

TABLE IV

Fraction	B.p., °C. (8 mm.)	Wt., g.	n_D^{25}
1	71-94	0.9	1.5408
2	94-96	1.4	1.5482
3	96-98	11.5	
4	98-99	7.3	1.5511
5	98.5	15.8	1.5515

tion 4 indicated that this material was largely *cis*-1,2-dibromocyclohexane contaminated with 1,3-dibromocyclohexane and *trans*-1,4-dibromocyclohexane. The bands at 14.65 μ (strong) and 11.9 μ (medium) which are present in the spectrum of *trans*-1,2-dibromocyclohexane but not in the spectra of the other dibromocyclohexanes were conspicuously absent in the spectrum of fraction 4 (and in the spectra of the other fractions). Fraction 5 was found to be essentially pure *cis*-1,2-dibromocyclohexane. Except for weak bands or shoulders at 10.5 (1,3-dibromo- and/or *trans*-1,4-dibromocyclohexane), 12.2, 13.6 and 13.8 μ (1,3-dibromocyclohexane), the spectrum of this fraction was indistinguishable from that of pure *cis*-1,2-dibromocyclohexane. Bands characteristic of *trans*-1,2-dibromocyclohexane, e.g., 10.0 μ (strong), 14.65 μ (strong), etc., were completely absent. It has previously been found³ that 2% of *trans*-1,2-dibromocyclohexane in *cis*-1,2-dibromocyclohexane can be detected by infrared analysis. Thus there is little doubt but that less than 2% of *trans*-1,2-dibromocyclohexane is present in any of the fractions, and there is no evidence that this material was present in any of the fractions.

1-Bromocyclohexene.—In previous work this compound was obtained in low yields from the dehydrobromination of *trans*-1,2-dibromocyclohexane. In the present work it was found that this compound can be prepared far more conveniently from 1-chlorocyclohexene. 1-Chlorocyclohexene was converted to 1,1-dibromocyclohexane as described above (expt. 4) and the latter compound was dehydrobrominated as follows: A mixture of 36.1 g. (0.15 mole) of 1,1-dibromocyclohexane and 50 g. of freshly distilled quinoline was refluxed for 1 hr. After cooling, the reaction mixture was diluted with 150 ml. of water and acidified with concentrated hydrochloric acid. The reaction mixture was extracted with ether. After drying (CaCl₂) the ether was removed by distillation. The residue was distilled and 17.5 g. (73%) of 1-bromocyclohexene, b.p. 44-46° (7 mm.), n_D^{25} 1.5109, was obtained. The infrared spectrum of this material was indistinguishable from that of 1-bromocyclohexene prepared from *trans*-1,2-dibromocyclohexane.³ By this method 1-bromocyclohexene can be prepared from the readily available 1-chlorocyclohexene²³ in yields of 50-60%.

Conversion of 1-Bromocyclohexene and Dihalocyclohexanes to *trans*-1,4-Dibromocyclohexane.—The same procedure as described above for the conversion of 1-chlorocyclohexane to *trans*-1,4-dibromocyclohexane (expt. 6) was used for these experiments. The results of these experiments are summarized in Table II which shows the amount of solid *trans*-1,4-dibromocyclohexane isolated in the various experiments. In experiment 8, 14 g. of liquid product, b.p. 95-98° (7 mm.), n_D^{25} 1.5500, was isolated in addition to the 2.2 g. of *trans*-1,4-dibromocyclohexane, m.p. 110-112°. The liquid fraction was fractionated carefully and the spectra of the various fractions showed that *trans*-1,4-, *cis*-1,2- and 1,3-dibromocyclohexane were present. That only dibromocyclohexanes were present was clearly shown by the chemical composition (carbon-hydrogen analysis) of each fraction. There was no evidence for the presence of *trans*-1,2-dibromocyclohexane. In experiment 14, a liquid product, 11.8 g., b.p. 92-97° (7 mm.), n_D^{25} 1.5490, was obtained together with 5.6 g. of *trans*-1,4-dibromocyclohexane. The liquid fraction had a spectrum essentially the same as that for 1,3-dibromocyclohexane. The chemical composition of the liquid fraction (carbon-hydrogen analysis) corresponded to that for dibromocyclohexane. *trans*-1,4-Dibromocyclohexane was the only product isolated in experiments 9-13.

Infrared Spectra of Dihalocyclohexanes.—Spectra of liquid films were used for comparison of liquid compounds and products. Spectra of 0.4 *M* carbon disulfide solutions were used for identification of the solid product as *trans*-1,4-dibromocyclohexane. The spectra of the dihalocyclohexanes differ sufficiently so that small amounts of any one can be detected in a mixture of dihalocyclohexanes. Several of the dihalides, *viz.*, 1,1-, *trans*-1,2- and 1,3-dibromocyclohexane, have strong characteristic bands that are absent or shifted in the spectra of the other dihalocyclohexanes. Thus the absence of any of these compounds in a mixture readily can be determined. The following bands were found especially useful for identification purposes (bands not present in the spectrum of any other dihalocyclohexane are marked with an asterisk): 1,1-Dibromocyclohexane, 11.35* and 14.20 μ ; 1-bromo-1-chlorocyclohexane, 13.55 and 13.85 μ ; *trans*-1,2-dibromocyclohexane, 10.00, 10.30, 11.60, 11.90 and 14.64* μ ; *cis*-1,2-dibromocyclohexane, 7.70, 8.23, 10.20 and 12.02 μ ; 1,3-dibromocyclohexane, 9.7* and 8.3 μ ; *trans*-1,4-dibromocyclohexane, 8.6, 10.1, 11.3, 11.5, 13.5 and 13.7 μ ; *cis*-1-bromo-2-chlorocyclohexane, 7.70, 9.22, 11.40, 12.02, 13.5, 14.4 and 15.1 μ ; *trans*-1-bromo-2-chlorocyclohexane, 9.98, 10.5, 11.6, 11.9, 13.5, 14.5 and 15.1 μ .

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Base-catalyzed Elimination and Aromatization of a Cyclohexadieneamine and its Methiodide¹

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Isomeric *n*-amylcyclohexadieneamines, prepared by rearrangement of the 2,4,6-trimethylbenzyltrimethylammonium ion and condensation of the resulting *exo*-methylenecyclohexadieneamine with butyllithium, was found to eliminate the carbanion of trimethylamine to form *n*-amylmesitylene with potassium amide in refluxing xylene and with potassium *n*-pentoxide in refluxing *n*-pentanol. A catalytic amount of potassium amide was sufficient for this aromatization. The methiodides of the *n*-amylcyclohexadieneamines underwent aromatization with potassium amide even in liquid ammonia, the carbanion of the tetramethylammonium ion being eliminated.

Recently² aromatic quaternary ammonium ion I was rearranged by sodium amide in liquid ammonia to *exo*-methylenecyclohexadieneamine II which was condensed with butyllithium in ether to form a mixture of isomeric *n*-amylcyclohexadieneamines IVa

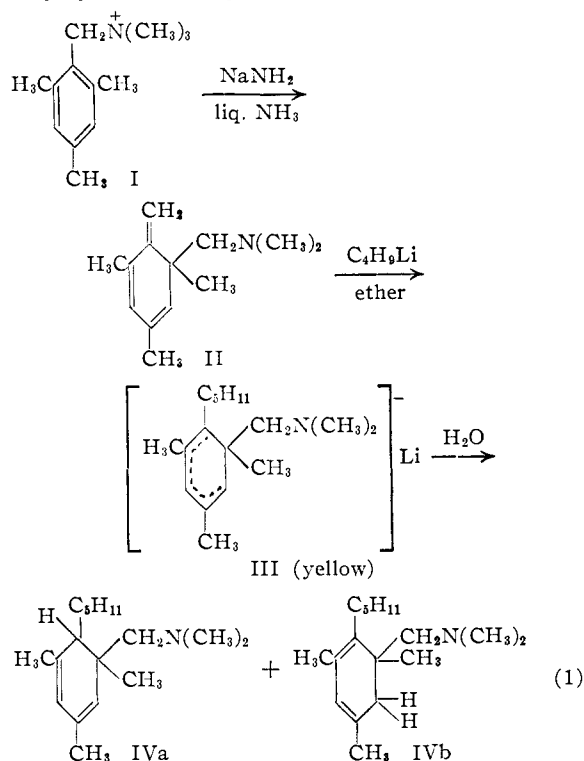
and IVb (equation 1). This condensation involved the attack of the potential butyl carbanion of the reagent at the *exo*-methylene group of II to form yellow *n*-amylcyclohexadienyl carbanion III which was hydrolyzed.

The mixture of isomeric alicyclic amines IVa and IVb was rearomatized by means of butyllithium in refluxing ether to produce *n*-amylmesitylene (V).

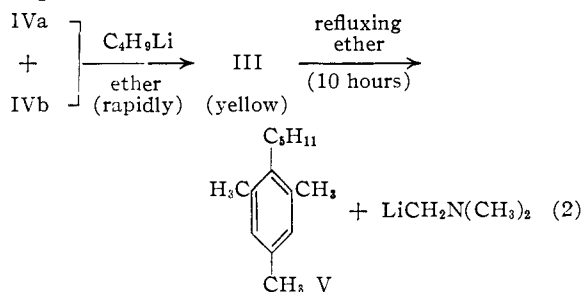
(1) Supported by the National Science Foundation.

(2) C. R. Hauser and D. N. Van Eenam, *THIS JOURNAL*, **78**, 5512 (1957).

This aromatization involved the reconversion of amines IVa-b, which function as acids, to yellow *n*-amylcyclohexadienyl carbanion III followed by the



slow elimination of trimethylamine as a carbanion (equation 2).²



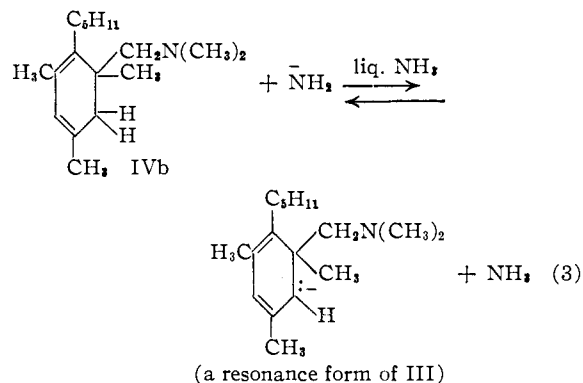
In the present investigation the aromatization of isomeric amines IVa-b and of their methiodides was effected by means of potassium amide or potassium *n*-pentoxide.

Whereas butyllithium in ether is a sufficiently strong base to convert amines IVa-b essentially completely to yellow carbanion III, the equilibrium of the acid-base reaction of these extremely weak acids with potassium amide in liquid ammonia (or ether) is evidently far on the side of the unchanged amines as illustrated for isomer IVb (equation 3).

Thus, although an immediate yellow-orange color is produced on adding amines IVa-b to potassium amide in liquid ammonia, the replacement of the ammonia by ether³ followed by carboxylation of the resulting yellow ether suspension failed to produce

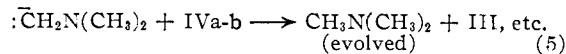
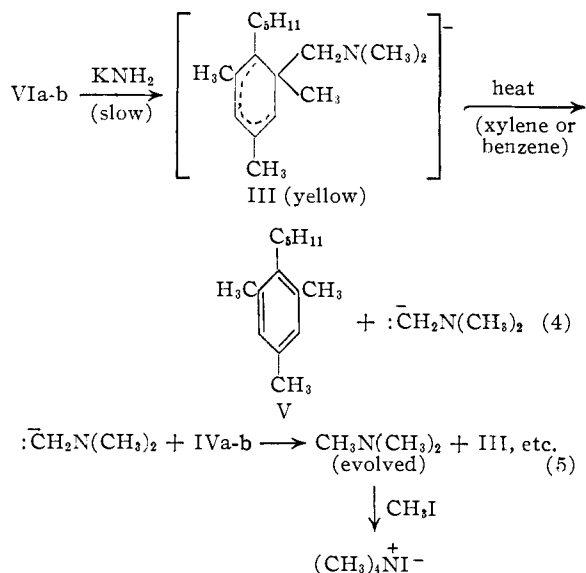
(3) Replacement of the liquid ammonia by ether might have caused some reversal of the acid-base reaction since such a reversal has been observed with certain other hydrocarbon acids; see C. R. Hauser, D. S. Hoffenberg, W. H. Puterbaugh and F. C. Frostick, *J. Org. Chem.*, **20**, 1531 (1955).

appreciable amino acid product. The corresponding carboxylation employing butyllithium in ether to prepare carbanion III previously has given a good yield of amino acid product.²



Moreover, potassium amide in liquid ammonia or ether failed to effect aromatization of amines IVa-b during 8 hr., and 97-98% of the original isomeric amines was recovered.

However, potassium amide⁴ brought about the aromatization of amines IVa-b in refluxing benzene and especially in refluxing xylene, in which solvent even 20 mole per cent. of this base produced a 93% yield of *n*-amylmesitylene (V) within 6 hr.⁵ Also trimethylamine was evolved and was caught in methyl iodide to form tetramethylammonium iodide in 91% yield. These reactions may be represented in equations 4 and 5, respectively.



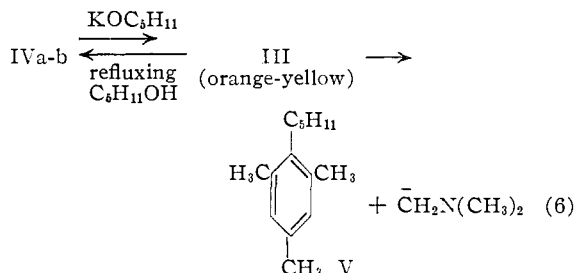
Although the amide ion initiates this aromatization, the more strongly basic trimethylamine carbanion that is eliminated in the process may be considered the main catalyst. This is because the latter base (as soon as formed) probably ionizes the unchanged amines IVa-b, thereby allowing the aromatization to be continued as indicated in equa-

(4) Lithium amide failed to produce color with amines IVa-b in liquid ammonia, and 99% of these amines was recovered after refluxing a benzene suspension of the reaction mixture for 24 hr.

(5) Most of the color disappeared on replacing the liquid ammonia by benzene or xylene, but it reappeared in the latter solvent at its refluxing temperature.

tion 5. Also, the trimethylamine carbanion evidently ionizes the ammonia that is formed when the amide ion initiates the aromatization, since the trimethylamine evolved was essentially uncontaminated with ammonia.

Similarly, potassium *n*-pentoxide effected the aromatization of amines IVa-b in refluxing 1-pentanol (140°) to form *n*-amylmesitylene (V) in 93% yield within 12 hr. (equation 6).

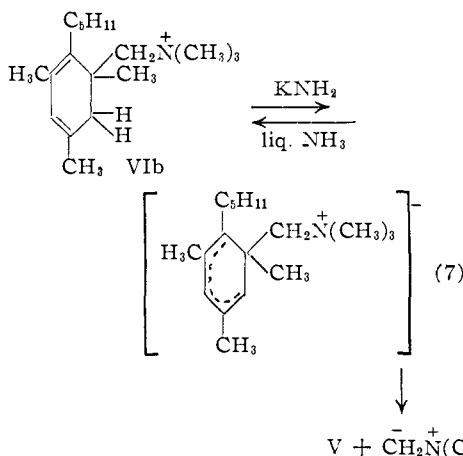


Since the reaction mixture was orange-yellow, carbanion III is apparently also an intermediate under these conditions. The eliminated carbanion of trimethylamine undoubtedly acquires a proton from the pentanol to regenerate the alkoxide ion. Therefore the aromatization presumably would occur with a catalytic amount of this base, although three equivalents were employed in the present experiment.

Sodium ethoxide in refluxing ethanol brought about the aromatization to the extent of only 5% within 24 hr.

These results indicate that, although the aromatization may require moderately strong bases (to effect some ionization of the extremely weak acids, amines IVa-b), the temperature at which the reaction is performed appears to be an important factor. Since the eliminated carbanion of trimethylamine is a relatively strong base, the driving force for the reaction seems to be associated with the production of the aromatic system.

It seemed likely that quaternization of alicyclic amines IVa-b would allow the aromatization to occur more readily since the carbanion of tetramethylammonium ion would then be eliminated, the rupture of the carbon-carbon bond being facilitated by the positively charged nitrogen atom. In agreement with this, the methiodides VIa-b of alicyclic amines IVa-b underwent aromatization with potas-



sium amide even in liquid ammonia (−33°) to give an 89% yield of *n*-amylmesitylene (V) within 10 minutes. Since the reaction was accompanied by the production of color, an intermediate carbanion may be assumed as illustrated with the methiodide of IVb, formula VIb (equation 7). The eliminated carbanion of the tetramethylammonium ion was shown to be colorless under similar conditions. The by-product carbanion of tetramethylammonium ion was hydrolyzed to form tetramethylammonium hydroxide, the latter being isolated as its picrate salt (88%).

Experimental⁶

***n*-Amylcyclohexadieneamines IVa-b.**—A mixture of these isomeric amines was prepared as described previously² by adding *exo*-methyleneamine(II) to butyllithium in ether and hydrolyzing the resulting reaction mixture after 10 minutes. The product distilled at 85–86° at 0.3 mm., n_D^{20} 1.4820, and had an ultraviolet absorption maximum occurring at 269 mμ (3.8).

Aromatization of *n*-Amylcyclohexadieneamines IVa-b with Potassium Amide.—To a solution of 0.008 mole of potassium amide in liquid ammonia contained in a 500-ml. 3-necked flask fitted with sealed stirrer, reflux condenser and addition funnel was added with stirring 10.0 g. (0.04 mole) of *n*-amylcyclohexadieneamines IVa-b in 25 ml. of sodium-dried ether. The resulting deep orange-yellow reaction mixture was stirred for 10 minutes, and the solvents then evaporated on the steam-bath during the addition of 250 ml. of sodium-dried xylenes (b.p. 138–140°). After most of the ammonia-ether had been removed, the orange-yellow color faded and a suspension of potassium amide appeared. The addition funnel was now replaced by a gas addition tube extending nearly to the bottom of the flask for the introduction of nitrogen (through a long soda lime tube). The last traces of ammonia were removed by bubbling nitrogen through the reaction mixture for 5 minutes while raising the temperature to 80° (heating mantle). A gas outlet tube leading from the condenser was then attached to a 20 cm. gas-drying tower filled with a large excess of methyl iodide in absolute ethanol. The reaction mixture was refluxed (140°) with stirring for 6 hr. while nitrogen was bubbled through the reaction train at the rate of approximately 2 bubbles per second. The orange color reappeared, and within 5 minutes a white, granular precipitate of tetramethylammonium iodide began to form and settle to the bottom of the tower; most of this salt was produced during the first 3 hr.

After cooling the xylene suspension to room temperature and stopping the flow of nitrogen, 50 ml. of water was added with stirring to hydrolyze the amide (distinct odor of ammonia detected) followed by 100 ml. of 6 *N* hydrochloric acid. The xylene layer was washed with water, dried over magnesium sulfate, filtered and the solution distilled through a 40-cm. Podbielniak type column to afford 7.1 g. (93%) of *n*-amylmesitylene (V), b.p. 103–104° at 3 mm., n_D^{20} 1.4983 (reported² b.p. 103–103.5° at 3 mm., n_D^{20} 1.4982). The sulfonamide of this hydrocarbon, after crystallization once from ethanol-water (after prior treatment with Norite) and twice from hexane containing 2% of benzene, melted at 102.5–104° (reported² m.p. 103–104°). This melting point was depressed by admixture with an authentic sample of the sulfonamide, m.p. 103–104°.

The aqueous acidified solution, on treatment with excess 50% sodium hydroxide, liberated 0.32 g. (3%) of crude unreacted starting material IVa-b, whose picrate melted at 139–140° (reported² m.p. 140–141°) after two crystallizations from 95% ethanol.

The contents of the gas-drying tower were cooled to 0° and the precipitated tetramethylammonium iodide collected on a funnel and washed once with 25 ml. of cold, absolute ethanol. After drying *in vacuo* there was obtained 7.3 g. (91%) of tetramethylammonium iodide⁷ decomposing at

(6) Melting and boiling points are uncorrected. The microanalysis is by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

(7) A sample of this methiodide, on treatment with refluxing concentrated sodium hydroxide, failed to evolve ammonia or amines (no effect on moist litmus paper), indicating that this quaternary salt was free from ammonium iodide or amine hydroiodides.

228° (reported⁸ decomposition point 230°). On admixture with an authentic sample of tetramethylammonium iodide, dec. pt. 228°, no depression in decomposition point was observed. A sample of the methiodide was converted to its picrate, melting and mixed melting point 313–314° dec. (reported⁹ m.p. 312–313° dec.).

When the reaction was repeated employing 0.12 mole of potassium amide and 10.0 g. (0.04 mole) of *n*-amylcyclohexadieneamines IVa-b in 250 ml. of sodium-dried refluxing xylenes, there was obtained 6.7 g. (89%) of *n*-amylmesitylene (V), b.p. 103–105° at 3 mm., *n*_D²⁰ 1.4987 (sulfonamide m.p. and mixed m.p. 102.5–104°), and 6.8 g. (85%) of tetramethylammonium iodide (dec. pt. and mixed dec. pt. 228°). In addition to these products there was recovered 0.63 g. (6%) of crude IVa-b, *n*_D²⁰ 1.4629 (picrate m.p. and mixed m.p. 139–140°).

In a similar experiment carried out with 0.08 mole of potassium amide and 10.0 g. (0.04 mole) of *n*-amylcyclohexadieneamines IVa-b in 250 ml. of sodium-dried refluxing benzene (80°) for 24 hr. (pale orange-gray reaction mixture), there was isolated 6.1 g. (80%) of *n*-amylmesitylene (V), b.p. 103–104.5° at 3 mm., *n*_D²⁰ 1.4983, and 1.4 g. (14%) of recovered *n*-amylcyclohexadieneamines IVa-b, b.p. 84–88° at 0.3 mm., picrate m.p. and mixed m.p. 139–140.5°.

Reaction of *n*-Amylcyclohexadieneamines IVa-b with Potassium *n*-Pentoxide.—To a solution of 0.12 mole of potassium amide in 200 ml. of liquid ammonia was added dropwise with stirring 250 ml. of dry 1-pentanol, and the ammonia then evaporated (steam-bath) from the resulting suspension of potassium *n*-pentoxide. The mixture was gradually heated to reflux on a heating mantle (solution attained), followed by the dropwise addition of 10.0 g. (0.04 mole) of *n*-amylcyclohexadieneamines IVa-b. The stirred reaction mixture, which rapidly became deep orange in color, was refluxed (137–138°) for 12 hr. (trimethylamine evolved). After cooling to room temperature, water was added slowly and the reaction mixture worked up (as described above) to

(8) 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. 296.

(9) W. Lossen, *Ann.*, **181**, 364 (1876).

give 7.1 g. (93%) of *n*-amylmesitylene (V), b.p. 102.5–104° at 3 mm., *n*_D²⁰ 1.4984. None of the starting compound was recovered.

When the reaction was carried out similarly with 0.12 mole of sodium ethoxide and 10.0 g. (0.04 mole) of *n*-amylcyclohexadieneamines IVa-b in 250 ml. of refluxing absolute ethanol (24 hr.), there was obtained from the pale orange reaction mixture 0.4 g. (5%) of crude *n*-amylmesitylene, *n*_D²⁰ 1.4986. Also, there was recovered 9.1 g. (91%) of amines IVa-b, b.p. 85–87° at 0.3 mm., *n*_D²⁰ 1.4822.

***n*-Amylcyclohexadieneamine Methiodides VIa-b.**—This product (m.p. 204–205° dec.) was obtained in 98% yield from 0.127 mole of *n*-amylcyclohexadieneamines (IVa-b) and 0.20 mole of methyl iodide in 50 ml. of absolute ethanol. A sample, recrystallized twice from absolute ethanol-ether and dried *in vacuo*, melted at 205–206° dec.

Anal. Calcd. for C₁₈H₃₄NI: C, 55.23; H, 8.75; N, 3.58. Found: C, 55.10; H, 8.74; N, 3.51.

Reaction of *n*-Amylcyclohexadieneamine Methiodides VIa-b with Potassium Amide.—To a stirred solution of 0.25 mole of potassium amide in 600 ml. of liquid ammonia was added rapidly (2 minutes) 48.7 g. (0.125 mole) of mixed methiodides VIa-b. The resulting bright red reaction mixture was allowed to react an additional 8 minutes, followed by the replacement of ammonia by ether (steam-bath) and the cautious addition of 150 ml. of water. The aqueous and ethereal layers were separated, the latter being worked up in the usual manner to give 21.2 g. (89%) of *n*-amylmesitylene (V), b.p. 103–104° at 3 mm., *n*_D²⁰ 1.4983 (sulfonamide m.p. and mixed m.p. 102–103°).

The aqueous alkaline layer containing tetramethylammonium hydroxide was neutralized carefully to pH 6 with hydrochloric acid with subsequent addition of 30.0 g. (0.13 mole) of picric acid. The resulting suspension was heated to boiling while additional water was put in to attain a clear solution. After cooling to 0°, the precipitated quaternary salt was collected on a funnel and recrystallized twice from a minimum of boiling water to afford 33.2 g. (88%) of tetramethylammonium picrate, m.p. and mixed m.p. 314–315° dec. (reported⁹ m.p. 312–313° dec.).

DURHAM, NORTH CAROLINA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

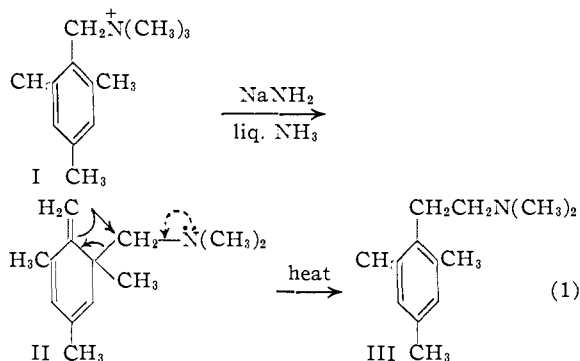
Thermal and Acid Induced Aromatizations of an *exo*-Methylenecyclohexadieneamine with Alcohols. Relation to *ortho* Substitution Rearrangement¹

BY CHARLES R. HAUSER AND DONALD N. VAN EENAM

RECEIVED JUNE 28, 1957

Two of the characteristic reactions of an *exo*-methylenecyclohexadieneamine, thermal isomerization to a β -arylethylamine and acid induced conversion to isodurene, were realized with certain alcohols and amines. Relatively more of the former reaction and relatively less of the latter occurred as the reactivity of the hydroxyl hydrogen of the alcohols was decreased and/or the temperature raised. These results furnish further evidence for the 1,3-shift mechanism of the thermal isomerization.

Recently² aromatic quaternary ammonium ion I was rearranged by sodium amide in liquid ammonia



(1) Supported by the National Science Foundation.

(2) C. R. Hauser and D. N. Van Eenam, *THIS JOURNAL*, **79**, 5512 (1957).

to *exo*-methylenecyclohexadieneamine II which was rearomatized in several ways. One of these processes involved the thermal isomerization of II to form β -arylethylamine III (as shown in eq. 1). Another mode of aromatization of II consisted in its treatment with cold dilute hydrochloric acid which produced isodurene (IV) and dimethylmethylenium chloride (equation 2).

In the present investigation both of these modes of aromatization were realized simultaneously with certain alcohols and amines. For example, on refluxing *exo*-methylenamine II in ethanol solution there were obtained both β -arylethylamine III and isodurene (IV) in yields of 25 and 71%, respectively. This predominant formation of isodurene was unexpected since amine III is formed exclusively on refluxing II in benzene. Evidently the *exo*-methylene group of II is so reactive toward acids that even ethanol functions largely in this manner