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 disulfoxide, 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
o-Methylstyrene[c]	2980	2.03					2460	3.36
o,α-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*,α-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 monoplanarity 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*-tolyldimethylcarbinol, b. p. 120-122° (25 mm.) and dehydration of the latter with boiling acetic anhydride, *o*,α-dimethylstyrene, b. p. 83-85° (25 mm.) in 70% yield.[8]

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[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).

[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 Lenhardt[1] record difficulty in coupling 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 Walker[2] 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 observed[3] that phenolic ethers couple with partial or complete dealkylation.

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

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[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, 1936, p. 112.

ditions. Here too, coupling took place with substantial cleavage of the ether. We were also unable to duplicate the results of Meyer and Lenhardt[1] using their 50% aqueous acetic acid solution. Coupling again was accompanied by demethylation, an observation which is in line with that of Jambuserwala and Mason[4] who found that 2-methoxy-3-naphthoic acid coupled with diazotized *p*-nitroaniline with complete removal of methoxyl,

Since the above coupling was conducted under strongly acid conditions, it seemed advisable to duplicate the process under conditions whereby the acidity of the sulfuric acid was neutralized by sodium acetate. When the acetic acid solution of *p*-nitrobenzenediazonium sulfate and (I) stood in contact with sodium acetate for several days, a red product was obtained on dilution with water. This was separated by adsorption methods into an amber glass, a red solid, and 1,3-bis-*p*-nitrophenyltriazene. The first two substances were not characterized. While the evidence here neither indicated nor precluded complete cleavage, it is pertinent to note that 1-methoxynaphthalene coupled with cleavage under these same buffered conditions.

Experimental

Coupling of 1-Naphthyl Tetraacetyl-β-D-glucopyranoside with Diazotized *p*-Nitroaniline.—Finely powdered sodium nitrite (1.7 g.) was added to 12 ml. of cold sulfuric acid. The mixture, warmed to about 70°, was stirred until completely dissolved, then was cooled to 20°. *p*-Nitroaniline (3 g.) was dissolved in hot acetic acid (36 ml.), and the mixture was cooled rapidly to room temperature. This solution was added slowly with stirring to the first solution.

One gram of 1-naphthyl tetraacetyl-β-D-glucopyranoside was dissolved in 20 g. of acetic acid. Into this mixture (at 20°) was added 15 ml. of the above diazonium solution. A pink coloration appeared. After standing for forty hours, the solution became intensely purple. On pouring into water (300 ml.), an orange solid resulted which rapidly became gummy. Extraction with ether (300 ml.) dissolved the gum but left a small amount of red solid which was filtered. The ether extract was washed with water and evaporated. The residue was redissolved in ether, and again a small amount of red solid remained undissolved. It was separated and combined with that above. The ether extract was dried over anhydrous sodium sulfate, filtered, and evaporated. There resulted 0.78 g. of reddish solid. This was recrystallized from 2-propanol to yield about 0.5 g. of the starting glucoside in slightly impure condition; m. p. 172-175°, mixed m. p. 175-177°.

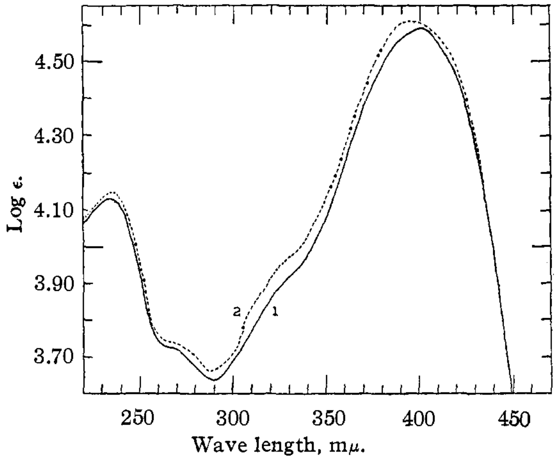

Fig. 1.—Absorption spectrum of 1,3-bis-*p*-nitrophenyltriazene: 1, known sample; 2, suspected sample.

The ether-insoluble red solids weighed 0.13 g. They were triturated with ether, air-dried, and found to melt at 275-278°. A mixed melting point of this material with 4-(*p*-nitrophenylazo)-1-naphthol (m. p. 284-285° (cor.)) gave the value 278-280°.

Attempts to couple 1-naphthyl tetraacetyl-β-D-glucoside with diazotized aniline or *p*-aminobenzoic acid under conditions comparable to those above led only to the isolation of starting material.

Several attempts were made to conduct the above coupling under well-buffered conditions. In a typical experiment 1-naphthyl tetraacetyl-β-D-glucoside (1.0 g.) in acetic acid (20 ml.) was treated with one-third (15 ml.) of the acetic acid solution of *p*-nitrobenzenediazonium sulfate prepared as described above. Anhydrous sodium acetate (12.3 g.) was added, the mixture shaken to an emulsion and permitted to stand for four days. The original yellow color became deep red, once the mixture was poured into water. The crude red solid was collected on a filter, suspended in water, collected again, and dried over phosphoric anhydride; yield, 1.80 g. Half a gram of this was dissolved in ethyl acetate (10 ml.) and ether (30 ml.). The red solution was filtered, and the filtrate was introduced into a column of alumina wet with ether. The absorbed band was developed with ether, but only a very thin orange band separated; this was not investigated. The effluent was evaporated to yield 0.19 g. of a reddish, amber glass, $[\alpha]^{25}{}_{\mathrm{D}}$ −48.5° (*c*, 1.90; chloroform). Attempts were made to crystallize this from 2-propanol, but only gummy crystals resulted. The main adsorbed band was extracted from the adsorbent in a Soxhlet thimble with ethyl acetate. Removal of the solvent left 0.22 g. of red solid. This was digested with methanol and filtered, leaving a gray-brown solid, m. p. 225-230° (dec.).

About 0.8 g. of the crude yield was digested twice with a total of 55 ml. of hot methanol, leaving 0.15 g. of orange solid, m. p. 228-229° (dec.). This was recrystallized from a mixture of acetone and water to give a yellow-gray solid, m. p. 229.5-230° (dec.). This was proven by melting point, mixed melting point, absorption spectrum (Fig. 1) and analysis to be 1,3-bis-*p*-nitrophenyltriazene.

Anal. Calcd. for $C_{12}H_9N_5O_4$: C, 50.2; H, 3.16; N, 24.4. Found: C, 49.62; H, 3.25; N, 24.56.

Coupling of 1-Methoxynaphthalene with Diazotized *p*-Nitroaniline.—1-Methoxynaphthalene (1 ml.) was dissolved in acetic acid (5 ml.) and sodium acetate (*ca.* 0.5 g.) was added. About 5 ml. of the non-aqueous diazo solution described above was added giving an immediate intense purple coloration. The homogeneous mixture was poured into water (100 ml.). A red product precipitated, which was collected on a filter and washed. A portion of the product was separated by means of its relative insolubility in hot ethanol. It was impure 4-(*p*-nitrophenylazo)-1-naphthol, m. p. 272-280°. The alcohol solution deposited solid on standing, m. p. around 120-125°. This was possibly a mixture of the previous high-melting solid plus the more soluble 4-(*p*-nitrophenylazo)-1-methoxynaphthalene of m. p. 169°.

The directions of Meyer and Lenhardt[5] for preparing *p*-nitrophenylazo-1-methoxynaphthalene are not specific, but it is stated that the coupling is carried out in 50% acetic acid. We attempted to duplicate these conditions by dissolving 1-methoxynaphthalene (1 ml.) in acetic acid (4 ml.) containing water (1 ml.) and adding this solution to a portion of the above diazo solution (3 ml.) diluted with water (13 ml.). A red solid formed instantly.

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[4] Jambuserwala and Mason, *J. Soc. Dyers Colourists*, **46**, 339 (1930).

This proved quite insoluble in ethanol and was treated as above. The recrystallized portion melted at 277–282°, and the alcohol-insoluble portion had an indistinct m. p. above 280°.

In an attempt to encourage coupling without cleavage by buffering, 1-methoxynaphthalene (2 ml.) was treated with a mixture of 15 ml. of the non-aqueous diazo solution, 15 ml. of acetic acid, and 12.3 g. of anhydrous sodium acetate. After addition of more acetic acid (15 ml.), the red-black mixture was shaken thoroughly and poured into water. The red solid was filtered, rinsed, and washed by suspension in methanol and refiltration. The insoluble portion, when dry, melted at 275–280°.

1,3-bis-*p*-Nitrophenyltriazene.—The procedure used in this preparation was a modification of that of Meldola and Streatfield.[5] *p*-Nitroaniline (2.76 g., 0.02 mole) was dissolved with heating in concd. hydrochloric acid (50 ml.). The solution was cooled and a solution of sodium nitrite (0.69 g., 0.01 mole) in water (5 ml.) was slowly added dropwise with stirring. Water (20 ml.) was added to the mixture, which then stood for nineteen hours. The clear yellow solution was thrown into excess water, and on standing fine yellow needles formed. These were filtered and dried *in vacuo;* yield, 0.70 g., m. p. 224–228° (dec.). The mother liquors deposited a second crop, weight 0.05 g., m. p. 228–230° (dec.).

In order to establish without doubt the identity of this material and the product from the previous buffered coupling reaction involving the 1-naphthyl tetraacetyl-β-D-glucoside, absorption spectra of both samples were measured and found identical (Fig. 1). Solutions 10^{-3} molar in each sample were made for the measurements. In taking the readings, it soon became apparent that Beer's law was failing to apply. Thus at 440 mμ the 10^{-3} molar solution of each sample had a density reading on the Beckman Model DU Spectrophotometer of 1.84. A 10^{-4} molar solution at the same wave length had a density of 0.860 instead of 0.184. Similarly, at 410 mμ the density of the 10^{-4} molar solution was 1.800, while that of a 10^{-5} molar solution was 0.360. As the wave length region between 445 and 400 mμ was crossed, the density readings for 10^{-3} molar and 10^{-4} molar solutions approached constant values within the range of the spectrophotometer scale, and it was necessary to use 10^{-5} molar solutions in order to cover the lower visible and ultraviolet spectrum. These effects were observed on two different spectrophotometers. They are probably attributable to the ionization of dinitrodiazoaminobenzene in alcoholic solution, and are currently under more extensive study.

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[5] Meldola and Streatfield, *J. Chem. Soc.*, **49**, 627 (1886).

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The Dissociation of Lead Chloride in Ethylene Glycol–Water Mixtures

BY J. C. JAMES

Norman and Garrett[1] have recently reported measurements of the conductance of lead chloride solutions at 25° in ethylene glycol–water mixtures, and conclude that activity and conductance data for such solutions show deviations from the Debye–Hückel and Onsager theories which cannot be accounted for by the assumption of incomplete dissociation. Discrepancies between theoretical and experimental values were attributed to differences between the macro and micro dielectric constants of the solutions, and "effective microdielectric constants" were calculated by comparison of experimental slopes with those predicted by the Debye–Hückel and Onsager theories.

These conclusions are surprising, as in aqueous solution previous workers[2–4] have assumed that the intermediate ion $PbCl^+$ was present, and have derived dissociation constants of the order of 0.02–0.03 from activity and conductance data; also, Fromherz and Kun-Hou Lih[5] have shown that the ultraviolet absorption spectra indicated presence of this ion. Similarly, conductance data for the salts zinc malonate, zinc sulfate and lanthanum ferricyanide in glycol–water mixtures have been accounted for satisfactorily by assuming dissociation to be incomplete.[6]

Norman and Garrett[1] have rejected this treatment on the grounds that as curves for the plots of both Λ *vs.* $\sqrt{m}$ and γ *vs.* $\sqrt{m}$ were straight in the lower concentration regions, a constant degree of dissociation would result in any solvent. Such behavior, however, does not necessarily imply complete dissociation, as the effect of actual variation in α may be cancelled out almost completely by the effect of higher terms neglected in the limiting Debye–Hückel and Onsager equations. Thus it has been shown by Davies[7] that dissociation is not complete in calcium mandelate solutions, although the Λ *vs.* $\sqrt{m}$ plot is linear up to $m = 0.02$, far beyond the limits of Onsager's equation. It is shown in this Note that the data of Norman and Garrett can be given an alternative explanation on the assumption that the intermediate ion $PbCl^+$ is formed in solution by the process $Pb^{++} + Cl^- \rightleftarrows PbCl^+$, further association to give the neutral salt being negligible.

Activity Data.—Dissociation constants for lead chloride in water at 25° have been calculated from the activity data of Carmody[8] using the method described by Davies,[9] and are given in Table I, γ being the stoichiometric activity coefficient, and f the true mean ionic activity coefficient. Dissociation constants in glycol–water mixtures have been calculated by the same method from the activity data of Garrett, Bryant and Kiefer,[10] up to concentrations of 0.006 N and are summarized in Table III. Mean ionic activity coefficients have been obtained from the empirical equation

$$-\log f = S\left[\frac{\sqrt{\mu}}{1+\sqrt{\mu}} - 0.20\,\mu\right]$$

where S is the limiting Debye–Hückel slope;

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[1] J. W. Norman and A. B. Garrett, THIS JOURNAL, **69**, 110 (1947).

[2] E. C. Righellato and C. W. Davies, *Trans. Faraday Soc.*, **26**, 592 (1930).

[3] G. Scatchard and R. F. Teft, THIS JOURNAL, **52**, 2272 (1930).

[4] H. S. Harned and M. E. Fitzgerald, *ibid.*, **58**, 2624 (1936).

[5] H. Fromherz and Kun-Hou Lih, *Z. physik. Chem.*, **A153**, 321 (1931).

[6] J. C. James, unpublished work.

[7] C. W. Davies, *J. Chem. Soc.*, 271 (1938).

[8] W. R. Carmody, THIS JOURNAL, **51**, 2905 (1929).

[9] C. W. Davies, *J. Chem. Soc.*, 349 (1939).

[10] A. B. Garrett, R. Bryant and G. F. Kiefer, THIS JOURNAL, **65**, 1905 (1943).