Synthesis of 4-Isoamyl-6-acetylresorcinol.—Molten resorcinol (9.3 g.) was treated with 1 ml. of isovaleryl chloride, which was sufficient to keep the mixture liquid at 95°. Additional isovaleryl chloride (total 10.2 g.) was added over a period of 10 min. and the mixture was heated at 95° for another 20 min. The crude 4-isovalerylresorcinol was used directly in the next step.

A mixture of zinc amalgam (prepared from 28 g. of zinc[11]) and 6 *N* hydrochloric acid (45 ml.) was treated with a solution of the above 4-isovalerylresorcinol (7.0 g.) in absolute ethanol (35 ml.), and the mixture was heated under reflux for 6 hr., at which time a negative ferric chloride test was noted. The mixture was diluted with an equal volume of water and extracted with three 60-ml. portions of methylene chloride. The extracts were washed with water, dried over anhydrous magnesium sulfate, filtered, and evaporated at reduced pressure to yield 6.0 g. of oil. This was distilled, b.p. 128–131° (0.5 mm.), to give 1.7 g. of distillate which solidified. This was recrystallized from ligroin–benzene (9:1), 1.5 g., m.p. 64–67°. A second recrystallization gave 0.9 g., m.p. 70–71.5°, and a final recrystallization gave m.p. 72.5–73.5°. Cox and co-workers[12] reported m.p. 61–62.5° for this compound, prepared in the same manner. The infrared spectrum of our material left no doubt as to its identity as 4-isoamylresorcinol. It is possible that polymorphism may explain the indicated melting point discrepancy.

A mixture of the above 4-isoamylresorcinol (0.50 g.) and acetyl chloride (0.50 g.) was warmed for 2 hr. on the steam bath, then evaporated to dryness at reduced pressure. The residue was dissolved in ether (10 ml.) and the solution was washed with saturated aqueous sodium bicarbonate (5 ml.). The bicarbonate layer was re-extracted with ether and the ether extracts were dried, filtered, and stripped of solvent *in vacuo* to yield 0.63 g. (85%) of oil, crude di-*O*-acetyl-4-isoamylresorcinol, whose infrared spectrum indicated that acetylation was complete.

A solution of the latter di-*O*-acetate (0.56 g.) and the above 4-isoamylresorcinol (0.38 g.) in nitrobenzene (7 ml.) was stirred vigorously and treated with anhydrous aluminum chloride (0.56 g.). The mixture was allowed to stand at room temperature overnight, then was warmed to 50–55° for 4 hr. and finally cooled and treated with ice and water. The mixture was acidified with concentrated hydrochloric acid (2 ml.) and stirred until solution was complete. The aqueous layer was separated and extracted with chloroform, and the combined organic phases were steam distilled until the distillate was clear. The cooled residue was extracted with ether and the extracts were dried, filtered, and stripped of solvent to yield a dark sirup. The latter was dissolved in benzene (5 ml.) and diluted with hexane (10 ml.); the dark tar depositing was removed by filtration and the filtrate was set aside to crystallize. The resulting product (0.60 g.) was collected and recrystallized four times from hexane–benzene, yielding 0.09 g. of 4-isoamyl-6-acetylresorcinol, m.p. 92.5–94.5°. The infrared spectrum of this material was identical with that of the above hydrogenolysis product of dehydrotremetone, and admixture of the two samples led to no melting point depression.

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[12] A. Dohme, E. Cox, and E. Miller, *ibid.*, **48**, 1688 (1926).

Oxidations of Substituted Azo- and Hydrazobenzenes with Peracetic Acid

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A series of substituted azobenzenes was oxidized with peracetic acid. The two isomers α- and β-3-nitroazoxybenzene were obtained from *trans*-3-nitroazobenzene by this method. Oxidation of 4,4′-dichloro-2-nitroazobenzene on the other hand gave only the *alpha* isomer of the azoxybenzene. By refluxiug with 30% hydrogen peroxide and glacial acetic acid or treatment with the former in acetic anhydride, some chlorinated azoxybenzenes were prepared from the stable azobenzenes. In this work, a series of dihalogenated and tetrasubstituted hydrazobenzenes was also oxidized by means of peracetic acid. Very good yields of the dihalogenated azoxybenzenes were generally achieved, the hydrazobenzenes were quite stable in the oxidizing medium, and several tetra-substituted azoxybenzenes were also obtained in improved yield.

The oxidation of azobenzenes to the corresponding azoxybenzenes has been a subject of some interest, particularly since peracetic acid was first employed as an oxidizing agent for this purpose. Swern has summarized the literature concerning this topic up to 1949 in a review,[1] and the peracetic acid oxidation of a series of halogenated azobenzenes was recently reported.[2] One of the objects of the present work was to study the oxidation of a variety of substituted azobenzenes by peracetic acid as a method of preparing the corresponding azoxybenzenes.

The oxidation of hydrazobenzenes to azobenzenes has been achieved with a wide variety of oxidizing agents. For instance, hydrazobenzene itself has been oxidized to azobenzene by mercuric oxide,[3] potassium dichromate and acetic acid,[4] lead peroxide in acetone,[5] and iodine.[6] Grammaticakis[7] reported the oxidation of a series of dichlorohydrazobenzenes to the corresponding azobenzenes by means of heating in air or potassium ferricyanide. The literature however, does not contain, as far as we know, any reference to the preparation of azoxybenzenes from the hydrazobenzenes by direct oxidation. Another object of this work was to prepare a series of azoxybenzenes from the hydrazobenzenes by means of oxidation with peracetic acid and to study the stability of the hydrazobenzenes in this oxidizing agent.

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[1] D. Swern, *Chem. Rev.*, **45**, 1 (1949).

[2] P. E. Gagnon and B. T. Newbold, *Can. J. Chem.*, **37**, 366 (1959).

[3] Willgerodt, *J. prakt. Chem.*, **37** (2), 355 (1873).

[4] H. V. Pechmann and A. Nold, *Ber.*, **31**, 564 (1898).

[5] H. Leemann and E. Grandmougin, *ibid.*, **41**, 1307 (1908).

[6] M. Gonze, *Bull. soc. chim. Belges.*, **43**, 483 (1934).

[7] M. P. Grammaticakis, *Bull. soc. chim. France*, 951 (1951).

Table I

Melting Points of Products

Substituents	Azoxybenzenes M.p., °C.	Azoxybenzenes Lit. m.p., °C.	Azobenzenes M.p., °C.	Azobenzenes Lit. m.p., °C.
2,2′-Dichloro-	55–56	56[a]	137–138	136[a]
3,3′-Dichloro-	97–98	97[b]	...	...
4,4′-Dichloro-	154–155	155–156[a]	...	...
2,2′-Dibromo-	114–115	114[c]	...	...
3,3′-Dibromo-	108–109	111–111.5[d]	...	...
4,4′-Dibromo-	171–173	172[e]	...	...
4,4′-Diiodo-	201–202	202–203[f]	...	...
3,3′-Diacetamino-	255–256	254–255[f]	...	...
4,4′-Dichloro-2-nitro-	132–134	134[g]	...	...
2,2′,3,3′-Tetrachloro-	138–139	138–138.5[h]	...	...
2,2′,4,4′-Tetrachloro-	128.5–129.5	130–130.5[i]	...	...
2,2′,5,5′-Tetrachloro-	145–146	147[i]	188–189	189[j]
3,3′,5,5′-Tetrachloro-	171–172	171–172[k]	194–196	194–194.5[l]
2,2′-Dimethyl-3,3′-dichloro-	122–123	122–123[m]	...	...
2,2′-Dimethoxy-5,5′-dichloro-	120–121	119[m]	...	...

[a] Ref. 22. [b] Ref. 25. [c] Ref. 26. [d] Ref. 20. [e] Ref. 27. [f] Ref. 28. [g] Ref. 17. [h] Ref. 2. [i] Ref. 23. [j] Ref. 24. [k] Ref. 29. [l] Ref. 30. [m] Ref. 19.

Table II

Oxidations of Azobenzenes

Azobenzenes	Amount, g.	H_2O_2, ml.	CH_3COOH, ml.	Temp., °C.	Time, hr.	Azoxy, %
Azobenzene	1.026	16	50	65–85	24	83
	0.297	25	50	70–90	16	72
	0.310	25	50	75–98	3	52
trans-3-Nitro-	0.407	25	50	62–69	19	89[a]
	0.600	25	50	80–90	1.2	90[a]
	0.530	25	50	75–80	1.5	95[a]
2,2′-Dichloro-	0.290	20	100	Reflux	3.5	91[b]
4,4′-Diiodo-	0.202	10	150	70–80	2	63
	0.197	10	150	80–85	2	87[b]
	0.111	10	50	Reflux	0.75	74
3,3′-Diacetamino-	0.225	25	100	75–80	2	47
	0.217	5	50	Reflux	0.25	65
4,4′-Dichloro-2-nitro-	0.050	25	50	67–75	1	79
2,2′,4,4′-Tetrachloro-	0.187	35	50	Reflux	6	88[b]
	0.200	50	100	Reflux	8	82
	0.103	30	50	Reflux	24	74
2,2′,5,5′-Tetrachloro-	0.201	60	125	Reflux	24	28
2,2′-Dimethyl-3,3′-dichloro-	0.160	25	100	66–80	18	74
	0.473	25	100	66–80	19	80
2,2′-Dimethoxy-5,5′-dichloro-	0.060	10	50	65–80	2	57
			$(CH_3CO)_2O$, ml.		Min.	
2,2′,4,4′-Tetrachloro-	0.200	10	100	Reflux	3	15
2,2′,5,5′-Tetrachloro-	0.200	10	100	Reflux	5	Trace
	0.200	5	100	Reflux	5	5
	0.122	10	100	Reflux	3	15

[a] Total yield of a mixture of two isomers. [b] Highest yield reported for an oxidation method.

Discussion

Oxidation of Mono- and Disubstituted Azobenzenes.—The melting points of the products obtained in this work are given in Table I. Some preliminary oxidations of azobenzene itself with hydrogen peroxide in glacial acetic acid under various conditions were performed to determine the stability of the compound in this oxidizing medium. Increasing the temperature and shortening the reaction time caused a greatly reduced yield of azoxybenzene (Table II).

The oxidation of 3- and 4-nitroazobenzene with peracetic acid has been reported[8–10] and the two structural isomers of 3- and of 4- nitroazoxybenzene were obtained. In the present work, the peracetic acid oxidation of *trans*-3-nitroazobenzene was studied. The latter is more stable than the *cis* isomer,[11] and since *cis*-3-nitroazobenzene would undoubtedly give the *trans*-3-nitroazoxybenzenes upon oxidation, the stable *trans* isomer was used. Oxidation with peracetic acid gave α- and β-3-nitroazoxybenzene in very good yield (Table II).

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[8] G. Leandri and A. Risalti, *Ann. Chim. (Rome)*, **44**, 1036 (1954).

[9] A. Angeli and L. Alessandri, *Atti. accad. Lincei.*, **20**(I), 170 (1911).

[10] A. Angeli and L. Alessandri, *ibid.*, **20**(I), 896 (1911).

[11] A. H. Cook and D. G. Jones, *J. Chem. Soc.*, 1309 (1939).

Meisenheimer in earlier work[12] also reported the formation of these compounds from the condensation of *m*-dinitrobenzene with phenylhydroxylamine.

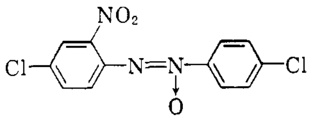
The infrared spectra of the α- and β-3-nitroazoxybenzenes were similar to that of azoxybenzene, the main difference being the presence of a band at 1510–1515 cm.$^{-1}$ in the spectrum of each isomer, which was assigned to the nitro group. The isomer designated α by Meisenheimer was not nitrated by nitric acid (d = 1.42) in sulfuric acid, which is evidence that the compound has the α structure.[13] Furthermore, the structures of the α- and β-3-nitroazoxybenzenes were recently established by independent synthesis,[14] and the same structures are indicated in this work. Since these compounds were prepared by peracetic acid oxidation, they probably possess the *trans* configuration.

In other experiments in this study, attempts were made to obtain 2,2′-dichloroazoxybenzene in good yield by oxidation of the corresponding azobenzene, several oxidizing agents being tried. There was no reaction with nitric acid in glacial acetic acid, while chromic oxide in acetic acid caused only decomposition. Complete oxidation was, however, achieved with hydrogen peroxide in acetic anhydride, but only traces of the azoxybenzene resulted. Finally, refluxing in hydrogen peroxide and acetic acid was employed and the 2,2′-dichloroazoxybenzene was obtained in very good yield, 90%.

The results given in Table II show that for azobenzenes that are stable, refluxing in hydrogen peroxide and acetic acid for a relatively short time is a good procedure for the preparation of azoxybenzenes. The advantages of this method are that the azobenzene is more soluble, the elevated temperature leads to effective oxidation, and the reaction time is shortened thus reducing decomposition.

Oxidations of Tri- and Tetrasubstituted Azobenzenes.—Oxidation of 4,4′-dichloro-2-nitroazobenzene with peracetic acid should give two structurally isomeric azoxybenzenes: namely, the α and β forms. 4,4′-Dichloro-2-nitroazoxybenzene, m.p. 133–134° and 134°, has been prepared by nitration of the azoxy compound,[15,16] and in later work, it was shown that nitration of 4,4′-dichloroazobenzene also gave the same compound.[17] In this work, 4,4′-dichloro-2-nitroazoxybenzene, m.p. 132–134°, was prepared by oxidation of the azo compound with hydrogen peroxide in glacial acetic acid and no second isomer was isolated (Table II).

It was also found that 4,4′-dichloro-2-nitroazoxybenzene was not nitrated by fuming nitric acid in acetic acid even after prolonged treatment using a method described previously.[17] This is evidence that the compound is the α isomer since the β isomer would certainly be expected to nitrate under these conditions. The infrared spectrum showed a strong band at 1540 cm.$^{-1}$, indicating the nitro group, and the remainder of the spectrum was similar to that of 4,4′-dichloroazoxybenzene. The ultraviolet spectrum possessed a K-band at 330 mμ, (log ϵ 4.01) and an E_2 band at 226 mμ, (log ϵ 4.21). The substance was also slowly steam volatile (0.02 g. distilled with 3.9 l. of water). Furthermore, all the methods employed for the preparation of this compound to date would be expected to give the α isomer on the basis of modern electronic theory. Since oxidation with peracetic acid also gave the *alpha* isomer, it is considered that the latter has the more stable *trans* configuration. The structure of α-4,4′-dichloro-2-nitroazoxybenzene is given below:



A series of tetrasubstituted azobenzenes was also oxidized with peracetic acid and the results are given in Table II.

Oxidations of Substituted Hydrazobenzenes.—The oxidation of 4-bromohydrazobenzene with peracetic acid has been reported by Angeli.[18] In this work, some dichloro and dibromohydrazobenzenes were oxidized with the same agent and the results are found in Table III. In general, the dihalogenated hydrazobenzenes were remarkably stable to the oxidizing medium and very good yields of the dihalogenated azoxybenzenes were achieved. A series of tetrasubstituted hydrazobenzenes was also oxidized (Table III), and in some cases improved yields of the azoxybenzenes were obtained.

Experimental

All melting points are uncorrected.

Preparation of Azobenzenes.—2,2′-Dichloro, 2,2′,4,4′-, and 2,2′,5,5′-tetrachloro, 2,2′-dimethyl-3,3′-dichloro, and 2,2′-dimethoxy-5,5′-dichloroazobenzenes were prepared from the corresponding azoxy compounds by reduction with zinc dust and alkali.[19] 4,4′-Diiodoazobenzene was obtained from the azoxybenzene by the action of concentrated sulfuric acid,[20] and 4,4′-dichloro-2-nitroazobenzene was made by reducing 4,4′-dichloro-2-nitroazoxybenzene with ammonium sulfide.[17] 3,3′-Diacetaminoazobenzene was prepared by acetylating 3,3′-diaminoazobenzene and *trans*-3-nitroazobenzene was synthesized by the method of Bamberger and Hubner.[21]

Preparation of Hydrazobenzenes.—The hydrazobenzenes used in this work were all prepared from the corresponding

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[12] J. Meisenheimer, *Ber.*, **53**, 358 (1920).

[13] H. E. Bigelow, *Chem. Rev.*, **9**, 117 (1931).

[14] C. L. Behr, E. G. Alley, and O. Levand, *J. Org. Chem.*, **27**, 65 (1962).

[15] K. Heumann, *Ber.*, **5**, 911 (1872).

[16] A. Calm and K. Heumann, *ibid.*, **13**, 1184 (1880).

[17] C. D. Houghton and W. A. Waters, *J. Chem. Soc.*, 1018 (1950).

[18] A. Angeli, *Atti. accad. Lincei*, **23** (I), 557 (1914).

[19] R. Gaudry and K. F. Keirstead, *Can. J. Research*, **27B**, 890 (1949).

[20] S. Gabriel, *Ber.*, **9**, 1405 (1876).

[21] E. Bamberger and R. Hubner, *ibid.*, **36**, 3818 (1903).

TABLE III

OXIDATIONS OF HYDRAZOBENZENES

Hydrazobenzenes	Amount, g.	H_2O_2, ml.	CH_3COOH, ml.	Temp., °C.	Time, hr.	Azoxy, %
2,2'-Dichloro-	1.149	50	150	60–70	48	79
	0.890	50	100	75–80	24	80
	0.357	25	50	Reflux	7.5	61
3,3'-Dichloro-	0.549	10	50	45–55	26.5	68
	0.443	10	50	65–70	18	Quant.
	0.396	10	50	80–85	2	85
4,4'-Dichloro-	0.515	10	100	65–85	2.5	81
	0.791	15	100	70–85	2.5	88
	0.846	20	100	75–90	1.75	86
2,2'-Dibromo-	0.221	10	50	60–77	1	Nil
	0.222	5	50	55–60	23.5	3
3,3'-Dibromo-	0.453	10	50	65–75	21	66
	0.405	5	50	80–85	5.75	80
4,4'-Dibromo-	0.438	10	100	70–80	3.25	91
	0.390	10	100	80–85	2	88
2,2',3,3'-Tetrachloro-	0.100	20	50	Reflux	3	71
2,2',4,4'-Tetrachloro-	0.102	40	50	Reflux	24	15
2,2',5,5'-Tetrachloro-	0.564	10	50	85–90	72	Nil[a]
	0.105	40	50	Reflux	24	35
3,3',5,5'-Tetrachloro-	0.204	20	100	55–80	24	85[b]
	0.105	10	50	Reflux	1	85
	0.087	30	50	Reflux	5	40
2,2'-Dimethyl-3,3'-dichloro-	0.286	25	100	62–80	6	89[c]
			$(CH_3CO)_2O$, ml.		Min.	
2,2',4,4'-Tetrachloro-	0.202	5	50	Reflux	3	37
2,2',5,5'-Tetrachloro-	0.270	5	100	60–70	105	47[c]
	0.200	10	100	60–70	160	
				Reflux	5	24
	0.202	5	50	Reflux	3	32

[a] 77% yield of the azobenzene. [b] Traces of the azobenzene. [c] Highest yield reported for an oxidation method.

azoxybenzenes by reduction with zinc dust and sodium hydroxide using the method previously reported.[19]

Preparation of α- and β-3-Nitroazoxybenzenes.—*trans*-3-Nitroazobenzene (0.600 g.) was dissolved in glacial acetic acid (50 ml.), 30% hydrogen peroxide (10 ml.) added, and the solution heated to 80–90°. This temperature was maintained for 1 hr. and 10 min., and further additions of hydrogen peroxide, 10 and 5 ml., were made after 10 and 20 min., respectively. Upon pouring into water, the solution gave a mixture of two 3-nitroazoxybenzenes; yield: 0.579 g., 90%. Fractional crystallization from acetone gave pale yellow needles of α-3-nitroazoxybenzene, m.p. 118.5–119.5°. (lit. m.p. 120–121°).[12]

Anal. Calcd. for $C_{12}H_9O_3N_3$: N, 17.28. Found: N, 17.50.

This compound was slightly soluble in ethanol. λ_{max} 315 and 269 mμ (log ε 4.49 and 4.50). The principal bands in the infrared spectrum were at: 1600, 1510, 1425, 1350, 1300, 1290, 1260, 1150, 1100, 1070, 1025, 945, 920, 900, 825, 810, 772, 741, 684, and 677 cm.$^{-1}$.

A second product was yellow β-3-nitroazoxybenzene, m.p. 87–88° (from ethanol) (lit. m.p. 86–88°).[12] This product was quite soluble in ethanol. λ_{max} 321 and 228 mμ (log ε 4.15 and 4.19). The main bands in the infrared spectrum were at: 1600, 1515, 1340, 1285, 1260, 1150, 1060, 1023, 972, 905, 877, 815, 773, 743, 702, and 684 cm.$^{-1}$.

Oxidations with Hydrogen Peroxide and Acetic Acid.—In this work, two procedures were employed for the oxidation of azo- and hydrazobenzenes using hydrogen peroxide and acetic acid. An example of each procedure is given.

Oxidation of 2,2'-Dichloroazobenzene.—2,2'-Dichloroazobenzene (0.290 g.) was dissolved in glacial acetic acid (100 ml.), 30% hydrogen peroxide (10 ml.) added, and the solution refluxed. Further additions of hydrogen peroxide (5 ml.) were made after 1.5 and 2.5 hr. The solution was refluxed for a total of 3.5 hr., cooled, and poured into water. The mixture was cooled overnight in the refrigerator and pale yellow 2,2'-dichloroazoxybenzene separated, m.p. 52–53°; yield: 0.279 g., 91%. One recrystallization from aqueous ethanol gave yellow needles, m.p. 55–56° (lit. m.p. 56°).[22]

Oxidation of 4,4'-Dichlorohydrazobenzene.—4,4'-Dichlorohydrazobenzene (0.846 g.) was dissolved in glacial acetic acid (100 ml.), the solution heated to 65°, and 30% hydrogen peroxide(10 ml.) added. The solution was then heated at 75–90° for 1.75 hr., when the color became pale yellow. The product was separated by the procedure described above, 4,4'-dichloroazoxybenzene being obtained; yield: 0.767 g., 86%, m.p. 154–155° (from ethanol) (lit. m.p. 155–156°).[22]

Oxidations with Hydrogen Peroxide and Acetic Anhydride.—Both azo- and hydrazobenzenes were oxidized using hydrogen peroxide in acetic anhydride. An example of the method employed is described.

Oxidation of 2,2',4,4'-Tetrachloroazobenzene.—2,2',4,4'-Tetrachloroazobenzene (0.202 g.) was dissolved in acetic anhydride (50 ml.), 30% hydrogen peroxide (5 ml.) added, and the solution heated to 100°. A very vigorous exothermic reaction took place and the solution boiled. Extremely rapid oxidation occurred and was accompanied by a rapid color change to yellow. The solution was quickly cooled and then poured into cold water with stirring. 2,2',4,4'-Tetrachloroazoxybenzene separated out on standing overnight in the refrigerator; yield: 0.078 g., 37%. Two recrystallizations from ethanol gave pale yellow needles, m.p. 128.5–129.5°, (lit. m.p. 130.5°).[23]

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(22) K. Brand, *J. prakt. Chem.*, **67**, 145 (1903).

(23) R. Gaudry and K. F. Keirstead, *Can. J. Research*, **27B**, 900 (1949).

(24) T. De Crauw, *Rec. trav. chim.*, **50**, 782 (1931).

(25) A. Laubenheimer, *Ber.*, **8**, 1623 (1875).

(26) L. Zechmeister and P. Rom, *Ann.*, **468**, 117 (1929).

Oxidation with Other Agents.—2,2′-Dichloroazobenzene (0.50 g.) was suspended in glacial acetic acid (10 ml.), chromic oxide (0.7 g.) dissolved in glacial acetic acid containing a few drops of water (5 ml.) added in portions with shaking, and the mixture warmed for 5 min. On cooling and dilution with water, unchanged 2,2′-dichloroazobenzene separated, 0.30 g., 60%, m.p. 137–138° (lit. m.p. 136°).[22]

2,2′-Dichloroazobenzene (0.30 g.) in glacial acetic acid (50 ml.) was treated with 100 ml. of nitric acid (50 ml. of water and 50 ml. of concentrated acid), and the mixture refluxed for 5.5 hr. On cooling, 2,2′-dichloroazobenzene was recovered in quantitative yield.

2,2′,5,5′-Tetrachloroazobenzene (1.0 g.) was suspended in a solution of sodium dichromate (3.5 g.) in water (5 ml.) and concentrated sulfuric acid (5 ml.) added. The mixture was shaken and cooled in water and finally heated on a steam bath for 2.5 hr. Extraction of the residue with benzene and evaporation of the extract gave recovered 2,2′,5,5′-tetrachloroazobenzene, 0.6 g., 60%, m.p. 188–189° (lit. m.p. 189°).[24]

Spectra.—Infrared absorption spectra were determined in Nujol on a Perkin–Elmer Model 137 Infracord spectrophotometer and the ultraviolet spectra were recorded on a Beckman Model DK-2 ratio recording spectrophotometer using absolute ethanol as solvent.

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The Pyrolysis of Alkyl Hydrogen Phthalates and Related Esters[2]

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The pyrolysis of alkyl hydrogen phthalates to alcohols and phthalic anhydride proceeds with retention of configuration. Primary alkyl and cycloalkyl groups are eliminated almost exclusively as alcohols, in contrast to secondary alkyl groups, which form olefin–alcohol mixtures. Alkyl hydrogen maleates and tetrachlorophthalates react similarly to form alcohols and anhydrides. The pyrolyses of dicyclohexyl phthalate and dibutyl phthalate give approximately equal mixtures of olefin and alcohol, consistent with a mechanism involving initial normal ester pyrolysis of dialkyl phthalate to olefin and alkyl hydrogen phthate, followed by displacement of alcohol by internal attack of the carboxyl group. Dibutyl maleate reacts more slowly to a mixture of alcohol and olefin.

In a previous paper[4] the pyrolysis of *sec*-alkyl hydrogen phthalates to olefins was reported. An appreciable amount of 4-heptanol was formed during the pyrolysis of 4-heptyl hydrogen phthalate. This investigation was initiated in order to survey the scope of the abnormal elimination reaction, both with respect to the nature of the alkyl group and the type of dicarboxylic acid employed, and to elucidate the mechanism of the reaction.

Methyl alkyl phthalates undergo pyrolytic decomposition to the appropriate alkene, methanol, and phthalic anhydride.[5] It appears certain that an intermediate stage in this reaction is the formation of methyl hydrogen phthalate and an alkene, followed by decomposition of the acid ester to methanol and phthalic anhydride. Otherwise higher alcohols would have been formed. Furthermore, dimethyl phthalate does not decompose under identical conditions, indicating that formation of methanol takes place from methyl hydrogen phthalate.

Dialkyl phthalates and maleates react similarly to the methyl alkyl phthalates, producing one mole of alcohol and one mole of olefin. The distillate from dicyclohexyl phthalate at atmospheric pressure consisted of 42% cyclohexanol and 56% cyclohexene. A predominance of cyclohexene, as a result of dehydration of cyclohexanol is to be expected. In a larger scale experiment, with longer contact time of acid (alkyl hydrogen phthalate) and pyrolytically formed alcohol, the extent of dehydration was greater, with a 28:72 ratio being observed. Similar distillation of dibutyl phthalate gives 63% of the theoretical yield of butanol, 54% of butene, or a 54:46 ratio. Dibutyl maleate decomposition proceeded relatively slowly, but led to a 56:44 ratio of butanol–butene.

Two mechanisms are likely for the pyrolysis of alkyl hydrogen phthalates. In the first, (mechanism I) proton transfer or hydrogen bonding leads to an intermediate species which decomposes by nucleophilic displacement at the carbonyl carbon to phthalic anhydride and an alcohol, or by carboxylate attack on the beta hydrogen to phthalic acid and olefin. In the light of Bender's work[6] on enhancement of hydrolysis rate with intra-

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