[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

# The Cleavage of Carbonyl Compounds by Alkalies. IX. Phenacylpyridinium Salts

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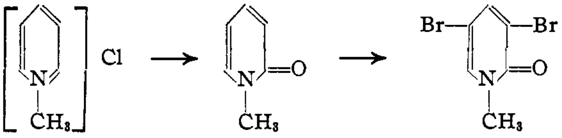
In the preceding paper[1] it was shown that when phenacylpyridinium halides are treated with aqueous alkalies they undergo chain cleavage, yielding the corresponding aromatic acids. Subsequent investigation has now disclosed that the remainder of the molecule appears in the form of the corresponding alkylpyridinium halide. Evidently, then, the reaction proceeds according to equation (1). Phenacylpyridinium chloride and *p*-bromo-*α*-methylphenacylpyridinium bromide react according to equations 2 and 3, respectively.[2]

$$[\mathrm{ArCOCH(R)NC_5H_5}]\mathrm{X} + \mathrm{NaOH} \longrightarrow \mathrm{ArCO_2Na} + [\mathrm{RCH_2NC_5H_5}]\mathrm{X} \qquad (1)$$

$$[\mathrm{C_6H_5COCH_2NC_5H_5}]\mathrm{Cl} + \mathrm{NaOH} \longrightarrow \mathrm{C_6H_5CO_2Na} + [\mathrm{CH_3NC_5H_5}]\mathrm{Cl} \qquad (2)$$

$$[p\text{-}\mathrm{BrC_6H_4COCH(CH_3)NC_5H_5}]\mathrm{Br} + \mathrm{NaOH} \longrightarrow p\text{-}\mathrm{BrC_6H_5CO_2Na} + [\mathrm{C_2H_5NC_5H_5}]\mathrm{Br} \qquad (3)$$

The alkylpyridinium halides have been identified by converting them into the dibromo derivatives of the corresponding 1-alkyl-2-pyridones. Methylpyridinium chloride, for example, when oxidized with potassium ferricyanide gave 1-methyl-2-pyridone (I) which when treated with bromine was converted into the known 3,5-dibromo-1-methyl-2-pyridone (II). The latter compound melted at 176°, which agrees with the findings of Decker and Kaufmann,[3] who also prepared the compound by the bromination of 1-methyl-2-pyridone.



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The *p*-bromo-*α*-methylphenacylpyridinium bromide was prepared by condensation of *α*-*p*-dibromopropiophenone with pyridine. Like the other phenacylpyridinium halides which proved to be sensitive to alkali,[4] it readily formed a monohydrate and was rapidly decomposed when dissolved in aqueous alkali. The ethylpyridinium bromide was isolated in the form of the 1-ethyl-2-pyridone, which in turn was characterized by transformation into the solid 3,5-dibromo-1-ethyl-2-pyridone. For

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[1] Babcock, Nakamura and Fuson, THIS JOURNAL, **54**, 4407 (1932). For paper VII of this series see Fuson, Bertetti and Ross, *ibid.*, **54**, 4380 (1932).

[2] A similar result was reported by Schmidt and van Ark [*Arch. Pharm.*, **238**, 321 (1900)], who decomposed phenacylpyridinium bromide with sodium carbonate solution. These authors based their conclusions on the isolation of methylpyridinium bromide in the form of a double salt.

[3] Decker and Kaufmann, *J. prakt. Chem.*, [2] **84**, 439 (1911).

[4] An exception was noted in the preceding paper. 2,4,6-Trimethylphenacylpyridinium chloride, though extremely soluble in water, showed no tendency to form a hydrate and could not be cleaved by treatment with alkalies.

comparison the latter was also synthesized directly from pyridine and diethyl sulfate.

The results presented above suffice to show that the cleavage of phenacylpyridinium halides is entirely analogous to other well-known types of cleavage of carbonyl compounds by alkalies. In particular, the remarkable ease with which the chain fission occurs bespeaks a close relationship between this cleavage and that involved in the haloform reaction. The presence of two $\alpha$-hydrogen atoms in the phenacyl salts, however, offers the possibility, not to be found in the trihalomethyl ketones, of introducing additional and varied substituents on the $\alpha$-carbon atom. The possibility of substitution of other amines, thio ethers, phosphines and similar compounds for the pyridine offers another means of introducing wide variations in the structure of the salts. From these points of view, the new example of cleavage promises a distinctly novel approach to an understanding of the general type of reaction which it illustrates. The work is being continued along these lines.

## Experimental

**The Preparation of 3,5-Dibromo-1-methyl-2-pyridone from Phenacylpyridinium Chloride.**—Twenty-five grams of phenacylpyridinium chloride was dissolved in 25 cc. of water, 25 cc. of 20% sodium hydroxide solution was added and the mixture was stirred for fifteen minutes. It was then acidified with hydrochloric acid, cooled to 10° and the precipitated benzoic acid was filtered. The yield of benzoic acid was 11.6 g. or 96% of the theoretical.

The filtrate, after first being exactly neutralized with sodium hydroxide, was then kept at a temperature between 0 and 10° and mechanically stirred. To it were added dropwise and simultaneously two solutions, the one containing 30 g. of potassium ferricyanide dissolved in 60 cc. of water, the other 15 g. of sodium hydroxide in 25 cc. of water. After these solutions had been added a second amount of potassium ferricyanide solution, equal to the first, was added in the same manner.

The solution was allowed to stand overnight. To it was then added 50 g. of sodium bicarbonate. It was then extracted with four 30-cc. portions of technical amyl alcohol. The extract was fractionally distilled under diminished pressure and yielded 3.5 g. of a liquid boiling at 127° (12 mm.). This corresponds to the boiling point of 1-methyl-2-pyridone. The pyridone was brominated following the direction of Decker and Kaufmann[3] and yielded the 3,5-dibromo-1-methyl-2-pyridone described by them.

**The Preparation of 3,5-Dibromo-1-ethyl-2-pyridone from *o*-Bromo-$\alpha$-methylphenacylpyridinium Bromide. (1) The Preparation of *p*-Bromo-$\alpha$-methylphenacylpyridinium Bromide.**—Twenty-four grams of $\alpha$,*p*-dibromopropiophenone was dissolved in 100 cc. of boiling alcohol and 20 cc. of pyridine was added. The mixture was boiled for five minutes when the *p*-bromo-$\alpha$-methylphenacylpyridinium bromide separated. The yield was 26 g. or 83% of the theoretical. The melting point was 232–233°.

*Anal.* Calcd. for $C_{14}H_{13}ONBr_2 \cdot H_2O$: Br, 20.6. Found: Br, 20.6, 20.7.

**(2) The Cleavage of *p*-Bromo-$\alpha$-methylphenacylpyridinium Bromide.**—Twenty-five grams of the *p*-bromo-$\alpha$-methylphenacylpyridinium bromide was dissolved in 100 cc. of warm water and a slight excess of 20% sodium hydroxide solution was added. The mixture was warmed slightly for ten minutes and then acidified with hydrobromic acid. The precipitated *p*-bromobenzoic acid was filtered and dried. It weighed 13 g., which corresponds to the theoretical yield.

(3) **The Preparation of 3,5-Dibromo-1-ethyl-2-pyridone.**—The filtrate obtained in the preceding experiment was treated in exactly the manner described for that obtained in the cleavage of phenacylpyridinium chloride. The final distillation yielded 2 g. of a liquid boiling at 124° (9 mm.). This compound was brominated according to the directions of Decker and Kaufmann for the bromination of 1-methyl-2-pyridone. The product obtained melted at 101–104°, and when recrystallized twice from 50% ethyl alcohol, melted sharply at 109°.

**The Preparation of 3,5-Dibromo-1-ethyl-2-pyridone from Pyridine and Diethyl Sulfate.**—Following the directions of Decker and Kaufmann[3] but substituting diethyl sulfate for dimethyl sulfate, 1-ethyl-2-pyridone was prepared in 30% yields from 2.7 g. of pyridine. It boiled at 124° (9 mm.); 132° (12 mm.). This was brominated by following the procedure of Decker and Kaufmann for the bromination of 1-methyl-2-pyridone. The 3,5-dibromo-1-ethyl-2-pyridone obtained was recrystallized from 50% ethyl alcohol; it melted at 109°.

*Anal.* Calcd. for $C_7H_7ONBr_2$: N, 5.0; Br, 56.9. Found: N, 5.0; Br, 56.7.

This compound when mixed with the compound prepared from *p*-bromo-$\alpha$-methylphenacylpyridinium bromide melted sharply at 109°.

## Summary

When phenacylpyridinium chloride and *p*-bromo-$\alpha$-methylphenacylpyridinium bromide are treated with aqueous alkalies they are cleaved into the corresponding aromatic acids and alkylpyridinium halides. The type of reaction involved is expressed by the equation

$$[ArCOCH(R)NC_5H_5]X + NaOH \longrightarrow ArCO_2Na + [RCH_2NC_5H_5]X$$

The relationship of this reaction to other types of cleavage of carbonyl compounds by alkalies is pointed out.

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# Studies of Organic Lead Compounds. V. Asymmetric Derivatives

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Optically active compounds containing asymmetric silicon, tin and germanium atoms have been known for some time. Analogous lead derivatives have been singularly resistant to resolution, although it seems reasonable to suppose that in organic combination the lead atom possesses a tetrahedral configuration. A large number of mixed lead alkyl-aryls have been prepared[2] and their resolution attempted by means of *d*-bromocamphorsulfonic acid.[3] Ethylpropylisobutyllead *d*-bromocamphorsulfonate (I) was found to be an oil which could not be crystallized. *n*-Propylisoamyllead bromo *d*-bromocamphorsulfonate (II) could be fractionally

[1] National Research Fellow in Chemistry.

[2] Krause and Schlöttig, *Ber.*, **58**, 427 (1925).

[3] Krause, Inaugural Dissertation, Berlin, July 1917, p. 56.