140° at atm. pressure). The infrared spectrum of methyl pyruvate was consistent with the α-keto ester structure and the n.m.r. showed two unsplit methyl peaks at 6.18 and 7.60 τ, with the expected integrated areas of 1:1.

Photolysis of α-Keto Esters.—Eighty-five milliliters of benzene solution usually 0.15 *M* in the esters mentioned in Table I were irradiated for 40–60 min. The gas evolved was collected in an eudiometer and analyzed by infrared. In all cases the gas was found to be carbon monoxide. The yield of carbon monoxide reported in Table I takes into account the amount of gas dissolved in solution. The benzene solutions were analyzed by v.p.c. (vapor phase chromatography). A 12-ft. β,β′-oxydipropionitrile (70°) column was used to isolate formaldehyde and acetaldehyde from methyl pyruvate while tricresyl phosphate (85°) was used for acetone and acetaldehyde determination from isopropyl pyruvate. The products from ethyl benzoylformate (benzaldehyde and acetaldehyde) were analyzed on an Apiezon J column at 150°. Identification of the products in all runs was made by comparing infrared spectra of samples collected from the v.p.c. with infrared spectra of authentic samples.

Quantum Yields.—Quantum yields were run using a standard optical bench, a PEK, 500-w. high pressure mercury arc with appropriate power supply, a columnating lens, and a Corning 7–39 filter to isolate mainly the 3660 Å. line. Benzene solutions, 0.2 *M* in ethyl pyruvate, served as an actinometer. The quantum yields were calculated relative to this system using $\phi = 0.17$.[2] Benzene solutions 0.2 *M* in ethyl pyruvate, isopropyl pyruvate, deuterioisopropyl pyruvate, methyl pyruvate, ethyl benzoylformate, and ethyl α-naphthoylformate were degassed in small Pyrex ampoules. The esters were 99% pure as shown by v.p.c. analysis. The actinometer and keto ester ampoules were irradiated simultaneously for 3 hr. The positions of the sample and actinometer were reversed after 1.5 hr. to compensate for any inhomogeneity in the light beam. The concentrations of the solutions were such that all of the light was absorbed. The amount of decomposition in quantum yield runs as well as in all product runs was determined by ultraviolet analysis before and after irradiation, with exception of ethyl benzoylformate, which was determined by v.p.c. analysis.

Acknowledgment.—This work has been supported in part by the Petroleum Research Fund of the American Chemical Society. The authors are greatly indebted to Angelo A. Lamola of the California Institute of Technology for obtaining the emission spectra reported in this paper.

(10) A. Weissberger and C. J. Kibler, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 611.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILL.]

Anchimerically Accelerated Bond Homolysis. V.[1] Decomposition of an Oxygen-18 Labeled *t*-Butyl Perester

BY J. C. MARTIN AND T. W. KOENIG

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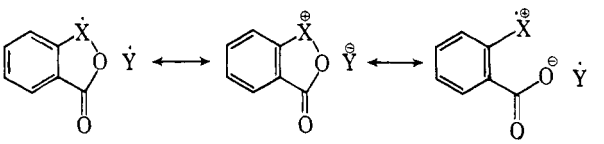
The decomposition of *t*-butyl *o*-(2,2-diphenylvinyl)perbenzoate labeled with O^{18} in the carbonyl position gives 3-benzhydrylphthalide with 88% retention of the identity of the carbonyl oxygen. This result is in accord with the proposed mechanism for anchimeric acceleration in the decomposition of *ortho*-substituted *t*-butyl perbenzoates and benzoyl peroxides. The bridging postulated from kinetic studies to be important in the transition state is maintained in the product radical as well, at least to the extent of 76%. A study of the basic hydrolysis of the product lactone gave evidence for a remarkably rapid exchange of the carboxylate oxygens with solvent water in basic media. We postulate neighboring hydroxyl electrophilic catalysis to explain this exchange.

Accelerations in the rates of decomposition of a number of *ortho*-substituted *t*-butyl perbenzoates and benzoyl peroxides have been reported previously. The substituents studied thus far include *o*-iodo,[2,3] *o*-vinyl,[1] *o*-methylthio,[2] and *o*-phenylthio[2] groups. The observed rates for these decompositions have been found to respond to solvent polarity[1,4,5] and ring substitution.[1,4,5] It has been proposed that the origin of these accelerations is a stabilization of the transition state leading to homolytic cleavage of the O–O bond by participation of the neighboring *o*-substituent. It has further been postulated that this transition state may be represented by canonical structures, I, II, and/or III. The inclusion of structure I is designed to reflect the resemblance of the transition state to the radical products of decomposition. Structure II is demanded to explain observed solvent and substituent effects. Structure III makes a contribution of undetermined magnitude.



I II III

X = I, $-S-CH_3$, $-S-C_6H_5$, vinyl; Y = $-OC(CH_3)_3$, $ArCO_2^-$

Accelerations have also been observed in the rates of decomposition of β-iodopropionyl peroxide[6] and *trans*-γ-benzylidenebutyryl peroxide.[7] From a kinetic study of the behavior of the latter compound in a variety of solvents, Lamb and co-workers have proposed a structure formally identical with III as the major contributor to the transition state for decomposition of this peroxide. Recent studies on the decompositions of the *t*-butyl peresters[8] and diacyl peroxides of *exo*- and *endo*-norbornene-5-carboxylic acids[9] indicate that there is little if any participation by the olefinic group in the decompositions of these compounds.

We now report the results of a study of the decomposition of *t*-butyl *o*-(2,2-diphenylvinyl)perbenzoate[10] labeled in the carbonyl group with oxygen-18.

(1) For part IV see T. W. Koenig and J. C. Martin, *J. Org. Chem.*, in press. This part was abstracted from the Ph.D. Thesis of T. W. K., University of Illinois, 1963.

(2) W. G. Bentrude and J. C. Martin, *J. Am. Chem. Soc.*, **84**, 1561 (1962).

(3) J. E. Leffler, R. D. Faulkner, and C. Petropoulos, *ibid.*, **80**, 5435 (1958).

(4) W. G. Bentrude, D. L. Tuleen, and J. C. Martin, *ibid.*, **85**, 1938 (1963).

(5) W. Honsberg and J. E. Leffler, *J. Org. Chem.*, **26**, 733 (1961).

(6) J. E. Leffler and J. S. West, *ibid.*, **27**, 4191 (1962).

(7) R. C. Lamb, F. F. Rogers, Jr., G. D. Dean, Jr., and F. W. Voight, Jr., *J. Am. Chem. Soc.*, **84**, 2635 (1962).

(8) M. M. Martin and D. C. DeJongh, *ibid.*, **84**, 3526 (1962).

(9) H. Hart and F. J. Chloupek, *ibid.*, **85**, 1155 (1963).

TABLE I

SAPONIFICATION OF 3-BENZHYDRYLPHTHALIDE AT 100° FOLLOWED BY ACIDIC RELACTONIZATION

Run	Starting lactone	Aqueous medium	Sapon. time, hr.	O^{18} analysis on product: Atom % excess	No. of O^{18} per molecule	Exchange, %
1	Unlabeled	2 *M* $NaO^{18}H$[a]	1	0.767	1.00	
2	Unlabeled	2 *M* $NaO^{18}H$[a]	3	.714	0.94	
3	Monolabeled prod. from run 1	2 *M* NaOH	1	.005	0.01	
4	Dilabeled[b]	2 *M* NaOH	1	0.780	1.02	
5	Monolabeled prod. from run 4	2 *M* NaOH	1	0.768	1.00	
6a[c]	Dilabeled	1 *M* KOH, 25% aq. methanol	1 min.	1.485	1.94	
6b[d]				1.135	1.48	
7a	Unlabeled	2 *M* $NaO^{18}H$	1	0.742	0.97	
7b	Monolabeled[e]	0.2 *M* $NaO^{18}H$[f]	1	.538		30
7c	Monolabeled[e]	0.2 *M* $NaO^{18}H$[f]	6	.065		100
7d	Monolabeled[e]	2 *M* $NaO^{18}H$[f]	1	.096		94

[a] 1.53 atom % excess O^{18}. [b] Prepared by reduction of 3-benzylidenephthalide with zinc dust and $NaO^{18}H$ in H_2O^{18} (1.53 atom % excess O^{18}) followed by lactonization with acid. [c] Temp. 25°; analysis of recovered unhydrolyzed fraction. [d] Analysis of hydrolyzed fraction from run 6a obtained by acidification of the aqueous phase. [e] Aliquots of solution of sodium salt which upon acidification give monolabeled lactone, hydrolysate in run 7a. [f] 0.15 atom % excess O^{18} (dilution of an aliquot from run 7a containing 1.53 atom % excess O^{18} with ordinary water and, in the case of run 7d, unlabeled 2 *M* NaOH solution).

Results and Discussion

Saponification–Relactonization of 3-Benzhydrylphthalide (IV).—Solid 3-benzhydrylphthalide is saponified in approximately 1 hr. in boiling aqueous sodium hydroxide (2 *M*). Acidification of the resulting homogeneous solution by pouring it into cold aqueous hydrochloric acid causes rapid lactonization and the only product isolated is identical with the starting lactone IV. Table I summarizes the oxygen-18 labeling experiments carried out involving this saponification–lactonization process. When unlabeled 3-benzhydrylphthalide was saponified with labeled aqueous base (2 *M*) by boiling for 1 hr., then acidified with cold aqueous acid in normal water,[11] the resulting lactone contained cleanly the equivalent of one labeled oxygen per molecule (Table I, run 1). Threefold extension of the reaction time in the basic medium caused no increase in the O^{18} content of the relactonized material (run 2). When the monolabeled material, obtained in this way, was subjected to the same cycle but using normal water as the saponification medium, the isolated lactone had lost effectively all of its excess O^{18} content (run 3). When doubly labeled 3-benzhydrylphthalide (prepared by acidification of the product mixture from reduction of 3-benzylidenephthalide with zinc in O^{18}-enriched NaOH solution[11]) was saponified in normal water, the lactone isolated after acidification contained one labeled oxygen per molecule (Table I, run 4). The labeling content of this material was essentially unchanged by again subjecting it to the hydrolysis–lactonization cycle in ordinary water (run 5).

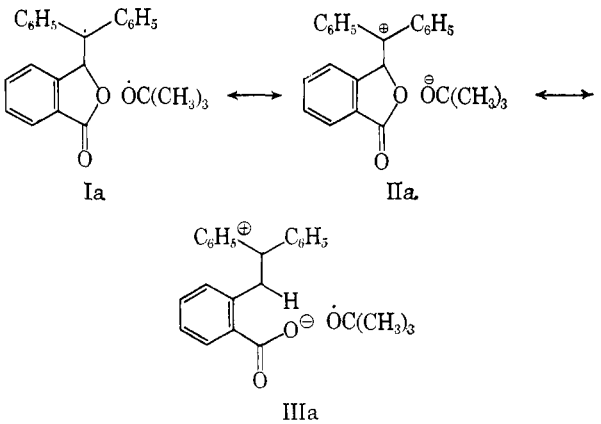
Runs 1–5 clearly demonstrate that the net effect of the saponification–lactonization cycle is the clean exchange of one of the oxygen atoms of the original lactone with the solvent while the other is retained throughout the sequence. If it is assumed that the basic hydrolysis step proceeds normally to give the carboxylate anion of the expected hydroxy acid V as the water-soluble species, then there appears to be no reasonable mechanism consistent with the above results which involves the specific exchange of the alkyl oxygen atom of the lactone structure.

The intermediacy of the hydroxy acid may be inferred from the results of an experiment in which a cold chloroform extract was obtained immediately after acidification of the saponification product mixture. The extract was shown to contain a material which could be extracted by aqueous bicarbonate and converted to the lactone upon acidification. The lactone is not extracted from chloroform by aqueous bicarbonate under these conditions. We therefore conclude that the exchange mechanism is one which cleanly gives exchange of the carbonyl oxygen with solvent. The intermediate hydroxy acid must have exchanged both carboxylate oxygen atoms with solvent before relactonization.

These results were met with mild surprise since it has been shown that the rates of hydrolysis of carboxylate esters and, in particular, of phthalide[12] itself greatly exceed their rates of O^{18} exchange in basic media. It was therefore considered unlikely that the exchange had occurred in the lactone before hydrolysis. The limited data available[13,14] also indicate that the rates of exchange of carboxylate anions are much too small to explain the results of runs 1–5.

The possibility that the large substituent on the methylene group of our phthalide might slow down

(10) Structures corresponding to the general structures I, II, and III for this particular compound are



(11) Exchange does not occur at the acidification step since in the preparation of the doubly labeled compound the lactonization was accomplished in normal water.

(12) M. L. Bender, *Chem. Rev.*, **60**, 53 (1960).

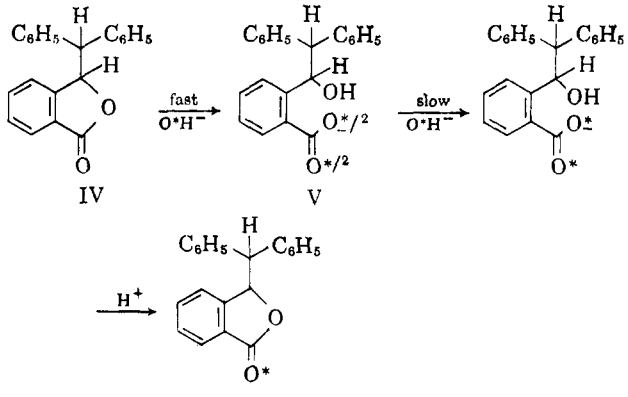
(13) C. A. Bunton and A. Konasiewicz, *J. Chem. Soc.*, 1354 (1955).

(14) R. D. Bentley, *J. Am. Chem. Soc.*, **71**, 2765 (1949).

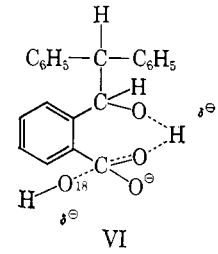
the hydrolysis sufficiently to invert the exchange-to-hydrolysis rate ratio quoted by Bender[12] for phthalide, made it seem desirable to run an appropriate control experiment. A sample of the doubly labeled lactone was dissolved in methanol, aqueous base added, and the resulting solution shaken for 1 min. at room temperature and quickly quenched in a large amount of water. Extraction of the basic mixture with ether was used to recover the unhydrolyzed lactone. Its analysis showed little decrease in O^{18} content (run 6a). Acidification of the basic hydrolysate from which the ether extract had been removed yielded the lactone from the hydroxy acid. Analysis of this material (run 6b) showed it to have retained 75% of the O^{18} enrichment of the original sample. These results suggest that the exchange occurs in a process slow relative to initial hydrolysis.

Runs 7a–d of Table I gives further evidence that the exchange occurs after hydrolysis. Unlabeled lactone was hydrolyzed as in run 1 using labeled solvent. After boiling for 1 hr. in the basic medium an aliquot was removed (run 7a) and acidified and the lactone isolated as a control (a duplication of run 1). Second and third aliquots of the original basic solution were diluted to ten times their volume with normal water and refluxed for 1 and 6 hr., respectively. The lactones isolated after this treatment had lost 30 and 100% of the O^{18} enrichment which must have been present after the initial basic hydrolysis (as evidence by run 7a). A fourth aliquot of the original basic solution was diluted to ten times its volume with 2 *M* sodium hydroxide in normal water and boiled for 1 hr. The isolated lactone showed that 94% of the O^{18} enrichment present after the initial hydrolysis had been re-exchanged with the diluted (in O^{18} content) solvent.

Thus the mechanism of this saponification–lactonization cycle consists of normal base-catalyzed hydrolysis of the lactone with acyl–oxygen cleavage. This is a relatively fast step (under homogeneous conditions) followed by a slower exchange of the oxygen atoms of the carboxylate anion. The acid-catalyzed lactonization then occurs, with loss of one of the carboxylate oxygen atoms.



Though the rate of exchange of the carboxylate anion is slow relative to the rate of hydrolysis of the lactone, it is of the order of 10^2–10^3 times as fast as the rate of exchange of sodium acetate in basic medium (calculated from the date of ref. 13). There are at least two reasonable postulates for the origin of this acceleration. Hydrogen bonding between the neighboring hydroxyl group and the carboxylate anion might render the carboxylate more susceptible to attack by the hydroxide ion. Such an effect has been postulated[12,15] to account for accelerations in the rates of saponification of hydroxy esters. In this case, a transition state for such intramolecular electrophilic catalysis by the neighboring hydroxyl group might resemble VI. This involvement of the hydroxy group provides



VI

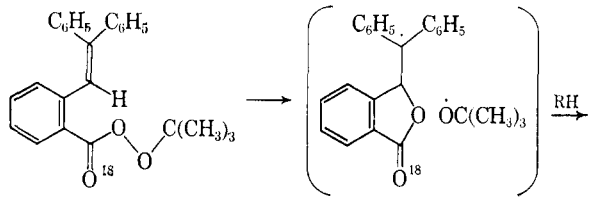
a way to avoid the concentration of two full negative charges on the carboxylate oxygens of the intermediate resulting from the attack of hydroxyl ion on the carboxylate carbon atom in the absence of neighboring hydroxyl. It would be expected to provide a substantial acceleration.

Alternatively, the exchange may be attributable to the presence of a small amount of the lactone in equilibrium with the carboxylate ion in the aqueous basic solution with the exchange occurring by the usual mechanism[12] involving the lactone. The last run of Table I argues against this possibility if the increase in the extent of exchange with increased NaOH concentration may be identified with the increase in hydroxide ion concentration. We have not, however, ruled out the possibility that the rapid exchange in the stronger base results from the operation of an unusually large kinetic salt effect. A choice between these two explanations is not possible from the available data, although the former seems much more likely.

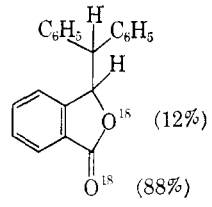
The remaining uncertainty in the mechanism of the exchange reaction does not detract from the utility of the saponification–lactonization cycle as a method for analyzing the O^{18} distribution in 3-benzhydrylphthalide. The excess O^{18} remaining after treatment with 2 *M* aqueous sodium hydroxide for at least 1 hr. is that which was originally present in the alkyl position of the lactone and the difference between this and the total excess O^{18} in the lactone before hydrolysis corresponds to the enrichment of the carbonyl oxygen.

Perester Decomposition.—The major (nonvolatile) products of the decomposition of *t*-butyl *o*-(2,2-diphenylvinyl)perbenzoate in chlorobenzene are 3-benzhydrylphthalide (IV, 35%), 3-benzylidenephthalide (16%), and dimeric material (35%).[1] Of these products the saturated lactone IV resulting from hydrogen abstraction by the bridged benzhydryl radical VII is the product most characteristic of free-radical processes and most difficult to explain by a nonradical pathway.[1] Pure 3-benzhydrylphthalide could not be isolated from this decomposition mixture, but when the reaction is carried out in the presence of 10% of the hydrogen donor 1,4-cyclohexadiene the yield of this lactone is increased to 60% and fractional recrystallization of the solid residue from the decomposition mixture gives the pure lactone.

(15) M. L. Bender, F. J. Kenzdy, and B. Zerner, *J. Am. Chem. Soc.*, **85**, 3017 (1963); T. C. Bruice and T. F. Fife, *ibid.*, **84**, 1973 (1962); S. M. Kupchan, S. P. Eriksen, and Y. Shen, *ibid.*, **85**, 350 (1963), and leading references.



VII VIII



IV

Table II summarizes the isotopic analyses on the decomposition product of *t*-butyl *o*-(2,2-diphenylvinyl)perbenzoate-*carbonyl*-O^{18}. It was shown that all of the excess O^{18} of the perester (1.01 atom % excess, per labeled oxygen) was in the carbonyl position by treating the labeled material with sodium methoxide and isolation and analysis of the resulting methyl *o*-(2,2-diphenylvinyl)benzoate (1.02 atom % excess, per labeled oxygen). The 3-benzhydrylphthalide obtained from the decomposition of the labeled perester in chlorobenzene containing 10% 1,4-cyclohexadiene contained the same excess of O^{18} as did the perester (adjusted for total oxygen content). Treatment of the solid residue from the crude product mixture with aqueous base (2 *M*) for 1 hr.[16] and isolation of 3-benzhydrylphthalide by acidification of the basic solution gave lactone in which 88% of the original label had been exchanged with the solvent, experiment 2. This provides a direct measure of the amount of O^{18} in the carbonyl position. Almost identical results were obtained from a second sample of perester with a lower level of labeling decomposed at 90° in chlorobenzene containing only 1% 1,4-cyclohexadiene, experiment 3.

TABLE II

DISTRIBUTION OF O^{18} IN 3-BENZHYDRYLPHTHALIDE (IV)

Expt.	Mole % 1,4-cyclohexadiene	Atom % O^{18}/molecule	Alkyl O^{18}, %
1[a]	10	0.517[b]	..
2[a]	10	.060[d]	12
3[c]	1	.036, 0.036[d]	12
4[c]	100	.074, 0.075[d]	25

[a] From the decomposition of *t*-butyl *o*-(2,2-diphenylvinyl)-perbenzoate containing 1.03 at. % excess O^{18} in the carbonyl position. [b] Isolated from the decomposition products without hydrolysis. [c] From the decomposition of *t*-butyl *o*-(2,2-diphenylvinyl)perbenzoate containing 0.59 atom % excess O^{18} in the carbonyl position. [d] After exchange of the carbonyl oxygen atom with ordinary water.

The observed degree of specificity (76% specific, 24% scrambled) supports the proposed[1] bonding in the transition state (*i.e.*, structures I and II) for the decomposition of this perester and further indicates that, at least for this 76% of the reaction, the product radical is bridged (as in VII) with the C–O bond initially formed remaining intact in the succeeding steps leading to isolable product. While this does not rule out an appreciable contribution of structure III to the description of the transition state, it does, in conjunction with kinetic evidence,[1] suggest that III is not the sole contributor. The preference for bonding to the peroxy oxygen of the carboxylate group and the magnitude of this preference are similar to those observed for the reaction of cyclic phthaloyl peroxide with stilbene[17] and also for the radical-induced decompositions of benzoyl peroxide by trityl,[18] cyclohexenyl,[18] and α-ethoxyethyl radicals.[18–20]

There are a number of possible origins for the 24% of lactone in which the two oxygens have become equivalent. Cage recombination of the initially formed radical pair VII to yield perester with scrambled labeling could account for this observation. Such a process does not occur in the decomposition of *t*-butyl perbenzoate,[21] but this does not unequivocally rule against it for the present compound. It is difficult to explain the greater scrambling of label in the product from the decomposition in cyclohexadiene solvent, over that when chlorobenzene was used as solvent, on the basis of this postulate. A more likely origin for the formation of the product with equilibrated oxygen atom is competitive unassisted cleavage of the perester to give a carboxy radical which would add to the neighboring olefinic function giving the same intermediate radical species as is formed directly during assisted decomposition. When the decomposition is carried out in pure 1,4-cyclohexadiene the lactone isolated after basic exchange of carbonyl oxygen atom still contains 25% of the labeling present in the original perester. Thus in this solvent the path which leads to the lactone with equilibrated oxygen atoms becomes as important as the specific one (50%). The magnitude of the acceleration in the rate of decomposition of this perester responds to solvent polarity (rel. rate 67 in methanol to 1 in cyclohexane at 90°). The unassisted cleavage is probably much less sensitive to medium effects. Since 1,4-cyclohexadiene would be expected to be less polar than chlorobenzene, the increase in the fraction of the product lactone in which the two oxygen atoms have been equilibrated could be a result of the decrease in the rate of assisted cleavage attributed to the change in the polarity of the medium while the rate of unassisted homolysis is relatively unaffected and therefore becomes competitively more important. This latter result also argues against the formation of the scrambled product by reversible formation of the bridged radical since the lifetime of this radical species should be decreased in pure cyclohexadiene.

There are several other possible origins for the observed 3-benzhydrylphthalide with O^{18} in the alkyl position, but the data presented here have no bearing for or against them. The postulate[1] that the homolytic decomposition of *t*-butyl *o*-(2,2-diphenylvinyl)perbenzoate proceeds through a transition state with bonding between the peroxy function and the neigh-

(16) The rate of saponification of 3-benzylidenephthalide was found to be much smaller than that for the 3-benzhydrylphthalide and the treatment with base for this length of time affords a crude separation of these two decomposition products.

(17) F. D. Greene and W. W. Rees, *J. Am. Chem. Soc.*, **82**, 893 (1960).

(18) W. von E. Doering, K. Okamoto, and H. Krauch, *ibid.*, **82**, 3579 (1960).

(19) E. H. Drew and J. C. Martin, *Chem. Ind.* (London), 925 (1959).

(20) D. B. Denney and G. Feig, *J. Am. Chem. Soc.*, **81**, 5322 (1959).

(21) E. H. Drew, unpublished work, observed no scrambling of label in *t*-butyl perbenzoate recovered after 75% decomposition.

boring olefinic substituent appears to be supported by this study of the decomposition of the labeled perester.

Experimental[22]

Materials.—Purification of materials has been described previously.[2] 1,4-Cyclohexadiene was obtained from Aldrich Chemical Co. and was used without further purification. The preparation of 3-benzhydrylphthalide has been described.[1]

Analysis for Oxygen-18.—The procedure and apparatus used for the O^{18} analysis were those of Doering and Dorfman[23] as modified by Denney and Greenbaum.[24]

Exchange Experiments with 3-Benzhydrylphthalide.—The general procedure used in all the exchange experiments of Table I (except run 6) was the same, except for the indicated variation in reflux time in the basic media and the isotopic composition of the solvent. In a typical run the solid lactone (0.5 g., 0.017 mole) was boiled in 2 *M* NaOH prepared by adding 1 g. of anhydrous sodium methoxide to 10 ml. of water (or H_2O^{18}). After refluxing for 1 hr. all of the solid material had dissolved. The solution was extracted with $CHCl_3$ and ether, then acidified by pouring it into a mixture of 25 ml. of concentrated HCl and 50 g. of ice. After 1 hr. the organic material was extracted with ether. The ether solution was washed with 2% aqueous bicarbonate and water and dried over sodium carbonate. After evaporation of the solvent the material was recrystallized from ethanol solution or from ether–pentane. The recovery was 0.3 g. (60%).

In run 6 of Table I a sample of doubly labeled 3-benzhydrylphthalide (150 mg.) was dissolved in 20 ml. of 10% dioxane in methanol, and 5 ml. of 25% aqueous KOH was added. The solution was shaken for 1 min. and quenched in a large amount of cold water. The resulting mixture was extracted with ether and the lactone isolated as outlined above (60% recovery, as lactone). The alkaline aqueous solution from the hydrolysis was then acidified to give 25 mg. (16%) of the lactone, isolated as above.

***t*-Butyl *o*-(2,2-Diphenylvinyl)perbenzoate-carbonyl-O^{18}. Procedure A.**—Carbonyl labeled *o*-(2,2-diphenylvinyl)benzoyl chloride was prepared by hydrolyzing the acid chloride (15 g. or 0.046 mole) with excess H_2O^{18} (1.53 atom % excess O^{18}). The resulting acid was treated with thionyl chloride and the acid chloride thus obtained hydrolyzed again with H_2O^{18}. The acid was again converted to the acid chloride, m.p. 112–114° (4 g., 0.012 mole, 30% recovery). This acid chloride was added to an ether solution of pyridine (1 g., 0.014 mole) and *t*-butyl hydroperoxide (1.2 g., 0.014 mole) at −20°. Isolation by the published method yielded 2.25 g. (0.006 mole, 50%) of perester.

Anal. Calcd. for $C_{25}H_{24}O_3$: C, 80.58; H, 6.49. Found: C, 80.75; H, 6.61; O^{18}, 0.345, 0.326 atom % excess/molecule.

A sample (200 mg.) of this labeled perester was treated with excess sodium methoxide in methanol at room temperature. The solvent was evaporated and the residue dissolved in ether and extracted with water. The methyl *o*-(2,2-diphenylvinyl)benzoate thus obtained was recrystallized from methanol; m.p. 95–96°.

Anal. Calcd. for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 83.99; H, 5.85; O^{18}, 0.508, 0.516 atom % excess/molecule.

Procedure B.—A second method for the synthesis of carbonyl labeled *t*-butyl *o*-(2,2-diphenylvinyl)perbenzoate involved the exchange of *o*-toluic acid (27 g., 0.2 mole) with H_2O^{18} (1.53 atom % excess O^{18}, 50 g., 2.75 moles) and a trace of HCl. This mixture was boiled for 15 hr. The acid was extracted with chloroform, methanol (100 ml.) and concentrated sulfuric acid (10 ml.) were added, and the mixture was refluxed for 8 hr. The methyl *o*-toluate was distilled (b.p. 53° at 0.2 mm., yield 30 g., 90%).

Anal. Calcd. for $C_9H_{10}O_2$: C, 72.01; H, 6.67. Found: C, 71.79; H, 6.84; O^{18}, 0.538 atom % excess/molecule.

The ester was brominated with N-bromosuccinimide and treated with triphenylphosphine to give the corresponding phosphonium salt. The phosphonium compound (75 g., 0.15 mole) was added to a stirred mixture of dimethyl sulfoxide (250 ml.) and sodium hydride (7.2 g. of a 50% dispersion, 0.15 mole).[25] After 30 min., benzophenone (27 g., 0.15 mole) was added. No apparent reaction occurred. The mixture was heated at 75° for 24 hr. and poured into a mixture of hydrobromic acid and ice. The precipitated oil was dissolved in ether and extracted with water. The solvent was evaporated and the residual oil heated with recovered H_2O^{18} with added sodium methoxide (10 g.). The basic solution was extracted with chloroform and acidified to give an oily solid. This material was recrystallized from 80% aqueous ethanol yielding 10 g. (0.03 mole, 20%) of the desired acid, m.p. 166–168°. This acid was converted to the acid chloride and this to the perester by the normal procedure (2.5 g., 0.007 mole, from 0.022 mole of acid chloride, 28%).

Anal. Found: C, 80.21; H, 6.53; O^{18}, 0.197, 0.194 atom % excess/molecule.

Perester Decompositions.—The perester decompositions were carried out by dissolving the labeled material in the appropriate solvent and degassing the solution, sealing it under vacuum. After the solution had been heated for the required length of time, the solvent and volatile products were removed under vacuum. The resulting solid residue was then treated exactly as outlined for the exchange studies on 3-benzhydrylphthalide. In one experiment, in which the labeled perester (0.536 g., 1.03 atom % excess O^{18} in the carbonyl position) was decomposed at 100° in chlorobenzene (9 ml.) containing 1,4-cyclohexadiene (1 ml.) for 12 hr., several recrystallizations of the solid residue from ether–pentane gave 25 mg. (6%) of 3-benzhydrylphthalide, m.p. 147–149°.

Anal. Calcd. for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 83.60; H, 5.42; O^{18}, 0.517 atom % excess/molecule.

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