697. *Quaternary Ammonium Salts. The Formation and Decomposition of Ethyldimethylanilinium Salts. The Synthesis of* N-*Ethyl*-N-*methylanilines.*

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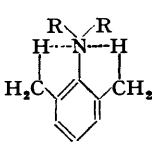
Preparation of some quaternary ethyldimethylanilinium salts containing substituted phenyl groups is described. The nature as well as the position of the substituent markedly influence both their formation and their decomposition. The readiness with which these salts are decomposed provides a valuable method for the synthesis of *N*-ethyl-*N*-methylanilines.

Formation of Quaternary Ammonium Salts.—All the quaternary ammonium salts investigated in this work were prepared by the action of ethyl sulphate on the dimethylanilines. Tertiary bases with substituents such as methyl, alkoxyl, or halogen react readily. Dimethyl-*p*-toluidine, in particular, added ethyl sulphate very smoothly, possibly owing to the relatively high electron-releasing power of the methyl group (cf. Baker and Nathan, *J.*, 1935, 1844).

Tertiary bases, with substituents such as NO_2, combined less readily. Of the three isomeric dimethylnitroanilines the *ortho*-isomer failed to give the quaternary ammonium salt when heated with ethyl sulphate or iodide. The nitro-group, especially in the *ortho*-position, generally hindered formation of quaternary salts (cf. Friedländer, *Monatsh.*, 1898, **19**, 627; Zaki and Fahim, *J.*, 1942, 270). *p*-Dimethylaminobenzaldehyde gave a very poor yield of the quaternary ammonium salt, probably owing to the large amount of tar formed.

Dimethyl-3-nitro-*p*-toluidine with excess of ethyl sulphate at 120—130° gave a product from which a picrate was isolated. This was not the quaternary picrate, but has not yet been identified.

The failure of *ortho*-substituted tertiary bases to give quaternary salts could be attributed to chelation. For example, the annexed structure is suggested for xylidine which does not add methyl iodide (Fischer and Windaus, *Ber.*, 1900, **33**, 345). Evans and his co-workers (*J.*, 1939, 1348) also discussed the possible existence of a semi-bond between the two nitrogen atoms of dimethyl-*o*-nitroaniline.



Decomposition of Quaternary Ammonium Salts.—The thermal decomposition of the ethyldimethylanilinium salts led to the tertiary base as usual, with the loss of the alkyl halide. Ten ethyldimethylanilinium halides decomposed with loss of methyl halide and formation of the corresponding *N*-ethyl-*N*-methylanilines. Ethyldimethyl-α- and -β-naphthylammonium iodides similarly decomposed to give *N*-ethyl-*N*-methyl-α- and -β-naphthylamine, respectively. On the other hand *N*-ethyl-*o*- and -*p*-ethoxy-*NN*-dimethylanilinium halides and ethyldimethyl-*p*-toluidinium halides gave a mixture of the corresponding *NN*-dimethyl- and *N*-ethyl-*N*-methyl-anilines.

In the ethyldimethylanilinium series a methyl group (which was the smallest group) left the molecule readily on thermal decomposition. This had been deduced by other investigators (Collie and Schryver, *J.*, 1890, 767; von Braun, *Annalen*, 1911, **382**, 1); but it proved not to be

always true, for in the diethylmethylanilinium series (unpublished work) the ethyl group tended to be the more readily eliminated. It is concluded only that in thermal decomposition of these quaternary salts the formation of the mixed alkyl-aromatic tertiary bases predominated.

Thermal decomposition of *N*-ethyl-2-methoxy-*NN*-dimethyl-4-nitroanilinium iodide gave 2-dimethylamino-5-nitrophenol.

With the exception of *N*-ethyl-2-methoxy-*NN*-dimethyl-4-nitro- and ethyldimethyl-4-nitroanilinium halides, which on decomposition by sodium ethoxide gave the corresponding phenetole derivatives, the quaternary ammonium salts investigated were decomposed by the alkali in the same way as by heat.

Experimental.

(The *compounds* prepared are recorded in the annexed tables.)

The following procedures were used in the preparation of ethyldimethylanilinium salts. The ethyl ethosulphates, which were hygroscopic or viscid, were prepared by heating the tertiary base with ethyl sulphate. The picrate, iodide, and perchlorate were prepared by adding to the fairly concentrated solution of the ethosulphate a saturated solution of picric acid, potassium iodide, and sodium perchlorate, respectively.

Compound.	M. p.	Crystn. solvent.	Found, %. C.	H.	N.	Formula.	Required, %. C.	H.	N.
N-Ethyl-*p*-methoxy-*NN*-dimethylanilinium picrate	148—149°	H_2O	50·3	4·9	13·6	$C_{17}H_{20}O_8N_4$	50·0	4·9	13·7
iodide	155—156	EtOH–Et_2O	(I, 41·7)			$C_{11}H_{16}ONI$	(I, 41·4)		
perchlorate	91—92	H_2O	(Cl, 12·3)			$C_{11}H_{16}O_5NCl$	(Cl, 12·7)		
Dimethyl-*p*-anisidine picrate	137—138	,,	47·5	4·1	14·5	$C_{15}H_{16}O_8N_4$	47·4	4·2	14·7
N-Ethyl-*N*-methyl-*p*-anisidine picrate	117—118	,,	48·6	4·7	14·2	$C_{16}H_{18}O_8N_4$	48·7	4·6	14·2
N-Ethyl-*o*-methoxy-*NN*-dimethylanilinium picrate	111—112	H_2O	50·2	4·9	13·6	$C_{17}H_{20}O_8N_4$	50·0	4·9	13·7
iodide	191—192	EtOH–Et_2O	(I, 41·2)			$C_{11}H_{16}ONI$	(I, 41·4)		
perchlorate	185—186	H_2O	(Cl, 12·7)			$C_{11}H_{16}O_5NCl$	(Cl, 12·7)		
Dimethyl-*o*-anisidine picrate	142—143	,,	47·4	4·1	14·6	$C_{15}H_{16}O_8N_4$	47·4	4·2	14·7
N-Ethyl-*N*-methyl-*o*-anisidine picrate	141—142	,,	48·7	4·5	13·9	$C_{16}H_{18}O_8N_4$	48·7	4·6	14·2
p-Ethoxy-*N*-ethyl-*NN*-dimethylanilinium picrate	109—110	H_2O	51·2	5·2	13·3	$C_{18}H_{22}O_8N_4$	51·2	5·2	13·3
chloride	85 (indef.)	$COMe_2$	(Cl, 15·4)			$C_{12}H_{20}ONCl$	(Cl, 15·5)		
perchlorate	93—94	H_2O	(Cl, 12·3)			$C_{12}H_{20}O_5NCl$	(Cl, 12·1)		
Dimethyl-*p*-phenetidine picrate	134—135	,,	48·9	4·6	14·2	$C_{16}H_{18}O_8N_4$	48·7	4·6	14·2
o-Ethoxy-*N*-ethyl-*NN*-dimethylanilinium picrate	132—133	H_2O	51·2	5·3	13·3	$C_{18}H_{22}O_8N_4$	51·2	5·2	13·3
iodide	179—180	EtOH–Et_2O	(I, 39·4)			$C_{12}H_{20}ONI$	(I, 39·6)		
perchlorate	184—185	H_2O	(Cl, 11·7)			$C_{12}H_{20}O_5NCl$	(Cl, 12·1)		
Dimethyl-*o*-phenetidine picrate	180 (decomp.)	,,	48·5	5·1	14·5	$C_{16}H_{18}O_8N_4$	48·7	4·6	14·2
N-Ethyl-*N*-methyl-*o*-phenetidine picrate	159—160	,,	49·7	4·7	13·4	$C_{17}H_{20}O_8N_4$	50·0	4·9	13·7
Ethyldimethyl-*p*-toluidinium picrate	144—145	H_2O	51·5	4·9	14·5	$C_{17}H_{20}O_7N_4$	52·0	5·1	14·3
iodide [1]	150—155	MeOH–Et_2O	(I, 44·0)			$C_{11}H_{18}NI$	(I, 43·6)		
perchlorate	169—710	$COMe_2$–pet.*	(Cl, 13·5)			$C_{11}H_{18}O_4NCl$	(Cl, 13·5)		
Ethyldimethyl-*m*-toluidinium picrate	131—132	H_2O	52·0	5·1	14·4	$C_{17}H_{20}O_7N_4$	52·0	5·1	14·3
iodide	115 (indef.)	EtOH–Et_2O	(I, 43·9)			$C_{11}H_{18}NI$	(I, 43·6)		
perchlorate	59—60	H_2O	(Cl 13·7)			$C_{11}H_{18}O_4NCl$	(Cl, 13·5)		
N-Ethyl-*N*-methyl-*m*-toluidine picrate	108	aq. EtOH	50·8	4·8	15·0	$C_{16}H_{18}O_7N_4$	50·8	4·8	14·8
Ethyldimethyl-*o*-toluidinium picrate	110—111	H_2O	52·0	5·1	13·8	$C_{17}H_{20}O_7N_4$	52·0	5·1	14·3
iodide	186—187	EtOH–Et_2O	(I, 43·5)			$C_{11}H_{18}NI$	(I, 43·6)		
perchlorate	151—152	H_2O	(Cl, 13·4)			$C_{11}H_{18}O_4NCl$	(Cl, 13·5)		
N-Ethyl-*N*-methyl-*o*-toluidine picrate	139	aq EtOH	50·7	4·6	15·0	$C_{16}H_{18}O_7N_4$	50·8	4·8	14·8

* Pet. = light petroleum.

Compound.	M. p.	Crystn. solvent.	Found, %. C.	H.	N.	Formula.	Required, %. C.	H.	N.
p-Bromophenyl-*N*-ethyl-*NN*-dimethylanilinium picrate	150°	H_2O	42·1	3·8	12·4 (Br, 17·6)	$C_{16}H_{17}O_7N_4Br$	42·0	3·7	12·3 (Br, 17·5)
iodide [2]	192	EtOH–Et_2O	—	—	—	—	—	—	—
perchlorate	198—199	H_2O	(total halogen, 35·5)			$C_{10}H_{15}O_4NClBr$	(total halogen 35·2)		
p-Bromo-*NN*-dimethylaniline picrate	136—137	,,	39·3	3·4	13·0 (Br, 18·5)	$C_{14}H_{13}O_7N_4Br$	39·2	3·0	13·1 (Br, 18·6)
m-Bromo-*N*-ethyl-*NN*-dimethylanilinium picrate	123	H_2O	41·9	3·7	12·3 (Br, 17·6)	$C_{16}H_{17}O_7N_4Br$	42·0	3·7	12·3 (Br, 17·5)
iodide	179	MeOH–Et_2O	(total halogen, 58·0)			$C_{10}H_{15}NBrI$	(total halogen, 58·1)		
perchlorate	113	H_2O	(total halogen, 35·3)			$C_{10}H_{15}O_4NClBr$	(total halogen, 35·2)		
m-Bromo-*NN*-dimethylaniline picrate [3]	137—138	aq. EtOH	39·2	3·0	12·8 (Br, 18·4)	$C_{14}H_{13}O_7N_4Br$	39·2	3·0	13·1 (Br, 18·6
m-Bromo-*N*-ethyl-*N*-methylaniline picrate	132	,,	40·6	3·3	12·6 (Br, 18·0)	$C_{15}H_{15}O_7N_4Br$	40·6	3·4	12·6 (Br, 18·1)
o-Chloro-*N*-ethyl-*NN*-dimethylanilinium picrate	128—129	H_2O	46·7	4·0	13·6 (Cl, 8·2)	$C_{16}H_{17}O_7N_4Cl$	46·5	4·1	13·6 (Cl, 8·6)
iodide	156—157	$COMe_2$–pet.*	(total halogen, 51·5)			$C_{10}H_{15}NClI$	(total halogen, 52·2)		
perchlorate	122—123	H_2O	(Cl, 25·2)			$C_{10}H_{15}O_4NCl_2$	(Cl, 25·0)		
o-Chloro-*N*-ethyl-*N*-methylaniline picrate	118	aq. EtOH	45·0	3·7	14·4 (Cl, 8·7)	$C_{15}H_{15}O_7N_4Cl$	45·2	3·8	14·1 (Cl, 8·9)
Ethyldimethyl-*p*-nitroanilinium picrate	154—155	H_2O	45·7	3·7	16·2	$C_{16}H_{17}O_9N_5$	45·4	4·0	16·5
iodide	157—167	MeOH	(I, 40·0)			$C_{10}H_{15}O_2N_2I$	(I, 39·4)		
perchlorate	169	H_2O	(Cl, 11·9)			$C_{10}H_{15}O_6N_2Cl$	(Cl, 12·1)		
N-Ethyl-*N*-methyl-*p*-nitroaniline	88	EtOH	59·9	6·6	15·4	$C_9H_{12}O_2N_2$	60·0	6·7	15·6
Ethyldimethyl-*m*-nitroanilinium picrate	150	H_2O	45·5	3·8	16·3	$C_{16}H_{17}O_9N_5$	45·4	4·0	16·5
iodide	166—167	MeOH	(I, 39·9)			$C_{10}H_{15}O_2N_2I$	(I, 39·4)		
perchlorate	181—182	H_2O	(Cl, 12·5)			$C_{10}H_{15}O_6N_2Cl$	(Cl, 12·1)		
N-Ethyl-*N*-methyl-*m*-nitroaniline picrate	126—127	aq. EtOH	44·0	3·4	17·4	$C_{15}H_{15}O_9N_5$	44·0	3·7	17·1
N-Ethyl-*p*-formyl-*NN*-dimethylanilinium picrate	142—143	H_2O	50·1	4·4	13·5	$C_{17}H_{18}O_8N_4$	50·2	4·4	13·8
N-Ethyl-2-methoxy-*NN*-dimethyl-4-nitroanilinium picrate	136—137	H_2O	45·3	4·2	15·5	$C_{17}H_{19}O_{10}N_5$	45·0	4·2	15·5
iodide	157	MeOH	(I, 36·3)			$C_{11}H_{17}O_3N_2I$	(I, 36·1)		
perchlorate	180	H_2O	(Cl, 11·1)			$C_{11}H_{17}O_7N_2Cl$	(Cl, 10·9)		
2-Dimethylamino-5-nitrophenol	100—101	Pet.*	52·6	5·5	15·1	$C_8H_{10}O_3N_2$	52·7	5·5	15·4
Ethyl-2 : *N* : *N*-trimethyl-5-nitroanilinium picrate	165	H_2O	46·7	4·3	16·1	$C_{17}H_{19}O_9N_5$	46·7	4·3	16·0
iodide	175	MeOH–Et_2O	(I, 38·2)			$C_{11}H_{17}O_2N_2I$	(I, 37·8)		
perchlorate	208—209	H_2O	(Cl, 11·8)			$C_{11}H_{17}O_6N_2Cl$	(Cl, 11·5)		
Dimethyl-4-nitro-*o*-toluidine picrate	167—168	,,	44·2	3·9	16·8	$C_{15}H_{15}O_9N_5$	44·0	3·7	17·1
N-Ethyl-*N*-methyl-4-nitro-*o*-toluidine picrate	154	aq. EtOH	45·5	4·1	16·8	$C_{16}H_{17}O_9N_5$	45·4	4·0	16·5
Ethyl-2 : *N* : *N*-trimethyl-*p*-nitroanilinium picrate	160—161	H_2O	46·8	4·3	16·1	$C_{17}H_{19}O_9N_5$	46·7	4·3	16·0
Dimethyl-5-nitro-*o*-toluidine picrate	135	,,	44·0	3·8	16·9	$C_{15}H_{15}O_9N_5$	44·0	3·7	17·1
Dimethyl-3-nitro-*p*-toluidine picrate	128	H_2O	43·9	3·7	16·8	$C_{15}H_{15}O_9N_5$	44·0	3·7	17·1
Ethyldimethyl-α-naphthylammonium picrate	100—101	H_2O	56·3	4·8	13·2	$C_{20}H_{20}O_7N_4$	56·1	4·7	13·1
iodide	166—167	MeOH–Et_2O	(I, 38·9)			$C_{14}H_{18}NI$	(I, 38·8)		
perchlorate	175	H_2O	(Cl, 11·8)			$C_{14}H_{18}O_4NCl$	(Cl, 11·9)		

Compound.	M. p.	Crystn. solvent.	Found, %. C.	H.	N.	Formula.	Required, %. C.	H.	N.
N-Ethyl-*N*-methyl-α-naphthylamine picrate	145°	aq. EtOH	55·0	4·4	13·3	$C_{19}H_{18}O_7N_4$	55·1	4·3	13·5
Ethyldimethyl-β-naphthylammonium picrate	133—134	aq. EtOH	56·0	4·6	12·8	$C_{20}H_{20}O_7N_4$	56·1	4·7	13·1
iodide [4]	154—155	MeOH–Et_2O	—	—	—	—	—	—	—
perchlorate	137—138	H_2O	(Cl, 11·8)			$C_{14}H_{18}O_4NCl$	(Cl, 11·9)		
N-Ethyl-*N*-methyl-β-naphthylamine picrate	188—189	$COMe_2$–H_2O	55·0	4·2	13·6	$C_{19}H_{18}O_7N_4$	55·1	4·3	13·5

[1] Doja (*J. Indian Chem. Soc.*, 1936, **13**, 528) gave m. p. 196°. [3] Jones and Hill (*J.*, 1907, 2083) gave m. p. 189°. [3] Vorländer and Siebert (*Ber.*, 1919, **52**, 295) gave m. p. 134—138°; Hodgson and Nicholson (*J.*, 1941, 766) gave m. p. 182°. [4] Reychler (*Bull. Soc. chim.*, 1902, **27**, 971) gave m. p. 152°.

Thermal decomposition of the quaternary ammonium salt (generally the iodide) was effected by heating the salt above its m. p. for some time. Decomposition with alkali was effected by heating the quaternary salt and slightly more than two equivs. of metallic sodium in absolute alcohol under reflux for 3 hours. The tertiary base left behind in both cases was identified generally as the picrate.

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