hard, gray cake. The yield of crude product was 64.2 g. (0.42 mole), or 85% based on the isopropyl halides.

The boiling points of a middle fraction of redistilled material at various pressures were obtained by distillation of a sample through a short Stedman column. The relation between temperature and pressure (in mm.) is given to within ±1.0 mm., which is within the accuracy of the measurements, by the equation $\log P = 7.987 - 1858/(t + 230)$.

Di-*s*-butylzinc.—By a procedure similar to that described above, di-*s*-butylzinc was prepared from 68.5 g. (0.5 mole) of *s*-butyl bromide, 92.0 g. (0.5 mole) of *s*-butyl iodide, and 140 g. (132 g. Zn, 2.0 g. atom) of zinc–copper couple. The starting temperature was 60°, and the reaction temperature 25°. The yield of crude product was 64.5 g. (0.36 mole), or 72%. On redistillation, the material distilled at 56° at 4 mm. *Anal.* Calcd. for $(C_4H_9)_2Zn$: Zn, 36.4. Found: Zn, 36.1.

Summary

Diisopropylzinc and di-*s*-butylzinc have been prepared from zinc–copper couple and secondary alkyl halides in good yield by a modification of the procedure usually used for preparation of the primary analogs.

DETROIT, MICHIGAN RECEIVED FEBRUARY 19, 1944

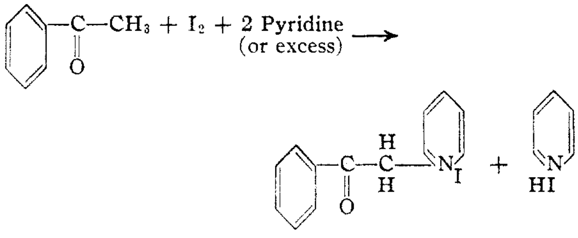
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

The Reaction of Iodine with Some Ketones in the Presence of Pyridine

BY L. CARROLL KING

In an investigation of the reactions of compounds containing reactive hydrogen atoms with iodine in the presence of a base it was observed that acetophenone, 1-naphthyl methyl ketone, 1-anthryl methyl ketone and propiophenone react directly with one mole of iodine and two moles (or excess) of pyridine to give excellent yields of 1-phenacylpyridinium iodide, 1-(1-naphthoylmethyl)-pyridinium iodide, 1-(1-anthroylmethyl)-pyridinium iodide and 1-(α-methylphenacyl)-pyridinium iodide, respectively, and, in each case, pyridine hydroiodide.

If acetophenone is used as an example the reaction may be formulated as follows



1-Phenacylpyridinium iodide has been reported.[1] It was further characterized by conversion to the known 1-phenacylpyridinium perchlorate.[2,3] 1-(α-Methylphenacyl)-pyridinium iodide was also characterized by conversion to the known 1-(α-methylphenacyl)-pyridinium perchlorate.[4]

It has been demonstrated previously that 1-phenacylpyridinium bromide[2,5] and 1-(α-methylphenacyl)-pyridinium bromide[3] can be cleaved by means of aqueous alkali to give benzoic acid. The 1-phenacylpyridinium iodide and the 1-(α-methylphenacyl)-pyridinium iodide described in this article when treated with aqueous sodium hydroxide also gave excellent yields of this substance.

The characterization of 1-(1-naphthoylmethyl)-pyridinium iodide and of 1-(1-anthroylmethyl)-pyridinium iodide depends on the mode of formation, the analysis, and on the fact that after treatment with aqueous alkali the respective 1-naphthoic and 1-anthroic acids were isolated in good yield from the cleavage products.[6]

In three of the four reactions carried out 74–92% yields (based on the ketones) of the expected substituted β-ketoalkylpyridinium iodides were obtained and in every case 87–95% of the expected yields of pyridine hydroiodide were observed. 1-(α-Methylphenacyl)-pyridinium iodide was obtained in only 41% yield. The low yield in this case was due to the solubility characteristics of this compound. When the 1-(α-methylphenacyl)-pyridinium compound was isolated as the perchlorate a 64% yield was obtained.

When excess pyridine was used as the solvent, the formation of the substituted β-ketoalkylpyridinium iodides, by means of the above reaction, proceeded smoothly with twenty to thirty minutes heating on the steam-bath and the reaction was complete after standing overnight. In most cases a solid began to separate soon after the heating was started. This substance consisted of pyridine hydroiodide and usually contained some of the substituted β-ketoalkylpyridinium iodide. In the four instances discussed in this paper, it was not found advantageous to use solvents other than an excess of the base when effecting this synthesis.

Preliminary experiments indicate that the above reaction is of value for the synthesis of derivatives of various nitrogeneous bases, particularly in those cases where an intermediate halogen compound is difficult to obtain. These experi-

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(1) F. Krohnke, *Ber.*, **66B**, 1386 (1933).

(2) E. Schmidt and H. VanArk, *Archiv. Pharm.*, **238**, 331 (1900).

(3) Krohnke, *Ber.*, **66**, 604 (1933).

(4) F. Krohnke, *ibid.*, **69**, 921 (1936).

(5) Babcock, Nakamura and Fuson, THIS JOURNAL, **54**, 4407 (1932); Babcock and Fuson, *ibid.*, **55**, 2949 (1933); E. Bamberger, *Ber.*, **20**, 3344 (1887).

(6) Krohnke[3] prepared 1-(1-naphthoylmethyl)-pyridinium bromide and showed that after treatment with aqueous alkali 1-naphthoic acid could be obtained from the cleavage products.

TABLE I

				Analyses, %					
				Found			Calcd.		
Pyridinium iodide	Formula	M. p.,[a] °C.	Yield, %	C	H	I	C	H	I
1-Phenacyl	$C_{13}H_{12}INO$	215–219	88[b]	48.36	3.72	38.9	48.01	3.7	39.03
1-(1-Naphthoylmethyl)-	$C_{17}H_{14}INO$	219–220	92[b]	55.20	3.74	33.9	54.41	3.76	33.82
1-(1-Anthroylmethyl)-	$C_{21}H_{16}INO$	235–237	74[b]	59.87	3.87	29.6	59.31	3.79	29.84
1-(α-Methylphenacyl)-	$C_{14}H_{14}INO$	152–153	41[b]	49.72	4.20	37.3	49.72	4.17	37.42
Pyridinium perchlorate									
1-Phenacyl	$C_{13}H_{12}ClNO_5$	189–190	90[c]	52.69	4.27		52.5	4.06	
1-(1-Naphthoylmethyl)-	$C_{17}H_{14}ClNO_5$	176–177	90[c]	59.32	4.12		58.69	4.05	
1-(1-Anthroylmethyl)-	$C_{21}H_{16}ClNO_5$	227–230	95[c]	63.81	4.25		63.40	4.05	
1-(α-Methylphenacyl)-	$C_{14}H_{14}ClNO_5$	141–142	64[d]–90[c]	54.29	4.49		53.94	4.52	

[a] All melting points were observed on a Fisher–Jones melting point apparatus. [b] Based on the ketone. [c] Based on the corresponding substituted β-ketoalkylpyridinium iodide. [d] This yield, based on the ketone, was obtained when the crude reaction mixture was converted directly into the perchlorate salt without preliminary isolation of the iodide.

ments also indicate that this reaction followed by alkaline cleavage, may be adapted to the preparation of acids from certain sensitive methyl ketones, particularly in those cases where the ordinary haloform reaction gives poor yields.

Extension of this reaction to other bases, to other halogens, and to various types of compounds containing active hydrogen atoms is in progress.

Experimental

Preparation of the Substituted β-Ketoalkylpyridinium Iodides.—The procedure was essentially the same for each of the four compounds prepared and was about as follows. To 0.1 mole of the appropriate ketone[7] dissolved in 30–50 ml. of pyridine 0.1 mole of iodine was added. The solution was heated thirty minutes on the steam-bath and let stand overnight. The excess pyridine was then removed and the mixture of pyridine hydroiodide and substituted β-ketoalkylpyridinium iodide separated by means of their solubility characteristics. 1-Phenacylpyridinium iodide, 1-(1-naphthoylmethyl)-pyridinium iodide and 1-(1-anthroylmethyl)-pyridinium iodide were comparatively insoluble in water and in methyl or ethyl alcohol and were easily separated from the more soluble pyridine hydroiodide. 1-(α-Methylphenacyl)-pyridinium iodide is very soluble in the solvents mentioned above but could be obtained pure from the concentrated methyl alcohol mother liquors after removal of most of the pyridine hydroiodide. In each case the substituted β-ketoalkylpyridinium iodide was crystallized from water or from dilute alcohol before analysis. The critical data for each of these compounds are listed in Table I.

The pyridine hydroiodide isolated in each case was identified by the usual procedures.

Preparation of the Substituted β-Ketoalkylpyridinium Perchlorates.—About 1 g. of each of the above substituted β-ketoalkylpyridinium iodides was dissolved in 50–400 ml. of hot water and 60% perchloric acid added until the solutions contained about 3% of it. The substituted β-ketoalkylpyridinium perchlorates separated at once or as the solution was cooled. The critical data for each of these substances are listed in Table I.

Alkaline Cleavage of the Substituted β-Ketoalkylpyridinium Iodides.—The method of cleavage of each of the four compounds was essentially the same. To suspensions of 1–5 g. of each of the substituted β-ketoalkylpyridinium iodides in 50–100 ml. of water or 50% ethyl alcohol, 1–3 g. of sodium hydroxide was added.

TABLE II

Starting iodide	Acid resulting from alkaline cleavage	Yield, %	M. p., °C.
1-Phenacylpyridinium	Benzoic	90	122
1-(α-Methylphenacyl)-pyridinium	Benzoic	88	122
1-(1-Naphthoylmethyl)-pyridinium	1-Naphthoic[a]	90	160–161
1-(1-Anthroylmethyl)-pyridinium	1-Anthroic[b]	80	251–252

[a] This substance was converted to the amide, m. p. 202–203°. [b] This substance was converted to the methyl ester, m. p. 101–102°.

The suspensions were heated one hour on the steam-bath and the acidic fractions isolated from the resulting homogeneous solutions. A summary of the results of this experiment appears in Table II.

Summary

1. It has been demonstrated that acetophenone, 1-naphthyl methyl ketone, 1-anthryl methyl ketone, and propiophenone react directly with one mole of iodine and two moles (or excess) of pyridine to give 1-phenacylpyridinium iodide, 1-(1-naphthoylmethyl)-pyridinium iodide, 1-(1-anthroylmethyl)-pyridinium iodide and 1-(α-methylphenacyl)-pyridinium iodide, respectively, and, in each case, pyridine hydroiodide.

2. Each of the substituted β-ketoalkylpyridinium iodides produced by the above reaction when treated with aqueous alkali was cleaved, and the corresponding carboxylic acid was isolated from the cleavage products.

EVANSTON, ILLINOIS RECEIVED JANUARY 31, 1944

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[7] The 1-anthryl methyl ketone, m. p. 108°, was prepared by Mr. Clair J. Collins. The author is also indebted to Mr. Collins for the procedure for purification of 1-anthroic acid, and for the authentic samples of 1-anthroic acid and its methyl ester.