compound reacted rapidly with dilute hydrochloric acid at room temperatures or even at 0° to form isodurene (89%) and presumably dimethylmethylene iminium chloride,[11] which was hydrolyzed, by further treatment of the reaction mixture with dilute sodium hydroxide, to give formaldehyde and dimethylamine (equations 4 and 5, respectively). The two latter compounds were isolated as appropriate derivatives.

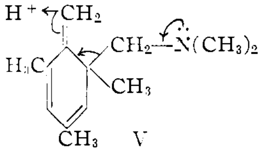


$$+ \; CH_2{=}\overset{+}{N}(CH_3)_2Cl^- \quad (4)$$



$$CH_2{=}\overset{+}{N}(CH_3)_2 \xrightarrow{OH^-} \left[\begin{array}{l}CH_2—N(CH_3)_2\\ |\\ OH\end{array}\right] \longrightarrow HCHO + (CH_3)_2NH \quad (5)$$

The mechanism of formation of the aromatic product is considered to involve the addition of a proton to the *exo*-methylene group of II accompanied by the simultaneous elimination of the dimethylmethylene iminium ion as indicated in V.

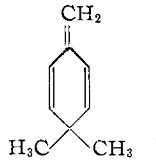

V

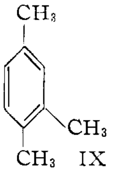
The proton may first add to the basic nitrogen of amine II to form cation VI, but, as might be expected from mechanism V, this ammonium type ion is relatively stable. Thus, saturation of a petroleum ether solution of amine II with dry hydrogen chloride precipitated the amine hydrochloride, from which the amine was largely recovered on adding this salt to cold alkali. On the other hand, the amine salt was converted rapidly to isodurene by cold water. This aromatization apparently involves the free amine and hydronium ion that are formed (in equilibrium) by an acid-base reaction between cation VI and water. These results are summarized in Scheme A.

It seemed possible that ammonium type ion VI was stable only because the salt was a crystalline solid, and that, in solution, the proton on the nitrogen was transferred intramolecularly to the *exo*-methylene carbon, accompanied by aromatization, as indicated in VII.

However, at least in glacial acetic acid, this intramolecular mechanism evidently does not operate, since the hydrochloride salt of amine II dissolves in this solvent at room temperatures without being converted immediately to isodurene. Thus, on neutralizing such solutions with alkali after one minute and thirty minutes, amine II was recovered in yields of 80 and 22%, respectively.[12] Even in 50% aqueous acetic acid, amine II was only slowly converted to isodurene. The fact that the ease of conversion of *exo*-methyleneamine II to isodurene is dependent not only on the strength of the acid but also on the basic strength of the solvent is further evidence for the intermolecular mechanism as indicated in V.

It should be mentioned that, although the present acid-catalyzed aromatization of amine II appears to be novel, several related reactions involving the addition of protons to *exo*-methylene groups are known. For example, alicyclic hydrocarbon VIII undergoes an acid-catalyzed rearrangement and aromatization to form IX.[13]


VIII


IX

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[9] See F. G. Young, F. C. Frostick, J. J. Sanderson and C. R. Hauser, THIS JOURNAL, **72**, 3635 (1950).

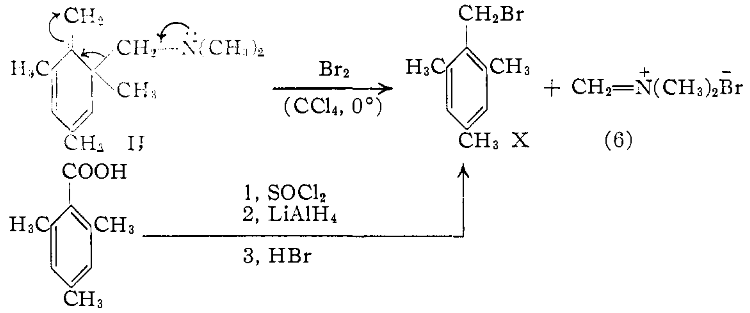
[10] W. M. Lauer and M. A. Spielman, *ibid.*, **55**, 4923 (1933).

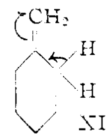
[11] This salt has been shown to be stable in acid but readily hydrolyzed by alkali; T. D. Stewart and W. E. Bradley, *ibid.*, **54**, 4172 (1932).

[12] The fact that isodurene is formed slowly in glacial acetic acid may be accounted for by an acid-base reaction between ammonium type ion VI and acetic acid (acting as the base) to give $(CH_3COOH_2)^+$, the proton of which reacts with amine II as indicated in V.

[13] K. von Auwers and K. Zeigler, *Ann.*, **425**, 217 (1921).

The reactions of *exo*-methyleneamine II with certain other electrophilic reagents also were studied.[14] Thus, II was converted by bromine in carbon tetrachloride at 0° to α^2-isoduryl bromide (X), the structure of which was established by an independent synthesis from mesitoic acid (equation 6).

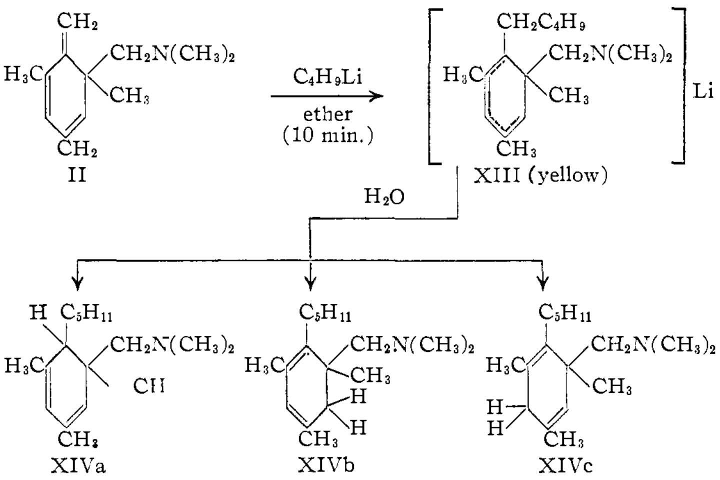

(6)


XI


XII

The yield of X from II was 85%, only one equivalent of bromine being used to avoid bromination of the aromatic ring. The mechanism of the reaction is considered to involve the addition of positive bromine or a polarized bromine molecule to the *exo*-methylene group of II accompanied by the elimination of dimethylmethylene iminium ion. This bromination is somewhat similar to the reaction of *exo*-methylene compound XI with chlorine to form mainly the allyl type chloride XII and hydrogen chloride observed by Arnold and Lee.[15] Incidentally bromine only added to the olefinic double bond of XI.[15]

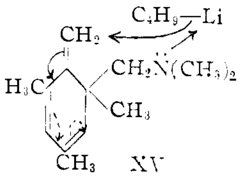
SCHEME B



Calcd. λ_{max} 267 mμ Calcd. λ_{max} 272 mμ Calcd. λ_{max} 252 mμ
Found λ_{max} 269 mμ (log ϵ 3.8)

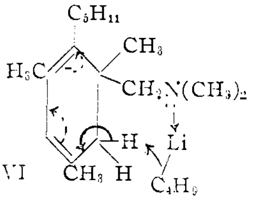
Reactions with *exo*-Methyleneamine II with Nucleophilic Reagents.—This compound reacted rapidly with butyllithium in ether at room temperatures to form a yellow lithium derivative (XIII) which, on hydrolysis, gave a *n*-amylcyclohexadieneamine product (Scheme B). On the basis of its ultraviolet absorption spectrum, this product may be regarded as a mixture of isomers XIVa and XIVb; little if any of isomer XIVc appeared to be present.

The mechanism of formation of yellow lithio derivative XIII evidently involves the nucleophilic attack of the potential butyl carbanion of butyllithium on the *exo*-methylene group of amine II.


XV

This reaction might occur within coördination complex XV in which the butyl group of the reagent should be activated as a carbanion, although an intermolecular process is also possible.

The *n*-amylcyclohexadieneamine product (XIVa and XIVb), obtained on hydrolysis of lithio derivative XIII (Scheme B), was reconverted rapidly to this yellow lithio derivative on treatment with butyllithium in ether. This acid-base reaction might occur within a coördination complex such as XVI, which would be formed from isomer XIVb, although an intermolecular process is possible. A similar intermediate complex could be formed with isomer XIVa.


XVI

Evidence that the reconversion of the *n*-amylcyclohexadieneamine product (XIVa and XIVb) to yellow lithio derivative XIII was essentially complete is the observation that approximately an equivalent of water was required to discharge the yellow color.[16] Also, carbonation of the yellow lithio derivative produced a good yield of a viscous

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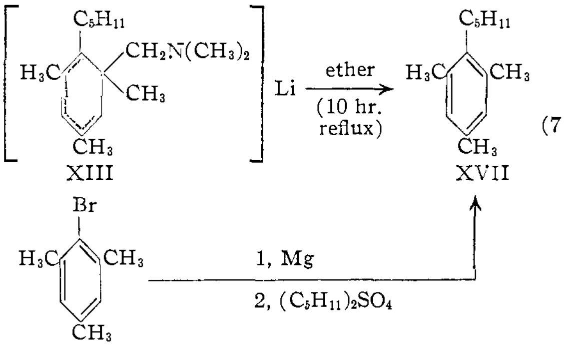
(14) Boron fluoride converted amine II in pentane to a relatively stable N-coördination complex which yielded isodurene only on treatment with hot water. Similarly acetic anhydride and acetyl chloride converted II in acetonitrile to relatively stable quaternary ammonium type salts.

(15) R. T. Arnold and W. W. Lee, THIS JOURNAL, **75**, 5396 (1953).

(16) The formation of the carbanion of lithio derivative XIII which has several resonance structures may furnish the driving force not only in this acid-base reaction (XVI), but also in the reaction of amine II with butyllithium (XV).

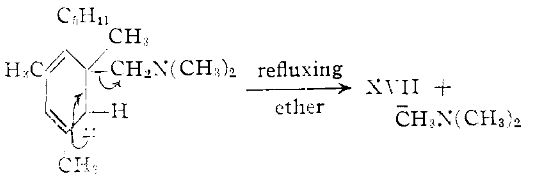
amino acid mixture which not only had a high decomposition temperature but was soluble in water and insoluble in ether. Similarly, lithio derivative XIII gave a viscous material with phenyl isocyanate. The formation of such products is not surprising since several isomers are possible.

Although lithio derivative XIII was relatively stable, it slowly decomposed in refluxing ether to form *n*-amylmesitylene (XVII). The structure of this aromatic hydrocarbon was established by an independent synthesis from bromomesitylene (equation 7).



(7)

The mechanism of formation of the *n*-amylmesitylene from lithio derivative XIII presumably involves the elimination of the carbanion of trimethylamine which was detected among the reaction products. This aromatization may be illustrated with one of the resonance structures of the carbanion of lithio derivative XIII, that of the conjugate base of acid XIVb (equation 8).



(8)

Similarly, *exo*-methyleneamine II reacted with butylsodium and butylmagnesium bromide in ether to form the corresponding organometallic derivatives of *n*-amylcyclohexadieneamines XIVa and XIVb which slowly decomposed to give *n*-amylmesitylene (XVII). In Table II are summarized the yields of products obtained on hydrolyzing the reaction mixtures after the color associated with the organometallic derivative appeared to be at a maximum. Also in this table are given the results with butyllithium. The general over-all reaction is illustrated in Scheme C.

SCHEME C

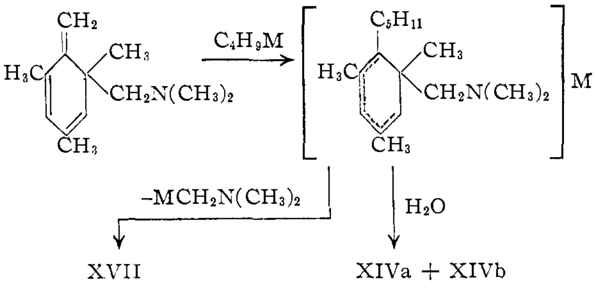


TABLE II

PRODUCTS XIVa-b AND XVII FROM *exo*-METHYLENEAMINE II AND BUTYL REAGENTS IN REFLUXING ETHER

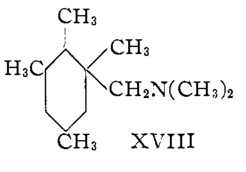
Butyl reagent	Ratio, reagent/II	Time, hr.	XIVa + XIVB Yield, %	XVII Yield, %
$C_4H_9Na^a$	2:1	2	72	17
$C_4H_9MgBr^b$	1:1	24	73	8
$C_4H_9Li^c$	2:1	0.33	73	9
$C_4H_9Li^c$	1:1	0.16	83	5
$C_4H_9Li^d$	2:1	10	17	67

[a] Yellow coloration of reaction mixture appeared after 15 minutes and intensified up to 2 hours. [b] Reaction mixture slowly became pale green after 3 hours and this color became more pronounced up to 24 hours. [c] Immediate deep yellow color appeared on the addition of II to the reagent. [d] In this experiment, the yellow lithio derivative was prepared from product XIVa + XIVb and butyllithium.

As can be seen from Table II the order of reactivity of the three butyl reagents with *exo*-methyleneamine II in ether was butyllithium > butylsodium > butylmagnesium bromide. The fact that butylsodium reacted more slowly than butyllithium may be ascribed at least partly to its insolubility in the ether.[17] Since both butyllithium and butylmagnesium bromide are soluble, the potential butyl carbanion of the former appears to be more available than that of the latter for attack on the *exo*-methlyene group of II.

Apparently only exceptionally strong bases such as the butyl carbanion of the organometallic compounds considered above react readily with *exo*-methylene amine II. Thus, the deep red color of the more weakly basic triphenylmethide ion was not discharged on standing with a twofold excess of II in ether at room temperature for two weeks. Neither does the amide ion react with II in liquid ammonia or ether. Indeed, II was prepared in the presence of this base in liquid ammonia.

Other Reactions of exo-Methyleneamine II.—In contrast to its reactivity toward certain electrophilic and nucleophilic reagents, this compound was found to be somewhat resistant to hydrogenation. Thus 90% of II was recovered after treatment with hydrogen over platinum (Adams catalyst) at room temperature and atmospheric pressure for one hour. However, II slowly underwent hydrogenation over Raney nickel catalyst at 55° under 4000 p.s.i.[18] On fractionation of the product there was obtained an amine which, by analysis, appeared to be a singly unsaturated compound rather than the expected saturated amine (XVIII).[19] Also, β-mesitylethyldimethylamine (III), which is the thermal isomerization product of II, was obtained as a minor product.



XVIII

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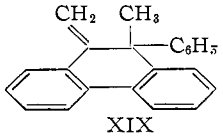
[17] The possible reaction of the butylsodium with the ether (β-elimination) need not be considered since an excess of the reagent was employed.

[18] We are indebted to the Eli Lilly Company (Dr. Nelson Easton and Mr. W. Scanlon) for carrying out this experiment.

[19] Only the nitrogen value was satisfactory for this amine.

The high degree of resistance of *exo*-methyleneamine II to hydrogenation suggests that the compound, which has polyalkyl substitution on the alicyclic ring, is adsorbed on the surface of the catalyst only with difficulty. This is in marked contrast to the relatively facile catalytic hydrogenation of *exo*-methylene compound XIX[20] and certain steroids where fused rings afford the molecular planarity and rigidity required for ready adsorption.



XIX

Attempts to effect reduction of *exo*-methyleneamine II with lithium aluminum hydride in refluxing ether (36 hours), and of its methiodide with 5% sodium amalgam and water (Emde method) were unsuccessful. In the former experiment some (36%) isomerization of II occurred to form β-mesitylethyldimethylamine (III).

exo-Methyleneamine II appeared to react with maleic anhydride in ether at room temperature, but only a small amount of material that might have been the Diels–Alder adduct was obtained after two months. The somewhat similar 1,1,3,5-tetramethylcyclohexadiene-3,5 has previously[21] been observed to give an adduct with maleic anhydride at approximately 200° but this relatively high temperature did not seem feasible with *exo*-methyleneamine II because of its tendency to isomerize.

Experimental[22]

2,4,6-Trimethylbenzyltrimethylammonium Chloride (I).—To a solution of 94.0 g. (0.56 mole) of α^2-isoduryl chloride, b.p. 124–126° at 20 mm., m.p. 36–37° (reported[23] b.p. 121–123° at 19 mm., m.p. 37°), in 200 ml. of absolute methanol was added with swirling 66 g. (1.12 moles) of liquefied anhydrous trimethylamine during 30 minutes. The flask was immersed in an ice-bath occasionally to minimize loss of trimethylamine. After standing at room temperature for 1 hour, 1 liter of anhydrous ether was added slowly to precipitate the quaternary ammonium chloride (I), which was collected on a funnel, washed with ether, and dried *in vacuo* in a desiccator. The somewhat hygroscopic salt melted at 219–220°, yield 98%. After one recrystallization from acetonitrile–ether it melted at 220–221°. Its picrate, after three recrystallizations from water, melted at 172–172.5°.

Anal. Calcd. for $C_{19}H_{24}N_4O_7$: C, 54.28; H, 5.75; N, 13.33. Found: C, 54.28; H, 5.79; N, 13.16.

Rearrangement of I to 6-Methylene-1,3,5-trimethyl-1-dimethylaminomethylcyclohexadiene-2,4 (II).—To a rapidly stirred suspension of 0.45 mole of sodium amide in 500 ml. of liquid ammonia in a 1-l. three-necked flask equipped with a Dry Ice reflux condenser and sealed stirrer was added during 5–10 minutes 34.2 g. (0.15 mole)[24] of finely powdered quaternary ammonium chloride I. The salt was kept dry by adding it from a 250-ml. erlenmeyer flask connected to the third neck of the reaction flask through Gooch tubing. The resulting light gray reaction mixture was stirred for approximately 2 hours,[25] and 16.5 g. (0.31 mole) of ammonium chloride was added (to destroy excess amide). Reagent grade ether (250 ml.) was added, and the liquid ammonia removed on the steam-bath. As soon as the ether began to reflux in the cold condenser the reaction mixture was cooled, and 50 ml. of 5 *N* sodium hydroxide solution was added with swirling. The resulting mixture was rapidly steam distilled[26] and the distillate (approximately 1 liter), after saturation with solid sodium carbonate, was extracted twice with 250-ml. portions of reagent grade ether. The combined ether extracts were washed with water and dried over anhydrous magnesium sulfate. Most of the solvent was distilled carefully on the steam-bath, the last traces being removed *in vacuo*, keeping the temperature near 35°. There was obtained 20.1 g. (70%) of essentially pure *exo*-methyleneamine II, $n^{25}\text{D}$ 1.5110, which was employed in some of the experiments described below. The product had a camphoric odor. A gummy residue (8.0 g., approximately 25%) was recovered from the steam distillation flask.

Analytically pure *exo*-methyleneamine was obtained by careful distillation of the above product (20.1 g.) through a 40-cm. Podbielniak type column at the lowest feasible pressure. There was obtained, after a trace of forerun (apparently isodurene), 13.6 g. (47%, based on the quaternary ammonium salt) of *exo*-methyleneamine II, b.p. 50–51° at 0.4 mm., $n^{25}\text{D}$ 1.5111.

Anal. Calcd. for $C_{13}H_{21}N$: C, 81.62; H, 11.07; N, 7.31. Found: C, 81.81; H, 10.93; N, 7.15. Ultraviolet absorption spectrum, calcd.[7] λ_{max} 313 mμ. Found λ_{max} 313 mμ (log ϵ 3.8).

Also there was obtained from the above distillation 2.0 g. (7%) of the thermal isomerization product, aromatic amine III, b.p. 73–74° at 0.4 mm., and 4.3 g. (15%) of polymeric residue.

exo-Methyleneamine II formed a quaternary ammonium iodide, m.p. 153–154° dec., with methyl iodide in acetonitrile, which partially decomposed on standing.

In an alternative method of work-up, 600 ml. of reagent grade ether was added to the reaction mixture (after prior addition of ammonium chloride), the liquid ammonia evaporated, and the ether suspension filtered. Most of the solvent was removed from the ethereal solution and the product isolated by steam distillation and worked-up as described above.

Thermal Isomerization of II to Form β-Mesitylethyldimethylamine (III).—An 11.5-g. (0.06 mole) sample of *exo*-methyleneamine II, b.p. 50–51° at 0.4 mm., was placed in a 100-ml. round-bottomed flask equipped with a reflux condenser, and the flask immersed in a Wood's metal-bath at 150° (electrically controlled) for one hour. The pale yellow product was distilled *in vacuo* to give 9.5 g. (83%) of colorless β-mesitylethyldimethylamine (III), b.p. 111.5–112° at 5 mm., $n^{25}\text{D}$ 1.5088.

Anal. Calcd. for $C_{13}H_{21}N$: C, 81.62; H, 11.07; N, 7.31. Found: C, 81.56; H, 10.96; N, 7.18.

The picrate, recrystallized three times from 95% ethanol, melted at 169.5–170.5°.

Anal. Calcd. for $C_{19}H_{24}N_4O_7$: C, 54.28; H, 5.75; N, 13.33. Found: C, 54.28; H, 5.67; N, 13.16.

The thermal isomerization of pure *exo*-methyleneamine II, b.p. 50–51° at 0.4 mm., was also effected at other temperatures with and without solvent. The results are summarized in Table I. In the experiments where solvent was employed, II was added to 100 ml. of sodium-dried solvent at the desired temperature for the specified time. The reactions at room temperature were run in tightly stoppered amber-colored bottles in the dark. The reaction mixtures

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[20] C. K. Bradsher, L. Rapaport and P. Anderson, THIS JOURNAL, **68**, 2153 (1946).

[21] J. Schmitt, *Ann.*, **547**, 256 (1941).

[22] 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.

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

[24] When the reaction was carried out on a larger scale (0.3 mole) the yield of II was somewhat lowered and relatively more of the thermal isomerization product III was obtained.

[25] In a 45-minute run employing the three to one ratio of amide to chloride I, and also in a three-hour run with a two to one ratio of the reactants, some 15–20% of unreacted chloride was recovered. This was isolated by extracting the solid salts of the reaction mixture with hot acetonitrile followed by precipitation with dry ether.

[26] This removed *exo*-methyleneamine II from polymeric material. In a preliminary experiment in which the crude product was directly distilled *in vacuo* at 5 mm., most of II underwent thermal isomerization to form aromatic amine III (58%).

were worked-up by adding 200 ml. of 6 *N* hydrochloric acid which converted unreacted II to isodurene. This hydrocarbon, b.p. 86–87° at 18 mm., $n^{25}\text{D}$ 1.5108, and the aromatic amine III, b.p. 111.5–112.5°, $n^{25}\text{D}$ 1.5089, were separated and isolated.

Independent Synthesis of β-Mesitylethyldimethylamine (III).—This amine was prepared in three steps, the first two of which were adaptations of the method of Speer and Hill[27] for the synthesis of substituted phenethyl alcohols and bromides.

To a cold, stirred solution of the Grignard reagent prepared from 39.8 g. (0.20 mole) of bromomesitylene and 5.1 g. (0.21 mole) of magnesium turnings in 150 ml. of ether was added during 15 minutes 17.6 g. (0.40 mole) of ethylene oxide in 50 ml. of dry benzene. After standing overnight at room temperature the reaction mixture was hydrolyzed with dilute acid and worked up to give 19.7 g. (60%) of β-mesitylethanol, b.p. 150–152° at 15 mm., m.p. 77–78° (reported[28] b.p. 145° at 17 mm., m.p. 79°).

To 19.7 g. (0.12 mole) of this alcohol in 50 ml. of benzene was added 27.0 g. (0.10 mole) of phosphorus tribromide in 100 ml. of benzene to give, after crystallization from absolute methanol, 19.8 g. (73%) of α^2-isoduryl bromide, m.p. 73.5–74° (reported[28] m.p. 74°).

To a solution of 19.8 g. (0.087 mole) of the bromide in 100 ml. of absolute methanol contained in a 300-ml. amber-colored screw cap bottle was added with shaking 40 g. (0.9 mole) of liquefied anhydrous dimethylamine. The cap was screwed on tightly and the mixture was allowed to stand in the dark at room temperature for 2 months. The solvent and excess dimethylamine were removed on the steam-bath, and the dark colored residue treated with excess 50% sodium hydroxide. The resulting oil was taken up in ether, and the solution extracted twice with 100-ml. portions of 6 *N* hydrochloric acid. The acid extract was again made alkaline with 50% sodium hydroxide, and the liberated amine was distilled *in vacuo* to give 12.1 g. (73%) of β-mesitylethyldimethylamine (III), b.p. 111–112.5° at 5 mm., $n^{25}\text{D}$ 1.5089. The picrate, recrystallized from 95% ethanol, melted at 170.5–171.5°. A mixed melting point with the picrate of the tertiary amine obtained from the thermal isomerization of II was the same.

Reactions of *exo*-Methyleneamine II with Acids to Form Isodurene. A. With Dilute Hydrochloric Acid.—To 19.1 g. (0.10 mole) of *exo*-methyleneamine II was added all at once with stirring 250 ml. of cold 6 *N* hydrochloric acid. The amine dissolved immediately with slight warming, and the solution became turbid within a few seconds. After standing for 5 minutes (when an oily layer had separated on the surface) the mixture was extracted with ether. The ether extract was dried and the solvent removed. The residue was distilled to give 12.0 g. (89%) of colorless isodurene, b.p. 85–86° at 18 mm., $n^{25}\text{D}$ 1.5108 (reported[29] b.p. 84.6–84.7° at 17 mm., $n^{25}\text{D}$ 1.5107). The dinitro derivative, after two recrystallizations from 95% ethanol, melted at 178–179.5° (reported[30] 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°.

The aqueous layer from the reaction mixture, containing dimethylmethylene iminium chloride, was boiled for 5 minutes to remove traces of ether and isodurene, cooled to 0°, and made alkaline (*p*H 9–10) with 50% sodium hydroxide. Formaldehyde and dimethylamine were isolated and identified from the resulting solution as described below.

Air was bubbled for 15 minutes through one of these solutions and the volatilized formaldehyde passed into a hot solution of 2,4-dinitrophenylhydrazine reagent to precipitate, on cooling, formaldehyde 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 164–165° (reported[31] m.p. 166°).

The dimethylamine was precipitated from the second solution as N,N-dimethylphenylthiourea by the addition of 13.0 g. (0.10 mole) of phenyl isothiocyanate with shaking. This derivative, after two recrystallizations from a minimum of refluxing ethanol, was obtained in 85% yield; melting and mixed melting point 134–135° (reported[32] m.p. 135°).

B. **With Hydrogen Chloride and Acetic Acid.**—Into a solution of 9.6 g. (0.05 mole) of *exo*-methyleneamine II in 100 ml. of sodium-dried petroleum ether (b.p. 30–60°) contained in a 500-ml. round-bottomed flask equipped with a calcium chloride drying tube was rapidly bubbled with swirling an excess of dry hydrogen chloride. The powdery salt, *exo*-methyleneamine hydrochloride (VI), which immediately precipitated in nearly quantitative yield, was freed from solvent by evaporation *in vacuo* on a water-bath maintained at 70°. This salt was added slowly to a rapidly stirred solution of a large excess of cold, 20% sodium hydroxide, and the resultant mixture extracted with ether, washed with water, dried over magnesium sulfate, and the solvent removed *in vacuo*. Methyl iodide (14.2 g., 0.10 mole) in a minimum of dry methanol was added to the residue, and the quaternary ammonium iodide of *exo*-methyleneamine II (14.4 g., 86% based on II), which precipitated on adding dry ether, was collected on a funnel and dried *in vacuo*. It melted at 153–154° dec., and did not depress the melting point of an authentic sample of this compound. From the filtrate of the quaternary ammonium salt was isolated, on careful distillation of the solvent, 0.7 g. (10%) of crude isodurene.

The preparation of *exo*-methyleneamine hydrochloride (VI) was repeated, and this salt was added to cold water to produce rapidly 5.9 g. (88%) of isodurene, b.p. 85–86° at 18 mm.

The preparation of VI was again repeated, and the salt was dissolved in 50 ml. of glacial acetic acid at room temperature. After 1 minute the solution was poured slowly onto excess cold 50% sodium hydroxide solution with stirring to give (on working-up as described above) 13.4 g. (80%) of *exo*-methyleneamine methiodide, m.p. and mixed m.p. 153–154° dec., and 1.0 g. (15%) of isodurene, b.p. 85–86° at 18 mm. In a similar experiment, permitted to run for 30 minutes (accompanied by a spontaneous gradual warming to 35–40°), there was isolated 3.6 g. (22%) of quaternary ammonium iodide and 5.0 g. (80%) of isodurene.

To 9.6 g. (0.05 mole) of *exo*-methyleneamine II was added with stirring 50 ml. of glacial acetic acid. The reaction mixture, which warmed considerably, was cooled to room temperature and allowed to stand for 1 hour. It was worked up as described above to give 15.1 g. (91%) of *exo*-methyleneamine methiodide, m.p. and mixed m.p. 153–154° dec., and 0.4 g. (6%) of crude isodurene.

Reaction of *exo*-Methyleneamine II with Bromine to Form α^2-Isoduryl Bromide (X).—To a stirred, ice-cooled solution of *exo*-methyleneamine II (19.1 g., 0.10 mole) in 200 ml. of dry carbon tetrachloride in a 1-l. three-necked flask fitted with a sealed stirrer, condenser and dropping funnel, was added dropwise over 30 minutes a solution of 19.2 g. (0.12 mole) of anhydrous bromine in 200 ml. of carbon tetrachloride. The reagent was added at such a rate that the bromine color was discharged between drops, a cream-colored precipitate being produced. The stirring was continued for one hour as the reaction mixture was allowed to warm to room temperature. After filtration, the solvent was distilled *in vacuo* and the residue, m.p. 47–49°, was crystallized once from petroleum ether (b.p. 30–60°) (cooled to −78°) to give 18.2 g. (85%) of α^2-isoduryl bromide (X), m.p. 50–51° (reported[33] m.p. 52°).

The mushy solid obtained by filtration consisted mainly of dimethylmethylene iminium bromide, which was hydrolyzed to formaldehyde and dimethylamine on treatment with a solution of sodium hydroxide.

Independent Synthesis of Bromide X.—This compound was prepared in an over-all yield of 87% from mesitoic acid. A solution of 45.7 g. (0.25 mole) of mesitoyl chloride (prepared in 98% yield from mesitoic acid, m.p. 151–153°) in 500 ml. of absolute ether was added dropwise to a stirred slurry of 9.5 g. (0.25 mole) of lithium aluminum hydride in 700 ml. of absolute ether to give, after standing overnight followed by hydrolysis, 37.1 g. (99%) of α^2-isoduryl alcohol (as white needles), m.p. 86.5–87.5° (reported[33] m.p. 88–89°).

A mixture of 20.0 g. (0.133 mole) of this alcohol and 250 g. (150 ml., 1.5 moles) of 48% hydrobromic acid was heated

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[27] J. H. Speer and A. J. Hill, *J. Org. Chem.*, **2**, 139 (1937).

[28] J. Sordes, *Compt. rend.*, **195**, 247 (1932).

[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] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," fourth ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 283.

[32] R. L. Shriner and R. C. Fuson, *ibid.*, p. 288.

[33] P. Carré, *Compt. rend.*, **151**, 149 (1910).

on the steam-bath for 4 hours with vigorous mechanical stirring. The crude bromide, which solidified on cooling, was collected on a funnel, washed with cold water, and crystallized from petroleum ether (b.p. 30–60°) (cooled to −78°) to give 25.6 g. (90%) of α^2-isoduryl bromide, m.p. 49.5–50.5°. This melting point was not depressed on admixture with the bromide prepared from *exo*-methyleneamine II and bromine.

Reaction of *exo*-Methyleneamine II with Butyllithium to Form 6-*n*-Amyl-1,3,5-trimethyl-1-dimethylaminomethylcyclohexadienes XIVa and XIVb.—A solution of butyllithium was prepared from 2.1 g. (0.30 g. atom) of lithium ribbon and 19.3 g. (0.133 mole) of *n*-butyl bromide in 250 ml. of ether in a 500-ml. 3-necked flask equipped with sealed stirrer, condenser and dropping funnel. To this vigorously stirred solution was rapidly added 19.1 g. (0.10 mole) of *exo*-methyleneamine II in 100 ml. of ether. An instantaneous, mildly exothermic reaction occurred with the formation of the bright yellow lithio derivative XIII. After stirring at room temperature for 10 minutes, the reaction mixture was cooled to 0° while cold water (100 ml.) was added dropwise to hydrolyze the organolithium compound (color destroyed after the addition of approximately 2 ml. of water). The ethereal layer was extracted with dilute acid, and the acid extract made alkaline with sodium hydroxide. The oily mixture was extracted with ether, washed with water, dried over magnesium sulfate, and the solvent evaporated. The residue was distilled slowly to give 20.8 g. (83%) of colorless *n*-amylcyclohexadieneamines (XIVa-b), b.p. 85–86° at 0.3 mm., $n^{25}D$ 1.4820.

Anal. Calcd. for $C_{17}H_{31}N$: C, 81.85; H, 12.53; N, 5.62. Found: C, 81.85; H, 12.35; N, 5.62; ultraviolet absorption spectrum, calcd.[7] λ_{max} 267–272 mμ; found: λ_{max} 269 mμ (log ϵ 3.8).

The picrate, after several crystallizations from 95% ethanol, melted at 140–141°.

Anal. Calcd. for $C_{23}H_{34}N_4O_7$: C, 57.72; H, 7.16; N, 11.71. Found: C, 58.03; H, 7.30; N, 11.58.

The ether extract (containing neutral products) was worked up to give 1.0 g. (5%) of crude *n*-amylmesitylene, $n^{25}D$ 1.4978.

Reconversion of *n*-Amylcyclohexadieneamines XIVa-b to Form Lithiocyclohexadienyl XIII and its Reactions. A. Carbonation.—A solution of 24.9 g. (0.10 mole) of *n*-amylcyclohexadieneamines XIVa-b in 100 ml. of ether was rapidly added to a stirred solution of butyllithium (prepared from 0.30 g. atom of lithium ribbon and 0.133 mole of *n*-butyl bromide) to produce immediately yellow lithio derivative XIII. This was poured onto 50 g. of Dry Ice consisting of small chunks, the color immediately fading. After the Dry Ice had evaporated, the mixture was shaken with 200 ml. of 25% sodium hydroxide and the two layers separated. The aqueous layer, containing amino acid, was acidified to a *p*H of 5. A viscous oil gradually formed above the aqueous salt solution amounting to 25 g. (approximately 85% yield, based on XIVa-b). It was soluble in water, alcohol and acetone, and almost completely insoluble in ether. Attempts to induce crystallization were unsuccessful. At temperatures approximating 300° trimethylamine was evolved, with the formation of a large amount of resinous material along with a trace of what appeared to be *n*-amylmesitylene.

B. **Reaction with Phenyl Isocyanate.**—*n*-Amylcyclohexadieneamine product XIVa-b (12.5 g., 0.05 mole) was reconverted to yellow lithio derivative XIII by means of butyllithium prepared from 0.15 g. atom of lithium and 0.067 mole of *n*-butyl bromide 200 ml. of ether. To this solution was added with stirring 5.4 g. (0.045 mole) of phenyl isocyanate in 25 ml. of ether. The yellow color of XIII abruptly changed to bright red-brown as the first few drops of phenyl isocyanate were added. After stirring for 10 minutes at room temperature, the reaction mixture was hydrolyzed with 100 ml. of cold water (color faded). The ethereal layer, on evaporation of the solvent, gave 15.5 g. (approximately 84% based on XIVa-b) of a viscous liquid (apparently an aminoanilide) which failed to crystallize.

C. **Thermal Decomposition to Form *n*-Amylmesitylene (XVII).**—The yellow lithio derivative XIII, prepared from 5.8 g. (0.84 g. atom) of lithium, 54.8 g. (0.40 mole) of *n*-butyl bromide and 33.0 g. (0.13 mole) of *n*-amylcyclohexadieneamines XIVa-b in 300 ml. of ether, was stirred and refluxed for 10 hours. Water (250 ml.) was cautiously added to the cooled reaction mixture (yellow color discharged), and the aqueous layer (smelling strongly of trimethylamine) was discarded. The ethereal layer was extracted with dilute acid to remove unreacted XIVa-b, 5.6 g. (17%) of which was recovered (b.p. 85–87° at 0.3 mm., $n^{25}D$ 1.4823). After washing with water, the ethereal solution was dried and the solvent evaporated. The residue was distilled to give 16.6 g. (67%) of *n*-amylmesitylene (XVII), b.p. 103–103.5° at 3 mm., $n^{25}D$ 1.4982, leaving 10.9 g. of residue.

Anal. Calcd. for $C_{14}H_{22}$: C, 88.35; H, 11.65. Found: C, 88.60; H, 11.44.

The sulfonamide of this hydrocarbon was prepared by a general procedure,[34] and crystallized once from ethanol-water (after prior treatment with Norite) and twice from hexane containing 2% of benzene. It melted at 103–104°.

Anal. Calcd. for $C_{14}H_{23}O_2SN$: C, 62.41; H, 8.60; N, 5.21. Found: C, 62.25; H, 8.64; N, 5.30.

Independent Synthesis of *n*-Amylmesitylene (XVII).—Di-*n*-amyl sulfate was prepared in 85% yield from di-*n*-amyl sulfite, b.p. 111–112° at 5 mm. (reported[35] b.p. 11.5° at 5 mm.) essentially as described by Suter and Gerhart[36] for the preparation of the corresponding di-*n*-butyl ester. The product distilled at 114–116° at 1 mm., $n^{25}D$ 1.4280 (reported[37] b.p. 117° at 2.5 mm., $n^{25}D$ 1.4270).

A solution of 152.5 g. (0.64 mole) of di-*n*-amyl sulfate in 100 ml. of ether was added dropwise during 45 minutes to a cooled (10°), stirred solution of mesitylmagnesium bromide prepared *via* the entrainment method from 8.1 g. (0.33 g. atom) of magnesium turnings, 31.9 g. (0.16 mole) of bromomesitylene and 17.6 g. (0.16 mole) of ethyl bromide in 200 ml. of ether.[38] The pasty reaction mixture was stirred for an additional 18 hours at room temperature and then hydrolyzed by the dropwise addition of 300 ml. of cold 6 *N* hydrochloric acid. The solvent was evaporated from the ether layer, and the residue added to a refluxing solution of sodium ethoxide (1 mole) in 350 ml. of ethanol. After 30 minutes the mixture was cooled and neutralized with dilute acid, and the product taken up in ether. Evaporation of the solvent followed by distillation *in vacuo* afforded 17.2 g. (57%) of *n*-amylmesitylene (XVII), b.p. 102–103° at 3 mm., $n^{25}D$ 1.4980. The identity of this and the product arising from the decomposition of XIII was established by a mixed melting point determination.

Reaction of *exo*-Methyleneamine II with Other Organobutyl Reagents.—In Table II are summarized the results obtained with butylsodium, butylmagnesium bromide and butyllithium with *exo*-methyleneamine II. The reactions of the first two reagents are described below.

A. **With Butylsodium.**—A suspension of butylsodium was prepared[39] from 11.5 g. (0.50 g. atom) of powdered sodium and 23.2 g. (0.25 mole) of *n*-butyl chloride in 100 ml. of ether in a 500-ml. three-necked flask fitted with a sealed stirrer, condenser and dropping funnel. After stirring for 2 hours at 0°, 19.1 g. (0.10 mole) of *exo*-methyleneamine II in 150 ml. of ether was added to this mixture during 5 minutes (became yellow within 15 minutes). After 2 hours, 50 ml. of ethanol was cautiously added (to destroy unreacted sodium), followed by water, and the ethereal layer extracted with 6 *N* hydrochloric acid. There was obtained 17.9 g. (72%) of *n*-amylcyclohexadieneamine product XIVa-b, b.p. 85–86° at 0.3 mm., $n^{25}D$ 1.4821, and 3.2 g. (17%) of *n*-amylmesitylene (XVII), b.p. 104–105° at 3 mm., $n^{25}D$ 1.4985. There was a combined undistillable residue of 2.4 g.

B. **With Butylmagnesium Bromide.**—To a stirred solution of butylmagnesium bromide prepared from 3.9 g. (0.16 g. atom) of magnesium turnings and 20.6 g. (0.15 mole) of *n*-butyl bromide in 100 ml. of ether was added 19.1 g. (0.10 mole) of II in 150 ml. of ether (mixture became pale green within 3 hours). After 24 hours the resulting solution was hydrolyzed with dilute hydrochloric acid, and the layers separated. The aqueous acid layer, on neutralization, gave 18.3 g. (73%) of *n*-amylcyclohexadieneamines XIVa-b, b.p. 85–87° at 0.3 mm., $n^{25}D$ 1.4824. The ethereal solution of

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(34) R. L. Shriner and R. C. Fuson, ref. 31, pp. 246–247.

(35) A. I. Vogel and D. M. Cowan, *J. Chem. Soc.*, 16 (1943).

(36) C. M. Suter and H. L. Gerhart, *Org. Syntheses*, **21**, 27 (1939).

(37) C. Barkenbus and J. J. Owen, THIS JOURNAL, **56**, 1204 (1934).

(38) This is a modification of the method of L. I. Smith, *Org. Syntheses*, **11**, 66 (1931).

(39) R. Paul and S. Tchelitcheff, *Compt. rend.*, **230**, 1473 (1950).

neutral products afforded, on distillation *in vacuo*, 2.6 g. (19%) of isodurene,[40] 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., $n^{25}D$ 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.[18] 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., $n^{25}D$ 1.4828.

Anal. Calcd.[41] for $C_{13}H_{25}N$: 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.[41] for $C_{19}H_{28}N_4O_7$: 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°, $n^{25}D$ 1.5076, consisted mainly of β-mesitylethyldimethylamine (III). A mixed melting point of the picrate of this product with an authentic sample of the picrate of III was not depressed.

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[40] This product arose from the acidic decomposition of unreacted starting material.

[41] These calculated values are those for the singly unsaturated amine and its picrate. The corresponding data for the fully saturated amine are $C_{13}H_{27}N$: C, 79.11; H, 13.70; N, 7.10; and those for the picrate, $C_{19}H_{30}N_4O_7$: 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[1]

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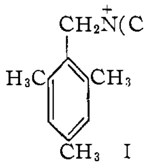
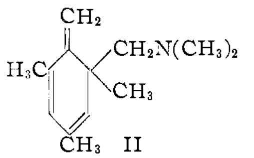
The 2,4,6-triisopropylbenzyltrimethylammonium ion was rearranged by sodium amide in liquid ammonia to form an *exo*-methylenecyclohexadieneamine that was rearranged thermally to a β-arylethylamine. The *exo*-methyleneamine was decomposed by acid to form an aromatic hydrocarbon and an aromatic amine, 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.

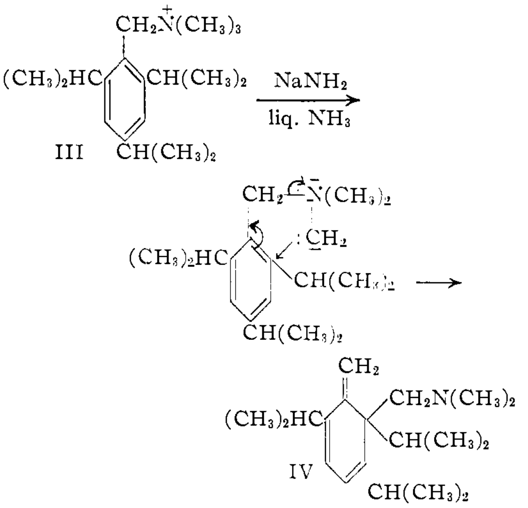
A previous paper[3] described the rearrangement of the 2,4,6-trimethylbenzyltrimethylammonium ion (I) by sodium amide in liquid ammonia to form *exo*-methyleneamine II and the thermal isomerization and reactions with electrophilic and nucleophilic reagents of this interesting alicyclic product.


I


II

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,[4] and its ultraviolet absorption spectrum agreed satisfactorily with that calculated[5] 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 accompanied 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.



(1)

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

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[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.