[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

Oxidation and Characterization of α,α'-Dichloro-*p*-xylene

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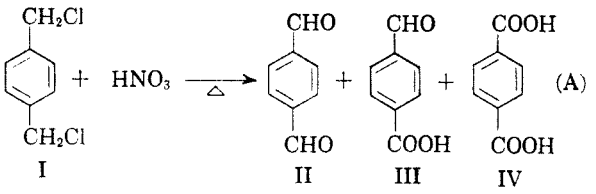
The major products of the oxidation of α,α'-dichloro-*p*-xylene (DCX) with dilute nitric acid at atmospheric pressure, are terephthalaldehyde and terephthalaldehydic acid; only small amounts of terephthalic acid are produced. An attempt to oxidize DCX with an alkaline three per cent hydrogen peroxide solution resulted in hydrolysis to the glycol, α,α'-dihydroxy-*p*-xylene. The characterization of DCX and terephthalaldehyde is described in detail.

This paper deals with some reactions of α,α'-dichloro-*p*-xylene, p-$ClCH_2C_6H_4CH_2Cl$. For convenience, the work is divided into the two categories of oxidation and characterization.

DISCUSSION

The oxidation of DCX. The oxidation of *p*-xylene to terepthahlic acid can be accomplished by the use of dilute nitric acid at both high temperatures and pressures.[1] The hydrocarbon, however, is resistant to oxidative attack by the same reagent at the milder experimental conditions of reflux temperature and atmospheric pressure. The conversion of the two methyl groups of the *p*-xylene into methylene groups, *e.g.*, by a substitution reaction, yields a compound with a bisbenzyl structure; the latter should then be more susceptible to oxidation at the moderate experimental conditions. In addition, if the substitution is by chlorine atoms as in DCX, then the oxidation will be further facilitated because the alcohols derived by hydrolysis should be oxidized with ease.

This is found to be the case. At atmospheric pressure and at the reflux temperature, DCX (I) is oxidized by dilute nitric acid to a mixture of terephthalaldehyde (II), terephthalaldehydic acid (III), and terephthalic acid (IV).[2]



The absence of the glycol, p-$HOCH_2C_6H_4CH_2OH$, as a reaction product indicates that a hydroxymethyl group is more readily oxidized by nitric acid than is a corresponding aldehydic group. This substantiates the previous report that the oxidation of α,α'-dihydroxy-*p*-xylene with concentrated nitric acid gives an 80 per cent yield of terephthalaldehyde.[3]

The results of the dilute nitric acid oxidation of DCX are summarized in Table I. They are consistent with the expectation that the product representing the lowest state of oxidation, terephthalaldehyde, is produced in greatest amount at the lower concentrations of oxidizing agent. The inverse is true for the product of the highest state of oxidation, terephthalic acid.[4]

It can be seen from Table I that although the short time oxidation of DCX with dilute nitric acid can lead to satisfactory yields of terephthalaldehyde, this single-stage oxidation process produces terephthalic acid in poor yield.

The characterization and reactions of DCX. The DCX used in the instant study was prepared by the interaction of sulfuryl chloride with *p*-xylene, in the presence of benzoyl peroxide.[5] The dihalide was characterized by the preparation of derivatives which are analogous to those obtained from benzyl chloride. As compared to the latter compound,

(1) (a) E. B. Bengtsson, *Acta Chem. Scand.*, **7**, 774 (1953); (*b*) E. B. Bengtsson, *Iva.*, **25**, 121 (1954); (*c*) I. N. Nazarov, N. V. Kuznetsov, and A. V. Semenovskii, *Doklady Akad. Nauk*, 99, 1003 (1954).

(2) E. Grimaux, *Compt. rend.*, **83**, 825 (1876) observed that terephthalaldehyde is produced by refluxing DCX with a lead nitrate solution. No qualitative data concerning the isolation of other products, or quantitative data with regard to the aldehyde, are mentioned. No further oxidative work with DCX is cited until 1954 when M. Kulka and R. H. F. Manske were issued U. S. Patent **2,666,786**, 19 January 1954, for its oxidation with concentrated nitric acid at super-atmospheric pressures. For a review and study of the oxidation of the dibromo analog, DBrX, one should consult the paper by R. Wegscheider and H. Suida, *Monatsh.*, **33**, 1006 (1912).

(3) B. Helferich, R. Streeck, and E. Gunther, *J. prakt. Chem.*, **151**, 251 (1938).

(4) After this work was completed, several recently published data concerning the nitric acid oxidation of DCX were discovered. J. Manka, J. Tomaszewski, and M. Wajnryb, *Zeszyty Naukowe Politechniki Lodzkiej*, No. 9, 31 (1955) concluded that the oxidation, in the presence of mercuric chloride as a catalyst, yielded a mixture of terephthalic acid and other oxidation products; the latter were not identified. The yields of terephthalic acid in this single-stage oxidation were poor and they finally evolved the following three-stage process for the oxidation of DCX to moderately good yields of terephthalic acid: (i) the hydrolysis of DCX to the glycol and other products, (ii) the oxidation of the hydrolysate with nitric acid, (iii) further oxidation of the product of (ii) with a fresh portion of nitric acid.

Independently of this paper, and the work of Manka, *et al.*, two patents were issued to Vereinigte-Glanzstoff-Fabriken (British Patent **724,921**, 23 February 1955 and U. S. Patent **2,740,811**, 3 April 1956) which also show that the single-stage oxidation of DCX with dilute nitric acid does not represent a feasible synthesis of terephthalic acid.

(5) M. Kulka, *Can. J. Research*, **23B**, 106 (1945).

TABLE I

OXIDATION OF DCX WITH DILUTE NITRIC ACID

Nitric Acid Conc., %	Temp.	Time, Hr.	Percentage Yield of		
			p-OHCC$_6$H$_4$CHO	*p*-HOOCC$_6$H$_4$CHO	*p*-HOOCC$_6$H$_4$COOH
10	106	7	56	23	15
15[a]	106	7	36	35	16
19	104	6	70[b]	23	5
40	107	4.2	3	63	29
50	106	8	2	43	49

[a] Used five mole per cent V_2O_5 as a catalyst. [b] The higher yield of terephthalaldehyde as compared to the 10 or 15 per cent nitric acid reaction is due to the shorter reaction time.

however, DCX exhibited a decreased reactivity towards displacement reactions. The use of more drastic experimental conditions (diethylene glycol monobutyl ether as solvent, and potassium iodide to effect halogen exchange) was necessary to prepare certain derivatives.

The reaction of sodium nitrite with DCX in methanolic solution was conducted in an attempt to prepare α,α'-dinitro-*p*-xylene. There is no recorded synthesis in the literature for this dinitro compound. It is of interest for it would lead to a novel synthesis of terephthalic acid.

$$p\text{-}O_2NCH_2C_6H_4CH_2NO_2 + 2H_2O \xrightarrow{H^+} p\text{-}HOOCC_6H_4COOH + 2NH_2OH$$

The infrared spectrum indicates that the small amount of reaction product isolated by distillation from a Hickmann micro still is *p*-chloromethylbenzyl alcohol with some *p*-chloromethylbenzaldehyde as an impurity. The fact that only one chloromethyl group of DCX was attacked indicates the slow reaction of DCX with sodium nitrite in methanol. Kornblum, *et al.*, has since reported that nitro compounds may be prepared from sodium nitrite and alkyl bromides or iodides, in dimethyl formamide as a solvent.[6] In corroboration of the experiment described above they also state that chlorides react too slowly to be satisfactorily employed in this reaction.

The treatment of DCX with sodium nitrate in aqueous solution yields *p*-hydroxymethylbenzaldehyde as a major reaction product. The DCX is apparently first hydrolyzed to the diol; one hydroxymethyl group is then oxidized by the nitrate salt to that of an aldehyde.

EXPERIMENTAL

General. All reagents are commercial chemicals which were used without further purification, unless otherwise noted. The 2,4-dinitrophenylhydrazone derivatives were prepared by a variation of Brady's method;[7] the reagent is prepared by dissolving 5 g. 2,4-dinitrophenylhydrazine in a solution of 37.5 ml. H_2SO_4 in 375 ml. methanol. The filtered reagent, when stored in a brown bottle, is stable for years. The derivative usually precipitates when the carbonyl compound is added at room temperature; slight warming is sometimes necessary. The preparation of other derivatives in the characterization of DCX and its oxidation products were carried out in standard manners.[8] All melting points are corrected unless otherwise noted.

Preparation of DCX. The dichloride was prepared by Kulka's method of the interaction of *p*-xylene and sulfuryl chloride in the presence of benzoyl peroxide;[5] this avoids impurities introduced by either multiple substitution (direct chlorination process) or the production of isomers (chloromethylation procedure). Kulka ran the reaction in sunlight for four hours using a molar ratio of xylene:chloride:peroxide of 1:2.5:0.006, and obtained a 58% yield of DCX. In diffuse room light for two hours and a respective molar ratio of 1:2.0:0.011, the instant experiment gave a 28% yield of DCX (white platelets from ethanol, m.p. 99–99.5°) and a 67% yield of *p*-methylbenzyl chloride (sweet-smelling liquid, b.p. 95–97°/20; lit. b.p. 92–94°/20[9]). Both materials are highly lachrymatory and should be manipulated in a hood.

Oxidation of DCX. All oxidations with dilute nitric acid were conducted in the following manner:

A suspension of DCX (3.5 g., 0.02 mole), in the appropriate concentration of nitric acid (molar ratio of HNO_3/DCX = 10) is refluxed for several hours at 106–108°. The solid DCX forms oily globules, at the reflux temperature, which gradually disappear as the hydrolysis and oxidation reactions proceed. Copious fumes of NO_2 are evolved and within two to three hours of reflux, a solid appears. On cooling to room temperature the reaction mixture deposits a mass of colorless crystals. The following scheme to separate the products (Fig. 1) was evolved after numerous tedious and unsuccessful separations were attempted by fractional crystallizations and sublimations, and by chromatographic techniques.

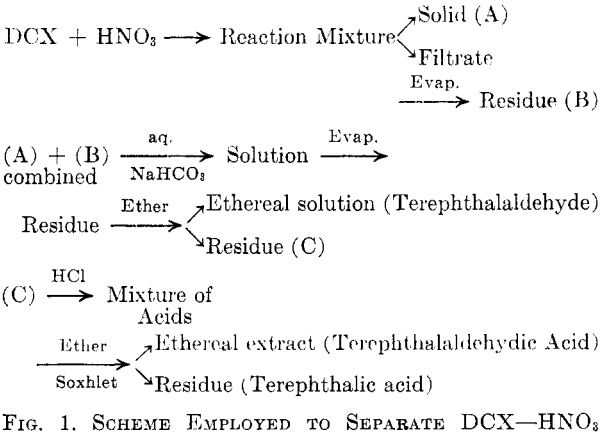


FIG. 1. SCHEME EMPLOYED TO SEPARATE DCX—HNO_3 REACTION PRODUCTS.

(6) N. Kornblum, H. O. Larson, D. D. Mooberry, R. K. Blackwood, E. P. Oliveto and G. E. Graham, *Chem. & Ind. (London)*, 443 (1955).

(7) O. L. Brady, *J. Chem. Soc.*, 756 (1931).

(8) R. L. Shriner, R. C. Fuson, D. Y. Curtin, *The Systematic Identification of Organic Compounds*, 4th Ed., John Wiley & Sons, Inc., New York (1956).

(9) H. Stephen, W. F. Short, G. Gladding, *J. Chem. Soc.*, **117**, 520 (1920).

TABLE II

ISOLATION AND IDENTIFICATION OF DCX-DILUTE HNO_3 PRODUCTS

Product or Derivative	Formula	M.P., °C.	% C		% H		Principal Infrared Bands (Cm.$^{-1}$)	Comments
			Calcd.	Obs.	Calcd.	Obs.		
Terephthalaldehyde	$C_8H_6O_2$	115–116	71.6	71.7	4.5	4.7	C=O at 1694 *p*-Subst. at 1198	Small white platelets. Positive Tollens' test
Terephthalaldehyde oxime	$C_8H_8N_2O_2$	211.5–212[a]	58.5	58.6	4.9	5.1	Broad OH at 3230 Weak C=N at 1652	Extremely water soluble colorless crystals
Terephthalal Dianiline	$C_{20}H_{16}N_2$	164–165	84.5	84.4	5.7	5.6	C=N at 1620 N=C—ArC=N at 1590[b]	% N calcd. 9.9; % N obsd. 10.1. Small yellow needles from ethanol
Terephthalal Di-*p*-toluidine	$C_{22}H_{20}O_2$	190–192	84.6	84.8	6.5	6.2	—	Yellow solid. Sublimed after recryst. from ethanol
Terephthalal Di-acetophenone	$C_{24}H_{18}O_2$	197–197.5[c]	85.2	84.7	5.4	5.4	—	Yellow tablets from ethanol
Terephthalaldehyde bis-*p*-nitrophenyl hydrazone	$C_{20}H_{16}N_6O_4$	294–295[d] (dec.)	59.4	59.4	4.0	3.8	—	Red crystals from ethanol
Terephthalaldehydic acid	$C_8H_6O_3$	Softens at 250, not molten at 320[e]	64.0	64.2	4.0	3.8	Broad OH in 3000 region C=O at 1680, 1698, 1728 COO— at 1616 C –O at 1248, 1292	Colorless, microcrystalline powder. Neut. equiv. calcd. 150; neut. equiv. obsd. 149
Terephthalaldehydic acid 2,4-dinitrophenylhydrazone	$C_{14}H_{10}N_4O_6$	326–327 (dec.) (uncorr.)[f]	50.9	50.5	3.1	2.6	—	Extremely insoluble orange solid. Analytical sample prepared by hot ethanol wash in Soxhlet extractor. % N calcd. 16.9; % N obsd. 16.4
Terephthalic acid	$C_8H_6O_4$	Not molten at 320	—	—	—	—	Broad OH in 3000 region —C=O at 1700 —COO at 1620 —C—O at 1285, 1292	Non-sublimeable solid. Purified by solution is base and reprecipitation with acid. Neut. equiv. calcd. 83.1; neut. equiv. obsd. 82.8. Prepared dimethyl terephthalate derivative, m.p. 140–141°

[a] K. W. Rosenmund, F. Zetzsche, and C. Flutsch, *Ber.*, **54**, 2888 (1921) list the m.p. 198°; B. Westenberger, *Ber.*, **16**, 2995 (1883) has m.p. 200°. [b] An authentic sample of benzalaniline (m.p. 50–51°) has the usual doublet at 1598 and 1587 cm.$^{-1}$ denoting Ar-conjugation. The replacement of these two bands by the singlet in the terephthalaldehyde derivative may be due to the symmetry of the *para*-conjugated groups. [c] H. V. Lendenfelt, *Monatsh.*, **27**, 969 (1906) lists m.p. 200–201°. [d] K. W. Rosenmund, *et al.* (*loc. cit.*) report m.p. 281° with sintering at 272°. [e] This behavior of the aldehyde-acid during a melting point determination had been observed previously by Wegscheider and Suida (*loc. cit.*). The use of a CO_2-filled, or an evacuated capillary tube leads to m.p. 248–250° [W. Davies, W. H. Perkin, and H. Clayton, *J. Chem. Soc.*, **121**, 2214 (1922) and N. V. Sidgwick and H. Clayton, *J. Chem. Soc.*, 2264 (1922)]. [f] J. B. Bowen and E. M. Wilkinson, *J. Chem. Soc.*, 750 (1950) observed m.p. 319.5–320.5° (uncorr.); J. W. Eustance, private communication recorded m.p. 322° (uncorr.).

TABLE III

CHARACTERIZATION AND REACTIONS OF DCX

Reagents	Product	Formula	M.P., °C.	% C		% H		% N		Comments
				Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	
Sodium benzoate, KI (butyl carbitol–water)	α,α′-*p*-xylenediol dibenzoate[a]	$C_{22}H_{18}O_4$	87–88.5	76.3	76.1	5.2	4.9	—	—	Refluxed 2 hr. Small white needles from ethanol. Similar reaction with sodium *p*-nitrobenzoate, in absence of KI, failed to yield derivative
Sodium phenoxide (butyl carbitol–water)	α,α′-diphenoxy-*p*-xylene	$C_{20}H_{18}O_2$	142[b]	82.7	83.2	6.3	6.2	—	—	Refluxed 100 min. White needles from ethanol
Thiourea, picric acid (ethanol)	α,α′-di-*S*-isothiuronium-*p*-xylene dipicrate	$C_{22}H_{20}N_{10}O_{14}S_2$	251–252 (dec.)	—	—	—	—	19.6	19.3	Refluxed 1.5 hr. Bright yellow needles from a water-ethanol-acetone mixture
Sodium *o*-benzoyl sulfimide (saccharin), KI (butyl carbitol–water)	*N*,*N*′-*p*-xylene disaccharin	$C_{22}H_{16}N_2O_6S_2$	315 (uncorr.)	—	—	—	—	6.0	5.8	Refluxed one hr. Twice recrystallized from dimethyl formamide–ethanol mixture. Attempts to prepare diphthalimido derivative only gave phthalimide
Sodium nitrite (methanol)	*p*-Chloromethyl benzyl alcohol (*p*-chloromethyl benzaldehyde)	C_8H_9ClO	B.p. 100–130/0.5	61.3	61.1	5.8	5.8	—	—	Refluxed 3 hr. Small amount of product as brown oil from a Hickman micro still. Positive Beilstein test. Immediate ppt. with silver nitrate. Broad OH at 3390 CH_2 at 2920, 2860. Formyl H at 2735. Aryl-CHO at 1700. CH_2OH at 1270, 1042. No NO_2 group absorption
Sodium nitrate (methanol)	*p*-Hydroxymethyl benzaldehyde (as *p*-nitrophenyl hydrazone)	$C_{14}H_{13}N_3O_3$	189–191	—	—	—	—	15.5	15.4	Small amount of product isolated as yellow oil
Hydrogen peroxide (NaOH, water)	(*i*) Terephthalic acid as dimethyl ester	$C_{10}H_{10}O_4$	141–142	—	—	—	—	—	—	Refluxed 12 hr. Molar ratio of NaOH:-H_2O_2:DCX = 5:4:1
	(*ii*) α,α′-dihydroxy-*p*-xylene	$C_8H_{10}O_2$	118–119[c]	69.5	69.2	7.3	7.6	—	—	Broad OH at 3280. CH_2OH at 1290, 1025[d]

[a] The monobenzoate (m.p. 73–74°) was prepared by E. Grimaux, *Compt. rend.*, **70,** 1363 (1870) by heating an alcoholic solution of DCX and sodium benzoate for 48 hr. at 100°. [b] The only previous mention is by J. v. Braun and H. Reich, *Ann.*, **445,** 225 (1925) who record m.p. 142°. They indicate that they investigated the reaction of the ether with hydrochloric acid and that it had not been prepared previously. No preparative or analytical data are presented. [c] I. Wender, H. Greenfield, S. Metlin, and M. Orchin, *J. Am. Chem. Soc.*, **74,** 4079 (1952) report m.p. 118–119.4°. [d] The infrared spectrum is identical with that of the glycol prepared by the lithium aluminum hydride reduction of dimethyl terephthalate (R. E. Burnett and J. R. Ladd, personal communication).

After this separation scheme was adopted, a somewhat similar plan was found to have been used by Low;[10] he had used chloroform instead of ether in the Soxhlet extractor. The latter was found to be a more selective solvent in this step. The terephthalaldehyde and terephthalaldehydic acid were then further purified by microsublimation at reduced pressure. Because of the aqueous insolubility of the acids produced, neutralization equivalents were found to be valid only if the acids were first dissolved in warm, standard alkali.

A detailed composite of the results of the isolation and identification of the DCX–HNO_3 reaction products is presented in Table II.

(10) W. Low, *Ann.*, **231**, 361 (1885).

Characterization and reactions of DCX. Table III summarizes the various reactions which were investigated with DCX. The most satisfactory derivative is α,α'-diphenoxy-*p*-xylene, p-$C_6H_5OCH_2C_6H_4CH_2OC_6H_5$; it is easily prepared and purified, and has a convenient melting point range.

Acknowledgment. I wish to thank the following Research Laboratory personnel for their invaluable assistance: Mr. Carl Hirt and Mrs. Florence Crouse for their aid in the interpretation and determination of infrared spectra, and Mrs. Joyce Northrup and Miss Beatrice Fey for their combustion analyses.

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Oxidation of 3-Phenoxymesitol

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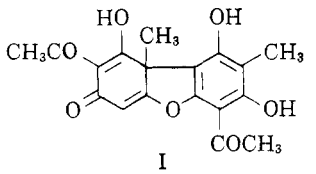
The synthesis of 3-phenoxymesitol (V) and the products of its alkaline ferricyanide oxidation are described.

The mold metabolite, usnic acid (I)[1,2] as well as the *p*-cresol oxidation product known as Pummerer's ketone (II)[2] are formed in one-electron



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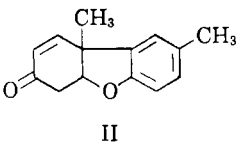
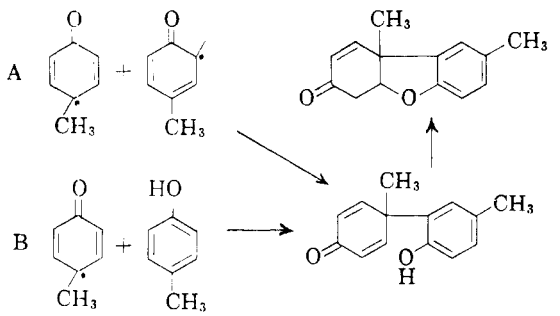
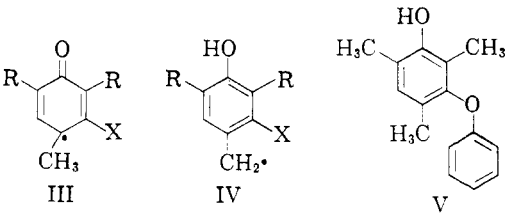


II

oxidation of methylphloracetophenone or *p*-cresol, respectively, by the pairing of radicals (A) or the substitution of one radical into a neutral phenol molecule followed by further oxidation (B).



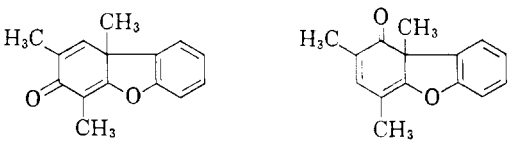
In the free radical oxidation of 2,6-dialkyl-4-methylphenols the nature of the products suggests the transient existence of radicals IIIa and IVa.[3] If in the one-electron oxidation of 3-phenoxymesitol (V) there occurred an internal condensation



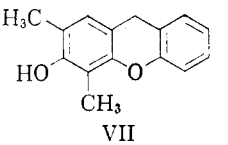
III IV V

a, R = R = alkyl; X = H
b, R = R = CH_3; X = $-OC_6H_5$

of the radicals IIIb and IVb as in reaction B there would be formed analogs of I (*i.e.*, VI) or the dibenzopyran VII.



VI



VII

The purpose of this study has been to ascertain whether the monomolecular ring closure of IIIb and or IVb could compete with the bimolecular dimerization and hydroxylation reactions which generally follow the formation of IIIa and IVa.

The synthesis of V was accomplished in the following manner. Bromonitromesitylene (IX), obtained by nitration of bromomesitylene,[4] was converted to nitrophenoxymesitylene by refluxing with sodium phenoxide and copper bronze in

(1) D. H. R. Barton, A. M. Deflorin, and O. E. Edwards, *J. Chem. Soc.*, 530 (1956).

(2) V. Arkley, F. M. Dean, A. Robertson, and P. Sidisunthorn, *J. Chem. Soc.*, 2322 (1956).

(3) For discussion and general references see H. E. Hey and W. A. Waters, *J. Chem. Soc.*, 2754 (1955).

(4) L. I. Smith, *Org. Syntheses*, **Coll. Vol. II** 95 (1943).