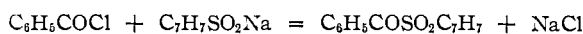


The Reaction between Carboxylic Acid Chlorides and Salts of *p*-Toluenesulfonic Acid

By H. T. HOOKWAY

During the course of an investigation of a series of α -methylene sulfones¹ it was found desirable to attempt the synthesis of α -ketosulfones, and an examination was made of the reaction between carboxylic acid chlorides and salts of *p*-toluenesulfonic acid.

By analogy with the reaction between *p*-toluenesulfonyl chloride and sodium *p*-toluenesulfinate to give an α -disulfone,² the reaction between benzoyl chloride and sodium *p*-toluenesulfinate was expected to follow the course shown below



Ethereal solutions of benzoyl and acetyl chlorides respectively were heated under pressure with sodium *p*-toluenesulfinate dihydrate and in both cases the products isolated were the corresponding carboxylic acids and di-*p*-tolyl disulfoxide (shown to be a thioisulfonate, $C_7H_7SO_2SC_7H_7$ ^{3,4}; no trace of a ketosulfone could be detected.

Since it does not appear possible to dehydrate sodium *p*-toluenesulfinate dihydrate without decomposition, this salt was used in the two experiments described above: presumably the acid chloride was first hydrolyzed to carboxylic acid and hydrochloric acid; the latter then liberated free *p*-toluenesulfonic acid which forms di-*p*-tolyl disulfoxide on heating alone or, more readily in the presence of aqueous acids^{5,6}

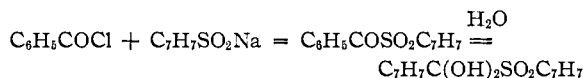


p-Nitrobenzoyl chloride was then heated with sodium *p*-toluenesulfinate: it was anticipated that this chloride, containing a strongly electron attractive nitro-group, would be more resistant to hydrolysis under the conditions obtaining in these experiments than either acetyl or benzoyl chlorides. Again, no ketosulfone was obtained, but a small amount of disulfoxide was isolated.

An attempt was made to avoid the use of a hydrated salt by preparing silver *p*-toluenesulfinate. This salt is stated to be anhydrous when obtained by precipitation by addition of silver nitrate to an aqueous solution of the sodium sulfinate.⁷ The analysis of the silver salt used in these experiments indicated that it still contained a small amount of water. When the silver salt and benzoyl chloride were heated together in ether, di-*p*-tolyl disulfoxide was obtained.

It is interesting to note Kohler and MacDonald claimed that by heating an ethereal solution of

benzoyl chloride with sodium *p*-toluenesulfinate an α -ketosulfone was obtained as an ether soluble oil which readily gave a solid hydrate on trituration with water²



A similar reaction was also stated to take place when other acid chlorides were used, but the properties of the reaction products were not described. It must also be noted that Kohler and MacDonald did not state whether they had prepared and used anhydrous sodium *p*-toluenesulfinate or a hydrated material in their experiments. These authors stated that their products gave crystalline derivatives with typical ketone reagents, such as hydroxylamine and phenylhydrazine. Reaction of di-*p*-tolyl disulfoxide with 2,4-dinitrophenylhydrazine in methanolic sulfuric acid, under conditions such that a ketone gives the corresponding dinitrophenylhydrazone, gave only unchanged disulfoxide. When di-*p*-tolyl disulfoxide was warmed with hydroxylamine in an acetic acid-sodium acetate buffer, however, amongst other products, di-*p*-tolyl disulfide was obtained. A similar breakdown of the disulfoxide was observed with phenylhydrazine in buffered solution: these observations will be the subject of a further communication.

Acknowledgment.—The author wishes to express his indebtedness to Dr. J. Kenyon, F.R.S., for his interest in this work.

Experimental

Reaction between Sodium *p*-Toluenesulfinate and Benzoyl Chloride.—Sodium *p*-toluenesulfinate dihydrate (4.0 g., 0.019 mole) was suspended in ether (10 cc.) in a stout walled glass tube and benzoyl chloride (3.0 g., 0.021 mole) was added. The tube was then sealed and heated at 100° for thirty-six hours. After cooling, the contents of the tube were extracted with sodium carbonate solution (25 cc. of 3 *N*); the residual ethereal solution after drying and evaporation to small bulk gave di-*p*-tolyl disulfoxide; yield, 1.0 g., m. p. 78.5–79° (after three recrystallizations from 96% ethanol). Found: C, 60.6; H, 4.7; S, 22.6. Calcd. for $C_{14}H_{14}O_2S_2$: C, 60.5; H, 5.04; S, 23.0. Mixed m. p. with authentic specimen of di-*p*-tolyl disulfoxide⁶ 78.5°. The alkaline extract on acidification gave 2.5 g. of benzoic acid, m. p. 122° (theoretical yield from hydrolysis of benzoyl chloride, 2.6 g.).

Reaction between Sodium *p*-Toluenesulfinate and Acetyl Chloride.—Sodium *p*-toluenesulfinate dihydrate (2.0 g., 0.009 mole) was suspended in ether (10 cc.) in a stout walled glass tube and acetyl chloride (0.84 g., 0.011 mole) was added. The tube was then sealed and heated at 100° for thirty-six hours. The reaction mixture was worked up as described in the previous experiment; yield of di-*p*-tolyl disulfoxide, 0.97 g., m. p. 78.5–79°; mixed m. p. with authentic specimen, 78°.

Reaction between Sodium *p*-Toluenesulfinate and *p*-Nitrobenzoyl Chloride.—Sodium *p*-toluenesulfinate dihydrate (8.0 g., 0.037 mole) was suspended in ether (100 cc.) in a stout-walled glass bottle and *p*-nitrobenzoyl chloride (6.92 g., 0.037 mole) was added. The reaction mixture was heated at 100° for twelve hours and gave 1.57 g. of di-*p*-tolyl disulfoxide, m. p. 78°, on working up.

(8) Prepared by the method of Smiles and Gibson, ref. 6.

(1) To be published shortly.

(2) Kohler and MacDonald, *Am. Chem. J.*, **22**, 219 (1899).

(3) Gilman, *et al.*, *THIS JOURNAL*, **47**, 851 (1925).

(4) Miller and Smiles, *J. Chem. Soc.*, **127**, 224 (1925).

(5) Otto, *Ber.*, **15**, 121 (1882).

(6) Smiles and Gibson, *J. Chem. Soc.*, **125**, 180 (1924).

(7) Otto, *Ann.*, **142**, 97 (1867).

Reaction between Silver *p*-Toluenesulfinate and Benzoyl Chloride.—Silver *p*-toluenesulfinate was prepared from the sodium salt and silver nitrate by precipitation from aqueous solution. The precipitated silver salt was washed with water and acetone and air dried. Found: Ag, 39.9. Calcd. for $C_7H_7O_2SAg$: Ag, 41. The silver salt (2.00 g., 0.0076 mole) was suspended in ether (20 cc. of sodium dried) in a stout-walled glass tube and benzoyl chloride (1.07 g., 0.0076 mole) was added. The tube was then sealed and heated at 100° for twelve hours. The reaction mixture yielded 0.2 g. of di-*p*-tolyl disulfide, m. p. 78°. All m. p.'s are uncorrected. Kohler and MacDonald quote 80° as m. p. for the keto-hydrate $C_{14}H_{14}O_4S$.

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The Influence of Substituents on the Ultraviolet Absorption Spectrum of Styrene

BY Y. HIRSCHBERG

In view of the recent paper by Murray and Gallaway,¹ the following measurements on the spectra of some substituted (ortho-, alpha- and beta-positions) styrenes may be recorded (alcohol as solvent).

Hydrocarbon	Max., Å.	Log ϵ	Max., Å.	Log ϵ	Max., Å.	Log ϵ	Max., Å.	Log ϵ
Styrene	2910	2.77	2820	2.88	2730	2.88	2440	4.23
β -Methylstyrene ^{a,b}	2930	2.84	2840	2.99			2460	4.25
α -Methylstyrene ^a							2435	3.96
α,β -Dimethylstyrene							2440	3.94
<i>o</i> -Methylstyrene ^c	2980	2.03					2460	3.86
<i>o,\alpha</i> -Dimethylstyrene ^{d,e}								

No maximum between 2100–3000 Å.

^a Ramart-Lucas and Amagat, *Bull. soc. chim.*, [4] **51**, 108 (1932); [5] **1**, 719 (1934). ^b Hillmer and Schorning, *Z. physik. Chem.*, **A167**, 407 (1934). ^c Ramart-Lucas and Hoch, *Bull. soc. chim.*, [5] **2**, 327 (1935). ^d Ref. (1). ^e Ramart-Lucas and Hoch, *Bull. soc. chim.*, [5] **5**, 848 (1938). ^f Campbell and co-workers, *THIS JOURNAL*, **69**, 880 (1947).

Introduction of a methyl group into the β -position of styrene has very little influence on the resonating system, whilst α -substitution, and to a minor degree *o*-substitution, destroys the resonance. This is particularly clear for the *o,\alpha*-dimethylstyrene for which no absorption maximum at all has been observed. It is reasonable to assume that the phenyl group is crowded out of the plane of the exocyclic double bond, and the mono-planarity required is thus destroyed.²

Materials

α -Methylstyrene was prepared according to Staudinger and Breusch,³ the β -isomer from ethylphenylcarbinol with acetic anhydride, according to Spaeth and Koller.⁴ For the synthesis of α,β -dimethylstyrene,⁵ acetophenone was converted by reaction with ethylmagnesium bromide into phenylmethylethylcarbinol and the crude product dehydrated with boiling acetic anhydride: b. p. 107–109° (21 mm.); yield 75.5%. *o*-Methylstyrene was obtained by reaction of *o*-tolylmagnesium bromide with acetaldehyde and adding the carbinol obtained (b. p. 120–130° (29 mm.)) dropwise to molten potassium hydrogen sulfate,

containing 1% of hydroquinone, at a bath temperature of 200° and in a vacuum of 100 mm.⁶ The product which distilled off immediately, was fractionated, b. p. 75–78° (21 mm.).⁷ Analogous reaction of *o*-tolylmagnesium bromide with acetone gave *o*-tolylmethylcarbinol, b. p. 120–122° (25 mm.) and dehydration of the latter with boiling acetic anhydride, *o,\alpha*-dimethylstyrene, b. p. 83–85° (25 mm.) in 70% yield.⁸

(6) Brooks, *THIS JOURNAL*, **66**, 1295 (1944).

(7) Eisenlohr and Schulz, *Ber.*, **57**, 1816 (1924); b. p. 170–174° at atmospheric pressure.

(8) Eisenlohr and Schulz, *loc. cit.*, b. p. 183–185° at atmospheric pressure.

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The Behavior of 1-Naphthyl Tetraacetyl- β -D-glucoside toward Diazotized *p*-Nitroaniline

BY CHARLES D. HURD AND WILLIAM A. BONNER

This note describes attempts to couple 1-naphthyl tetraacetyl- β -D-glucopyranoside (I) with diazo compounds. The ease of coupling should compare with that of 1-methoxynaphthalene.

Meyer and Lenhardt¹ record difficulty in cou-

pling diazotized *p*-nitroaniline with anisole but claim that 4-(*p*-nitrophenylazo)-1-methoxynaphthalene, m. p. 169°, is formed on coupling with 1-methoxynaphthalene.

Attempts to couple (I) with aqueous solutions of diazotized *p*-nitroaniline led to difficulties caused by the insolubility of the acetylated glucoside. When a solution of *p*-nitrobenzenediazonium sulfate was prepared in glacial acetic acid after the manner of Hodgson and Walker² and mixed with a solution of the acetylated glucoside in acetic acid, a slight color developed. In the course of several days, however, this mixture assumed the intense purple coloration characteristic of control experiments with 1-methoxynaphthalene. The only product found was 4-(*p*-nitrophenylazo)-1-naphthol in 22% yield, showing cleavage as well as coupling. About half of the starting glucoside was recovered. It has frequently been observed³ that phenolic ethers couple with partial or complete dealkylation.

In view of this result we studied 1-methoxynaphthalene under approximately identical con-

(1) Meyer and Lenhardt, *Ann.*, **398**, 78 (1913).

(2) Hodgson and Walker, *J. Chem. Soc.*, 1620 (1933).

(3) K. H. Saunders, "The Aromatic Diazo Compounds," Edward Arnold and Co., London, 1938, p. 112.

(1) Murray and Gallaway, *THIS JOURNAL*, **70**, 3867 (1948).

(2) Compare, Buck, Kennedy, Morton and Tanner, *Nature*, **162**, 103 (1948), and the dipole measurements of Everard and Sutton, *ibid.*, **162**, 104 (1948).

(3) Staudinger and Breusch, *Ber.*, **62**, 449 (1929).

(4) Spaeth and Koller, *ibid.*, **58**, 1268 (1925).

(5) Klages, *ibid.*, **35**, 2641 (1902).