black in color, was divided into two parts for gas chromatographic analysis. The lower boiling compounds (2-butanone and chloroform) were determined on an F & M Model 5750 gas chromatograph equipped with a Mosley recorder and disk integrator using a 15 ft by 0.25 in. column packed with 17% E-600 on Chromosorb W. Ethyl acetate was used as the internal standard for these analyses. The higher boiling components of the reaction mixture (unreacted I and *p*-cresol) were determined on the same chromatograph using a 5 ft by 0.125 in. column packed with 10% W-98 on Chromosorb W. Diphenyl ether was used as an internal standard for these analyses. The results for three different runs are given in Table I.

The presence of 2-butanone and *p*-cresol as reaction products was demonstrated by isolation of these materials from another reaction mixture. 2-Butanone was distilled from the reaction mixture at 80°: 2,4-dinitrophenylhydrazone mp 114–115.5° (lit.[11] mp 117°); semicarbazone mp 143–144° (lit.[11] mp 146°). After removal of the lower boiling components, *p*-cresol was extracted from the reaction mixture with a 20% sodium hydroxide solution. The 2,6-dibromo-*p*-cresol prepared from the extracted material melted at 47.5–48° (lit.[11] mp 49°). The aryloxyacetic acid derivative melted at 136.5–137° (lit.[11] mp 136°).

Other Reactions of I.—Sealed tubes containing I, 1-butanol, and *t*-butyl peroxide in one case and I, *t*-butyl alcohol, and *t*-butyl peroxide in another (initial ratios of components 7:1:0.01) were heated for 24 hr at 125°. The 1-butanol reaction mixture turned dark during this period and gas chromatographic analysis showed the presence of *p*-cresol as a reaction product. No detectable amounts of *p*-cresol were found in the tube containing *t*-butyl alcohol nor did the contents of the tube become highly colored during the heating period but assumed only a pale yellow color.

In another reaction a mixture of I, 2-butanol, and azobisisobutyrylnitrile was heated at 80° for several hours. Gas chromatographic analysis indicated formation of *p*-cresol, chloroform, and 2-butanone.

Registry No.—I, 3274-12-2; 2-butanol, 78-92-2; *t*-butyl peroxide, 110-05-4.

(11) R. L. Shriner, R. C. Fuson, and D. Y. Curtin," The Systematic Identification of Organic Compounds," 4th ed, John Wiley and Sons, Inc., New York, N. Y., 1956.

Decomposition Reactions of 1-Phenyl-1-cyclohexyl Peracetate

H. HAUBENSTOCK[1]

Esso Research and Engineering Company., Linden, New Jersey

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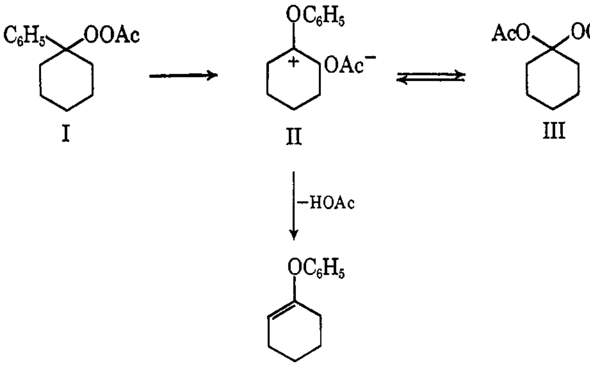
In a study of the decomposition of 1-phenyl-1-cyclohexyl peracetate (I) in several solvents, we have observed that the products obtained depend strikingly on the solvent employed.

Table I summarizes the major decomposition products determined by gas chromatographic analysis. In absolute ethanol, the major products formed were phenol and cyclohexanone. The same result was found in *n*-butyl alcohol. These products are the result of an ionic Criegee type of rearrangement,[2a] involving migration of the phenyl group to electron-deficient oxygen.[2b] Ring opening has been observed[2b] in the reaction of 1-phenylcyclohexyl hydroperoxide with acetic acid–CrO_3, and other cases are known where alkyl migration to electron-deficient oxygen is more highly favored than phenyl migration.[3] It has been shown that the decomposition of 1-methyl-1-cyclohexyl peracetate in ethanol and acetic acid gave 6-ketoheptanol and 6-ketoheptyl acetate, respectively.[4] These reactions presumably involve migration of a ring carbon atom to electron-deficient oxygen.

In the decomposition of I in glacial acetic acid, 1-phenoxycyclohexene was found to be a major product, along with phenol and cyclohexanone (Table I). The isolated 1-phenoxycyclohexene was characterized by its infrared and nuclear magnetic resonance spectra and elemental analysis.

The nature of the products formed in ethanol and acetic acid rule out a homolytic reaction path. Homolytic cleavage of the peroxide linkage would generate 1-phenylcyclohexyloxy radicals, and the expected products would be those derived from ring opening, *e.g.*, caprophenone[5] and possibly also 1-phenylcyclohexanol. The major products actually found (Table I) can be interpreted as having been formed from an intermediate phenoxycarbonium ion[6] (II). Although 1-phenoxycyclohexene was a major decomposition product in acetic acid,[7] it was not detected in ethanol. This product may be formed in acetic acid directly from the cation II, or from an acylal (III).



In ethanol, apparently II is trapped and converted into ketal; however further work is needed to establish this pathway.

Decomposition of I in heptane and in pyridine produced a mixture of mainly 1-phenoxycyclohexene and caprophenone, with virtually no phenol or cyclohexanone (Table I). Therefore, it appears that in these solvents the decomposition takes both an ionic path and a radical path. The ionic pathway did not lead to phenol or cyclohexanone, and this suggests that in the absence of a nucleophilic solvent such as ethanol the phenoxycyclohexene is formed directly from the intermediate phenoxycarbonium ion (or the phenoxy acylal III).

The peracetate I is an example of a system which decomposes by an ionic or radical pathway depending on the solvent. A similar example is the decomposition of

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[1] Address all correspondence to the author at Richmond College, Staten Island, N. Y. 10301.

[2] (a) R. Criegee, *Ann.*, **560**, 127 (1948); (b) H. Kwart and R. T. Keen, *J. Amer. Chem. Soc.*, **81**, 943 (1959).

[3] S. L. Friess and N. Farnham, *ibid.*, **72**, 5518 (1950).

[4] H. Francois, G. Bex, and R. Lalande, *Bull. Soc. Chim. Fr.*, 3702 (1965).

[5] D. H. Hey, C. J. M. Stirling, and G. H. Williams, *J. Chem. Soc.*, 1054 (1957).

[6] E. Hedaya and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 1661 (1967); see also references cited in this paper.

[7] Cumyl perbenzoate rearranges to $PhOCMe_2OCOPh$ in *n*-octane–$PhNO_2$ which decomposes to $PhOCMe{=}CH_2$ and PhCOOH. See N. V. Yablokova, V. A. Yablokova, and O. F. Rachkova, *Reaktsionnaya Sposobnost Organ. Soedin., Tartusk. Gos. Univ.*, **3** (2), 223 (1966); *Chem. Abstr.*, **67**, 2670*a* (1967).

TABLE I

DECOMPOSITION OF 1-PHENYL-1-CYCLOHEXYL PERACETATE (I)

Solvent[a]	Reaction time, hr	Product composition, %[b]				
		Phenol	Cyclohexanone	1-Phenoxycyclohexene	Caprophenone	Miscellaneous
Ethanol	62	53	34			*c*
Acetic acid[d]	52	20	30	44		*e*
Acetic acid[f]	72	11	12	72		*g*
Heptane	25			34	58	*h*
Pyridine	22	*i*	*i*	*Ca.* 75	*Ca.* 25	

[a] Reaction was carried out in refluxing solvent, unless otherwise noted. [b] Percentages of peak areas obtained in gc analysis with a Carbowax 20M column at *ca.* 200°. These data do not represent accurate mole per cent composition, but do indicate approximate relative amounts of the indicated products. [c] Two peaks (13%) were found at very short retention times, one of them probably being solvent. [d] Reaction temperature, 80°. [e] 5% phenyl acetate was detected, also unidentified high boiling material, *ca.* 15% of total observed area. [f] Reaction carried out at room temperature (*ca.* 25°). [g] There was also 5% unidentified material. [h] 8% of what appears to be 1-phenylcyclohexanol was detected. Some unidentified higher boiling material was present. [i] Traces of phenol and cyclohexanone were detected.

t-butylperoxy chloroformate, the mechanism of which is solvent dependent.[8] Furthermore, the nature of the ionic products in the decomposition of I depends on the particular solvent employed, as discussed above.

Experimental Section

Gas chromatographic analyses were carried out with a Perkin-Elmer Model 154 instrument using a Carbowax 20M column (10% on 70–80 mesh Anakrom ABS) at 200°, and with an F & M Model 500 instrument using a 2-ft 10% silicone rubber (SE 30) on 60–70 mesh Anakrom ABS column. The F & M instrument was programmed for 70–340° at 21°/min. Peak areas were calculated by the peak height-width at half-height method.

1-Phenyl-1-cyclohexyl Peracetate.—1-Phenylcyclohexyl hydroperoxide was prepared from the corresponding alcohol with 90% (or 70%) hydrogen peroxide using the procedure of Hey, Stirling, and Williams.[5] Reaction of the pure hydroperoxide with acetyl chloride in pyridine gave the liquid peracetate in 87% yield. The identity of the peracetate was confirmed by its infrared spectrum (neat); strong bands at 1754 (C=O), 1183 (C–O), and 754 and 694 cm^{-1} (monosubstituted aromatic). The nmr spectrum (CCl_4) confirmed the structure of the peracetate, showing a multiplet (5 H) in the aromatic region near δ 7.3 ppm and a broad signal for the ring protons from *ca.* 1.4 to 2.3 ppm, which included a sharp singlet for $-OCOCH_3$ at δ 1.72 ppm (total 13 H).

Decomposition of the Peracetate in Ethanol.—1-Phenyl-1-cyclohexyl peracetate (6 g) was heated under reflux for 62 hr in absolute ethanol. The cooled reaction mixture was diluted with salt solution and extracted with ether. The ether solution was washed with sodium bicarbonate and salt solution and dried over $MgSO_4$. An infrared spectrum of the recovered product, 3.7 g, showed no evidence of starting peracetate. Strong hydroxyl and carbonyl (1689 cm^{-1}) bands were present. The product was analyzed by gas chromatography on a Carbowax 20M column at 198° (Table I). Further analysis on the silicone rubber column programmed to 340° confirmed phenol and cyclohexanone as the only significant components in the mixture.

Decomposition of I in Acetic Acid.—Compound I (3 g) was decomposed in 30 ml of glacial acetic acid at 80° for 52 hr. The product (2 g) was worked up as described above, except that methylene chloride was used for extraction. Analysis of the product was carried out by gas chromatography on the Carbowax 20M and silicone rubber columns (Table I).

In a similar decomposition, the crude product was washed with 10% sodium hydroxide and distilled, giving 1-phenoxycyclohexene, bp 66–68° (0.15 mm).

Anal. Calcd for $C_{12}H_{14}O$: C, 82.71; H, 8.09. Found: C, 82.04; H, 8.19.

The infrared spectrum (10% CCl_4) showed bands at 1220 (s) (aromatic ether), 1669 (C=C str), 862 cm^{-1} (=CH out of plane deformation). The structure of the vinyl ether was confirmed by its nmr spectrum, which showed a multiplet (5 H) in the aromatic region near 7 ppm, an olefin proton (multiplet, 1 H) at about δ 4.94 ppm, and the ring methylene protons (8 H) in the range 1.4–2.4 ppm composed of two major overlapped multiplets corresponding to the ring allylic and nonallylic protons. Strong irradiation in the allylic proton region (175.8 cps upfield from the olefin signal) collapsed the olefin proton signal to a broad singlet.

Decomposition of I in Heptane and Pyridine.—Compound I (2 g) was decomposed in 20 ml of refluxing heptane under nitrogen for 25 hr. The product (1.7 g) had an infrared spectrum which showed very little hydroxyl absorption and no cyclohexanone. There was a strong band at 1667 [$C_6H_5-C(=O)-$] and at 1220 cm^{-1}. Analysis of the product was carried out on the Carbowax 20M and silicone rubber columns (Table I).

The peracetate (1.3 g) was decomposed in 20 ml of refluxing pyridine under nitrogen for 22 hr. The infrared spectrum of the product showed virtually no hydroxyl absorption but showed strong bands at 1667 and 1215 cm^{-1}. Product analysis was carried out on a Carbowax 20M column (Table I).

Registry No.—I, 17012-34-9; 1-phenoxycyclohexene, 17012-35-0.

Acknowledgments.—Thanks are extended to Dr. P. E. Butler of the Analytical Research Division for performing the nmr decoupling experiment and also to Mr. Jack Oliver for his technical assistance.

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Reaction of 2-Acetylcyclohexanone with Malononitrile and Cyanoacetamide

FILLMORE FREEMAN, DONALD K. FARQUHAR,
AND ROBERT L. WALKER

Department of Chemistry, California State College at Long Beach, Long Beach, California 90801

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It has been reported,[1,2] without structure proof, that the pyridine-catalyzed reaction of cyanoacetamide (I) and 2-acetylcyclohexanone (II) gave a mixture of 3-cyano-2-hydroxy-4-methyl-5,6,7,8-tetrahydroquinoline (III) and 4-cyano-3-hydroxy-1-methyl-5,-6,7,8-tetrahydroisoquinoline (IV). During studies of the reaction of malonic acid derivatives and dicarbonyl compounds, we found that the diethylamine-catalyzed reaction of malononitrile (V) or I with II gave a solid with the empirical formula $C_{11}H_{12}N_2O$. We have shown this product to have structure IV *via* elemental analysis, spectral analyses, and chemical reactivity. Also, we have prepared several previously unknown derivatives of IV. The nmr spectrum of IV in trifluoroacetic acid, which shows resonances at τ 6.98 (m), 7.35 (m), 7.48 (s, $C-CH_3$), and 8.17 (m), does not distinguish

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(2) H. K. Sen and U. Bose, *J. Indian Chem. Soc.*, **4**, 51 (1929).