Attempts to isolate intermediates in the rearrangements of α-bromomethylethylacetyl azide and α-bromomethylneopentylacetyl azide were unsuccessful. Steric factors may play a part in the occurrence of dehydrohalogenation and the stability of the olefinic isocyanate.

Experimental

α-Bromodineopentylacetyl Azide.—Dineopentylacetyl chloride was made from 200 g. of Butlerow acid (mostly α)[4] and 238 g. of thionyl chloride. The product was fractionated through an 18-plate column to give twelve fractions, 131 g., boiling at 108° at 22 mm., $n^{20}\text{D}$ 1.4430–1.4436. Fifty-one grams (0.233 mole) of the acyl halide was treated with 1 ml. of phosphorus trichloride and 41 g. (0.256 mole) of bromine. The mixture was heated overnight on the steam-bath and excess bromine then removed through a water aspirator. The crude acyl halide was dissolved in 100 ml. of acetone and added over a period of two hours to a solution of 30 g. of sodium azide in 100 ml. of water. The temperature was maintained at 5–10° throughout the addition. Two liquid phases were formed. The upper layer contained most of the dineopentylacetyl azide.

Curtius Rearrangement.—The azide layer from the above preparation was added slowly to 300 ml. of boiling benzene, and the mixture was refluxed for two hours. Ninety per cent. of the calculated amount of nitrogen gas was evolved based on a theoretical yield of the acyl azide. The solution was cooled and stirred vigorously for 24 hours with 1 l. of cold water. Fractionation of the benzene layer through a 12-plate column gave six fractions, 13.9 g. (27% over-all) of olefinic isocyanate, b.p. 85–87° at 8 mm., $n^{20}\text{D}$ 1.4487–1.4490. After refractionation through a micro column, the product had $n^{20}\text{D}$ 1.4485–1.4487.

Anal. Calcd. for $C_{12}H_{21}ON$: C, 73.79; H, 10.84; N, 7.17. Found: C, 74.06; H, 10.90; N (Dumas), 7.14.

Five similar preparations were carried out. Inadequate stirring of the benzene layer with cold water gave the α-bromo isocyanate which decomposed to a gas and tar upon distillation. When isolation of the product was effected by steam distillation of the benzene solution from 400 ml. of 20% hydrochloric acid, the product was mixed with dineopentyl ketone from which it could be separated by fractionation through a 10-plate column. A 32% over-all yield of the intermediate isocyanate was isolated in one experiment.

Two drops of the compound decolorized more than 80 drops of 1% bromine in carbon tetrachloride and more than 40 drops of 1% aqueous potassium permanganate. α-Naphthyl isocyanate gave negative tests with these reagents.

The product exhibited continuous absorption of light with no maximum in the region 2200–3000 Å. The results are consistent with absorption characteristics of the isocyanate group[5] and a compound containing a double bond.

The compound reacted with phenylmagnesium bromide to give an amide, m.p. 145–146.5°.

Anal. Calcd. for $C_{18}H_{27}ON$: N, 5.13. Found: N (Kjeldahl), 4.98.

Before drying in a vacuum over phosphorus pentoxide, the m.p. was 139–140° and the nitrogen analysis indicated that a molecule of water of crystallization was present.

An N-phenylurea, m.p. 169°, was formed by heating the compound with a solution of aniline in methanol.

Ozonolysis of 1 g. of the product was carried out in methylene chloride. The ozonide was decomposed by boiling water followed by steam distillation. A 2,4-dinitrophenylhydrazone prepared on a drop of the distillate melted at 203°. Admixture with an authentic sample of the 2,4-dinitrophenylhydrazone of trimethylacetaldehyde gave no depression in melting point.

The olefinic isocyanate was unchanged when stored for three months in corked vials in the ice-box or in a sealed tube at room temperature. However, when stored in corked vials at room temperature, some of the fractions underwent an increase in refractive index and viscosity; others deposited crystals, m.p. 155–158° after recrystallization from ethanol. The crystals absorbed bromine in carbon tetrachloride and may be the corresponding olefinic symmetrical urea.

Hydrolysis to Dineopentyl Ketone.—A mixture of 30 g. of the olefinic isocyanate, 30 ml. of concentrated hydrochloric acid and 100 ml. of water was refluxed for two days. The product was isolated by steam distillation and dried by fractionation with 25 ml. of benzene through a 10-plate column. Dineopentyl ketone was obtained in six fractions, 20.6 g. (80%), b.p. 61° at 10 mm., $n^{20}\text{D}$ 1.4200, oxime, m.p. 76–78°.

As further proof that the compound was an isocyanate, an 0.80 millimole sample was hydrolyzed with 1:1 sulfuric acid in a modified Kjeldahl apparatus. Carbon dioxide was swept by nitrogen into standard barium hydroxide solution, and ammonia was determined in the residue by alkaline distillation according to the standard Kjeldahl procedure. Obtained were 0.15 millimole of carbon dioxide and 0.13 millimole of ammonia. Thus, although only about 20% of the compound was hydrolyzed during the heating period and much distilled unchanged with the nitrogen stream, equivalent quantities of ammonia and carbon dioxide were formed in the hydrolysis.

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[4] F. C. Whitmore and C. D. Wilson, THIS JOURNAL, **56**, 1397 (1934).

[5] S. Woo and T. Liu, *J. Chem. Phys.*, **3**, 544 (1935).

STATE COLLEGE, PENNSYLVANIA

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

A Kinetic Study of the Rearrangement of Some Benzoates of 9-Decalyl Hydroperoxide

BY PAUL D. BARTLETT AND JOHN L. KICE[1]

RECEIVED JUNE 12, 1953

The Criegee rearrangement of the benzoate of 9-decalyl hydroperoxide into 1-benzoyloxy-1,6-epoxycyclodecane has been followed kinetically by means of an iodometric titration of the perester. An unsaturated ether has been isolated as a by-product. The rearrangement is of the first order, shows only moderate acid catalysis, and is intramolecular in the sense that rearrangement in the presence of sodium *p*-bromobenzoate does not lead to bromine-containing product. The rates of rearrangement of the substituted benzoates bearing the nitro, bromo, methyl and methoxyl substituents in the para position fit the Hammett equation with a value of $\rho = 1.34$.

The benzoate of 9-decalyl hydroperoxide has the property, in common with camphene hydrochloride, of undergoing molecular rearrangement rapidly in solvents of high ionizing power and slowly in poorly ionizing solvents.[2] Criegee and Kaspar[2] have shown convincingly that this rearrangement involves an ionic fission of the oxygen–oxygen link and takes a course analogous to the Wagner–Meerwein rearrangement in which there is an ionic fission of a carbon–halogen or carbon–oxygen link. Recent progress in formulating the intermediates in the Wagner–Meerwein rearrangement[3–6] raises the

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[1] National Science Foundation Fellow, 1952–1953.

[2] R. Criegee and R. Kaspar, *Ann.*, **560**, 127 (1948).

[3] S. Winstein and D. Trifan, THIS JOURNAL, **71**, 2953 (1949).

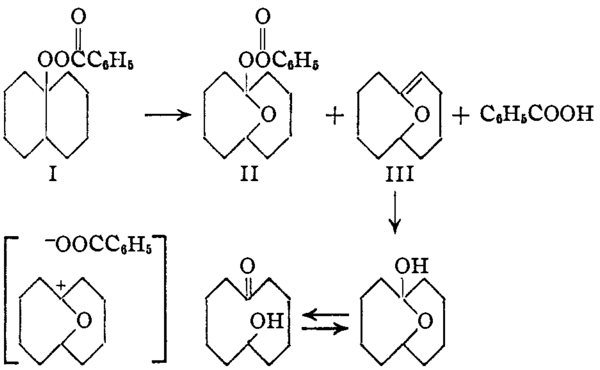
[4] D. J. Cram, *ibid.*, **71**, 3863 (1949).

[5] J. D. Roberts, *ibid.*, **73**, 3542 (1951).

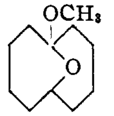
[6] F. Brown, E. D. Hughes, C. K. Ingold and J. F. Smith, *Nature*, **168**, 65 (1951).

hope of understanding the Criegee rearrangement in similar detail. We have undertaken a quantitative study of the reaction as a first step in this direction.

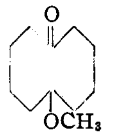
The Products of the Rearrangement.—The benzoate I of 9-decalyl hydroperoxide underwent rearrangement on standing in methanol at room temperature for 26 hours into 1-benzoyloxy-1,6-epoxycyclodecane (II) in a yield of 80.6%. From the mother liquors benzoic acid was isolated by extraction in a yield of 9.4%. The only other product was a colorless unsaturated oil which was readily hydrated in the presence of acetic acid to 6-hydroxycyclodecanone-1 (IV) and which could be hydrogenated to a product having, according to its infrared spectrum, no double bond and no hydroxyl group. This product of the reaction is accordingly formulated as 1,6-epoxycyclodecene-1 (III), a product of the elimination of benzoic acid, representable as arising from the loss of a proton from the intermediate V.



This product was impure, absorbing only 75% of the calculated hydrogen, and may well have included some of the acetal VI, an expected product from intervention of the solvent and some 6-methoxycyclodecanone (VII), arising from the acid catalyzed isomerization of VI.[7]



VI



VII

The Kinetics of the Rearrangement.—It was found possible to titrate the perester by alcoholyzing it quantitatively with sodium methoxide solution and titrating the resulting 9-decalyl hydroperoxide iodometrically. The reaction was cleanly of the first order when followed in this way over 88% of its course in methanol at 24.6° (open circles Fig. 2) and showed a rate constant of 4.89 and 4.94×10^{-5} sec.$^{-1}$ in two runs.[8] Measurements at 40.0° gave a rate constant of 3.40×10^{-4} sec.$^{-1}$ and 22.7 kcal./mole as the enthalpy of activation.

Acid Catalysis.—In view of evidence in other cases[9] showing the importance of acid catalysis in the ionization processes of esters, we investigated the effect of hydrochloric acid at a constant ionic strength of 0.20 upon the rate of this rearrangement. The results are shown in Table I. There is clear acceleration by acid, but the rate in the absence of all acid is greater than the additional rate produced by hydrochloric acid at a concentration of 0.2 *M*.

The question of competition for an ionic intermediate is important in establishing the extent to which the ion is free, and is of special interest here in view of the possible occurrence of an ion with a positive charge on an electronically deficient oxygen atom.[10] When 9-decalyl perbenzoate was rearranged in methanol in the presence of slightly over an equivalent quantity of sodium *p*-bromobenzoate and *p*-bromobenzoic acid, the product (isolated by evaporating an ether extract washed with sodium carbonate, but without recrystallization to effect any fractionation of the product) contained only 0.13% bromine out of 22.62 calculated for the *p*-bromobenzoate of decalyl hydroperoxide or its rearrangement product. In the converse experiment the *p*-bromobenzoate was rearranged in an equivalent benzoate buffer and the product, isolated in identical fashion, was found by analysis to contain 21.01% bromine. In view of the probable presence in the non-acidic fraction of some of the elimination product reported above, this result cannot be taken to indicate that a corresponding amount of exchange of anion has occurred. The evidence is rather that, from the first experiment, not over 0.6% of labeled benzoate ion from the outside entered into the product of the rearrangement. It is evident, then, that the cation produced in the Criegee rearrangement exists only in an ion pair or in a "solvent cage," and reacts in this way more exclusively than do the ion pairs in the internal Wagner–Meerwin rearrangements or allylic rearrangements which have been reported.[11-13]

The Effect of Substituents on the Rate of Rearrangement.—If the rearrangement is ionic in character its rate should respond to substituents in the benzoate group in the same qualitative way as the ionization of benzoic acids. We have measured the rates of rearrangement of the 9-decalyl perbenzoates bearing the nitro, bromo, methyl and methoxyl substituents in the para position, with the results shown in Table II and Fig. 1. When plotted according to the Hammett equation (Fig. 2) a straight line is obtained with the usual degree of precision, and its slope indicates a ρ factor for the

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(7) R. Criegee and W. Schnorrenberg, *Ann.*, **560**, 141 (1948).

(8) Compare the values of $k_1 = 4.1 \times 10^{-5}$ and $E = 23.1 \pm 0.5$ obtained by a different method of following the reaction (H. L. Goering and A. C. Olson, THIS JOURNAL, **75**, Dec. 5 (1953)).

(9) E. A. Braude, *Annual Reports of the Chem. Soc.*, **46**, 126 (1949).

(10) For a fuller discussion of the nature of this cation, see Goering and Olson, ref. 8. These authors formulate the ion, by analogy with the work cited above on the Wagner–Meerwin rearrangement, as a bridged structure with the charge distributed between oxygen and carbon. Because of the inherently greater stability of a carbon cation (with its oxonium resonance structure) than of the isomeric species with electronically deficient oxygen, one might expect a bridged structure to provide less stabilization in this case than in one involving only carbon as a possible seat of charge. Since present evidence suggests that bridged structures are not universal among carbonium ions, we tend to think of the present cation as being formed directly in the carbonium–oxonium $\left({>}\overset{+}{C}OR \longleftrightarrow {>}C{=}\overset{+}{O}R \right)$ form.

(11) S. Winstein and D. Trifan, THIS JOURNAL, **74**, 1154 (1952).

(12) S. Winstein and K. Schreiber, *ibid.*, **74**, 2171 (1952); **74**, 2165 (1952).

(13) H. L. Goering, W. G. Young and S. Winstein, *ibid.*, **73**, 1958 (1951).

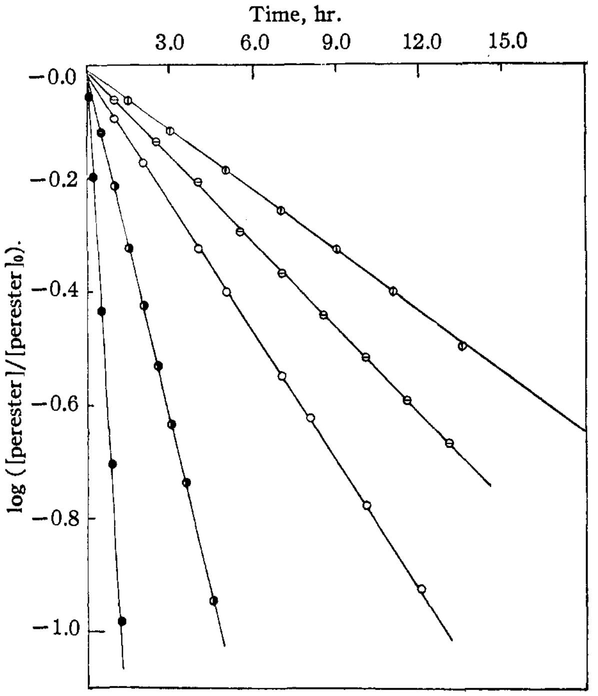

Fig. 1.—Rearrangement of esters of decalyl hydroperoxide in methanol at 24.6°: ●, *p*-nitrobenzoate; ◑, *p*-bromobenzoate; O, benzoate; ⊖, *p*-methylbenzoate; ⦶, *p*-methoxybenzoate.

Criegee rearrangement of 1.34 compared to 1.00 for the ionization of benzoic acids. This is in accord with the polarizability of the O–O link indicated by other facts in this field, and confirms the essentially ionic nature of the rearrangement.

TABLE I

EFFECT OF ACID ON REARRANGEMENT OF DECALYL PERBENZOATE IN METHANOL

Ester, 10^2 *M*	LiCl, 10^2 *M*	HCl, 10^2 *M*	$k_1 \times 10^5$, sec.$^{-1}$	Distance followed, %
7.41	19.9	0.00	5.69	81
7.44	9.9	10.1	7.08	83
8.16	0.0	20.0	8.42	92

TABLE II

REARRANGEMENT OF ESTERS OF DECALYL HYDROPEROXIDE IN METHANOL AT 24.6°

Ester	Initial concn. ester, 10^2 *M*	$k_1 \times 10^5$, sec.$^{-1}$	Distance followed, %
p-Nitrobenzoate	0.32	55.0	80
	0.37	55.3	90
p-Bromobenzoate	3.00	13.2	89
Benzoate	8.84	4.89	88
	6.82	4.94	77
p-Methylbenzoate	6.13	3.25	79
	5.97	3.19	66
p-Methoxybenzoate	5.75	2.24	89
	6.11	2.28	83

Experimental

***trans*-9-Decalyl Hydroperoxide.**—This was prepared according to the method of Cope and Holtzman.[14]

Esters of *trans*-9-Decalyl Hydroperoxide. Benzoate.—Prepared by the method of Cope and Holtzman.[14] The material used for further work was recrystallized from methanol until it showed a melting point of 67–68°.

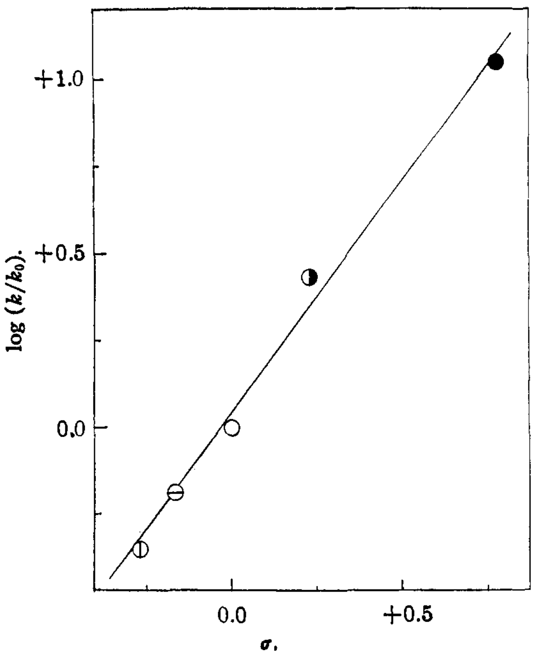

Fig. 2.—log ($k/k_{\text{unsubstituted}}$) *vs.* Hammett's σ for esters of decalyl hydroperoxide: ●, *p*-nitrobenzoate; ◑, *p*-bromobenzoate; O, benzoate; ⊖, *p*-methylbenzoate; ⦶, *p*-methoxybenzoate.

***p*-Nitrobenzoate.**—Prepared by the method of Criegee and Kaspar[2] and recrystallized twice from benzene–petroleum ether, it melted sharply at 94° dec.

***p*-Bromobenzoate.**—Four grams (0.024 mole) of decalyl hydroperoxide was dissolved in 25 ml. of absolute pyridine, and the solution was cooled to 0°. To the cold solution was added in small portions over the course of 5 minutes 6.0 g. (0.028 mole) of *p*-bromobenzoyl chloride. The mixture was removed from the ice-bath and allowed to stand with frequent shaking at room temperature for 45 minutes. It was then poured into about 200 ml. of cold 10% sulfuric acid. The solid which separated was filtered off, washed first with water and then with 2 ice-cold 10-ml. portions of methanol, and dried *in vacuo* at room temperature. The crude solid was treated with 50 ml. of benzene, the insoluble material removed by filtration, and the benzene removed under reduced pressure at room temperature.

The crude product was recrystallized from petroleum ether, yielding 2.8 g. of perester, m.p. 87–88° (34%).

Anal. Calcd. for $C_{17}H_{21}O_3Br$: C, 57.80; H, 5.99; Br, 22.62. Found: C, 58.13; H, 6.02; Br, 22.65.

***p*-Methylbenzoate.**—This was prepared by a method exactly analogous to that used by Cope and Holtzman for the preparation of decalyl perbenzoate. From 6.0 g. (0.036 mole) of decalin hydroperoxide and 6.2 g. (0.040 mole) of *p*-methylbenzoyl chloride there was obtained, after recrystallization from methanol, 5.4 g. of the perester (52%), m.p. 82–83°.

Anal. Calcd. for $C_{18}H_{24}O_3$: C, 74.96; H, 8.35. Found: C, 74.65; H, 8.29.

***p*-Methoxybenzoate** was prepared in exactly the same manner as the *p*-methylbenzoate. From 6.0 g. (0.036 mole) of decalin hydroperoxide and 6.3 g. (0.038 mole) of *p*-methoxybenzoyl chloride the yield, after recrystallization from methanol, was 5.9 g. (63%) of perester, m.p. 77–78°.

Anal. Calcd. for $C_{18}H_{24}O_4$: C, 71.03; H, 7.95. Found: C, 71.16; H, 8.19.

Rearrangement of Decalyl Perbenzoates in Methanol.—All of the peresters yield as the major product on rearrangement in methanol the corresponding ester of the hemiacetal, 1,6-epoxycyclodecanol-1. The properties of the benzoate and *p*-nitrobenzoate have been previously reported.[3] The properties of the remaining three are listed below.

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(14) A. C. Cope and G. Holtzman, *ibid.*, **72**, 3062 (1950).

Esters of 1,6-Epoxycyclodecanol-1: *p*-bromobenzoate, m.p. 100–100.5°. *Anal.* Calcd. for $C_{17}H_{21}BrO_3$: C, 57.80; H, 5.99; Br, 22.62. Found: C, 58.20; H, 6.10; Br, 22.77.

***p*-Methylbenzoate**, m.p. 112–113°. *Anal.* Calcd. for $C_{18}H_{24}O_3$: C, 74.96; H, 8.35. Found: C, 74.47; H, 8.19.

***p*-Methoxybenzoate**, m.p. 117–118°. *Anal.* Calcd. for $C_{18}H_{24}O_4$: C, 71.03; H, 7.95. Found: C, 71.02; H, 7.85.

For a quantitative study of the products of the rearrangement, however, experiments were carried out only on decalyl perbenzoate.

Product Study.—A sample of 1.195 g. of decalyl perbenzoate was dissolved in 40 ml. of absolute methanol and allowed to stand at 24.6° for 26 hours. The methanol was removed under reduced pressure at room temperature, and the distillate collected in a flask immersed in a Dry Ice trap. The residue, which crystallized almost immediately, was recrystallized from about 15 ml. of 80% methanol. The crystalline material was filtered, washed and dried. It amounted to 0.926 g. (77%) of 1-benzoyloxy-1,6-epoxycyclodecane, m.p. 97–97.5°.

The filtrate from the crystallization was diluted and made alkaline with sodium carbonate solution and extracted with two 10-ml. portions of methylene chloride. It was then extracted with two 10-ml. portions of ether. The filtrate was concentrated to about 5 ml. volume, acidified with concentrated hydrochloric acid, and the precipitate which formed was recrystallized from hot water. Benzoic acid (0.050 g., 9.4%), m.p. 121–122°, identical in all respects with a known sample, was obtained.

The methylene chloride extracts were dried over sodium sulfate, and the solvent removed by distillation through a column. A residue of 0.131 g. of oily material was obtained. An infrared spectrum showed that it still contained some epoxyester. However, the presence of a fairly intense band at 5.99 μ suggested that one of the by-products was olefinic in nature. The residue also gave a positive test with dilute permanganate, which is not the case with the pure epoxyester. From the residue on treatment with a little 80% methanol was obtained an additional 0.040 g. of 1-benzoyloxy-1,6-epoxycyclodecane.

The methanol distillate and the ether extract were both fractionated through a column. No residue could be found in either case.

SUMMARY OF RESULTS

1-Benzoyloxy-1,6-epoxycyclodecane	0.966 g.	80.6%
Benzoic acid	.050 g.	9.4%
Unidentified material (containing an olefin)	.091 g.	....
Total recovery	1.107 g.	

The nature of the olefinic material was investigated in larger scale experiments.

Seven grams of decalyl perbenzoate was decomposed by heating in 20 ml. of methanol at reflux. At the end of 1.5 hours, 2 ml. of water was added, the solution was cooled and the crystalline epoxyester filtered off. It weighed 5.4 g. (77%).

To the filtrate was added about 40 ml. of 10% sodium carbonate solution, and the experiment continued as before. The oily residue from the methylene chloride extracts was distilled at 15 mm., yielding about 0.5 ml. of water-white liquid, boiling about 110° (15 mm.). The residue in the pot solidified on cooling and was found to be epoxyester.

The distillate gave a strong positive test with aqueous permanganate. Its infrared spectrum showed strong double bond absorption at 5.99 μ, but the presence of weak absorption in the carbonyl region showed that carbonyl impurities also were present. It was redistilled at reduced pressure, which afforded some purification, but the amount of carbonyl impurity was still sufficient to make an elementary analysis infeasible. Accordingly the nature of the olefinic material was tentatively established by the following reaction.

A sample of 0.264 g. of the redistilled material was heated on the steam-bath with 4 ml. of 50% acetic acid for 30 minutes. The solution was diluted with 5 ml. of water, neutralized with solid sodium carbonate, and extracted with three 10-ml. portions of methylene chloride. The methylene chloride extracts were dried, and the solvent removed under reduced pressure. The residue was an oil which solidified on standing and weighed 0.250 g. An infrared spectrum of the crude material was identical with that of a known sample of 6-hydroxycyclodecanone, except for the presence of a weak band at 5.81 μ, doubtless due to the carbonyl impurities present in the starting material. Recrystallized from petroleum ether–cyclohexane, it melted at 69–70.5°, and showed no depression of the melting point on mixture with a known sample of 6-hydroxycyclodecanone. The yield of 6-hydroxycyclodecanone, based on the weight of the crude product, is 84.6%. On the basis of this experiment the olefinic material was tentatively identified as 11-oxabicyclo[4,4,1]hendecene-1 (III).

Also, 0.545 g. of once-distilled material was hydrogenated over prereduced platinum oxide in ethyl alcohol. Seventy-five per cent. of the theoretical amount of hydrogen (based on one double bond and the formula $C_{10}H_{16}O$) was rapidly absorbed. The catalyst was filtered off, the solution diluted with water and extracted with three 25-ml. portions of petroleum ether. The petroleum ether extracts were dried and the solvent removed. The residue was distilled under reduced pressure, and an infrared spectrum taken on the colorless distillate. It showed that the absorption at 5.99 μ due to the carbon–carbon double bond had disappeared, the weak absorption in the region around 5.8 was still present, and there was no absorption due to hydroxyl groups. This indicates that a carbon–carbon double bond has been reduced and not a carbon–oxygen double bond.

Competition Experiments.—(Run 1): 0.6520 g. (2.92×10^{-3} mole) of sodium *p*-bromobenzoate, 0.5999 g. (2.98×10^{-3} mole) of *p*-bromobenzoic acid and 0.6463 g. (2.36×10^{-3} mole) of decalyl perbenzoate were dissolved in 50 ml. of absolute methanol and allowed to stand at 24.6° for 26 hours. The methanol was then removed under reduced pressure at room temperature. The residue was treated alternately with 15-ml. portions of ether and 5% sodium carbonate solution, 2 portions of each being used; these solutions were poured into a separatory funnel, and after extraction, the carbonate layer was drawn off. The ether layer was subsequently extracted four more times with 15-ml. portions of carbonate solution to ensure complete removal of all the acid. It was washed once with water, dried over sodium sulfate, filtered, and the ether removed. The crystalline residue was dried and analyzed for bromine content.

An 84.59-mg. sample gave only 0.27 mg. of AgBr, corresponding to a bromine content of 0.13%, a value so small that it is within the experimental error of the analysis.

Run 2: 0.5270 g. (1.49×10^{-3} mole) of decalyl per-*p*-bromobenzoate, 0.2210 g. (1.81×10^{-3} mole) of benzoic acid and 0.2495 g. (1.73×10^{-3} mole) of sodium benzoate were dissolved in 50 ml. of absolute methanol and the solution allowed to stand for 24 hours at 24.6°. At the end of this time the solution was worked up in exactly the same way as in the previous experiment.

An analysis gave Br, 21.01; calcd. for pure 1-(*p*-bromobenzoxy)-1,6-epoxycyclodecane, 22.62. Therefore the sample is 92.9% pure. This may be due not to exchange by benzoate, but to the presence of the very slowly vaporized by-products (see Products Study), which would not contain bromine, and which are not removed by drying.

Kinetic Studies.—The procedure for the kinetic runs was as follows.

A sample of the perester was weighed out, dissolved and made up to volume with absolute methanol previously thermostated to 24.6°, and the solution placed in a glass stoppered flask in a thermostat set at 24.60 ± 0.01°.

At intervals 5- or 10-ml. aliquots were removed in pipets calibrated for methanol at 25°. The aliquots were chilled rapidly and 1 ml. of 2 *N* sodium methoxide solution added. The solution was then allowed to stand for 10 minutes (20 minutes in the case of the per-*p*-methoxybenzoate). Fifty ml. of isopropyl alcohol was then added, followed by 4 ml. of glacial acetic acid. The flask was flushed with carbon dioxide for 5 minutes, after which the gas flow was stopped, and 10 ml. of a saturated solution of sodium iodide in isopropyl alcohol was added. The solution was heated to gentle boiling on the steam-bath and kept there for 5 to 10 minutes. Heating was then discontinued, and the gas flow resumed. Five ml. of water was added, and the solution was titrated to the disappearance of the iodine color with standard thiosulfate.

For those runs in which lithium chloride and hydrochloric acid were used, standard solutions of these reagents in methanol were prepared and standardized at 24.6°.

The proper amounts of these thermostated solutions were added to the weighed sample of perester, followed by sufficient thermostated absolute methanol to bring the solution to the desired volume.

Also, in these runs, an amount of 2 N methoxide sufficient to neutralize the hydrochloric acid present in the aliquot was added in addition to the 1 ml. normally used during the analysis.

That the method of analysis employed is satisfactory for determining the amount of perester present is shown by the following analyses on pure samples of the peresters using the method described above.

Decalyl perbenzoate

Wt. taken, g.	Vol. 0.05087 N S_2O_3 required, ml.	Wt. found, g.	Purity, %
0.2172	30.79	0.2148	98.9
.2784	39.70	.2770	99.4

Decalyl per-p-methylbenzoate

	Vol. 0.03708 N S_2O_3 required, ml.		
0.1792	32.40	0.1736	96.9

Decalyl per-p-nitrobenzoate

	Vol. 0.02548 N S_2O_3 required, ml.		
0.1270	30.83	0.1253	98.7

Similar results were obtained with the other two peresters.

The rate constants for the different runs were usually determined graphically, but in those cases in which there was any doubt as to the best straight line, the method of least squares was employed. Rate constants in all cases were reproducible to within 3%.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM CHANDLER LABORATORY, COLUMBIA UNIVERSITY]

Mechanism of the Peracid Ketone–Ester Conversion. Analysis of Organic Compounds for Oxygen-18[1]

BY W. VON E. DOERING[2] AND EDWIN DORFMAN

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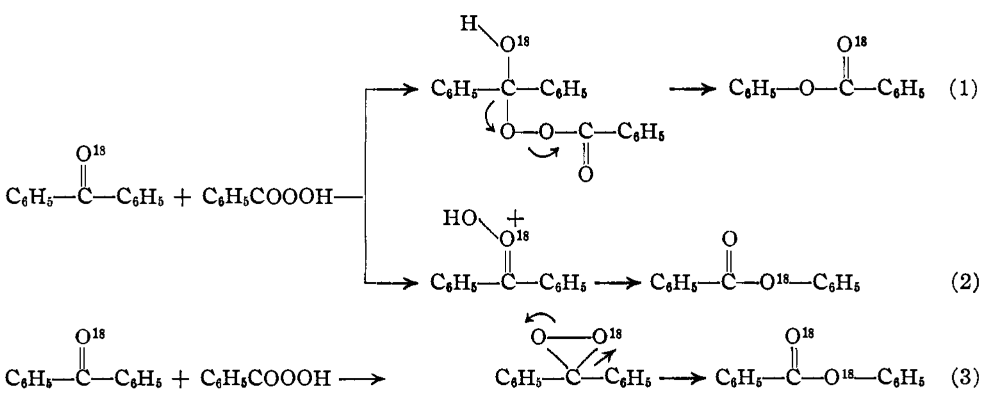
When benzophenone-O^{18} is oxidized with perbenzoic acid, phenylbenzoate-*carbonyl-O*^{18} results. The position of oxygen-18 is shown by reduction with lithium aluminum hydride to benzyl alcohol containing the excess oxygen-18 and phenol having the normal abundance. These analyses are carried out mass-spectrometrically on carbon dioxide obtained from the organic material by a modification of the Schütze–Untersaucher method for quantitative oxygen analysis.

At the conclusion of a paper dealing with migration aptitude in the peracid ketone–ester conversion, three consistent mechanisms were considered although, at the time, no experimentally supported distinction could be made between them.[3] These mechanisms were also considered to be consistent with kinetic studies.[4] They were in theory distinguishable by the different fates they would impose on the carbonyl oxygen atom. Using, as example, the reaction of benzophenone-O^{18} and perbenzoic acid to give phenylbenzoate, the "Criegee" mechanism (1)[3,5,6] would lead to phenylbenzoate-*carbonyl-O*^{18}; the "Wittig" mechanism (2)[8] would give the reverse result—phenylbenzoate-*ether-O*^{18}; whereas the "v. Baeyer" mechanism (3)[3,7] would lead to ester in which the oxygen-18 was equally distributed between both oxygen atoms. In this paper, the results of such an experiment are reported.



The bulk of the work was concerned with developing a general method of getting oxygen-18 out of organic molecules in a form suitable for mass-spectrometric analysis. The ter Meulen method of oxygen analysis[8] has been used by Urey and Roberts[9] for the analysis of methanol-O^{18} and by Bunton and Frei[10] for phenol-O^{18}. The latter workers report a 10% isotope dilution, a result which would accord with the large blank usually observed when the method is used for oxygen analyses.[11] Another method which was considered was a modification

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[2] Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut.

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