Aromatic Peracids. The Effects of Solvent on the Ozone-Initiated Autoxidation of Benzaldehydes

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The yields of perbenzoic acids from the corresponding aldehydes are solvent dependent. In methyl or ethyl acetate solutions, perbenzoic acid was prepared in 90% yields at 98+% aldehyde consumption by the action of ozone and oxygen. In a like manner the 2-Cl, 4-Cl, 3-NO_2, and 4-NO_2 peracids were prepared in 83 to 60% yields.

Perbenzoic acid (I) has been known for years and its effectiveness as an epoxidizing agent is unquestioned. The preparation of I from benzoyl peroxide[2] is effective, but at the same time cumbersome and not readily applied to large-scale work. Jorissen and Van der Beek[3] reported the preparation of I in 65% yield by sunlight-initiated autoxidation of benzaldehyde (II) in carbon tetrachloride. More recently, Swern[4] reported a large-scale preparation of I in 40% yield by air oxidation of II in an acetone solution under ultraviolet irradiation.

The ozone-initiated oxidation of II has been documented by Briner[5] and co-workers, but their studies were directed more toward the effect of ozone as a catalyst than the preparation of I *per se*. Using carbon tetrachloride, *n*-hexane, and cyclohexane as solvents, they obtained at best a 25% yield of I, while the remainder of II was converted to benzoic acid (III).

The relatively low yields of I from II could result from the peracid forming a hemiacetal-type adduct with the aldehyde, such as are formed with the aliphatic aldehydes. Such a reaction would preclude any one-step, high yield perbenzoic acid synthesis as it does in the acetaldehyde–peracetic acid system. Phillips[6] and co-workers have described an elegant method of surmounting this problem in the case of peracetic acid, but an analogous preparation of I does not seem feasible owing to its high boiling point. On the other hand, it should be noted that there is no report of such an adduct being formed from I and II.

To determine whether I and II form an adduct, equimolar amounts were dissolved in ethyl acetate, cooled to −70°, and allowed to warm slowly in the beam of an infrared spectrophotometer with periodic scanning. The relative concentrations of I and II did not change as the sample warmed. Similarly, the room temperature spectrum of the mixture indicated no adduct formation. It was concluded, therefore, that, if any adduct formed,[7] it was not a major product as it is in the case of the aliphatics.

In order to determine if solvents could effect a change in the yield of I, a series of runs, using ozone as initiator, was made at 20–22°, with 0.25 moles of II as a 0.50 molar solution and constant oxygen–ozone feed rate. The results are listed in Table I.

The data clearly demonstrate the ability of methyl and ethyl acetates to promote the formation of high yields of I at high conversions of II. The effectiveness of these esters, particularly ethyl acetate, is seen in runs 1, 3, 7, and 10, wherein the yield of I increases with increasing amounts of ethyl acetate, the polar component of the solvent.

The effects of solvent on the consumption of ozone are listed in the last column of Table I. The apparent reactivity of the solvent toward ozone would be greatly suppressed in the presence of the more reactive II, but it would become significant at high conversions of II. Bearing in mind that the consumption of II is directly proportional to the rate of ozone input, it appears that there is some relation between the data in columns 4, 5, and 7 in Table I. Thus, a more reactive solvent results in a higher ozone consumption and a longer reaction time. The yield of I is independent of oxygen solubility, within the limits of the data in col. 6.

In view of the work of Van der Beek[8] and associates, who found only traces of 3- and 4-chloroperbenzoic acid when acetone solutions of the respective aldehydes were air oxidized in the presence of light, the process herein described was extended to various substituted benzaldehydes (Table II).

From the data in Table I it is seen that the yields are low in nonpolar solvents (*e.g.*, CCl_4) and in solvents which are relatively reactive toward ozone (*e.g.*, benzene). In general, the yields in ester solvents tend to be higher with decreasing aliphatic character and an increase in polar character. The yield in ethyl acetate is an exception to this generality, being higher than in methyl acetate, although the difference is not large. It is not possible to ascribe the high yield in the lower molecular weight esters to the polar nature of the solvent alone, since other polar solvents have not been investigated. However, it is thought that the relatively short reaction times obtained by the use of ozone and the presence of a solvent capable of minimizing the interaction of peracid with aldehyde combine to reduce the extent of reaction of I with II with a resulting increase in yield.

Experimental[9a]

Preparation of Perbenzoic Acid (I).—All reactions were carried out in an all-glass, 500-ml. cylindrical reactor having a central cold finger as well as an exterior cooling jacket. The distance between the cooling surfaces was $^3/_8$ in. The reactor was equipped

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[1] To whom inquiries should be directed.

[2] H. Gilman and A. H. Blatt, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 431.

[3] W. P. Jorissen and P. A. A. Van der Beek, *Rec. trav. chim.*, **45**, 245 (1926).

[4] D. Swern, T. W. Findley, and J. T. Scanlan, *J. Am. Chem. Soc.*, **66**, 1925 (1944).

[5] For a review, see E. Briner, *Advan. Chem. Ser.*, **21**, 184 (1959).

[6] B. Phillips, F. C. Frostick, Jr., and P. S. Starcher, *J. Am. Chem. Soc.*, **79**, 5982 (1957).

[7] In consideration of accuracy limits, the adduct cannot be present in concentrations exceeding ±3% of amount present. This experiment was carried out only in ethyl acetate. The results might differ significantly in other solvents.

[8] P. A. A. Van der Beek, *Rec. trav. chim.*, **51**, 411 (1932).

[9] (a) All melting points and boiling points are uncorrected. (b) SCFM is standard cubic feet per minute.

TABLE I

OXIDATION OF BENZALDEHYDE

Run no.[a]	Solvent	% yield of I at 99% conversion of II	Reaction time, hr.	Moles of O_3/mole of II consumed	Soly. of O_2, ml. of O_2/l. of solvent at 22°	Consumption of O_3 by solvent[b]
1	Ethylacetate (EA)	90	1.7	0.078	24	0 ± 0.5
2	EA/dichloromethane[c]	90	2.0	0.089	17	0
3	EA/carbontetrachloride[c]	87	1.7	0.061	23	0
4	Methyl acetate	85	1.1	0.037	21	0
5	Methyl propionate	83	1.7	0.102		
6	Methyl butyrate	80	1.7	0.104	24	
7	EA/carbontetrachloride[d]	77	1.5	0.068	23	0.5
8	Ethyl butyrate	72	2.7	0.113	23	6
9	Dichloromethane	72	3.0	0.136	13	7
10	Carbon tetrachloride	67	1.5	0.085	23	0.5
11	Butyl butyrate	64	4.7	0.207		
12	Isoamyl acetate	59	5.0	0.208	23	22
13	Chlorobenzene	57	4.1	0.224	15	58
14	Benzene	47	4.0	0.226		58

[a] Data is average of three runs, excepting run 2 which was made only once. [b] Solvent (100 ml.) was treated at 25° with O_3/O_2 at the rate of 0.2 mmole of O_3/min. and the concentration of O_3 in exit gas was determined after 6-min. equilibration time. The per cent decrease in the ozone concentration is reported. [c] 50 vol. % ethyl acetate. [d] 10 vol. % ethyl acetate.

TABLE II[a]

OXIDATION OF SUBSTITUTED BENZALDEHYDES

Substituted benzaldehyde	% yield of peracid	Reaction time,[b] hr.
4-CH_3	87	2
2-Cl	83	4
3-NO_2	73	7
4-Cl	72	2.5
4-NO_2	60	14

[a] 0.25 mole of aldehyde used as a 0.5 *N* ethyl acetate solution. [b] Time for 99% aldehyde consumption.

with a 1-in. glass frit in the bottom, a side sampling drain, a thermowell, and two top vents. The gas stream entered the reactor through the bottom frit and was vented through (in this order) a Dry Ice trap, a three-way stopcock, and two parallel 500-ml. scrubbers containing 5% potassium iodide solution. The ozone was prepared with a Welsbach T-23 generator.

A simplified apparatus used for preparative work consisted of a well-stirred, 2-l., baffled, round-bottom flask equipped with thermometer, gas dispersion tube, and sampling point.

A typical run was as follows. While purging with dry nitrogen, 203 g. of dry ethyl acetate and 26.9 g. of freshly distilled (under nitrogen) benzaldehyde were charged into the precooled reactor. While this mixture was being cooled to the reaction temperature of 20–22°, the ozone generator was purged with dry oxygen and finally adjusted at a gas flow of 0.055 SCFM[9b] containing 0.22 mmole of ozone per minute. At this point, the nitrogen purge was stopped and the oxygen–ozone stream was admitted into the reactor. At random time intervals during the run, the potassium iodide traps (wash bottles) were switched, removed, titrated with standard thiosulfate to starch end point, refilled with fresh 5% potassium iodide solution, and replaced, all in such a manner as to lose only a minimal amount of gas.[10]

The results of previous experiments indicated that the approximate time required to reach 98+% conversion was 1.4 hr.; hence, the reaction mixture was not sampled until this time period had elapsed. At this point, a 1-ml. aliquot was withdrawn through the side arm and the conversion of the aldehyde was determined by vapor phase chromatographic analysis. If the reaction had not reached at least 98.3% conversion, the flow was continued for a short time, depending on the extent of reaction, and the analysis was repeated. In this experiment the reaction was stopped after 91 min. The conversion was 99.6% of the aldehyde.

At this stage, the gas flow through the reactor was stopped, and the reactor was drained. The contents of the reactor, 229.7 g., were analyzed by the potassium iodide–thiosulfate procedure and found to contain 0.229 moles of I as peroxide. This corresponds to a 90% yield. The total ozone consumed was 18.6 mmoles, based on an input of 0.22 mmole/min. or 20 mmoles total minus 1.4 mmoles calculated from the titration of the contents of the potassium iodide scrubbers.

It should be noted that there is considerable latitude in reaction conditions, *i.e.*, 20 to 35°, 0.1 to 0.5 *M* aldehyde, and any ozone feed rate below that of the general procedure.

Analysis.—Since the standard sodium thiosulfate–potassium iodide method is not specific for peracids, an infrared method was used to confirm the titration data. Standard I was prepared from benzoyl peroxide, and the spectrum was determined. Subsequently, a fresh sample of I from the ozonator was analyzed both by titration and infrared. Typical results of triplicate determinations are shown in Table III.

TABLE III

EQUIVALENTS OF I FORMED

Thiosulfate	Infrared	Reaction solvent
0.404	0.405	Ethyl acetate
0.402	0.382	Ethyl acetate
0.073	0.077	Chlorobenzene

The vapor phase chromatographic analysis was carried out on a 5 ft. × 0.25 in. column of 20% Oronite NIW on 80–100-mesh Chromosorb-W at 160° and 15 p.s.i.g. of helium.

Effect of Temperature on the Benzaldehyde–Perbenzoic Acid Interactions.—To determine this effect, various amounts of benzoic acid, perbenzoic acid, and benzaldehyde were added to ethyl acetate and the solutions were cooled to Dry Ice temperatures. Infrared spectra were recorded at regular time intervals over the temperature range of −60 to 30°. The spectra were recorded with a Baird double beam instrument employing a Dry Ice-cooled cell equipped with a thermocouple. The cell was constructed with sodium chloride windows with a path length of 0.15 mm. Sample handling and recording operations were performed in a dry nitrogen atmosphere. Component concentrations were determined at the following wave lengths: perbenzoic acid, 11.35 μ; benzoic acid, 8.87 and 14.9 μ; benzaldehyde, 12.1 and 13.35 μ; and ethyl acetate, 5.30 and 10.9 μ. Standard blends of benzaldehyde and ethyl acetate without the two acids were scanned first under the above conditions to determine temperature effects upon analytical absorptions and cell path length. The resulting data on absorption variations were in agreement with the variations predicted on the basis of cell path length changes indicating that the absorptions were not temperature sensitive under these conditions.

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[10] The loss of ozone-containing gas was that volume of gas in the line between the switching (3-way) valve and the surface of the potassium iodide solution in the scrubber—approximately 3 ml.

The blends of perbenzoic acid, benzoic acid, benzaldehyde, and ethyl acetate then were scanned at four 15-min. intervals over the indicated temperature range. The initial spectrum was recorded at −60° and the final one at 30°.

The absorptions of the two acids and benzaldehyde changed concomitantly with the changes of the ethyl acetate absorption and were perfectly consistent with the variations observed from the previous runs due to path length differences.

These results constituted unequivocal evidence that, between −60 and 30°, temperature has no effect upon the benzaldehyde–benzoic acid–perbenzoic acid equilibrium in ethyl acetate.

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The Synthesis and Cyclization of 2-(1-Naphthylmethyl)-2′-carboxybenzophenone[1,2]

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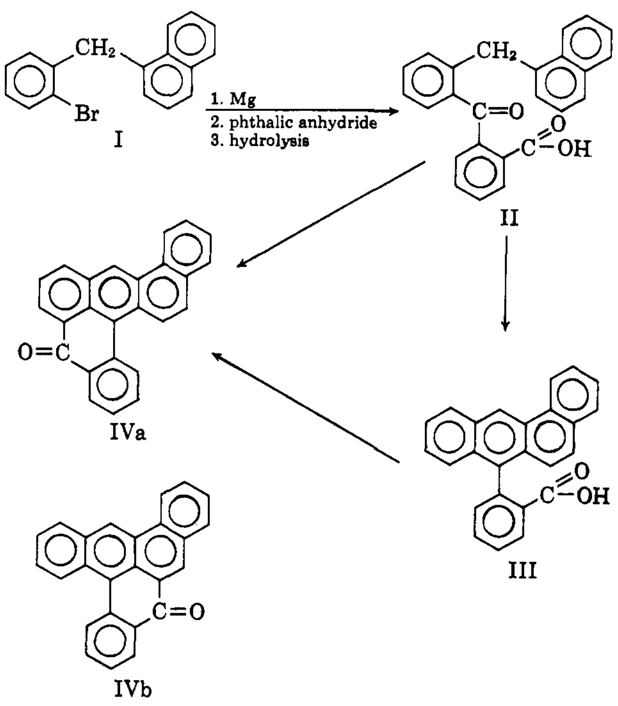
2-(1-Naphthylmethyl)-2′-carboxybenzophenone has been synthesized and cyclized to dibenzo[*hi,l*]chrysen-9-one under one set of conditions, and to 7-(2-carboxyphenyl)benz[*a*]anthracene under different conditions. One of the optically active forms of this acid has been isolated.

A study of the cyclization of 2-(1-naphthylmethyl)-2′-carboxybenzophenone (II) is interesting for several reasons. First, II might lose 1 mole of water to give 7-(2-carboxyphenyl)benz[*a*]anthracene (III). This should be resolvable into optically active forms owing to restricted rotation about the 7-1′ bond as a result of molecular overcrowding; it is of further interest because of its close relationship to 7-phenylbenz[*a*]anthracene.[4] Second, II might lose 2 moles of water to give dibenzo[*hi,l*]chrysen-9-one (IVa) and/or naphtho[3,2,1-*fg*]naphthacen-9-one (IVb).

The keto acid (II) was prepared in satisfactory yield by the addition of the Grignard reagent of 2-(1-naphthylmethyl)bromobenzene[5] (I) to a boiling solution of phthalic anhydride in benzene (see Chart I). The structure of II was established by carbon–hydrogen analysis, neutralization equivalent titration, infrared spectrum, and by conversion to its methyl ester which was characterized by carbon–hydrogen analysis and by its infrared spectrum.

The keto acid (II) lost 1 mole of water when heated with a mixture of hydrobromic and acetic acids for 1 hr. to give 90% of 7-(2-carboxyphenyl)benz[*a*]anthracene (III).[6] It is interesting to note that when Bradsher and Vingiello[7] cyclized an analogous keto acid, 2-benzyl-2′-carboxybenzophenone, to 9-(2-carboxyphenyl)anthracene they obtained an 80% yield after 20 hr. of heating. The greater ease of aromatic cyclodehydration into the 2-position of the naphthyl system as compared with the phenyl system is consistent with a proposed mechanism for aromatic cyclodehydration.[8]

CHART I



The ease of cyclization of II to III was further illustrated when the reaction was accomplished in 60% yield by simply treating II with concentrated sulfuric acid for a few minutes at −40°.

The acid (III) was first isolated as an alcoholate as indicated by carbon, hydrogen analysis, neutralization equivalent titration, and gas chromatographic analysis. Heating *in vacuo* at 110° for 48 hr. gave the acid III.

The acid III should be optically active owing to restricted rotation about the 7-1′ bond, and preliminary experiments using brucine as a resolving agent confirm this.

On dehydration, III might be expected to give IVa and/or IVb. However, if one assumes that the reaction proceeds *via* an attack of the positive carboxylic acid carbon on an electron-rich ring position, one would predict ring closure at C-8 in preference to C-6. The calculation of the localization energies for the 7-(2-carboxyphenyl)benz[*a*]anthracene system (III) is com-

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[1] The nomenclature used in this paper is that presented in the "Definitive Rules for Nomenclature of Organic Chemistry," *J. Am. Chem. Soc.*, **82**, 5545 (1960).

[2] Presented before the Division of Organic Chemistry at the Southeastern Regional Meeting of the American Chemical Society, Gatlinburg, Tenn., Nov., 1962.

[3] Abstracted from the M.S. thesis of E. J. Greenwood presented to the Virginia Polytechnic Institute, 1961.

[4] This compound, NSC #14080, showed slight activity against S-180 and L-1210 (private communication from the National Institutes of Health, Bethesda, Md.).

[5] For an improved method of preparation see P. Polss, Ph.D. dissertation, Virginia Polytechnic Institute, Blacksburg, Va., 1962.

[6] This compound, NSC #76322, which is currently being tested, showed activity against S-180 (private communication from the National Institutes of Health, Bethesda, Md.).

[7] C. K. Bradsher and F. A. Vingiello, *J. Org. Chem.*, **13**, 786 (1948).

[8] C. K. Bradsher and F. A. Vingiello, *J. Am. Chem. Soc.*, **71**, 1434 (1949).