prepared by condensation in acetic anhydride (method B). The general applicability of acetic anhydride for such condensations has been reported on by Kaslow and Stayner[13] and by Shaw and Wagstaff.[14] An inferior yield of 13% was reported by Tipson[15] for use of this method in preparing 2-(*p*-dimethylaminostyryl)-quinoline (XI). The 87% yield reported here can be attributed to the longer heating period employed.

Experimental

Piperidine-catalyzed Condensation of Quinaldinium Salts with Aromatic Aldehydes. Method A.—1-Methylquinaldinium methosulfate was purified by several recrystallizations from isopropyl alcohol, m.p. 151–152° (lit.[16] m.p. 223–224°).

Anal. Calcd. for $C_{12}H_{15}NO_4S$: C, 53.51; H, 5.62; N, 5.20. Found: C, 53.60; H, 5.81; N, 5.37.

After recrystallizations from isopropyl alcohol 1-methyl-6-ethoxyquinaldinium methosulfate melted 134–135° (lit.[10] m.p. 98°).

Anal. Calcd. for $C_{14}H_{19}NO_5S$: C, 53.64; H, 6.11; N, 4.47. Found: C, 53.50; H, 6.08; N, 4.38.

The preparation of all the 2-styrylquinolinium compounds shown in Table I was essentially the same as that described below for 1-methyl-2-(*m*-nitrostyryl)-6-ethoxyquinolinium methosulfate (VI).

A mixture of 18.8 g. (0.06 mole) of 1-methyl-6-ethoxyquinaldinium methosulfate, 9.1 g. (0.06 mole) of *m*-nitrobenzaldehyde and 1 ml. of piperidine in 100 ml. of isopropyl alcohol was brought to reflux temperature in two minutes. Refluxing then was continued for an additional 40 minutes. The reaction mixture was cooled and the product collected by filtration. After washing with ice-water and drying, there was obtained 25 g. of the styryl salt, which melted at 266–267°, yield 93%.

Condensation of Quinaldines with Aromatic Aldehydes in Acetic Anhydride. Method B.—All the 2-styrylquinolines shown in Table II were prepared essentially as described below for 2-(*m*-nitrostyryl)-6-ethoxyquinoline (XIII). This procedure is essentially analogous to that described by Kaslow and Stayner.[13]

A mixture of 18.7 g. (0.1 mole) of 6-ethoxyquinaldine, 15.1 g. (0.1 mole) of *m*-nitrobenzaldehyde and 8.0 g. (0.06 mole) of acetic anhydride was heated under reflux for six hours. The hot solution was poured into excess cold water. After standing overnight the product was collected by filtration. The crude material was dried, yield 31 g. (98%), m.p. 137–139°.

Quaternation was effected by heating 5 g. (0.016 mole) of the above base with 3.8 g. (0.03 mole) of methyl sulfate in 10 ml. of nitrobenzene on the steam-bath until a solution was obtained (about 5 minutes). After cooling, the product (XX) was collected by filtration, washed well with ether, and dried; yield 6.1 g. (89%), m.p. 252–253°, after recrystallizations from methanol.

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[13] C. E. Kaslow and R. O. Stayner, THIS JOURNAL, **67**, 1717 (1945).

[14] B. D. Shaw and E. A. Wagstaff, *J. Chem. Soc.*, 77 (1933).

[15] R. S. Tipson, THIS JOURNAL, **67**, 507 (1945).

[16] H. Rupe, H. Hagenbach and A. Collin, *Helv. Chim. Acta*, **18**, 1395 (1935).

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The Reductive Decomposition of an Azo Compound

BY J. E. LEFFLER AND L. M. BARBATO

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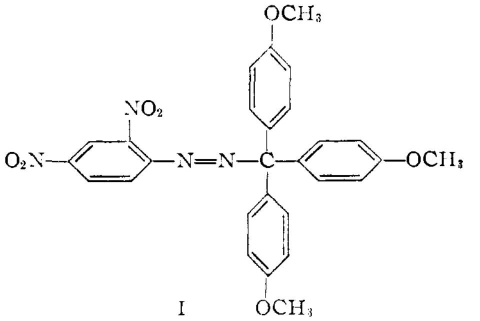
In connection with a study of the effects of solvent and structural changes on the free radical decomposition of organic compounds and on the shift to polar reaction mechanisms we have studied the azo compound 2,4-dinitrophenylazotris-(*p*-anisyl)-methane (I).



I

We found, however, that we were hampered in our original purpose by the tendency of the azo compound to be reduced to the corresponding hydrazo compound. With three nitro substituents the effect should be still more pronounced and we were in fact unable to prepare 2,4,6-trinitrophenyl-azo-tris-(*p*-anisyl)-methane by oxidation of the hydrazo compound.

In benzene at 75° the dinitro compound I is half reduced to the hydrazo compound and half decomposed to a complicated mixture of products suggestive of a radical reaction. In other radical decomposition reactions a frequent feature has been the displacement of hydrogen atoms from the solvent by attacking free radicals.[1] It is not generally believed that atomic hydrogen is set free in such reactions but only that a second radical accepts the hydrogen atom at some stage, perhaps by reaction with a radical–solvent complex. We suspect that in the decomposition of the azo compound I, molecules of the undecomposed azo compound play the role ordinarily played by a second free radical, accepting hydrogen from a solvent–radical complex and becoming reduced to the hydrazo compound. The first-order rate constant for the formation of radicals from the azo compound in benzene at 75° in the presence of α,α-diphenyl-β-picrylhydrazyl is about 10^{-4} sec.$^{-1}$ as determined by the fading of the diphenylpicrylhydrazyl color. Since α,α-diphenyl-β-picrylhydrazyl reacts, but not instantaneously, with 2,4-dinitrophenylhydrazo-tris-(*p*-anisyl)-methane, the rate constant is only an approximate one.

Experimental

2,4-Dinitrophenylhydrazotris-(*p*-anisyl)-methane.—To a boiling benzene solution of 1.3 g. of 2,4-dinitrophenylhydrazine is added 1 g. of trianisylmethyl chloride, the mixture boiled for one hour, filtered and the filtrate concentrated to dryness. The residue after washing with warm alcohol is crystallized several times from chloroform–alcohol; the product melts at 165–168°.

Anal.[3] Calcd. for $C_{28}H_{26}N_4O_7$: C, 63.38; H, 4.94. Found: C, 63.08, 62.82; H, 4.86, 4.73.

2,4-Dinitrophenylazotris-(*p*-anisyl)-methane.—The hydrazo compound in chloroform solution is shaken with excess lead dioxide and anhydrous sodium sulfate for one week at room temperature. Crystallization from chloroform–alcohol gives orange crystals, m.p. 132–133°. Unless the characteristic hydrazo absorption band at 3300 cm.$^{-1}$ is absent, the oxidation is repeated. The infrared spectrum of

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[1] D. I. Relyea and D. F. DeTar, THIS JOURNAL, **76**, 1202 (1954); D. F. DeTar and S. V. Sagmanli, *ibid.*, **72**, 965 (1950); C. E. Boozer and G. S. Hammond, *ibid.*, **76**, 3862 (1954); G. S. Hammond, J. T. Rudesill and F. J. Modic, *ibid.*, **73**, 3229 (1951).

the product is very much like that of *p*-nitrophenylazotris-(*p*-anisyl)-methane.[2]

Anal.[3] Calcd. for $C_{28}H_{24}N_4O_7$: C, 63.6; H, 4.58; N, 10.6. Found: C, 63.63; H, 4.71; N, 10.24.

Decomposition of 2,4-Dinitrophenylazotris-(*p*-anisyl)-methane in Benzene at 75°.—The decomposition was carried out in degassed ampoules. The major product, obtained by adding petroleum ether to the benzene solution, was the hydrazo compound, identified by melting point and visible spectrum. By removing solvent from an aliquot of the benzene solution of the decomposition products and dissolving the residue in a mixture of acetic and perchloric acids the amount of hydrazo compound can be estimated spectrophotometrically as tris-*p*-anisylcarbonium ion. The yield on this basis was close to one-half of the theoretical (50.6%). Chromatography of the mother liquor from the isolation of the hydrazo compound on alumina failed to isolate additional pure products, but one fraction gave a color with acetone and sodium hydroxide in methanol, the spectrum of which closely resembles that produced by the action of the same reagents on *m*-dinitrobenzene. The hydrazo compound does not give such a color test.

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[2] M. D. Cohen, J. E. Leffler and L. M. Barbato, THIS JOURNAL, **76**, 4169 (1954)

[3] Analysis by Clark Microanalytical Laboratory, Urbana, Ill.

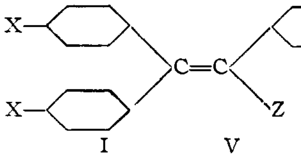
Triphenylethylene Derivatives. I

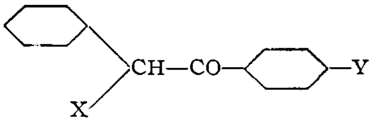
BY TOYOYUKI NAGANO

RECEIVED JULY 23, 1954

We have applied the Friedel–Crafts reaction to the preparation of estrogenic triphenylethylene derivatives with the thought that this method might be preferable to the Grignard synthesis.

4-Methoxydesoxybenzoin was converted to 4-methoxy-α′-chlorostilbene which reacted with anisole to give 1,1-dianisyl-2-phenylethylene (I), while α-chlorostilbene failed to react with benzene under these conditions. 4-Methoxydesyl bromide (II) condensed with benzene to give a mixture of 4-methoxy-α-phenyldesoxybenzoin (IV) and 4-hydroxy-α-phenyldesoxybenzoin (III), the extent of the demethylation depending on the conditions. When IV was heated with phosphorus pentachloride, 1,1-diphenyl-2-anisyl-2-chloroethylene (V) was formed. Attempts to condense II with anisole were unsuccessful.





	I	V	II	III	IV
X	OCH_3	H	Br	phenyl	phenyl
Y	H	OCH_3	OCH_3	OH	OCH_3
Z	H	Cl			

Chloroacetyl chloride was treated with an excess of anisole in an attempt to prepared desoxyanisoin; the product, however, was *p*-methoxy-ω-chloroacetophenone and under more drastic conditions a dark resin was obtained.

Acknowledgment.—The author is indebted to Mr. Konomu Matsumura for his advice and encouragement.

Experimental

4-Methoxy-α′-chlorostilbene.—Phosphorus pentachloride (2.3 g., 0.011 mole) was added to a solution of 4-methoxydesoxybenzoin (2.3 g., 0.01 mole) in benzene (5 ml.) and the mixture allowed to stand for 15 hours at room temperature with occasional shaking. The resulting red solution was poured into ice-water and extracted with ether. On evaporation of the dried ether–benzene extract and washing of the residue with methanol (10 ml.), colorless crystals (1.8 g., 75%) were obtained, which were recrystallized from ethanol as colorless plates, m.p. 74–75°.

Anal. Calcd. for $C_{15}H_{13}OCl$: C, 73.62; H, 5.32; Cl, 14.52. Found: C, 73.56; H, 4.97; Cl, 14.18.

1,1-Dianisyl-2-phenylethylene (I).—Pulverized aluminum chloride (1.7 g., 0.013 mole) was added with shaking over a 15-minute period to a solution of 4-methoxy-α′-chlorostilbene (2.4 g., 0.01 mole) and anisole (1.3 g., 0.012 mole) in carbon disulfide (5 ml.). After standing for 4 hours at room temperature, the deep red solution was poured into crushed ice and extracted with ether (40 ml.). On evaporation of the dried extract, the residual oil yielded crystals which were treated with ethanol (10 ml.); yield 2.7 g. (85.4%), m.p. 63–64° with preliminary softening around 60°. For analytical purposes, a portion (0.1 g.) was recrystallized from ethanol (10 ml.) giving colorless prisms, m.p. 64–65°, reported[1] m.p. 62–64°.

Anal. Calcd. for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37. Found: C, 83.58; H, 6.30.

A portion of the crude material (m.p. 63–64°) was brominated in carbon tetrachloride to give colorless prisms, m.p. 114–115°, reported[1] m.p. 114–115°.

4-Methoxydesyl Bromide.—This compound was obtained in 80% yield by brominating 4-methoxydesoxybenzoin with bromine in carbon tetrachloride. A poorer yield was obtained by bromination with phosphorus pentabromide in boiling benzene.

4-Hydroxy-α-phenyldesoxybenzoin (III).—Pulverized aluminum chloride (3 g., 0.022 mole) was added to a solution of 4-methoxydesyl bromide (3 g., 0.01 mole) in benzene (30 ml.) and the mixture gently refluxed for 3 hours. After standing overnight at room temperature, the reaction mixture was treated with ice and hydrochloric acid and extracted with benzene. After removal of the solvent, the residue was treated with sodium hydroxide solution (1%, 20 ml.). The alkali-insoluble portion (0.2 g.) was washed with ethanol and recrystallized to give IV, m.p. 128–130°. When the alkaline solution was acidified with hydrochloric acid, a light brown solid (2.6 g.) separated which crystallized from benzene as colorless plates, m.p. 181–182°. The ethanol solution of this material gave an orange color with ferric chloride.

Anal. Calcd. for $C_{20}H_{16}O_2$: C, 83.26; H, 5.59. Found: C, 83.32; H, 5.75.

The acetyl derivative separated as colorless prismatic needles from glacial acetic acid, m.p. 114–116°. The cold ethanol solution of the acetylated compound gave no color reaction with ferric chloride, but developed an orange color instantly on warming.

Anal. Calcd. for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49. Found: C, 79.97; H, 5.36.

4-Methoxy-α-phenyldesoxybenzoin (IV).—4-Methoxydesyl bromide (3 g.) and aluminum chloride (2 g., 0.015 mole) in benzene were heated at 70° for an hour. After standing for about 20 hours at room temperature, the solution was treated with ice and hydrochloric acid and extracted with ether (30 ml.). The ether–benzene layer was shaken with sodium hydroxide solution (1%, 20 ml.). When the alkaline layer was acidified, 0.9 g. of the 4-hydroxy compound III was obtained which after two recrystallizations from benzene melted at 181–182°. The residue obtained by evaporation of the ether–benzene solution was recrystallized twice from ethanol to give colorless needles; yield 1.7 g., m.p.

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[1] R. S. Shelton, THIS JOURNAL, **75**, 5493 (1953).