Ionic Peroxide Fragmentations[1]

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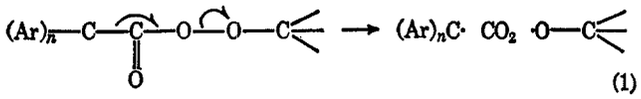
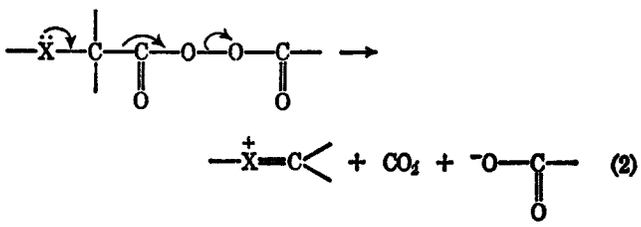
The reaction of α-oxy acids with peroxy acids and N,N′-dicyclohexylcarbodiimide yielded the expected diacyl peroxide only under carefully controlled conditions and then only when the α-oxy group was part of a three-membered ring. The reactions of these peroxides have been studied. Based largely on an examination of products, an ionic fragmentation mechanism has been proposed for their decompositions.

A number of factors influence the ease with which the peroxide bond is broken. For example, location of aryl substituents α to a peroxy ester carbonyl dramatically enhances the rate of homolytic decomposition.[2] This rate acceleration has been attributed to delocalization in the product carbon radical which in turn requires cleavage of both the O–O and C–C bonds in the initial transition state (eq 1). We would like to report



(1)

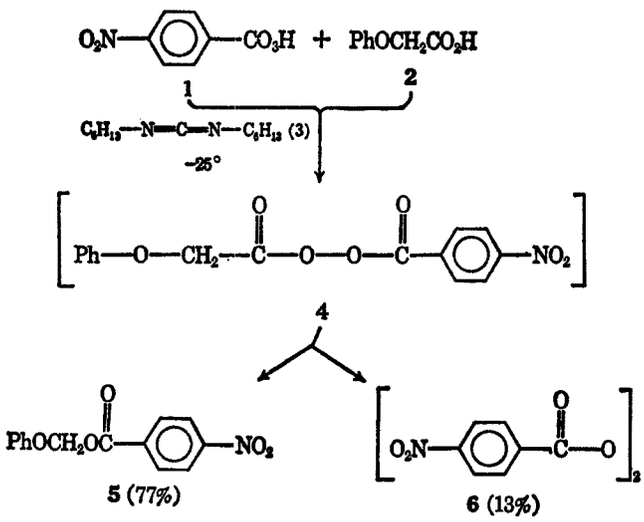
evidence for an ionic concerted cleavage (fragmentation[3]) which is apparently characteristic of certain α-substituted diacylperoxides (eq 2).



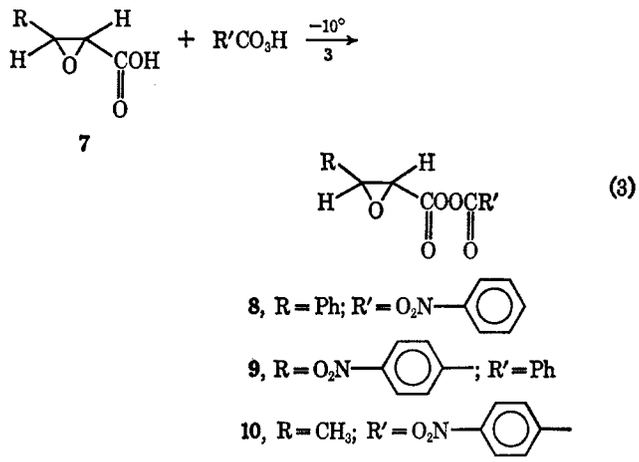
(2)

Our attention was directed to these ionic decompositions by the discovery that the reaction of *p*-nitroperbenzoic acid (**1**) and phenoxyacetic acid (**2**) with N,N′-dicyclohexylcarbodiimide (**3**)[4] failed to yield the expected unsymmetrical peroxide (**4**). The only products which could be isolated were **5** and **6** (Scheme I). Although **4** was considered a possible source of these products, all attempts to isolate or detect this peroxide failed.[5] To understand this remarkably facile reaction, it was necessary to find an isolable analog of **4** and examine its breakdown in a controlled manner.

SCHEME I



If **4** was in fact the precursor of **5** and **6**, the unshared electrons appeared to represent the most probable locus of its instability. Since constraint of a heteroatom within a three-membered ring has been of previous utility in moderating heteroatom electron release,[6] oxirane analogs of **1** (glycidic acids, **7**) were prepared and allowed to react with peroxy acids and **3** at −10° in carbon tetrachloride. Under carefully controlled conditions, unsymmetrical peroxides **8–10** could be prepared and isolated (eq 3). These compounds differed greatly



(3)

in their stability. Solid **10**[7] decomposed quickly at room temperature, whereas solid **8** was stable for several days and solid **9** was unchanged after several weeks at room temperature. Inclusion of nitro groups proved necessary to facilitate isolation and purification of these peroxides.

The initial decomposition of peroxide **8** was observed in deuteriochloroform at room temperature. The product was identified as aldehyde **11** (Scheme II). To investigate this reaction further, peroxide **8** was decomposed in methanol. This solvent was selected because of its nucleophilicity in ionic reactions and its hydrogen-donating ability toward radicals. The major products of this reaction were aldehyde (**12**),

(1) Support of this research by National Science Foundation Grants GP-5531 and GP-8044 is gratefully acknowledged.

(2) P. D. Bartlett and R. R. Hiatt, *J. Amer. Chem. Soc.*, **80**, 1398 (1958).

(3) C. A. Grob, "Theoretical Organic Chemistry," Butterworth and Co. (Publishers) Ltd., London, 1959, p 114.

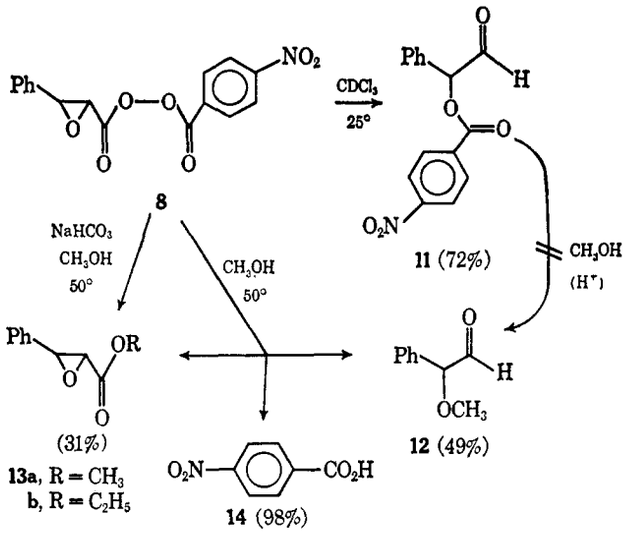
(4) Procedure of F. D. Greene and J. Kazan, *J. Org. Chem.*, **28**, 2168 (1963).

(5) Other methods for the preparation of unsymmetrical peroxides (*cf.* A. G. Davies, "Organic Peroxides," Butterworth and Co. (Publishers) Ltd., London, 1961, p 64) gave the same products in lower yields

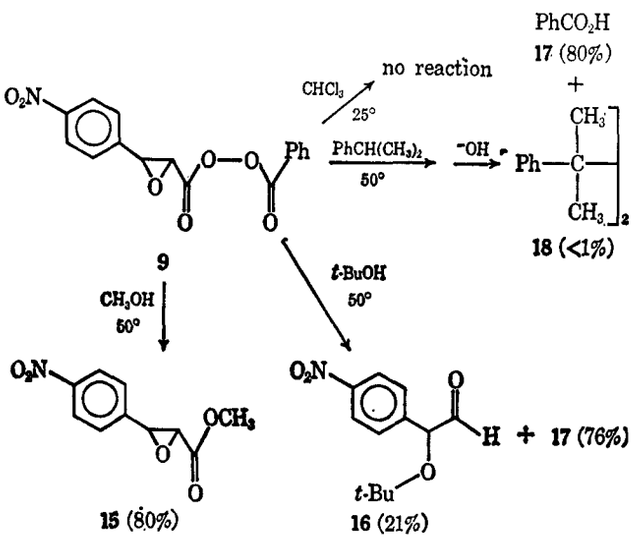
(6) J. A. Deyrup and R. B. Greenwald, *J. Amer. Chem. Soc.*, **87**, 4538 (1965).

(7) The great instability of **10** precluded attainment of analytical purity and thus its further study was not attempted.

SCHEME II



SCHEME III



glycidic ester (**13a**), and *p*-nitrobenzoic acid (**14**). Ester **13a** was apparently the result of solvolytic attack by methanol on the glycidyl carbonyl group. This solvolytic attack was enhanced by added base. Added *p*-nitrobenzoic acid, however, did not affect the product distribution.

The formation of **11** and **12** are indicative of the mechanism of this reaction. Although esters are often observed as minor products of radical coupling,[8] there is no obvious manner or precedent for a radical process leading to ether **12**.[9] Failure to observe hydrogen abstraction from methanol or other products of radical coupling also argues against a radical process. The isolation of *p*-nitrobenzoic acid (**14**) in high yield is in agreement with a nonradical path since aroyloxy radicals generally undergo facile decarboxylation (in the absence of efficient scavangers).[10]

Study of the decomposition of peroxide **9** was complicated by its greater stability and the lability of its products. For example, this peroxide failed to decompose in chloroform after 2 days at room temperature, whereas peroxide **8** was totally decomposed under identical conditions.[11,12]

Attempted decomposition of **9** in methanol resulted solely in methanolysis of the peroxide to give ester **15**[13] (Scheme III). To diminish solvent attack on the carbonyl group, a bulkier alcohol, *t*-butyl alcohol, was chosen. In this solvent, aldehyde **16** and benzoic acid were the only identifiable products. The yield of the latter again points to a nonradical process.

Although it is difficult to choose an appropriate standard for comparison, qualitative results indicate that the decomposition of **9** in *t*-butyl alcohol is considerably faster than that of benzoyl peroxide which is known to break (homolytically) only one O–O bond in the rate-determining step. Thus, 80% of the initial amount of benzoyl peroxide failed to react under those conditions which result in the complete decomposition of **9** (in *t*-BuOH).[14] As a final test of the nonradical nature of the decomposition of **9**, this peroxide was decomposed in cumene at 50°. After all of the material had reacted, the mixture was examined. Less than 1% dicumyl (**18**) was detected along with 80% recoverable benzoic acid (after hydrolysis). No other products could be isolated owing to the difficulty of removing the cumene. It can be concluded that at least 99% of the reaction proceeded *via* an ionic route in spite of the relatively nonpolar nature of this solvent. Efficient geminate recombination of radicals would, of course, invalidate the above argument. The ease with which these reaction intermediates can be intercepted by nucleophilic solvents to yield ethers suggests the absence of cage processes in these decompositions.

The elimination from consideration of possible radical processes requires an ionic mechanism and that this ionic reaction be of lower energy than homolytic alternatives. Attempts to construct a detailed mechanistic picture for the ionic decomposition of these peroxides suggested several alternative possibilities. One such possibility concerns the question of whether the oxirane ring opens in a slow step to some intermediate which could undergo rapid decomposition. Routes of this type were excluded *via* suitable controls which tested the stability of the oxirane ring towards nucleophilic ring opening under the reaction conditions. For example, glycidic ester **13b** was *quantitatively* recovered from methanol in the presence of an equimolar amount of *p*-nitrobenzoic acid. Similar complete inertness to ring opening was also observed for a mixture of **15** and benzoic acid in *t*-BuOH.

Another possible route to the observed products is a carboxy inversion process leading to **20** (eq 4) which could subsequently form the observed products.

(8) D. F. DeTar, 17th Organic Symposium, June 1961, as reported in W. P. Pryor, "Free Radicals," McGraw-Hill, Book Co. Inc., New York, N. Y. 1966, p 257; H. Erlenmeyer and W. Shoenauer, *Helv. Chim. Acta*, **19**, 338 (1936).

(9) It was possible to show (see Experimental Section) that **12** was not formed *via* methanolysis of **11**.

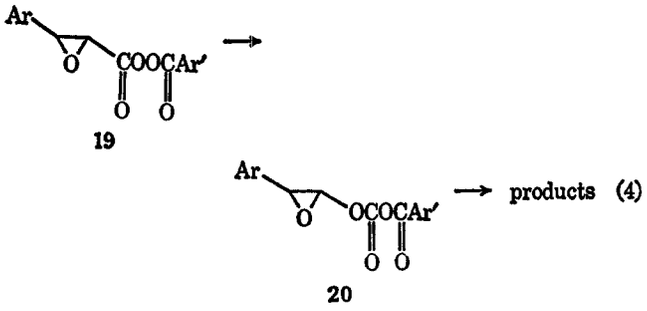
(10) *Cf.* E. Hedaya and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 1661 (1967).

(11) At higher temperatures, although decomposition took place, the products were not stable enough to allow isolation.

(12) The greater stability of **8** is in qualitative agreement with an ionic mechanism which involves electron flow from the oxirane ring toward an aryloate leaving group.

(13) The enhanced formation of glycidic ester at the expense of aldehyde from **9** (compared with **8**) supports the formation of **13** by a methanolysis mechanism.

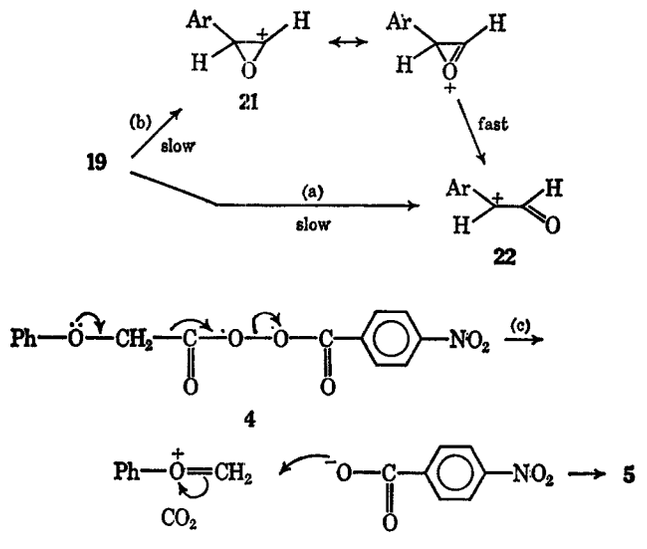
(14) At 83° in *t*-BuOH, benzoyl peroxide required 2 days to react and, after that time, the reaction mixture yielded only 9.9% benzoic acid after base hydrolysis.



Carboxy inversion has ample precedent and constitutes a major path for some diacyl peroxides.[15] It was possible, however, to follow the decomposition of **8** in deuteriochloroform by nmr spectroscopy and in this way ascertain that no detectable amount of **20** was present during or after the reaction. If the carbonate was formed, it must have an exceptionally short lifetime. Although independent preparation of **20** does not seem feasible, existing knowledge concerning carboxy inversion products (carbonates) suggests that **20** should be isolable under our reaction conditions (*i.e.*, room temperature in chloroform).[16-18]

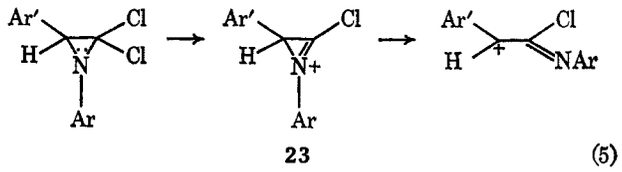
Two paths (Scheme IV) for the decomposition of these peroxides are consistent with the mechanistic

SCHEME IV



requirements discussed above. Both paths a and b yield carbonium ion **22** which is an obvious and reasonable precursor of the observed ester (**11**) and ethers **12** and **16**. Path a implies direct electrocyclic ring opening, whereas path b is a two-step process in which oxirane carbonium ion **21** serves as an intermediate. By analogy to the first step of path b, path c may be written for the decomposition of the unisolated diacyl peroxide **4**.[19-21]

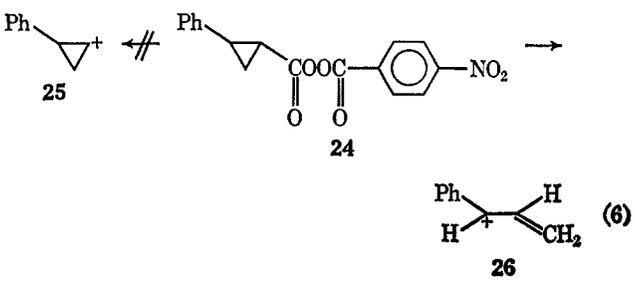
Direct electrocyclic ring opening has been experimentally verified and theoretically discussed for the reactions of cyclopropanol derivatives.[22] The two step process finds ample precedent in the ring opening reactions of 2-haloaziridines (eq 5).[23] For these



(5)

reactions, the intermediacy and properties of **23**,[23] as well as its analogs,[6] have been demonstrated.

In an attempt to distinguish between paths a and b, a homocyclic analog (**24**) of **8** was prepared. The lack of electron-pair stabilization in **25** requires that any heterolytic decomposition of **24** proceed with concerted formation of **26** (eq 6). Since the allylic carbonium ion



(6)

26 should be more stable than ketocarbonium ion **22**,[24] we expected that, if **19** yields **22** directly, **24** should be even more reactive.[25] In fact **24** was exceptionally stable and *no* change was detected in **24** after 2 weeks at 50° in $CDCl_3$.[27] We conclude from this experiment that **21** is a discrete intermediate in the decomposition of **19**. In other words, we conclude that electron donation from oxygen (as in the case of nitrogen[6,23]) *followed* by ring opening offers an energetically more favorable route to ionization than the totally concerted process exhibited by the cyclopropane analogs.

In a recent series of papers, McDonald and coworkers have examined the rearrangement of chloroepoxides (**27**) to chloro ketones (**29**).[28] These workers concluded that **28** is produced without intervention of a cyclic

(15) J. E. Leffler, *J. Amer. Chem. Soc.*, **72**, 67 (1950); D. B. Denney, *ibid.*, **78**, 590 (1956); J. E. Leffler and C. D. Petropoulus, *ibid.*, **79**, 3068, (1957).

(16) C. J. Michejda, D. S. Tarbell, and W. H. Saunders, *ibid.*, **84**, 4113 (1962); D. B. Denny and N. Sherman, *J. Org. Chem.*, **30**, 3760 (1965).

(17) It should be pointed out that Greene has also observed ester formation without intervention of carbonate products in the decomposition of certain diacyl peroxides. In contrast to our reactions, however, he apparently observed several simultaneous (including carboxy inversion) decomposition modes.[18]

(18) F. D. Greene, C. C. Chu, H. P. Stein, and F. M. Vane, *J. Amer. Chem. Soc.*, **86**, 2080 (1964).

(19) The *t*-butyl peroxy ester analog of **4** has recently been prepared and a *homolytic* fragmentation process postulated for it and several closely related compounds.[20] The ability of the leaving group to accommodate negative charge thus appears to play a key role in determining the decomposition mode.

(20) C. Ruchardt, H. Bock, and I. Ruthardt, *Angew. Chem. Intern. Ed. Engl.*, **5**, 253 (1966); D. R. Dixon and A. Pajaczkowski, *Chem. Commun.*, 337 (1966).

(21) The formation of **6** could occur directly from the reaction of **1** and **3** or *via* attack by *p*-nitroperbenzoate on **5**.

(22) *Cf.* C. H. DePuy, *Accounts Chem. Res.*, **1**, 33 (1968).

(23) R. E. Brooks, J. O. Edwards, G. Levy, and F. Smyth, *Tetrahedron*, **22**, 1279 (1966).

(24) *E.g.*, J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 169.

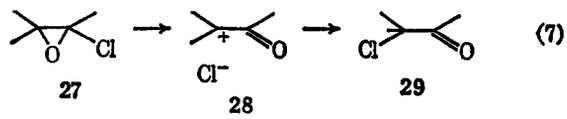
(25) This argument requires that the strain energy of cyclopropane and that of oxirane are essentially the same. Values of 27.5 and 28 kcal (respectively) have been reported.[26]

(26) J. D. Cox, *Tetrahedron*, **19**, 1175 (1963).

(27) In contrast to **8** which had completely reacted within 2 days at 25° in the same solvent.

(28) R. N. McDonald and T. E. Tabor, *J. Amer. Chem. Soc.*, **89**, 6573 (1967), and references therein.

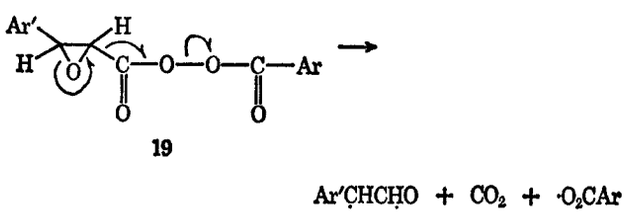
carbonium ion[29] (eq 7). A detailed study of subsituent effects on these reactions is now in progress in hopes of clarifying the mechanism of these ring-opening reactions.



27 28 29 (7)

The failure to observe radical processes deserves some comment. Free-radical substitution α to an ether oxygen has been extensively documented.[30] The oxirane radical itself is known as an intermediate in the free-radical chlorination of epoxides by *t*-BuOCl at 70°.[31] It is interesting to note that, in contrast to the ionic reactions discussed above, the radical chlorination apparently can proceed without ring opening under the reaction conditions. In addition to concerted homolytic O–O rupture, a second free-radical path is also avaliable to **19**. The importance of multiple-bond homolyses which yield delocalized free radicals has already been mentioned and suggested the possibility shown in Scheme V. Although the product radical, **30**,

SCHEME V

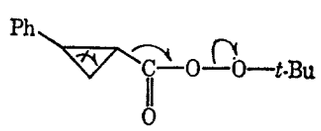


19

Ar'ĊHCH̥O + CO_2 + $\cdot O_2CAr$

30

would meet the delocalization requirement, this radical fragmentation is not observed. A similar failure to observe either multiple bond homolysis or ring opening in the free-radical decomposition of **31** and other related cyclopropyl peroxy esters has been described.[32]



31

The ionic character of these peroxide decompositions, in spite of reasonable homolytic alternatives, indicates a considerable driving force for the heterolytic route. Our results suggest that other suitably located electron-rich sites (*i.e.*, those carbon and heteroatom systems which can serve as neighboring groups in solvolytic ionization) might also promote similar ionic fragmentations. In addition to providing new carbonium ion sources, it is also possible that these mild fragmentations in nonpolar solvents could be of degradative, synthetic, and protective utility. Explorations of these possibilities as well as further examination of the chemistry of oxirane carbonium ions are in progress.

(29) R. N. McDonald and P. A. Schwab, *J. Org. Chem.*, **29**, 2459 (1964).
(30) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, p 479.
(31) C. Walling and P. S. Fredericks, *J. Amer. Chem. Soc.*, **84**, 3326 (1962).
(32) R. D. Swigert, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1964.

Experimental Section[33]

***trans*-3-Methylglycidyl *p*-Nitrobenzoyl Peroxide.**—To a cold solution of 100 ml of carbon tetrachloride and 630 mg (6.2 mmol) of *trans*-3-methylglycidic acid[34] was added 1.28 g (6.2 mmol) of N,N′-dicyclohexylcarbodiimide (Aldrich) and 1.13 g (6.2 mmol) of *p*-nitroperbenzoic acid[35] and the mixture was allowed to stir at 0° for 4 hr. The N,N′-dicyclohexylurea (1.2 g, 87%) was filtered and washed with chloroform. The filtrate was evaporated at 0° under reduced pressure to give 1.51 g (92%) of crude product. Some purification (by nmr analysis) was achieved by redissolving the residue in CCl_4 and reevaporation. As solids started to separate, they were filtered, and the center cuts gave a relatively pure sample of white solid: mp 70° (with explosion); ir (Nujol) 1780 and 1810 cm^{-1} (C=O); nmr ($CDCl_3$) δ 8.54–8.14 (m, 4, aromatic), 3.64–3.36 (m, 2, CHCH), 1.50 (d, 3, J = 5 Hz, CH_3). The sample starts to decompose noticeably within 1 hr with development of ir absorption at 1700 cm^{-1}.

Potassium *trans*-3-Phenylglycidate.—A solution of 5 g of potassium hydroxide in 30 ml of ethanol was added with stirring to a solution of 10 g (52 mmol) of ethyl *trans*-3-phenylglycidate in 20 ml of ethanol at a temperature below 15°. The precipitate was immediately filtered, washed with 30 ml of ethanol, and dried [room temperature (0.5 mm)] yielding 7.2 g (70%) of the salt: nmr (D_2O) δ 7.71 (s, 5, Ph), 4.37 (d, 1, J = 2 Hz, CHCO), 3.94 (d, 1, J = 2 Hz, CHCO), 3.94 (d, 1, J = 2 Hz, CHPh).

***trans*-3-Phenylglycidic Acid.**—Potassium *trans*-3-phenylglycidate (3 g, 15 mmol) was dissolved in a minimum amount of water and 140 ml of 0.1 *N* hydrochloric acid was added. The acid solution was extracted five times with 25 ml of chloroform. The solution was dried over sodium sulfate, 25 ml of carbon tetrachloride was added, and the solution was evaporated yielding 2 g (88%) of a white solid: mp 80–84° (lit.[36] mp 83–84°); nmr ($CDCl_3$) δ 7.30 (s, 5, Ph), 4.12 (d, 1, J = 1.5 Hz, CHCO), 3.53 (d, 1, J = 1.5 Hz, CHPh). The acid was used immediately since it decomposes on standing.

***p*-Nitrobenzoyl *trans*-3-Phenylglycidyl Peroxide.**—To a cooled (−9°) solution of 175 ml of carbon tetrachloride and 1 g (6.1 mmol) of *trans*-3-phenylglycidic acid, 1.26 (6.1 mmol) of N,N′-dicyclohexylcarbodiimide (Aldrich) and 1.11 g (6.1 mmol) of *p*-nitroperbenzoic acid (90% active oxygen) were added simultaneously. The mixture was stirred at −9° for 5 hr. The carbon tetrachloride was evaporated, 50 ml of chloroform was added, and the urea was removed by filtration. The chloroform solution was evaporated and the remaining solid was washed with methanol, 1.7 g (85%). The peroxide was recrystallized from chloroform by addition of methanol giving white plates: mp 88° with rapid decomposition; ir (Nujol) 1760 and 1790 cm^{-1} (C=O); nmr ($CDCl_3$) δ 8.28 (d, 4, J = 1.7 Hz, NO_2Ph), 7.36 (s, 5, Ph), 4.32 (d, 1, J = 1.5 Hz, CHPh).

Anal. Calcd for $C_{16}H_{11}O_7N$: C, 58.36; H, 3.27; N, 4.25. Found: C, 58.50; H, 3.40; N, 4.18.

2-*p*-Nitrobenzoyloxy-2-phenylacetaldehyde.—*p*-Nitrobenzoyl *trans*-3-phenylglycidyl peroxide was dissolved in deuteriochloroform and allowed to stand at room temperature for 2 days. The deuteriochloroform was then evaporated and the residue was dissolved in carbon tetrachloride: ir (CCl_4) 1750 cm^{-1} (C=O); nmr (CCl_4) δ 9.22 (s, 1, HCO), 7.94 (s, 4, HO_2Ph), 7.14 (s, 5, Ph), 6.00 (s, 1, PhCH). Based on the integrated relative areas of the δ 9.22 or 6.00 singlets *vs.* the 7.14 aryl absorption, the percentage conversion into 2-*p*-nitrobenzoyloxy-2-phenylacetaldehyde was 72%. This reaction product was dissolved in methanol and converted to 2-*p*-nitrobenzoyloxy-2-phenylacetaldehyde 2,4-dinitrophenylhydrazone according to standard procedure.[37] The sparingly soluble orange solid was recrystallized from ethanol–ethyl acetate: mp 187–189°; ir (Nujol) 1710 cm^{-1} (C=O).

(33) All melting points are uncorrected. Chemical shifts of nmr spectra run in organic solvents are reported in parts per million downfield from internal tetramethylsilane (δ). Chemical shifts of nmr spectra run in D_2O are reported in parts per million downfield from a point 4.99 ppm upfield from the DOH peak.
(34) G. Braun, *J. Amer. Chem. Soc.*, **52**, 3185 (1930).
(35) L. S. Silbert, E. Siegel, and D. Swern, *J. Org. Chem.*, **27**, 1336 (1962).
(36) W. Dieckman, *Ber.*, **43**, 1035 (1910).
(37) D. Y. Curtin, R. C. Fuson, and R. L. Shriner, "The Systematic Identification of Organic Compounds," 5th ed, John Wiley & Sons, Inc., New York, N. Y., 1964, p 256.

Anal. Calcd for $C_{21}H_{15}O_8N_5$: C, 54.20; H, 3.25; N, 15.05. Found: C, 54.04; H, 3.49; N, 15.10.

Decomposition of *p*-Nitrobenzoyl *trans*-3-Phenylglycidyl Peroxide in Methanol.—To 20 ml of methanol at 50° was added 208 mg (0.63 mmol) of *p*-nitrobenzoyl *trans*-3-phenylglycidyl peroxide. The mixture was allowed to stand at 50° for 20 hr and then the methanol was evaporated. The solids were washed with carbon tetrachloride yielding 104 mg (98%) of *p*-nitrobenzoic acid, mp 240–242° (lit.[38] mp 241.5°). The ir spectrum was identical with that of an authentic sample. The nmr spectrum of the carbon tetrachloride filtrate showed 2-methoxy-2-phenylacetaldehyde (49%) and methyl *trans*-3-phenylglycidate (31%).[39] A small (*ca.* 5% of the total OCH_3 peaks) absorption due to methyl *p*-nitrobenzoate was also detected.

This product identification was confirmed by molecular distillation of the crude reaction mixture at 50–60° (hot air-bath temperature) under vacuum (0.5 mm). In this manner, two fractions were obtained.

The more volatile (collected at 0°) was nearly pure 2-methoxy-2-phenylacetaldehyde: ir (neat) 1740 cm^{-1} (C=O); nmr (CCl_4) δ 9.32 (d, 1, J = 2 Hz, CHO), 7.18 (s, 5, Ph), 4.34 (d, 1, J = 2 Hz, PhCH), 3.36 (s, 3, CH_3). Traces of impurity could not be removed by distillation on this scale and thus structure proof was accomplished *via* oxidation of the aldehyde to 2-methoxy-2-phenylacetic acid. For this purpose, a solution of 105 mg (0.36 mmol) of potassium dichromate in 3.6 ml of aqueous sulfuric acid was added to 152 mg (1 mmol) of the distilled 2-methoxy-2-phenylacetaldehyde. The suspension was stirred on a steam bath for 5 min, cooled, and extracted with ethyl ether. The ether was evaporated and the resulting oil was dissolved in benzene and dried over magnesium sulfate. The oil from benzene evaporation crystallized on standing at room temperature. The acid was recrystallized from petroleum ether yielding 95 mg (57%) of transparent crystals: mp 69–70° (lit.[40] mp 68°); ir (Nujol) 1745 cm^{-1} (C=O); nmr (CCl_4) δ 11.6 (s, 1, OH), 7.30 (s, 4, Ph), 4.46 (s, 1, CH), 3.36 (s, 3, OCH_3).

The less volatile fraction consisted of methyl *trans*-3-phenylglycidate in addition to smaller amounts of the aldehyde and methyl *p*-nitrobenzoate. The absorption pattern of the major component was characteristic and identical with that of the product formed from the decomposition of this peroxide in methanol in the presence of sodium bicarbonate.

Decomposition of *p*-Nitrobenzoyl *trans*-3-Phenylglycidyl Peroxide in Methanol in the Presence of *p*-Nitrobenzoic Acid.—A mixture of 166 mg (0.51 mmol) of the above peroxide, 84 mg (0.51 mmol) of *p*-nitrobenzoic acid, and 15 ml of methanol was heated at 50° for 24 hr. The methanol was removed and the residue was taken up in CCl_4. The resultant nmr spectrum was almost identical with that of the product obtained without added acid. No detectable change was observed in the aldehyde/ester ratio.

Decomposition of *p*-Nitrobenzoyl *trans*-3-Phenylglycidyl Peroxide in Methanol in the Presence of Sodium Bicarbonate.—A mixture of 279 mg (0.82 mmol) of *p*-nitrobenzoyl *trans*-3-phenylglycidyl peroxide, 10 ml of methanol, and a twofold excess of sodium bicarbonate was allowed to stand at 50° for 24 hr. The methanol was evaporated and the solid was washed with carbon tetrachloride. The solid was identified as *p*-nitrobenzoic acid by its mp 240–242° (lit.[38] mp 241.5°) and its ir spectrum which was superimposable on that of an authentic sample. Evaporation of the CCl_4 yielded an oil. Analysis of this oil by nmr spectroscopy indicated the presence of methyl 3-phenylglycidate [nmr (CCl_4) δ 7.26 (s, 5, Ph), 3.98 (d, 1, J = 1.5 Hz, CHCO), 3.76 (s, 3, CH_3), 3.32 (d, 1, J = 1.5 Hz, CHPh)] and methyl *p*-nitrobenzoate (1.7:1). No other products were present. This oil was dissolved in ethanol and an excess of potassium hydroxide was added at 0°. After 7 min, the precipitate was filtered and dried at room temperature under vacuum for 3 hr. The nmr spectrum (D_2O) of this material was superimposable on that previously described for potassium *trans*-3-phenylglycidate.

Reaction of 2-*p*-Nitrobenzoyloxy-2-phenylacetaldehyde in Methanol.—A sample of *p*-nitrobenzoyl *trans*-3-phenylglycidyl peroxide was allowed to decompose in deuteriochloroform at room temperature for 2 days. The deuteriochloroform was evaporated. The nmr spectrum showed 2-*p*-nitrobenzoyloxy-2-phenylacetaldehyde. The oil, which contained some *p*-nitrobenzoic acid, was dissolved in methanol and the solution was allowed to stand at 50° overnight. After evaporation of the methanol, neither 2-*p*-nitrobenzoyloxy-2-phenylacetaldehyde nor 2-methoxy-2-phenylacetaldehyde was observed in the complex nmr spectrum.

Methyl *trans*-3-*p*-Nitrophenylglycidate.—In a flame-dried apparatus flushed with nitrogen, a mixture of 15.1 g (0.1 *m*) of *p*-nitrobenzaldehyde and 17.4 g (0.16 *m*) methyl α-chloroacetate in 50 ml of 1,2-dimethoxyethane was cooled in a salt–ice bath and 18.2 g (0.16 *m*) powdered potassium *t*-butoxide added over 1 hr. The dark mixture was allowed to stir at that temperature for 2 hr, then slowly brought to room temperature, and stirred overnight. Dilute hydrochloric acid was added to neutralize the base and 300 ml of water added. The gummy residue was filtered and washed with 300 ml ethyl ether to yield a tan solid. The solid was recrystallized from ethanol yielding 7.1 g (31.8%) of long pale yellow needles: mp 139–140.5°; ir (Nujol) 1750 cm^{-1} (C=O); nmr ($CDCl_3$) δ 8.3–7.4 (m, 4, NO_2Ph), 4.24 (d, 1, J = 2 Hz, $CHNO_2Ph$), 3.87 (s, 3, OCH_3), 3.51 (d, 1, J = 2 Hz, CHCO).

Anal. Calcd for $C_{10}H_9NO_5$: C, 53.81; H, 4.06; N, 6.28. Found: C, 53.60; H, 3.94; N, 6.14.

***trans*-3-*p*-Nitrophenylglycidic Acid.**—An excess of potassium hydroxide was added to a mixture of 5 g (22.4 mmol) of methyl *trans*-3-*p*-nitrophenylglycidate in 10 ml of water at 0°. Enough ethanol was added to dissolve the ester. After a few minutes, the solution was acidified with excess hydrochloric acid and the ethanol was evaporated. The acid precipitated out of water and was recrystallized from ethanol yielding 4.6 g (96%) of pale yellow platelets: mp 186–188° (lit.[41] mp 186–188°); ir (Nujol) 1700 cm^{-1} (C=O).

Benzoyl *trans*-3-*p*-Nitrophenylglycidyl Peroxide.—To a cooled solution of 150 ml of carbon tetrachloride and 2 g (14 mmol) of *trans*-*p*-nitrophenylglycidic acid, 1.95 g (14 mmol) of N,N′-dicyclohexylcarbodiimide and 1.31 g (14 mmol) of perbenzoic acid were added simultaneously. The mixture was stirred at salt–ice bath temperature for 5 hr. The carbon tetrachloride was evaporated, 50 ml of chloroform was added, and the N,N′-dicyclohexylurea was removed by filtration. The chloroform filtrate was evaporated and the residual solid was recrystallized from chloroform by addition of methanol, yielding 1.45 g (30%) of peroxide: mp 108–108.5° with vigorous decomposition; ir (Nujol) 1760 and 1800 cm^{-1} (C=O); nmr ($CDCl_3$) δ 8.40–7.48 (m, 9, aromatic), 4.44 (d, 1, J = 1.5 Hz, CHCO), 3.77 (d, 1, J = 1.5 Hz, CHPh).

Anal. Calcd for $C_{16}H_{11}O_7N$: C, 58.36; H, 3.37; N, 4.25. Found: C, 58.40; H, 3.44; N, 4.23.

Decomposition of Benzoyl *trans*-3-*p*-Nitrophenylglycidyl Peroxide in Methanol.—A mixture of 0.257 g (0.78 mmol) of benzoyl *trans*-3-*p*-nitrophenylglycidyl peroxide and 10 ml of methanol was allowed to stand at 50° for 3 days. The methanol was evaporated and the solids were washed with carbon tetrachloride. The solid (127 mg, 80%) was identified as methyl *trans*-3-*p*-nitrophenylglycidate, mp 138–140°. The ir and nmr spectra were identical with those of the previously prepared sample.

Decomposition of Benzoyl *trans*-3-*p*-Nitrophenylglycidyl Peroxide in *t*-Butyl Alcohol.—A mixture of 255 mg (0.78 mmol) of benzoyl *trans*-3-*p*-nitrophenylglycidyl peroxide and 10 ml of *t*-BuOH was heated at 50° for 3 days. The alcohol was evaporated under vacuum.

The residue was dissolved in $CHCl_3$ and extracted with dilute sodium bicarbonate. Acidification of the aqueous solution and extraction with ether yielded, after drying and solvent removal, a solid. This solid was sublimed to give 72 mg (76%) of benzoic acid, mp 119–122°, which was identified by melting point and ir spectrum. Repetition of this decomposition in *t*-BuOH at 50° in which the entire original reaction residue was hydrolyzed at room temperature with aqueous sodium hydroxide yielded, after repetition of the above isolation procedure, 82% benzoic acid.

(38) "Dictionary of Organic Compounds," 4th ed, J. R. A. Pollock and R. S. Stevens, Ed., Oxford University Press, New York, N. Y., 1965, p 2437.

(39) Since the major products could not be quantitatively isolated, these percentage yields were calculated from the nmr spectrum. The total area of the aryl region was defined as 100%. Five times the integrated area of a single proton divided by the area of the aryl region thus represents the percentage yield of a given component.

(40) A. McKenzie, *J. Chem. Soc.*, **75**, 753 (1899).

(41) E. Kleucker, *Ber.*, **55**, 1634 (1922).

The nmr spectrum of the neutral material revealed a major product which was assigned as 2-*t*-butoxy-2-*p*-nitrophenylacetaldehyde: nmr (CCl_4) δ 9.30 (d, 1, J = 2 Hz, CHCO), 8.2–7.2 (m, aromatic), 4.82 (d, 1, J = 2 Hz, CHPh), 1.26 (s, 9, C_4H_9). The structure was assigned on the basis of the nmr spectrum which is analogous to the that of 2-methoxy-2-phenylacetaldehyde. This aldehyde was formed in 20% yield. A second decomposition under the same conditions gave a yield of 22%.[42] Equal-intensity singlets present in several runs at δ 9.58 and 6.16 can tentatively be assigned (by analogy) to 2-benzoyloxy-2-*p*-nitrophenylacetaldehyde.

Attempts at isolating the 2-*t*-butoxy-2-phenylacetaldehyde by crystallization, chromatography, or distillation were unsuccessful. For this reason, several chemical transformations of the reaction mixture were explored.

The residue (191 mg) from the decomposition of 0.675 mmol of benzoyl 3-*p*-nitrophenylglycidyl peroxide was stirred at steam-bath temperature for 10 min in 10% sulfuric acid solution containing 105 mg of potassium dichromate. Only *p*-nitrobenzoic acid 43 mg (38%) was recovered in the acid fraction. The reaction was run at room temperature overnight and again yielded the identical acid. Oxidation was attempted at room temperature in a water–acetone system with excess silver oxide, but *p*-nitrobenzoic acid was again the sole product.

The residue from the decomposition of 304 mg (0.92 mmol) of benzoyl *trans*-3-*p*-nitrophenylglycidyl peroxide in *t*-BuOH was dissolved in 3 ml of ethanol and added to a solution 350 mg (9.2 mmol) of sodium borohydride in 20 ml of ethanol. The solution was allowed to stir overnight. About 20 ml of water was added and the solution was heated on the steam bath for 5 min. After cooling, the ethanol was evaporated and the product extracted into chloroform. The components were separated by thick layer chromatography on alumina with chloroform. The 2-*t*-butoxy-2-*p*-nitrophenylethanol was collected at R_F 0.6 as an oil: nmr (CCl_4) δ 8.2–7.4 (m, 4, aromatic), 4.6 (*t*, 1, J = 7 Hz, $CHCH_2OH$), 3.4 (broad *t*, 2, CH_2OH), 2.0 (broad t, 1, OH), 1.17 (s, 9, OC_4H_9). This oil could not be crystallized and was, therefore, converted into a phenylurethan derivative according to a standard procedure.[43] A white solid was obtained from CCl_4–petroleum ether (bp 00–00°): mp 69–71°; nmr (CCl_4) δ 8.3–7.0 (m, aromatic), 4.74 (t, 1, J = 7 Hz, $CHCH_2$), 4.00 (d, 2, J = 6 Hz, $CHCH_2$), 1.13 (s, 9, OC_4H_9); mass spectrum (70 eV) *m/e* (rel intensity) 358 (2.2), 328 (0.6), 208 (0.4), 119 (57.5), 117 (53.3), 57 (100) (expected: 358). Difficulties in obtaining and purifying this material did not permit obtaining a sample of analytical purity.

Decomposition of Benzoyl Peroxide in *t*-Butyl Alcohol.—A mixture of 500 mg (2.1 mmol) of benzoyl peroxide and 10 ml of *t*-BuOH was allowed to stand at 50° for 3 days. The alcohol was evaporated. The melting point and ir spectrum of the remaining white solid (416 mg, 83%) were identical with those of the starting material.

A mixture of 550 mg (2.3 mmol) of benzoyl peroxide and 15 ml of *t*-BuOH was refluxed for 2 days. The alcohol was evaporated and the product was hydrolyzed in aqueous sodium hydroxide at room temperature overnight. The basic solution was washed with chloroform and acidified with hydrochloric acid and the product was extracted into chloroform. The chloroform was evaporated and the residue was sublimed at 50° under vacuum to yield 54 mg (9.9%) of a white solid, mp 96–115°. The ir spectrum showed benzoic acid.

Decomposition of Benzoyl 3-*p*-Nitrophenylglycidyl Peroxide in Cumene.—Cumene was shaken with concentrated sulfuric acid until the acid remained colorless. It was washed three times with aqueous sodium bicarbonate solution and four times with water, dried over magnesium sulfate, and passed through activated silica. The cumene was then refluxed over sodium under nitrogen for 24 hr and distilled under nitrogen through a 40-cm, helices-packed, vacuum-jacketed column at a reflux ratio of 10:1. Cumene was collected at 152° (760 mm) and stored in the dark under nitrogen.

A sample of 101 mg (0.307 mmol) of benzoyl *trans*-3-*p*-nitrophenylglycidyl peroxide in about 10 ml of cumene was degassed and sealed under nitrogen. It was allowed to stand at 50° for 4 days in the dark. The sample was brought to exactly 10 ml and examined by gas chromatography. Comparison with an authentic equimolar solution of dicumyl showed the peroxide decomposition mixture to contain no detectable dicumyl. After distillation of cumene, the reaction mixture was hydrolyzed and the acidic products were sublimed to give 80% of benzoic acid, mp 120–122°.

Stability of Substituted Oxiranes toward Acid-Catalyzed Decomposition in Alcohol. A.—A solution of 121 mg (0.63 mmol) of ethyl *trans*-3-phenylglycidate and 105 mg (0.63 mmol) of *p*-nitrobenzoic acid in 20 ml of methanol was allowed to stand at 50° for 20 hr and the methanol was evaporated. The residue was separated into its components by extraction of the ester with carbon tetrachloride. The nmr spectra and weights of the two fractions revealed that the original materials had been recovered in quantitative yield.

B.—A mixture of 95 mg (0.78 mmol) of benzoic acid and 174 mg of (0.78 mmol) methyl *trans*-3-*p*-nitrophenylglycidate in 10 ml of *t*-BuOH was heated at 50° for 3 days. The mixture was then cooled and evaporated to give 269 mg of residue which was identified by nmr spectroscopy as an equimolar mixture of two starting materials.

Phenoxymethyl *p*-Nitrobenzoate.—A solution of 732 mg (4 mmol) *p*-nitroperbenzoic acid and 760 mg (5 mmol) phenoxyacetic acid in 40 ml each of CH_2Cl_2 and Et_2O was cooled to −25°. A cooled solution of N,N′-dicyclohexydicarbodiimide in 10 ml of CH_2Cl_2 was added rapidly with stirring. The urea began to precipitate within 45 sec. After 24 hr at −25°, the reaction was filtered and the filtrate was washed with water and 10% Na_2CO_3. After the mixture was dried, the solvents were evaporated. The residue was extracted with hot cyclohexane which yielded 840 mg (77%) of phenoxymethyl *p*-nitrobenzoate: mp 101–101.5°; ir ($CHCl_3$) 1773 cm^{-1} (C=O); nmr $CDCl_3$ δ 6.7–8.25 (m, 9, aromatic), 6.0 (s, 2, OCH_2O); mass spectrum (70 eV) *m/e* (rel intensity) 273 (13), 243 (31), 150 (100), 120 (13), 104 (32).

Anal. Calcd for $C_{14}H_{11}NO_5$: C, 61.55; H, 4.06. Found: C, 61.64; H, 4.17.

The cyclohexane-insoluble residue was extracted with chloroform. Evaporation of the chloroform gave 900 mg of material which was spectrally identified as 4,4′-dinitrobenzoyl peroxide. The yield of phenoxymethyl *p*-nitrobenzoate based on available peracid was 90%.

***p*-Nitrobenzoyl *trans*-2-Phenylcyclopropylcarboxoyl Peroxide.**—*p*-Nitroperbenzoic acid (100 g, 0.55 mmol) and N,N′-dicyclohexylcarbodiimide (1.00 g, 0.62 mmol) were added simultaneously to a cooled solution of *trans*-2-phenylcyclopropanecarboxylic acid (1.27 g, 0.62 mmol) in 150 ml of carbon tetrachloride. The mixture was allowed to stir at ice-bath temperature for 5 hr. The carbon tetrachloride was evaporated, 50 ml of chloroform was added and the N,N′-dicyclohexyl urea was removed by filtration. The chloroform was evaporated and the residual solid was recrystallized from chloroform by addition of ethanol yielding 1.08 g (57%) of the peroxide. The analytical sample was prepared by dissolving a sample partially in chloroform, filtering, eluting the solution through a 2-cm column of 20% deactivated alumina with chloroform, and recrystallizing the peroxide twice by addition of ethanol with about 50% loss of material. The sample was dried at room temperature under vacuum (0.2 mm) for 12 hr: mp 114–116° with evolution of gas; ir (Nujol) 1760 with a shoulder at 1780 cm^{-1} (C=O); nmr ($CDCl_3$) δ 7.1–8.34 (m, aromatic), 2.52–2.9 (m, 1, CHPh), 1.4–2.23 (m, 3, ring protons).

Anal. Calcd for $C_{17}H_{13}O_6N$: C, 62.38; H, 4.00; N, 4.28. Found: C, 62.17; H, 4.06; N, 4.13.

Decomposition of *p*-Nitrobenzoyl *trans*-2-Phenylcyclopropylcarboxyl Peroxide.—A saturated solution (about 10%) of *p*-nitrobenzoyl *trans*-2-phenylcyclopropylcarboxyl peroxide in deuterated chloroform failed to show any change in the nmr spectrum after standing at 50° for 2 weeks.

Registry No.—*trans*-3-Methylglycidyl *p*-nitrobenzoyl peroxide, 19190-77-3; potassium *trans*-3-phenylglycidate, 19190-78-4; *trans*-3-phenylglycidic acid, 1566-68-3; *p*-nitrobenzoyl *trans*-3-phenylglycidyl peroxide, 19190-79-5; 2-*p*-nitrobenzoyloxy-2-phenylacetaldehyde hydrazone, 19202-49-4; 2-methoxy-2-phenylacetaldehyde, 19190-53-5; methyl *trans*-3-phenylglycidate, 19190-80-8; methyl *trans*-3-*p*-

(42) The same method of calculating yields was used as previously described.[34] In this case, however, the integrated area of a single proton was multiplied by four.

(43) Reference 37, p 229.

nitrophenylglycidate, 19202-48-3; benzoyl *trans*-3-*p*-nitrophenylglycidyl peroxide, 19190-81-9; 2-*t*-butoxy-2-*p*-nitrophenylacetaldehyde, 19202-50-7; 2-*t*-butoxy-2-*p*-nitrophenylethanol, 19190-54-6; 2-*t*-butoxy-2-*p*-nitrophenylethanol phenylurethan derivative, 19190-55-7; phenoxymethyl *p*-nitrobenzoate, 19190-56-8; *p*-nitrobenzoyl *trans*-2-phenylcyclopropylcarboxoyl peroxide, 19202-51-8.

Synthesis of Perfluoroalkyl Vinyl Ether Acids and Derivatives

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Potassium salts of certain perfluorodicarboxylic acids have been found to undergo a monodecarboxylation to yield perfluoroalkyl vinyl ether acid salts in low yield. Various carboxyl derivatives were prepared.

Although alkyl trifluorovinyl ethers, $ROCF{=}CF_2$, in which R is a hydrocarbon alkyl group can be prepared by the reaction of an alkali metal alkoxide with tetrafluoroethylene (TFE), this procedure generally fails when an alkali metal perfluoroalkoxide is used. An exception is the reaction of potassium perfluoroisopropoxide with fluorinated cyclobutene to give the vinyl ether.[2] In most cases the fluoroalkoxide anion prefers to lose fluoride ion rather than react with the fluoroolefin. The most convenient preparation of perfluoroalkyl vinyl ethers is by pyrolysis of certain fluorinated ether acid salts *via* the following reaction.

$$R_FOCF(CF_3)CO_2M \xrightarrow{\Delta} R_FOCF{=}CF_2$$[3]

This general procedure has now been refined so that a selective pyrolysis of only one of the carboxyl groups to certain perfluoroalkyldicarboxylic acid salts can be carried out. Thus the reaction can now be used of prepare, although in low over-all yield, functionally substituted perfluoroalkyl vinyl ethers, a new class of compounds. The vinyl ether esters and nitriles can be copolymerized with other fluorinated monomers such as TFE and vinylidene fluoride and other perfluoroalkyl vinyl ethers.

The type of dicarboxylic acid salt used is illustrated in IV, in which the rate of pyrolysis of the carboxyl group on the more substituted α-carbon (b) is faster than the rate of pyrolysis of the other end (a). Pyrolyses of this nature in the perfluorocarbon series are thought to proceed through a carbanion intermediate. The carbanion resulting from pyrolysis at (b) should be more stable due to the delocalizing ability of the α-CF_3 group. A fluorine α to a carbanion is known to have much less delocalizing ability than a fluorine β to the negative charge[4] due to an inductive effect through space.[5]

Compound I is easily prepared by the reaction of hexafluoropropylene epoxide (HFPO)[6] with a diacid fluoride to give the unsymmetrical adduct.[7] This reaction, carried out at $-30°$ in diglyme with cesium fluoride catalyst, involves initial reaction of cesium fluoride with a carbonyl group to give a perfluoroalkoxide, which then attacks the electrophilic center carbon of HFPO to produce I in about 70% yield.

$$CF_3CF\underset{}{\overset{O}{\diagdown\diagup}}CF_2 + FC(=O)(CF_2)_{n-1}CF(=O) \xrightarrow{CsF} FC(=O)(CF_2)_nOCF(CF_3)CF(=O)F_3C$$

Ia, $n = 3$
b, $n = 4$

$$Ib \xrightarrow{KOH} KO_2C(CF_2)_4OCF(CF_3)CO_2K \xrightarrow{\Delta} CF_2{=}CF(CF_2)_2OCF{=}CF_2$$

(a) (b) IVb II

$$IV \xrightarrow[k_1]{\Delta} {}^-CF_2(CF_2)_{n-1}OCF(CF_3)CO_2K \quad (a)$$

$$IV \xrightarrow[k_2]{\Delta} KO_2C(CF_2)_nOCF^- \quad (b)$$

$k_2 > k_1$

Evidence of such a difference in the rate of pyrolysis came from the discovery of small amounts of monodecarboxylated product in the pyrolysis of the potassium salt IVb during preparation of the diene II. This product was isolated as the vinyl ether acid, perfluoro-6-oxa-7-octenoic acid (III). The normal temperature

$$CF_2{=}CFO(CF_2)_4CO_2H$$
III

for complete pyrolysis of IVb to the diene II[8] is 200–225°. Infrared and glpc analyses of the product from complete pyrolysis also give evidence of smaller amounts of the internal olefin $CF_3CF{=}CFCF_2OCF{=}CF_2$, which is produced by double-bond migration. For mono-

$$KO_2C(CF_2)_nOCF(CF_3)CO_2K \xrightarrow{185°} KO_2C(CF_2)_nOCF{=}CF_2 +$$
IV Va, b, 25%

$$FC(=O)(CF_2)_nOCF{=}CF_2 + KO_2C(CF_2)_nOCHFCF_3$$
VIa, b, ~2% VII

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(2) R. W. Anderson, N. L. Madison, and C. I. Merrill, Abstracts, Fourth International Symposium on Fluorine Chemistry, Estes Park, Colo., July 1967, p 64.

(3) C. G. Fritz and S. Selman, U. S. Patent 3,291,843 (1966).

(4) S. Andreades, *J. Amer. Chem. Soc.*, **86**, 2003 (1964).

(5) A. Streitwieser, Jr., and D. Holtz, *ibid.*, **89**, 692 (1967); A. Streitwieser, Jr., A. P. Marchand, and A. H. Pudjaatmaka, *ibid.*, **89**, 693 (1967).

(6) For a synthesis of HFPO see British Patent 904,877 (1962); *Chem. Eng. News*, **45**, (33), 18 (1967).

(7) C. G. Fritz and E. P. Moore, U. S. Patent 3,250,807 (1966).

(8) Compound II was first synthesized by this method by Dr. Charles G. Fritz, Plastics Department, E. I. duPont de Nemours & Co., Inc.