butoxide. A vapor phase chromatogram taken of a hydrolyzate of this salt showed the presence of *t*-butyl hydroperoxide and small amounts of *t*-butyl alcohol, but no trace of di-*t*-butyl peroxide.

Ozonization of Solid Potassium *t*-Perbutoxide.—Finely powdered potassium *t*-perbutoxide (1.9 g.) was ozonized at −78° in the course of 3 hr. following the same procedure used with the first experiment on potassium *t*-butoxide. As in the previous experiments, the white solid assumed an orange-red color immediately upon coming in contact with the ozone. On the basis of the net oxygen evolved, at the end of the experiment, the over-all conversion was 39%. Moreover, the rate of oxygen evolution between −30° and −10° was very rapid as compared with that of the experiments with either potassium dioxide or potassium *t*-butoxide. It was, therefore, suspected that, in this case, an unstable intermediate must have been formed at −78° and decomposed spontaneously above −30°.

In another experiment, potassium *t*-perbutoxide (3.36 g. equivalent to 0.0257 mole of 100% $(CH_3)_3COOK$) was dropped into the vessel A (Fig. 2) in small portions at −78°, with magnetic stirring, in the course of 4 hr. while dry oxygen containing 6% ozone was allowed to pass through the apparatus countercurrently at the rate of about 0.230 mmole per min. At the end of the experiment the orange-red solid was extracted several times at −78° with liquid propane and the extracts filtered as before using the same technique which already has been described. The propane of the combined filtrates was then allowed to evaporate slowly until the temperature of the flask reached −30° which is 12° above the b.p. of propane. The flask was connected quickly to an Orsat apparatus and the white crystalline residue which remained began to disintegrate, with gas evolution, as the temperature of the flask was allowed to rise. The cooling bath was then removed and the temperature of the flask allowed to rise to 18°, at the temperature of which all the solid had changed into a liquid and the gas evolution stopped. The same operation was repeated with the flask empty to measure the gas due to expansion between −30° and +18°. Both volumes were converted to S.T.P. and the difference between the two gave the gas evolved (36.00 ml.) from the disintegration of the solid residue. A vapor phase chromatogram of the liquid showed the presence of 168 mg. of di-*t*-butyl peroxide and 26.9 mg. of acetone. The amount of *t*-butyl alcohol which was also present was not estimated since the original potassium *t*-perbutoxide contained *t*-butyl alcohol of crystallization.

On the basis of these figures and eq. 3 and 4, the over-all conversion to the di-*t*-butyl tetroxide was calculated to be 10.75%. Since the tetroxide is assumed to decompose into oxygen and *t*-butoxy radicals, and the latter either couple to form di-*t*-butyl peroxide or decompose to give acetone and ethane, one could easily calculate the volume of oxygen produced. This comes out as 30.95 ml. But the volume actually obtained was 36.00 ml., so that the difference, 5.05 ml., must be due to ethane. Unfortunately, the presence or quantity of ethane was not determined. However, when calculated from the amount of acetone obtained, it comes out as 5.2 ml. which is close to the estimated volume.

In another experiment, samples of the orange-red solid in vessel A, after the propane filtrations, were taken in capillary tubes which were sealed in nitrogen at low temperatures and the paramagnetic spin resonance measured at −196°. Spectrum B of Fig. 1 shows the results of the measurements which give a *g*-value of 2.00.

Acknowledgment.—The authors wish to thank Dr. David H. Douglass, Jr., Paul F. Keller and John D. Kierstead of the Research Laboratory of Electronics for the paramagnetic spin measurements, Mrs. Mary H. Kerr for technical assistance and Lucidol Division of Wallace and Tiernan, Inc., for financial support of this investigation.

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY, CAMBRIDGE 38, MASS.]

Peresters. VIII. Di-*tert*-butyl Monoperoxyoxalate

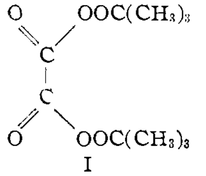
BY PAUL D. BARTLETT, BORIS A. GONTAREV AND HIDEKI SAKURAI

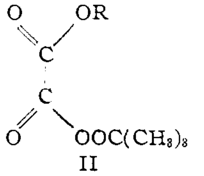
RECEIVED FEBRUARY 15, 1962

Di-*tert*-butyl monoperoxyoxalate (II, R = *tert*-butyl) decomposes in the temperature range 25–55° in benzene solution about three times as fast as di-*tert*-butyl diperoxyoxalate (I). In contrast to the latter ester, which in cumene solution yields 2 moles of carbon dioxide and 1.98 moles of free *tert*-butoxy radicals per mole of perester, the new compound affords 1.5 moles of carbon dioxide, 0.98 mole of scavengeable free radicals and 0.37–0.44 mole of di-*tert*-butyl carbonate. Most of the latter is shown to be formed by a cage effect; for in the presence of the efficient scavenger galvinoxyl[6] 0.348 mole of it is still formed from 1 mole of perester, while the carbon dioxide yield is cut to 1.01 moles. It follows that (1) the O–O and central C–C bond break in concert in the decomposition of di-*tert*-butyl monoperoxyoxalate; and (2) the carbo-*tert*-butoxy radical, $COOC(CH_3)_3$, is unstable but scavengeable, in contrast to the unscavengeable carbo-*tert*-butylperoxy radical $COOOC(CH_3)_3$. The present evidence is ambiguous as to whether the rapid decomposition of di-*tert*-butyl diperoxyoxalate (I) involves the concerted fission of three bonds or only two, but reasons are given for continuing to consider the former alternative.

Introduction

In previous work it has been found that the double perester, di-*tert*-butyl diperoxyoxalate (I), is an efficient initiator of chain reactions at temperatures as low as 25°, and shows no cage effect amounting to more than 1%.[1,2] This rapid decomposition could be approached, but not equaled, by esters of mono-*tert*-butylperoxyoxalic acid such as the ethyl (II, R = C_2H_5) or *p*-methoxybenzyl ester[3] (II, R = *p*-$CH_3OC_6H_4CH_2$).


I


II

The dependence of the decomposition rate of the substituted benzyl[3] and benzhydryl[4] esters of the type II upon the polar character of the substituents suggested the investigation of di-*tert*-butyl monoperoxyoxalate (II, R = *tert*-butyl) where electron release by the R group might be higher than in the previously examined cases.

Di-*tert*-butyl monoperoxyoxalate was prepared without difficulty by the reaction of *tert*-butylperoxyoxalyl chloride with *tert*-butyl alcohol in pentane solution in the presence of pyridine at −8 to −2°. It was isolated without warming, by

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(1) P. D. Bartlett, E. P. Benzing and R. E. Pincock, *J. Am. Chem. Soc.*, **82**, 1762 (1960).

(2) P. D. Bartlett and T. Funahashi, *ibid.*, **84**, 2596 (1962).

(3) P. D. Bartlett and R. E. Pincock, *ibid.*, **82**, 1769 (1960).

(4) P. D. Bartlett and N. L. Bauld, to be published.

washing and extraction of the solution, and gave only one fraction by chromatography on Florisil. It showed typical perester absorption at 5.58 μ and ester absorption at 5.72 μ; the former peak disappeared on decomposition of the perester and could be used to follow its decomposition quantitatively.

Products.—A study of the products of decomposition in degassed cumene solution gave the results shown in Table I. Di-*tert*-butyl diperoxyoxalate yields only carbon dioxide (2 moles), *tert*-butyl alcohol (2 moles) and bicumyl in this solvent. In contrast, di-*tert*-butyl monoperoxyoxalate produces 37–44% of one mole of di-*tert*-butyl carbonate; that fraction of the carbo-*tert*-butoxy radical which does not survive to recombine into this product is accounted for as carbon dioxide. Isobutane and isobutylene are also found, but in a total amount of only 0.24–0.27 mole per mole of perester out of 0.53–0.57 mole of *tert*-butyl radical that must have been formed along with the carbon dioxide.

TABLE I

DECOMPOSITION PRODUCTS OF DI-*tert*-BUTYL MONOPEROXYOXALATE IN CUMENE AT 24.60°

Compound	Amount, millimoles Run 1	Amount, millimoles Run 2	Mole/mole perester Run 1	Mole/mole perester Run 2
Original perester	2.58	2.52	1.00	1.00
Carbon dioxide				
by weight	3.97	3.96	1.54	1.57
by volume	4.00	3.86	1.55	1.53
Isobutane	0.54	0.70	0.21	0.37
Isobutylene	0.08		.03	
tert-Butyl alcohol	1.48	1.52	.57	0.60
Di-*tert*-butyl carbonate	1.10	0.93	.44	.37
Bicumyl	1.05	1.05	.41	.42

TABLE II

FIRST-ORDER RATE CONSTANTS[b] FOR DECOMPOSITION OF DI-*tert*-BUTYL MONOPEROXYOXALATE IN BENZENE

Temp., °C.	Concn., mole/l.	$k \times 10^5$, sec.$^{-1}$
25.5[a]	0.02333	6.33
25.5	.01785	6.91
25.7	.02516	6.59
25.7	.2516	5.00
40.3	.2500	47.7
40.3	.2500	50.2
40.3	.5023	37.0
54.2	.2508	182
55.7	.02508	288
55.7	.2508	210

[a] This run in cumene. [b] Observed by infrared absorption.

TABLE III

EFFECT OF GALVINOXYL[6] ON DECOMPOSITION OF DI-*tert*-BUTYL MONOPEROXYOXALATE

Rate constant × 10^5 at 25.5°	Perester alone	Perester with G.
In benzene		
Perester disappearance	6.90	
Scavenger disappearance		3.39
In cumene		
Perester disappearance	6.33	
Scavenger disappearance		2.95
Products in cumene (moles/mole perester)		
CO_2	1.55	1.01
Di-*tert*-butyl carbonate	0.37, 0.44	0.35
C_4-Hydrocarbons	0.24, 0.27	<0.03

Reaction Rate.—Table II summarizes the results of the rate studies over the temperature range 25.5–55.7°. There is little difference in rate between cumene and benzene solutions. In contrast to some other peresters, the first-order rate constant appears slightly but consistently higher in 0.025 *M* than in 0.25 *M* solutions in benzene. The most striking fact about the rate constants is that they are three times as great as for the related compound with twice as many perester groups, di-*t*-butyl diperoxyoxalate (I), under the same conditions.

The enthalpy and entropy of activation are determined to be 24.0 kcal. and 2.5 e.u., respectively, at the lower concentration, and 23.7 kcal. and 1.1 e.u. at the higher concentration, compared to 25.6 kcal. and 5.1 e.u. for di-*tert*-butyl diperoxyoxalate, all in benzene.

Effect of a Scavenger.—The zero cage effect seen in the decomposition of di-*tert*-butyl diperoxyoxalate (I)[2] despite the stability of di-*tert*-butyl monoperoxycarbonate[5] under the reaction conditions indicates that the carbo-*tert*-butylperoxy radical, $COOOC(CH_3)_3$, is so unstable that it decomposes in less than the time required to recombine with a *tert*-butoxy radical within the solvent cage. This conclusion is reinforced by the finding of so much di-*tert*-butyl carbonate as a reaction product of the monoperoxyoxalate in the present study. To verify that this carbonate is indeed formed by radical coupling within the solvent cage, di-*tert*-butyl monoperoxyoxalate was decomposed in the presence of an equivalent of the stable free radical and efficient scavenger galvinoxyl.[6] The results of rate studies with small amounts of this scavenger and of a quantitative determination of the carbon dioxide and di-*tert*-butyl carbonate, are shown in Table III. The carbonate is still found to the extent of 35%, the carbon dioxide is reduced cleanly to one mole per mole of perester, and the rate studies show that only 49% in benzene, and 47% in cumene, of the perester molecules decomposing produce scavengeable radical pairs. In the presence of galvinoxyl the decomposition of the carbo-*tert*-butoxy radical is completely forestalled, presumably by the formation of its addition product with the scavenger; but di-*tert*-butyl carbonate is formed in almost the same amount as without the scavenger. Thus the carbonate is formed by a true cage effect. Furthermore, the carbo-*tert*-butoxy and carbo-*tert*-butylperoxy radicals differ so greatly in their rates of decomposition that the one is fully scavengeable by galvinoxyl while the other cannot be scavenged at all.

Discussion

It is clear from the nature of the products that the decomposition of the peresters of type II involves concerted breaking of not more than two bonds, while the rate can scarcely be accounted for without the participation of both of these bond

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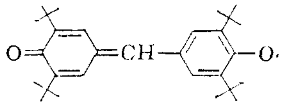
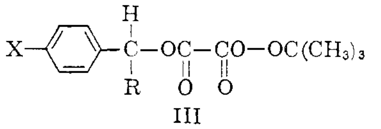
(5) P. D. Bartlett and H. Sakurai, forthcoming publication.

(6) Galvinoxyl[2,9] is



fissions in the rate-determining step. Therefore, the high rate of these decompositions is a consequence of a weakness of the oxalate carbon–carbon bond, a bond between two positively polarized carbon atoms. This conclusion would not necessarily imply the nature and magnitude of the effect of changes in the group R on the reactivity of II, and this question requires some discussion. In monoperoxyoxalates of the type III[3,4] where R =

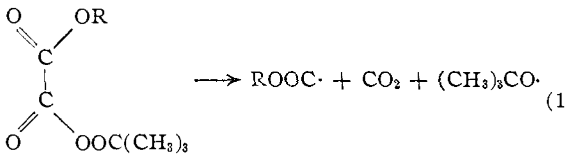


$X-C_6H_4-CH(R)-OC(=O)-C(=O)-O-OC(CH_3)_3$

III

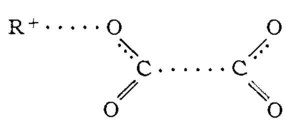
H, C_6H_5 or XC_6H_4, the dependence of decomposition rate on X is intermediate between a σ- and a σ^+-relationship; that is, the resonance effects of the groups X (including methoxyl) are more important than in the ionization of benzoic acids, but not as important as in the solvolysis of cumyl chlorides. It would be far-fetched to regard this effect as operating on the O–O bond, chemically and probably spatially remote from the perturbing substituent. An electron-releasing *inductive* effect on the oxalate C–C bond could scarcely do other than to strengthen the bond, whereas groups with negative σ in fact increase the rate. As with the decompositions of other peresters, we conclude that the activating effect must operate to lower the energy of the transition state more than to destabilize the perester.

If we compare the products from the ethyl and *tert*-butyl esters of *tert*-butylperoxyoxalic acid we conclude that the carbo-*tert*-butoxy radical is more unstable than the carbethoxy radical. The latter is intercepted by cumene to the point where only 12% of decarboxylation occurs,[3] compared with 53–57% from the carbo-*tert*-butoxy radical. If these figures are referred to those carboalkoxy radicals which escape the solvent cage, they become 17 and 87–98%, respectively, the last two figures being those for runs 1 and 2. It is entirely expected that an increased stability of the radical R should be attended by an increasing rate of decarboxylation of the radical COOR. What needs to be explained is the translation of this increased stability of R into a greatly increased rate (16-fold between ethyl and *t*-butyl) of reaction 1 in



$$ROOC-COOOC(CH_3)_3 \longrightarrow ROOC\cdot + CO_2 + (CH_3)_3CO\cdot \quad (1)$$

which no R· is set free. The evidence suggests that a channel exists in the transition state for the cationic stability of R to set up the contributing ionic bond structure IV. It must not be necessary



IV

in IV for the R–O bond to be stretched anywhere near the point of no return as are the C–C and O–O bonds which actually break. This suggestion appears quite consistent with the comparative activation parameters of the *tert*-butyl and the other monoperoxyoxalates (see above).

Although experiments of the kind here reported were undertaken in part to gain evidence on the mechanism of decomposition of di-*tert*-butyl diperoxyoxalate, DBPO (I), they provide no clear answer to the question whether two or three bonds are breaking in the rate-determining step for this double perester. The most efficient scavenger fails to capture any product short of the two *tert*-butoxy radicals and two carbon dioxide molecules corresponding to a one-step decomposition.[2] On the other hand, the rate of DBPO decomposition, which was the original basis of the suspicion that three bonds might be breaking in concert, is threefold less than that of di-*tert*-butyl monoperoxyoxalate in which the carbalkoxy radical can be scavenged. It would appear from the discussion above that the activation parameters would not be characteristically different for the two mechanisms, since the amount of orientation required for a transition state with the component IV is the same as that required for a concerted fission of three bonds. However, the symmetry of I and the polar character of the *tert*-butoxy radical seem to fit this perester poorly into the proposed mechanism for decomposition of the monoperoxyoxalates II, unless in the case of I the inductive effect of *tert*-butoxy brings about a direct weakening of the C–C bond of the oxalate. Concerning the hypothetical carbo-*tert*-butylperoxy radical we can say only that if it occurs in the decomposition of DBPO at all, it is of even shorter life than the acyloxy radicals from acetyl and other acyl peroxides, for no way has been found to capture this radical, in or out of the solvent cage.[6a]

Experimental

Materials. *tert*-**Butylhydroperoxide.**—Lucidol *t*-butyl hydroperoxide was purified as described in Part V.[1] After a large forerun the third fraction distilling at 34–37° at 2 mm. pressure was collected and stored at −25°.

Oxalyl Chloride.—Eastman Kodak Co. oxalyl chloride was used without further purification.

Pentane.—Phillips pure grade pentane was distilled from sodium through a 35-cm. Vigreux column at 35.2 ° and stored over sodium wire.

Pyridine.—Fisher certified reagent pyridine was refluxed overnight with barium oxide and distilled through a 37-cm. column packed with glass helices. The middle fraction boiling at 114° was collected and stored over sodium hydroxide pellets.

Cumene.—Eastman Kodak Co. white label cumene was stirred three times with concd. sulfuric acid in a ratio of about 10:1, until the acid layer became only light yellow on long stirring. After washing twice with water, 10% sodium bicarbonate solution and twice with water again, the cumene was dried with anhydrous magnesium sulfate and fractionated over sodium through a 37-cm. column packed with glass helices. The middle fraction boiling at 152.0–152.5° was collected and stored in the dark under nitrogen.

Di-*tert*-butyl carbonate was synthesized by the procedure of Choppin and Rogers.[7]

Anal. Calcd. for $C_9H_{18}O_3$: C, 62.04; H, 10.41. Found: C, 61.86; H, 10.89.

4,4′-Dihydroxy-3,5,3′,5′-tetra-*tert*-butyldiphenylmethane was prepared from 2,6-di-*tert*-butylphenol and 36% form-

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(6a) Compare L. Herk, M. Feld and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 2998 (1961).

(7) A. R. Choppin and J. W. Rogers, *ibid.*, **70**, 2967 (1948).

aldehyde.[8] Recrystallization of this compound from absolute ethanol gave colorless crystals; yield 80%, m.p. 156.8–157.6°. 2,6-Di-*t*-butylphenol (Eastman Kodak Co.) was recrystallized from ethanol; m.p. 37.0–38.0°.

Galvinoxyl was prepared after Coppinger[9] and recrystallized five times by dissolving in Merck reagent grade carbon tetrachloride and evaporating slowly under a stream of prepurified nitrogen at room temperature. It was of 98.0% purity based on optical density at 770 mμ, and the value of ϵ_{770} = 607 observed for a previous sample of 100.2% purity by titration.[2]

***tert*-Butylperoxyoxalyl chloride** was synthesized as described in Part VI[3] and used without further purification.

Di-*tert*-butyl Monoperoxyoxalate.—A solution of 2.50 g. of *tert*-butyl alcohol and 2.8 g. of pyridine in 15 ml. of pentane was added dropwise over an hour to a solution of 5.95 g. of freshly prepared *tert*-butylperoxyoxalyl chloride in 15 ml. of pentane at −2 to −8° with stirring. The precipitation of white pyridinium chloride occurred immediately. After stirring for 30 minutes longer the mixture was carefully washed twice each with 10% sulfuric acid, water, 10% sodium bicarbonate solution and water. The pentane layer was dried with anhydrous magnesium sulfate overnight at −25°. The pentane was evaporated under vacuum at 0° to leave 5.0 g. (69%) of colorless liquid di-*tert*-butyl monoperoxyoxalate.

Anal. Calcd. for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31. Found: C, 55.96; H, 8.52.

Chromatography on Florisil afforded only one fraction, identical in its infrared spectrum with the original material. The infrared spectrum could not be determined without the intrusion of absorptions due to decomposition products. The principal peaks observed in carbon tetrachloride which did not increase, or which decreased, with time were at 3.33, 5.58, 5.73, 6.87, 7.20, 7.32, 7.79, 8.05, 8.95 and 9.74 μ.

Di-*tert*-butyl monoperoxyoxalate decomposes at room temperature with evolution of carbon dioxide. When it is not diluted the decomposition may become violent. After a short time at room temperature the solutions used for determination of the infrared spectrum showed an increasing peak at 4.25 μ due to carbon dioxide.

Analysis of Decomposition Products.—The methods used were essentially those previously described.[1] In one run a solution of 0.5620 g. of di-*tert*-butyl monoperoxyoxalate in 10 ml. of cumene was degassed four times and allowed to decompose at 24.6° for 36 hours. There was 4.62 millimoles of condensable gas formed, and no non-condensable gas. After complete absorption of the carbon dioxide on Ascarite, 0.62 millimole of gas remained whose infrared spectrum showed bands corresponding to the known spectra of isobutane and isobutylene.[10,11] The residual gas was shown by its mass spectrum to be a mixture of 0.54 millimole of isobutane with 0.08 millimole of isobutylene, by comparison with published spectra.[12] The peaks at masses 43 and 56 being taken as standards, the intensities at 41, 42, 50, 51, 53, 55, 57 and 58 agreed with those calculated for this mixture within a mean deviation of 3.6 units on the scale of 660 for the most intense peak.

Comparison of the infrared spectrum of the volatile, nongaseous products in cumene with the spectra of authentic *tert*-butyl alcohol and di-*tert*-butyl carbonate indicated that only these compounds were present and that they had been formed in the amounts of 1.48 and 1.10 millimoles, respectively. A mixture of *tert*-butyl alcohol and di-*tert*-butyl carbonate in these proportions gave an infrared spectrum in cumene identical with that of the reaction product.

The residue in the reaction flask amounted to 0.2492 g. of a white solid melting over the range from 90 to 100°, which was identified as dicumyl.

The product study in the presence of galvinoxyl was carried out in a similar manner, except that the non-volatile residue was not isolated or characterized.

Kinetic Studies.—The rate measurements were made by the infrared technique described in earlier papers of this series.[13] A calibration curve of the intensity of the characteristic perester peak at 5.58 μ as a function of concentration of the perester was prepared, and this curve was used in determining perester concentration in the aliquots taken from the thermostated solution of the perester in cumene.

The rate determinations in the presence of galvinoxyl were made as described by Bartlett and Funahashi,[2] the disappearance of the scavenger being followed by its ultraviolet absorption.

Acknowledgment.—We thank the National Institutes of Health for a grant in support of this work.

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[8] M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1435 (1957).

[9] G. M. Coppinger, *J. Am. Chem. Soc.*, **79**, 501 (1957).

[10] R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.*, **15**, 120 (1947).

[11] R. S. Rasmussen, *ibid.*, **16**, 712 (1948).

[12] American Petroleum Institute Research Project 44, Mass Spectral Data, Serial Nos. 5 and 28.

[13] P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1404 (1958).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASS.]

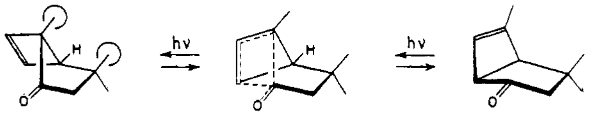
Photochemical Reactions. X.[1,2] Experiments with 1,3,5-Cycloöctatrien-7-one and Cycloöctatetraene Epoxide

BY G. BÜCHI AND EDWARD M. BURGESS[3]

RECEIVED DECEMBER 18, 1961

Irradiation of 1,3,5-cycloöctatrien-7-one in hexane solution yielded bicyclo[4.2.0]octa-4,7-dien-2-one. The anticipated bicyclo[2.2.2]octadienone was not detected. On exposure to ultraviolet light in methanol solution the monocyclic ketone was transformed to a methyl octa-1,3,5-trienoate of unknown configuration which on subsequent equilibration was partly converted to the known *trans-trans*-ester. Pyrolysis of cycloöctatrienone and its photoisomer furnished benzene, *o*-vinylphenol and *o*-vinylphenyl acetate. Cycloöctatetraene epoxide rapidly polymerizes to unrecognizable products on irradiation, but on pyrolysis at 260° it is isomerized to β-cycloheptatrienecarboxaldehyde which in turn is transformed to the γ-isomer by heating at 330°. Thermal treatment of all three isomers at 400° yielded phenylacetaldehyde. Possible mechanisms of the various transformations are discussed.

In an earlier paper we discussed the reversible photochemical equilibration of the two ketones (**1** and **3**) which may proceed through an activated complex (**2**).



1 2 3

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[1] Part of a program of research supported by a grant from the Godfrey L. Cabot Fund, Publication No. 74, M.I.T. Solar Energy Conversion Project.

[2] Part IX, G. Büchi and Edward M. Burgess, *J. Am. Chem. Soc.*, **82**, 4333 (1960).

[3] National Science Foundation Predoctoral Fellow 1960–.