of 6 *N* hydrochloric acid and 500 g. of crushed ice. The mixture of solids (*i.e.*, 2,2-diphenyl-4-methyl-1,2-dihydroquinoline and 2-phenyl-4-methylquinoline hydrochloride) which precipitated was filtered and separated into its components in the following way. The mixed solids were treated with 5% sodium hydroxide to free the 2-phenyl-4-methylquinoline from its salt and the mixture then extracted with several portions of ether. In this way the ether-soluble 2-phenyl-4-methylquinoline was separated from the ether-insoluble 2,2-diphenyl-4-methyl-1,2-dihydroquinoline. Thus, 14.9 g. (25%) of 2,2-diphenyl-4-methyl-1,2-dihydroquinoline, m.p. 163–164° (from 95% ethanol) was obtained. *Anal.* Calcd. for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71. Found: C, 88.42; H, 6.83; N, 4.62. This dihydroquinoline gave a yellow picrate, m.p. 198–200° dec. *Anal.* Calcd. for $C_{28}H_{22}N_4O_7$: C, 63.87; H, 4.21; N, 10.64. Found: C, 63.51; H, 3.89; N, 10.72.

From the ether solution mentioned above there was obtained (56.6 g., 64.6%) of 2-phenyl-4-methylquinoline, b.p. 161–164° at 1.3 mm. This amine gave a methiodide, m.p. 183.5–185°.[6] It also gave a yellow picrate, m.p. 212–213.5° (from 95% ethanol) and a hydrochloride, m.p. 233–235°. *Anal.* of picrate: Calcd. for $C_{22}H_{16}N_4O_7$: C, 58.93; H, 3.60; N, 12.50. Found: C, 58.96; H, 3.31; N, 12.42. *Anal.* of the hydrochloride: Calcd. for $C_{16}H_{14}NCl$: N, 5.49. Found: N, 5.48.

Similar results were obtained when the ether solution of the tar base and phenyllithium was treated with methyl benzoate, benzoyl chloride or carbon dioxide.

**Proof of Structure of 2,2-Diphenyl-4-methyl-1,2-dihydroquinoline.**—Using the procedure described for similar compounds[7-9] 5.0 g. of 2,2-diphenyl-4-methyl-1,2-dihydroquinoline was oxidized to give a mixture of 4.2 g. of starting material and 0.02 g. of 2,2-diphenyl-1,2-dihydroquinoline, m.p. 86–87°[10] (from 95% ethanol).

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# The Preparation of Some ω-Bromoalkyl Quaternary Ammonium Salts

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RECEIVED JANUARY 31, 1955

In conjunction with the investigation of unsymmetrical bis-quaternary salts, which is being carried on in these laboratories, a convenient route to ω-bromoalkyl monoquaternary intermediates was required. A preliminary search of the literature revealed that little had been done in this field. Maréchal and Bagot,[1] who adequately reviewed the earlier literature, prepared two of the desired type of bromoalkylammonium bromide salts by what appeared to be the simplest approach: reaction of a dibromoalkane with a slight excess of trimethylamine in benzene solution. In our hands, however, their procedure afforded salt mixtures containing a high proportion of the bis-quaternary derivative.[2] After some experimentation a modification was adopted, which afforded the monoquaternary salts in yields of 50 to 90%. The technique involved the slow addition of 65 to 75% of the calculated amount of the appropriate tertiary amine to a benzene solution of the dibromoalkane. In this way, a large excess of the dihalide was maintained in solution throughout the operation and the mono salt precipitated before it was given the opportunity to react further. Unreacted dibromide was recovered from combined mother liquors. Even under these conditions appreciable amounts of the bis-quaternary by-products often formed; these were isolated in a few instances. Occasionally, the crude mono salt containing (as indicated by ionic halogen determination) roughly 5 to 10% of bis-quaternary material, was not purified and was found to be satisfactory for the preparation of desired derivatives.

An alternative approach was attempted for the synthesis of some of the propyl salts. This, involving the reaction of a hydroxypropyl quaternary ammonium bromide with 48% hydrobromic acid, was found to be less satisfactory and not generally applicable. V and VIII were successfully prepared by both methods.

There was, of course, no difficulty in the preparation of mono salt derivatives of dibromoethane.

## Experimental[3]

**Tertiary Amines.**—N-Methylpyrrolidine, b.p. 78.5–79.5°, $n^{26}D$ 1.4204,[4] picrate m.p. 219–221°, was prepared from pyrrolidine by the Eschweiler–Clarke process[5] or, less satisfactorily, from 1,4-dibromobutane and methylamine.[6]

*Anal.* Calcd. for $C_5H_{11}N$: N, 16.34. Found: N, 16.59.

N-Methylpiperidine, b.p. 105–107°, $n^{25}D$ 1.4355, and methyldiethylamine, b.p. 65°, were prepared by the Eschweiler–Clarke method.

**3-Bromopropyltrimethylammonium Bromide** (III).—This compound was prepared a number of times in yields of 50 to 90%. As an example, anhydrous trimethylamine was bubbled slowly into a solution of 135 g. (0.67 mole) of 1,3-dibromopropane in 300 ml. of benzene at room temperature until 26.4 g. (0.45 mole) had been absorbed. This took approximately 5 hours. After 16 hours the white crystalline precipitate, 99.5 g. (85% yield) of analytically satisfactory III, m.p. 205° dec., was collected. Occasionally, the precipitate obtained directly from the reaction mixture was found to be contaminated with bis salt; in the event of this, one recrystallization from alcohol afforded pure III.[7]

**3-Bromopropylmethyldiethylammonium Bromide (V).**—Over a period of 1.5 hours a solution of 14.3 g. (0.16 mole) of methyldiethylamine in 50 ml. of benzene was added dropwise with stirring to 50.5 g. (0.25 mole) of 1,3-dibromopropane, warmed on a steam-bath. After completion of the addition, the reaction mixture was allowed to stand overnight at room temperature. The supernatant liquid was decanted from the oily product which was washed with fresh benzene, taken to dryness twice under reduced pressure with the addition of more benzene, and finally dried *in vacuo* over phosphorus pentoxide. There was obtained 27.9 g. (59% yield) of white, hygroscopic material, melting 120–130°.

**6-Bromohexyltrimethylammonium Bromide (XIII).**—Into a solution of 14.6 g. (0.06 mole) of dibromohexane in 25 ml. of benzene at room temperature, was bubbled slowly 2.4 g. (0.04 mole) of trimethylamine. The reaction mixture was allowed to stand overnight, the white precipitate was collected and recrystallized from *t*-butyl alcohol. A yield of 11.5 g. (95%) of XIII, m.p. 106–108°, was obtained.

**3-Bromopropylmethylpiperidinium Bromide (Alternative Procedure) (VIII).**—3-Piperidinopropanol, b.p. 109–110° (19 mm.), was prepared by the reaction of 3-bromopropanol with piperidine and sodium carbonate in aqueous alcohol. The methobromide, prepared in benzene, melted at 128–129°.

A solution of 10.7 g. of the methobromide salt in 20 ml.

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[1] R. Maréchal and J. Bagot, *Ann. pharm. franç.*, **4**, 172 (1946).

[2] See also, K. J. M. Andrews, F. Bergel and A. L. Morrison, *J. Chem. Soc.*, 2998 (1953).

[3] Melting points are corrected for stem exposure.

[4] N. D. Zelinsky and J. K. Jurjew, *Ber.*, **62**, 2589 (1929), report $n^{20}$ 1.4480. Their product may have been contaminated with N-methylpyrrole.

[5] H. T. Clarke, H. B. Gillespie and S. Z. Weisshaus, THIS JOURNAL, **55**, 4571 (1933).

[6] J. v. Braun, *Ber.*, **49**, 966 (1916).

[7] When present in appreciable amounts, the bis-quaternary impurities sometimes crystallized first out of alcoholic solvents. The mono salts were obtained from the mother liquors by the addition of ether. In the purification of longer chain monoquaternaries, advantage could be taken of their relatively high solubility in acetone

TABLE I

ω-BROMOALKYL QUATERNARY AMMONIUM SALTS: Br—$(CH_2)_n$—N⊕R′$R_2$Br⊖

|  | $n$ | $NR_2$ | R′ | M.p., °C. | Formula | Ionic bromine, % Calcd. | Ionic bromine, % Found |
|---|---|---|---|---|---|---|---|
| I | 2 | $N(CH_3)_2$ | $CH_3$ | 229[b] | $C_5H_{13}Br_2N$ | 32.35 | 32.47 |
| II | 2 | Pyrrolidino | $CH_3$ | 223 | $C_7H_{15}Br_2N$ | 29.27 | 29.42 |
| III | 3 | $N(CH_3)_2$ | $CH_3$ | 205[c] | $C_6H_{15}Br_2N$ | 30.61 | 30.93 |
| IV | 3 | $N(CH_3)_2$ | $C_6H_5CH_2$ | 156–158 | $C_{12}H_{19}Br_2N$ | 23.70 | 24.09 |
| V | 3 | $N(C_2H_5)_2$ | $CH_3$ | 120–130 | $C_8H_{19}Br_2N$ | 27.64 | 27.71 |
| VI | 3 | $N(C_2H_5)_2$ | $C_2H_5$ | 146–148[d] | $C_9H_{21}Br_2N$ | 26.33 | 26.55 |
| VII | 3 | Pyrrolidino | $CH_3$ | 177–179 | $C_8H_{17}Br_2N$ | 27.84 | 27.96 |
| VIII | 3 | Piperidino | $CH_3$ | 190–193 | $C_9H_{19}Br_2N$ | 26.54 | 26.60 |
| IX | 3 | Morpholino | $CH_3$ | 143–145 | $C_8H_{17}Br_2NO$ | 26.37 | 26.58 |
| X | 3 | $C_5H_5N$[a] |  | 128–129[e] |  |  |  |
| XI | 4 | Pyrrolidino | $CH_3$ | 96[f] |  |  |  |
| XII | 5 | $N(CH_3)_2$ | $CH_3$ | 133–136 | $C_8H_{19}Br_2N$ | 27.64 | 28.10 |
| XIII | 6 | $N(CH_3)_2$ | $CH_3$ | 106–108 | $C_9H_{21}Br_2N$ | 26.36 | 26.49 |
| XIV | 10 | $N(CH_3)_2$ | $CH_3$ | 122–128 | $C_{13}H_{29}Br_2N$ | 22.25 | 22.28 |

[a] Pyridine derivative. [b] M. Krüger and P. Bergell, *Ber.*, **36**, 2901 (1903), reported m.p. 230–231°. [c] R. Lucius, *Arch. Pharm.*, **245**, 249 (1907), reported m.p. 208°. [d] R. Lucius, *ibid.*, p. 254, gave m.p. 227–228° for this compound. [e] M.p. of the crude material (ionic halogen determination indicated it to contain 9% of the bis salt). [f] M.p. of the crude material containing *ca.* 6% of the bis salt.

of 48% hydrobromic acid and 4 ml. of ethanol was refluxed for 15 hours. The solution was concentrated *in vacuo* to an oily residue. The oil was dissolved in alcohol, precipitated with ether and then taken to dryness several times under reduced pressure with the addition of benzene. There was obtained 10.5 g. of hygroscopic product, m.p. 190–193°, representing a 70% yield in the final step.

**Acknowledgment.**—Ionic halogen determinations were performed by Mr. Donald L. Miller.

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## Structure of the Cyclic Condensation Product of Adiponitrile

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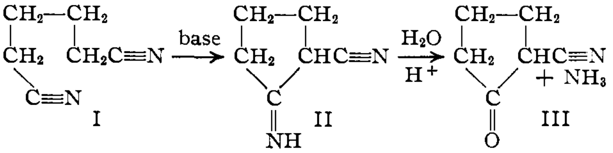
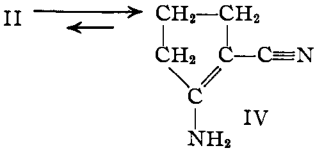
RECEIVED FEBRUARY 26, 1955

The base-catalyzed cyclization of adiponitrile (I) is a well-known reaction.[1,2] Previously, the cyclic reaction product has been assigned the structure of 2-cyanocyclopentylidene imine (II),[2] largely because it is hydrolyzed very readily to 2-cyanocyclopentanone (III), as indicated by the equation



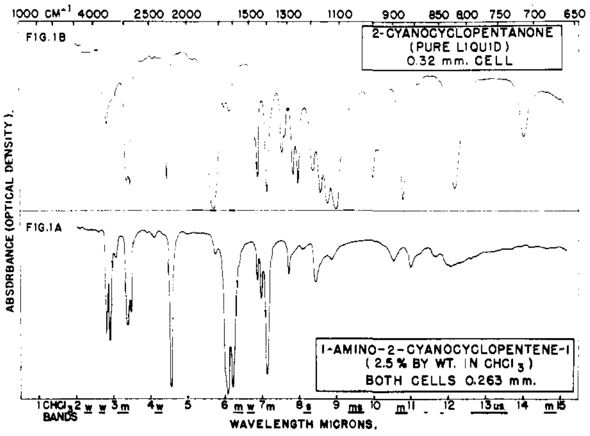
However, we propose that the cyclic product obtained from I exists principally as the enamine of II, 1-amino-2-cyanocyclopentene-1 (IV)



IV

The evidence for this enamine structure is found in the infrared and ultraviolet spectra of the cyclic product. An analogous situation for conjugated aminoesters exists with respect to ethyl aminocrotonate.[3,4]

The infrared spectrum of the product obtained by cyclization of I is shown in Fig. 1-A. The absorption at 2189 cm.$^{-1}$ indicates a rather unusual conjugated nitrile; the presence of an $-NH_2$ group is indicated by absorptions at 3512, 3420 and 1645 cm.$^{-1}$; and an olefinic linkage characteristic of cyclopentene is indicated by absorption at 1605 cm.$^{-1}$. Since it has been shown by Kitson and Griffith[5] that unconjugated nitriles absorb at 2250 cm.$^{-1}$ and that normal conjugated nitriles absorb at 2225 cm.$^{-1}$, it may be presumed that the further shift of the nitrile absorption to 2189 cm.$^{-1}$ is due to the influence of the amine group. The location of the absorption peak at 2189 cm.$^{-1}$ was determined more accurately by scanning this region at higher resolution with the use of a calcium fluoride prism.



The infrared spectrum of the hydrolysis product III is shown in Fig. 1-B. In contrast to the spectrum of Fig. 1-A, this shows absorption of a normal unconjugated nitrile at 2250 cm.$^{-1}$ and of a ketone at 1755 cm.$^{-1}$; there is no olefinic absorption at 1605 cm.$^{-1}$. Therefore, it is evident that in this

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(1) S. R. Best and J. F. Thorpe, *J. Chem. Soc.*, **95**, 685 (1909).

(2) J. F. Thorpe, *ibid.*, **95**, 1901 (1909).

(3) K. von Auwers and W. Susemihl, *Ber.*, **63**, 1072 (1930).

(4) S. A. Glickman and A. C. Cope, THIS JOURNAL, **67**, 1017 (1945).

(5) R. E. Kitson and N. E. Griffith, *Anal. Chem.*, **24**, 334 (1952).