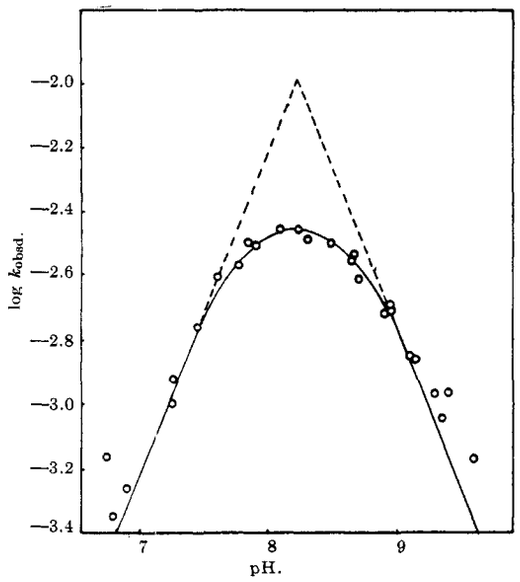

Figure 2.—Second-order rate constant for decomposition of peroxypivalic acid as a function of pH at 25.0°.

the results obtained are given in graphical form in Figure 2 in order to illustrate the pH dependence of the decomposition.

Once the general pattern of decomposition was established, the decomposition of a sample of peroxypivalic acid in which 1.2% of the peroxidic oxygen was doubly labeled in O^{18}, $(CH_3)_3C(=O)O^{18}O^{18}H$, was carried out. The oxygen gas evolved contained an amount of O_2^{36} consistent with 24% of the decomposition proceeding by attack on carbon (eq 1) and 76% attack on oxygen (eq 2). See Table I.

TABLE I

MASS SPECTROGRAPHIC ANALYSIS OF GAS SAMPLES FROM THE DECOMPOSITION OF DOUBLY LABELED PEROXYPIVALIC ACID

	Peak heights		
	O^{32}	O^{34}	O^{36}
I. H_2O_2[a]			
Oxygen	2100	16.4	25.9
Oxygen percentage	98.06	0.73	1.21
II. Peroxypivalic Acid[b]			
Oxygen	2150	57.2	6.4
Oxygen percentage	97.12	2.59	0.29

$$\% \text{ unscrambled} = \frac{0.29}{1.21} \times 100 = 24$$

[a] Oxygen liberated by ceric oxidation of H_2O_2 in perchloric acid solution.[2] [b] In carbonate buffer at pH 8.4.

Thus, we were able to alter the mechanism of decomposition by sterically hindering the carbonyl site of peroxyacetic acid, lending additional support to the original postulate of a dual mechanism.

When this investigation was near completion, Edwards and coworkers[6] reported a similar study using monoperoxyphthalic acid. Even though this compound is not as similar in nature to peroxyacetic acid as the one being reported here, the results appear to be in complete agreement.[7] As a matter of convenience, the results obtained on the systems studied to date are listed in Table II.

TABLE II

Monosubstituted peroxy acid	Attack on O_2, %[a]	Attack on C or S, %[a]
Peroxyacetic acid	17	83
Peroxysulfuric acid	90	10
Peroxyphthalic acid	74	26
Peroxypivalic acid	76	24

[a] Based on the results of doubly labeled isotope tracer experiments.

Experimental Section

The procedures used in the kinetic and labeling experiments have been previously reported.[1,2] Peroxypivalic acid was prepared in yields of up to 80% as follows. To 11.6 ml of concentrated sulfuric acid at 0°, 5.6 ml of pivalic acid (mp 34–35°) was slowly added. This was followed by 3.4 ml of deionized water which was in turn followed by 5.1 ml (dropwise) of 50% hydrogen peroxide. The resulting mixture was allowed to stand at 20° for 1 hr after which it was extracted with two 50-ml aliquots of methylene chloride. Removal of the methylene chloride by means of a water aspirator and a rotary evaporator left an oily residue which possessed a sharp odor characteristic of peroxycarboxylic acids. Analysis of the residue by both basic and iodimetric titration[8] confirmed that it contained only pivalic and peroxypivalic acids.

If this material is diluted with 25 ml of water and then brought to a pH of 6.2 with 3 *M* NaOH, extraction with two 50-ml portions of methylene chloride leads to a product of 95% purity.

Registry No.—Peroxypivalic acid, 14909-78-5.

Acknowledgments.—This work was supported in part by the Office of Naval Research. We also wish to thank Dr. Fred Saalfeld of the Naval Research Laboratories for the mass spectral analysis.

(6) R. E. Ball, J. O. Edwards, M. L. Haggett, and P. Jones, *J. Am. Chem. Soc.*, **89**, 2331 (1967).

(7) However, it may be noted that in the case of monoperoxyphthalic acid, in addition to sterically hindering the carbonyl center, attack may also be preferred at oxygen due to a loss of conjugation following attack on carbon. For this reason it is likely that benzoic acid[5] also undergoes decomposition *via* attack upon oxygen to a greater extent than that found for peroxyacetic acid.

(8) F. P. Greenspan and D. G. MacKellar, *Anal. Chem.*, **20**, 1061 (1948).

2,2′-Dihydroxydiphenyl Sulfone and Its Monoethers

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Because of a need for a quantity of very pure 2,2′-dihydroxydiphenyl sulfone (I), the synthetic methods reported in the literature were surveyed. The earliest work, that by Tassinari,[2] was misleading in that he believed he had prepared the 3,3′ isomer when in fact he had prepared I. Mauthner[3] prepared I by a somewhat different route, but his product was impure, as was demonstrated by Machek and Haas.[4] This previous work was summarized by Gump and Vitucci,[5]

(1) To whom requests for reprints should be addressed.
(2) G. Tassinari, *Gazz. Chim. Ital.*, **17**, 90 (1887); **19**, 343 (1889).
(3) F. Mauthner, *Ber.*, **39**, 1351 (1906).
(4) G. Machek and H. Haas, *J. Prakt. Chem.*, **160**, 41 (1942).
(5) W. Gump and J. Vitucci, *J. Am. Chem. Soc.*, **67**, 238 (1945).

TABLE I

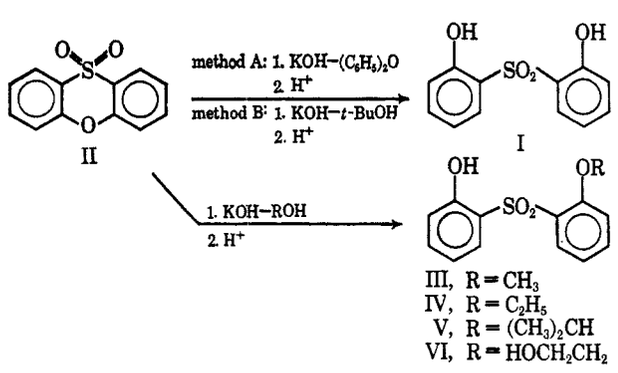
Compd	Alkoxy group	Mp, °C	Yield, %	Calcd, % C	Calcd, % H	Calcd, % S	Found, % C	Found, % H	Found, % S
III	Methoxy[a]	173–174	81[b]	59.09	4.58	12.07	59.17	4.72	11.89
IV	Ethoxy[c]	128–129	80[b]	60.41	5.07	11.51	60.53	5.36	11.42
V	isoPropoxy	112–114	84[b]	61.64	5.52	10.95	61.89	5.57	11.07
VI	β-Hydroxyethoxy	149–150	62[d]	57.14	4.80	10.88	57.28	4.90	10.97

[a] Characterized by preparing 2,2′-dimethoxydiphenyl sulfone, using dimethyl sulfate; mp 195–196°, lit.[3] mp 197°. Infraredsp ectrum identical with that published for the authentic compound: Sadtler Standard Spectra Index, Spectrum No. 17826.[12b] [b] Recrystallized from ethanol. [c] Acetate derivative: mp 184–186°. *Anal.* Calcd for $C_{16}H_{16}O_5S$: C, 59.98; H, 5.03; S, 10.0. Found: C, 60.26; H, 5.19; S, 10.18. [d] Recrystallized from benzene.

who improved upon the tedious and time-consuming earlier procedures. This paper describes a new and simpler synthesis of I, wherein both high yield and purity are achieved. Also reported herein are four new 2-hydroxy-2′-alkoxydiphenyl sulfones, readily prepared by this method but which would otherwise be difficult to synthesize.

Phenoxathin was prepared in 85% yield by the reaction of phenyl ether with sulfur in the presence of aluminum chloride.[6] It was then oxidized by hydrogen peroxide to phenoxathin 10-dioxide (II) in greater than 90% yield.[7] It has been found that the ether linkage of II can readily be cleaved by potassium hydroxide in phenyl ether at 200° to give an 85–90% yield of I. The only previous attempt at cleavage of II was with lithium. After carbonation, acidic tar was the only product.[8]

Compound II is also capable of undergoing ether interchange with certain alkanols in the presence of potassium hydroxide to give 2-hydroxy-2′-alkoxydiphenyl sulfones. In such a manner, 2-hydroxy-2′-methoxydiphenyl sulfone (III) and the corresponding 2′-ethoxy (IV), 2′-isopropoxy (V), and 2′-(β-hydroxyethoxy) (VI) compounds were prepared. The yield, melting point, and elemental analyses are reported in Table I. However, in *t*-butyl alcohol, interchange did not occur, and the product was compound I. The *t*-butoxide ion must be prevented from reacting by steric hindrance, which gives preference to the less basic hydroxide. This is supported by the fact that no reaction occurred in tetrahydrofuran with potassium *t*-butoxide as the base.



It is postulated that the relative positive charge on the sulfur atom of II causes the aromatic rings joined through the ether linkage to be activated toward nucleophilic attack by the base. Szmant and Suld[9] have shown the acidity of *p*-(4-substituted phenylsulfonyl)phenols to be a function of the substituted groups, which alter the relative positive charge on the sulfur atom of the sulfone group and, hence, increase or decrease the acidity of the phenolic hydroxyl group. Ogata and Okano[10] have demonstrated that ether interchange will occur with phenolic ethers when reacted with an alcohol and potassium hydroxide if strong electronegative groups are present, such as in 2,4-dinitrophenylalkyl (or -aryl) ethers. The activating effect of the sulfone group on the reactivity of the ether linkage was further illustrated by the inability of phenoxathin to undergo cleavage in *t*-butyl alcohol and potassium hydroxide. Even the carbonyl group in xanthone is not sufficiently activating to cause cleavage in *t*-butyl alcohol.

Experimental Section[11]

2,2′-Dihydroxydiphenyl Sulfone. Method A.—Phenoxathin 10-dioxide (II) was prepared by the method of Gilman and Esmay[7] and recrystallized from benzene (1.25 ml/g) with a 10% loss. Compound II (36.7 g), pulverized potassium hydroxide pellets (132 g), and phenyl ether (785 ml, Dow Chemical Co.) were stirred at 200° for 23 hr in a stainless-steel, 5-l resin flask. Water (880 ml) was added to the cooled reaction mixture and the aqueous phase was separated. The pH of the solution was adjusted to 8–9 with hydrochloric acid. After cooling the solution to 20° to freeze the remaining phenyl ether, the solution was filtered, and the filtrate was treated with activated charcoal and filtered. The cooled solution was then brought to pH 6 to precipitate I: 37.0 g (93%), mp 189–190°. Recrystallization from ethanol–water (264:379, v/v) gave a 94% recovery: mp 189.5–191°, lit.[4] mp 191°. Recrystallization from ethylene dichloride (96% recovery) did not alter the melting point. This product was free of impurities as determined by thin layer chromatography, and its infrared spectrum was identical with that published for the authentic compound.[12] The melting point of its diacetate derivative was 185.5–187.0°, lit.[4] mp 186–188°.

Method B.—A solution of II (2.32 g) in *t*-butyl alcohol (40 ml) was refluxed for 22 hr with 5.6 g of potassium hydroxide pellets (87% assay). Water was added to the reaction mixture, and the alcohol was removed under reduced pressure. After filtering the unreacted starting material (0.05 g), compound I was precipitated by acidification to pH 6 to give 2.5 g, mp 182–188°. Recrystallization from ethanol–water gave pure I (2.0 g): mp 189.5–191.0°.

Phenoxathin and xanthone were treated similarly but with no detectable reaction. Compound II was also refluxed in tetrahydrofuran with 3 molecular equiv of potassium *t*-butoxide, but only unreacted II was recovered (100%).

2-Hydroxy-2′-alkoxydiphenyl Sulfones.—A solution of II in the appropriate alcohol was refluxed with potassium hydroxide

(6) C. Suter and C. Maxwell, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 485.
(7) H. Gilman and D. Esmay, *J. Am. Chem. Soc.*, **74**, 2021 (1952).
(8) H. Gilman and J. Dietrich, *ibid.*, **80**, 380 (1958).
(9) H. Szmant and G. Suld, *ibid.*, **78**, 3400 (1956).
(10) Y. Ogata and M. Okano, *ibid.*, **71**, 3211, 3212 (1949).
(11) Melting points are uncorrected; analyses were performed by the Chemicals Division, Applied Research Laboratory, U. S. Steel Corp.
(12) (a) Sadtler Standard Spectra Index, Spectrum No. 17827.[12b] (b) The Sadtler Research Laboratories, Philadelphia, Pa., 1962.

as in method B, with the exception that where ethylene glycol was used, the reaction temperature was 100°.

Registry No.—I, 15038-67-2; III, 14909-73-0; IV, 14909-74-1; acetate of IV, 14909-75-2; V, 14909-76-3; VI, 14909-77-4.

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A Study of the *p*-Methoxybenzylidene Derivatives of Succinic and Malonic Acids[1a]

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An interest in the methoxyindenone **1** as a possible synthetic intermediate for certain gibberellins lead us to study several transformations of the Stobbe condensation product **2** (Scheme I). Based on previous studies[2] of acid-catalyzed intramolecular acylations, we anticipated that cyclization of the *trans* acid **2** or anhydride **3** would yield the naphthol **4**, whereas cyclization of the *cis* acid **5** or one of its derivatives **6** or **7** might yield the desired indenone **1**. The indicated photochemical isomerizations (**2** ⇌ **5** and **8** ⇌ **7**) provided the previously unknown *cis* acid **5** and its derivatives. A variety of attempts to convert the *cis* acid **5**, *cis* anhydride **6**, or derivatives of the *cis*-monomethyl ester **7** to the indenone **1** resulted in formation of the naphthol **4**, the *trans* anhydride **3**, or intractable materials. It appears that the acid-catalyzed interconversion of the *cis* and *trans* anhydrides is more rapid than cyclization, presumably because of the charge delocalization possible in the acyl cation **16** which gives this intermediate a sufficiently long lifetime to permit *cis–trans* isomerization.[2c]

Because of the reported[3] difficulties in acid-catalyzed cyclizations of 3-(4-methoxyphenyl)propionic acid derivatives (**13**) and related materials, we examined briefly the cyclization of the pure acid chloride **13c** under various conditions (Scheme II). Cyclization in the presence of aluminum chloride and methylene chloride gave a moderate yield (38%) of the indanone **15** (no attempt was made to optimize this yield). In earlier work,[3a,b] the addition of a benzene solution of the acid chloride **13c** to aluminum chloride had been found to give the indanone **15** in 93–100% yield. Repeated attempts to duplicate this result gave mixtures of the indanone **15** (*ca.* 20% yield) and the previously unreported phenyl ketone **14** (*ca.* 40% yield). It is possible that this differing behavior of benzene solutions of the acid chloride **13c** is attributable to a significant difference in the quality and purity of the commercial aluminum chloride available at the times when the two sets of experiments were performed.

(1) (a) This research has been supported by a grant from the National Science Foundation (Grant No. GP-5685). (b) Woodrow Wilson Predoctoral Fellow, 1963–1964; National Institutes of Health Predoctoral Fellow, 1964–1967.

(2) (a) W. S. Johnson, *Org. Reactions*, **2**, 114 (1944); (b) W. S. Johnson and G. H. Daub, *ibid.*, **6**, 1 (1951); (c) W. S. Johnson and R. P. Graber, *J. Am. Chem. Soc.*, **72**, 925 (1950).

(3) (a) W. S. Johnson and W. E. Shelberg, *ibid.*, **67**, 1853 (1945); (b) W. S. Johnson and H. J. Glenn, *ibid.*, **71**, 1092 (1949); (c) J. Sam and J. N. Plampin, *ibid.* **82**, 5205 (1960).

Experimental Section[4]

Preparation of the *trans* Acid 2 and Its Derivatives.—Following previously described procedures,[5] the diacid **2** was obtained as white needles from water: mp 193–201° dec (decomposition temperature dependent on rate of heating) (lit. mp 202–203°,[5b] 188–191°,[6a] 194–195°[6b]); ultraviolet maximum, 290 mμ (ε 20,500); infrared (KBr), 1695 (carboxyl C=O), 1670 (conjugated carboxyl C=O), and 1602 cm^{-1} (conjugated C=C); nmr ($(CD_3)_2NCDO$), δ 7.89 (1 H singlet, vinyl C–H), 7.54 (2 H doublet with J = 9 cps, aryl CH), 7.11 (2 H doublet with J = 9 cps, aryl CH), 3.89 (3 H singlet, O–CH_3), and 3.59 (2 H singlet, CH_2–CO). Reaction of the *trans* acid **2** with acetic anhydride afforded the anhydride **3** which crystallized from a benzene–cyclohexane mixture as colorless plates: mp 161–162° (lit.[5a] mp 166–167°); infrared ($CHCl_3$), 1840 and 1770 cm^{-1} (anhydride C=O) and 1645 cm^{-1} (conjugated C=C); ultraviolet maximum (CH_3CN), 233 mμ (ε 9900) and 321 (29,800); nmr ($(CD_3)_2NCDO$), δ *ca.* 7.7 (1 H superimposed on an adjacent peak, vinyl CH), 7.77 (2 H doublet with J = 9 cps, aryl CH), 7.16 (2 H doublet with J = 9 cps, aryl CH), *ca.* 4.1 (2 H, partially resolved AB pattern with $J \sim 20$ cps, CH_2–CO), and 3.94 (3 H singlet, O–CH_3).

Reaction of the anhydride **3** with methanol yielded, after crystallization from a benzene–cyclohexane mixture, the monomethyl ester **8** as white needles: mp 136–137° (lit.[5a] mp 139–140°); infrared ($CHCl_3$), 1735 (ester C=O), 1680 (conjugated carboxyl C=O), and 1630 cm^{-1} (conjugated C=C); ultraviolet maximum, 289 mμ (ε 19,700); nmr ($CDCl_3$), δ 8.04 (1 H singlet, vinyl CH), 7.42 (2 H doublet with J = 9 cps, aryl CH), 6.99 (2 H doublet with J = 9 cps, aryl CH), 3.87 (3 H singlet, O–CH_3), 3.79 (3 H singlet, O–CH_3), and 3.63 (2 H singlet, CH_2–CO); pK_{MCS}* 6.82.[7]

In the preparation of the acid **2**, a minor higher melting byproduct, the diarylidene acid **9**, was isolated as a yellow solid: mp 254–257° dec (decomposition point dependent on rate of heating) (lit.[5c] mp 260–261°); infrared (KBr), 1675 cm^{-1} (conjugated carboxyl C=O). Reaction of this diacid **9** with acetic anhydride followed by recrystallization from a benzene–hexane mixture gave the anhydride **10** (stereochemistry unknown) as yellow plates: mp 174–176° (lit.[5c] mp 179–180°); infrared ($CHCl_3$), 1760 and 1820 cm^{-1} (anhydride C=O); ultraviolet maxima (CH_3CN), 227 mμ (ε 14,100), 255 (10,100), 319 (27,700), and 407 (14,000); nmr ($CDCl_3$), δ 7.89 (2 H singlet, vinyl C–H), 6.76 (4 H doublet, J = 9 cps, aryl CH), 6.46 (4 H doublet, J = 9 cps, aryl CH), and 3.78 (6 H singlet, O–CH_3).

Preparation of the *cis* Acid 5 and Its Derivatives.—A solution of the disodium salt derived from 37 g (0.16 mole) of the *trans* acid **2** in 300 ml of water was irradiated under a nitrogen atmosphere with a Hanovia mercury lamp (450 w) for 24 hr. The solution was acidified and the crude acid was collected and fractionally crystallized from water to separate 10 g (27%) of the less soluble starting *trans* acid **2** and 18 g (49%) of the more soluble *cis* acid **5** as a white solid: mp 165–168° dec (decomposition point dependent on rate of heating); infrared (KBr), 1705

(4) All melting points are corrected and all boiling points are uncorrected. Unless otherwise stated magnesium sulfate was employed as a drying agent. The infrared spectra were determined with a Perkin-Elmer Model 237 infrared recording spectrophotometer fitted with a grating. Unless otherwise noted, all ultraviolet spectra were determined in 95% ethanol with a Cary recording spectrophotometer, Model 14. The nmr spectra were determined at 60 Mc with a Varian Model A-60 nmr spectrometer. The chemical-shift values are expressed either in cycles per second or δ values (parts per million) relative to a tetramethylsilane internal standard. The mass spectra were obtained with a CEC Model 21-130 mass spectrometer. The microanalyses were performed by Dr. S. M. Nagy and his associates and by the Scandinavian Microanalytical Laboratory.

(5) (a) A. M. El-Abbady and L. S. El-Assal, *J. Chem. Soc.*, 1024 (1959); (b) F. G. Badder, L. S. El-Assal, N. A. Doss, and A. H. Shehab, *ibid.*, 1016 (1959); (c) F. G. Baddar, L. S. El-Assal, and M. Gindy, *ibid.*, 1270 (1948).

(6) (a) K. N. Campbell, J. A. Cella, and B. K. Campbell, *J. Am. Chem. Soc.*, **75**, 4681 (1953); (b) A. L. S. Buckle, A. McGookin, and A. Robertson, *J. Chem. Soc.*, 3981 (1954).

(7) The values pK_{MCS}*, the apparent pK_a value in a mixture of 80% Methyl Cellosolve and 20% water, were determined by Dr. W. Simon. For discussion and leading references, see W. Simon, *Angew. Chem. Intern. Ed. Engl.*, **3**, 661 (1964)