neutralize the base present. Ether was added to help precipitate the sodium chloride, and the precipitate was filtered off. The solvent was then removed and the residue was re-ketalized in the standard manner. The product was then worked up and distilled, b.p. 90–100° (0.15 mm.). The yield of crude ketal alcohol was 25.25 g.

In a flask fitted with a stirrer, dropping funnel, and an efficient fractionation take-off were placed, after drying under nitrogen, 500 cc. of *t*-butyl alcohol and 25.25 g. of the above ketone. Potassium (17.0 g.) was then added and the flask was heated to promote solution of the metal. When all of the metal had dissolved, about one-half of the alcohol was distilled off. Then 500 cc. of dry benzene was added and the benzene–*t*-butyl alcohol azeotrope was distilled off. Another 500 cc. of benzene was added and the distillation continued until about 700 cc. had been distilled. Methyl iodide (40 ml.) was then added and the suspension was refluxed with stirring for 3 days. The solution was cooled, and then filtered by inverted filtration. The solvent was removed and the oil was distilled, b.p. 125–128° (18 mm.), $n^{25.7}\text{D}$ 1.4605. The yield was 20.32 g. of product which still contained some alcohol, as shown by its infrared spectrum. The crude product was then treated with benzoyl chloride and pyridine in chloroform to react with the alcohol still present. After working up and then refluxing for 2 hr. with 5% hydrochloric acid to cleave the ketal, an oily layer remained which was taken up in ether and worked up to give an oil which was distilled, b.p. 83–87.5° (9 mm.), $n^{25.8}\text{D}$ 1.4506. The yield was 7.42 g.

The 2,4-dinitrophenylhydrazone, m.p. 128–128.8°, was prepared and recrystallized from 95% ethanol.

Anal. Calcd. for $C_{15}H_{20}N_4O_5$: C, 53.56; H, 5.99. Found: C, 53.82; H, 6.08.

The mixture m.p. with the derivative of the isomeric XV was 114.7–122.5°.

7α,10β-Dimethyl-6β-methoxy-$\Delta^{1,9}$-octalone-2 (XXIIa) and 7α,10α-Dimethyl-6β-methoxy-$\Delta^{1,9}$-octalone-2 (XXIIb).—A mixture (*ca.* 50:50) of these two octalones was prepared by two routes. The first was the same as for the octalone XVI. Starting with 3.83 g. (0.0245 mole) of ketone XXI, we obtained 1.32 g. of recovered starting material and 1.84 g. (55%) of product, b.p. 96–115° (0.01 mm.).

A 2,4-dinitrophenylhydrazone was prepared. It seemed to be a mixture, the melting point of which was raised with difficulty to 157.5–160.6°, with softening at 150.5°.

The other procedure was modeled on that of Yanagita, *et al.*[34] In a 10-cc. flat-bottom flask fitted with a magnetic stirrer, reflux condenser, and dropping funnel, and flamed under nitrogen, was placed 7.0 g. (0.0448 mole) of ketone XXI. The liquid was thoroughly degassed to remove oxygen. Sodium (0.1 g.) in very small pieces was added slowly at room temperature (2 hr.), and the solution was stirred until all of the sodium had dissolved (1 hr.). Then 3.01 g. of 4-diethylamino-2-butanone, which had been previously degassed, was added rapidly. After 1 hr. the solution was slowly heated to 135° during 1 hr. and maintained there for 3 hr. The product was worked up and the oil was distilled to give 3.83 g. of recovered starting material and 2.92 g. (69.3%) of product, b.p 95–103° (0.01 mm.).

A 2,4-dinitrophenylhydrazone was prepared and recrystallized from ethyl acetate and 95% ethanol to give an erratically melting derivative, m.p. 140.5–145.3°, with softening at 137° (presumably a mixture of C_{10}-epimers (see below)).

Anal. Calcd. for $C_{19}H_{24}O_5N_4$: C, 58.75; H, 6.23. Found: C, 58.89; H, 5.96.

Mixture of 3α,9β-Dimethyl-2β-methoxydecalin and 3α,9α-Dimethyl-2β-methoxydecalin.—This decalin mixture was prepared from the octalone mixture XXIIa and XXIIb by the same procedure used for the preparation of the decalin XVIII. The corresponding decalol mixture was prepared in 94% yield; the decalone mixture XXIIIa and XXIIIb in 71% yield.

A pure 2,4-dinitrophenylhydrazone was obtained from the decalone mixture after recrystallization from ethyl acetate; m.p. 199.1–200.2°.

Anal. Calcd. for $C_{19}H_{26}N_4O_5$: C, 58.45; H, 6.71. Found: C, 58.91; H, 6.46.

The decalin mixture was prepared in 72% yield by the usual Wolff–Kishner reduction and the product was subjected to v.p.c. on a Craig polyester succinate column; two peaks were obtained. The first peak corresponded to 55 ± 3% and the second peak to 45 ± 3% of the mixture of decalins.

Degradation of the Decalin Mixture to *trans*-1-Methyl-1,2-cyclohexanediacetic Acid (XII).—The above decalin mixture was degraded by the same procedure used to degrade the decalin XVIII. A crystalline acid was obtained which, when recrystallized once from acetic acid and water, gave a white crystalline product, m.p. 193.9–195.8°. A mixture melting point with the authentic *trans*-1-methylcyclohexane-1,2-diacetic acid gave no depression.

In order to show that if one of the components of the decalin mixture had been *ca.* 50% of the *cis* isomer the acids could not have been separated by a simple crystallization, a mixture of pure *cis*- and *trans*-acids was prepared and an attempt was made to recrystallize the mixture as in the oxidative work-ups. Pure acid(s) could not be obtained.

Acknowledgment.—This work was supported in part by the National Science Foundation and the National Institutes of Health.

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[34] M. Yanagita, M. Hirakura, and F. Seki, *J. Org. Chem.*, **23**, 841 (1958).

[CONTRIBUTION FROM THE HALL LABORATORY OF CHEMISTRY, WESLEYAN UNIVERSITY, MIDDLETOWN, CONN.]

The Photochemistry of α-Keto Acids and α-Keto Esters. II. Solution Phase Photodecomposition of α-Keto Esters[1]

BY PETER A. LEERMAKERS, PAUL C. WARREN, AND GEORGE F. VESLEY

RECEIVED NOVEMBER 26, 1963

Methyl, ethyl, isopropyl, and 2-deuterioisopropyl pyruvate, ethyl benzoylformate, and ethyl α-naphthoylformate have been irradiated at 3660 Å. in benzene solution. Products have been isolated and quantum yields for the decompositions measured. The evidence presented indicates a mechanism involving photodecarbonylation in the primary process leaving caged radicals which can disproportionate to give the aldehyde derived from the acid fraction and the aldehyde or ketone derived from the alcohol fraction of the ester. A brief discussion of the excited states involved and a novel approach to the synthesis of pyruvic esters is presented.

Introduction

In a brief communication Hammond and co-workers reported that ethyl pyruvate was a triplet excitation acceptor for benzophenone leading to relatively efficient decomposition of the ester yielding acetaldehyde and carbon monoxide as the only isolable products.[2] Since those authors used this reaction only as an example of an energy transfer process, we have undertaken to study the novel photochemical reactions of α-keto esters from the organic chemist's standpoint, and have attempted to elucidate the general mechanism of the photodecarbonylation reaction.

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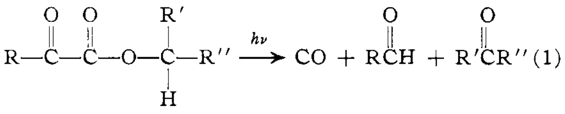
[1] Part I of this series is P. A. Leermakers and G. F. Vesley, *J. Am. Chem. Soc.*, **85**, 3776 (1963).

[2] G. S. Hammond, P. A. Leermakers, and N. J. Turro, *ibid.*, **83**, 2395 (1961).

The photochemistry of simple esters in solution, reported by Ausloos,[3] appears to have little relevance to the photochemistry of esters containing the α-carbonyl substituent. In the simple esters, in which the light absorbed was of considerably shorter wave lengths than in our studies, complex fragmentation with apparently low quantum yield was found to occur, and for esters other than formates, decarboxylation was significantly more important then decarbonylation. We now wish to report our rather different observations in the photolyses of various α-keto esters in solution.

Results and Discussion

Although a material balance has not been obtained for any of the keto esters studied, the following general reaction is an important decomposition path in the photoreaction of α-keto esters



$$R-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-O-\underset{\underset{H}{|}}{\overset{\overset{R'}{|}}{C}}-R'' \xrightarrow{h\nu} CO + R\overset{\overset{O}{\|}}{C}H + R'\overset{\overset{O}{\|}}{C}R'' \quad (1)$$

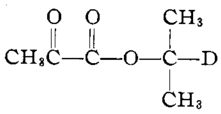
where R′ and R″ = alkyl and/or hydrogen and R = alkyl or aryl.

Table I lists the products and approximate net yields in the decompositions of the various esters in benzene. The concentration of starting material was generally 0.15 *M*, and reactions were run to 60–80% completion. The products not accounted for in the table were colored intractable residues.

TABLE I

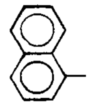
Ester	Products	Net yield, %
$CH_3COCOOCH_3$	CH_3CHO	20
	CH_2O	8
	CO	65
$CH_3COCOOCH_2CH_3$	CH_3CHO	60
	CO	80
$CH_3COCOOCH(CH_3)_2$	CH_3CHO	15
	CH_3COCH_3	83
	CO	50
$C_6H_5COCOOCH_2CH_3$	C_6H_5CHO	30
	CH_3CHO	25
	CO	30

Formally, the reaction involves migration of a hydrogen atom from the 1-carbon of the alcohol portion of the ester to the *ketone* carbonyl group of the acid portion with removal of the ester carbonyl. It was of interest to us to determine whether the shift of hydrogen occurred in the *primary* photochemical process (concerted with the decarbonylation), or whether decarbonylation took place leaving caged acyl and alkoxy radicals which could then disproportionate to give the indicated products. If the primary process involves a concerted hydrogen migration, then the quantum yield for 2-deuterioisopropyl pyruvate could be somewhat lower than that for the same undeuterated ester provided the *vibrational* energy of the electronically excited ester is not high enough to nullify the importance of the difference in activation energies for hydrogen *vs.* deuterium transfer. This particular compound was selected because of the high net yield of acetone produced, indicating that a large percentage of the photodecomposition of this ester proceeds *via* the reaction path with which we are concerned. Table II lists the quantum yields at 3360 Å. for the photodecompositions of the various esters studied.



$$CH_3\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-D$$

TABLE II

Ester[a]	φ
$CH_3COCOOCH_2CH_3$	0.17[b]
$CH_3COCOOCH_3$	.15 ± 0.02
$CH_3COCOOCH(CH_3)_2$	.18 ± .01
$CH_3COCOOCD(CH_3)_2$	.19 ± .02
$C_6H_5COCOOCH_2CH_3$	.056 ± .005
 $-COCOOCH_2CH_3$	<0.01

[a] Concentration in all cases was 0.20 *M*, and photolyses were carried to less than 30% conversion. [b] Used as the actinometer; ref. 2.

From the data one sees that in fact there is no isotope effect in the isopropyl ester; closer inspection of the data reveals that *all* of the *pyruvate* esters decompose with very similar quantum efficiencies. Thus one finds little or no effect of primary *vs.* secondary *vs.* tertiary migrating hydrogen (and one would then probably not expect an isotope effect in the isopropyl esters).

If hydrogen were being transferred in the primary process, it is reasonable to assume (but not rigorously so, owing to the high excitation energies possessed by these reacting species) that the difference in the kind of hydrogen atom transferred would manifest itself in the quantum yields. Thus, although we should not completely exclude the possibility of the intramolecular mechanism, it is our opinion that the data best fit a mechanism in which the primary, irrevocable photochemical act is loss of carbon monoxide (both bonds to the carbon probably being broken simultaneously or nearly so), this loss *not* being influenced by the nature of the alkoxy substituent, with subsequent formation of an acyl and an alkoxy radical in a solvent cage. The radicals then may disproportionate giving the products indicated in the general reaction of interest (1) or they may become "free" and react in a number of ways leading to the intractable high molecular weight products. Unsuccessful attempts were made to isolate ethoxybenzene and acetophenone from the reaction of ethyl pyruvate in benzene. It is significant that no product obtained by coupling or the geminate radical pair (the simple ester) was ever observed in the decomposition of any of the keto esters studied. Such products would have been easily observable under the analytical conditions. Although we cannot with any certainty account for this phenomenon, it is possible that if the reaction does take place in the triplet state (*vide infra*), and the spins of the radical pair do not become uncorrelated, the disproportionation reaction (and other side reactions) could overrule radical coupling.

Available evidence indicates that ethyl pyruvate[2,4] decomposes in its triplet state, and this would almost surely be true in the case of the methyl and isopropyl esters as well. Both ethyl[4] and isopropyl pyruvate

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(3) P. Ausloos, *J. Am. Chem. Soc.*, **80**, 1310 (1958).

(4) N. J. Turro, Ph.D. Thesis, California Institute of Technology, 1963.

phosphoresce strongly at 77°K. The 0–0 band of ethyl pyruvate in EPA corresponds to a triplet energy of 65.0 kcal. The spectrum of isopropyl pyruvate has been analyzed in more detail, showing the 0–0 band in an ethanol glass at 64.5 kcal. and the 0–0 band in MCIP (methyl cyclohexane–isopentane) at 63.9 kcal. The vibrational spacing between the 0–0 and 0–1 bands in both cases is about 1700 cm.$^{-1}$. The higher energy in the more polar glass and especially the 1700 cm.$^{-1}$ gap between the first and second bands are highly indicative that the emission is from the n–π^* triplet.

One notices in Table II that the phenyl analog of ethyl pyruvate, namely ethyl benzoylformate, decomposes only about one-third as efficiently as the pyruvic esters, and that the naphthyl analog, ethyl naphthoylformate, has a quantum yield of zero (within experimental error). Although the emission spectrum of ethyl benzoylformate has not been recorded, one feels with reasonable confidence that its triplet state will lie approximately 5–8 kcal. lower than that of the pyruvic esters (although probably still n–π^*)[5]; thus its lower reactivity could be due to lower excitation energy.

The phosphorescence spectrum of ethyl naphthoylformate indicates a triplet state of yet lower energy with 0–0 band at 19,700 cm.$^{-1}$ (56.6 kcal.) in both ethanol and MCIP. The 0–1 band is 590 cm.$^{-1}$ further to the red and the (0–1) – (0–2) spacing is 640 cm.$^{-1}$. The lack of a solvent effect, the vibrational structure of the phosphorescence, and analogy to other naphthoyl compounds,[6] leads one to conclude that the emitting (and potentially chemically active) species is the π–π^* triplet. Thus the center of excitation is not located specifically in the carbonyl groups, and the molecule is apparently inert to photodecarbonylation.

A Convenient Synthesis of Pyruvic Esters.—Except for the ethyl ester, pyruvic esters are exceedingly difficult to prepare by conventional methods (Fischer esterification, *via* the acid chloride, etc.) due to the inherent sensitivity of pyruvic acid to these usually rather harsh conditions. We have found that refluxing a mixture of 12 g. of pyruvic acid, 100 g. of anhydrous calcium sulfate (powdered), and 100 ml. of the appropriate alcohol for 3 hr. gives about a 40% yield of both the methyl and isopropyl esters. This method should be suitable for the esterification of other sensitive acids as well.

Experimental

Materials.—Pyruvic acid was Matheson, Coleman and Bell 99% reagent grade, which was distilled prior to use, b.p. 39–42° at 1 mm. Ethyl pyruvate, Aldrich Chemical Co., Inc., was freshly distilled, b.p. 50–52° at 15 mm. Similarly, ethyl benzoylformate (Eastman White Label) was distilled prior to use, b.p. 75° at 1 mm. Organic solvents were reagent grade and were used without further purification.

Apparatus.—All product runs were carried out using a Hanovia 450-w. high pressure mercury arc with a quartz immersion reactor equipped with a eudiometer for collecting gases. A 2800 Å. cut-off filter was used in all cases. A Cary Model 14 recording spectrophotometer was used for all ultraviolet spectra. Infrared spectra were recorded on a Perkin–Elmer Model 137 Infracord spectrophotometer. Gas phase spectra were taken in a 10-cm. path-length cell; solution spectra were taken in chloroform using a 0.1-mm. cell.

Ethyl α-Naphthoylformate.[7]—Eighty-five grams (0.67 mole) of naphthalene and 100 g. (0.74 mole) of ethyl oxalyl chloride (Eastman White Label) were dissolved in 550 ml. of dried tetrachloroethane. This mixture was poured into a 3-l., three-necked round-bottom flask fitted with a True-bore stirrer and reflux condenser. The other neck of the flask was fitted with a piece of wide rubber tubing connecting an inverted 500-ml. erlenmeyer flask, held by a ring stand; 113 g. (0.85 mole) of aluminum chloride, placed in the erlenmeyer flask, was added to the mixture by adjusting two pinch clamps. The addition was made over a 3-hr. period at ice bath temperature. After the addition was completed, the mixture was stirred at room temperature for 12 hr. The mixture was poured over ice and ether added. The organic layer was separated and the aqueous layer extracted with several portions of ether. The ether layer was dried with magnesium sulfate. The ether was removed under vacuum and the tetrachloroethane distilled, b.p. 50° (35 mm.). The oily residue, a mixture of the α- and β-esters, was distilled, b.p. 155–174° at 1 mm., yielding 105 g. of product (69%).

The α- and β-esters were separated by dissolving the above yellow oil in 172 ml. of absolute alcohol, followed by the addition of 100 g. of picric acid. Upon heating, a clear yellow solution was obtained which produced a crystalline precipitate when cooled. The precipitate was filtered and washed with cold alcohol and the filtrate discarded since only the α-ester was desired. The picric acid compound was suspended in 1 l. of water and 10% sodium carbonate was added until the solution was alkaline. The oily ethyl α-naphthoylformate which separated was extracted with 1 l. of carbon tetrachloride which was subsequently removed under vacuum; 55 g. of α-ethyl naphthoylformate distilled at 158–163°[8] at 1 mm.; 53% of the α- and β-mixture was isolated as the α-ester.

Isopropyl Pyruvate.—In a 100-ml. flask, fitted with a reflux condenser, 10 ml. of freshly distilled pyruvic acid, 100 ml. of dry isopropyl alcohol, and 100 g. of finely powdered calcium sulfate were mixed. The anhydrous mixture was refluxed on a steam bath for 3 hr. with periodic agitation. The solution was filtered with a medium porosity sintered glass filter and then fractionally distilled under vacuum. The crude ester was mixed with 10% sodium bicarbonate, extracted with ether, and dried over magnesium sulfate; 5 g. (37%) of isopropyl pyruvate was obtained which distilled at 55–57° at 17 mm. pressure (lit.[9] 50.5–51° at 13 mm.).

Isopropyl pyruvate was identified by its infrared spectrum showing characteristic ester absorptions and its n.m.r. spectrum which showed an unsplit acetyl methyl at 7.68 and a methyl doublet at 8.75 τ, based on tetramethylsilane as an internal standard. The tertiary proton, a septet, appears at 4.90 τ. The integrated areas are in the expected ratio 3:6:1.

2-Deuterio-2-propanol.—In a 500-ml. three-necked flask 2.5 g. (0.060 mole) of lithium aluminum deuteride, 98% (Metal Hydrides Inc.), was dissolved in 150 ml. of anhydrous ether. To this well-stirred mixture was added a solution of 20 ml. of acetone (distilled from potassium permanganate and dried) in 100 ml. of anhydrous ether over a period of 1 hr. After the addition was complete, the mixture was refluxed for 3 hr. while being constantly stirred; 6 ml. of water was slowly added and the mixture was then filtered, dried with magnesium sulfate, and distilled, b.p. 80–82°; 6 g. of 2-deuterio-2-propanol was obtained (40%).

Deuterioisopropyl Pyruvate.—Deuterioisopropyl pyruvate was prepared by the procedure outlined for the nondeuterated compound using 6 g. of 2-deuterio-2-propanol as the limiting reagent; 3 ml. of deuterioisopropyl pyruvate was obtained, b.p. 61–62° (22 mm.). The n.m.r. spectrum of the deuterated ester showed two unsplit methyl peaks at 7.68 and 8.75 τ, whose integrated areas are in the ratio of 1:2. There was no evidence of a tertiary proton in the region of 5 τ; therefore it was assumed that the isopropyl pyruvate was completely monodeuterated.

Methyl Pyruvate.—Using the procedure described above, from 10 ml. (0.144 mole) of pyruvic acid there was obtained 6 g. (41%) of methyl pyruvate, b.p. 35–36° at 9 mm. (lit.[10] 136–

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[5] Pyruvic acid and pyruvic esters have exceedingly similar emission spectra, both with respect to energy and to the nature of the triplet states (n–π).[1] The triplet state of benzoylformic acid (and, hence, by analogy perhaps its ethyl ester) lies about 60 kcal. above the ground state,[1] and is n–π^*.

[6] G. S. Hammond and P. A. Leermakers, *J. Am. Chem. Soc.*, **84**, 207 (1962).

[7] F. F. Blieke and R. F. Feldkamp, *ibid.*, **66**, 1087 (1944).

[8] Reported[7] b.p. 167° (2–3 mm.).

[9] Byk-Guldenwerke, German Patent 526,366 (1928); *Frld.*, **17**, 279 (1928); no author given.

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.

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(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.]

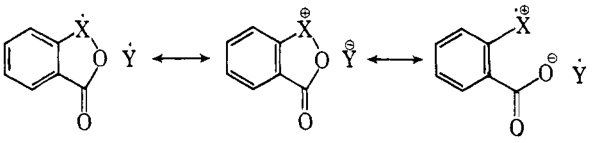
Anchimerically Accelerated Bond Homolysis. V.[1] Decomposition of an Oxygen-18 Labeled *t*-Butyl Perester

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

RECEIVED NOVEMBER 30, 1963

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.

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[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).