39. *Quaternary Ammonium Salts. Part III.**

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On degradation of the quaternary ammonium salts of two esters, the ester groups were hydrolysed before decomposition affected the ammonium group. Quaternary ammonium derivatives have been prepared from some *as*-diphenylethylenes. Condensation of dimethylaniline with acetyl chloride in presence of fused zinc chloride gave rise to ααα-tris-*p*-dimethylaminophenylethane.

Degradation of *p*-carbomethoxyphenyltrimethylammonium iodide (Tadros and Kamel, unpublished work) and 2-carbethoxy-1 : 1-diphenylethylene-*pp*′-bistrimethylammonium iodide, $CO_2Et{\cdot}CH{:}C(C_6H_4{\cdot}NMe_3I)_2$, with boiling methanolic sodium methoxide gave *p*-dimethylaminobenzoic and bis-*p*-dimethylaminophenylacrylic acid respectively. In view of the electron-attracting properties of the carbomethoxy- and carbethoxy-groups (see, *e.g.*, Zaki, *J.*, 1928, 983) it was expected that the degradation of the above two ester quaternary ammonium iodides would have resulted in the production of some methyl *p*-anisoate and ethyl di-*p*-methoxyphenylacrylate (or the derived sodium salts) as in known cases (Zaki and Tadros, *J.*, 1941, 350; Zaki and Fahim, *J.*, 1942, 271; Tadros and Latif, *J.*, 1949, 3337). It was found that with both the ester quaternary iodides in methanolic sodium methoxide at room temperature the ester group was hydrolysed before degradation affected the ammonium group. This result probably explains the failure to obtain the expected methoxy-esters, since (*a*) the carboxyl ion has little or no attraction for electrons and (*b*) *p*-carboxyphenyltrimethylammonium chloride and sodium ethoxide (Zaki and Tadros, *J.*, 1941, 562) did not give *p*-ethoxybenzoic acid.

The preparative work recorded in the Experimental followed substantially known procedures.

Experimental

M. p.s are uncorrected. Microanalyses are by Drs. Weiler and Strauss, Oxford.

Ethyl ββ-*Bis*-p-*dimethylaminophenylacrylate*.—This was prepared by Reformatsky's reaction (zinc needles, 32·7 g.; dry benzene, 300 c.c.; Michler's ketone, 26·6 g.; ethyl bromoacetate, 33·5 g.). When the reaction subsided, the mixture was refluxed for 3 hours, and the cooled benzene solution decanted from black material. The benzene solution was shaken twice with hydrochloric acid (1 : 1). To the acid extract sodium hydroxide solution was added until the solution became weakly acidic and the precipitated Michler's ketone was filtered off. The

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* Part II, *J.*, 1951, 1890.

filtrate was made alkaline and the semi-solid material thus precipitated was taken up with ether. The ethereal extract was extracted with hydrochloric acid and the acid solution treated with sodium hydroxide as before, this being repeated until the *ester* was obtained free from unchanged ketone. It separated from light petroleum (b. p. 40—60°) in yellow crystals, m. p. 98—100° (Found: C, 74·4; H, 7·7; N, 8·3. $C_{21}H_{26}O_2N_2$ requires C, 74·5; H, 7·7; N, 8·3%). The black residue was dissolved in concentrated hydrochloric acid, the mixture filtered, and the filtrate made alkaline with sodium hydroxide solution. The precipitate thus obtained was filtered off and the process repeated twice. The final material was redissolved in hydrochloric acid and the solution treated with sodium hydroxide drop by drop and the precipitate (5 g.) which separated in the slightly acid medium was collected. This separated after several crystallisations from benzene–light petroleum (b. p. 60—80°) in almost colourless crystals, m. p. 211°. It proved to be tetrakis-*p*-dimethylaminophenylpinacol, showing no depression in m. p. on admixture with an authentic sample (Gomberg and Bachmann, *J. Amer. Chem. Soc.*, 1927, **49**, 236) (Found: C, 76·2; H, 7·6; N, 10·4. Calc. for $C_{34}H_{42}O_2N_4$: C, 75·8; H, 7·7; N, 10·4%). The slightly acid filtrate was made alkaline and more acrylic ester was obtained (total yield, 10%).

ββ-*Bis*-p-*dimethylaminophenylacrylic Acid.*—(*a*) The ester (3 g.) and methyl-alcoholic sodium methoxide (from 1 g. of sodium in 20 c.c. of methyl alcohol) was refluxed for 2 hours. The alcohol was distilled off and the residue taken up with water and filtered off. Dilute acetic acid was added drop by drop to the filtrate whereupon the *acid* separated. It crystallised from benzene in greenish crystals, m. p. 172—173° (Found: C, 73·7; H, 7·1; N, 9·2. $C_{19}H_{22}O_2N_2$ requires C, 73·6; H, 7·1; N, 9·0%).

(*b*) *as*-Bis-*p*-dimethylaminophenylethylene (2·5 g.) and oxalyl chloride (4·5 g.) were refluxed for 2 hours. Excess of oxalyl chloride was removed *in vacuo* and the semi-solid dark residue was treated with excess of 10% sodium carbonate solution. The mixture was boiled and then filtered. The filtrate was neutralised with dilute acetic acid whereupon the acid separated (yield, 2%).

ααα-*Tris*-p-*dimethylaminophenylethane.*—Acetyl chloride (10 g.), dimethylaniline (50 g.), and fused zinc chloride (5 g.) were heated on the water-bath with stirring for 4 hours, decomposed with water, made alkaline, and steam-distilled and the semi-solid black *triamine* was crystallised several times from benzene–ether from which it separated in almost colourless crystals, m. p. 205—206° (30%) (Found: C, 80·4; H, 8·7; N, 10·3. $C_{26}H_{33}N_3$ requires C, 80·6; H, 8·5; N, 10·8%).

Tetrakis-p-*dimethylaminophenylethylene.*—To the Grignard reagent prepared from magnesium (5·8 g.), *iso*propyl iodide (42·5 g.), and ether (200 c.c.), Michler's ketone (13·3 g.) was added (cf. Lemoult, *Compt. rend.*, 1912, **154**, 1622). The solution was stirred for 4 hours on the water-bath, decomposed with aqueous ammonium chloride, and extracted with ether. A part of the residue left after removal of the ether dissolved in alcohol and proved to be 1 : 1-bis-*p*-dimethylaminophenyl*iso*butene. The alcohol-insoluble *tetra-amine* (3 g.) separated from benzene–light petroleum (b. p. 60—80°) in greenish crystals, m. p. 296° (Found: C, 80·4; H, 7·9; N, 11·3. Calc. for $C_{34}H_{40}N_4$: C, 80·9; H, 7·9; N, 11·1%).

as-*Bis*-p-*dimethylaminophenylethylene.*—To the Grignard reagent prepared from magnesium (1·2 g.), *p*-bromodimethylaniline (9·7 g.), and ether (100 c.c.), redistilled ethyl acetate (5 g.) was added. After 2 hours' stirring, the solution was left overnight and then decomposed with aqueous ammonium chloride. Ether was distilled off and the residue gave after several crystallisations from alcohol 50 mg. of the pure ethylene, m. p. 118° alone or mixed with an authentic sample.

Oxidation of 1 : 1-*Diphenylethylene*-pp′-*bistrimethylammonium Chloride.*—A solution of the salt (1·0 g.) in concentrated nitric acid (20 c.c.; *d* 1·42) was refluxed on a sand-bath for 4 hours, then evaporated to dryness on the water-bath, and the residue was treated twice with 10 c.c. of concentrated hydrochloric acid and evaporated almost to dryness after each treatment. The dipicrate prepared from the residue proved to be benzophenone-*pp*′-bis(trimethylammonium picrate) (Tadros and Latif, *loc. cit.*), m. p. and mixed m. p. 206—208°.

Quaternary Ammonium Salts of as-*Diphenylethylenes.*—*The dipicrates.* The base (1 mol.) and methyl sulphate (4 mol.) were heated on the water-bath, the vigorous exothermic reaction being controlled by cooling. The mixture was then heated on the water-bath for 3 hours. The methosulphates were not isolated and were converted into the dipicrates from which the dichlorides, dibromides, di-iodides (also obtained by refluxing for several hours the base with excess of methyl iodide in methyl alcohol and then distilling off the solvent and excess of methyl iodide), and diperchlorates were obtained as previously reported (cf. Zaki and Tadros, *loc. cit.*).

Products are reported in the Table. They are soluble in water and alcohol, but insoluble in ether, benzene, or acetone. The dichlorides, dibromides, and di-iodides are hygroscopic and retain solvent of crystallisation (particularly alcohol) which could only be removed after heating at 100° for considerable time *in vacuo* over P_2O_5 or $CaCl_2$.

p-Carbomethoxyphenyltrimethylammonium iodide, m. p. 170° (cf. Willstätter and Kahn, *Ber.*, 1904, **37**, 401), was prepared from the ester (5 g.) and methyl iodide (50 g.) on the water-bath for 10 hours. The derived *picrate*, m. p. 180°, crystallised from alcohol in yellow crystals (Found: C, 48·3; H, 4·5; N, 13·9. $C_{17}H_{18}O_9N_4$ requires C, 48·3; H, 4·3; N, 13·3%). *p*-Carboxyphenyltrimethylammonium chloride, m. p. 240° (decomp.), which was obtained from *p*-carboxyphenyltrimethylammonium picrate, m. p. 206—207° (Zaki and Tadros, *loc. cit.*), was also obtained on treatment of the ester picrate with concentrated hydrochloric acid.

Decomposition of the quaternary ammonium salts. A mixture of the halide (5 g.) and methyl-alcoholic sodium methoxide (20 c.c.; 2·5 atoms of sodium per 1 mol. of the salt) was refluxed for 4 hours on the water-bath. Methyl alcohol was evaporated off and the residue treated with hydrochloric acid. A clear solution was obtained which was neutralised with sodium hydroxide drop by drop until a precipitate was formed. This separated from alcohol and was proved by m. p. and mixed m. p. to be the corresponding tertiary base.

The same result was obtained on decomposition with alcoholic sodium ethoxide, phenoxide, or benzyloxide.

		Found, %:					Required, %:			
Salt	M. p.	C	H	N	Hal	Formula	C	H	N	Hal
1 : 1-*Diphenylethylene*-pp′-*bistrimethylammonium*										
picrate	216—218°	51·0	4·3	14·3	—	$C_{32}H_{32}O_{14}N_8$	51·1	4·3	14·9	—
chloride	122—135 *†	65·1	7·7	7·8	18·2	$C_{20}H_{28}N_2Cl_2$	65·4	7·6	7·6	19·4
bromide	218 *	52·3	6·2	6·0	34·9	$C_{20}H_{28}N_2Br_2$	52·6	6·1	6·1	35·1
iodide	198 *	43·4	5·5	4·9	45·9	$C_{20}H_{28}N_2I_2$	43·6	5·1	5·1	46·2
perchlorate ...	242 *	48·1	5·7	6·1	14·8	$C_{20}H_{28}N_2Cl_2O_8$	48·5	5·7	5·7	14·4
1 : 1-*Diphenyl-2-methylethylene*-pp′-*bistrimethylammonium*										
picrate	181—184	51·6	4·5	14·2	—	$C_{33}H_{34}O_{14}N_8$	51·7	4·4	14·6	—
chloride	164 *	66·6	8·1	6·8	18·3	$C_{21}H_{30}N_2Cl_2$	66·1	7·9	7·4	18·6
bromide	180 *	53·1	6·1	6·2	34·5	$C_{21}H_{30}N_2Br_2$	53·6	6·4	5·9	34·1
iodide	160 *	45·1	5·1	5·5	44·7	$C_{21}H_{30}N_2I_2$	44·7	5·3	5·0	45·0
perchlorate ...	250—252 *	50·0	6·0	5·3	14·7	$C_{21}H_{30}N_2Cl_2O_8$	49·5	5·9	5·5	13·9
1 : 1-*Diphenyl-2-ethylethylene*-pp′-*bistrimethylammonium*										
picrate	148—150	51·9	4·3	14·5	—	$C_{34}H_{36}O_{14}N_8$	52·3	4·6	14·4	—
chloride	169 *	66·6	8·0	6·8	17·9	$C_{22}H_{32}N_2Cl_2$	66·8	8·1	7·1	18·0
bromide	231—232 *	54·3	6·1	6·2	32·8	$C_{22}H_{32}N_2Br_2$	54·5	6·6	5·9	33·0
iodide	224 *	45·4	5·5	4·3	43·5	$C_{22}H_{32}N_2I_2$	45·6	5·5	4·9	43·9
perchlorate ...	248—250 *	50·1	6·1	5·2	13·8	$C_{22}H_{32}O_8N_2Cl_2$	50·5	6·1	5·4	13·6
1 : 1-*Diphenyl*-2 : 2-*dimethylethylene*-pp′-*bistrimethylammonium*										
picrate	205—206	52·4	4·3	14·3	—	$C_{34}H_{36}O_{14}N_8$	52·3	4·6	14·4	—
chloride	143 *	66·5	8·3	6·8	17·8	$C_{22}H_{32}N_2Cl_2$	66·8	8·1	7·1	18·0
bromide	200—201 *	54·1	6·8	6·2	33·5	$C_{22}H_{32}N_2Br_2$	54·5	6·6	5·8	33·0
iodide	218 *	45·9	5·6	4·5	43·6	$C_{22}H_{32}N_2I_2$	45·6	5·5	4·9	43·9
perchlorate ...	280 *	50·1	6·1	5·3	13·9	$C_{22}H_{32}O_8N_2Cl_2$	50·5	6·1	5·4	13·6
2-*Carbethoxy*-1 : 1-*diphenylethylene*-pp′-*bistrimethylammonium*										
iodide	174	44·4	5·1	4·4	40·6	$C_{23}H_{32}O_2N_2I_2$	44·5	5·1	4·5	40·8
picrate	85—90	—	—	13·7	—	$C_{35}H_{36}O_{16}N_8$	—	—	13·6	—
2-*Carboxy*-1 : 1-*diphenylethylene*-pp′-*bistrimethylammonium*										
picrate	122—124	—	—	13·8	—	$C_{33}H_{32}O_{16}N_8$	—	—	14·1	—

* With decomp. Most of the salts become green some degrees below the m. p. † Extremely hygroscopic and retains HCl, the latter being removed *in vacuo* at 100° over P_2O_5.

Hydrolyses of the ester group before decomposition of the quaternary ammonium group. (*a*) Methyl-alcoholic sodium methoxide (from 0·1 g. of sodium in 20 c.c. of methyl alcohol) containing *p*-carbomethoxyphenyltrimethylammonium iodide (1 g.) was left at room temperature (25—30°). A sample was daily left to evaporate at room temperature and the residue converted into the picrate. The picrate obtained after 4 days had m. p. 206—208° alone or mixed with *p*-carboxyphenyltrimethylammonium picrate (Zaki and Tadros, *loc. cit.*). (*b*) 2-Carbethoxy-1 : 1-diphenylethylene-*pp*′-bistrimethylammonium iodide, when treated as above, gave the carboxymethylene salt, m. p. 122—124°.

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