oil (A) which exhibited strong azide and conjugated carbonyl absorptions in the i.r. spectrum (2100, 1719, 1590 cm^{-1}) but no signals below δ 3.00 in the n.m.r. spectrum. This material decomposed to a black tar within minutes when solvent was removed. The t.l.c. indicated the presence of only the material with R_f 0.64.

2-Iodo-2-cyclohexenone

The reaction was run in exactly the same manner using the same molar quantities of reactants. Evaporation of the dried solution gave 5.6 g of a dark brown oil; n.m.r. δ 7.90 (t, J = 6 Hz), 4.83 (br), 4.60 (br d), 4.24 (mult), 3.7–1.5 (mult); i.r. 3030, 2960, 2880, 2110, 1715, 1690, 1590, 1575 cm^{-1}.

Assignment of the first three n.m.r. absorptions to **8***a*, **7***b*, and **7***a* (2) respectively gives a product distribution by n.m.r. integration of 9:7:7

Chromatography of the mixture on silica gel using benzene – petroleum ether as eluent gave a mixture of **7***a* and **7***b* in 20% yield

Anal. Calcd. for $C_6H_8N_3IO$: C, 27.17; H, 3.02. Found: C, 27.31; H, 2.93.

Further elution of the column with benzene and benzene–ethanol afforded **8***a* (2.53 g, 44%) as white crystals from petroleum ether, m.p. 46.0–47.0°: i.r. 3030, 2960, 2940, 2890, 2870, 1690, 1593 cm^{-1}; n.m.r. δ 7.90 (1H, t) 2.87–1.82 (6H, mult).

Anal. Calcd. for C_6H_7IO: C, 32.46; H, 3.18; I, 57.16. Found: C, 32.76; H, 3.46; I, 56.76.

Crude adduct (3.0 g) was dissolved in 100 ml ether and 5 ml of triethyl amine was added. The mixture was stirred at room temperature for 18 h, filtered, washed with two 50 ml portions of water, dried, and evaporated to give a dark oil; n.m.r. blank between δ 4.0 and 7.5; i.r. 2110, 1695 cm^{-1}. Purification as previously outlined afforded 1.65 g (55%) of **8***a*. A dark immobile band on the column may have been **8***b* or its decomposition products.

The financial assistance of the National Research Council of Canada and the technical assistance of Mr. D. Hill are gratefully acknowledged.

1. (*a*) A. HASSNER. Accts. Chem. Res. **4**, 9 (1971). (*b*) F. W. FOWLER, A. HASSNER, and L. A. LEVY. J. Am. Chem. Soc. **89**, 2077 (1967).
2. G. L'ABBÉ and A. HASSNER. J. Org. Chem. **36**, 258 (1971).
3. A. HASSNER, G. L'ABBÉ, and M. J. MILLER. J. Am. Chem. Soc. **93**, 981 (1971).
4. H. SCHECHTER, M. J. CULLIS, R. E. DESSEY, Y. OKUZUMI, and A. CHEN. J. Am. Chem. Soc. **84**, 2905 (1962).

Ozonation of Naphthalene with Water as Participating Solvent. Preparation of *o*-Phthalaldehyde

MURRAY G. STURROCK, BETTY J. CRAVY, AND VIRGINIA ALLEN WING
Department of Chemistry, Texas Woman's University, T.W.U. Station, Denton, Texas 76204

Received April 14, 1971

The water in aqueous acetone solutions acts as a participating solvent in the reaction of naphthalene with ozone forming hydroperoxy intermediates which are reduced to *o*-phthalaldehyde by conventional agents. The results are markedly different from those obtained in anhydrous solvents. Yields of product requiring no purification are 63%.

Dans des solutions aqueuses d'acétone, l'eau agit comme solvant de participation dans la réaction de l'ozone avec le naphtalène. Il se forme des hydropéroxy intermédiaires que sont réduits en *o*-phthaladéhyde par les agents conventionnels. Les résultats sont très différents de ceux obtenus dans des solvants anhydres. Les rendements en produit (ne demandant aucune purification) sont de 63%.

Canadian Journal of Chemistry, 49, 3047 (1971)

The profound effect that the presence of water in the solvent can have on the course of the reaction of a polycyclic aromatic hydrocarbon with ozone was first demonstrated some ten years ago (1) when yields of anthraquinone obtained directly from anthracene without the aid of reducing agents were improved from 28% in glacial acetic acid (2) to 73% in aqueous *t*-butanol (1). The anthracene reaction gave no useful isolable intermediate products and the mechanism of the ozonation reaction in aqueous media was studied first with phenanthrene (3) and later with pyrene (4). This is therefore the third in a series of reports devoted to the subject of ozonation in aqueous solvents.

The results of the work with anthracene, phenanthrene, and pyrene suggested that the effect of the presence of water during the ozonation of naphthalene would be to promote the formation of *o*-phthalaldehyde. This interesting but expensive dialdehyde has not been prepared heretofore in reasonable yield by the ozonation of naphthalene followed by conventional sodium iodide in acetic acid reduction of the ozonation products.

The reaction of ozone with naphthalene has been investigated by a number of workers (5–9). After some uncertainty (9), Bailey and co-workers concluded (10) that the explosive ozonation product isolated from the inert solvents used in all these studies was indeed the diozonide of naphthalene as originally reported by Harries (5). This group also made an extensive study of the reaction in anhydrous aliphatic alcohols, particularly anhydrous methanol, and isolated intermediate cyclic alkoxyhydroxyperoxides. They found, however, that the intermediates were completely resistant to reduction by sodium iodide in acetic acid (10). Only *o*-phthalaldehydic acid, or derivatives of it depending on the nature of the alcohol used as solvent and the type of work-up procedure, was recovered. Pappas and co-workers (11, 12) confirmed the surprising resistance of the cyclic hydroxymethoxyperoxide intermediate to reduction by sodium iodide. He was successful in obtaining a 40–50% yield of *o*-phthalaldehyde (as the bis[(2,4-dinitrophenyl)-hydrazone] derivative) by treating the cold methanolic ozonation product with dimethyl sulfide (11) and a 57% yield using triphenylphosphine (12).

The work with phenanthrene in aqueous *t*-butanol (3) had shown that water, like the aliphatic alcohols, acts as a participating solvent in the ozonation reaction and that the analogous cyclic dihydroxyperoxide decomposes quantitatively to biphenaldehyde on heating in aqueous solution. On the other hand, the cyclic methoxyhydroxyperoxide from phenanthrene yielded biphenaldehydic acid (13). The dihydroxyperoxide intermediate had not been isolated from the ozonation of phenanthrene in this earlier work (3) but had been prepared from biphenaldehyde and 30% hydrogen peroxide. Later it was prepared by the ozonation of phenanthrene in aqueous acetone (M. G. Sturrock, unpublished results). A series of equilibria including the open chain hydroxyhydroperoxide had been postulated to explain the results (3).

Considered in the light of the difference in the course of the reactions of ozone with phenanthrene and with anthracene in anhydrous and in aqueous solvents, it seemed probable that *o*-phthalaldehyde would result if the ozonation conditions were such that the formation of the intermediate hydroxyhydroperoxide would be favored, or better, that the formation of the cyclic alkoxyhydroxyperoxide would be precluded. Further support for the belief that *o*-phthalaldehyde could be prepared in this way was to be found in the process which had been patented for the removal of thionaphthene from crude coal tar naphthalene by the selective reaction of the thionaphthene using a deficiency of ozone and aqueous *t*-butanol as solvent (14). *o*-Phthalaldehyde had been detected qualitatively in these ozonation products (15).[1]

Accordingly, naphthalene was treated with two molar equivalents of ozone using aqueous acetone solutions as solvents. After conventional reduction with potassium iodide in acetic acid, removal of the acetone by evaporation, reduction of the liberated iodine with sodium thiosulfate solution, extracted with chloroform, and sublimation of the chloroform residue, pure *o*-phthalaldehyde was recovered. Yields of 63% were obtained consistently by this procedure. The principal product recovered when aqueous methanol was used as solvent was methyl-*o*-phthalaldehydate although *o*-phthalaldehyde could be detected qualitatively (15).[1] Yields of *o*-phthalaldehyde from ozonations made in aqueous *t*-butanol were slightly less than those in aqueous acetone, averaging 58% in a series of several experiments.

The conditions outlined in the Experimental evidently represent the optimum for this reaction in acetone–water solutions. Changes made in the ratio of acetone to water, in the quantity of naphthalene charged and, rather surprisingly, in the temperature of the ozonation step, had no significant effect on the yield. The results of typical experiments are given in Table 1.

It was evident at an early point in this work that the critical operation was the extraction of the *o*-phthalaldehyde from the aqueous solution after the reduction and evaporation of the acetone. Substitution of ethyl acetate or ethyl ether for chloroform made little difference in the

---

[1] *o*-Phthalaldehyde gives an intense blue–black coloration when treated with ammonia followed by acetic acid. The same color is developed when *o*-phthalaldehyde comes into contact with the skin.

TABLE 1. Ozonation of naphthalene in acetone–water mixtures

Naphthalene (g charged)	Ozone (M equiv)	Solvent (ml)		Temperature (°C) ozonation	*o*-Phthalaldehyde (% Yield)
		Acetone	Water		
5.0	2.1	105	45	27	61.6
5.0	2.1	105	45	27	63.9
5.0	2.1	105	45	26	60.1
5.0	2.1	75	75	27	57.5
2.5	2.1	62	22	26	61.5
5.0	2.1	105	45	−20	62.0
2.5	2.1	62	22	−20	59.0

yields obtained on sublimation. Steam distillation of the reduced product prior to extraction markedly reduced the efficiency of extraction probably as the result of increased hydration of the *o*-phthalaldehyde. The possibility of multipoint attack by ozone on the naphthalene molecule was discounted because unreacted naphthalene was not recovered when the amount of ozone absorbed was in the 2.1–2.2 M equiv range. A reddish gummy substance always remained at the end of the sublimation. This is believed to be a polymer of *o*-phthalaldehyde. A positive "Thiele test" (15) was obtained with it by treatment with ammonium hydroxide followed by acidification with acetic acid but the product could not be decomposed to any identifiable material. *o*-Phthalaldehydic acid formation was not a problem since the purity of the sublimed product remained high (m.p. 54–56°; lit. (16) 55.5–56°) regardless of the yield and of the final temperature used in sublimation. Undoubtedly some product was lost in the atmospheric temperature and pressure evaporation of the acetone after the reduction step. When the acetone was removed with a Rinco evaporator, the distillate gave positive "Thiele" tests. In a single experiment performed in acetone–water followed by a non-reductive work-up procedure, *o*-phthalaldehydic acid (m.p. 96–99°) was recovered in 62.5% yield. The literature (10) reports 88% yield of *o*-phthalaldehydic acid (m.p. 99°) from the low temperature ozonation of naphthalene in anhydrous methanol. Although the difference is believed to lie in incomplete extraction, the matter was not further investigated.

Aqueous methanol and aqueous ethanol proved to be unsuitable solvents for the preparation of *o*-phthalaldehyde. After treatment of the ozonation product with potassium iodide and acetic acid, the materials extracted with chloroform were esters of *o*-phthalaldehydic acid. This observation serves to illustrate the tendency of ethyl and methyl alcohols to form cyclic alkoxyhydroxyperoxides. In the case of phenanthrene these alkoxyhydroxyperoxides were found to decompose in a manner which retained the three atoms of oxygen of the original ozone molecule forming acidic products. The analogous hydroxyperoxides yield carbonyl derivatives (1, 3).

The results of this work have again demonstrated that water can act as a participating solvent in the ozonation of aromatic compounds and that its use is advantageous, particularly when aldehydic rather than acidic products are desired. *o*-Phthalaldehyde requiring no further purification is obtained by the ozonation of naphthalene in aqueous acetone solutions in yields which compare favorably with or exceed those reported by any procedure.

Experimental

The equipment and procedures used were those previously described (4). The naphthalene was reagent grade, m.p. 79–80°.[2] It was established that purification to m.p. 80.2° (14) had no discernable effect on the yields of *o*-phthalaldehyde. All other chemicals employed were also of reagent grade.

o-Phthalaldehyde by the Ozonation of Naphthalene

(A) Ozonation in Acetone–Water with Potassium Iodide Reduction

A stream of ozonized oxygen containing 1.73 g/ft^3 of ozone was passed into a solution 5.0 g (0.039 mol) of naphthalene in 105 ml of acetone and 45 ml of water at a rate of 0.010 ft^3/min. Under these conditions 98–99% of the ozone being introduced was absorbed. After 4 h the ozone absorption decreased to about 95% of that being introduced. A total of 4.1 g of ozone was passed into the reaction mixture of which 4.0 g (0.0834 mol) was absorbed. Immediately after completion of the ozonation, the product was treated with excess potassium iodide (13 g) and 5 ml of glacial acetic acid. The iodine released was reduced with 10% aqueous sodium thiosulfate solution and the acetone removed under reduced pressure at room temperature using a Rinco evaporator. The aqueous solution was extracted several times with

---

[2] Melting points were determined with an Electrothermal Melting Point Apparatus, standardized thermometer.

25 ml portions of chloroform. It was then saturated with sodium bicarbonate and again extracted several times with chloroform until the extract gave a negative test for *o*-phthalaldehyde (15). The chloroform was allowed to evaporate by overnight standing in an open beaker under mild magnetic stirrer agitation. The residue remaining, a light red or pinkish solid, was sublimed at a temperature of 45–60° under reduced pressure using ice-water in the cold finger of the sublimation apparatus. The sublimed product (3.33 g) light yellowish well formed crystals of *o*-phthalaldehyde, melted at 55–56°; lit. (16) 55.5–56°. The yield, 63.6% of theory, was typical of runs made in this manner.

Anal.[3] Calcd. for $C_8H_6O_2$: C, 71.65; H, 4.53. Found: C, 71.58; H, 4.50.

The n.m.r. spectrum obtained in $CDCl_3$ showed a singlet at $-0.7\ \tau$ equivalent to two hydrogens and a multiplet from 1.8–2.2 τ equivalent to four hydrogens.[4]

After the sublimations were completed, that is to say when no further material was condensed on raising the temperature of the bath to 80–90°, a small quantity of red glass-like substance remained. The n.m.r. spectra, run on several different samples of the glass dissolved in acetone, invariably showed a singlet at $-0.7\ \tau$ indicative of the aldehyde protons on *o*-phthalaldehyde and peaks at 1.7 τ to 2.7 τ corresponding to aromatic ring hydrogens. It is believed to be a polymeric phthalaldehyde.

(B) Ozonation in t-Butanol–Water with Potassium Iodide Reduction

A solution of 5.0 g of naphthalene in 105 ml of *t*-butanol and 45 ml of water was treated with a stream of ozonized oxygen containing 1.56 g/ft^3 of ozone at a rate of 0.0125 ft^3/min. Under these conditions 99% of the ozone introduced was absorbed. A total of 4.1 g of ozone was passed through the reaction mixture. Upon completion of the ozonation the product was treated in the manner described under section *A*. The yield of *o*-phthalaldehyde (m.p. 54–56°) was 3.05 g (58.3%).

(C) Ozonation in Acetone–Water with Dimethyl Sulfide Reduction

The ozonation was carried out using 5.0 g of naphthalene in a mixture of acetone and water as described under section *A*. Dimethyl sulfide (4 ml) was immediately added and the acetone allowed to evaporate at room temperature under gentle agitation. An additional 6 ml of reducing agent was added over the course of the next 3 h. Tests for active oxygen (potassium iodide) were made periodically until, after 4 h, a negative test was obtained. The solution was allowed to stand overnight to assure complete evaporation of the acetone. It was then extracted several times with chloroform and the extract allowed to evaporate. The yellow oil remaining was sublimed as previously described. The sublimed product gave a heavy "Thiele Test" (15) but was pasty and smelled strongly of dimethyl sulfoxide. An unsuccessful attempt was made to avoid the dimethyl sulfoxide difficulty by steam distillation prior to extraction. It is possible that this problem using dimethyl sulfide in the preparation of *o*-phthalaldehyde was encountered by Pappas *et al.* (12) since yields of this particular aldehyde were reported as the bis[(2,4-dinitrophenyl)hydrazone] derivative.

(D) Ozonation in Aqueous Methanol

A solution of 5.0 g of naphthalene in 105 ml of methanol and 45 ml of water was treated with 4.1 g of ozone as described in section *A*. After removal of the alcohol (Rinco, reduced pressure, bath temperature 34°), a brown oil separated. The aqueous solution was decanted and extracted with chloroform. The oil and the chloroform extract, were combined and the solvent removed by evaporation. The product remaining was crude methyl-*o*-phthalaldehydate. An n.m.r. spectrum of the oil in acetone showed a singlet at −0.7, a multiplet from 1.8 to 2.5, a broad singlet at 2.9, a broad singlet at 4.9, a singlet at 6.0, and several small peaks from 6.3 to 6.8 τ as well as a very small peak at about 9 τ. The peaks can be given the following assignments according to their chemical shifts: −0.7, aromatic aldehyde; 1.8 to 2.5, phenyl hydrogens; 4.9, hydroxyl proton; and 6.0 τ $C_6H_5COOC\mathit{H}_3$. On hydrolysis with sodium hydroxide solution followed by acidification, the oil yielded crude *o*-phthalaldehydic acid.

(E) Ozonation in Aqueous Ethanol

In a similar experiment using aqueous ethanol as solvent, the orange oil recovered was crude ethyl-*o*-phthalaldehydate. An n.m.r. spectrum of the oil in acetone showed a singlet at −0.7, a multiplet from 1.7 to 2.5, a quartet from 5.3 to 5.7 (centered at 5.5), a triplet from 8.5 to 8.7 τ (centered at 8.6), and a small impurity peak due to ethanol. The peaks can be given the following assignments according to their chemical shifts: −0.7, aromatic aldehyde; 1.7 to 2.5, phenyl hydrogens; quartet from 5.3 to 5.7, $C_6H_5COOC\mathit{H}_2CH_3$; and the triplet from 8.5 to 8.7 τ, $C_6H_5COOCH_2C\mathit{H}_3$.

3,6-Dihydroxy-4,5-benzo-1,2-dioxane (the Cyclic Dihydroxyperoxide)

(A) From o-Phthalaldehyde

o-Phthalaldehyde (1 g) was covered with 30% hydrogen peroxide and allowed to stand overnight in a refrigerator. White crystals, 0.39 g, (31 2%) m.p. 108–111° crude product separated. Recrystallization from ethyl acetate and petroleum ether gave 0.20 g of product m.p. 127–128°; lit. (18) 127–128°.

Anal. Calcd. for $C_8H_8O_4$: C, 57.15; H, 4.76. Found: C, 57.06; H, 4.72.

Three attempts were made to determine the active oxygen content of the product using the room temperature procedure (17) which had been used successfully in previous work (3, 4). The results were 26.7, 25.9, and 21.8% respectively, of the theoretical. The procedure of Rieche and Schmitz (18) which involves the use of higher temperatures during the reduction gave only 66.6% of theory.

(B) From the Ozonation of Naphthalene in Acetone–Water

A solution of 5.0 g of naphthalene in 105 ml of acetone and 45 ml of water was treated with 4.1 g of ozone in the manner described for the preparation of *o*-phthalaldehyde, section *A*. Removal of the acetone formed a cloudy solution which could not be induced to yield a crystalline product after standing several hours in an ice bath. The solution was extracted twice with 25 ml portions of ethyl

---

[3] Microanalyses were carried out using a Perkin–Elmer 240 Elemental Analyser.

[4] All n.m.r. spectra were obtained using a Varian A-60A Analytical Nuclear Magnetic Resonance Spectrometer.

acetate. The white crystals which formed as the ethyl acetate evaporated melted 99–150°. Recrystallization from ethyl acetate – petroleum ether (3:2), gave a product m.p. 129.5–131°, not depressed by an authentic sample of the cyclic dihydroxyperoxide m.p. 127–128°. The yield was low, 0.39 g, 6.0%. A quantity of crystals, 1.4 g, meanwhile had separated from the solution which had been extracted. The m.p. 107–115° was narrowed to 99–100° on recrystallization from water. Identification as *o*-phthalaldehydic acid was confirmed by elemental analysis.

Anal. Calcd. for $C_8H_6O_3$: C, 64.0; H, 4.0. Found: C, 64.12; H, 3.89.

o-Phthalaldehydic Acid by Ozonation in Aqueous Acetone, Alkaline Work-up

A solution of 2.5 g of naphthalene in 105 ml of acetone and 45 ml of water was treated with 2.05 g of ozone in the manner previously described. The product was refluxed with 25 ml of 15% sodium hydroxide solution for 30 min, cooled, acidified with hydrochloric acid and extracted five times with 25-ml portions of ethyl ether. The combined extracts were allowed to evaporate by overnight standing. The oil which remained was treated with a few drops of water and placed in the ice-bath. After several hours 1.83 g (62.4%) of *o*-phthalaldehydic acid, m.p. 96–99° separated, no depression with an authentic sample.

The authors are grateful to The Robert A. Welch Foundation, Houston, Texas, for the financial support of this work.

1. M. G. Sturrock, E. L. Cline, and K. R. Robinson. U.S. Pat. 2 898 350. August 4, 1959.
2. P. S. Bailey and J. B. Ashton. J. Org. Chem. **22**, 98 (1957). See also P. S. Bailey, P. Kolsaker, B. Sinha, J. B. Ashton, F. Dobinson, and J. E. Batterbee. J. Org. Chem. **29**, 1400 (1964).
3. M. G. Sturrock, E. L. Cline, and K. R. Robinson. J. Org. Chem. **28**, 2340 (1963).
4. M. G. Sturrock and R. A. Duncan. J. Org. Chem. **33**, 2149 (1968).
5. C. Harries. Ann. **343**, 336, 372 (1905).
6. L. Seekles. Rec. trav. chim. **42**, 706 (1923).
7. J. P. Wibaut, L. W. F. Kampschmidt. Koninkl. Ned. Akad. Wet. Proc. 53, 1109 (1950).
8. L. W. F. Kampschmidt and J. P. Wibaut. Rec. trav. chim. **73**, 431 (1954).
9. P. S. Bailey and F. J. Garcia-Sharp. J. Org. Chem. **22**, 1008 (1957).
10. P. S. Bailey, S. S. Bath, F. Dobinson, F. J. Garcia-Sharp, and C. D. Johnson. J. Org. Chem. **29**, 697 (1964).
11. J. J. Pappas, W. P. Keaveney, E. Gaucher, and M. Berger. Tetrahedron Lett. No. 26, 4273 (1966).
12. J. J. Pappas, W. P. Keaveney, M. Berger, and R. V. Rush. J. Org. Chem. **33**, 787 (1968).
13. P. S. Bailey. J. Am. Chem. Soc. **77**, 3811 (1956).
14. M. G. Sturrock, E. L. Cline, K. R. Robinson, and R. J. Lovin. U.S. Pat. 3 016 401. January 9, 1962.
15. J. Thiele and E. Winter. Ann. **311**, 260 (1900).
16. J. C. Bill and D. S. Tarbell. Org. Synth. **14**, 82 (1954).
17. G. Lohaus. Ann. **583**, 6 (1953) and endorsed by S. Fliszar, D. Gravel, and E. Cavallieri. Can. J. Chem. **44**, 67 (1966).
18. A. Rieche and E. Schmitz. Chem. Ber. **90**, 1082 (1957).

Ouverture normale d'époxydes aromatiques para-substitués par des α-mercapto esters

CASIMIR BERSE ET RONALD COULOMBE[1]

Département de chimie, Université de Montréal, Montréal, Québec

Reçu le 19 février 1971

Les α-mercaptoesters peuvent ouvrir le cycle oxirannique des époxydes aromatiques. Les produits formés résultent en grande majorité d'une ouverture normale du cycle et l'influence du substituant sur le noyau aromatique est de peu d'importance.

The three-membered ring of aromatic epoxides can be opened by α-mercaptoesters. The reaction products arise to a great extent by a normal opening of the ring and the substituent effect of the aromatic epoxide is of little importance.

Canadian Journal of Chemistry, 49, 3051 (1971)

Beaucoup de travaux (1–4) ont été effectués sur l'ouverture des époxydes par des acides aminés et nous avons été amenés à étudier cette réaction d'ouverture par des α-mercaptoesters aliphatiques. Même si le comportement des époxydes a déjà été étudié (5) en présence de thiols légers, aucun travail n'a été effectué avec des mercaptoesters.

Le schéma 1 résume les réactions effectuées dans la pyridine à reflux.

---

[1] Boursier pré-doctoral du CNRC 1969–1971.