[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, CAIRO UNIVERSITY]

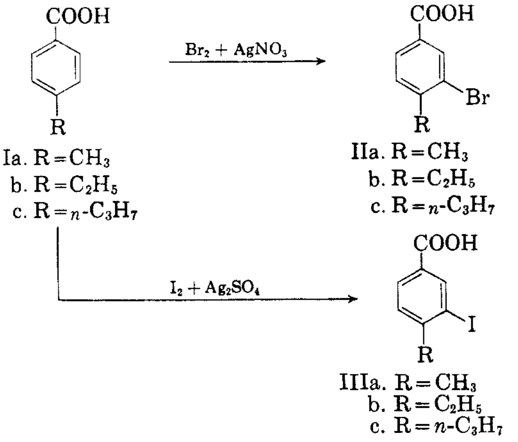
Bromination and Iodination of Some *p*-Alkylbenzoic Acids

ABDALLAH M. FLEIFEL

Received November 11, 1959

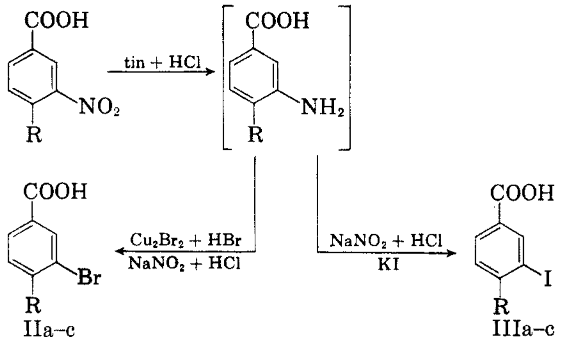
Bromination and iodination of some *p*-alkylbenzoic acids may be effected in almost quantitative yields. Bromination of the *p*-alkylbenzoic acids (Ia–c) with bromine in the presence of silver nitrate in acidic medium (*cf.* Derbyshire and Waters[1]) gives 3-bromo-4-alkylbenzoic acids (IIa–c).

Iodination of the *p*-alkylbenzoic acids (Ia–c) with iodine in the presence of silver sulfate in concentrated sulfuric acid (cf. Derbyshire and Waters[2]) affords 3-iodo-4-alkylbenzoic acids (IIIa–c):



Scheme A

Authentic specimens of IIa–c and IIIa–c were prepared from the corresponding 4-alkyl-3-nitrobenzoic acids (*cf.* Fahim and Fleifel[3]) which were reduced with tin and hydrochloric acid to give 3-amino-4-alkylbenzoic acids. These were subjected without isolation to Sandmeyer's reaction to give samples of 3-bromo-4-alkylbenzoic acids or 3-iodo-4-alkylbenzoic acids (*cf.* Kloeppel[4]) which were found to be identical with IIa–c and IIIa–c, respectively (Scheme B).



Scheme B

An authentic specimen of IIa was also prepared by another route, starting with *p*-nitrotoluene (*cf.* Claus and Kunath,[5] and Higginbottom *et al.*[6]).

The preceding facts indicate that the halonium ion aromatic substitution is aided by the *ortho* activating alkyl group in the 4-position. The *meta* directing in the 1-position is deactivating. It only allows substitution in the 3-position; it does not aid it as in fact the alkyl group does.

EXPERIMENTAL

General procedure. (a) *Bromination of p-alkylbenzoic acids.* The *p*-alkylbenzoic acid (Ia–c) (0.1 mole) (prepared according to Fahim and Fleifel[3]) was mixed with nitric acid (66 ml.; *d.*, 1.40), distilled water (50 ml.), glacial acetic acid (300 ml.), and bromine (17.6 g.; 0.11 mole) in a 3-necked ground-joint flask provided with a mechanical stirrer, a reflux condenser, and a tap funnel. An aqueous solution of silver nitrate (17 g.; 0.1 mole) in distilled water (50 ml.) was added dropwise during $^1/_2$ hr. with vigorous stirring and the reaction mixture was stirred for 2 hr. longer at room temperature (25°). It was then poured into ice-cold water and the precipitate collected. The solid product, which consisted of the organic acid and silver bromide, was digested with sodium carbonate and filtered off. The carbonate extract was boiled with charcoal, filtered, cooled, and acidified (a little amount of sodium bisulfite being added). The precipitated acid was collected, dried, and crystallized.

(b) *Iodination of p-alkylbenzoic acids.* Finely powdered iodine (26 g.; 0.11 mole) was added portionwise during $^1/_2$ hr. to the mixture of *p*-alkylbenzoic acid (Ia–c) (0.1 mole), silver sulfate (16 g.; 0.05 mole) in conc. sulfuric acid (240 ml.) and a little distilled water (30 ml.) on the boiling water bath with efficient stirring. The reaction mixture was refluxed for Ia, 0.5 hr., Ib, 2.5 hr., Ic, 5 hr. with vigorous stirring. It was then poured into ice-cold water and worked up as mentioned before. The iodo acids (IIIa–c) obtained on acidification of the sodium carbonate extract were filtered, dried, and crystallized.

Authentic specimens of IIa–c *and* IIIa–c. 4-Alkyl-3-nitrobenzoic acid (0.1 mole) (prepared as recommended by Fahim and Fleifel[3]) was refluxed with tin foil (25 g.) and concd. hydrochloric acid (100 ml.) on a steam bath for 5 hr. The product was decanted from any unchanged tin, cooled, and then diazotized with a solution of sodium nitrite (6.9 g.; 0.1 mole) in water (30 ml.). The diazonium solution was treated either with cuprous bromide (29 g.; 0.1 mole) in

---

(1) D. H. Derbyshire and W. A. Waters, *J. Chem. Soc.*, 573 (1950).

(2) D. H. Derbyshire and W. A. Waters, *J. Chem. Soc.*, 3694 (1950).

(3) H. A. Fahim and A. M. Fleifel, *J. Chem. Soc.*, 4519 (1952).

(4) E. Kloeppel, *Ber.*, **26**, 1733 (1893).

(5) Ad. Claus and H. Kunath, *J. prakt. Chem.*, **39**, 487 (1889).

(6) A. Higginbottom, P. Hill, and W. F. Short, *J. Chem. Soc.*, 264 (1937).

TABLE I

3-Bromo-4-alkyl- and 3-Iodo-4-alkyl-benzoic Acids

Compound	Solvent	M.P.,°	Yield, %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Bromine, % Calcd.	Bromine, % Found
IIa	C_2H_5OH	204	100	$C_8H_7O_2Br$[4]	44.65	44.25	3.20	3.10	37.20	36.80
IIb	C_2H_5OH	165	100	$C_9H_9O_2Br$	47.16	46.89	3.93	3.75	34.93	34.87
IIc	Benzene-ligroin	89–90	95	$C_{10}H_{11}O_2Br$	49.38	48.97	4.52	4.41	32.92	32.50
									Iodine, % Calcd.	Iodine, % Found
IIIa	C_2H_5OH	205–206	100	$C_8H_7O_2I$[5]	36.64	36.85	2.67	2.50	48.47	48.15
IIIb	C_6H_6	191–192	100	$C_9H_9O_2I$	39.13	38.86	3.26	3.38	46.08	45.42
IIIc	C_2H_5OH	232–233	100	$C_{10}H_{11}O_2I$	41.37	41.0	3.79	3.58	43.79	43.40

hydrobromic acid (100 ml.; 48%) or with an aqueous solution of potassium iodide (18 g.; 0.11 mole). The reaction mixture was stirred for 1 hr. at room temperature, a little sodium bisulfite added, the precipitated acids collected after acidification and crystallized. Mixed melting point determination was carried out between the bromo- acids and IIa–c, and between the iodo- acids and IIIa–c, respectively, and in each case no depression was observed.

An authentic specimen of IIa was also prepared by a series of already known reactions starting with *p*-nitrotoluene (*cf.*[5,6]) which was brominated according to procedure (a) to give 2-bromo-4-nitrotoluene in 100% yield (*cf.*[6]). The latter was converted to the corresponding nitrile which on hydrolysis gave 3-bromo-4-methylbenzoic acid (2-bromo-*p*-toluic acid), m.p. 204°, undepressed when mixed with IIa. The 3-bromo-4-alkyl- and 3-iodo-4-alkyl-benzoic acids are listed in Table I.

Chemistry Department
Faculty of Science
Cairo University
Giza, Cario, Egypt, U. A. R.

[Contribution from the Department of Chemistry, University of Notre Dame]

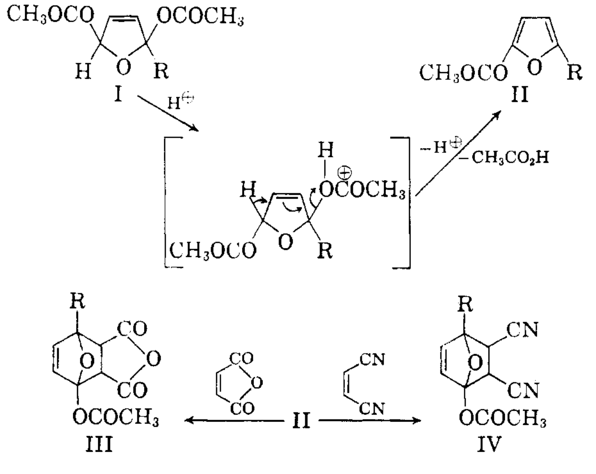
Reactions of Furan Compounds. XVIII. Nuclear Acetoxylation[1]

G. FRANK D'ALELIO, CARL J. WILLIAMS, Jr.,[2] and CHRISTOPHER L. WILSON

Received December 8, 1959

The acid-catalyzed pyrolysis of 2,5-diacetoxy-2,5-dihydrofuran resulting in the elimination of acetic acid and the formation of 2-acetoxyfuran and γ-crotonolactone has been studied further. Lactone formation is believed to involve further pyrolysis of 2-acetoxyfuran in the presence of acetic acid to give the lactone and acetic anhydride. The syntheses of diacetoxylated α-substituted furans by the action of bromine and potassium acetate in acetic acid acetic anhydride on α-substituted furans did not yield the expected products. However, their unstable formation is suspected because of the isolation of 2-acetoxy-5-methylfuran, anemonin, 2-oxo-5-acetoxymethylene-2,5-dihydrofuran, and 2-oxo-5-methoxymethylene-2,5-dihydrofuran from 2-methylfuran, furfuryl acetate, furfural diacetate, and furfuryl methyl ether, respectively.

The synthesis of 2-acetoxyfuran has been previously described; vapor-phase pyrolysis of 2,5-diacetoxy-2,5-dihydrofuran (I. R = –H) at 400–450° gave 7–40% 2-acetoxyfuran (II. R = –H) and varying amounts of a by-product, γ-crotonolactone (V).[3] Milder acid-catalyzed liquid-phase pyrolysis (100°) in the presence of a high-boiling diluent was subsequently reported to give much-improved yields (80%) of 2-acetoxyfuran.[4] The pyrolysis failed in the presence of a basic substance such as sodium acetate, and it was reasoned that the production of 2-acetoxyfuran was an acid-catalyzed



elimination of acetic acid. Pyrolysis in the absence of acid was attributed to traces of residual acid and/or by-products of the pyrolysis itself (*e.g.*, acetic

---

[1] Abstracted from a portion of the Ph.D. dissertation of C. J. Williams, University of Notre Dame, 1958. Part XVII, *J. Am. Chem. Soc.*, **81**, 2440 (1959).

[2] Present address: Research Laboratories, Eastman Kodak Co.

[3] N. Clauson-Kaas and N. Elming, *Acta Chem. Scand.*, **6**, 560 (1952).

[4] C. L. Wilson, M. P. Cava, and C. J. Williams, Jr., *J. Am. Chem. Soc.*, **78**, 2306 (1956).