

action with aqueous sodium thiosulfate, nor did it absorb hydrogen chloride from ether solution.

Treatment of I with aqueous acid or base causes rapid hydrolysis to glycolaldehyde and acetic acid. Acetoxyacetaldehyde itself is known to hydrolyze readily in water.⁴ The hydrolysis of I also appears to occur slowly in the absence of acid or base. Thus, a freshly prepared aqueous solution of I could be titrated slowly with 0.1 N sodium hydroxide, while a similar solution aged twenty-four hours could be titrated rapidly. The equivalent weight by titration was 105 (calcd. 102). These reactions indicate that the compound could be either I or acetoxyacetaldehyde. A comparison of their infrared and ultraviolet spectra as well as their refractive indices serves to distinguish between the two compounds.

The infrared spectrum of I contained bands at 3.35, 5.7, 6.8 (w), 7.0 (w), 7.35, 7.82, 8.2, 8.78 (w), 9.0, 9.25 (w), 9.55 (w), 9.9, 10.2, 10.4 (w), 10.75 (w), 11.25, 11.87, and 12.8 μ . The vinyl double bond absorption of vinyl acetate at 6.1 and 10.5 μ had disappeared. The strong peak at 9.0 μ was new. The acetate carbonyl absorption at 5.7 μ and the peak at 8.2 μ were present in both I and vinyl acetate.

The infrared spectrum of acetoxyacetaldehyde contained bands at 2.90 (w), 3.45 (w), 3.55 (w), 3.70 (w), 5.72–5.8 (broad), 7.10 (w), 7.3, 8.2, 8.7 (w), 9.2 (w), 9.50, 10.0 (w), 10.4 (w), 11.3 (w), 11.8 (w), and 12.8 μ (w). The peaks at 3.55 and 3.70 μ are assigned to the aldehyde C—H absorption. The peak for carbonyl CO absorption at 5.7–5.8 μ did not appear to be split as determined on a Perkin-Elmer Infracord.

The ultraviolet spectrum of acetoxyacetaldehyde has a peak at 287 m μ , ϵ (CCl₄) 9.3. At the same wave length, for I, ϵ 0.9.

Experimental

Vinyl Acetate Epoxide (I).—To a filtered solution of 24 g. of perbenzoic acid⁵ in 400 ml. of chloroform was added 15 ml. of vinyl acetate. The mixture was stored at 5° for 6 days. The solution was decanted from the precipitate of benzoic acid and then extracted with 40 ml. of a saturated aqueous solution of potassium bicarbonate. The chloroform layer was dried over anhydrous sodium sulfate and the solvent stripped off under vacuum at 0° in a spinning band still. The residual liquid was then distilled in the spinning band to give 4 g. (25%) of colorless liquid distilling at 35–40°/5 mm., 140°/760 mm., n_{25}^D 1.4071, d_{25}^{25} 1.13 g./ml. (NOTE: the compound should be handled with care until its explosive properties have been determined.)

Anal. Calcd. for C₄H₆O₃: C, 47.06; H, 5.92; O, 47.02. Found: C, 46.62, 46.62; H, 5.84, 5.97; O, 46.70, 47.15.

Vapor phase chromatography (silicone grease on Celite) indicated that the sample contained 99% I and 1% acetic acid. For comparison, the b.p. of acetoxyacetaldehyde is reported as 108–112°/760 mm.² and 90°/50 mm.³

(4) C. D. Hurd and E. M. Filachione, *J. Am. Chem. Soc.*, **61**, 1156 (1939).

(5) G. Brown, "Organic Syntheses," Coll. Vol. I, Wiley, New York, N. Y., 1941, p. 431.

The phenylhydrazone of acetoxyacetaldehyde was prepared by treating I with phenylhydrazine acetate according to the standard procedure.⁶ Its melting point was 126° (lit., 128°²).

The *p*-nitrophenylhydrazone of acetoxyacetaldehyde, prepared from I, melted at 300°.

Anal. Calcd. for C₁₀H₁₁N₃O₄: C, 50.65; H, 4.64. Found: C, 51.11; H, 4.73.

Acetoxyacetaldehyde.—To 38.0 g. of 1,2-diacetoxy-1-ethoxyethane⁷ was added 3.6 g. of water and one drop of concentrated hydrochloric acid. The water was immiscible. The mixture was stirred vigorously at room temperature for 15 hr. At the end of this period, a homogeneous solution was obtained and distilled through a 15-in. spinning band column at 50 mm. The first distillate, 38–45°, was a mixture of acetic acid and ethyl acetate (approx. 11.3 g.). A second fraction which distilled at 75° was the acetoxyacetaldehyde, n_{25}^D 1.4220, d_{25}^{25} 1.21 g./ml. (yield, approx. 5.2 g.). The material is hygroscopic.

Anal. Calcd. for C₄H₆O₃: C, 47.06; H, 5.92; O, 47.02. Found: C, 46.80, 46.64; H, 6.25, 6.10; O, 46.90, 47.03.

The acetoxyacetaldehyde on being shaken with an aqueous solution of semicarbazide hydrochloride formed a semicarbazone which was recrystallized from water to give white crystals, m.p. 170–172° (lit. 170°).⁷

Anal. Calcd. for C₅H₈N₂O₃: C, 37.8; H, 5.69; N, 26.4. Found: C, 37.90; H, 5.70; N, 26.14.

(6) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, 1956, p. 131.

(7) Criegee, "Neuere Methoden Preparativen Organische Chemie," Vol. II, 266.

Tetrachloro-*o*-benzoquinone by Direct Oxidation of Pentachlorophenol

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It is generally accepted that *o*-benzoquinones are formed only if there are two *ortho* substituents attached to the benzene ring, such as in catechol and *o*-aminophenols.^{1,2} Reed³ recently oxidized pentachlorophenol with nitric acid in trifluoroacetic acid and trifluoroacetic anhydride at –20° and obtained 2,3,4,5,6-pentachloro-4-pentachlorophenoxy-2,5-cyclohexadienone in 64% yield. Baral⁴ reported oxidation of pentachlorophenol with fuming nitric acid under two experimental conditions, the only isolated product being chloranil in 16.6 and 40% yield.

We found⁵ that fuming nitric acid, unlike the system used by Reed,³ did not react with penta-

(1) J. Cason, *Org. Reactions*, IV, 313 (1948).

(2) Z. E. Jolles in E. H. Rodd, Ed., "Chemistry of Carbon Compounds," Vol. IIIB, Elsevier Publishing Co., New York, 1956, p. 689.

(3) R. Reed, Jr., *J. Am. Chem. Soc.*, **80**, 219 (1958).

(4) M. E. Baral, *Bull. soc. chim. France*, [3] **27**, 2710 (1902).

(5) While this manuscript was in preparation, A. L. Rocklin disclosed the preparation of tetrachloro-*o*-benzoquinone by nitric acid oxidation of pentachlorophenol, U.S. Patent 2,920,082 (1960).

chlorophenol at very low temperatures (below -20°) at an appreciable rate, but at higher temperatures the reaction was instantaneous. When fuming nitric acid was added dropwise to pentachlorophenol which was dispersed in a refluxing hydrocarbon mixture (boiling around 0°), the only product was 2,3,4,5,6-pentachloro-4-pentachlorophenoxy-2,5-cyclohexadienone, isolated in good yield. When fuming nitric acid was added dropwise to pentachlorophenol dispersed in refluxing pentane, the product was mainly tetrachloro-*o*-benzoquinone (67%) together with a small amount of chloranil. Under similar conditions but using boiling hexane, the product was also mainly tetrachloro-*o*-benzoquinone (57%). Again a little chloranil was found.

Possibly the initial yield of tetrachloro-*o*-benzoquinone in the reaction at the higher temperature was much higher because this quinone was unstable in fuming nitric acid, especially at this high temperature.^{6,7} Since 2,3,4,5,6-pentachloro-4-pentachlorophenoxy-2,5-cyclohexadienone was also unstable under the reaction conditions, Reed could oxidize it with nitric acid at 0° to an 80% yield of chloranil.⁸ It was found in this laboratory that oxidation of 2,3,4,5,6-pentachloro-4-pentachlorophenoxy-2,5-cyclohexadienone with fuming nitric acid at conditions more resembling those under which tetrachloro-*o*-benzoquinone was obtained, afforded 59% of chloranil, and this may explain why no detectable amount of the cyclohexadienone was found in the above drastic oxidation of pentachlorophenol.

The above experimental results indicated that at 0° fuming nitric acid would oxidize pentachlorophenol mainly to substituted cyclohexadienone, whereas at higher temperatures (30 – 60°) the reaction product was mainly tetrachloro-*o*-benzoquinone and a small amount of chloranil. Since the *ortho*-quinone is not formed by the further reaction of the cyclohexadienone, the oxidation must take different courses at different temperatures. The chloranil may arise either from the further oxidation of the cyclohexadienone or from the direct oxidation of pentachlorophenol, or by both courses.

Experimental⁸

Pentachlorophenol.—To a three-necked flask equipped with an efficient stirrer, refluxing condenser, and thermometer there were added 4.0 moles of water, 4.20 moles of sodium hydroxide, and 1 l. of ethylene glycol. To the above solution at 130 – 140° solid hexachlorobenzene (2.00 moles) was added slowly in two hours. After the hexachlorobenzene had been added, the reaction mixture was kept at 140° for 2 hr., at which time all solid was dissolved. The product was then poured into 3 l. of water and the mixture was filtered through a filtering aid. The filtrate was then neutralized

with concentrated hydrochloric acid and the solid formed was collected by filtration. Two recrystallizations from xylene gave 498 g. (93.5%) of a product, m.p. 187.5 – 190° . Reported⁹ m.p., 190 – 191° . No melting depression was observed when mixed with an authentic sample.

2,3,4,5,6-Pentachloro-4-pentachlorophenoxy-2,5-cyclohexadienone.—The reaction has been repeated twice with similar results. To a 500-ml. three-necked flask equipped with a stirrer, a condenser cooled by a solid carbon dioxide-acetone mixture, a thermometer, and a gas inlet tube, there was added 20 g. of pentachlorophenol (0.075 mole, m.p. 189 – 190°) and 60 ml. of ligroin, b.p. 35 – 57.5° . A certain amount of propane was introduced from the gas inlet tube so that the highly agitated mixture boiled at 0° . The gas tube was removed and a dropping funnel was attached. Fuming nitric acid (40 ml., d 1.50) was added dropwise and the reaction mixture changed its color to deep red. After the mixture had been stirred for 40 min., 20 ml. of glacial acetic acid was added to facilitate separation of products. The mixture was stirred for another 20 min. and was then filtered through a coarse sintered-glass funnel. The reddish yellow filter cake was washed with 40 ml. of glacial acetic acid and was sucked to dryness, m.p. 135 – 136° , 11.5 g.

An excess of ice cubes was added to the filtrate causing the temperature to drop below -10° . After 25 min., the solid which formed in the freezing mixture was filtered again; yield, 4.2 g., m.p. 156 – 157° , total yield: 15.7 g. (79.2%). Both products gave very similar infrared spectra. They were mixed to obtain product m.p. 130 – 146° . This product was recrystallized from benzene to give a yield of 12.0 g., m.p. 173 – 174° and gave a correct analysis for the cyclohexadienone (reported³ m.p. 177 – 178°). However there were some differences in the infrared spectra from that reported.³ These bands were found in Nujol mull, strong: 5.95, 6.35, 7.45, 9.02, 9.22, 9.98, 11.55, 12.62, 13.55, 13.66, 14.43 μ ; medium: 7.92, 8.81, 11.72, 12.90, 14.12 μ ; weak but sharp bands: 6.22 and 7.73 μ . Reported³: 5.90, 6.35, 9.00, 11.56, 11.74, 12.65, 12.95, 13.74, and 14.44 μ .

Tetrachloro-*o*-benzoquinone.—To a 3-l. three-necked flask equipped with a glass stirrer, a condenser cooled by a mixture of solid carbon dioxide and acetone, a thermometer, and a dropping funnel there were added 400 g. of pentachlorophenol (1.50 moles), 450 ml. of ligroin (b.p. 32 – 57°), and 0.5 g. of anhydrous ferric chloride. The mixture boiled at 32° . To this refluxing mixture fuming nitric acid (300 ml.) was added in 20 min. because of the evolution of gaseous by-products, the boiling temperature dropped to 19° . This mixture was further stirred at the refluxing temperature for 10 min. Propane gas was introduced into the reaction mixture through a gas inlet tube and the temperature of the mixture dropped to -20° . Water was added and the temperature went up to -15° . The product was filtered through a coarse sintered-glass funnel. The deep red filter cake obtained, wt. 350 g., m.p. 108 – 110° , was 95% yield of a crude mixture of chloranil and tetrachloro-*o*-benzoquinone.

The filter cake was extracted with 500 ml. of ether until the reddish color was removed. The residue was 56 g. (17.2%) of pure chloranil, m.p. 292° . Reported m.p.¹⁰ 291 – 293° . No melting point depression was observed when mixed with an authentic sample.

From the filtrate there was isolated tetrachloro-*o*-benzoquinone, 199 g. of m.p. 122 – 127 , whose melting point was not improved by recrystallization from ether solution, and 47 g., m.p. 93 – 101° . Recrystallized from ether, the latter gave product m.p. 121 – 126° , wt., 40 g.; total yield, 246 g. (66.7%). The melting point reported¹¹ was 130° . In spite of the low melting point, the product of m.p. 122 – 127° gave the correct analysis for the benzoquinone.

(6) T. Zincke, *Ann.*, **435**, 145 (1924).

(7) C. L. Jackson and P. W. Carleton, *Am. Chem. J.*, **39**, 493 (1908).

(8) Melting points are uncorrected. Analysis by Dr. H. W. Galbraith, Knoxville, Tennessee.

(9) G. J. Tiessens, *Rec. trav. chim.*, **50**, 112 (1931).

(10) E. Koenigs and H. Greiner, *Ber.*, **64**, 1047 (1931).

(11) R. L. Datta and J. C. Rbounik, *J. Am. Chem. Soc.*, **43**, 313 (1921).

Anal. Calcd. for $C_6Cl_4O_2$: C, 29.1; Cl, 57.3. Found: C, 28.93; Cl, 57.50.

Under the same reaction conditions as above, except that refluxing hexane was used as solvent (b.p. 68°), the reaction of fuming nitric acid with the phenol was violently fast, and the product was worked up right after the addition. By filtering the reaction product through a sintered-glass funnel, from 20 g. of pentachlorophenol used, there was isolated 2.8 g. (15.2%) of chloranil, m.p. 280–290°. From the filtrate which was treated with ice water, there was isolated 10.5 g. of red product, m.p. 118–119°. Infrared analysis indicated that this was tetrachloro-*o*-benzoquinone, 56.9% yield. No 2,3,4,5,6-pentachloro-4-pentachlorophenoxy-2,5-cyclohexadiene was isolated or detected.

Chloranil from 2,3,4,5,6-Pentachloro-4-pentachlorophenoxy-2,5-cyclohexadiene.—To 2.0 g. of the cyclohexadiene there was added 4.0 ml. of fuming nitric acid. The solution turned red instantaneously and a yellow solid precipitated. This mixture was kept at room temperature overnight whereupon the red color of the solution disappeared. Excess of water was added to the reaction product and the mixture was filtered to give pure chloranil, m.p. 290°, wt., 1.1 g. or 59.2%.

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Preparation of Mono- and Difluorobenzoic Acids and Their Vinyl Esters

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All isomeric fluorobenzoic acids are known. Many methods may be used for their preparation, of which that from the amino acids^{2a,b,c} and their esters,^{2d} employing the Schiemann reaction, is the most common. The oxidation of fluorotoluenes with potassium permanganate and chromic acid is also reported, but has been found to lead predominantly to nuclear oxidation.³ Nitric acid oxidation of fluorobenzyl chlorides is more satisfactory.⁴

Fluorotoluenes can be oxidized at high temperature under pressure with yields up to 95% with a 20% nitric acid solution to essentially pure carboxylic acids. The oxidation is carried out in an autoclave, and the nitric acid solution used is calculated to be 10% in excess in nitric acid. More concentrated solution or more excess nitric

acid causes nuclear oxidation and depresses the yield. The oxidation under the described conditions starts at 140–150°, but for a rapid and complete reaction, higher temperatures must be used. When the reaction is kept at 180–200°, or, better, at 190–195°, heating for three to four hours is sufficient. Since the oxidation is an exothermic reaction, care must be taken to keep below 200°. For better results, pressure is needed. Conditions at which a pressure of 930 p.s.i. was developed led to a 10% better yield than for 720 p.s.i.

Difluorotoluenes⁵ are advantageously oxidized likewise, but with 15% nitric acid solution. The difluorobenzoic acids thus prepared are the 2,5-, 2,4-, and 3,4-difluorobenzoic acids, of which the 3,4-difluorobenzoic acid prepared by the iodoform reaction on the corresponding difluoroacetophenone is known.⁶ As shown in Table I, smaller yields result in the case of oxidation of difluorotoluenes, although still in the region of 65–70%. It is characteristic that the melting points of fluoro- and difluorobenzoic acids are very close to that of benzoic acid except when fluorine is in the 4-position; however, 3,4-difluorobenzoic acid is no exception.

TABLE I

Benzoic acid	Yield, %	M.p., °C.
<i>p</i> -Fluoro-	96	181–182
<i>m</i> -Fluoro-	89	121–122
<i>o</i> -Fluoro-	82	120–121
2,5-Difluoro-	69	118–119
3,4-Difluoro-	70	119–120
2,4-Difluoro-	65	182–184

Preparation of the vinyl esters of the three mono-fluorobenzoic acids followed the transesterification method of Adelman.⁷ Difficulty was encountered in finding an efficient inhibitor for the polymerization reaction during the transesterification. At a reaction temperature of 60°, hydroquinone was found inefficient, and low-molecular-weight polymers of polyvinyl acetate and polyvinyl fluoro-benzoate were formed. With traces of sulfur, however, the vinyl fluoro-benzoates were obtained free of polymeric impurities. The transesterification reaction proceeds slower with the *p*-fluorobenzoic acid.

TABLE II

Vinyl-benzoate	Yield, %	B.p., °C., 14 mm.	n_D^{20}
<i>p</i> -Fluoro-	82.5	78–79	1.4843
<i>m</i> -Fluoro-	89.0	80–81	1.4725
<i>o</i> -Fluoro-	84.2	89–89.5	1.5048

All three vinyl fluoro-benzoates prepared polymerize readily when treated with benzoyl peroxide.

(1) To whom inquiries should be addressed.

(2) (a) J. Pippy and F. Williams, *J. Chem. Soc.*, 1466 (1934); (b) E. D. Bergmann, J. Berkovic, and R. Ikan, *J. Am. Chem. Soc.*, **78**, 6039 (1956); (c) L. S. Fosdick and E. E. Campaigne, *ibid.*, **63**, 974 (1941); (d) E. Bennet and C. Niemann, *ibid.*, **72**, 1800 (1950).

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