Table VI

Solvent	Relative [PC]$_{wt.}$	Relative [PC]$_{peak\ area}$
Benzene	1.057	1.057
Thiolacetic acid	1.013	1.034
1-Hexyne	1.000	1.000

and 0.4542 g. of monoadducts (73.8% cis isomer) was added to 10 ml. of 4% aqueous sodium hydroxide solution containing 0.4888 g. of thiolacetic acid. This mixture was shaken well at room temperature and then stored in a refrigerator at ~5°. After 4 days, the organic layer was analyzed by v.p.c.; the mixture contained 73.4% cis isomer and the measured peak area of the monoadducts relative to phenylcyclohexane was 2.89, while the calculated unchanged value was 2.81.

Equilibration of cis- and trans-1-Hexenyl Thiolacetate. A. Two samples of the monoadduct mixture containing 77 and 17% cis isomer, respectively, were heated under nitrogen on a steam bath (ca. 90°) for several days. The mixtures were analyzed periodically by v.p.c. Both samples were converted to the same mixture after 11–12 days as shown in Table III. Further heating had no effect. Neither iodine nor *t*-butylthiol accelerated the isomerization.

B. Approximately 1 mole % of thiophenol was added to two samples of monoadduct containing 73 and 20% cis isomer, respectively. The samples were irradiated in Pyrex tubes with a General Electric sunlamp at 21–25° and analyzed periodically. Both samples gave the same mixture after 2–3 days as shown in Table III. The addition of more thiophenol and further irradiation had no effect.

C. Approximately 5 mole % of thiolacetic acid was added to a sample of monoadduct containing 74% cis isomer. After 4 days at 5°, the mixture contained 71% cis isomer and the thiolacetic acid could not be detected by v.p.c.

Photochemistry of 1,3-Cyclobutanediones. Decomposition Modes and Chemical Intermediates[1]

Nicholas J. Turro,[2] Peter A. Leermakers, H. R. Wilson, D. C. Neckers, G. W. Byers, and G. F. Vesley

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Several tetrasubstituted 1,3-cyclobutanediones have been photolyzed, with remarkably high quantum yield, in inert solvents (in the presence and absence of oxygen), in hydroxylic solvents, and in the vapor phase. Chemical evidence, supported by a recent report of spectroscopic evidence, indicates that in solution one of the primary intermediates, formed by monodecarbonylation, is the corresponding cyclopropanone. The latter reacts with alcohols (to form hemiketals which subsequently may react thermally), with dienes, and with oxygen. In the absence of the above scavengers, further decarbonylation occurs to give a tetraalkyl olefin in good yield. The vapor phase photolysis of tetramethyl-1,3-cyclobutanedione involves complex radical processes but one of the primary photolytic paths is apparently cleavage to yield 2 moles of dimethylketene which is subsequently photolyzed to carbon monoxide, propylene, and methane. Some tetramethylethylene is also formed. It is proposed that the chemically active excited state of the diones may be an n–π* singlet.

Introduction

Cyclopropanone and its derivatives are believed to be intermediates in the Favorskii reaction.[3] A 2,3-diazocyclopropanone was recently prepared[4] and possesses remarkable thermal stability and low reactivity toward nucleophiles. In contrast, no example of the unambiguous isolation and characterization of a cyclopropanone has been reported.[5,6] The photochemistry of tetraalkyl-1,3-cyclobutanediones was undertaken to determine if tetraalkylcyclopropanones are produced by monodecarbonylation and whether they exist as short-lived intermediates (perhaps capable of

(1) Preliminary accounts of part of this work have appeared previously: (a) N. J. Turro, G. W. Byers, and P. A. Leermakers, *J. Am. Chem. Soc.*, **86**, 955 (1964); (b) P. A. Leermakers, G. F. Vesley, N. J. Turro, and D. C. Neckers, *ibid.*, **86**, 4213 (1964).

(2) Visiting scientist, summer, 1964, Dow Chemical Co., Eastern Research Laboratory, Framingham, Mass.; National Science Foundation Postdoctoral Fellow, Harvard University, 1963–1964.

(3) See, for example, A. S. Kende, *Org. Reactions*, **11**, 261 (1960); A. W. Fort, *J. Am. Chem. Soc.*, **84**, 2620, 2625 (1962); **82**, 4979 (1960); R. C. Cookson and M. J. Nye, *Proc. Chem. Soc.*, 129 (1963).

(4) F. D. Green and J. C. Stowell, *J. Am. Chem. Soc.*, **86**, 3569 (1964).

(5) Although a number of cyclopropanones are claimed to have been prepared and isolated, none of these cases have been substantiated. See, for example, J. F. Cogdell, *Dissertation Abstr.*, **19**, 2751 (1959); H. K. Ingold, *et al.*, *J. Chem. Soc.*, **119**, 305 (1921); **121**, 1177 (1922); F. B. LaForge and F. Acree, *J. Org. Chem.*, **5**, 430 (1940); **6**, 208 (1941).

(6) The elegant attempts of Lipp and co-workers to prepare cyclopropanone indicate the difficulties to be encountered in isolation of this compound and its relatives: P. Lipp, J. Buchkremer, and H. Seeles, *Ann.*, **499**, 1 (1933); P. Lipp and R. Köster, *Ber.*, **64**, 2823 (1931); P. Lipp and H. Seeles, *ibid.*, **62**, 2456 (1929). See also: D. A. Semenow, E. F. Cox, and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 3221 (1956).

being isolated) in fluid solutions at 25°. In this paper we shall present evidence that our goals have been partially achieved and we shall attempt to correlate our results with those of other workers[7–9] in the field and present a general mechanism which accounts for the known photochemistry of tetrasubstituted 1,3-cyclobutanediones.

Spectral Properties of Tetraalkyl-1,3-cyclobutanediones. The electronic absorption spectra of a number of tetrasubstituted 1,3-cyclobutanediones are very similar.[10–12] The ultraviolet absorption spectrum[10–12] of tetramethyl-1,3-cyclobutanedione (I), as an example of this class of compounds, exhibits *two* distinct n–π* transitions. The higher energy transition, termed

I II

III
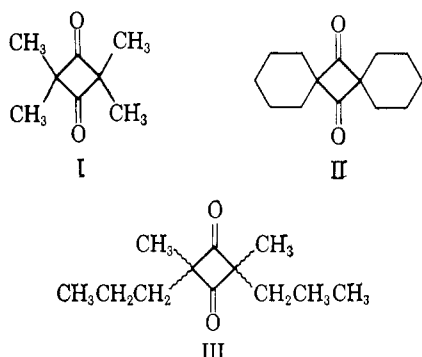
n → (π* − π*), possesses a highly structured absorption band which exhibits a maximum in isooctane at 3078 Å. (ϵ_{max} 40). The lower energy transition, termed n → (π* + π*), possesses a broad structureless absorption band which maximizes in isooctane at 3480 Å. (ϵ_{max} 20). The presence of two distinct n–π* transitions has been attributed to 1,3-π interactions in the excited states of I. Both n–π* absorption bands exhibit slight blue shifts of about 40 Å. in going from isooctane to ethanol.[11,12] No fluorescence or phosphorescence (a yield of 0.001 of either would have been detectable) from I was obtained at 77°K. in an ethanol–ether–isopentane glass.[13]
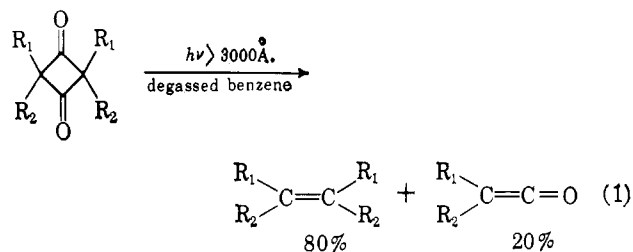
Photolysis of Tetraalkyl-1,3-cyclobutanediones in Inert Solvents. Photolysis of degassed solutions of tetraalkyl-1,3-cyclobutanediones results in the rapid evolution of carbon monoxide and a good yield of the corresponding tetraalkylethylene. Thus, the quantum yield for the disappearance of I in degassed benzene solution is 0.38 ± 0.01 and tetramethylethylene is formed as the major product (in 80% yield after exhaustive photolysis). The quantum yields for disappearance of the dispirodione II in degassed benzene or methylene chloride are 0.31 ± 01 and 0.34 ± 0.01, respectively, and bicyclohexylidene is produced (in 70% yield after exhaustive photolysis).

Ketenes are also formed in these photolyses. Photolyzed solutions quickly develop a yellow color and strong infrared band[14] at 4.7 μ, which is immediately

discharged by the addition of a few drops of alcohol. The total amount of dione which is photolyzed to yield ketene is difficult to evaluate quantitatively because dimerization of dialkylketenes to regenerate the diones proceeds at a rapid rate under the photolysis conditions.[15] We estimate that about 20% of the photolyzed dione yields ketene (at low conversions).

Preliminary experiments designed to determine the stereospecificity of olefin formation were performed with 2,4-dimethyl-2,4-di-*n*-propyl-1,3-cyclobutanedione (III). The photolysis of an 82% isomerically pure sample of III yields an olefin which is 75% isomerically pure. Thus, the reaction appears to be about 90% stereospecific, although it has not yet been possible to differentiate the *cis* from the *trans* form in either the dione or ethylene. This conclusion is not demanded until experiments with the other isomer of III have been performed.

In order to investigate whether intermolecular reactions contribute significantly to olefin formation, a benzene solution of comparable concentrations of I and tetraethyl-1,3-cyclobutanedione(IV)was photolyzed. Although tetramethylethylene and tetraethylethylene were formed in good yield, *no* diethyldimethylethylene could be detected by vapor phase chromatography (limit of detection about 0.1%).

$$R_1 \begin{matrix} \\ \\ \end{matrix} C = C \begin{matrix} R_1 \\ \\ R_2 \end{matrix} + R_1 \begin{matrix} \\ \\ \end{matrix} C = C = O \quad (1)$$

80% 20%

Vapor phase chromatographic (v.p.c.) analysis of a solution of I which was photolyzed *to low conversion* revealed the presence of a new component whose area in the vapor phase chromatograms corresponded to a significant portion of the photolyzed dione. This material was isolated by preparative v.p.c. and was shown to be isopropenyl isopropyl ketone (V) by comparison of its mass spectrum, infrared spectrum, and n.m.r. spectrum with those of an authentic sample.[16] As the photolysis of I progressed the yield of V approaches a steady state as shown in Figure 1. Analysis of the crude reaction mixture by n.m.r. and infrared spectroscopy showed that V *was completely absent;* consequently, we conclude that a *precursor* to V exists in the crude reaction mixture and this precursor rearranged to V during the v.p.c. analysis. If the reaction mixture is allowed to stand in the dark for 15 hr. the concentration of V by v.p.c. drops to about one-fourth of its initial value.

Photolysis of Tetraalkyl-1,3-cyclobutanediones in Inert Solvents in the Presence of Oxygen. The photolysis of tetraalkyl-1,3-cyclobutanediones in inert solvents in the presence of oxygen results in the formation of carbon monoxide, carbon dioxide, and a ketone

(7) R. C. Cookson, M. J. Nye, and G. Sabrahamanyam, *Proc. Chem. Soc.*, 144 (1964).

(8) H. G. Richey, J. M. Richey, and D. C. Clagett, *J. Am. Chem. Soc.*, 86, 3907 (1964).

(9) I. Haller and R. Srinivasan, *ibid.*, 87, 1144 (1965).

(10) E. A. LaLancette and R. E. Benson, *ibid.*, 83, 4867 (1961).

(11) E. M. Kosower, *J. Chem. Phys.*, 38, 2813 (1963).

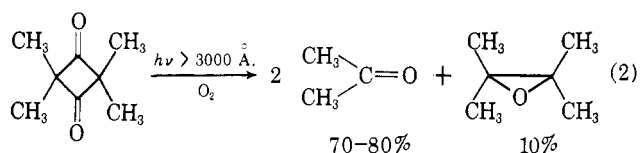(12) J. E. Fernandez and A. A. More, *Quart. J. Florida Acad. Sci.*, 26, 217 (1963).

(13) We wish to thank Professor A. A. Lamola for obtaining this information for us.

(14) Dimethylketene possesses strong absorption at 4.7 μ: R. A. Holroyd and F. E. Blacet, *J. Am. Chem. Soc.*, 79, 4830 (1957).

(15) H. Standinger, K. Kyckerhoff, H. W. Klever, and L. Ruzicka, *Ber.*, 58, 1083 (1925).

(16) B. H. Smith, Ph.D. Dissertation, Emory University, 1951; *Dissertation Abstr.*, 19, 2480 (1959).

and epoxide as the major nongaseous products. Thus, photolysis of a benzene solution of I under a pressure of about 530 mm. of oxygen results in a 70–80% yield of acetone (based on 1 mole of I yielding 2 moles of acetone) and about 10% yield of tetramethylethylene oxide. Similarly, photolyses of II and III in the presence of oxygen yield cyclohexanone and 2-pentanone as the major products.

$$CH_3 \underset{CH_3}{\overset{O}{\diamond}} CH_3 \xrightarrow[O_2]{h\nu\ \rangle\ 3000\ \text{Å.}} 2\ \underset{CH_3}{\overset{CH_3}{>}}C{=}O\ +\ \underset{CH_3\quad O\quad CH_3}{\overset{CH_3\qquad CH_3}{\diamond}} \quad (2)$$
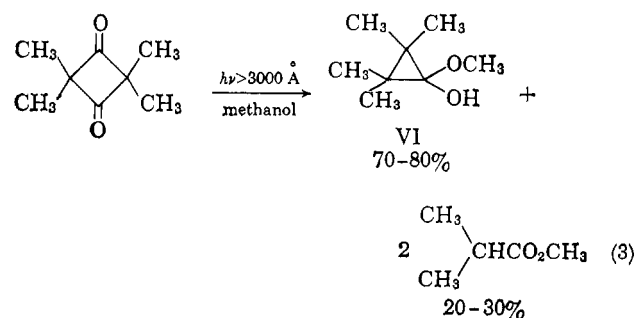
70–80%   10%

The disappearance of I and the formation of acetone and tetramethylethylene oxide were followed by v.p.c., and the evolution of carbon monoxide and carbon dioxide were followed by mass spectrometric analysis. The results of these measurements are given in Table I. When a partially photolyzed, degassed benzene solution of I was treated with oxygen *in the dark*, carbon monoxide, carbon dioxide, acetone, and tetramethylethylene oxide were formed. The tetramethylethylene which was formed in the degassed photolysis remained constant and cannot, therefore, be a precursor to the oxidation products.

Table I. Millimoles of Products from Photolysis of I in the Presence of Oxygen (660 mm.)

Time, min.	$>{=}O$	$\overset{O}{\diamond}$	CO	CO$_2$	Conversion, %
15	0.072	0.0034	0.06	0.03	3
30	0.18	0.014	0.12	0.06	7
60	0.44	0.031	0.32	0.16	22

Photolysis of Tetramethyl-1,3-cyclobutanedione in Alcohols. The quantum yield for the disappearance of I in methanol is 0.49 ± 0.03. Methyl isobutryate (20–30% based on 1 mole of I yielding 2 moles of ester) and the methyl hemiketal of tetramethylcyclopropanone (VI, 70–80%) are the only products detected by n.m.r. analysis of the crude reaction mixture, although some tetramethylethylene (5%) could be detected by v.p.c. Compound VI is easily purified by flash evaporation of the excess methanol and ester at 25° on a rotary evaporator. A crude isolated yield of about 75% of VI may be obtained in this manner.

$$CH_3 \underset{CH_3}{\overset{O}{\diamond}} CH_3 \xrightarrow[\text{methanol}]{h\nu>3000\ \text{Å}} CH_3 \underset{CH_3}{\overset{CH_3}{\triangle}}\underset{OH}{\overset{OCH_3}{}}\ +$$

VI
70–80%

$$2\ \underset{CH_3}{\overset{CH_3}{>}}CHCO_2CH_3 \quad (3)$$

20–30%

Similar results are observed in the photolysis of I in isopropyl alcohol, although the hemiketal was not worked up in this case. In the latter case, attempts to purify the hemiketal by chromatography or distillation
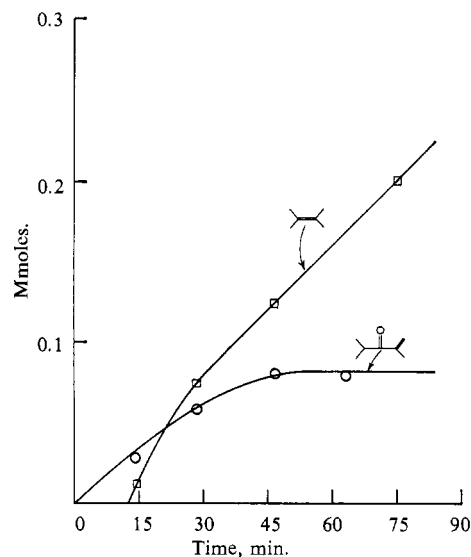
Figure 1. Formation of tetramethylethylene and isopropenyl isopropyl ketone (V) with time (the number of millimoles of V is calculated from vapor chromatograms on the assumption that V has the same thermal conductivity as I). At 60 min., conversion of the dione was 20%.

lead to decomposition. Upon standing, the hemiketals of tetramethylcyclopropanone decompose[1,8] to compounds of the type VII and VIII in a ratio of *ca.* 3:1.

$$\underset{\underset{\text{VII}}{}}{H-\overset{CH_3}{\underset{CH_3}{\overset{|}{C}}}-\overset{CH_2O}{\underset{CH_3}{\overset{\|}{C}}}-\overset{O}{\overset{\|}{C}}-OR} \qquad \underset{\underset{\text{VIII}}{}}{H-\overset{CH_3O}{\underset{CH_3}{\overset{|}{C}}}-\overset{O}{\underset{CH_3}{\overset{\|}{C}}}-\overset{CH_3}{\overset{}{C}}-OR}$$

These compounds were identified by spectral analysis and, in the case of R = isopropyl, by preparation and comparison of authentic samples.

The structure of the hemiketal VI was established by its mass spectrum, infrared spectrum, and n.m.r. spectrum (see Experimental section) in addition to its chemical reactions to form VII (R = CH$_3$) and VIII (R = CH$_3$).

Photolysis of I in the Vapor Phase. Complete photolysis of low pressures of the tetramethyldione I yielded, per mole of dione consumed, 2.0 moles of carbon monoxide, 0.078 mole of propylene, 0.026 mole of tetramethylethylene, 0.0024 mole of methane, and a trace of propane. The low yields of hydrocarbons compared to carbon monoxide are attributed to polymer formation which becomes apparent on the walls of the reaction vessel.

Figures 2 and 3 show the rate of formation of carbon monoxide and propylene, respectively. In the former case there appears to be a slight induction time; in the case of propylene it is quite obvious. The rapid buildup of carbon monoxide before the formation of appreciable amounts of either propylene or tetramethylene (after 4 hr. less than 0.003 mole of the olefin per mole of I had been formed) indicates the early formation of high molecular weight products not observable in either the chromatograms of the gaseous or condensible portions of the reaction mixture (presumably polymer, *vide supra*).

Irradiation of I in the presence of 100 mm. of oxygen leads to the formation of acetone and carbon dioxide,
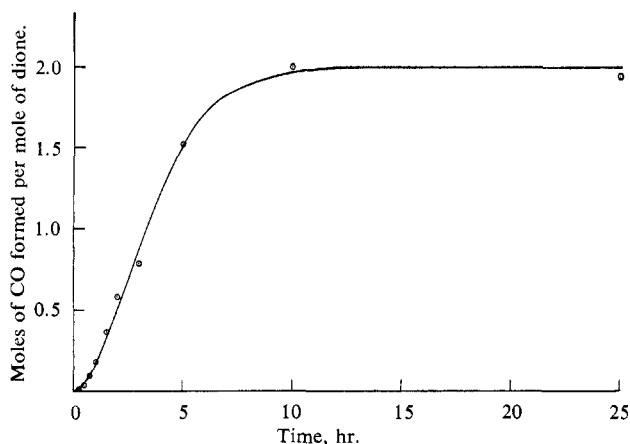
Figure 2. Formation of CO as a function of time in the gas phase photolysis of tetramethyl-1,3-cyclobutanedione.

Figure 3. Formation of propylene as a function of time in the gas phase photolysis of tetramethyl-1,3-cyclobutanedione.

as well as all of the other products listed in the absence of oxygen. In a typical run, irradiation for 4 hr. yielded 0.0062 mole of tetramethylethylene per mole of I initially present and 0.013 mole of acetone. This result is hard to interpret since both an intermediate such as tetramethylcyclopropanone (vide infra) and dimethylketene should both be oxidized to acetone.[15,1]

The Nature of the Chemically Active State in the Photolysis of Tetraalkyl-1,3-cyclobutanediones. Pyrex vessels and mercury arcs were employed in these studies so that excitation was primarily located in the lowest energy transition of the 1,3-cyclobutanediones. Filtration of the exciting radiation with either a Corning 7-37 filter or grating monochromometer in order to isolate pure 3660-Å. light did not appear to alter the course of the photolysis of I. The lack of emission from I implies that an extremely rapid path(s) of deactivation for the lowest excited singlet state (S_1) of I exists. Since the quantum yield for destruction of I is high, the two most likely paths for deactivation of S_1 are (1) photochemical reaction or (2) intersystem crossing to the lowest triplet, T_1, followed by decomposition. However, the photolysis of I could not be sensitized by benzophenone or be quenched by a high concentration (0.3 *M*) of 1,3-pentadiene. These facts *imply* that T_1 is not involved in these photolyses. However, such results *do not demand* this conclusion since (1) benzophenone's triplet $(E_T = 69$ kcal./mole) may be of insufficient energy to excite I and (2) photoreaction in T_1 may be much more rapid than energy transfer[18] to 1,3-pentadiene. Thus, indirect evidence indicates that the n–π* singlet is the chemically reactive state in the solution and gas phase photolysis of I.

The Intermediacy of Tetraalkylcyclopropanones. The results[1] presented above in conjunction with those of other investigators[7–9] compel the conclusion that tetraalkylcyclopropanones are intermediates (possessing half-lives of at least several hours at 25°) in the photolysis of tetraalkyl-1,3-cyclobutanediones. Haller and Srinivasan[9] found that brief irradiation of I in solution at 25°, followed by rapid scanning of the infrared spectrum of the photolyzed solution, produced absorption bands at 1840 and at 2124 cm.−¹. The latter

absorption is clearly attributed to dimethylketene and the former can be reasonably assigned to the carbonyl stretch[19,20] of tetramethylcyclopropanone (IX). We have found that at greater conversions (30–50%) the intensity of the band at 1840 cm.−¹ does not increase to a significant extent. This result is consistent with the data in Figure 1 which show that the formation of tetramethylcyclopropanone (assayed as V in our v.p.c. analysis) quickly reaches a steady-state concentration. Cookson, *et al.*,[7] and Richey, *et al.*,[8] were able to trap the cyclopropanone as a furan adduct, X. This result is in accord with other experiments in which proposed cyclopropanone intermediates have been trapped with dienes.[3] Richey, *et al.*,[8] and the present authors have
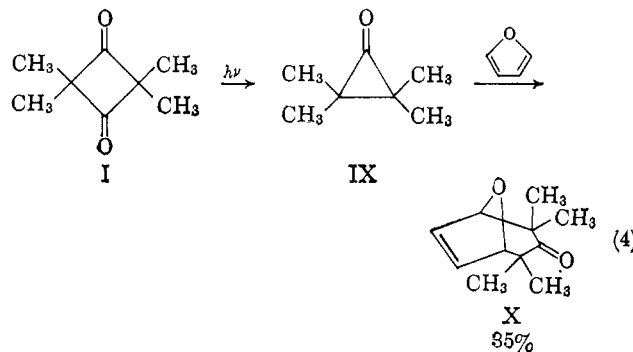
found that tetramethylcyclopropanone is trapped in high yield (70–80%) by alcohols.

The nearly complete inhibition of tetramethylethylene formation when I is photolyzed in the presence of oxygen indicates that a precursor of the ethylene is trapped by oxygen. The simultaneous formation of acetone and tetramethylethylene oxide are probably the result of formation and destruction of the peroxides XI and XII as shown below. The fact that these oxidations occur *in the dark* offers good evidence that a transient intermediate and *not* an electronically excited state is involved.

Finally, the formation of isopropenyl isopropyl ketone in the vapor chromatograph indicates that IX is capable of undergoing unimolecular rearrangements.

(17) R. A. Holroyd and F. E. Blacet, *J. Am. Chem. Soc.*, 79, 4830 (1957).
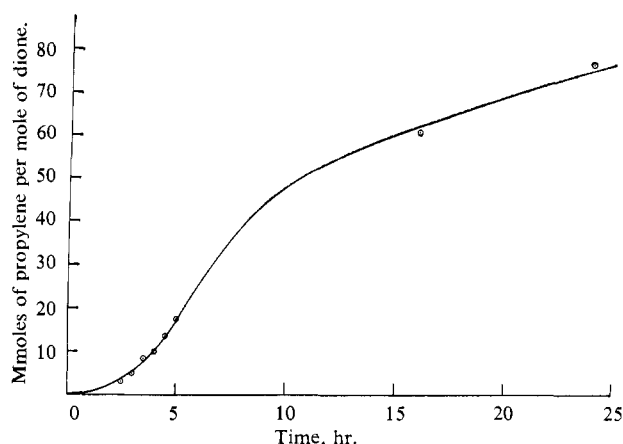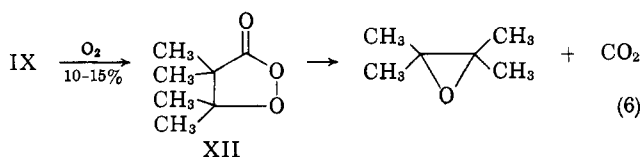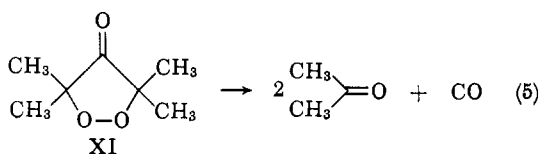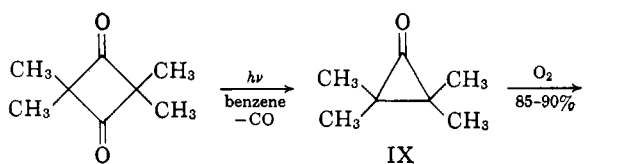(18) G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, 66, 1144 (1962).

(19) W. D. DeMore, H. O. Pritchard, and N. Davidson, *J. Am. Chem. Soc.*, 81, 5874 (1959).
(20) A. S. Kende, Ph.D. Thesis, Harvard University, 1956.

$$CH_3 \overset{O}{\diamond} CH_3 \quad \xrightarrow[\substack{benzene \\ -CO}]{h\nu} \quad CH_3 \overset{O}{\triangle} CH_3 \quad \xrightarrow[85-90\%]{O_2}$$

IX

$$CH_3 \overset{O}{\diamond} CH_3 \quad (O-O) \quad \longrightarrow \quad 2\, {}^{CH_3}_{CH_3}{>}{=}O \;+\; CO \quad (5)$$

XI

We are not sure if some tetramethylethylene is also formed by thermolysis of IX.

$$IX \quad \xrightarrow{O_2}_{10-15\%} \quad CH_3 \cdots O \quad \longrightarrow \quad {}^{CH_3}_{CH_3}{>}\!\!\triangle\!\!{<}^{CH_3}_{CH_3} \;+\; CO_2$$

XII

(6)
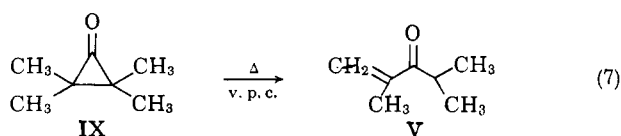
The remarkable reactivity of IX as demonstrated by the above reactions may be a result of a cyclic intermediate such as formed from tetracyanoethylene oxide. Thus, the rate-determining step in the reactions of IX may be the formation of a 1,3-dipole or a 1,3-diradical. The rate-determining step in the cycloadditions of tetracyanoethylene oxide is believed[21] to be ring opening to form 1,3-dipole. Should a biradical be involved in the oxidation reactions, these results would be the first instance, to the authors' knowledge, of the intermolecular trapping of a hydrocarbon 1,3-biradical.[22] The

$$CH_3 \overset{O}{\triangle} CH_3 \quad \xrightarrow{\Delta}_{v.\,p.\,c.} \quad CH_2{=} \cdots CH_3 \quad (7)$$
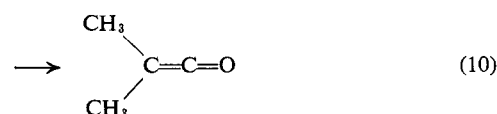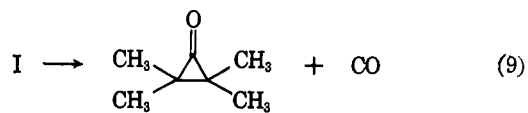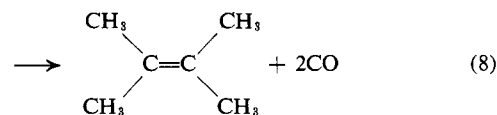
IX   V
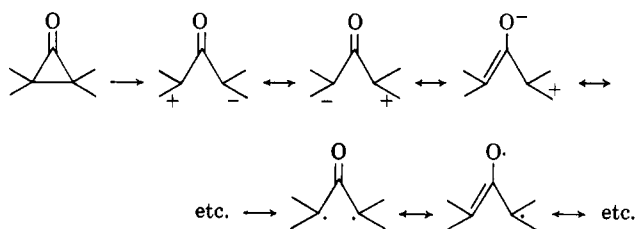
mechanism of adduct formation from IX and furan is unknown and could conceivably arise from a biradical, bipolar, or concerted mechanism.

In summary, tetraalkylcyclopropanones are remarkably versatile in their reactions and may undergo unimolecular reactions and in addition behave as biradicals or dipolar intermediates depending on the demands of attacking reagents.

Primary Processes in the Photolysis of I. The photochemistry of I and other tetrasubstituted 1,3-cyclobutanediones in solution can be accounted for by three primary processes (eq. 8-10). Equation 10 ap-

(21) W. J. Linn, O. W. Webster, and R. E. Benson, *J. Am. Chem. Soc.*, **85**, 2032 (1963).
(22) For references on attempts to trap 1,3-trimethylene radicals in the vapor phase see R. Srinivasan in "Advances in Photochemistry," Vol. I, W. A. Noyes, Jr., G. S. Hammon, and J. N. Pitts, Jr., Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p. 83.

$$\longrightarrow \quad {}^{CH_3}_{CH_3}{>}C{=}C{<}^{CH_3}_{CH_3} \;+\; 2CO \quad (8)$$

$$I \quad \longrightarrow \quad CH_3 \overset{O}{\triangle} CH_3 \;+\; CO \quad (9)$$

$$\longrightarrow \quad {}^{CH_3}_{CH_3}{>}C{=}C{=}O \quad (10)$$

parently accounts for about 20-30% of the dione which reacts in the systems studied. Thus, the yield of methyl isobutryate (20-30%) and isopropyl isobutryate (30%) obtained by us and the yield of ethyl isobutryate (20-25%) obtained by Richey, *et al.*,[8] are consistent with the formation of about 20-30% dimethylketene in these photolyses. The yield of CO_2 given in Table I represents an *upper* limit for the amount of dimethylketene formed from photolysis of I in the presence of oxygen in inert solvents, since this ketene is known to react with oxygen to yield acetone and carbon dioxide[16,17] in the ratio of 0.85 to 1. A value of about 25% for process 10 is obtained from this assumption.

The extent of reaction proceeding *via* paths 8 and 9 is more difficult to estimate because at conversions greater than 20% the cyclopropanone apparently is converted to tetramethylethylene as fast as it is formed (see Figure 1).

Since the nature of the process which converts IX to tetramethylethylene is not known, we cannot unequivocally make a quantitative measure of processes 8 and 9. However, direct photolysis of IX is unlikely at low conversion, so that perhaps singlet–singlet energy transfer from I to IX results in decarbonylation of the latter compound to form tetramethylethylene. We can conclude that reaction 8 occurs to the extent of about 5% from trapping experiments. Such a conclusion is not unambiguous if (1) oxygen and alcohol react with excited I *before* process 8 can occur or (2) a solvent effect alters the photochemistry of I in alcohol solvents. The fact that *some* tetramethylethylene is formed in the photolysis of I in the vapor phase *even in the presence of a high pressure of oxygen* is consistent with the occurance of process 8.

The occurrence of reaction 10 accounts for the induction period in the formation of propylene in the gas phase photolysis of I. Secondary photolysis of dimethylketene to yield propylene and carbon monoxide is delayed until enough ketene has been formed to absorb competitively light with I (the absorption coefficients of dimethylketene and I are quite similar[17] at 3660 Å.).

Experimental

Materials. The diones were supplied by Tennessee Eastman Co., courtesy of Dr. Kent C. Brannock, and were used as furnished. Vapor chromatography indicated that they were of high purity. Other chemicals and solvents were of reagent grade and supplied by normal commercial outlets. Mass spectra were determined on either a Consolidated 21-301C spectrometer[1] or Hitachi Perkin-Elmer Model D spectrometer. All

n.m.r. spectra were taken at 60 Mc. on a Varian A-60. The solvent for spectra was carbon tetrachloride unless specified; tetramethylsilane was employed as an external standard.

Bulk Photolyses. Samples of the diones from 3 to 15 g. were dissolved in 150 ml. of the appropriate solvent and irradiated from 2 to 8 hr. in a Hanovia 450-w. immersion reactor. Light of wave lengths below 3000 Å. was filtered out through Pyrex. In runs in which the hemiketal was desired, the entire assembly was placed in a 4-l. beaker containing ice. The reactor was connected to an eudiometer for collecting and measuring evolved gas. Conversion of reactant and formation of products were usually determined by gas chromatography. Standard solutions of reactants and products were injected for quantitative determinations. A detailed account of the preparation of cyclohexylidenecyclohexane will appear elsewhere.[23]

Tetramethylcyclopropanone Methyl Hemiketal. Tetramethylcyclobutane-1,3-dione (44.5 g.) was added to methanol (200 g.) and photolyzed for 12 hr. in a Hanovia 450-w. immersion apparatus at 25°. A stirring bar was helpful to assist solution of the excess dione (which goes into solution as the photolysis progresses). The n.m.r. spectrum of a sample of the crude reaction mixture showed the presence of only two products (in addition to the methanol), the methyl hemiketal of tetramethylcyclopropanone ($\sim$80%) and methyl isobutyrate ($\sim$40%), yields based on dione consumed. The crude reaction mixture was placed in a 500-ml., round-bottom flask and the excess methanol and most of the methyl isobutyrate were removed by flash distillation on a rotary evaporator. A white, low-melting solid resulted (36.5 g., 76%) which, after recrystallization at $-78°$ in pentane, showed the following properties: partial mass spectrum (values in parenthesis indicate the assignment and per cent of base peak) 144 (molecular ion, 2%), 129 ($M^+ - CH_3$, 11%), 112 ($M^+ - CH_3OH$, 5%), 102 ($M^+ - C_3H_6$), and 41 ($C_3H_5^+$, 100%); partial infrared spectrum 3370, 1220, 1145, 1101, 1090, and 1015 cm.$^{-1}$; n.m.r. (in carbon tetrachloride) singlets at 3.40 (1 proton), 2.95 (3 protons), and 0.70 p.p.m. (12 protons); the latter splits into a doublet in pyridine.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.6; H, 11.2. Found: C, 66.6; H, 11.3.

Photoproducts of I in Methanol and Isopropyl Alcohol. Reaction mixtures which were not worked up right away to give the hemiketal but rather were allowed to stand for 24 to 48 hr. yielded, after separation on a β,β,β-triscyanoethoxypropane column at 100°, the following compounds (depending upon which solvent was employed): Isopropyl isobutyrate was identified by comparison of its infrared spectrum with that of an authentic sample. Isopropyl 2,2,3-trimethylbutyrate was identified by elementary analysis (*Anal.* Calcd. for $C_{10}H_{20}O_2$: C, 69.6; H, 11.7. Found: C, 69.2; H, 11.8), its n.m.r. spectrum consisting of two septets centered at 4.8 (one proton) and 1.65 (one proton), two doublets centered at 1.10 (six protons) and 0.70 (six protons), and a singlet at 0.90 p.p.m. (six protons), and by comparison of its infrared spectrum with that of an authentic sample prepared by esterification of 2,2,3-trimethyl-

butyric acid, the latter prepared by the method of Haaf and Koch.[24] 2,4-Dimethyl-4-isopropoxy-3-pentanone (VIII) was identified by its n.m.r. spectrum consisting of two septets centered at 3.6 (one proton) and 3.2 (one proton), two overlapping doublets centered at 1.0 (six protons) and 0.8 (six protons), and a singlet at 1.1 p.p.m. (six protons) (*Anal.* Calcd. for $C_{10}H_{20}O_2$: C, 69.6; H, 11.7. Found: C, 70.3; H, 11.7). In addition, the infrared spectrum matched that of the compound prepared in the following alternate manner. Bromine (40 g., 0.25 mole) was added slowly to 57 g. (0.5 mole) of isopropyl ketone with the evolution of hydrogen bromide gas. A large excess of isopropyl alcohol was added and the solution was refluxed for 4 hr. The product was purified by preparative v.p.c. using a Carbowax column by injecting the reaction mixture directly. Methyl isobutyrate was identified by comparison of its infrared spectrum with that of an authentic sample. Methyl 2,2,3-trimethylbutyrate was identified by its n.m.r. consisting of a sharp singlet at 3.40 (3 protons), a septet centered at 1.6 (one proton), a sharp singlet at 0.82 (six protons), and a doublet centered at 0.60 p.p.m. (six protons) (*Anal.* Calcd. for $C_8H_{16}O_2$: C, 66.6; H, 11.2. Found: C, 66.7; H, 11.2). In addition, its infrared spectrum compared with that of a sample prepared by esterification of 2,2,3-trimethylbutyric acid (*vide supra*). 2,4-Dimethyl-4-methoxy-3-pentanone was identified by its n.m.r. spectrum, showing a doublet centered at 0.85 (six protons), a singlet at 1.12 (six protons), a singlet at 3.7 (three protons), and a multiplet (septet) centered at 1.8 p.p.m. (one proton). Its partial mass spectrum showed m/e 144 (molecular ion, 0.2%), 127 ($M^+ - CH_3$, 12%), and 73 ($> = O^+ - CH_3$, 100%); partial infrared spectrum, 5.82 (carbonyl) and a doublet at 7.30, 7.40 μ (*gem*-dimethyl).

Photoproducts from Inert Solvents (Nonoxygenated). Carbon monoxide was identified by its infrared spectrum. Tetramethylethylene was identified by comparison of its infrared spectrum with that of an authentic sample. Cyclohexylidenecyclohexane was identified by its melting point, 53–54° (lit.[25] 54–55°), and its n.m.r. spectrum consisting of two broad peaks at 1.5 (twelve protons) and 2.2 p.p.m. (eight protons), the spectrum being virtually identical with that of *exo*-methylenecyclohexane[26] except that it showed no proton resonance in the vinyl region.

Photoproducts from Inert Solvents under Oxygen. Acetone (from I) was identified by infrared analysis. Tetramethylethylene oxide (from I) was identified by comparison of its mass spectrum, infrared spectrum, and v.p.c. retention time (Carbowax 20 M) with authentic material. Carbon dioxide (from I) was identified and analyzed by mass spectrometry. 2-Pentanone (from III) was identified by comparison of its infrared spectrum with that of an authentic sample. Cyclohexanone (from II) was identified by comparison of its infrared spectrum with that of an authentic sample.

Quantitative Product Analyses under Controlled Oxygen and Argon Pressure. A photolysis cell was con-

(23) N. J. Turro, P. A. Leermakers, and G. F. Vesley, *Org. Syn.*, in press.

(24) von W. Haaf and H. Koch, *Ann.*, **638**, 122 (1960).
(25) J. Jaques and C. Weidmann-Hattier, *Bull. soc. chim. France*, 1478 (1958).
(26) "High Resolution N.M.R. Catalogue," Vol. I, No. 180, Varian Associates, Palo Alto, Calif.

structed with side arm for sample withdrawal for v.p.c. analysis and stopcock arrangement for gas withdrawal for mass spectral analysis. The apparatus and technique were adopted from those of Traylor.[27] For the oxygenation experiments, the sample was degassed by a series of freeze–thaw cycles and then filled with a known pressure of gas consisting of about 90% oxygen and 10% argon (as an internal standard). Samples for mass spectral and v.p.c. (Carbowax 20 M) analyses were withdrawn simultaneously. The yields of gases were calculated by the method of Traylor.[27] The values were corrected for the solubility of the gas in the solvent employed.

Determination of the Stereospecificity of the Photolytic Decomposition of 2,4-Dimethyl-2,4-dipropyl-1,3-cyclobutanedione (III). Separation of a sample of 2,4-dimethyl-2,4-dipropyl-1,3-cyclobutanedione into its stereoisomeric forms was accomplished by repeated injections of a mixture of the stereoisomers into a vapor phase chromatograph using a di-*n*-decyl phthalate column at 160°. The dione thus collected was run through the chromatograph a second time to repurify. In this manner about 100 μl. was collected and dissolved in CH$_2$Cl$_2$. A chromatogram of this solution was taken under the same conditions to record the purity of the solution. A 4.00-ml. sample of this solution was irradiated for 2 hr., then analyzed to determine the ratio of the stereoisomers of the olefins formed by injection into the chromatograph using a di-*n*-decyl phthalate column at 110°.

Quantum Yields. The actinometer used in the determination of the quantum yields of tetramethyl-1,3-cyclobutanedione in benzene and in isopropyl alcohol and of dispiro[5.1.5.1.]tetradecan-7,14-dione in benzene and in methylene chloride was the benzophenone–benzhydrol system discussed by Moore, Hammond, and Foss.[28] A 4.00-ml. aliquot of a 0.3 *M* solution of each of the diones was placed in a drawn tube, degassed, and sealed off. Similar tubes, 0.3 *M* in both benzophenone and benzhydrol, were prepared as actinometers. Each sample tube was then irradiated along with an actinometer for 2 hr. The percentage of the tetramethyldione decomposed was determined by the ratio of peak areas for the photolyzed and unphotolyzed diones on a vapor phase chromatograph using a di-*n*-decyl phthalate column at 140°. Similar data on the dispiro solutions was obtained through analysis on a Cary Model 14 spectrophotometer, the absorptivity at 3440 Å. being taken as a measure of the concentration of the solution. All of the actinometer tubes were similarly analyzed on a

Cary spectrophotometer, the wave length of maximum absorption being again taken as 3440 Å. The quantum yield of the actinometer was calculated to be 0.86.[28]

Vapor Phase Photolyses of I. All photolyses of I in the vapor phase were carried out in a 4.0-l. reaction vessel. Samples containing 30–35 mg. of the dione was placed in a cold finger in the bottom of the vessel and cooled at Dry Ice temperature. The system was connected to a vacuum system, evacuated, oxygen added if desired, and sealed off, after which the dione was vaporized and the vessel was placed in a Rayonet reactor. For all gaseous product work, the reaction vessel, still in the reactor, was connected to a vacuum line in such a way as to permit 1.0% samples of the entire gaseous contents to be passed into a flame ionization gas chromatograph during the course of the reaction. All gaseous products were determined by a comparison of retention times with those of standard samples. For quantitative work, 25-μl. samples of the standards were injected into the chromatograph through the vacuum line. The following column and temperature conditions were used in work with the samples indicated: carbon monoxide, 3-ft. silica gel or molecular sieve column at room temperature in series with a nickel nitrate column at 280–350°; methane, propylene, and propane, 3-ft. silica gel column at 70–100°.

The collection of condensable products was accomplished by joining a long neck of glass tubing to the top of the reaction vessel. After irradiation this neck was immersed in liquid nitrogen to condense the products and sealed off. Analyses for tetramethylethylene and acetone were carried out by opening the tube, dissolving the products in 75 μl. of benzene or toluene, and injecting this solution into the gas chromatograph. For solutions containing only tetramethylethylene, a di-*n*-decyl phthalate column at 70–100° was used. When both tetramethylethylene and acetone were present it was necessary to use a Carbowax column at a similar temperature to achieve separation. In both cases product identification was by comparison of retention times of reaction samples with those of standard 1.0% by volume solutions of tetramethylethylene and acetone in benzene. As with the gaseous products, quantitative yields were determined from a comparison of sample and standard peak areas.

(27) T. G. Traylor, *J. Am. Chem. Soc.*, **85**, 2411 (1963).
(28) W. M. Moore, G. S. Hammond, and R. P. Foss, *ibid.*, **83**, 2789 (1961).