

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 $C_7H_7O_2S$ Ag: 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

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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

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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).