The Oxidation of Ortho-Substituted Azobenzenes as Followed by Tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)europium Proton Magnetic Resonance Spectral Clarification. Regioselective Routes to Azoxybenzenes[1]

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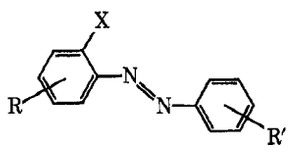
The ratio of isomeric azoxybenzenes produced *via* the peracetic acid oxidation of *o*- ($-CH_3$, $-OCH_3$, $-Cl$, $-CO_2H$, $-CO_2CH_3$, $-OAc$, and $-OH$) azobenzenes has been examined directly using Eu(fod)$_3$ to separate isomeric pmr signals. With the exception of the hydroxyl group, which favored oxidation of the nitrogen adjacent to the ortho-substituted benzenoid ring, all other substituents favor oxidation of the nonadjacent nitrogen with varying degrees of regioselectivity. Oxidation of azobenzene-2-carboxylic acids gave azoxybenzene-2-carboxylic acids which were >98% isomerically pure. Decarboxylation of these azoxybenzene-2-carboxylic acids proceeded readily and completed a convenient, two-step, regioselective entry into the azoxybenzenes. The differences provided by $-CO_2H$ and $-CO_2CH_3$ are discussed with regard to the role of internal hydrogen bonding.

The peracid oxidation of unsymmetrical azobenzenes (**1**) generally proceeds to yield a mixture of azoxybenzene isomers (**2a,b**). With no ortho substituent (**1**, X = H), the ratio of azoxybenzene isomers is generally[2] close to 1:1. With the exception of a report[3] examining the influence of simultaneous (2,2′) ortho substitution, the effect of ortho substituents upon the oxidation of azobenzenes has not been well studied,[4] particularly with regard to quantitative measurements of the minor azoxybenzene isomer formed. The apparent simplicity of this problem is offset by the inherent difficulties associated with analysis[5] by column chromatography or fractional recrystallization followed by chemical degradation to known compounds.



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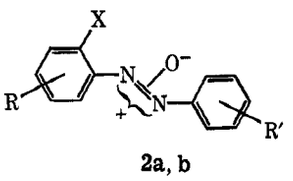


2a, b

The importance of developing room temperature nematic systems for display[6] and spectroscopic[7] applications coupled with the ability of some azoxybenzene mixtures[2b,8,9] to form excellent low-temperature nematic mesophases prompted us to develop[9] a rapid analytical technique utilizing the lanthanide pmr shifting agent, tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)europium[10] [Eu(fod)$_3$], for analysis of isomeric azoxybenzene mixtures. This ability to observe accurate azoxybenzene isomeric distributions *via* a direct method prompted us to examine the azoxybenzene isomeric distribution produced in the oxidation of azobenzenes possessing single ortho substituents. The ortho substituents were selected from those expected to depress[11,12] crystalline–mesomorphic transitions without destruction[12] of mesomorphic behavior.

The azobenzenes were all synthesized by two basic methods involving amine–nitroso[13] or phenol–diazonium[14] condensations. The oxidations were conducted in acetic acid at 25° using 90% hydrogen peroxide and a catalytic amount of sulfuric acid. The azoxybenzene isomer ratios were shown to be stable to these conditions for >20 hr. Purification of the crude products was accomplished without disturbing the isomeric distributions. Yields of azoxybenzenes were generally >85% of theoretical. Prior to analysis with Eu(fod)$_3$, phenols and acids were converted to acetates and esters.

The magnitude and direction of the regioselectivity of oxidation was measured by pmr analysis using Eu(fod)$_3$ to separate coincidental or closely coincidental isomeric resonances. These results are summarized in Table I. For ease of quantitative analysis, the azobenzenes were chosen to provide azoxybenzene mix-

(1) Presented in part at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971.

(2) (a) C. S. Hahn and H. H. Jaffé, *J. Amer. Chem. Soc.*, **84**, 949 (1962); (b) R. Steinstrasser and L. Pohl, *Tetrahedron Lett.*, 1921 (1971).

(3) V. M. Dzimoko and K. A. Dunaevskaya, *Zh. Obshch. Khim.*, **31**, 3385 (1961).

(4) For a convenient summary of early work in this area, see K. H. Schundehutte, "Methoden der Organische Chemie," Georg Thieme Verlag, Stuttgart, 1965, p 745.

(5) The individual isomers of azoxybenzene mixtures possess remarkably similar ir, uv, nmr, and glpc parameters. In any case, degradation to known compounds is usually required for rigorous identification.

(6) G. H. Heilmeier and J. E. Goldmacher, *Proc. IEEE*, **57**, 34 (1969).

(7) Nmr and esr: (a) C. T. Yim and F. R. Gilson, *Can. J. Chem.*, **47**, 1057 (1969); (b) P. Diehl and C. L. Khetrapal, *Mol. Phys.*, **15**, 633 (1968); (c) A. Saupé, *Angew. Chem., Int. Ed. Engl.*, **7**, 97 (1968); (d) C. F. Schwerdtferger and P. Diehl, *Mol. Phys.*, **17**, 417 (1969). Ir and uv: (e) R. A. Levenson, H. B. Gray and G. P. Ceasar, *J. Amer. Chem. Soc.*, **92**, 3653 (1970).

(8) H. Kelker, B. Scheule, R. Hatz, and W. Bartsch, *Angew. Chem., Int. Ed. Engl.*, **9**, 962 (1970).

(9) R. E. Rondeau, M. A. Berwick, R. N. Steppel, and M. P. Servé, *J. Amer. Chem. Soc.*, **94**, 1096 (1972).

(10) R. E. Rondeau and R. E. Sievers, *ibid.*, **93**, 1552 (1971).

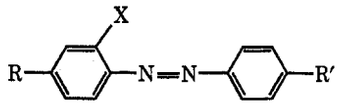
(11) (a) Available reports[11b] indicate that ortho substitution imparts a less favorable crystal lattice packing relative to the unsubstituted analog. (b) For examples, see W. Kast in "Landolt-Börnstein," 6th ed, Vol. II, Springer-Verlag, West Berlin, 1960, Part 2a.

(12) (a) No azoxybenzenes in this study were expected to show mesomorphism, although the ortho substituents of interest to us were those which could ultimately be incorporated into mesomorphic compounds. Large, bulky substituents would destroy[12b] mesomorphic behavior even through greater regioselectivity might be expected from their usage. (b) G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Academic Press, New York, N. Y., 1962.

(13) H. D. Anspon, "Organic Syntheses," Collect Vol. III, Wiley, New York, N. Y., 1943, p 711.

(14) J. L. Hartwell and L. Fieser, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 145.

TABLE I
OXIDATION OF AZOBENZENES



Compd	X	R	R′	Nitrogen oxidized, N_α[a]:N_β	Relative pmr shifting relationships[b]
3a	CH_3	H	H	1:15	$S_{N\alpha} > S_{N\beta}$ (2,2′-methyl)
3b	H	4-CH_3	H	1:1.1[c]	
4a	Cl	H	4-CH_3	1:24	$S_{N\beta} > S_{N\alpha}$ (4,4′-methyl)[d]
4b	H	4-Cl	4-CH_3	1:1.1[c]	
5a	OCH_3	H	H	1:8.3	$S_{N\alpha} > S_{N\beta}$ (2,2′-methoxy)
5b	H	4-OCH_3	H	1:1.2[c]	
6a	CO_2CH_3	H	H	1:5.7	$S_{N\beta} > S_{N\alpha}$ (2,2′-carbomethoxy)
6b	H	4-CO_2CH_3	H	1:1.4[c]	
7	CO_2H	H	H	1:18	
8a	CO_2CH_3	H	4-Cl	1:5.0	$S_{N\beta} > S_{N\alpha}$ (2,2′-carbomethoxy)
8b	H	4-CO_2Et	4-Cl	1:1.0	
9	CO_2H	H	4-Cl	1:20	
10	CO_2CH_3	H	4-OCH_3	1:3.8	$S_{N\beta} > S_{N\alpha}$ (2,2′-carbomethoxy)
11	CH_3	H	2-CO_2CH_3	1:3.2	
12	OH	5-CH_3	H	2.6:1	
13	OC(=O)CH_3	5-CH_3	H	1:9.3	$S_{N\beta} > S_{N\alpha}$ (2,2′-acetoxy)

[a] N_α is the nitrogen attached to the X-substituted ring. [b] Shifts are downfield except as indicated. Relative shifting relationships are measured as the slope (S) of the induced pmr shift of the N_α or N_β isomer *vs.* concentration of added Eu(fod)$_3$. The protons used for the comparison are indicated in parenthesis. [c] No regioselectivity implied. [d] The methyl protons of the N_α isomer are shifted slightly upfield.

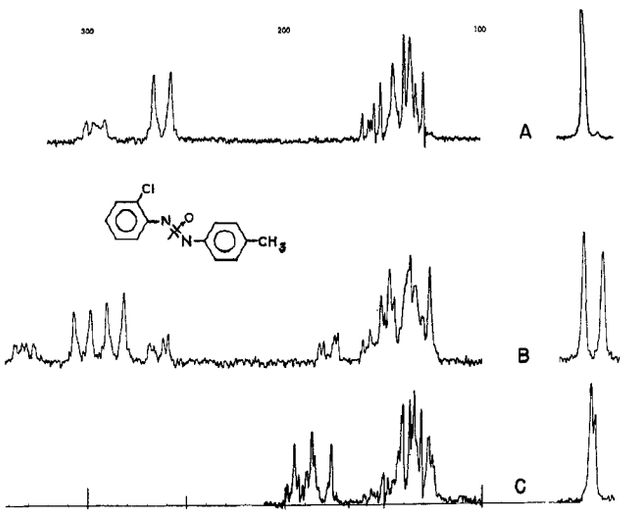


Figure 1.—Spectral clarification of the 2- and 2′-chloro-4′- and -4-methylazoxybenzenes. Pmr spectra in 0.5 ml of CCl_4 with added TMS (500-Hz sweep; methyls offset 100 Hz; aromatics offset 300 Hz): A, oxidized 2-chloro-4′-methylazobenzene mixture (25.5 mg) with 35.1 mg of added Eu(fod)$_3$; B, solution C with 42.0 mg of added Eu(fod)$_3$; C, mixture of 13.4 mg of 4-methyl and 14.9 mg of 4′-methyl isomers with no Eu(fod)$_3$.

tures which possessed, or could be converted to derivatives which possessed, singlet resonances. In most cases, a methyl function giving a singlet pmr signal was used. Structural assignments based upon lanthanide shifting patterns have been established only for 4,4′-substituted azoxybenzenes[9] in which the lanthanide interaction is at the azoxy oxygen and in which at least one of the para substituents bears a hydrogen. In instances where the coordination site was other than the central linkage, as with acetoxy and carbomethoxy azoxybenzene esters, or no para substituents bearing hydrogen were present, new rules relating shifting patterns to stereochemistry were required.[15] This was accomplished *via* synthesis of both isomers by known regiospecific methods, followed by Eu(fod)$_3$ pmr comparison of known mixtures with the mixtures obtained by oxidation of the azobenzenes. Figure 1 illustrates this process for the 2- and 2′-chloro-4′- (and -4-) azoxybenzenes.[16] In cases in which only one of the azoxybenzene isomers could be synthesized by known methods, the Eu(fod)$_3$ pmr shifting patterns were first observed and subsequently related to structure after degradation to known compounds. For example, 2′-carbomethoxy-4-methylazoxybenzene, which was obtained as the minor isomer upon oxidation of the corresponding azobenzene, was accessible in low yields through direct synthesis,[17] but the structure of the major isomer required confirmation by decarboxylation to 4′-methylazoxybenzene. Structural assignments of the oxidation products of **12** and **13** were made on the basis of the interrelationships of the major isomers obtained from each: *i.e.*, conversion by acetylation of the major product of phenol oxidation, 2′-hydroxy-5′-methylazoxybenzene, to the minor product of acetoxy oxidation, 2′-acetoxy-5′-methylazoxybenzene, and conversion by deacetylation of the major product of acetoxy oxidation, 2-acetoxy-5-methylazoxybenzene, to the minor product of phenol oxidation, 2-hydroxyl-5-methylazoxybenzene.

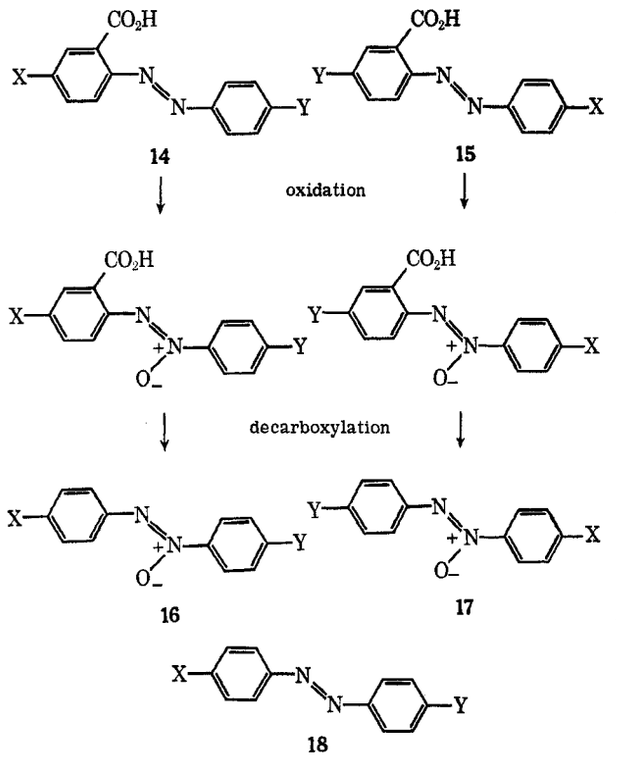
(15) (a) The pmr shifting associated with lanthanide reagents is a function[9,15b-e] of the strength of the interaction, proton distance, and angle to the lanthanide interaction site, as well as the nature of the lanthanide employed. (b) C. C. Hinckley, M. R. Klotz, and F. Patil, *J. Amer. Chem. Soc.*, **93**, 2417 (1971), and references cited therein. (c) B. L. Shapiro, J. R. Hlubecek, G. R. Sullivan, and L. F. Johnson, *ibid.*, **93**, 3281 (1971). (d) T. H. Siddal, *Chem. Commun.*, 452 (1971). (e) G. M. Whitesides and D. W. Lewis, *J. Amer. Chem. Soc.*, **93**, 5914 (1971).

(16) (a) The nomenclature[15b] is used which utilizes primed numbers to refer to substituents on the benzenoid nucleus adjacent to the N–O linkage. (b) G. G. Spence, E. C. Taylor, and O. Buchardt, *Chem. Rev.*, 231 (1970).

(17) L. C. Behr, E. G. Alley, and O. Levand, *J. Org. Chem.*, **27**, 65 (1962), and references cited therein.

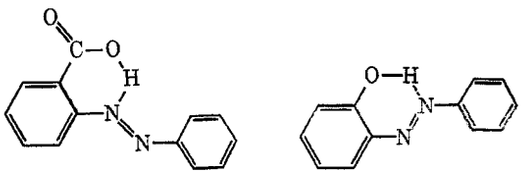
Two excellent, and totally distinct, regiospecific routes to azoxybenzenes have been reported. The first[17] involves vigorous oxidation of an intermediate indazole oxide followed by decarboxylation; the second[18] proceeds by the reaction of Grignard reagents with arylnitrosohydroxylamine derivatives. The first method proceeded poorly through the oxidation step in some instances,[19] and the second was limited by the need to employ a Grignard in the synthetic scheme. The results in Table I suggested an attractive alternative synthesis. Oxidation of the azobenzene-2-carboxylic acids **14** and **15** [(X = H, Y = $-CH_3$, $-Cl$, $-NO_2$ or $-OCH_3$, and X = $-CH_3$, $-Cl$, $-NO_2$ or $-OCH_3$, Y = H) Scheme I] gave highly crystalline azoxybenzene-2-carboxylic acid mixtures with a 14–20:1 preference for oxidation of the nitrogen nonadjacent (N_β) to the benzenoid ring possessing the 2-carboxylic acid moiety. The intermediate azoxybenzene-2-carboxylic acids (obtained with >98% isomeric integrity by one recrystallization of the crude oxidation product) underwent decarboxylation under the same conditions reported[17] for azoxybenzene-2′-carboxylic acid derivatives. Optimum purification of the final product required a simple column chromatographic separation of the azoxybenzenes **16** or **17** from the azobenzene **18**, which was formed in low yields by partial reduction of the azoxy linkage under the decarboxylation conditions.

SCHEME I
REGIOSELECTIVE SYNTHESES OF AZOXYBENZENES



With the exception of the hydroxyl group, the principle influence of the ortho substituent was, not unexpectedly, to direct oxidation to the nitrogen furthest removed (N_β) from the ortho-substituted benzenoid ring. This was attributed primarily to inductive and steric effects, since resonance contributions appeared to be of little consequence as shown by the control oxidations of **3b**, **4b**, **5b**, **6b**, and **8b**. More interesting, however, were the relative magnitudes of this N_β selectivity. The N_β selectivity imparted by the 2-carboxylic acid function was two to three times greater than that associated with the corresponding 2-carbomethoxy group, which is the larger substituent. While we cannot rigorously exclude the possibility that this is due to an increased steric N_β selectivity provided by solvent coordination[20] with azobenzene-2-carboxylic acid, internal hydrogen bonding appeared to offer a more logical explanation.

Azobenzene-2-carboxylic acids **19** should be capable of forming an internal hydrogen bond, a phenomenon which has been established[21] for 2-hydroxyazobenzenes **20**. The overall result of this internal hydrogen



bonding should be both to shield the nitrogen involved and decrease its nucleophilicity, and thereby lower[22] the probability of oxidation at that site. Such an argument implies that peracetic acid oxidation of 2-hydroxyazobenzenes could show an increased N_α oxidation selectivity. The only report pertinent to this conclusion examined the oxidation of 2-hydroxy 2′-substituted azobenzenes.[3] In these examples, the observed exclusive oxidation of the nitrogen adjacent to the 2-hydroxyl function may be due to either an internal hydrogen bonding effect promoting N_α oxidation or the expected N_β directing influence of the other 2′ substituent or both. Accordingly, we reexamined the original report[23] of the oxidation of 2-hydroxy-5-methylazobenzene (**12**) and indeed found a slight reversal of the expected N_β oxidation pattern.

Experimental Section[24,25]

General.—Tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)europium [Eu(fod)$_3$] was synthesized according to known procedures.[26] The oxidizing solution was composed of acetic acid, 90% hydrogen peroxide, and concentrated sulfuric acid in a volume ratio of 100:15:0.5. All oxidations were conducted in a thermostated reaction vessel rigidly maintained at 25°. Glpc was accomplished on a Varian Series 1200 instrument using a 6 ft × 0.250 in. diameter aluminum column packed with 3% SE-30 on 100/120 mesh Aeropak 30. The pmr spectra were recorded with a Varian HA601L spectrometer operating in

(18) T. E. Stevens, *J. Org. Chem.*, **29**, 311 (1964).
(19) Particularly with hydroxyl or benzyl substituents.
(20) The ortho position of the acid function should hinder coordination.
(21) (a) W. R. Brode, J. H. Gould, and G. M. Wyman, *J. Amer. Chem. Soc.*, **74**, 4641 (1952); (b) L. M. Reeves, *Can. J. Chem.*, **38**, 748 (1960).
(22) Reduction of electron density at a specific nitrogen hampers[2-4] its oxidation.
(23) D. Bigiani and R. Poggl, *Gazz. Chim. Ital.*, **54**, 114 (1924).
(24) Melting points are uncorrected. Elemental analyses are by J. Kern, Air Force Materials Laboratory, Wright-Patterson AFB, Dayton, Ohio.
(25) Eu(fod)$_3$ pmr shifting behavior of other azoxybenzene isomeric pairs will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JOC-72-2409. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.
(26) G. S. Springer, D. W. Mark, and R. E. Sievers, *Inorg. Chem.*, **6**, 1105 (1967).

the frequency sweep mode. The unknown azoxybenzenes, which are cited without experimental preparations, were made according to the procedure detailed for 2′-methylazoxybenzene.

2′-Methylazoxybenzene.—*N*-2-Methylphenyl-*N*′-tosyloxydiimide *N*-oxide[27] (6.1 g, 0.02 mol) was dissolved in 50 ml of methylene chloride and cooled in an ice–water bath while phenylmagnesium bromide [Grignard prepared from bromobenzene (3.2 g, 0.02 mol) and magnesium (0.69 g, 0.03 g-atom) in 30 ml of dry tetrahydrofuran] solution was added through a fritted glass filter to remove unreacted magnesium. The solution was stirred at room temperature for 18 hr. An additional 100 ml of methylene chloride was then added, and the methylene chloride was extracted with 10% hydrochloric acid and 10% sodium hydroxide and dried ($MgSO_4$). Glpc analysis indicated the presence of a complex mixture of products from which the desired azoxybenzene was isolated after concentration and column chromatography on 100 g of neutral alumina (activity I) using petroleum ether (bp 30–60°)–ether (95:5) as solvent, yielding 0.57 g (14%) of a yellow oil: bp 124–125° (1 mm);[28] ir (neat) 3060, 1470, 763, and 685 cm^{-1}; uv max (cyclohexane) 228 nm (ϵ 8830) and 303 (13,300); nmr (CCl_4) δ ~6.50 and 5.66 (m, 9, aromatic protons) and 2.44 ppm (s, 3, $-CH_3$). *Anal.* Calcd for $C_{13}H_{12}N_2O$: C, 73.56; H, 5.70; N, 13.20. Found: C, 73.55; H, 5.62; N, 13.46.

Oxidation of 2-Methylazobenzene.—2-Methylazobenzene[29] (1.96 g, 0.01 mol) was added to 75 ml of the oxidizing solution and stirred for 18 hr. The yellow solution was then poured onto ice–water and extracted into ether, and the ether was extracted with 10% sodium hydroxide, then dried ($MgSO_4$), concentrated, and quickly chromatographed on 100 g of neutral alumina (activity I) using petroleum ether–ether (95:5), yielding 1.83 g (86%) of a yellow liquid, bp 123–126° (1 mm).[28] Eu(fod)$_3$ pmr analysis prior to distillation indicated that the major isomer predominated by 15:1, a ratio which was not altered upon rechromatography under the same conditions. The pmr absorbances associated with the major isomer were enhanced upon the addition of known 2-methylazoxybenzene: bp 128–130° (1.2 mm);[28] ir (neat) 3090, 1480, 763, and 685 cm^{-1}; uv max (cyclohexane) 243 nm (ϵ 9270), 256 (shoulder, 7910), and 332 (10,100); nmr (CCl_4) δ ~6.50 and 5.66 (m, 9, aromatic protons) and 2.40 ppm (s, 3, $-CH_3$). *Anal.* Calcd for $C_{13}H_{12}N_2O$: C, 73.56; H, 5.70; N, 13.20. Found: C, 73.32; H, 5.66; N, 13.38.

2-Chloro-4′-methylazobenzene.—2-Chloronitrosobenzene[30] (5.00 g, 0.035 mol) was dissolved in 50 ml of glacial acetic acid by gentle heating and added to 4-methylaniline (3.85 g, 0.035 mol) previously dissolved in 10 ml of glacial acetic acid. The solution was heated on a steam bath for 0.5 hr and allowed to stand at room temperature for 12 hr. The solution was then poured onto water and the resulting orange solid was collected by filtration. The crude product was dissolved in a minimal amount of ether and chromatographed on 100 g of neutral alumina (activity I) using pentane–ether (4:1), yielding 5.9 g (73%) of a product which, when recrystallized from 35 ml of hexane, gave orange needles: mp 43.5–44.0°; ir (KBr) 1630, 1060, 830, and 760 cm^{-1}; uv max (cyclohexane) 238 nm (ϵ 13,000), 333 18,500) and 456 (541); nmr (CCl_4) δ ~5.83 (m, 8, aromatic protons) and 2.43 ppm (s, 3, $-CH_3$). *Anal.* Calcd for $C_{13}H_{11}N_2Cl$: C, 67.68; H, 4.81; N, 12.14; Cl, 15.37. Found: C, 67.94; H, 4.71; N, 12.25; Cl, 15.47.

Oxidation of 2-Chloro-4′-methylazobenzene.—2-Chloro-4′-methylazobenzene (1.16 g, 0.005 mol) was dissolved in 100 ml of oxidizing solution and stirred for 18 hr. Work-up of the yellow solution was identical with the procedure for the oxidation of 2-methylazobenzene, yielding 1.1 g (89%) of a light yellow solid. Nuclear magnetic resonance (in CCl_4) (confer Figure 1, spectrum A) indicated that the major isomer predominated by 24:1 and underwent a pmr shifting behavior with added Eu(fod)$_3$ different from that observed for 2′-chloro-4-methylazoxybenzene: mp 63–64°; ir (KBr) 1470, 1340, 910, and 760 cm^{-1}; uv max (cyclohexane) 233 nm (ϵ 10,700) and 310 (16,700); nmr (CCl_4) δ ~6.45 and 5.58 (m, 8, aromatic protons) and 2.36 ppm (s, 3, $-CH_3$). *Anal.* Calcd for $C_{13}H_{11}N_2OCl$: C, 63.29; H, 4.49; N, 11.36; Cl, 14.37. Found: C, 63.22; H, 4.49; N, 11.50; Cl, 14.51.

2-Chloro-4′-methylazoxybenzene.—Two recrystallizations of the oxidized 2-chloro-4′-methylazobenzene gave 2-chloro-4′-methylazoxybenzene as yellow needles: mp 67.5–68.0°; ir (KBr) 1690, 1450, 915, and 755 cm^{-1}; uv max (cyclohexane) 242 nm (ϵ 9660), 273 (9080), and 328 (1200); nmr (CCl_4) δ ~6.58 and 5.58 (m, 8, aromatic protons) and 2.42 ppm (s, 3, $-CH_3$). *Anal.* Calcd for $C_{13}H_{11}N_2OCl$: C, 63.29; H, 4.49; N, 11.36; Cl, 14.37. Found: C, 63.08; H, 4.59; H, 11.54; Cl, 14.62.

Azobenzene-2-carboxylic Acids. 4′-Methylazobenzene-2-carboxylic Acid.—The general procedure is illustrated by the preparation of 4′-methylazobenzene-2-carboxylic acid. 4-Methylnitrosobenzene[30] (6.05 g, 0.05 mol) was dissolved in 25 ml of acetic acid by gentle heating and added to 2-carbomethoxyaniline (7.55 g, 0.05 mol) previously dissolved in 25 ml of acetic acid. The solution was heated on a steam bath for 45 min and allowed to stand at room temperature for 12 hr. The solution was then poured onto water and extracted into ether, and the ether was dried ($MgSO_4$) and removed under vacuum. Chromatography of the residue on ~100 g of neutral alumina (activity II) with petroleum ether–ether (2:1) gave 9.2 g (70%) of a red oil, bp 155–158° (0.03 mm). The red oil (4.57 g, 0.018 mol) was dissolved in 100 ml of ethanol, and 10 g of sodium hydroxide in 100 ml of water was added. The mixture was refluxed for 12 hr and added to 300 ml of ice–water, and the solids were suction filtered and discarded. The resulting orange filtrate was extracted with ether and the aqueous phase was neutralized with concentrated hydrochloric acid. The crude, suspended solids were filtered and recrystallized from ethanol–hexane, yielding 3.5 g (82% based on ester) of orange-yellow needles: mp 118.5–119.0°; ir (KBr) 2760 (broad), 1740, 835, 776, and 683 cm^{-1}; uv max (methanol) 230 nm (ϵ 13,600), 327 (19,200), and 435 (689); nmr ($DCCl_3$) δ ~6.0 (m, 9, aromatic protons and $-CO_2H$) and 2.42 ppm (s, 3, $-CH_3$). *Anal.* Calcd for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 70.00; H, 5.08; N, 11.72.

Oxidation of Azobenzene-2-carboxylic Acids. 4′-Chloroazoxybenzene-2-carboxylic Acid.—The general procedure is illustrated by the oxidation of 4′-chloroazobenzene-2-carboxylic acid. 4′-Chloroazobenzene-2-carboxylic acid (5.20 g, 0.02 mol) was added to 200 ml of the oxidizing solution and stirred for 12 hr. The yellow solution was then poured onto ice–water and stirred for 3 hr, the resultant solid suction was filtered and dissolved in ether, and the ether was dried ($MgSO_4$) and removed under reduced pressure to give 5.10 g (92%) of a yellow powder, which was homogenized with mortar and pestle. A small fraction of the powder (~250 mg) was treated with diazomethane; the resulting analysis of the esters by the Eu(fod)$_3$ pmr spectral clarification technique indicated that the major isomer predominated by 20:1. Recrystallization from ethanol–water gave 4′-chloroazoxybenzene-2-carboxylic acid as yellow crystals: mp 151–152°; ir (KBr) 2900 (broad), 1740, 1475, 840, and 761 cm^{-1}; uv max (methanol) 256 nm (ϵ 12,100) and 324 (9900); nmr ($DCCl_3$) δ 8.17 (broad singlet, 1, $-CO_2H$), ~6.50 and 5.83 (m, 8, aromatic protons). *Anal.* Calcd for $C_{13}H_9N_2O_3Cl$: C, 56.43; H, 3.28; N, 10.13; Cl, 12.82. Found: C, 56.45; H, 3.36; N, 10.13; Cl, 12.77.

Decarboxylation of 4-Methylazoxybenzene-2-carboxylic Acid and 4′-Methylazoxybenzene-2-carboxylic Acid.—4-Methylazoxybenzene-2-carboxylic acid (0.71 g, 2.8 mol) was added to 50 ml of pyridine and powdered copper (~1.5 g) along with a crystal of cupric acetate. The mixture was stirred magnetically at reflux and monitored periodically by glpc. When the ratio of 4-methylazobenzene to azoxybenzene product was 0.16:1.00 (~12 hr) the mixture was added to 200 ml of 10% hydrochloric acid and extracted with ether. The ether was extracted with additional 10% hydrochloric acid and 10% sodium hydroxide, dried ($MgSO_4$), and concentrated under reduced pressure. Column chromatography on 100 g of neutral alumina (activity I) with pentane–ether (20:1) yielded first the 4-methylazobenzene and then a yellow-white powder identified as 4- or 4′-methylazoxybenzene. Pmr analysis with Eu(fod)$_3$ indicated <5% of the minor isomer to be present. Recrystallization from hexane gave 0.36 g (61%) of 4-methylazoxybenzene, mp 50.5–51.0° (lit.[18] mp 50°). Decarboxylation of 4′-methylazoxybenzene-2-carboxylic acid under the same conditions gave 4′-methylazoxybenzene, mp 63.5–64.0° (lit.[2a] mp 65°), in 72% yield.

Oxidation of 2-Acetoxy-5-methylazobenzene.—2-Acetoxy-5-methylazobenzene (2.54 g, 0.01 mol) was dissolved in 100 ml of

(27) Synthesized according to the method of Stevens.[18]

(28) S. Oae, T. Fukumoto, and M. Yamagami, *Bull. Chem. Soc. Jap.*, **36**, 601 (1963), report bp 127–129° (2 mm) for an undetermined mixture of 2- and 2′-methylazoxybenzene.

(29) J. Burns, H. McCombie, and H. A. Scarborough, *J. Chem. Soc.*, 2928 (1928).

(30) R. E. Lutz and M. R. Lytton, *J. Org. Chem.*, **2**, 773 (1939).

oxidizing solution and stirred for 18 hr. The yellow solution was poured onto ice–water and stirred for an additional 3 hr, the resultant solid was filtered and dissolved in ether, the ether was dried ($MgSO_4$), and the sample was concentrated under reduced pressure. The concentrated solution was chromatographed on 100 g of Florisil with hexane–ether (1:1) yielding 2.21 g (82%) of a yellow-white solid. The individual azoxybenzene isomers were partially separable *via* glpc (205°, the minor azoxyacetate preceding the major isomer), in this instance indicating that no fractionation of the mixture had occurred under the conditions of chromatography. Both glpc and Eu(fod)$_3$ pmr analysis indicated that the major isomer predominated by 9.3:1.

2-Acetoxy-5-methylazoxybenzene.—Two recrystallizations from hexane–ethanol of the oxidized 2-acetoxy-5-methylazobenzene mixture gave the major isomer, 2-acetoxy-5-methylazoxybenzene, as pale yellow needles: mp 76.5–77.0°; ir (KBr) 1760, 1225, 1193, 774, and 684 cm^{-1}; uv max (methanol) 243 nm (ϵ 10,600) and 324 (11,200); nmr (CCl_4) δ ~6.50 and 5.57 (m, 8, aromatic protons), 2.38 (s, 3, C-5 $-CH_3$), and 2.21 ppm (s, 3, $-COCH_3$). *Anal.* Calcd for $C_{15}H_{14}N_2O_3$: C, 66.66; H, 5.22; N, 10.37. Found: C, 66.48; H, 5.26; N, 10.33.

2-Hydroxyl-5-methylazoxybenzene.—2-Acetoxy-5-methylazoxybenzene (2.70 g, 0.01 mol) was dissolved in 100 ml of ethanol–water (1:1), and 15 g of potassium hydroxide was added. The solution was refluxed for 30 min, acidified with 10% hydrochloric acid, and poured onto 300 ml of ice–water. After stirring overnight, the crude product was suction filtered and dissolved in ether, and the ether was dried ($MgSO_4$) and removed under vacuum. Recrystallization from hexane–ethanol gave 1.8 g (79%) of yellow-orange needles, mp 72.5–73.0° (lit.[23] mp 74°).

Oxidation of 2-Hydroxyl-5-methylazobenzene.—2-Hydroxy-5-methylazobenzene[21] (2.12 g, 0.01 mol) was dissolved in 100 ml of the oxidizing solution and stirred for 24 hr. The yellow-orange solution was then poured onto ice–water and stirred for 3 hr at room temperature. The resultant crude solid was collected by suction filtration and dissolved in ether, and the ether was dried ($MgSO_4$) and removed under vacuum, yielding 1.9 g (90%) of a yellow-orange solid. The individual azoxybenzene isomers were partially separable *via* glpc (195°, the major azoxyphenol preceding the minor isomer). Conversion of the crude azoxyphenols to the acetates by treatment with pyridine–acetic anhydride as detailed for 2′-acetoxy-5′-methylazoxybenzene, and glpc (205°, the major azoxyacetate preceding the minor isomer) coupled with Eu(fod)$_3$ pmr spectral clarification, indicated that the major azoxyphenol isomer predominated by 2.6:1.

2′-Hydroxy-5′-methylazoxybenzene.—Two recrystallizations from hexane–ethanol of the oxidized 2-hydroxy-5-methylazobenzene mixture gave the major isomer, 2′-hydroxy-5′-methylazoxybenzene, as yellow needles, mp 124.5–125.0° (lit.[23] mp 125°).

2′-Acetoxy-5′-methylazoxybenzene.—2′-Hydroxy-5′-methylazoxybenzene (1.06 g, 0.005 mol) was dissolved in 30 ml of pyridine, and 3 ml of acetic anhydride was added. The solution was stirred for 1 hr, poured onto 300 ml of hydrochloric acid (20%) at 0°, and extracted into ether, and the ether was dried ($MgSO_4$) and concentrated under reduced pressure. The concentrated solution was chromatographed on 50 g of Florisil using pentane–ether (1:1) and the product corresponding to the yellow band was collected, yielding 0.9 g (67%) of a viscous yellow oil which resisted crystallization. Distillation in a microstill at 0.5 mm with a pot temperature of 165° gave a clear yellow oil: ir (neat) 1780, 1205, 769, and 688 cm^{-1}; uv max (methanol) 230 nm (ϵ 10,500) and 310 (14,500); nmr (CCl_4) δ ~6.50 and 5.57 (m, 8, aromatic protons), 2.38 (s, 3, C-5 $-CH_3$) and 2.16 ppm (s, 3, $COCH_3$). *Anal.* Calcd for $C_{15}H_{14}N_2O_3$: C, 66.66; H, 5.22; N, 10.37. Found: C, 66.63; H, 5.25; N, 10.54. Glpc (205°) and Eu(fod)$_3$ treatment of this azoxyacetate revealed it to be isomerically pure and to possess glpc and Eu(fod)$_3$ behavior identical with those of the minor azoxyacetate formed from the oxidation of 2-acetoxy-5-methylazoxybenzene.

Registry No.—Eu(fod)$_3$, 17631-68-4; 2′-methylazoxybenzene, 34810-71-4; 2-methylazoxybenzene, 34810-72-5; 2-chloro-4′-methylazobenzene, 34810-73-6; 2′-chloro-4-methylazoxybenzene, 34810-74-7; 2-chloro-4′-methylazoxybenzene, 34810-75-8; 4′-methylazobenzene-2-carboxylic acid, 13304-23-9; 4′-chloroazoxybenzene-2-carboxylic acid, 34810-77-0; 2-acetoxy-5-methylazoxybenzene, 34810-78-1; 2′-acetoxy-5′-methylazoxybenzene, 34810-79-2.

Thermal Decomposition of Methyl and Phenyl Triphenylmethylazocarboxylates[1a,b]

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Products from the decomposition of methyl and phenyl triphenylmethylazocarboxylates at 60° in benzene or cumene are reported. These and other results indicate that these tritylazocarboxylates decompose to trityl radicals, nitrogen, and the corresponding alkoxycarbonyl radicals (ROĊ=O) which can escape from a solvent cage and couple with other radicals before decarboxylating or decarbonylating. These alkoxycarbonyl radicals seem to be relatively unreactive radicals since no evidence for the addition into benzene or the abstraction of the α-hydrogen atom of cumene by these radicals was obtained.

Several reports of a class of free radicals which we prefer to call alkoxycarbonyl radicals (ROĊ=O) have been published.[2-15] The most detailed remarks on alkoxycarbonyl radicals came from decomposition studies of ethyl and benzyl *tert*-butyl monoperoxyoxalates as well as di-*tert*-butyl monoperoxyoxalate.[5,6] These studies demonstrated that alkoxycarbonyl radicals were stable enough to escape from the solvent cage to be trapped by molecules of solvent such as benzene or cumene or by molecules of a scavenger such as galvinoxyl, and to abstract a hydrogen atom from some active hydrogen atom donating species such as cumene.

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