[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE ILLINOIS INSTITUTE OF TECHNOLOGY]

The Reaction of *p*-Bromophenacyl Bromide with Chloride Ion[1]

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Halogen interchange between organic halides and alkali halides usually goes in the direction RCl → RBr → RI.[2] For example, Collet[3] has obtained *p*-bromophenacyl iodide from the reaction of *p*-bromophenacyl chloride with potassium iodide in alcohol. However, in the present investigation it has been found that, using sodium chloride in 62% aqueous ethanol, the ω-bromine atom in *p*-bromophenacyl bromide easily can be replaced by a chlorine atom.

The resulting *p*-bromophenacyl chloride was identified by elementary analysis and comparison with an independently synthesized sample.[4] The mixed melting points of the chloride, m. p. 117–118°, and the bromide, m. p. 109–110°, were found to lie between the melting points of the two pure samples. The melting point diagram of the system is shown in Fig. 1. This figure was of value in estimating the purity of the reaction products.

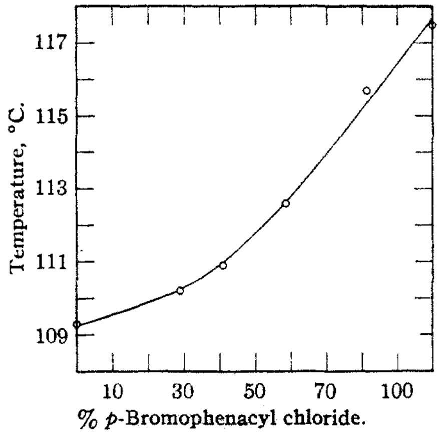

Fig. 1.—Melting point–composition diagram.

Experiments in which *p*-bromophenacyl bromide and a large excess of sodium chloride were heated together under conditions generally used to prepare the *p*-bromophenacyl esters[5] always gave the chloride, which, after one recrystallization, melted at 117–118°. An experiment with potassium chloride gave identical results. The presence of hydrochloric acid has no appreciable effect. However, when equi-molar quantities of the two reactants were used, as in Runs 8 and 9 (Table I), only a partial conversion was noted. This fact, together with the almost complete conversion with a large excess of sodium chloride (Expts. A and 1, Table I), indicates the equilibrium nature of the process

$$\mathrm{BrC_6H_4COCH_2Br + Cl^- \rightleftarrows BrC_6H_4COCH_2Cl + Br^-}$$

This equilibrium has been noted in other recently described halogen interchanges.[6] To see whether the reverse reaction would occur, experiments using sodium bromide and *p*-bromophenacyl chloride were performed. In two experiments a first crop of crystals was obtained which started melting at 110°. This could not be *p*-bromophenacyl bromide (m. p. 109–110°) because a subsequent recrystallization raised the melting point about 2°. In expt. 3 a small quantity of a substance melting at 130–134° was isolated. This was probably *p*-bromophenacyl alcohol, m. p. 136.6.[4b] Hence it is not clear that the reverse replacement occurred and further study will be necessary to clear up the point.

It is improbable that the interchange can be explained in terms of the differential solubility of the organic halides involved. Rough determinations of the solubilities of the two organic compounds were made. At 25 ± 0.5° the solubility of *p*-bromophenacyl bromide in 100 ml. of 62% ethanol was 0.332 ± 0.008 g., while that of *p*-bromophenacyl chloride was 0.278 ± 0.010 g. The solubility of the inorganic salts need not be considered since they are not precipitated.

This replacement reaction is of interest in qualitative organic analysis. *p*-Bromophenacyl bromide is generally used to form solid esters from the sodium salts of acids.[5] Should sodium chloride be present as a contaminant due to a previous reaction, the resulting *p*-bromophenacyl chloride

TABLE I[a]

Expt.	Compounds reacting, mg.	Crop 1 Wt., mg.	Crop 1 M. p., °C.	Crop 2[c] Wt., mg.	Crop 2[c] M. p., °C.
8	556 RBr, 118 NaCl	352	113.5–114.5	83	110.5–111.5
9	556 RBr, 118 NaCl	361	113.5–114.5	72	111–112.5
A	750 RBr, 750 NaCl	475	116–117	85	112–114
1	750 RBr, 750 NaCl, 2 drops dil. HCl		116–117		116–117
7	750 RBr, 1000 KCl	530	116.5–117.5	80	115–116
2	750 RBr, 750 NaCl 250 NaOAc, 2 drops dil. HCl	265	112–115	325	67–71
5	250 RBr, 750 NaCl 250 NaOAc, 2 drops dil. HCl	50	114.5–116	180	80–95
3	750 RCl, 1000 NaBr	495	110–111 112–114[b]	104	99–102 109–111.5[b]
6	750 RCl, 1000 NaBr	557	110–112 111–113.5[b]	120	105–107 109–111[b]

[a] R = *p*-$\mathrm{BrC_6H_4COCH_2^-}$. [b] M. p. upon recryst. [c] Obtained by dilution of mother liquor with water.

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(1) Presented before the Organic Division of the American Chemical Society, Detroit, April 12, 1943.

(2) Houben, "Die Methoden der organischen Chemie," Georg Thieme Verlag, Leipzig, 1930, 3rd ed., Vol. III, pp. 1195–1198. See also Wilson, *Chem. Rev.*, **16**, 149 (1935).

(3) Collet, *Bull. soc. chim.*, (3) **23**, 830 (1900).

(4) (a) Collet, *Compt. rend.*, **125**, 718 (1897); (b) Judefind and Reid, THIS JOURNAL, **42**, 1043 (1920).

(5) Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, New York, N. Y., 2nd ed., 1940, p 132.

(6) Moelwyn-Hughes, *Trans. Faraday Soc.*, **35**, 368 (1939); Bennett and Vernon, *J. Chem. Soc.*, 1783 (1938).

might cause confusion. The present investigation was initiated by such a set of circumstances. Table I includes some typical experiments we have performed attempting to produce the ester from sodium acetate in the presence of sodium chloride. The first product to crystallize was always impure *p*-bromophenacyl chloride.

Experimental[7]

Replacement Reactions.—Weighed quantities of the organic halide and the alkali halide were placed in a 25-ml. round-bottom flask and 30 ml. of 62% ethanol added. The resulting solution was refluxed for one and one-half hours, after which time it was allowed to cool. The crystals which formed were filtered, dried and weighed.

Anal.[8] Calcd. for C_8H_6BrClO: C, 41.15; H, 2.60. Found: C, 40.89; H, 2.62.

Synthesis of *p*-Bromophenacyl Chloride.—This compound was synthesized from bromobenzene, chloroacetyl chloride, and aluminum chloride by the method of Collet[4a] as modified by Judefind and Reid.[4b] We obtained white needles from aqueous alcohol, m. p. 117–118°, yield 80%.

Melting Point–Composition Curve.—Weighed quantities of the two compounds were mixed intimately. Since the mixtures gave melting ranges of 1.5–2°, the mean of the first and last values was used as the experimental points.

Solubility Determination.—Twenty-five ml. of the respective saturated halide solutions, properly thermostated, was removed and delivered into a weighed dish. The alcohol was evaporated at 45° and the weight of the residue determined.

Summary

1. *p*-Bromophenacyl chloride was shown to be formed from *p*-bromophenacyl bromide and sodium or potassium chloride in 62% ethanol.

2. The possibility of this replacement causing confusion when *p*-bromophenacyl bromide is used to identify acids in the presence of sodium chloride was shown.

3. The melting point–composition diagram and the solubility in aqueous ethanol of the two halides are given.

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[7] Melting points uncorrected.

[8] The microanalysis was performed by Dr. T. S. Ma, University of Chicago.

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The Permanent Fading of Alkaline Phenolphthalein Solutions

BY MAX H. HUBACHER

It is common knowledge that solutions of phenolphthalein in strong alkali are red when freshly prepared, but soon become colorless. This color fading is reversible, as the red color reappears when alkalinity is decreased.

Irreversible or permanent fading takes place when solutions of phenolphthalein in dilute alkali are exposed to the air for months. This permanent fading was observed by others and was attributed to the formation of a "tertiary carbinol-carbonate ion," but no experimental proof was submitted.[1]

It is known that alkaline phenolphthalein solutions are oxidized very slowly by atmospheric oxygen.[2] Now it has been found that irreversible fading is likewise due to air oxidation.

The following two compounds were isolated from faded phenolphthalein solutions: 2-(4′-hydroxybenzoyl)-benzoic acid (I) in a yield of 39–45% and a small quantity of phthalic acid. The remaining reaction product was a brown semisolid mass on which further investigation is in progress, to isolate additional compounds. Up to the present time, no evidence has been revealed of the fate of the third benzene ring of the phenolphthalein molecule. It may be mentioned here that acid I can also be obtained from phenolphthalein in a yield of 80%, by hydrolysis of its oxime.[3]

Red phenolphthalein solutions sealed into Pyrex glass tubes retained their color for two years, at which time only pure phenolphthalein could be recovered.

In the colorimetric determination of phenolphthalein, these two types of fading should be taken into consideration, otherwise the results will be low.

Alkaline *o*-cresolphthalein solutions faded more slowly than phenolphthalein solutions and yielded 2-(3′-methyl-4′-hydroxybenzoyl)-benzoic acid (II) and a trace of phthalic acid. On the other hand, 3,4-dihydroxydiphenylphthalide fades rather rapidly and the compounds isolated from its faded solutions, in yields of 43%, were phenol and phthalic acid. This leads to the conclusion that not all phthaleins are air-oxidized to substituted *o*-benzoylbenzoic acids. The phenol obtained from the 3,4-dihydroxydiphenylphthalide must come from the unsubstituted benzene ring.

Eugenia H. Maechling[4] found that phenolphthalein can be oxidized in alkaline solution by hydrogen peroxide to phthalic acid. As a second reaction product, hydroquinone was isolated in this Laboratory. *o*-Cresolphthalein likewise yielded phthalic acid and toluhydroquinone. This is another example of the reaction first described by Dakin, who obtained catechol by hydrogen peroxide oxidation of salicylaldehyde and hydroquinone from *p*-hydroxyacetophenone.[5]

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[1] A. Thiel and G. Coch, *Z. anorg. allgem. Chem.*, **217**, 254 (1934).

[2] M. H. Hubacher, U. S. Patent 1,940,495 (*C. A.* **28**, 1366 (1934)).

[3] P. Friedlaender, *Ber.*, **26**, 176 (1893). He reports a m. p. of 210° dec. for the 2-(4′-hydroxybenzoyl)-benzoic acid.

[4] E. H. Maechling, *Ind. Eng. Chem., Anal. Ed.*, **10**, 586 (1938).

[5] H. D. Dakin, *Am. Chem. J.*, **42**, 477 (1909), and "Organic Syntheses," Coll. Vol. I, 141 (1941).