The Reactions of Acetophenone and Iodine with Some Nitrogenous Bases[1]

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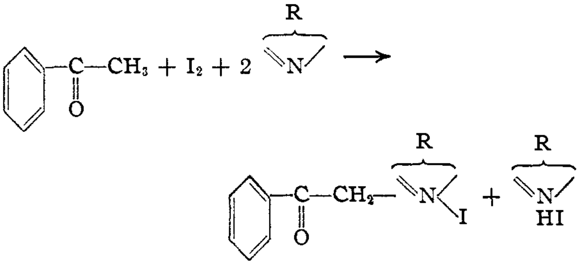
In recent papers from this Laboratory[2] the reaction of ketones with iodine and pyridine to give substituted β-ketoalkylpyridinium iodides was reported. This reaction has now been extended to certain other bases, namely, α, β and γ-picoline, quinoline, isoquinoline and 4-amylpyridine. A suitable excess of each of these bases reacted with iodine and acetophenone to give a quaternary salt corresponding to the base used. The course of the reactions was analogous to that reported in previous papers[2] and may be formulated as



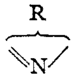
where  represents α, β or γ-picoline, quinoline, isoquinoline or 4-amylpyridine.

TABLE I

Iodide	Compound Number	Formula	M. p.,[a] °C.	Yield,[b] %	Analyses, %[c] Nitrogen Calcd.	Nitrogen Found	Iodide Calcd.	Iodide Found
1-Phenacyl-2-picolinium	I	$C_{14}H_{14}INO$	200–202	24	4.13	4.24	37.5	37.5
1-Phenacyl-3-picolinium	II	$C_{14}H_{14}INO$	182–184	56	4.13	3.97	37.4	37.3
1-Phenacyl-4-picolinium	III	$C_{14}H_{14}INO$	195–198	12	4.13	3.93	37.5	37.8
1-Phenacylquinolinium	IV	$C_{17}H_{14}INO$	187–192	43	3.76	3.83	33.8	33.4
2-Phenacylisoquinolinium	V	$C_{17}H_{14}INO$	178–180	95	3.76	3.60	33.8	33.9
1-Phenacyl-4-amylpyridinium	VI	$C_{18}H_{22}INO$	173–175	20	3.53	3.52	32.1	32.6
Perchlorate								
1-Phenacyl-2-picolinium	Ia	$C_{14}H_{14}ClNO_5$	185–189	d	4.49	4.40		
1-Phenacyl-3-picolinium	IIa	$C_{14}H_{14}ClNO_5$	180–181	d	4.49	4.48		
1-Phenacyl-4-picolinium	IIIa	$C_{14}H_{14}ClNO_5$	175–176	d	4.49	4.52		
1-Phenylacylquinolinium	IVa	$C_{17}H_{14}ClNO_5$	193–195	d	4.03	4.21		
2-Phenacylisoquinolinium	Va	$C_{17}H_{14}ClNO_5$	194–197	d	4.03	4.10		
1-Phenacyl-4-amylpyridinium	VIa	$C_{18}H_{22}ClNO_5$	130–131	d	3.81	4.22		

[a] All melting points were observed on a Fisher–Jones melting point block and represent the range where the crystalline salt becomes an orange to black liquid. [b] Yield of pure product isolated based on the ketone. [c] Nitrogen analysis by M. Ledyard. [d] See note 3.

The analytical, melting point and yield data for each of the iodides produced and for the corresponding perchlorate[3] derivative of each is listed in the Table I. The structures[4] of II, III and IV depend on the mode of formation, on the analyses of the iodide and of a perchlorate derivative and on the fact that alkaline cleavage of each of these gave benzoic acid.[5] The structure of I was confirmed by conversion to 2-phenylpyrrocoline.[6] The structure of V was identified by comparison of the melting point of its perchlorate derivative, Va, with that of the corresponding substance prepared by Krohnke.[7] The structure of VI depends on the mode of formation and on the analyses of the iodide and perchlorate derivative.

The reactions used for preparation of the quaternary iodides described in this paper, when considered in connection with the more extensive survey of similar reactions wherein pyridinium salts were prepared,[2] establish the generality of this type of reaction. Further work is in progress.

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Experimental

The preparation of each of the quaternary salts was effected in about the same way.

To a solution of 0.1 mole of acetophenone in 30 g. of the appropriate base, 0.1 mole of iodine was added. The reaction mixture was heated overnight on the steam-bath, cooled and thoroughly washed with ethyl ether. Each quaternary salt was separated from the appropriate crude reaction products by one of the methods described below.

I and IV separated slowly from a clarified acetone solution of the appropriate crude reaction products. Both of them were recrystallized from acetone–alcohol containing a small amount of water. V and VI crystallized from an acetone–alcohol solution of the appropriate crude reaction products. III crystallized slowly from the mother liquors after removal of most of the γ-picoline hydroiodide from an acetone solution of the crude reaction products. II crystallized from a water solution of the clarified crude reaction products.

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(1) Some of the compounds described in this paper were prepared independently and simultaneously by Dr. Jonathan L. Hartwell and Sylvia R. L. Kornberg, THIS JOURNAL, **68**, in press (1946).

(2) L. C. King, THIS JOURNAL, **66**, 894 (1944); **66**, 1612 (1944); **67**, 2089 (1945).

(3) Prepared as described in previous papers (ref. 2). The yield was 90–95% in each case.

(4) For identification of compounds see the table.

(5) The cleavage reactions were effected in a manner similar to that described previously (ref. 2). Only about 10% of the theoretical yield of benzoic acid was obtained from IV and V.

(6) The method of Tschitschibabin, *Ber.*, **60**, 1607 (1927), was used. The product obtained in this Laboratory melted at 214–215° after crystallization from acetone–alcohol. *Anal.* Calcd. for $C_{14}H_{11}N$: N, 7.24. Found: N, 7.40.

(7) Krohnke, *Ber.*, **68**, 1177 (1935).