Anal. Calcd. for $C_8H_4OCl_4$: Cl, 55.0. Found: Cl, 55.1.

2,4,6-Trichlorobenzoic Acid from 2,4,6-Trichloroacetophenone.—Five-tenths gram of 2,4,6-trichloroacetophenone was shaken with a mixture of 100 cc. of 10% sodium hypochlorite solution and 20 cc. of pyridine for seventy-two hours at room temperature. The solution was acidified with hydrochloric acid and extracted with ether. The material obtained on evaporation of the ether was dissolved in dilute sodium hydroxide solution and reprecipitated with hydrochloric acid. It melted from 159–162°. The conversion of the ketone to the acid was practically quantitative.

2,4,6-Trichlorobenzoic Acid from α,2,4,6-Tetrachloroacetophenone.—Five-tenths gram of α,2,4,6-tetrachloroacetophenone was stirred with 100 cc. of 10% sodium hypochlorite solution and 10 cc. of pyridine at 90° for twenty-four hours. The solution obtained on evaporation of the ether was dissolved in dilute sodium hydroxide solution and reprecipitated with hydrochloric acid. It melted at 160°. The yield of the acid was 97% of the theoretical.

Summary

2,4,6-Trichloroacetophenone has been prepared and its reaction with solutions of sodium hypohalites has been studied. When hypobromite solutions were used, α,α,α-tribromo-2,4,6-trichloroacetophenone was obtained. Treatment with hot, concentrated solutions of sodium hydroxide converted this ketone into 2,4,6-trichlorobenzoic acid.

With sodium hypochlorite solutions 2,4,6-trichloroacetophenone gave α,2,4,6-tetrachloroacetophenone. Prolonged treatment with the hypochlorite solutions converted both the trichloro and the tetrachloro compounds into 2,4,6-trichlorobenzoic acid.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF HOLY CROSS COLLEGE]

PHENACYL AND *p*-BROMOPHENACYL ESTERS OF MONOSUBSTITUTED BENZOIC ACIDS[1]

BY T. LEONARD KELLY AND HARTLEY W. HOWARD

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The use of phenacyl and *p*-bromophenacyl esters was introduced by Reid and co-workers[2] as a means of identifying acids. Since easily prepared and easily purified esters of organic acids are highly desirable the present investigation was undertaken.

Experimental

The procedure for the preparation of the esters was essentially the same as that of Reid. In the case of the amino acids, however, a modified procedure was used. By using the method of Reid on the amino acids very low yields were obtained. It was then considered possible that one mole

[1] This paper is constructed from a thesis submitted by Hartley W. Howard to the Faculty of Holy Cross College in partial fulfilment of the requirements for the degree of Master of Science.

[2] Reid and co-workers, THIS JOURNAL, **41**, 75 (1919); *ibid.*, **42**, 1043 (1920).

of the reagent might substitute in place of an amino hydrogen, thereby forming a N-phenacyl derivative of the acid as well as the ester of this derivative. A search revealed that Scholtz[3] had prepared the N-phenacyl acids of *o*-, *m*- and *p*-aminobenzoic acids. He also prepared and analyzed the phenacyl esters of the N-phenacyl *o*- and *p*-amino acids. The procedure we used was to take 0.005 equivalent of the acid, which was not quite neutralized with sodium carbonate in 5 cc. of water, and 2 g. of the reagent dissolved in alcohol and reflux for ninety minutes. After cooling, the precipitate was filtered and washed. It was then stirred into 100 cc. of 1% sodium hydroxide to dissolve the N-substituted acid. The ester, insoluble in alkali, was filtered and washed. The N-substituted acid was recovered by acidifying the alkaline filtrate with hydrochloric acid. The ester was then recrystallized to constant melting point.

Results

The results are expressed in tabular form, the first column giving the melting point of the acid used, the second the melting point of the ester and the third the percentage yield.

TABLE I

PHENACYL AND *p*-BROMOPHENACYL ESTERS

Acid	M. p., °C.	Phenacyl esters Ester m. p., °C.	Yield, %	*p*-Bromophenacyl esters Ester m. p., °C.	Yield, %
o-Bromobenzoic	147	83.2	99	101.6	86
m-Bromobenzoic	154	113.4	88	126.4	85
p-Bromobenzoic	252	...	..	133.8	84
o-Chlorobenzoic	138	83	97	106	80
m-Chlorobenzoic	153	116.4	98	117.2	82
p-Chlorobenzoic	235	87.6	98	126	80
o-Iodobenzoic	162	71	96	110.2	91
m-Iodobenzoic	185	115.6	78	127.6	81
p-Iodobenzoic	268	101 dec.	84	146.4	61
o-Nitrobenzoic	144	124.5	83	100.6	88
m-Nitrobenzoic	139	104.5	86	133.6	85
p-Nitrobenzoic	237	...	..	134	89
m-Hydroxybenzoic	196	146.5	79	168	79
p-Hydroxybenzoic	211	178	91	184	79
o-Nitrocinnamic	243	126	91	141.5	92
m-Nitrocinnamic	197	145.5	89	177.5	91
p-Nitrocinnamic	285	146.2		190.5	89

TABLE II

p-BROMOPHENACYL ESTERS OF N-*p*-BROMOPHENACYL AMINOBENZOIC ACIDS

Acid	M. p., °C.	Ester m. p., °C.	Yield, %
o-Aminobenzoic	144	172	52
m-Aminobenzoic	169	190	36
p-Aminobenzoic	187	200	62

[3] Scholtz, *Ber.*, **51**, 1645 (1918).

These three esters were analyzed for bromine and checked with the calculated percentages. Acetone was used as solvent for recrystallizations. No precipitate was obtained upon acidifying the alkaline filtrate from the ortho acid. From the meta acid a precipitate, presumably N-*p*-bromophenacyl-*m*-aminobenzoic acid, was obtained. It melted at 198°. From the para acid a precipitate, presumably N-*p*-bromophenacyl-*p*-aminobenzoic acid, was obtained which melted at 208°.

Summary

1. The esters formed by phenacyl bromide and *p*-bromophenacyl bromide with the aminobenzoic acids are shown to be substituted in the amine group as well as the carboxyl group.

2. A number of substituted benzoic acids have been converted to the phenacyl and *p*-bromophenacyl esters and their melting points recorded.

WORCESTER, MASSACHUSETTS

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

REARRANGEMENT OF UNSATURATED 1,4-GLYCOLS. 2-METHYL-2-BUTENE-1,4-DIOL

BY A. F. SHEPARD[1] AND JOHN R. JOHNSON

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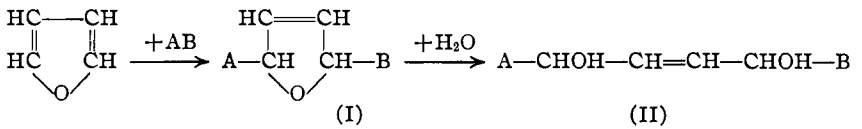
It has been suggested that the mechanism of a number of reactions of furan and its simple derivatives involves a preliminary 1,4-addition to the furan ring. Such reactions include the processes of halogenation[2] and nitration,[3] as well as the rearrangement of the α-furfuryl group in metathesis[4] and in ring opening reactions.[5,6] The postulation of 1,4-addition leads to the formulation of an intermediate 2,5-dihydrofuran derivative (I), which is merely the cyclic ether of a substituted 2-butene-1,4-diol (II).



(I) (II)

[1] This article is an abstract of a portion of a thesis submitted by A. F. Shepard to the Faculty of the Graduate School of Cornell University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, in June, 1929.

[2] Gilman and Wright, THIS JOURNAL, **52**, 3349 (1930).

[3] Freure and Johnson, *ibid.*, **53**, 1142 (1931).

[4] (a) Reichstein, *Ber.*, **63**, 749 (1930); (b) Runde, Scott and Johnson, THIS JOURNAL, **52**, 1284 (1930).

[5] Pummerer and Gump, *Ber.*, **56**, 999 (1923).

[6] In dealing with furan derivatives such as C_4H_3O—CH=CH—CO—R, in which the conjugated system extends into the side chain, it has been suggested that 1,6- or 1,8-addition may occur.[2]