Photochemistry of Some Cyclopropyl Conjugated 1,2-Diketones. Part 2.[1] Fragmentation Reactions and Reduction by Aldehydes

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The photochemistry of some cyclopropyl conjugated and some related 1,2-diketones in benzene as solvent in the absence and presence of an aliphatic aldehyde as hydrogen donor has been studied. In benzene no photodecomposition occurs with λ > 403 nm, but with radiation of lower wavelength (>300 nm) the 1,2-diketones, with the exception of dicyclopropylethanedione, undergo photodecomposition. The products arise from initial bond rupture between the two carbonyl groups, subsequent decarbonylation of part of the acyl radicals (and not of the relatively stable cyclopropylcarbonyl radicals), and eventual combination of the various types of radicals present. Upon irradiation of a mixture of biacetyl and dicyclopropylethanedione, acyl interchange was observed. The photoreaction of 1,2-diketones in the presence of aliphatic aldehydes led to the formation of dihydrodimers (2), αα-diacylalkanols (3), and esters (4). The mechanisms of formation of these products from the semidione radical formed from triplet excited 1,2-diketone by hydrogen abstraction from the aldehyde, are discussed.

OUR interest in the photoreduction of cyclopropyl conjugated 1,2-diketones prompted us to examine their behaviour upon irradiation (i) in an inert solvent (benzene) and (ii) in the presence of an aldehyde as hydrogen donor. Previously we reported that the photoreduction of the three cyclopropyl conjugated 1,2-diketones (1a—c) and the two related ones (1d and e) in propan-2-ol leads to the exclusive formation of the diastereoisomeric dihydrodimers (2a—e).[1] The solution photochemistry of biacetyl has been studied before. In perfluoro-octane at 25° with λ 366 or 436 nm almost no decomposition occurred.[2] At higher temperatures formation

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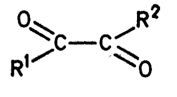
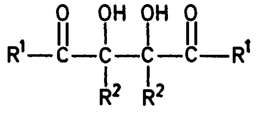
[1] Part 1, J. Kelder and H. Cerfontain, *Tetrahedron Letters*, 1972, 1307.

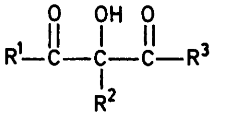
[2] S. A. Greenberg and L. S. Forster, *J. Amer. Chem. Soc.*, 1961, **83**, 4339.

of CO, methane, and ethane was observed and the quantum yield of biacetyl disappearance at 100° with λ 366 nm was reported to be 2.5×10^{-3}. Irradiation of biacetyl in aqueous solution with shorter wavelengths leads to an efficient photoenolization.[3]


(1)


(2)

$R^1{-}CO{-}C(OH)(R^2){-}C(OH)(R^2){-}CO{-}R^1$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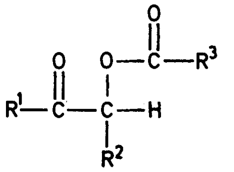
$R^1{-}CO{-}C(OH)(R^2){-}CO{-}R^3$


(4)

$R^1{-}CO{-}CH(R^2){-}O{-}CO{-}R^3$

a; R^1=R^2=R^3= △
b; R^1= △; R^2=R^3=Me
c; R^1= △; R^2=Ph; R^3=Me
d; R^1=R^2=R^3=Me
e; R^1=R^3=Me; R^2=Ph
f; R^1=R^2= △; R^3=Me
g; R^1=R^3= △; R^2=Me
h; R^1=Me; R^2=Ph; R^3= △
i; R^1=Ph; R^2=Me; R^3= △
j; R^1=Ph; R^2=R^3=Me
k; R^1= △; R^2=Pr^n
l; R^1=Ph; R^2=Pr^n

RESULTS

Irradiations in Benzene.—The products obtained upon irradiation of 0.50M solutions of the 1,2-diketones (1a—d) in benzene in a Pyrex vessel at room temperature under nitrogen with a Philips SP 500 mercury lamp (λ > 300 nm) are shown in Table 1. No relative yields have been determined. The conversion of (1a) was very small in comparison with those of (1b—d). This is shown quantitatively for the 1,2-diketones (1a, c, and d) in the Figure. The three diketones under study do not undergo photodecomposition upon irradiation with λ 403 nm (Figure A). The photostability of dicyclopropylethanedione (1a) under conditions where the other 1,2-diketones are photoreactive, *i.e.* with λ > 300 nm (Figure B), is remarkable. Upon irradiation of (1a) in CCl_4 as radical scavenger[4] with the same radiation for 12 h only small amounts (<1%) of cyclopropanecarbonyl chloride and hexachloroethane with trace amounts of ethene and CO are obtained.

TABLE 1

Photoproducts of 1,2-diketone in benzene upon irradiation with the full radiation >300 nm from a Philips SP 500 mercury lamp at 25°

Substrate	Products
(1a)	CO, C_2H_4, $(cPr)_2CO$ (all only in trace amounts)[a]
(1b)	CO, CH_4, C_2H_6, Me_2CO, cPrCOMe, cPr·CO·CO·cPr
(1c)	CO, incomplete analysis
(1d)	CO, CH_4, C_2H_6, Me_2CO
(1a + d; equimolar)	cPr·CO·CO·Me (amongst others)

[a] cPr = Cyclopropyl.

Irradiation of a mixture of equimolar amounts of dicyclopropylethanedione and biacetyl in benzene with the same radiation yields 1-cyclopropylpropane-1,2-dione (1b).

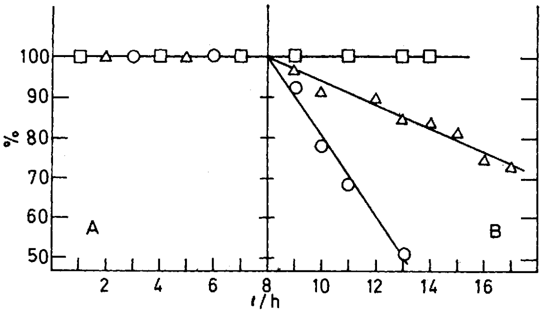
Irradiations in the Presence of Aldehydes.—The products formed upon irradiation of the five 1,2-diketones (1a—e) in the presence of an aldehyde (ethanal in all cases but one) in benzene with λ 403 nm are given in Table 2. The irradiations of these experiments were continued until the yellow 1,2-diketone colour faded completely. In all cases formation of a mixture of diastereoisomeric dihydrodimers (2a—e) was observed. Due to their thermal instability[1] most of the dihydrodimers decomposed on the injection side of the g.l.c. columns to yield 1,2-diketones and α-hydroxyketones.* In most cases the dihydrodimers could, however, be obtained pure by removal of the solvent from

TABLE 2

Photoreductions of 1,2-diketones in the presence of an aldehyde with λ 403 nm

Substrate	Aldehyde	Major products	Minor products
(1a)	MeCHO	(2a); (3f)	(2b);[a] (3b); (3g)
(1b)	MeCHO	(2b);[a] (3b); (3d)	(2d);[a] cPrCHO[b]
(1c)	MeCHO	(2c);[a] (4c)	(4h); (4i)
(1d)	MeCHO	(2d); (3d)	
(1e)	MeCHO	(2e); (4e); (4j)	
(1a)	cPrCHO	(2a); (3a); (4a)	

[a] The presence of these dihydrodimers in the reaction mixture is very likely in view of the presence of their pyrolysis products [1,2-diketone and the α-hydroxyketone(s)] upon separation of the crude reaction mixture by g.l.c. [b] The presence of cyclopropane carbaldehyde (cPrCHO) was established by the presence of the corresponding acid (identified by comparison with an authentic sample) among the photoproducts.



Photoconversion of the 1,2-diketones (1a) (□), (1c) (△), and (1d) (○) in benzene (0.5M) upon irradiation with: A, λ 403 nm and B, 300 < λ < 450 nm, *i.e.* after removal of the '403 nm' filter

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* Injection of the pure dihydrodimers did in fact show that this decomposition occurred under the g.l.c. conditions employed.

[3] J. Lemaire, *J. Phys. Chem.*, 1967, **71**, 2653; J. Lemaire, M. Niclause, X. Deglise, J. C. André, G. Persson, and M. Bouchy, *Compt. rend.*, 1968, **267C**, 33; D. Phillips, *J. Chem. Educ.*, 1971, **48**, 198.

[4] S. Winstein and S. H. Seubold, *J. Amer. Chem. Soc.*, 1947, **69**, 2916.

the reaction mixture under reduced pressure. The compounds listed in Table 2 account for >90% of the *fully* converted 1,2-diketone substrate.

The dihydrodimers obtained in the present study are the same as observed in the photoreduction using propan-2-ol.[1] In Part 1 we misinterpreted the ^{1}H n.m.r. spectral data of the dihydrodimers, obtained from the phenyl substituted diketones (1c and e). Based on the large deshielding of the *ortho*-protons of these dimers (to an extent similar in *e.g.* acetophenone) we had assigned structures with the phenyl groups α to the carbonyl groups. The ^{1}H n.m.r. spectra of the products other than the dihydrodimers obtained in the present study forced us to reconsider the original structure assignment of the dihydrodimers, and prompted us to record the u.v. absorption spectra of all the dihydrodimers. The u.v. spectra of the dimers (2) obtained from (1c and e) were found to be similar in shape to that of *e.g.* benzylmethylketone,[5a] but to be strongly different from that of *e.g.* acetophenone.[5b,6a] Accordingly the revised assigned structures (2c and e) are proposed. Compound (2e) was also obtained by electrochemical reduction of (1e) in an ethanolic dilute sulphuric acid solution.[7]

Butyryl Radical Additions.—In order to obtain information on the possible occurrence of acyl interchange with the 1,2-diketones the reaction of butyryl radicals, generated by thermal decomposition of benzoyl peroxide in refluxing butanal,[8] with both dicyclopropylethanedione (1a) and 1-phenylpropane-1,2-dione (1e), was studied. The main products proved to be 1-cyclopropylpentane-1,2-dione (1k) and 1-phenylpentane-1,2-dione (1l) respectively.

DISCUSSION

Photolyses in Benzene.—The energy required to decompose *e.g.* biacetyl into two acetyl radicals is 65—70 kcal mol^{-1}.[6b,9] Excitation of biacetyl in the first $S_0 \longrightarrow S_1$ $n\pi^*$ absorption band (at 470—340 nm)[10] corresponds to an energy uptake of 61—84 kcal mol^{-1}. Because the lowest vibrational level of this singlet $n\pi^*$ excited state has an energy of 61 kcal mol^{-1}, excitation of 1,2-diketones in the liquid phase in this band is expected to be ineffective in cleaving the bond between the two carbonyl groups.* This is in fact observed for irradiation in benzene as solvent (see Figure A). Irradiation of 1,2-diketones with λ 403 nm does not lead to photodecomposition, whereas irradiation with lower wavelength >300 nm does (Figure B), apparently because this radiation effects excitation into the second singlet excited $n\pi^*$ state (at 330—240 nm),[10] the lowest vibrational state of which has sufficient energy for the rupture of the bond between the two carbonyl groups. The observed products in the photolysis of the 1,2-diketones in benzene with λ > 300 nm can be explained by the reactions (1)—(8). With 1-cyclopropylpropane-1,2-dione (1b), the formation of the main non-volatile

$$\mathrm{R^1{\cdot}CO{\cdot}CO{\cdot}R^2 \xrightarrow{h\nu} [R^1{\cdot}CO{\cdot}CO{\cdot}R^2]^*} \tag{1}$$

$$\mathrm{[R^1{\cdot}CO{\cdot}CO{\cdot}R^2]^* \longrightarrow R^1\dot{C}O + R^2\dot{C}O} \tag{2}$$

$$\mathrm{R^1\dot{C}O \longrightarrow R^1{\cdot} + CO} \tag{3}$$

$$\mathrm{R^2\dot{C}O \longrightarrow R^2{\cdot} + CO} \tag{4}$$

$$\mathrm{R^1\dot{C}O + R^1{\cdot} \longrightarrow R^1{}_2CO} \tag{5}$$

$$\mathrm{R^2\dot{C}O + R^1{\cdot} \longrightarrow R^1COR^2} \tag{6}$$

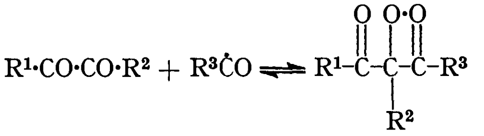
$$\mathrm{2R^1\dot{C}O \longrightarrow R^1{\cdot}CO{\cdot}CO{\cdot}R^1} \tag{7}$$

$$\mathrm{Me{\cdot} + R^1{\cdot}CO{\cdot}CO{\cdot}Me \longrightarrow MeH + R^1{\cdot}CO{\cdot}CO{\cdot}\dot{C}H_2} \tag{8}$$

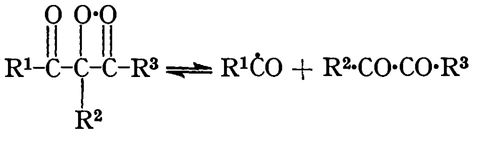
$$\mathrm{R^1\dot{C}O + R^2\dot{C}O \longrightarrow R^1{\cdot}CO{\cdot}CO{\cdot}R^2} \tag{9}$$

product dicyclopropylethanedione (1a) can be explained by steps (1), (2), and (7) with R^1 = cyclopropyl. Dicyclopropylethanedione was also observed as one of the main products upon irradiation of cyclopropanecarbaldehyde.[11] Cyclopropylcarbonyl radicals are remarkably stable towards decarbonylation,[12] probably as a result of the very high strength of bonds to a cyclopropyl group. This argument also explains the extremely low degree of photodecomposition of dicyclopropylethanedione (1a), as the resulting cyclopropylcarbonyl radicals do not decompose and thus can only recombine with formation of the starting diketone [step (7)]. The relatively low yield of cyclopropylcarbonyl chloride upon irradiation of (1a) in carbon tetrachloride indicates that the cyclopropylcarbonyl radicals are present in the system mainly as radical pairs and not as free radicals.

The formation of the mixed diketone (1b) upon irradiation of an equimolar mixture of dicyclopropylethanedione and biacetyl can be explained in terms of combination of free acetyl and cyclopropylcarbonyl radicals, or in terms of an acyl exchange mechanism [steps (10a) and (11a), with R^1 = R^2 = cyclopropyl, R^3 = Me, and with



$$\mathrm{R^1{\cdot}CO{\cdot}CO{\cdot}R^2 + R^3\dot{C}O \rightleftharpoons R^1{-}\overset{\overset{O}{\|}}{C}{-}\underset{\underset{R^2}{|}}{\overset{\overset{O\cdot}{|}}{C}}{-}\overset{\overset{O}{\|}}{C}{-}R^3} \tag{10a}$$



$$\mathrm{R^1{-}\overset{\overset{O}{\|}}{C}{-}\underset{\underset{R^2}{|}}{\overset{\overset{O\cdot}{|}}{C}}{-}\overset{\overset{O}{\|}}{C}{-}R^3 \rightleftharpoons R^1\dot{C}O + R^2{\cdot}CO{\cdot}CO{\cdot}R^3} \tag{11a}$$

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* In the gas-phase 366 nm excitation of biacetyl leads to dissociation from both the first excited singlet and triplet states, and 313 nm excitation to dissociation from the second and first excited singlet state.[6c]

[5] U.v. spectra collection, S. P. Sadtler, Philadelphia, 1961, (*a*) 2927U; (*b*) 3226U.

[6] J. G. Calvert and J. N. Pitts, ' Photochemistry,' Wiley, 1966, (*a*) p. 378; (*b*) p. 825; (*c*) p. 421.

[7] T. Arai, *Denki Kagaku*, 1962, **30**, 175 (*Chem. Abs.*, 1965, **62**, 15760g).

[8] R. L. Huang, *J. Chem. Soc.*, 1956, 1749.

[9] E. Murad and M. G. Ingram, *J. Chem. Phys.*, 1964, **41**, 404.

[10] J. Kelder, H. Cerfontain, B. R. Higginson, and D. R. Lloyd, *Tetrahedron Letters*, 1974, 739.

[11] J. J. I. Overwater, Thesis (in English), University of Amsterdam, 1969, p. 83; C. W. Funke, J. A. J. Geenevasen, J. L. M. de Boer, and H. Cerfontain, *J.C.S. Perkin II*, 1976, 1083.

[12] D. I. Schuster and J. D. Roberts, *J. Org. Chem.*, 1962, **27**, 51.

$R^1 = R^2 =$ Me, $R^3 =$ cyclopropyl]. The first explanation (radical combination) is very unlikely in view of the carbon tetrachloride experiment with (1a) which indicated the absence of free cyclopropylcarbonyl radicals in that system. The absence of these radicals also renders sequence (10a) and (11a) with $R^1 = R^2 =$ Me, $R^3 =$ cyclopropyl unlikely. Acyl exchange between (1a and d) thus proceeds by addition of an acetyl radical to ground state (1a) and subsequent loss of a cyclopropylcarbonyl radical from the radical intermediate.

Photoreduction with Aldehydes.—The formation of the products formed in the photoreduction of 1,2-diketones in the presence of an aldehyde may be explained in terms of the reactions (1) and (10)—(18).* The chemically reactive excited state in the photoreduction of 1,2-diketones upon λ 403 nm irradiation is the lowest excited triplet state.[13] With λ 403 nm, step (2) does not occur and the only reaction of the triplet excited diketone is abstraction of the weakly bonded acyl hydrogen from the aldehyde [step (12)], yielding an acyl and a semidione radical, probably as a triplet radical pair. After spin inversion, combination of these radicals leads to the formation of the αα-dicarbonylalkanol. It is remarkable that carbon–carbon combination products [of type (3b, f, and g)] are not observed with the phenyl-containing 1,2-diketones (1c and e). Instead esters (4c and h) were obtained which are formed by recombination of the same radicals, but now by coupling on the oxygen instead of the carbon atom of the semidione radical.† Very recently ester formation was also observed in the photoreaction of some *ortho*-quinones with aldehydes.[14] The factors that determine carbonyl carbon *versus* carbonyl oxygen addition are not very well understood [15] and may be polar [16] and/or steric in origin. A further complication is that the dihydrodimer (2c) and the ester (3c), both resulting from the same 1,2-diketone, originate from two different tautomeric semidione radicals, (5) and (6) respectively.

$$[R^1\cdot CO\cdot CO\cdot R^2]^* + R^3CHO \longrightarrow R^1\cdot CO\cdot \dot{C}OH\cdot R^2 + R^3\dot{C}O \quad (12a)$$

$$R^1\cdot CO\cdot \dot{C}OH\cdot R^2 + R^3\dot{C}O \longrightarrow R^1\cdot CO\cdot CR^2OH\cdot CO\cdot R^3 \quad (13a)$$

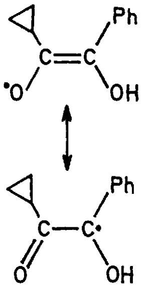
$$\longrightarrow R^2HOC{=}CR^1OCO\cdot R^3 \quad (14a)$$

$$R^1\cdot HOC{=}CR^2OCO\cdot R^3 \xrightarrow{\circ} R^1\cdot CO\cdot CHR^2OCO\cdot R^3 \quad (15a)$$

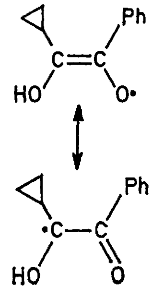
$$2R^1\cdot CO\cdot \dot{C}OH\cdot R^2 \longrightarrow R^1\cdot CO\cdot CR^2OH\cdot CR^2OH\cdot COR^1 \quad (16a)$$

$$R^1\dot{C}O + R^3CHO \longrightarrow R^1CHO + R^3\dot{C}O \quad (17)$$

$$2\,R^3\dot{C}O \longrightarrow R^3\cdot CO\cdot CO\cdot R^3 \quad (18)$$



(5)



(6)

Recombination of free semidione radicals [step (16)] is known to be an important process for semidione radicals originating from flexible (*E*)-1,2-diketones,[17] and this process takes place in fact with all the presently studied substrates. Recombination of the free $R^3\dot{C}O$ radicals [step (18)] is in general of minor importance. Only with 1-cyclopropylpropane-1,2-dione (1b) as substrate considerable amounts of (2d) and (3d) were isolated, which apparently originated from substantial amounts of biacetyl.‡ Further with dicyclopropylethanedione as substrate small amounts of products derived from 1-cyclopropylpropane-1,2-dione were isolated. It is proposed that the biacetyl and 1-cyclopropylpropane-1,2-dione occurring as intermediates are formed mainly by steps (10) and (11). The formation of 1-cyclopropylpentane-1,2-dione § and 1-phenylpentane-1,2-dione in the reaction of butanoyl radicals with (1c and e) respectively seems to substantiate this proposal (*cf.* also ref. 16*b*).

The formation of cyclopropanecarbaldehyde upon irradiation of 1-cyclopropylpropane-1,2-dione (1b) with ethanal is thought to arise by hydrogen abstraction by the cyclopropylcarbonyl radicals from ethanal [step (17)]; these cyclopropylcarbonyl radicals are formed by acyl

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* With unsymmetrical 1,2-diketones in addition to steps (10a)–(16a) a similar set of steps (10b)–(16b) must in fact also be considered, in which the position of the groups R^1 and R^2 are exchanged. This set is omitted for reasons of simplicity.

† It may be of related interest that with the phenyl-containing 1,2-diketones only very weak broad e.s.r. signals were obtained which could not be resolved, whereas with the other diketones neatly resolved e.s.r. signals of the semidione radicals were observed.[1]

‡ All irradiations were continued until complete decolourization of the yellow diketone solution.

§ 1-Cyclopropylpentane-1,2-dione could also result from a combination of free cyclopropylcarbonyl and butyryl radicals. In the radical induced reaction of (1c) with butanal, the cyclopropylcarbonyl radicals could in principle also be formed by a sequence analogous to (10) and (11) in which the attacking entity is the reactive phenyl radical.[16b] This alternative seems, however, unlikely, in view of the absence of cyclopropyl phenyl ketone amongst the reaction products.

[13] H. J. Bäckstrom and K. Sandros, *Acta Chem. Scand.*, 1958, **12**, 823; N. J. Turro and R. Engel, *Mol. Photochem.*, 1969, **1**, 143.

[14] K. Maruyama, T. Miyazawa, and Y. Kishi, *Chem. Letters*, 1974, 721; K. Maruyama and T. Takahashi, *ibid.*, p. 467; K. Maruyama and A. Takuwa, *ibid.*, p. 471.

[15] M. G. Vinogradov and G. I. Nihishin, *Russian Chem. Rev.*, 1971, **40**, 916.

[16] (*a*) W. H. Urry, A. Nishihara, and J. H. Y. Niu, *J. Org. Chem.*, 1967, **32**, 347; (*b*) W. G. Bentrude and K. R. Darnall, *J. Amer. Chem. Soc.*, 1968, **90**, 3588.

[17] S. A. Weiner, E. J. Hamilton, and B. M. Monroe, *J. Amer. Chem. Soc.*, 1969, **91**, 6350.

exchange on reaction of $\mathrm{Me\dot{C}O}$ radicals with the starting diketone [steps (10) and (11)].

A priori the esters (4c and e) could also arise from attack of an acetyl radical on one of the carbonyl oxygens of the starting (ground state) 1,2-diketone [step (19)] and subsequent hydrogen abstraction by the resulting carbon radical from ethanal [step (20)]. Similar chain reaction types of addition to aryl monoketones were reported by Kaplan.[18] In the present case there is little evidence for this alternative mechanism for the ester formation, as no esters were found upon the thermal decomposition of benzoyl peroxide in the presence of butanal and 1-phenylpropane-1,2-dione.

$$\mathrm{Me\dot{C}O + R^1{\cdot}CO{\cdot}CO{\cdot}R^2 \longrightarrow R^1{\cdot}CO{\cdot}\dot{C}R^2OCOMe} \quad (19)$$

$$\mathrm{R^1{\cdot}CO{\cdot}\dot{C}R^2OCOMe + MeCHO \longrightarrow R^1{\cdot}CO{\cdot}CHR^2OCOMe + Me\dot{C}O} \quad (20)$$

The formation of small amounts of the esters (4h and i) is unexpected and at present one can only speculate on the mechanism by which they are formed.

Upon irradiation of a mixture of dicyclopropylethanedione and cyclopropanecarbaldehyde dihydrodimer (2a), α,α-diacylalkanol (3a), and ester (4a) are all formed (Table 2). The occurrence of ester formation may be ascribed to steric retardation of carbon–carbon combination of the dicyclopropylsemidione radicals with cyclopropylcarbonyl radicals, thus relatively favouring the ester formation. Rubin and Ben-Bassat [19] have in fact ascertained that the photoreduction of camphorquinone with aromatic aldehydes, butanal, or 2,2-dimethylpropanal leads exclusively to carbon–oxygen radical combination with formation of esters, whereas with ethanal as the hydrogen donor (yielding the less bulky $\mathrm{Me\dot{C}O}$ radical), both carbon–carbon and carbon–oxygen radical combination occurred.

EXPERIMENTAL

The cyclopropyl conjugated 1,2-diketones were synthesized as described.[20]

Photolyses.—The irradiations of the solutions were carried out in a water-jacketted Pyrex vessel using the radiation from a Philips SP 500 mercury lamp with or without a Jena '403 nm' glass filter (type PAL no. 80332.03; $\lambda_{\max.}$ 403 nm; $T_{\max.}$ 41%; half bandwidth 23 nm), all placed in a fixed arrangement on an optical rail. The solutions were prepared by dissolving the 1,2-diketones (0.002—0.010 mol) with or without five equivalents of the aldehyde in dry benzene or in CCl_4 (10 ml; freed from oxygen by bubbling nitrogen through), and then irradiated under nitrogen. The irradiations of the solutions containing an added aldehyde were continued until the yellow colour of the diketones had completely faded (within a few hours).

Free Radical Reactions.—1,2-Diketone (0.8 g) was dissolved in freshly distilled butanal (10 ml). To the refluxing solution (which was kept under nitrogen) were added within 6 h benzoyl peroxide (3 × 0.04 g). The reaction mixture was left refluxing for 15 h and was then worked up. By this procedure [8] *ca.* 10% of the starting 1,2-diketone was converted.

Analysis.—The products were isolated, except for the dihydrodimers, by means of preparative g.l.c. The dihydrodimers were isolated directly from the irradiated mixture and obtained crystalline by careful removal of the solvent under reduced pressure. The structures of the products were assigned on the basis of g.l.c. retention times, i.r., u.v., and ^{1}H n.m.r. spectra, and in two cases [(1k and l)] also by on-line g.l.c.–mass spectrometric analysis. The spectral data of the products listed in Table 2, and the g.l.c. columns used for the separation of the products listed in Table 1, have been reported elsewhere.[21] The products listed in Table 2 were separated using g.l.c. columns containing dinonyl phthalate, SE-30, diethyleneglycol succinate, or Carbowax, all on Chromosorb, 45—60 mesh.

[6/1158 *Received*, 17th *June*, 1976]

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[18] L. Kaplan, *J. Amer. Chem. Soc.*, 1966, **88**, 1833, 4970.

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