Quaternary Ammonium Salts. Part III. The Formation and Decomposition of* p-*Aroylphenylethyldimethylammonium Salts.*

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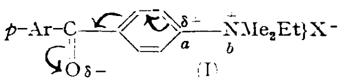
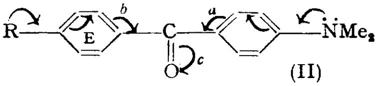
The formation of these salts (I) is governed by the $-M$ effect of the aroyl group, which is the combined effect of the electronic displacements due to the carbonyl and the aryl group. Thermal decomposition of the iodides (I; X = I) leads, with one exception, to formation of the corresponding *N*-ethyl-*N*-methylaminobenzophenones (B). However, decomposition with alcoholic sodium methoxide gives rise to a mixture of the base (B) and the methyl ether (A). The ratio of A to B depends on the nature and on the position of the substituent in the aryl group.

This work deals with the effect of the *p*-aroyl group on the formation and decomposition of quaternary ammonium salts (cf. Part I, Fahim and Galaby, *J.*, 1950, 3529; Part II *). *N*-*p*-Aroylphenyl-*N*-ethyl-*NN*-dimethylammonium ethyl sulphates (I; X = $EtSO_4$) were formed by heating the corresponding tertiary bases with ethyl sulphate at 115—130°. The quaternary salt was estimated as picrate or iodide. Formation of the quaternary salt is inhibited by increase of the $-M$ effect of the aroyl group, which is the combined effect of the electronic displacements due to the carbonyl and the aryl group. The relative ease of formation of the quaternary salt from 4-dimethylamino-4′-methylbenzophenone (II; R = Me) is due to the decrease in the $-M$ effect of the carbonyl group caused by the $+I$ and probably by the hyperconjugation effect of the methyl group.



(I)



(II)

The results showed, however, that process (*a*) (see II) is retarded by electron-repelling substituents, and enhanced by electron-attracting ones in ring E. This explains the low tendency of certain bases to form quaternary ammonium salts, *e.g.*, *p*-dimethylaminobenzaldehyde (cf. Part I, *loc. cit.*) and 4-dimethylamino-4′-nitrobenzophenone.

The final decomposition of the quaternary iodides led [except with (I; Ar = *o*-bromophenyl, X = I), which gives the corresponding dimethylamino-base] to the corresponding *N*-ethyl-*N*-methylaminobenzophenone (B); a similar result was reported in Parts I and II (*locc. cit.*).

However, when the same quaternary ammonium iodides were decomposed by alcoholic sodium methoxide the same *N*-ethyl-*N*-methylaminobenzophenones (B) were obtained mixed

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* Part II, *J.*, 1951, 2761.

with the corresponding methyl ethers (A). The ratio of A to B varied from one iodide to another, depending mainly on the nature and on the position of the substituent already

(A) *p*-Ar·CO·C_6H_4·OMe *p*-Ar·CO·C_6H_4·NMeEt (B)

present in the aryl group. This formation of two products suggests the presence of two positive centres (*a*) and (*b*) in the molecule (I), the ratio A : B being governed by the relative electron densities there. The formation of the ether (A) seems to proceed by the bimolecular nucleophilic substitution mechanism S_N2 (cf. Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 802). The increase in the ratio A : B in the order Ar = *p*- < *m*- < *o*-bromophenyl indicates that the bromine atom is probably operating by its —*I* effect only.

This explains why the *m*-acetyl quaternary iodide gave only the tertiary base when decomposed by alkaline sodium methoxide, since the *m*-oriented acetyl group will impart a very weak positive charge on a carbon atom attached to nitrogen by its —*I* effect, which is not sufficient for the nucleophilic attack by the methoxyl ion.

EXPERIMENTAL

The quaternary ammonium salts (ethosulphate, picrate, and iodide) were prepared as described in Part I (*loc. cit.*). The quaternary ammonium iodides were decomposed by heating them above the m. p. for some time. The resulting tertiary base was extracted with a suitable solvent (ether, alcohol, or toluene) and identified by analysis and by mixed m. p. with the starting tertiary base.

The decomposition with alkali was effected by refluxing the quaternary iodide (0·005 mole) with methyl-alcoholic sodium methoxide [from sodium (0·3 g.) and absolute methyl alcohol (20 ml.)] for 3 hr. Alcohol was then evaporated and the product was extracted with 5N-hydrochloric acid (30 ml.). The neutral product was the corresponding *p*-methoxybenzophenone. The acid solution was made alkaline, and the base liberated was identified by m. p. and mixed m. p. with the product obtained from the thermal decomposition. The recorded ratios of the neutral portion (A) to the base (B) are semiquantitative, since a blank experiment on the base showed that it could be recovered in 95% yield. The yields recorded were the mean of at least two concordant results. A higher concentration of sodium methoxide caused resinification in the case of the 4-*m*-nitrobenzoyl quaternary iodide.

4-Dimethylaminobenzophenone.—p-Benzoylphenylethyldimethylammonium picrate (95% yield from the ethosulphate; 5 hr. at 115—120°), crystallised from alcohol, had m. p. 175—176° (Found: C, 57·4; H, 4·7. $C_{23}H_{22}O_8N_4$ requires C, 57·3; H, 4·6%). The *iodide*, crystallised from methanol–ether, had m. p. 154° (decomp.) (Found: I, 33·3. $C_{17}H_{20}ONI$ requires I, 33·3%). On thermal decomposition, the iodide gave *4-ethylmethylaminobenzophenone*, colourless crystals (from ethanol), m. p. 77—78° (Found: C, 79·6; H, 7·1. $C_{16}H_{17}ON$ requires C, 80·3; H, 7·1%). The alkaline decomposition gave the same compound (B) (0·75 g.), m. p. 76°, and 4-methoxybenzophenone (A) (0·1 g.), m. p. 61° (Ullmann and Goldberg, *Ber.*, 1902, **35**, 2814, gave m. p. 61—62°). The molar ratio B : A was 1 : 0·15.

*4-Dimethylamino-4′-methylbenzophenone.—Ethyldimethyl-*p*-toluoylphenylammonium picrate*, obtained in 90% yield from the ethosulphate (3 hr. at 115—120°) and crystallised from ethanol, had m. p. 178—179° (Found: C, 57·9; H, 4·7. $C_{24}H_{24}O_8N_4$ requires C, 58·1; H, 4·8%). The *iodide*, crystallised from methanol–ether, had m. p. 135° (decomp.) (Found: I, 32·1. $C_{18}H_{22}ONI$ requires I, 32·2%). Thermal decomposition of the iodide gave *4-ethylmethylamino-4′-methylbenzophenone*, colourless crystals (from ethanol), m. p. 103—104° (Found: C, 80·0; H, 7·6. $C_{17}H_{19}ON$ requires C, 80·6; H, 7·5%). The alkaline decomposition gave the same product (0·85 g.) and 4-methoxy-4′-methylbenzophenone (0·2 g.), m. p. 89° (Jones, *J.*, 1936, 1854, gave m. p. 90—91°). Molar ratio B : A = 1 : 0·26.

*4-Dimethylamino-4′-methoxybenzophenone.—4-*p*-Anisoylphenylethyldimethylammonium picrate* (88% from the ethosulphate; 6 hr. at 115—120°), crystallised from water, had m. p. 185° (Found: C, 56·4; H, 4·6. $C_{24}H_{24}O_9N_4$ requires C, 56·3; H, 4·7%); the *iodide*, crystallised from methanol–ether, had m. p. 137—138° (decomp.) (Found: I, 31·3. $C_{18}H_{22}O_2NI$ requires I, 30·9%). On thermal decomposition, the iodide gave *4-ethylmethylamino-4′-methoxybenzophenone*, colourless crystals (from ethanol), m. p. 107° (Found: C, 75·5; H, 7·2. $C_{17}H_{19}O_2N$ requires C, 75·8; H, 7·1%). The alkaline decomposition gave the same compound (0·7 g.), m. p. 106°, and 4 : 4′-dimethoxybenzophenone (0·18 g.), m. p. 144° (Unger, *Annalen*, 1933, **504**, 285, gave m. p. 146°). Molar ratio B : A = 1 : 0·28.

4-*Bromo-4′-dimethylaminobenzophenone*.—4-p-*Bromobenzoylphenylethyldimethylammonium picrate*, formed in 85% yield from the ethosulphate (10 hr. at 120—125°) and crystallised from ethanol, had m. p. 178° (Found: C, 49·2; H, 3·9. $C_{23}H_{21}O_8N_4Br$ requires C, 49·2; H, 3·7%). The colourless *iodide* (from methanol) had m. p. 160° (decomp.) (Found: I, 27·7. $C_{17}H_{19}ONBrI$ requires I, 27·6%). Thermal decomposition gave 4-*bromo-4′-ethylmethylaminobenzophenone*, m. p. 83—84° (from ethanol) (Found: C, 59·9; H, 5·0. $C_{16}H_{16}ONBr$ requires C, 60·4; H, 5·0%). The alkaline decomposition gave the same ketone (0·75 g.), m. p. 82°, and 4-bromo-4′-methoxybenzophenone (0·29 g.), m. p. 154° (Jones, *loc. cit.*, gave m. p. 154°). Molar ratio B : A = 1 : 0·43.

3-*Bromo-4′-dimethylaminobenzophenone*.—This *ketone*, prepared by a method similar to that of Shah, Deshpande, and Chaubal (*J.*, 1932, 642), had m. p. 97·5—98·5° (from ethanol) (Found: C, 59·5; H, 4·8; N, 4·75; Br, 25·8. $C_{15}H_{14}ONBr$ requires C, 59·2; H, 4·6; N, 4·6; Br, 26·3%). 4-m-*Bromobenzoylphenylethyldimethylammonium picrate*, obtained in 80% yield from the ethosulphate (10 hr. at 120—125°) and crystallised from ethanol, had m. p. 156—157° (Found: C, 49·8; H, 3·7. $C_{23}H_{21}O_8N_4Br$ requires C, 49·2; H, 3·7%). The *iodide*, crystallised from methanol, had m. p. 159° (decomp.) (Found: I, 27·2. $C_{17}H_{19}ONBrI$ requires I, 27·6%). Thermal decomposition gave 3-*bromo-4′-ethylmethylaminobenzophenone*, colourless crystals, m. p. 82—83° (Found: C, 60·3; H, 5·2. $C_{16}H_{16}ONBr$ requires C, 60·4; H, 5·0%), and alkaline decomposition gave the same product (0·66 g.), m. p. 82°, and 3-bromo-4′-methoxybenzophenone (0·33 g.), m. p. 80° (Jones, *loc. cit.*, gave m. p. 80°). Molar ratio B : A = 1 : 0·54.

2-*Bromo-4′-dimethylaminobenzophenone*.—Prepared like the 3′-bromo-isomer, and crystallised from methanol, this *ketone* had m. p. 85° (Found: 60·0; H, 4·9; N, 4·4%). 4-o-*Bromobenzoylphenylethyldimethylammonium picrate*, made from the ethosulphate in 96% yield (6 hr. at 120—125°) and crystallised from ethanol, had m. p. 168—169° (Found: C, 49·6; H, 3·7%), and the *iodide* had m. p. 154° (decomp.) (from methanol–ether) (Found: I, 26·9%). Thermal decomposition of the latter gave 2-bromo-4′-dimethylaminobenzophenone, m. p. 85°, and alkaline decomposition gave this ketone (0·35 g.), m. p. 83°, together with 2-bromo-4′-methoxybenzophenone (0·7 g.), m. p. 94° (Jones, *loc. cit.*, gave m. p. 96°). Molar ratio B : A = 1 : 2·18.

4-*Dimethylamino-4′-nitrobenzophenone*.—*Ethyldimethyl*-p-*nitrobenzoylphenylammonium picrate* (75% yield from the ethosulphate; 12—13 hours' heating at 125—130°), crystallised from acetone, had m. p. 201—202° (Found: C, 52·3; H, 4·0. $C_{23}H_{21}O_{10}N_5$ requires C, 52·4; H, 4·0%), and the *iodide* crystallised from methanol–ether in deep red crystals, m. p. 123° (decomp.) (Found: I, 29·4. $C_{17}H_{19}O_3N_2I$ requires I, 29·8%). The thermal decomposition product of the iodide was crystallised from toluene to give 4-*ethylmethylamino-4′-nitrobenzophenone* in deep orange-coloured plates, m. p. 168—170° (Found: 68·2; H, 5·5. $C_{16}H_{16}O_3N_2$ requires C, 67·6; H, 5·6%). The alkaline decomposition gave a mixture of two unidentified products.

4-*Dimethylamino-3′-nitrobenzophenone*.—*Ethyldimethyl*-m-*nitrobenzoylphenylammonium picrate* (83% yield from the ethosulphate; 7 hr. at 120—125°), crystallised from acetone–light petroleum (b. p. 50—60°), had m. p. 136—137° (Found: C, 52·4; H, 4·1. $C_{23}H_{21}O_{10}N_5$ requires C, 52·4; H, 4·0%). The *iodide* formed needles (from methanol–ether), m. p. 153° (decomp.) (Found: I, 29·4. $C_{17}H_{19}O_3N_2I$ requires I, 29·8%). On thermal decomposition it gave 4-*ethylmethylamino-3′-nitrobenzophenone*, yellow plates [from toluene–light petroleum (b. p. 50—60°)], m. p. 136—137° (Found: C, 68·2; H, 5·6%), and alkaline decomposition gave the same product (0·26 g.), m. p. 135°, and 4-methoxy-3′-nitrobenzophenone (0·23 g.), m. p. 91° (Jones, *loc. cit.*, gave m. p. 93°). Molar ratio B : A = 1 : 1.

3-*Acetyl*-NN-*dimethylaniline*.—This was obtained from methyl sulphate and a methyl-alcoholic solution of *m*-aminoacetophenone, b. p. 148°/13 mm. (Rupe, Braun, and von Zembruski, *Ber.*, 1901, **34**, 3522); its *picrate* crystallised from water in yellow needles, m. p. 139—141° (Found: C, 48·7; H, 4·1. $C_{16}H_{16}O_8N_4$ requires C, 49·0; H, 4·1%), and its *ethiodide* (from methanol–ether) had m. p. 175—178° (decomp.) (Found: I, 38·8. $C_{12}H_{18}ONI$ requires I, 39·8%). The quaternary *picrate* (from the iodide) formed yellow crystals, m. p. 125—126° (Found: C, 51·5; H, 4·7. $C_{18}H_{20}O_8N_4$ requires C, 51·4; H, 4·8%), from water. Thermal decomposition of the quaternary iodide gave 3-acetyl-*N*-ethyl-*N*-methylaniline; its *picrate*, crystallised from water, had m. p. 129—131° (Found: C, 50·2; H, 4·3. $C_{17}H_{18}O_8N_4$ requires C, 50·2; H, 4·4%). The alkaline decomposition of the same iodide gave only 3-acetyl-*N*-ethyl-*N*-methylaniline, the picrate of which was identical with that of the thermal decomposition product.

The iodine in the iodides was determined by boiling them with alcoholic silver nitrate.

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