of refraction of each imine[10] and freshly distilled amino alcohol[11] was an accepted value.

Approximately a 0.1 *M* solution of reagent grade perchloric acid was prepared and its molarity determined to three figures. The acid solution and the imine were cooled to about 20°. The imine was then added quickly from a weight buret to the acid in a vessel in a constant temperature bath at 25.0 ± 0.1°. In later runs it was found to be more convenient to add the imine from a calibrated syringe (precision = ±0.004 g. for a two-gram aliquot).

The temperature of the mixture rose to 25° as a result of the heat of neutralization and remained constant after about 30 seconds. The *p*H was measured with a Beckman model G *p*H meter after equilibrium was reached (about two minutes).

In a solution containing the weak organic base (symbol, B) and its conjugate acid (symbol, HB^+), it can be shown that

$$[\mathrm{OH}^-] = K_{\mathrm{B}} \frac{[\mathrm{B}]}{[\mathrm{HB}^+]}$$

When [B] and $[\mathrm{HB}^+]$ are present in equivalent amounts, $[\mathrm{OH}^-]$ equals K_{B} and it follows (assuming pK_a is independent of ionic strength) that $pK_{\mathrm{B}} = 14.00 - p\mathrm{H}$. The values given in Table I are the averages of ten runs (after a series of preliminary runs) for each imine. The average deviation from the mean *p*H value was 0.010.

At an ionic strength of 0.1, there was a drift in the *p*H of the solution (under a nitrogen atmosphere) in the case of 2,2-dimethylethylenimine from 8.63 to 8.50 over a 5-hour period. When the solution was diluted threefold, no drifting occurred in one hour. The *p*H value was identical with the highest value obtained at the higher concentration. The drift to a lower *p*H is not due to hydrolysis to an amino-alcohol since the *p*H should increase in that case.

The observed stability of the imines in this system suggested the possibility of obtaining complete neutralization curves. Accordingly an aqueous solution was titrated with dilute perchloric acid and the *p*H measured after addition of each acid increment. All the imines gave sharp endpoints and the *p*H values at the points of half-neutralization were identical with those obtained by direct addition of imine to acid.

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[11] C. D. Hodgman, "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, Ed. 36, 1954.

[JOINT CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, ACTON TECHNICAL COLLEGE, AND THE INSTITUTO DE QUÍMICA, UNIVERSIDAD NACIONAL AUTÓNOMA DE MÉXICO]

The Absorption Spectra of Aromatic Azo and Related Compounds. I. Azoxybenzenes

BY PETER H. GORE[1a] AND OWEN H. WHEELER[1b]

RECEIVED SEPTEMBER 12, 1955

The ultraviolet absorption of a number of azoxybenzenes has been measured. The results are interpreted in terms of the electronic and steric effects of the substituents.

Apart from some early studies[2] of the effects of substituents on the absorption spectra of azoxybenzene, no systematic study has been attempted. It is the purpose of this paper to give such data, in particular for symmetrically disubstituted *trans*-azoxybenzenes.

The ultraviolet absorption of aliphatic azoxy compounds recently has been shown[3] to consist of two bands, a maximum near 220 mμ (ϵ 7,000) and an inflection near 275 mμ (ϵ 50); however, an assignment of the two bands was not attempted. It seems probable that the band near 220 mμ, being of high intensity, is due to an electronic transition (E-band) involving the –N=N– system and, as would be expected, alkyl groups shift this band by 4–7 mμ. The weaker band near 270 mμ is probably due to a radical transition (R-band) in the azoxy groups, corresponding to the band near 350 mμ ($\epsilon \sim 10$) in azomethane.[4] Coördination of an oxygen atom leads to a hypsochromic shift, as well as an increase in absorption intensity, and this is the typical effect of substitution on R-bands.[5]

A series of disubstituted azoxybenzenes has been prepared and their spectra taken (see Table I). Absorption occurs in three main regions: *ca.* 230, 260 and 320 mμ (designated E_1-, E_2- and K-bands). The R-band of aliphatic azoxy compounds will be submerged in the high intensity band at *ca.* 320 mμ. This is a point of distinction from the otherwise very similar spectra of azobenzenes,[6] in which the R-bands occur in the visible region, since the R-band of aliphatic azo compounds is at a higher wave length,[4] and undergoes a bathochromic shift in the benzene derivatives into the near visible region.

The band (E_1) at *ca.* 230 mμ[7] is not appreciably affected in wave length by substitution, changes only occurring in the absorption intensity. A similar band is also present in the spectra of phenylnitrones[8a] and azobenzenes,[8b] and is attributed to electronic transitions in the benzene rings, arising from the E-band of benzene (*ca.* 205 mμ, ϵ 6,300)[9] which has been displaced by substitution of the azoxy group to *ca.* 230 mμ, and is not appreciably displaced by further substitution. This E_1-band sometimes appears as two separate peaks, which may be due to unequal polarization of the two benzene rings[10] by the unsymmetrical azoxy group; such double maxima are not found in azo compounds.[8b]

A second band (E_2) is shown by azoxybenzene itself and a few of its derivatives. The actual position of the absorption band (at *ca.* 250 mμ) suggests that the E_2-transition involves one of the benzene rings and the azoxy linkage. In many of the disub-

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[1] (a) Acton Technical College, London; (b) Universidad Nacional Autónoma de México, Mexico.

[2] (a) E. Müller and E. Hory, *Z. physik. Chem.*, **A162**, 281 (1932); (b) L. Szegö, *Ber.*, **61**, 2087 (1928); **62**, 736 (1929).

[3] B. W. Langley, B. Lythgoe and N. V. Riggs, *J. Chem. Soc.*, 2309 (1951); B. W. Langley, B. Lythgoe and L. S. Rayner, *ibid.*, 4191 (1952).

[4] A. Hantzsch and J. Lifschitz, *Ber.*, **45**, 3011 (1912).

[5] A. Buraway, *J. Chem. Soc.*, 1177 (1939).

[6] A. Buraway, *ibid.*, 1865 (1937); A. H. Cook, D. G. Jones and J. B. Polya, *ibid.*, 1315 (1939).

[7] This band was not detected in much of the early work.

[8] (a) Part II, THIS JOURNAL, **78**, in press (1956); (b) Part III, in preparation.

[9] K. Bowden and E. A. Braude, *J. Chem. Soc.*, 1068 (1952).

[10] α denotes substitution in the ring remote from the N→O group, and β in the other ring.

TABLE I

ABSORPTION SPECTRA OF DERIVATIVES OF AZOXYBENZENE[a]

			Absorption maxima[b]		
Substituents	E_1	E_2	*K*	$\Delta\lambda/2$[c]	$\Delta\epsilon$[d]
......	231(8300)	260(7000)	323(14,500)	....	......
β-4′-$NMe_2 \rightarrow O$	......	264.5(9020)	341(19,200)	+18	+ 4,700
4,4′-DiMe	$\left.\begin{matrix}227\\236\end{matrix}\right\}(9400)$	......	330(18,100)	+ 3.5	+ 3,600
4,4′-DiPh[e]	......	......	366(28,300)	+21.5	+13,800
4,4′-DiMeO	242(11,500)	......	356(25,600)	+16.5	+11,100
4,4′-DiNO_2	227(7530)	$\left.\begin{matrix}267\\281\end{matrix}\right\}(5650)$	342(13,900)	+ 9.5	− 600
4,4′-DiF	234.5(11,000)	261(7040)	325(16,200)	+ 1	+ 1,700
4,4′-DiCl	$\left.\begin{matrix}223\\236\end{matrix}\right\}(9080)$	......	330(18,700)	+ 3.5	+ 4,200
4,4′-DiBr	220–230[f](~12,000)	......	333(22,100)	+ 5	+ 7,600
4,4′-DiI	223(12,900)	......	295(22,500)	−14	+ 8,000
3,3′-DiNO_2[e]	......	$\left.\begin{matrix}251\\257\end{matrix}\right\}(20,700)$	$\left.\begin{matrix}314\\324\end{matrix}\right\}(14,400)$	+ 0.5	− 100
3,5,3′,5′-TetraNO_2	$\left.\begin{matrix}227\\236\end{matrix}\right\}(32,100)$	$\left.\begin{matrix}251\\256\end{matrix}\right\}(24,100)$	315(14,400) 324(11,300)	+ 0.2	− 3,200
3,3′-DiF	227(6080)	......	324(13,100)	+ 0.5	− 1,400
3,3′-DiCl	$\left.\begin{matrix}227\\236\end{matrix}\right\}(9880)$	251(4810)	324(12,000)	+ 0.5	− 2,500
3,3′-DiBr	$\left.\begin{matrix}228\\237\end{matrix}\right\}(14,200)$	......	323(15,700)	0	+ 1,600
3,3′-DiI	227(27,900)	$\left.\begin{matrix}251\\257\end{matrix}\right\}(15,800)$	328(13,900)	+ 2.5	− 600
2,2′-DiMe	$\left.\begin{matrix}228\\238\end{matrix}\right\}(6840)$	......	312(11,100)	− 5.5	− 3,400
2,2′-DiMeO	227(3870)	......	304(2580) $\left.\begin{matrix}330\\342\end{matrix}\right\}(2320)$	− 4[g]	−12,000
2,2′-DiCl	223(10,900)	......	304(7500)	− 9.5	− 7,000
2,2′-DiBr	227(14,900) 237(10,700)	......	310(5700)	− 6.5	− 8,800
2,2′-DiI	227(23,800)	......	$\left.\begin{matrix}280\\305\end{matrix}\right\}(6750)$ 312(5850)	−15.5[h]	− 7,700

[a] Determinations are present work, and values are for ethanol solution unless otherwise stated. [b] Wave lengths in mμ, ε max. in parentheses. [c] Mean Δλ for K-band, for one substituent. [d] Δε max. for K-band. [e] Determined in chloroform solution. [f] Fine structure. [g] Center of K-band taken as λ 315 mμ, ε 2500. [h] Center of K-band taken as λ 292 mμ, ε 6800.

stituted compounds the E_2-band will be submerged by the E_1-band, which is always of higher intensity.

The K-band in the 4,4′-disubstituted derivatives (Table I) shows a series of pronounced bathochromic shifts, with $I < F < Me < Cl < Br < NO_2 < OMe < Ph$. The hypsochromic shift of iodine is abnormal, but this has been observed in the spectra of other benzenoid compounds.[9] The bathochromic sequence for the other atoms is the one usually observed,[9,11] and is in the reverse order of the inductive effects in chemical reactivity.[12] However, the order of mesomeric effects,[13] *viz.*, $F < Me < Cl < Br < I < OMe < Ph$, indeed follows a very similar sequence to that of the bathochromic displacements, suggesting that the mesomeric effect is the most important. This effect will lower the energy level of the excited state, thus decreasing the energy of the transition, *i.e.*, causing displacement to longer wave length.

The mesomeric effect is inoperative in a *meta* position and the effect of substituents in the 3,3′-positions of azoxybenzene will be very small, since the only effect operating is the inductive effect. The dihalogeno derivatives have essentially the same spectra as the parent compound. A nitro group is a powerful −M substituent and substitution in the *meta* position will reduce the electron availability in the benzene rings, and make conjugate transitions throughout the whole molecule more difficult. This accounts for the appearance of new bands (at 314–315 mμ) in the spectra of 3,3′-dinitro- and 3,5,3′,5′-tetranitroazoxybenzene, and possibly also for the low intensity of the K-band of 4,4′-dinitroazoxybenzene.

Substitution in the 2,2′-positions results in pronounced hypsochromic shifts and diminution of intensity of the K-band[14] (Table I). This has previously been noted for azoxybenzene derivatives,[2a,15] and for related compounds of the 1-

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(11) J. W. Baker and H. B. Hopkins, *J. Chem. Soc.*, 1089 (1949).

(12) E. A. Braude and E. Stern, *ibid.*, 1096 (1947).

(13) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapt. III.

(14) As a result many 2,2′-disubstituted azoxybenzenes are very light in color, *e.g.*, 2,2′-dichloro-6,6′-dimethoxyazoxybenzene is almost colorless. R. Adams, R. R. Holmes and J. W. Way, THIS JOURNAL, **75**, 5901 (1953).

(15) G. M. Badger and R. G. Buttery, *J. Chem. Soc.*, 2156 (1953)

naphthyl series.[15] This double effect indicates pronounced steric hindrance to coplanarity,[16] and considerable hindrance is to be expected from the size of the *ortho* substituents and their proximity to the coördinated oxygen atom of the azoxy group. Steric inhibition of resonance raises the energy level of the excited state relative to that of the ground state leading to hypsochromic displacement and decreased absorption intensity. For very large groups, *e.g.*, 2,2'-dimethoxy and diiodo, degeneracy of the energy levels[16] produces splitting of the main maximum into several additional maxima.

The absorption spectra of a number of mono *para* substituted azoxybenzenes was measured by Szegö.[2b] He found that the effect of substituents on the K-band was in the order Me < Br < NO_2 < OMe < OEt < OH < NH_2, which is the same order as noted above. Substitution in the α-4-position produces greater bathochromic shifts than in the β-4-position, since in the former case polarization of the central azoxy linkage is easier. The wave length shifts are greater for mono substitution (α-Me, 11; β-Me, 10; α-OMe, 31; β-OMe, 13; α-Br, 12; β-Br, 10; α-NO_2, 17; β-NO_2, 17 mμ) than the mean effect of disubstitution (*cf.* Table I), showing that the introduction of a second group has less effect than that produced by the first.

A dimethylamino group with unshared electrons produces the greatest shift (β-4-dimethylaminoazoxybenzene has $\lambda_{\max}$ 395 mμ, ϵ 28,200)[17] but when these electrons are coördinated to an oxygen atom (as in the β-4-$\underset{\overset{\downarrow}{\mathrm{O}}}{\mathrm{N}}$-$\mathrm{Me_2}$ compound) this shift is reduced (see Table I).

cis-Azoxybenzenes have been prepared,[2a, 18] but since they exist in a configuration in which there must be appreciable interference between the *ortho* hydrogen atoms of the two rings, they are of low stability, and *ortho* substituted *cis*-azoxybenzenes are very unstable.[2a,18d] The ultraviolet absorption of some disubstituted *cis*-azoxybenzenes was measured by Müller and Hory[2a] and the bathochromic shifts for the K-bands are smaller and the absorption intensities much less (4,000–7,000) than for the corresponding *trans* derivatives, due to this strained configuration about the central linkage.

On the assumption that the molar extinction of the K-band of the 2,2'-disubstituted azoxybenzenes (ϵ_2), in the absence of steric effects, should be as high as the molar extinction of the 4,4'-disubstituted compounds (ϵ_0), the angle of distortion can be calculated. The total deformation (non-coplanarity) angle is variously given by $\cos\theta_1 = \epsilon_2/\epsilon_0$,[16b] or by $\cos^2\theta_2 = \epsilon_2/\epsilon_0$.[19] It has been found that these deformation angles (see Table II) increase with the effective size of the substituent, *viz.*, Me < Cl < Br < I < OMe, confirming the previous qualitative discussion. The angle for the *cis*-dimethyl compound is essentially the same as for the *trans* derivative, but *cis*-azoxybenzene and the *cis*-4,4'-disubstituted azoxybenzenes are probably not planar themselves,[20] and the above treatment will only give the additional departure from co-planarity.

TABLE II

DEFORMATION ANGLES FOR 2,2'-DISUBSTITUTED AZOXYBENZENES[a]

Substituent	ϵ_2	ϵ_0	θ_1	θ_2
trans-DiMe	11,100	18,100	52°	38°
cis-DiMe[b]	4,000	6,500	50°	37°
trans-DiMeO	2,500	25,000	84°	72°
trans-DiCl	7,500	18,700	66°	51°
trans-DiBr	5,700	22,100	75°	59°
trans-DiI	5,850	22,500	75°	59°

[a] Data from present work, unless otherwise stated. [b] Data from ref. 18b.

The relationship between the spectra of azoxybenzenes and azobenzenes, as well as phenylnitrones, will be discussed in later papers.[8a,b]

Experimental

Compounds.—The azoxybenzenes (see Table III) were prepared by reduction of the corresponding nitro com-

TABLE III

Substituent	Prepn. method	M.p., °C.	Literature, °C.
. . . . . .	. .[a]	35	35.5–36.5[a]
β,4-$NMe_2 \rightarrow O$	B	136–137	128[b]
4,4'-DiMe	A	68	69[c]
4,4'-DiPh	A	203–204	205[d]
4,4'-DiMeO	. .	118 (136)[f]	118.5 (135.6)[g]
4,4'-DiNO_2	B	192	192[h]
4,4'-DiF	B	86–87	. .
4,4'-DiCl	A	155–156	155–156[i]
4,4'-DiBr	B	172	172[j]
4,4'-DiI	A	198	199.5[k]
3,3'-DiNO_2	A	143	144–145[l]
3,5,3',5'-TetraNO_2	A	185	185[m]
3,3'-DiF	B	51.5	51.5[n]
3,3'-DiCl	A	96	97[o]
3,3'-DiBr	A	111	113[k]
3,3'-DiI	A	120.5–121.5	118–119[k]
2,2'-DiMe	A	60	59–60[p]
2,2'-DiMeO	A	81–82	81[q]
2,2'-DiCl	A	55–56	56[q]
2,2'-DiBr	A	115	114[r]
2,2'-DiI	. .[r]	148	148[s]

[a] H. E. Bigelow and A. Palmer, *Org. Syntheses*, Coll. Vol. II, 57 (1943). [b] A. Angeli, *Atti. R. Accad. Lincei*, **24**, 1190 (1915). [c] E. Bamberg and E. Renauld, *Ber.*, **30**, 2278 (1897). [d] W. Zimmermann, *ibid.*, **13**, 1961 (1880). [e] Commercial sample. [f] Optically anisotropic and double melting point. [g] T. Svedberg, *Ann. Physik*, **44**, 1132 (1914). [h] A. Werner and E. Stiasny, *Ber.*, **32**, 3274 (1899). [i] K. Heumann, *ibid.*, **5**, 911 (1872). [j] M. D. Farrow and C. K. Ingold, *J. Chem. Soc.*, 2543 (1924). [k] S. Gabriel, *Ber.*, **9**, 1405 (1876). [l] E. Bamburger and R. Hübner, *ibid.*, **36**, 3803 (1903). [m] C. A. Lobry, de Bruyn and A. van Leent, *Rev. trav. chim.*, **13**, 151 (1894). [n] P. H. Gore and G. K. Hughes, *Austr. J. Sci. Res.*, **4A**, 185 (1951). [o] A. Laubenheimer, *Ber.*, **8**, 1623 (1875). [p] H. Klinger and R. Pitschke, *ibid.*, **18**, 2551 (1885). [q] K. Brand, *J. prakt. Chem.*, **67**, 145 (1903). [r] Ref. 20. [s] A. H. Cook and D. G. Jones, *J. Chem. Soc.*, 1309 (1938), with improved yield (35%).

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(16) (a) E. A. Braude, E. R. H. Jones, H. P. Koch, R. W. Richardson, F. Sondheimer and J. B. Toogood, *J. Chem. Soc.*, 1890 (1949); (b) E. A. Braude, W. F. Forbes and F. Sondheimer, *Nature*, **173**, 117 (1954).

(17) W. Anderson, *J. Chem. Soc.*, 1722 (1952).

(18) (a) G. M. Badger, R. G. Buttery and G. E. Lewis, *ibid.*, 2143 (1953); (b) E. Müller and W. Kreutzmann, *Ann.*, **495**, 132 (1932); (c) K. Calderbank and R. J. W. LeFevre, *J. Chem. Soc.*, 1949 (1948); (d) E. Müller, *Ann.*, **493**, 166 (1932).

(19) H. B. Klevens and J. R. Platt, THIS JOURNAL, **71**, 1714 (1949).

(20) *cis*-Azobenzene has been shown to be non-planar: G. C. Hampson and J. M. Robertson, *J. Chem. Soc.*, 409 (1941).

pound with sodium hydroxide in methanol[21] (method A) or by oxidation of the corresponding azobenzene with peracetic acid[22] (method B), unless otherwise stated. They were recrystallized from ethanol to constant melting point (see Table III).

4,4-Difluoroazoxybenzene, a new compound, was prepared by peracetic acid oxidation[22] of 4,4'-difluoroazobenzene,[23] and recrystallized from alcohol as pale yellow needles, m.p. 86–87°.

Anal. Calcd. for $C_{12}H_8N_2OF_2$: C, 61.5; H, 3.4. Found: C, 61.3; H, 3.5.

Absorption Spectra.—The absorption spectra were determined in absolute ethanol, or A. R. chloroform, with a Unicam S.P. 500 spectrophotometer.

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[21] L. Zechmeister and P. Rom, *Ber.*, **59**, 867 (1926); *Ann.*, **468**, 129 (1929).

[22] A. Angeli, *Atti. R. Accad. Lincei*, **19**, 793 (1910).

[23] J. Lichtenberger and R. Dormet, *Bull. soc. chim. France*, 318 (1951).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Oxidation of Thianthrene to Thianthrene-5-oxide by Diazonium Salts

BY HENRY GILMAN AND DHAIRYASHEEL R. SWAYAMPATI

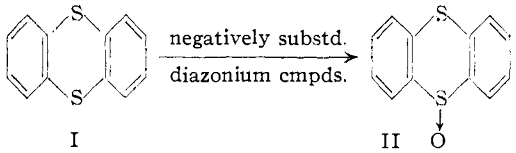
RECEIVED NOVEMBER 16, 1955

Thianthrene was oxidized to thianthrene-5-oxide in good yields by treatment with negatively substituted benzenediazonium salts in glacial acetic acid. The best results were obtained with *o*- and *p*-nitrobenzenediazonium sulfates. Thianthrene was prepared in improved yields by a modification of an earlier procedure.

Diazonium compounds react with a large number of "coupling components" such as phenols, aromatic amines, substances containing reactive methylene groups, phenolic ethers and hydrocarbons to give azo derivatives.[1] Although phenols and aromatic amines couple readily with diazotized amines, phenolic ethers and hydrocarbons require special conditions. Meyer and Tochtermann[2] were able to couple diazotized picramide with mesitylene, and Smith and Paden[3] used the same diazonium compound for successful coupling with pentamethylbenzene and with isodurene. Meyer and Lenhardt[4] were the first to couple phenolic ethers with diazonium salts. They found that phenolic ethers couple very slowly with diazonium compounds, but that the coupling reaction is greatly facilitated by the presence of more alkoxy groups in the "coupling component" and of nitro groups, particularly in the *ortho* and *para* positions, in the diazonium compound. Schoutissen[5] found that the coupling of anisole proceeds only if two nitro groups are present in the *ortho* and *para* positions in the diazonium compound, and that no coupling occurred if the two nitro groups were present in the *meta* positions.

The action of diazonium compounds on thianthrene (I), which is a thioether, was studied in the present investigation. The reaction consisted in adding a diazonium salt solution to a suspension of thianthrene in glacial acetic acid, and stirring the mixture for 12–24 hours. At the end of the reaction period the mixture was filtered, if necessary, and the solution diluted with water and the product which separated was collected and identified. It was found that thianthrene was oxidized to thianthrene-5-oxide (II) by *o*-nitro-, *p*-nitro-, 2,4-dinitro- and *p*-carboxybenzenediazonium salts. When nitrosylsulfuric acid was used for the diazotization of *o*-nitro-, *p*-nitro- and 2,4-dinitroaniline the yields of the sulfoxide were 98, 94 and 66%, respectively. With *o*-nitro- and *p*-carboxybenzenediazonium chloride only a part of the thianthrene dissolved to give the sulfoxide in 39% (90%, on the basis of unrecovered thianthrene) and 56% (93.5%, on the basis of unrecovered thianthrene), respectively.

It was found that either the nitro or the diazonium group by itself was not sufficient for the oxidation, since *m*-dinitrobenzene as well as benzenediazonium chloride failed to oxidize thianthrene.



I II

Since oxidation was more effective with sulfates than with chlorides it was thought that sulfuric acid may be partly responsible for the reaction. Fries and Engelbertz[6] have reported that thianthrene forms a complex with sulfuric acid, which upon hydrolysis gives a mixture of thianthrene and thianthrene-5-oxide. In an experiment in which a mixture of sulfuric acid, acetic acid and thianthrene in the usual experimental proportions was stirred at room temperature for 24 hours, no oxidation was detected. The starting material, thianthrene, was recovered in 97% yield.

It has been frequently observed that phenolic ethers couple with partial or complete elimination of the alkyl group from the ether.[7] Although

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[1] H. A. Lubs, "The Chemistry of Synthetic Dyes and Pigments," Reinhold Publishing Corporation, New York, N. Y., 1955, p. 101; see also H. W. Grimmel in H. Gilman, "Organic Chemistry," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 243.

[2] K. H. Meyer and H. Tochtermann, *Ber.*, **54**, 2283 (1921).

[3] L. I. Smith and J. H. Paden, THIS JOURNAL, **56**, 2169 (1934).

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[5] H. A. J. Schoutissen, THIS JOURNAL, **55**, 4541 (1933).

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