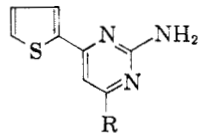
TABLE I

PYRIMIDINES OF TYPE

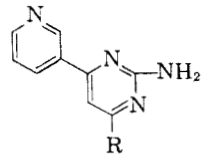


R	Molecular Formula	M.P.	% Nitrogen Calcd.	% Nitrogen Found[a]	Molecular Formula	M.P.[b]	% Nitrogen Calcd.	% Nitrogen Found[a]
—CH_3	$C_9H_9N_3S$	172°	21.97	21.50	$C_{15}H_{12}N_6O_7S$	243–248°	19.93	19.94
—C_2H_5	$C_{10}H_{11}N_3S$	139°	20.47	20.32	$C_{16}H_{14}N_6O_7S$	233–237°	19.34	19.25
—*n*-C_3H_7	$C_{11}H_{13}N_3S$	116°	19.16	19.13	$C_{17}H_{16}N_6O_7S$	213–214°	18.74	18.81
—*i*-C_3H_7	$C_{11}H_{13}N_3S$	115°	19.16	19.03	$C_{17}H_{16}N_6O_7S$	220–222°	18.74	18.65
n-C_4H_9	$C_{12}H_{15}N_3S$	79°	18.01	18.27	$C_{18}H_{18}N_6O_7S$	196–199°	18.17	18.00–
i-C_4H_9	$C_{12}H_{15}N_3S$	110°	18.01	18.17	$C_{18}H_{18}N_6O_7S$	175–176°	18.17	17.92
n-C_5H_{11}	$C_{13}H_{17}N_3S$	82°	16.99	16.88	$C_{19}H_{20}N_6O_7S$	163–164°	17.64	17.60
—OH	$C_8H_7N_3OS$	306° dec.	21.74	21.95	$C_8H_7N_3O_8S$	241–248°	19.90	19.72

[a] Nitrogen analyses by Micro-Tech Laboratories, Skokie, Ill. [b] Melting points of the picrates were taken in a sealed evacuated capillary tube, are uncorrected, and all melt with decomposition.

TABLE II

PYRIMIDINES OF TYPE



R	Molecular Formula	M.P.	% Nitrogen Calcd.	% Nitrogen Found[a]	Molecular Formula	M.P.[b]	% Nitrogen Calcd.	% Nitrogen Found[a]
—CH_3	$C_{10}H_{10}N_4$	205°	30.09	29.83	$C_{16}H_{13}N_7O_7$	245–249°	23.60	23.75
t-Butyl	$C_{13}H_{16}N_4$	138°	24.43	24.43	$C_{19}H_{19}N_7O_7$	210–212°	21.43	21.34
i-Butyl	$C_{13}H_{16}N_4$	149°	24.66	24.66	$C_{19}H_{19}N_7O_7$	206–207°	21.43	21.38
Phenyl	$C_{15}H_{12}N_4$	166°	22.57	22.57	$C_{21}H_{15}N_7O_7$	223–225°	20.53	20.78

[a] Nitrogen analyses by Micro-Tech Laboratories, Skokie, Ill. [b] Melting points of the picrates were taken in a sealed evacuated capillary tube, are uncorrected, and all melt with decomposition.

Preparation of I. A 3.5-g. sample of ethylnicotinoylacetate and 5 g. of guanidine carbonate was heated at 140° for 1 hr. The molten mass was allowed to cool and recrystallized from 80% alcohol, and light colored crystals were obtained melting at 283–288° dec.

Anal. Calcd. for $C_9H_{10}O_2N_4$: N, 27.37. Found: N, 27.17.

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Quaternary Ammonium Salts. IV. Synthesis and Decomposition of *N*-Methyl-*N*,*N*-di-*n*-propylanilinium Salts

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In continuation of the research done by Fahim and Galaby,[1] Fahim and Fleifel,[2] and Fahim *et al.*,[3] we now have studied the synthesis and decomposition of some *N*-methyl-*N*,*N*-di-*n*-propylanilinium salts. The tertiary bases, used as starting materials in this investigation, were prepared by propylation of the corresponding primary aromatic amines with tri-*n*-propyl phosphate as recommended by Bilman *et al.*[4] for the preparation of dipropylaniline. The dipropylanilines obtained were identified through the picrate. The boiling points and the yields of the tertiary bases are recorded in Table I.

TABLE I
TERTIARY BASES

Primary aromatic amine	Boiling point of the dipropylaniline	Yield, %
p-Anisidine	158–160/15 mm.	70
o-Anisidine	142–145/15 mm.	45
p-Phenetidine	166–168/60 mm.	44
o-Phenetidine	173–175/60 mm.	45
p-Toluidine	165–168/65 mm.	51
m-Toluidine	170–173/60 mm.	51
o-Toluidine	144–146/55 mm.	58

(1) H. A. Fahim and M. Galaby, *J. Chem. Soc.*, 3529 (1950).
(2) H. A. Fahim and A. M. Fleifel, *J. Chem. Soc.*, 2761 (1951).
(3) H. A. Fahim, F. G. Baddar, and M. Galaby, *J. Chem. Soc.*, 317 (1955).
(4) J. H. Bilman, A. Radike, and A. W. Mundy, *J. Am. Chem. Soc.*, **64**, 2977 (1942).

TABLE II

QUATERNARY IODIDES, QUATERNARY PICRATES, PICRATES OF STARTING MATERIALS AND PRODUCTS

Starting Material	Compound	Solvent[c]	M.P.	Yield, %	Formula	Carbon, % Calcd. (Found)	Hydrogen, % Calcd. (Found)	Iodine, % Calcd. (Found)
Ia	*N*-Methyl-*N*,*N*-di-*n*-propyl-*p*-anisidinium iodide	A	142–143	100[a]	$C_{14}H_{24}ONI$			36.39 (36.3)
	N-Methyl-*N*,*N*-di-*n*-propyl-*p*-anisidinium picrate	B	103–104		$C_{20}H_{26}O_8N_4$	53.33 (53.40)	5.77 (5.80)	
	N,*N*-di-*n*-propyl-*p*-anisidine picrate	B	93–94		$C_{19}H_{24}O_8N_4$	52.3 (52.40)	5.50 (5.70)	
	N-Methyl-*N*-propyl-*p*-anisidine picrate	B	102		$C_{17}H_{20}O_8N_4$	50.0 (49.80)	4.90 (4.95)	
Ib	*N*-Methyl-*N*,*N*-di-*n*-propyl-*o*-anisidinium iodide	A	238–239	45	$C_{14}H_{24}ONI$			36.39 (36.9)
	N-Methyl-*N*,*N*-di-*n*-propyl-*o*-anisidinium picrate	B	143–144		$C_{20}H_{26}O_8N_4$	53.33 (53.75)	5.77 (5.90)	
	N,*N*-di-*n*-propyl-*o*-anisidine picrate	B	110		$C_{19}H_{24}O_8N_4$	52.3 (52.14)	5.50 (5.70)	
	N-Methyl-*N*-propyl-*o*-anisidine picrate	B	139–140		$C_{17}H_{20}O_8N_4$	50.0 (49.50)	4.90 (5.0)	
Ic	*N*-Methyl-*N*,*N*-di-*n*-propyl-*p*-phenetidinium iodide	A	241–242	100	$C_{15}H_{26}ONI$			35.59 (36.2)
	N-Methyl-*N*,*N*-di-*n*-propyl-*p*-phenetidinium picrate	B	117		$C_{21}H_{28}O_8N_4$	54.31 (53.90)	6.03 (5.90)	
	N,*N*-di-*n*-propyl-*p*-phenetidine picrate	B	105–106		$C_{20}H_{26}O_8N_4$	53.33 (53.98)	5.77 (6.05)	
	N-Methyl-*N*-propyl-*p*-phenetidine picrate	B	137–138		$C_{18}H_{22}O_8N_4$	51.18 (51.65)	5.21 (5.10)	
Id	*N*-Methyl-*N*,*N*-di-*n*-propyl-*o*-phenetidinium iodide	A	233–234	53	$C_{15}H_{26}ONI$			35.59 (36.2)
	N-Methyl-*N*,*N*-di-*n*-propyl-*o*-phenetidinium picrate	B	139–140		$C_{21}H_{28}O_8N_4$	54.31 (53.80)	6.03 (5.90)	
	N,*N*-di-*n*-propyl-*o*-phenetidine picrate	B	96		$C_{20}H_{26}O_8N_4$	53.33 (53.01)	5.77 (5.79)	
	N-Methyl-*N*-propyl-*o*-phenetidine picrate	B	184–185		$C_{18}H_{22}O_8N_4$	51.18 (51.75)	5.21 (5.30)	
Ie	*N*-Methyl-*N*,*N*-di-*n*-propyl-*p*-toluidinium iodide	A	133–134	80	$C_{14}H_{24}NI$			38.02 (38.76)
	N-Methyl-*N*,*N*-di-*n*-propyl-*p*-toluidinium picrate[b]	B	140–141		$C_{20}H_{26}O_7N_4$	55.27 (55.26)	6.0 (6.09)	
	N,*N*-di-*n*-propyl-*p*-toluidine picrate	B	109		$C_{19}H_{24}O_7N_4$	54.28 (53.97)	5.71 (5.67)	
	N-Methyl-*N*-propyl-*p*-toluidine picrate	B	284–285		$C_{17}H_{20}O_7N_4$	51.0 (50.86)	5.0 (4.85)	
If	*N*-Methyl-*N*,*N*-di-*n*-propyl-*m*-toluidinium iodide	A	148–149	37	$C_{14}H_{24}NI$			38.02 (38.6)
	N,*N*-di-*n*-propyl-*m*-toluidine picrate	B	128–129[d]		$C_{19}H_{24}O_7N_4$	54.28 (54.27)	5.71 (5.74)	
	N-Methyl-*N*-propyl-*m*-toluidine picrate	B	89–90		$C_{17}H_{20}O_7N_4$	51.0 (50.59)	5.0 (5.12)	
Ig	*N*,*N*-di-*n*-propyl-*o*-toluidine picrate	B	140–141		$C_{19}H_{24}O_7N_4$	54.28 (54.29)	5.71 (5.90)	

[a] The yields of *N*-methyl-*N*,*N*-di-*n*-propylanilinium salts were calculated on the basis of the iodide. [b] *N*-Methyl-*N*,*N*-di-*n*-propyl-*m*-toluidinium picrate was obtained as a yellow oil which could not be solidified. [c] A = methanol-ether; B = ethanol. [d] F. J. Wobb, W. S. Cook, H. E. Albert, and G. E. P. Smith, *Ind. Eng. Chem.*, **46**, 1711 (1954) (*Chem. Abstr.*, 14282 (1954)), gave the same m.p. for the picrate, when they prepared the tertiary base (If) by the action of *n*-propyl bromide in aqueous potassium carbonate.

N-Methyl-*N*,*N*-di-*n*-propylanilinium salts of the tertiary bases (Ia–g) were prepared by the action of methyl iodide on the corresponding *N*,*N*-di-*n*-propylanilines.

$$\underset{\text{I}}{ArN(C_3H_7)_2} + CH_3I \longrightarrow \underset{\text{II}}{[ArN(C_3H_7)_2CH_3]^+I^-}$$

Ia.	Ar = *p*-$CH_3OC_6H_4$—	IIa.	Ar = *p*-$CH_3OC_6H_4$—
b.	Ar = *o*-$CH_3OC_6H_4$—	b.	Ar = *o*-$CH_3OC_6H_4$—
c.	Ar = *p*-$C_2H_5OC_6H_4$—	c.	Ar = *p*-$C_2H_5OC_6H_4$—
d.	Ar = *o*-$C_2H_5OC_6H_4$—	d.	Ar = *o*-$C_2H_5OC_6H_4$—
e.	Ar = *p*-$CH_3C_6H_4$—	e.	Ar = *p*-$CH_3C_6H_4$—
f.	Ar = *m*-$CH_3C_6H_4$—	f.	Ar = *m*-$CH_3C_6H_4$—
g.	Ar = *o*-$CH_3C_6H_4$—		

Only in the case of *N*,*N*-di-*n*-propyl-*o*-toluidine, could the formation of the quaternary ammonium salt not be achieved under normal conditions, when the tertiary base was treated with methyl iodide or methyl sulfate, due probably to steric effect.[1,2]

The thermal decomposition of the quaternary ammonium iodides was affected by heating above their melting points. The remaining tertiary bases, left after decomposition, were identified as the corresponding picrates. Mixed melting-point determination of the picrates of the starting materials (Ia–f) and the picrates obtained on thermal decomposition, showed depression in each case. This fact, together with the analytical figures obtained from decomposition picrates, indicated that thermal decomposition led to the formation of the mixed dialkylaniline, i.e., *n*-propyl iodide was always eliminated and *N*-methyl-*N*-propyl aromatic base was left. A similar result has been reported previously.[1–3]

Decomposition of the iodides IIa–f with ethanolic sodium ethoxide followed the same route observed in the thermal decomposition. Mixed melting-point determination of the picrates obtained on thermal decomposition and those from alkaline decomposition showed no depression, indicating that they are identical. The quaternary iodides, the quaternary picrates, the picrates of the starting materials, and the picrates of the products of decomposition are listed in Table II.

EXPERIMENTAL

Preparation of the dipropylanilines (Ia–g). Tri-*n*-propyl phosphate was prepared according to the general procedure described for the synthesis of *n*-alkyl phosphates.[5]

The method used for the preparation of Ia–g was that adopted by Bilman *et al.*[4] The corresponding picrates were prepared by mixing an ethanolic solution of the freshly distilled tertiary base with saturated ethanolic solution of picric acid. The products were filtered and crystallized.

Preparation of the quaternary ammonium iodides. Equimolecular proportions of the tertiary base Ia–g and methyl iodide were mixed in a sealed tube and left for some days at room temperature (20°) (in case of Ia, Ic, and Ie), or heated at 100° for 5–10 hr. (Ib, Id, and If), (40 hr. in case of Ig). The solid products were washed with ether and crystallized.

Preparation of the quaternary ammonium picrates. The quaternary ammonium picrates were obtained when an aqueous solution of the corresponding iodide was added to an excess of a saturated aqueous solution of picric acid. The precipitate was collected, dried, and crystallized.

Decomposition of the quaternary ammonium iodides. (a) *By heat.* The thermal decomposition of the iodides IIa–f was effected by heating 0.5 g. of the pure substance in a Pyrex tube above its melting point until bubbles ceased to evolve. The oily residue was extracted with ether, filtered to remove any undecomposed iodide and the ether removed. A few drops of ethanol were added, followed by a saturated ethanolic solution of picric acid. The picrate was filtered off and crystallized.

(b) *By ethanolic sodium ethoxide.* The decomposition of the iodides IIa–f was carried out by heating (1.5 g.) with ethanolic sodium ethoxide [from metallic sodium (0.3 g.) and absolute ethanol (20 ml.)] for 5 hr. on the steam bath. Sodium iodide, formed as a result of decomposition, was filtered, the ethanol was concentrated and a few ml. of water added. The oil that separated was taken up in ether, dried, and the ether removed. The oily residue was converted into the picrate, which was then filtered and crystallized.

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(5) G. R. Dutton and C. R. Noller, *Org. Synthesis*, **Vol. XVI**, p. 9.

Thiophosgenation of Dimethylammonium Chloride[1]

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In continuation of studies[3] on the preparation and properties of the thiatriazole ring system a supply of dimethylthiocarbamyl chloride (II) was required. Billiter and Rivier[4,5] report a convenient procedure using dimethylammonium chloride (I) and thiophosgene in the presence of aqueous sodium hydroxide. The thiophosgene (in alcohol-free chloroform) is added to an aqueous solution of I followed by slow addition of sodium hydroxide, the temperature being maintained at 25° by addition of ice. Yields of 65 to 95% of II were reported. Two moles of alkali are used per mole of I and at the end of the reaction the aqueous phase was reported[4] to be alkaline. At this point the chloroform layer changes from red to yellow in color. In our hands the repetition of this procedure failed to confirm any of these observations; only a 7%

(1) The authors gratefully acknowledge the support of these studies by the Air Force Office of Scientific Research.

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(5) Houben-Weyl, *Methoden der Organischen Chemie*, Georg Thieme Verlog, Stuttgart, Germany, volume IX, page 830 (1955).