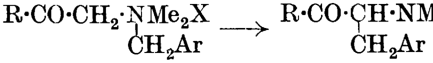
263. *Degradation of Quaternary Ammonium Salts. Part VII. New Cases of Radical Migration.*

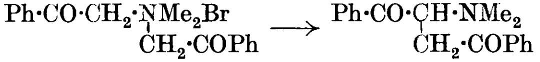
By THOMAS THOMSON and THOMAS STEVENS STEVENS.

THE rearrangements described in previous work have been of the type

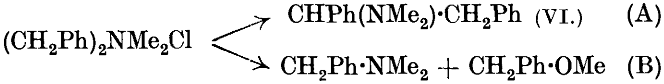
(I.)  (II.)

$$\mathrm{R{\cdot}CO{\cdot}CH_2{\cdot}\underset{CH_2Ar}{NMe_2X}} \longrightarrow \mathrm{R{\cdot}CO{\cdot}\underset{CH_2Ar}{CH}{\cdot}NMe_2}$$

and the reaction involves migration of a substituted benzyl group to the methylene carbon atom of a phenacyl or acetonyl radical. It has now been found possible to effect rearrangements such that the *migrating* radical is phenacyl (III ⟶ IV), or such that the methylene carbon atom *to* which wandering takes place is that of a benzyl group (V ⟶ VI).

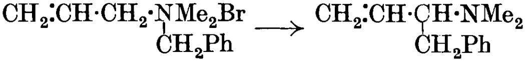
(III.)  (IV.)

$$\mathrm{Ph{\cdot}CO{\cdot}CH_2{\cdot}\underset{CH_2{\cdot}COPh}{NMe_2Br}} \longrightarrow \mathrm{Ph{\cdot}CO{\cdot}\underset{CH_2{\cdot}COPh}{CH}{\cdot}NMe_2}$$

(V.) 

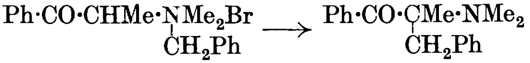
$$\mathrm{(CH_2Ph)_2NMe_2Cl} \begin{cases} \longrightarrow \mathrm{CHPh(NMe_2){\cdot}CH_2Ph} \text{ (VI.)} & \text{(A)} \\ \longrightarrow \mathrm{CH_2Ph{\cdot}NMe_2 + CH_2Ph{\cdot}OMe} & \text{(B)} \end{cases}$$

This interchangeability of function seems to confirm the view that the same characteristic of a radical (presumably some degree of anionic stability) which enables it to lose a hydrogen ion and act as recipient of the migrating group, is also that which enables it to function as the migrating radical itself. Parallel attempts to bring about rearrangement of *di*-p-*bromophenacyldimethylammonium bromide* and of diacetonyldimethylammonium chloride (analogues of III), and also of *di*-p-*bromobenzyldimethylammonium bromide* (compare V), led to decomposition. On the other hand, the rearrangement of phenyldibenzylmethylammonium iodide (see below) and of *benzyldimethylallylammonium bromide* (potential analogues of V) was accomplished. The latter case was suggested by the observation that the allyl radical can replace CH_2Ar in the reaction (I ⟶ II); it was found, however, that migration takes place wholly in the direction

 (VII.)

$$\mathrm{CH_2{:}CH{\cdot}CH_2{\cdot}\underset{CH_2Ph}{NMe_2Br}} \longrightarrow \mathrm{CH_2{:}CH{\cdot}\underset{CH_2Ph}{CH}{\cdot}NMe_2}$$

It was thought that the replacement of the two hydrogen atoms of the phenacyl methylene group might change the sense of the reaction (I ⟶ II), so that the substituted phenacyl radical would migrate into the benzyl group, and the preparation of such substituted quaternary salts was undertaken. The monomethylated substance (VIII) gives (IX) readily, but salts in which one of the hydrogen atoms in question is replaced by phenyl, or both by methyl, could not be prepared.

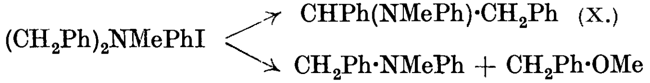
(VIII.)  (IX.)

$$\underset{\displaystyle CH_2Ph}{Ph{\cdot}CO{\cdot}CHMe{\cdot}NMe_2Br} \longrightarrow Ph{\cdot}CO{\cdot}\underset{\displaystyle CH_2Ph}{CMe}{\cdot}NMe_2$$

In this series the progressive replacement of the hydrogen atoms of the phenacyl methylene group leads to a progressive decrease in the facility of quaternary salt formation. Thus bromopropiophenone and benzyldimethylamine do not combine in the cold, and the interaction of α-dimethylaminopropiophenone and benzyl chloride is sluggish. Similarly, although chlorodeoxybenzoin reacts with dimethylamine, it will not combine with benzyldimethylamine, nor will *dimethylaminodeoxybenzoin* unite with benzyl chloride or iodide; and bromo*iso*butyrophenone gives no quaternary salt with benzyldimethylamine, and only traces of tertiary base with dimethylamine. The interaction of bromopropiophenone and benzyldimethylamine in *hot* benzene produces, not (VIII), but dibenzyldimethylammonium bromide (identified as the iodide), probably by a dissociation and combination of the type discovered by Wedekind (*Ber.*, 1902, **35**, 767): (VIII) ⟶ $Ph{\cdot}CO{\cdot}CHMe{\cdot}NMe_2 + CH_2PhBr$, followed by $CH_2Ph{\cdot}NMe_2 + CH_2PhBr \longrightarrow (CH_2Ph)_2NMe_2Br$.

The change (V ⟶ VI) and its analogues require far more drastic conditions than have hitherto been used in this series of investigations. Thus the salt (V) is unaffected by boiling with methyl-alcoholic sodium methoxide or with *iso*propyl-alcoholic sodium *iso*propoxide solutions. With methyl-alcoholic sodium methoxide solution at 120—140°, the salt is decomposed wholly according to scheme (B) above, and a similar result is obtained on refluxing with amyl-alcoholic sodium amyloxide solution (compare Achmatowicz, Perkin, and Robinson, this vol., p. 500). Treatment with solid sodium methoxide at 140° results in 50% of the salt being rearranged according to scheme (A) and 50% decomposed according to (B). When the salt is fused with sodamide (140—150°), the degradation proceeds wholly in the direction (A); a small amount of stilbene is also produced. These results suggest that, when the hydrogen atom which is to be replaced by the migrating radical has little mobility, its extraction becomes the primary condition of the rearrangement, a conclusion which contrasts with the experience of Dunn and Stevens (previous paper) with more acidic quaternary salts. Such removal of a hydrogen ion may be regarded, moreover, as the initial and determining stage of the observed conversion of (VI) into stilbene by further treatment with sodamide, an apparently paradoxical elimination of dimethylamine by a powerfully *alkaline* reagent which has already effected removal of the elements of hydrogen chloride from (V).

The degradation of phenyldibenzylmethylammonium iodide was investigated in view of a possible influence of an aryl radical attached to the nitrogen on the course of the rearrangement. The salt, on refluxing with methyl-alcoholic sodium methoxide solution, is wholly decomposed according to scheme (D) below, and fusion with sodamide results in some 70% being decomposed to benzylmethylaniline (compare D) and some 20% being rearranged according to scheme (C)



$$(CH_2Ph)_2NMePhI \begin{array}{l} \nearrow CHPh(NMePh)\cdot CH_2Ph \ (X.) \quad (C) \\ \searrow CH_2Ph\cdot NMePh + CH_2Ph\cdot OMe \quad (D) \end{array}$$

The use of sodamide favours rearrangement (C) as in the case of the analogous salt (V), while the replacement of a methyl group in (V) by phenyl definitely facilitates the decomposition (D).

Attempts to prepare phenacylphenylbenzylmethylammonium bromide were unsuccessful. According to Wedekind (*Ber.*, 1908, **41**, 2804) the salt is formed by the interaction of ω-bromoacetophenone and benzylmethylaniline, but it has now been found that the product is actually *phenyldibenzylmethylammonium bromide*, which probably arises in a similar manner to the formation of (V) from bromopropiophenone and benzyldimethylamine (see above). ω-Methylanilinoacetophenone could not be combined with benzyl chloride or iodide.

Constitution of the Rearrangement Products.—The substance (IV) was converted into the methosulphate and reduced, giving diphenacyl, $Ph\cdot CO\cdot CH_2\cdot CH_2\cdot COPh$. The methosulphates of (VI), (VII), (IX), and (X), on treatment with alkali, yielded respectively stilbene, α-phenylbutadiene, α-benzylidenepropiophenone, and stilbene. The confirmation of the structure of (VII) by synthesis from benzylmagnesium chloride and α-dimethylaminovinylacetonitrile (compare Stevens, Cowan, and MacKinnon, J., 1931, 2568) was impracticable, since the interaction of acraldehyde, dimethylamine, and hydrogen cyanide gave rise, not to the unsaturated substance, but to the diaminonitrile, $CH_2(NMe_2)\cdot CH_2\cdot CH(NMe_2)\cdot CN$ (compare Bruylants, *Bull. Acad. roy. Belg.*, 1925, **7**, 270). Catalytic reduction of (VII) gives β-dimethylamino-α-phenylbutane, which was synthesised by the action of ethylmagnesium bromide on α-dimethylamino-β-phenylpropionitrile.

EXPERIMENTAL.

When diphenacyldimethylammonium bromide (Rumpel, *Arch. Pharm.*, 1899, **237**, 235) was warmed with aqueous caustic soda, ω-dimethylamino-ω-phenacylacetophenone was obtained as a gummy solid; *picrate*, small yellow prisms, m. p. 128—130°, from methyl alcohol (Found: $C_6H_3O_7N_3$, 44·9. $C_{18}H_{19}O_2N,C_6H_3O_7N_3$ requires $C_6H_3O_7N_3$, 44·9%).

Constitution of ω-Dimethylamino-ω-phenacylacetophenone.—By treatment of ω-bromoacetophenone with alcoholic sodium ethoxide, Fritz (*Ber.*, 1895, **28**, 3032) obtained a so-called "bromodiphenacyl," m. p. 161—162°, which on reduction in absolute alcohol with zinc dust gave diphenacyl, m. p. 143—145°, of well-established constitution. ω-Dimethylamino-ω-phenacylacetophenone, refluxed in benzene with methyl sulphate (1 equiv.), yielded an oily methosulphate which was reduced by zinc dust and dilute sulphuric acid to diphenacyl, m. p. and mixed m. p. 143—145°. An attempt to synthesise ω-dimethylamino-ω-phenacylacetophenone from "bromodiphenacyl" and dimethylamine in alcohol yielded a substance, the picrate of which formed small yellow prisms, m. p. 184—186°, from benzene (Found: $C_6H_3O_7N_3$, 45·5%). Several "bromodiphenacyls" are known whose structures are a matter of doubt.

*Di-*p*-bromophenacyldimethylammonium Bromide.*—*p*-Bromophenacyl bromide (2 mols.) and dimethylamine (1 mol.) in alcohol gave almost instantaneously a mass of colourless crystals. The unchanged bromide having been removed with boiling benzene, the residue crystallised from alcohol in prisms, m. p. 215° (decomp.) (Found: ionisable Br, 15·0. $C_{18}H_{18}O_2NBr_2{\cdot}Br$ requires ionisable Br, 15·4%).

When the foregoing ammonium bromide was warmed with methyl-alcoholic sodium methoxide, dimethylamine was evolved: an ethereal extract of the diluted solution, on treatment with dilute hydrochloric acid, deposited an orange-red solid, m. p. 170—171° (decomp.). The acid layer, made alkaline with ammonia, yielded a cream-coloured solid, m. p. 253—255°, which did not redissolve in dilute acid. The main product was a black-red tar, and no unchanged quaternary salt was obtained. Neither of the solid products, both small in quantity, was identical with di-*p*-bromobenzoylethylene (Conant and Lutz, *J. Amer. Chem. Soc.*, 1925, **47**, 891), which might have been formed from the expected rearrangement product.

Diacetonyldimethylammonium Chloride.—Prepared from chloroacetone (2 mols.) and dimethylamine (1 mol.) in alcohol, the chloride was obtained as a brownish mobile oil; *picrate*, yellow prismatic needles, m. p. 198—199° (decomp.), from methyl alcohol (Found: $C_6H_2O_7N_3'$, 59·4. $C_8H_{16}O_2N{\cdot}C_6H_2O_7N_3$ requires $C_6H_2O_7N_3'$, 59·1%). The quaternary chloride was completely destroyed by aqueous caustic soda or methyl-alcoholic sodium methoxide and no isolable products were obtained.

Dibenzyldimethylammonium Chloride.—Prepared from benzyldimethylamine and benzyl chloride in cold benzene, this separated as an oil; after solidifying, it crystallised from acetone in stout prisms, m. p. 93—95° (Found: Cl, 13·7. $C_{16}H_{20}NCl$ requires Cl, 13·6%). The *iodide* crystallised from alcohol in stout prisms, m. p. 192° (Found: I, 35·9. $C_{16}H_{20}NI$ requires I, 36·0%), and the picrate from methyl alcohol in yellow leaflets, m. p. 148—150° (Goss, Ingold, and Wilson, J., 1926, 2462, give m. p. 146°) (Found: $C_6H_2O_7N_3'$, 50·4. Calc. for $C_{16}H_{20}N{\cdot}C_6H_2O_7N_3$: $C_6H_2O_7N_3'$, 50·2%).

The quaternary chloride was heated at 120—140° for 2 hours with methyl-alcoholic sodium methoxide. An ethereal extract of the diluted solution yielded benzyldimethylamine (isolated as picrate) to dilute hydrochloric acid and then contained benzyl methyl ether, b. p. 169—170°: the amounts of these two products accounted satisfactorily for the original quaternary salt used.

From the quaternary chloride and solid sodium methoxide (not alcohol-free) at 140°, the product being worked up as just described, there resulted benzyl methyl ether and a mixture of bases which were separated by crystallisation of the picrates from methyl alcohol. αβ-Diphenylethyldimethylamine picrate was deposited first; yellow leaflets from methyl alcohol, m. p. 156—157° (softening markedly at about 130°) even after repeated crystallisation (compare Stevens, Cowan, and MacKinnon, J., 1931, 2571). The mother-liquor deposited benzyldimethylamine picrate, m. p. and mixed m. p. 93—95°. A very small amount of unchanged quaternary salt was isolated as picrate, m. p. and mixed m. p. 148—150°.

Constitution of αβ-Diphenylethyldimethylamine.—The base and methyl sulphate (equal mols.) were refluxed in benzene for an hour and the oily quaternary salt was boiled with caustic soda solution; stilbene, m. p. and mixed m. p. 123—125°, was obtained. Treatment of αβ-diphenylethyldimethylamine with sodamide at 200° also gave stilbene.

*Di-*p*-bromobenzyldimethylammonium Bromide.*—This was prepared from *p*-bromobenzyl bromide (Stevens, Snedden, Stiller, and Thomson, J., 1930, 2122) (2 mols.) and dimethylamine (1 mol.) in alcohol. After distillation of most of the alcohol, addition of ether precipitated an oil, which solidified and then crystallised from alcohol–ether in long prismatic needles, m. p. 193—195° after softening at about 170° (Found: ionisable Br, 17·0. $C_{16}H_{18}NBr_2{\cdot}Br$ requires ionisable Br, 17·2%). This *bromide* was completely destroyed by sodamide at 160—170° and no product of the degradation could be isolated.

α-Dimethylaminopropiophenone.—Bromopropiophenone (1 mol.) and dimethylamine (2—3 mols.) were heated in alcohol for 2 hours at 100—110°, most of the solvent was distilled, and the residue poured into water and extracted with ether. *α-Dimethylaminopropiophenone picrate*, isolated in the first place from ether, crystallised from methyl alcohol in yellow prismatic needles, m. p. 128—130° (Found : $C_6H_3O_7N_3$, 56·7. $C_{11}H_{15}ON,C_6H_3O_7N_3$ requires $C_6H_3O_7N_3$, 56·4%).

α-Methylphenacylbenzyldimethylammonium Iodide (as VIII).—Prolonged interaction of α-dimethylaminopropiophenone and benzyl chloride in cold benzene gave an oil, which was converted into the *iodide*; this crystallised from alcohol–ether in minute prisms and from water in clusters of rather irregular prisms, m. p. 160—161° (decomp.) (Found : I, 32·7. $C_{18}H_{22}ONI$ requires I, 32·2%).

Treatment of the iodide with hot aqueous caustic soda produced a dark oil, an ethereal extract of which yielded an almost colourless oil to dilute hydrochloric acid. *α-Dimethylamino-α-benzylpropiophenone picrate* crystallised from aqueous methyl alcohol in short, stout, yellow prisms, m. p. 161—162° (Found : $C_6H_3O_7N_3$, 46·0. $C_{18}H_{21}ON,C_6H_3O_7N_3$ requires $C_6H_3O_7N_3$, 46·2%).

Constitution of α-Dimethylamino-α-benzylpropiophenone.—The base was refluxed for several hours in benzene solution with methyl sulphate (1 equiv.), and the methosulphate, which separated in fine needles on cooling, was heated to boiling with aqueous caustic soda; the oil obtained was removed by ether and gave a phenylhydrazone as fine yellow needles, m. p. 127—128° (softening at 115°) alone or mixed with authentic benzylidenepropiophenonephenylhydrazone (Abell, J., 1901, **79**, 935).

α-Dimethylaminodeoxybenzoin.—Chlorodeoxybenzoin (m. p. 66—68°; compare Schroeter, *Ber.*, 1909, **42**, 2348) was treated with dimethylamine (2—3 mols.) in alcohol at 100—110°, and *α-dimethylaminodeoxybenzoin* obtained as a yellow viscous oil which slowly solidified in the cold to stout prismatic crystals, m. p. 59—61° after washing with ether (Found : N, 5·95. $C_{16}H_{17}ON$ requires N, 5·9%); *hydrochloride*, prismatic needles, m. p. 222—225° (decomp.), from alcohol–ether (Found : HCl, 13·5. $C_{16}H_{17}ON,HCl$ requires HCl, 13·2%).

*α-Dimethylamino*iso*butyrophenone.*—*iso*Butyrophenone may be prepared from *iso*propylmagnesium chloride and benzonitrile. By treatment of α-bromo*iso*butyrophenone (Collet, *Bull. Soc. chim.*, 1897, **17**, 78) with dimethylamine in alcohol at 100—110°, or at 140—160° for 6 hours, only a very small amount of basic material was obtained as a yellow oil, most of the α-bromo*iso*butyrophenone being recovered unchanged. *α-Dimethylamino*iso*butyrophenone picrate* crystallised from methyl alcohol in yellow prisms, m. p. 153—155° (Found : $C_6H_3O_7N_3$, 55·0. $C_{12}H_{17}ON,C_6H_3O_7N_3$ requires $C_6H_3O_7N_3$, 54·5%).

Phenyldibenzylmethylammonium Bromide and Iodide.—Benzylmethylaniline and ω-bromoacetophenone, reacting under the conditions described by Wedekind (*loc. cit.*), gave *phenyldibenzylmethylammonium bromide*, fine colourless needles, m. p. 144—146°, after recrystallisation from alcohol–ether (Wedekind gives decomp., 149—150°) (Found : Br, 21·9. $C_{22}H_{22}ONBr$ requires Br, 20·2%. $C_{21}H_{22}NBr$ requires Br, 21·7%). It was converted into the iodide, colourless prisms, m. p. and mixed m. p. (see below) 132—134°, from alcohol–ether.

Benzylmethylaniline could not be combined with benzyl chloride, and its interaction with benzyl iodide required a much longer time than was used by Jones (J., 1903, **83**, 1410). Phenyldibenzylmethylammonium iodide crystallised from alcohol in prismatic needles, m. p. 133—135° (Jones gives m. p. 134—135°). When it was refluxed with methyl-alcoholic sodium methoxide for an hour, benzylmethylaniline (picrate, m. p. and mixed m. p. 105—107°) and benzyl methyl ether, b. p. 169—170°, were obtained in amounts which accounted satisfactorily for the quaternary salt used. *Benzylmethylaniline picrate*, prepared in ether, crystallised from methyl alcohol in stout yellow prisms, m. p. 105—107° (Found : $C_6H_3O_7N_3$, 54·2. $C_{14}H_{15}N,C_6H_3O_7N_3$ requires $C_6H_3O_7N_3$, 53·8%).

The quaternary iodide was heated at 160—170° with sodamide (2 equivs.), and the reaction mass treated with water. An ethereal extract, treated with dilute hydrochloric acid, deposited αβ-*diphenylethylmethylaniline hydrochloride,* which crystallised from alcohol or water in fine prismatic needles, m. p. 230—232° (Found : HCl, 11·3. $C_{21}H_{21}N,HCl$ requires HCl, 11·3%); αβ-*diphenylethylmethylaniline*, liberated by sodium hydroxide formed leaflets, m. p. 92—93°, from methyl alcohol (Found: N, 5·1. $C_{21}H_{21}N$ requires N, 4·9%). The hydrochloric acid extract, made alkaline with ammonia, yielded benzylmethylaniline (picrate, m. p. and mixed m. p. 105—107°). No unchanged quaternary salt was isolated.

The constitution of αβ-diphenylethylmethylaniline was determined in the same way as that of α-dimethylamino-α-benzylpropiophenone, the methosulphate, however, being decomposed with aqueous methyl-alcoholic caustic soda; the ethereal extract yielded stilbene, m. p. and mixed m. p. 123—125°.

Benzyldimethylallylammonium Bromide.—From allyl bromide and benzyldimethylamine in cold benzene, a viscous oil separated which slowly solidified. The crystals were washed with acetone and obtained as stout, extremely deliquescent prisms, m. p. 98—100° (Found: Br, 31·2. $C_{12}H_{18}NBr$ requires Br, 31·3%); *picrate*, clusters of short yellow prisms, m. p. 108—110°, from acetone (Found: $C_6H_2O_7N_3'$, 56·6. $C_{12}H_{18}N{\cdot}C_6H_2O_7N_3$ requires $C_6H_2O_7N_3'$, 56·4%).

The quaternary *bromide* reacted violently with sodamide at about 80° and a pungent odour was perceptible. The reaction mixture was treated with water, and an ethereal extract then yielded to dilute hydrochloric acid an almost colourless basic oil, b. p. 121—124°/45 mm., in a yield corresponding to some 60% of the quaternary salt used; *picrate*, yellow prismatic needles, m. p. 147—149°, from aqueous methyl alcohol (Found: $C_6H_3O_7N_3$, 57·0. $C_{12}H_{17}N,C_6H_3O_7N_3$ requires $C_6H_3O_7N_3$, 56·7%). No unchanged quaternary salt was obtained.

The basic oil, which may be $CH_2{:}CH{\cdot}CH_2{\cdot}CHPh{\cdot}NMe_2$ or $CH_2{:}CH{\cdot}CH(CH_2Ph){\cdot}NMe_2$, was refluxed in benzene with methyl sulphate (1 mol.), the methosulphate boiled for a short time with caustic soda solution, and the oil obtained extracted, dried, and treated with bromine in chloroform; after removal of the warm solvent by aspiration, phenylbutadiene dibromide remained, m. p. 94° after crystallisation from ligroin (compare Riiber, *Ber.*, 1903, **36**, 1404).

The interaction of benzylmagnesium chloride and $\alpha\gamma$-bisdimethylaminobutyronitrile gave $\beta\delta$-bisdimethylamino-α-phenylbutane, $Me_2N{\cdot}CH_2{\cdot}CH_2{\cdot}CH(NMe_2){\cdot}CH_2Ph$, a pale yellow liquid, b. p. 150—160°/17 mm.; *picrate*, minute yellow prisms, m. p. 193—195° (decomp.), from acetone (Found: $C_6H_3O_7N_3$, 67·2. $C_{14}H_{24}N_2,2C_6H_3O_7N_3$ requires $C_6H_3O_7N_3$, 67·6%).

The rearrangement product (VII) in acetic acid was shaken with activated palladium on charcoal in hydrogen. The oil obtained gave a *hydrobromide* from alcohol–ether in prismatic needles, m. p. 161—163° (Found: HBr, 31·4. $C_{12}H_{19}N,HBr$ requires HBr, 31·4%), depressed in admixture with α-dimethylamino-α-phenylbutane hydrobromide but not with β-dimethylamino-α-phenylbutane hydrobromide. The *p*-bromophenacylobromide also was identical (m. p. and mixed m. p.) with that of β-dimethylamino-α-phenylbutane. The reduced compound, therefore, is β-dimethylamino-α-phenylbutane, and the original degradation product β-dimethylamino-α-phenyl-Δ^{γ}-butylene (VII).

α-Dimethylamino-α-phenylbutane.—The interaction of *n*-propylmagnesium bromide and α-dimethylaminophenylacetonitrile, or of phenylmagnesium bromide and α-dimethylaminovaleronitrile (Henry, *Bull. Acad. roy. Belg.*, 1898, **36**, 245), yielded an almost colourless liquid, b. p. 130—132°/40 mm.

α-*Dimethylamino*-α-*phenylbutane picrate* crystallised from methyl alcohol in yellow leaflets, m. p. 139—140° (Found : $C_6H_3O_7N_3$, 56·0. $C_{12}H_{19}N,C_6H_3O_7N_3$ requires $C_6H_3O_7N_3$, 56·4%), the *hydrobromide* from alcohol–ether in fine needles, m. p. 162—163° (Found : HBr, 31·1. $C_{12}H_{19}N,HBr$ requires HBr, 31·4%), and the p-*bromophenacylobromide*, obtained by refluxing the components for a short time in benzene solution, in minute prisms, m. p. 208—210° (decomp.) (Found : ionisable Br, 17·4. $C_{20}H_{25}ONBr{\cdot}Br$ requires ionisable Br, 17·6%).

β-*Dimethylamino*-α-*phenylbutane.*—α-Dimethylamino-β-phenylpropionitrile (Stevens, Cowan, and MacKinnon, *loc. cit.*) gave with ethylmagnesium iodide an almost colourless liquid, b. p. 133—138°/36 mm. β-*Dimethylamino*-α-*phenylbutane hydrobromide* crystallised from alcohol–ether in prismatic needles, m. p. 161—163° (Found : HBr, 31·3%), and the p-*bromophenacylobromide* in minute prisms, m. p. 188—190° (decomp.) (Found : ionisable Br, 17·4%).

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