PERACETIC ACID OXIDATION OF HALOGENATED AZOBENZENES[1]

PAUL E. GAGNON AND BRIAN T. NEWBOLD[2]

ABSTRACT

A series of dihalogenated and five tetrachloroazobenzenes were oxidized to the corresponding azoxy compounds by means of 30% hydrogen peroxide in glacial acetic acid, the reaction being carried out at about 60–70° C, for 24 hours.

As expected, the yields, in general, obtained from azobenzenes containing substituents in the 2,2′-positions were lower than those from compounds having substituents in the 3,3′- and 4,4′-positions, which gave very good results.

INTRODUCTION

One of the most useful methods for the preparation of azoxybenzenes is the reduction of the appropriate nitrobenzene with a suitable reagent. However, azoxy compounds have also been obtained by oxidation of amines by means of peracids. For example, aniline when oxidized with an equimolar quantity of perbenzoic acid (1), or with peracetic acid (2), gave rise to azoxybenzene. D'Ans and Kneip (2) stated that primary amines can give rise to azo and azoxy compounds when treated with concentrated peracids under various conditions. Later, Greenspan (3) obtained a much better yield, 85%, of azoxybenzene from aniline by oxidation with 45% peracetic acid.

A third method of obtaining azoxybenzenes is the oxidation of the corresponding azobenzenes. For instance, azobenzene gave azoxybenzene when treated with an acetic acid solution of chromic acid in a sealed tube at 150–250° C (4) and 4,4′-dinitroazoxybenzene was obtained from the azo compound by the action of fuming nitric acid at room temperature (5).

The direct oxidation of azobenzenes to azoxybenzenes by means of organic peracids has been a subject of interest for many years. Angeli and others (6, 7, 8, 9) studied this reaction. For example, when azobenzene was treated for several days with peracetic acid, made by combining glacial acetic acid with 30% hydrogen peroxide, azoxybenzene was obtained (6). In a review (10), Swern states that this reaction proceeds readily under mild conditions and quantitative yields are frequently obtained, and he lists the azoxybenzenes prepared by this method up to 1949. In recent work, azobenzene was also oxidized by perbenzoic acid (11).

There are some examples of peracid oxidation of halogenated azobenzenes mentioned in the literature. For instance, 4-bromo-, 4,4′-dibromo-, and 2-bromo-4-nitro-azobenzene have been oxidized to the corresponding azoxy compounds by 30% hydrogen peroxide in glacial acetic acid (12, 13). Badger *et al.* (14) recently oxidized 3-bromo-, 4-bromo-, and 4-chloro-azobenzene with perbenzoic acid. However, only one dichloroazobenzene, namely, the 4,4′-derivative, has been oxidized to the azoxy compound by means of peracetic acid (15). Recently (16), 3,3′- and 4,4′-difluoroazoxybenzenes were prepared from the azo compounds by oxidation with peracetic acid using the method of Angeli.

The main object of the present work was to oxidize a series of dihalogenated and tetrachloroazobenzenes to the corresponding azoxy derivatives by means of 30% hydrogen peroxide in glacial acetic acid and to compare the yields obtained.

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Contribution from the Department of Chemistry, Laval University, Quebec, Que., and St. Joseph's University, Moncton, New Brunswick.

[2] *Head of the Department of Chemistry, St. Joseph's University, Moncton, New Brunswick.*

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THEORETICAL PART

In the present work, many oxidations of dihalogenated azobenzenes were carried out using 30% hydrogen peroxide in glacial acetic acid. The manner in which the hydrogen peroxide was added to the solution of the azo compound was found to be important. The best results were obtained when most of the hydrogen peroxide was added regularly in small portions during the first 2 hours. The solubility of the azobenzene in glacial acetic acid was of considerable importance. It was found that the azobenzenes which were very soluble were the most easily oxidized. The time of the reaction was also critical, for instance, when the period of heating at 60–70° C was only a few hours, the yields of the azoxy derivatives were low. Therefore, the period of heating for the oxidations described in this work was extended to 24 hours.

The experimental conditions for the best yields of the dihalogenated azoxybenzenes are given in Table I. It is seen that only a low yield, 28%, of 2,2′-dichloroazoxybenzene was obtained, and that almost half of the starting material was recovered. It is evident that 2,2′-dichloroazobenzene was quite stable to oxidation with peracetic acid. Bigelow *et al.* (17) found that 4-amino-azobenzene was very difficult to oxidize, there being incomplete oxidation even after 6 days of refluxing in 30% hydrogen peroxide. In the present work, however, very good yields of 3,3′- and 4,4′dichloroazoxybenzene were obtained.

TABLE I

Oxidation of halogenated azobenzenes

Azobenzenes	Amount, g	30% H_2O_2, ml	CH_3COOH, ml	Temp., ° C	Azoxy compound			Starting material rec., %
					Yield, %	M.p., ° C	Lit. m.p., ° C	
			Dihalogenated azobenzenes					
2,2′-Dichloro-	2.000	41	150	60–70	28	56	56 (23)	47
3,3′-Dichloro-	2.000	41	200	62–75	93	98–99	97 (24)	Nil
4,4′-Dichloro-	0.512	31	200	60–82	89	154–155	155–156 (21)	"
2,2′-Dibromo-	0.232	10	50	63–66	13	112–113	114 (25)	"
3,3′-Dibromo-	0.300	10	50	64–65	Quant.	111–112	111.5 (26)	"
4,4′-Dibromo-	0.202	16	100	65–68	Quant.	171–171.5	172 (27)	"
3,3′-Diiodo-	0.200	10	100	62–67	96	116–117	117–118 (20)	"
			Tetrachloroazobenzenes					
2,2′;3,3′-Tetrachloro-	0.042	20	150	66–70	71	136–138	— *	Nil
2,2′;4,4′- "	0.098	30	100	65–67	26	128–129	130.5 (20)	72
2,2′;5,5′- "	0.088	35	100	65–68	25	145–146	147 (28)	75
3,3′;4,4′- "	0.160	22	150	62–68	98	137.5–138.5	137–138 (29)	Nil
3,3′;5,5′- "	0.095	20	150	61–70	71	172–173	171–172 (30)	"

*2,2′;3,3′-Tetrachloroazoxybenzene also prepared from 2,2-dichloronitrobenzene using dextrose in alkaline medium was pale yellow, m.p. 138–138.5° C. Yield, 2%. Anal. calc. for $C_{12}H_6N_2OCl_4$: Cl, 42.20%. Found: Cl, 41.22%.

By contrast, the yield of 2,2′-dibromoazoxybenzene was low, 13%, and there was apparently considerable complete oxidation, there being no recovery of unreacted starting material. Bigelow *et al.* (17) showed that both 4-nitro-4′-hydroxyazobenzene and 4-hydroxyazobenzene were completely oxidized to carbon dioxide and nitrogen by prolonged refluxing with 30% hydrogen peroxide. Quantitative yields of 3,3′- and 4,4′-dibromoazoxybenzene were obtained in the present study. As shown in Table I, the yield of 3,3′-diiodoazoxybenzene was very good, but here again, in some experiments, considerable decomposition occurred.

As far as we know, there are no instances of oxidation of tetrachloroazobenzenes with peracetic acid that have been recorded in the literature. In the present work, five tetrachloroazoxybenzenes were prepared from the azo compounds by oxidation with 30% hydrogen peroxide in glacial acetic acid. The solubility of the tetrachloroazobenzene in glacial acetic acid, the manner in which the hydrogen peroxide was added, and the time of heating were of importance.

The experimental conditions and best results are given in Table I. It is seen that the yield of 2,2′;3,3′-tetrachloroazoxybenzene, which is described for the first time, was 71%, whereas the yields of 2,2′;4,4′- and 2,2′;5,5′-tetrachloroazoxybenzene were only 26 and 25% respectively. By comparison, both 3,3′;4,4′- and 3,3′;5,5′-tetrachloroazobenzene gave good yields of the azoxy derivatives.

In general, it may be said that oxidation of halogenated azobenzenes with peracetic acid is a good method for the preparation of azoxybenzene derivatives having no substituents in the 2,2′-positions.

EXPERIMENTAL PART*

Preparation of Halogenated Azobenzenes

The halogenated azobenzenes were prepared from the corresponding nitrobenzenes by standard methods given in the literature. For example, 4,4′-dichloroazobenzene was made by reducing 4-chloronitrobenzene with magnesium and absolute methanol (18). In the case of 3,3′;4,4′-tetrachloroazobenzene, the azoxy compound (19) was reduced with zinc dust and sodium hydroxide, followed by oxidation in air, as previously described (20).

Peracetic Acid Oxidation

The procedure followed was essentially the same in every case; therefore the preparation of only one compound needs to be described in detail.

4,4′-Dichloroazobenzene (0.512 g) was dissolved in glacial acetic acid (200 ml) at 80° C, and then 30% hydrogen peroxide (2 ml) was added. Further additions of 30% hydrogen peroxide (2 ml) were made every 15 minutes during the first 2 hours, when a further 5 ml was added. The heating was continued at about 65° C, then after 3 hours, 3 ml of 30% hydrogen peroxide was added. To complete the reaction, after 19 and 20 hours 2- and 5-ml portions of hydrogen peroxide, respectively, were added. Heating was continued until the 24-hour period was over, the solution being then allowed to cool to room temperature. The original orange color had changed to pale yellow. The solution was poured into an excess of water (300 ml) and a pale yellow product separated out. It was washed with water and dried. Crude yield, 89%. The 4,4′-dichloroazoxybenzene was recrystallized several times from ethanol as pale yellow needles, m.p. 154–155° C, alone or with an authentic sample (lit. m.p. 155–156° C (21)).

In some cases, the aqueous filtrate, obtained after precipitation with water and filtration, yielded a small amount of product after standing in a refrigerator. In some experiments, precipitation took place after several portions of hydrogen peroxide had been added and glacial acetic acid was used to restore the solution. In cases where there was incomplete oxidation, that is, where a mixture of azoxy compound and starting material was obtained, separation was achieved either by crystallization or chromatography. The latter method was used particularly for the separation of products obtained from the oxidation of the tetrachloroazobenzenes. The chromatography was carried out with columns containing a (4:1) mixture of salicylic acid – celite as absorbant. The celite was celite 535. The products were placed on the column in ligroin solution and

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**All melting points are uncorrected.*

development was carried out with ligroin (b.p. 66–75° C). Elution was achieved with 95% ethanol. The azoxy compound was absorbed high on the column as a yellow band and the starting material (orange band) moved down to the bottom or was passed into the filtrate. The products separated by chromatography were further purified by recrystallizations from ethanol. In order to verify the oxidation method used in the present work, azobenzene was employed as a reference compound. Azobenzene (2 g), glacial acetic acid (50 ml), 30% hydrogen peroxide (18 ml) were heated at 65° C for 24 hours. The crude yield of azoxybenzene was 83%: m.p. 35–36° C, alone or with an authentic sample (lit. m.p. 35.5–36.5° C (22)).

The experimental details and results for all the halogenated azoxybenzenes prepared are given in Table I.

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REFERENCES

1. Prileschajew, N. Ber. **42**, 4811 (1909).
2. D'Ans, J. and Kneip, A. Ber. **48**, 1136 (1915).
3. Greenspan, F. P. Ind. Eng. Chem. **39**, 847 (1947).
4. Petriew, H. Ber. **6**, 557 (1873).
5. Weiner, A. and Stiasmy, E. Ber. 3263 (1899).
6. Angeli, A. Atti accad. nazl. Lincei, **19** [I], 793 (1910).
7. Angeli, A. and Alessandri, L. Atti accad. nazl. Lincei, **20** [I], 896 (1911).
8. Angeli, A. Gazz. chim. ital. **46** (2), 67 (1916).
9. Bigiavi, D. and Sabatelli, V. Gazz. chim. ital. **57**, 559 (1927).
10. Swern, D. Chem. Revs. **45**, 1 (1949).
11. Badger, G. M., Buttery, R. C., and Lewis, G. E. J. Chem. Soc. 2143 (1953).
12. Angeli, A. and Valori, B. Atti. accad. nazl. Lincei, **21** [I], 155 (1912).
13. Bigiavi, D., Albanese, C., and Poggi, I. Gazz. chim. ital. **61**, 392 (1931).
14. Badger, G. M., Buttery, R. C., and Lewis, G. E. J. Chem. Soc. 2147 (1953).
15. Burns, J., McCombie, H., and Scarborough, H. A. J. Chem. Soc. 2928 (1928).
16. Gore, P. H. and Wheeler, O. H. J. Am. Chem. Soc. **78**, 2160 (1956).
17. Bigelow, H. E., Holder, C. H., and Linton, E. P. Can. J. Research, B, **19**, 132 (1941).
18. Keirstead, K. F. Can. J. Chem. **31**, 1064 (1953).
19. Gaudry, R. and Keirstead, K. F. Can. J. Research, B, **27**, 893 (1949).
20. Gaudry, R. and Keirstead, K. F. Can. J. Research, B, **27**, 900 (1949).
21. Heumann, K. Ber. **5**, 911 (1872).
22. Bigelow, H. E. and Palmer, A. Org. Syntheses, Collective Vol. **II**, 57 (1943).
23. Brand, K. J. prakt. Chem. **67**, 145 (1903).
24. Laubenheimer, A. Ber. **8**, 1623 (1875).
25. Zechmeister, L. and Rom, P. Ann. **468**, 117 (1928).
26. Gabriel, S. Ber. **9**, 1405 (1876).
27. Farrow, M. D. and Ingold, C. K. J. Chem. Soc. 2543 (1924).
28. De Crauw, T. Rec. trav. chim. **50**, 782 (1931).
29. Dains, F. B. and Kenyon, W. O. J. Am. Chem. Soc. **52**, 2357 (1931).
30. Beilstein, F. and Kurbatow, A. Ann. **197**, 84 (1879).