# Photoreduction of Cycloalkanecarbaldehydes

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The photochemistry of cyclopropane- and cyclobutane-carbaldehyde in propan-2-ol with λ 300 nm has been studied. The primary chemical process upon irradiation of each of the two aldehydes in propan-2-ol is abstraction of the solvent methine hydrogen by both the $^1S$ and $^1T$ excited states of cyclopropanecarbaldehyde and only the $^1T$ excited state of cyclobutanecarbaldehyde. The resulting α-hydroxycycloalkylmethyl radicals (i) recombine with the 1-hydroxy-1-methylethyl radicals, (ii) abstract hydrogen from the solvent (and not from the 1-hydroxy-1-methylethyl radicals, as was demonstrated for cyclopropanecarbaldehyde using *O*-deuteriopropan-2-ol) and in the case of cyclopropanecarbaldehyde also from the parent aldehyde, and (iii) rearrange in the case of the cyclopropyl derivative into 4-oxobutyl radicals. Detailed mechanisms for the formation of the various photoproducts (nine identified for cyclopropane- and six for cyclobutane-carbaldehyde) also based on triplet quenching and radical scavenging experiments are proposed. The fate of the radical pair cyclo-$C_4H_7\dot{C}HOH$ and R· formed upon irradiation of cyclobutanecarbaldehyde in the presence of a hydrogen-donor RH seems to depend on the steric accessibility of the radical site of R•. For R = benzyl and α-hydroxybenzyl the (unlike) radicals mainly combine, whereas for R = cumyl and α-hydroxy-α-phenylbenzyl mainly cyclobutylmethanol is formed. For R = 1-hydroxy-1-methylethyl, radical combination and cyclobutylmethanol formation are of equal importance.

THE gas-phase photolysis of aliphatic aldehydes and ketones has been studied extensively.[1] Less attention has been paid to the photochemistry of aliphatic aldehydes in solution. Some quantitative studies on Norrish Type II process in non-cyclic aliphatic aldehydes have been made by Coyle.[2] Therefore we thought it of interest to initiate a systematic study of the photochemistry of cycloalkanecarbaldehydes in solution. This paper describes the photochemical behaviour of cyclopropane- and cyclobutane-carbaldehyde in the presence of hydrogen donating compounds (usually the solvent). The photochemical conversion of these two aldehydes in alkenes or alka-1,3-dienes as solvent into oxetans and the photochemistry of the first four members of the cycloalkanecarbaldehyde series in inert solvents will be reported in subsequent papers.

Recently a number of CIDNP studies on irradiated simple aliphatic aldehydes have been reported.[3] The gas-phase photolysis of cyclopropanecarbaldehyde has been studied extensively.[4]

## RESULTS

Cyclopropanecarbaldehyde in propan-2-ol is stable and in contrast to the general behaviour of aliphatic aldehydes (including cyclobutanecarbaldehyde †) does not yield any acetal. The photoreduction of cyclopropanecarbaldehyde was studied in propan-2-ol, that of cyclobutanecarbaldehyde in propan-2-ol, but also in the presence of other hydrogen donors.

*Cyclopropanecarbaldehyde in propan-2-ol.*—Irradiation of this aldehyde (0.5 mol) in propan-2-ol as solvent with λ *ca.* 300 nm yielded acetone (1), 2,3-dihydroxy-2,3-dimethylbutane (2), butanal (3), dicyclopropylethanedione (4a), 1,2-dicyclopropyl-2-hydroxyethanone (5a), 1,2,3-tricyclopropyl-2-hydroxypropane-1,3-dione (6a), cyclopropylmethanol (7a), 1-cyclopropyl-2-methylpropane-1,2-diol (8a), and 5-cyclopropyl-5-oxopentanal (9). The major products are (1), (3), and (6a)—(8a). *E.g.* for an irradiation time of 90 h at −90° the product ratio (1) : (2) : (3) : (4a) : (5a) : (6a) : (7a) : (8a) : (9) was 35 : 3 : <1 : 2 : 2 : 15 : 20 : 18 : 5; and no CO, ethylene, and cyclopropane were formed. The ratio (3) : (7a) increases strongly with increasing temperature (Table 1). At −90° mainly (7a) is formed but at room temperature mainly (3).

TABLE 1

Relative amounts of photoproducts

| Temp. (°C) | (1) | (3) | (7a) | (8a) |
|---|---|---|---|---|
| −90 | 1.0 [a] | <0.1 | 0.6 | 0.6 |
| −30 | 1.0 [a] | 0.5 | 0.3 | 0.7 |
| +25 | 1.0 [a] | 0.5 | <0.1 | 0.6 |

[a] Taken as reference compound.

Irradiation (λ 300 nm) of the aldehyde (0.15 mol) in propan-2-ol in the presence of carbon tetrachloride (4 mol) as a free radical scavenger yielded as major products acetone and chloroform, and in addition some 4-chlorobutanal, isopropyl cyclopropanecarboxylate, and hexachloroethane, formed in about equal amounts.

In order to obtain information on the mechanism of formation of cyclopropylmethanol, cyclopropanecarbaldehyde (0.5 mol) was irradiated with λ 300 nm in *O*-deuteriopropan-2-ol at −90°. The identified products were (1), (4a)—(8a), and (9). As was apparent from the mass spectra of all these compounds and from the $^1H$ n.m.r. spectra of (6a)—(8a), no carbon bonded deuterium was present in any of them, the upper limit being *ca.* 10%.

Irradiation of cyclopropanecarbaldehyde (1.0 mol) in propan-2-ol with λ 300 nm in the presence of either biphenyl (0.3 mol) at 0° or (*Z*)-penta-1,3-diene (0.3 mol) at −90° as a triplet quencher yielded only 1-cyclopropyl-2-methylpropane-1,2-diol (8a), the amount of which was roughly the

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† Upon dissolving cyclobutanecarbaldehyde (0.05 mol) in propan-2-ol at 20° the extinction at λ 300 nm decreases with time. From the zero time and the final constant (after *ca.* 20 h) extinction the equilibrium composition was calculated to contain *ca.* 40% aldehyde and *ca.* 60% acetal.

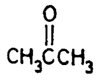
[1] J. G. Calvert and J. N. Pitts, ' Photochemistry,' Wiley, 1966, pp. 368—427; ' Photochemistry,' The Chemical Society, vol. 1, 1970, pp. 68—82; vol. 2, 1971, pp. 183—199; vol. 3, 1972, pp. 250—260; vol. 4, 1973, pp. 266—286; vol. 5, 1974, pp. 219—228.

[2] J. D. Coyle, *J. Chem. Soc.* (*B*), 1971, 2254.

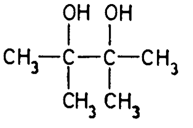
[3] J. Bargon and K. G. Seifert, *Ber. Bunsengesellschaft. Phys. Chem.*, 1974, **78**, 187; K. G. Seifert and J. Bargon, *Angew. Chem. Internat. Edn.*, 1973, **12**, 763; H. E. Chen, S. P. Vaish, and M. Cocivera, *J. Amer. Chem. Soc.*, 1973, **95**, 7586; K. Schaffner, H. Solf, S. M. Rosenfeld, R. G. Lawler, and H. R. Ward, *J. Amer. Chem. Soc.*, 1972, **94**, 6553; H. E. Chen, A. Groen, and M. Cocivera, *Canad. J. Chem.*, 1973, **51**, 3032.

[4] G. Greig and J. C. J. Thynne, *Trans. Faraday Soc.*, 1967, **63**, 1369; J. J. I. Overwater and H. Cerfontain, *Rec. Trav. chim.*, 1968, **87**, 73; 1970, **89**, 705, 719, 729.

same as in the absence of the triplet quenchers. This result strongly indicates that (8a) is formed mainly from the first excited singlet state and all the other products [(1)—(3), (4a)—(7a), and (9)] only from the first excited triplet state.


$CH_3C(=O)CH_3$

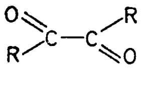
(1)

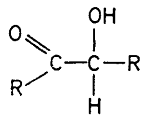

$CH_3-C(OH)(CH_3)-C(OH)(CH_3)-CH_3$

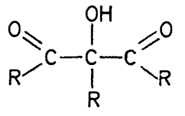
(2)

$CH_3(CH_2)_2CHO$

(3)

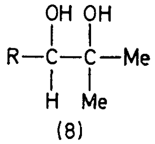

(4)


(5)

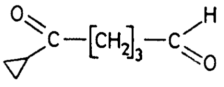

(6)

$RCH_2OH$

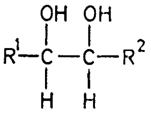
(7)


$R-C(OH)(H)-C(OH)(Me)-Me$

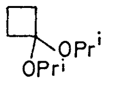
(8)

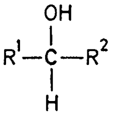

(9)


(10)

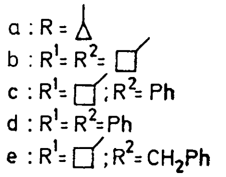

$R^1-C(OH)(H)-C(OH)(H)-R^2$

(11)


(12)


$R^1-C(OH)(H)-R^2$

(13)



*Cyclobutanecarbaldehyde in Propan-2-ol.*—Irradiation of this aldehyde (0.15 mol) in propan-2-ol at 20° with λ *ca.* 300 nm yielded as identified products cyclobutane (10), acetone (1), 2,3-dihydroxy-2,3-dimethylbutane (2), cyclobutylmethanol (7b), 1-cyclobutyl-2-methylpropane-1,2-diol (8b), 1,2-dicyclobutylethane-1,2-diol (11b), and cyclobutanecarbaldehyde di-isopropyl acetal (12), but no (4b)—(6b). In a dark experiment it was shown that the acetal is not a photochemical but a thermal product. The major photochemical products are (7b) and (8b). *E.g.* for an irradiation time of 10 h at 20° the ratio of (10) : (1) : (2) : (7b) : (8b) : (11b) : (12) was found to be 2 : 7 : <0.1 : 4 : 4 : 1 : 160. At higher temperatures the relative amounts of cyclobutane and the acetal amongst the products are significantly greater.

Irradiation of cyclobutanecarbaldehyde in propan-2-ol as solvent in the presence of carbon tetrachloride (5 mol) as a radical scavenger yielded only the acetal (12).* Apparently, (1), (7b), (8b), and (11b) are formed *via* free radical processes.

Irradiation of cyclobutanecarbaldehyde (0.15 mol) in propan-2-ol with λ *ca.* 300 nm in the presence of (*Z*)-penta-1,3-diene (0.1 mol) as a triplet quencher yielded only the acetal (12) traces of oxetans, and possibly (8b) [the oxetans have the same g.l.c. retention times as (8b)]. The formation of the other products was quenched completely. Hence the photoproducts with the possible exception of small amounts of (8b) all arise by reaction of the excited triplet state.

*Cyclobutanecarbaldehyde with Other Hydrogen Donors.*—Cumene, diphenylmethanol, benzyl alcohol, and toluene were employed as hydrogen donors. Irradiation of the aldehyde (0.15 mol) in cumene at 20° with λ 300 nm yielded as main products cyclobutane and cyclobutylmethanol in a ratio of 0.25, and small amounts of other non-identified products. Irradiation of the aldehyde (0.15 mol) in benzene in the presence of diphenylmethanol (2.0 mol) at 20° with λ 300 nm afforded cyclobutane, cyclobutylmethanol, benzophenone (in the ratio 4 : 14 : 1), and tetraphenylethane-1,2-diol. None of these products is formed if naphthalene (0.5 mol) is added to the mixture to be irradiated.† This indicates that the photoproducts all arise from the excited triplet state of the aldehyde.

Irradiation of the aldehyde (0.5 m) in benzyl alcohol as solvent at 0° with λ 300 nm yielded 1-cyclobutyl-2-phenylethane-1,2-diol (11c) and 1,2-diphenylethane-1,2-diol (11d) in the ratio 3 : 1, a thermally unstable product, possibly cyclobutanecarbaldehyde dibenzyl acetal, and virtually no cyclobutylmethanol or benzaldehyde. 1,2-Dicyclobutylethane-1,2-diol could not be excluded as a product since the g.l.c. retention time of this compound is similar to that of benzyl alcohol.

Irradiation of the aldehyde (0.15 mol) in toluene as solvent at 5° with λ 300 nm yielded carbon monoxide, cyclobutane, dicyclobutylmethanol (13b), 1,2-dicyclobutyl-2-hydroxyethanone (5b), 1-cyclobutyl-2-phenylethanol (13e), bibenzyl, and no cyclobutylmethanol. After 20 h irradiation the ratio of the liquid products in the given order was roughly 1 : 2 : 3 : 1. The first four products are the main primary products in photolysis of cyclobutanecarbaldehyde in inert solvents.[6]

## DISCUSSION

The formation of the photoproducts (1), (2), (7), and (8) upon irradiation of cyclopropane- and cyclobutanecarbaldehyde in propan-2-ol may be explained by the reaction steps (1)—(12). A, $R^1$, $R^2$, and Q stand for aldehyde, cycloalkyl, $Me_2\dot{C}OH$, and quencher respectively; the superscripts 1 and 3 denote the multiplicity of an excited electronic state (*e.g.* $^3A$) or an intimate radical pair (*e.g.* ${}^{1}\overline{R^1\dot{C}HOH\ R^{\cdot 2}}$).

$$A + h\nu \longrightarrow {}^1A \qquad (1)$$

$${}^1A + R^2H \longrightarrow {}^{1}\overline{R^1\dot{C}HOH\ R^{2\cdot}} \qquad (2)$$

$${}^{1}\overline{R^1\dot{C}HOH\ R^{2\cdot}} \longrightarrow (8) \qquad (3)$$

$${}^1A \longrightarrow {}^3A \qquad (4)$$

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* No search was made for cyclobutane.

† Naphthalene will absorb most of the radiation but will act as a singlet sensitizer. Wagner[5] has recommended 1-methylnaphthalene as both singlet sensitizer and triplet quencher for several ketones. We observed, however, that this compound is not stable on irradiation in the presence of cyclobutanecarbaldehyde, probably on account of hydrogen abstraction from the methyl group.

[5] P. J. Wagner, *Mol. Photochem.*, 1971, **3**, 169.

[6] C. W. Funke and H. Cerfontain, *Tetrahedron Letters*, 1973, 487.

$$^3A + Q \longrightarrow A + {}^3Q \qquad (5)$$

$$^3A + R^2H \longrightarrow {}^{3}\overline{R^1\dot{C}HOH\ R^{2\cdot}} \qquad (6)$$

$${}^{3}\overline{R^1\dot{C}HOH\ R^{2\cdot}} \longrightarrow R^1\dot{C}HOH + R^{2\cdot} \qquad (7)$$

$$R^1\dot{C}HOH + R^{2\cdot} \longrightarrow (8) \qquad (8)$$

$$R^1\dot{C}HOH + R^2H \longrightarrow (7) + R^{2\cdot} \qquad (9)$$

$$2\ R^1\dot{C}HOH \longrightarrow (R^1HOHC)_2 \qquad (10)$$

$$2\ R^{2\cdot} \longrightarrow (1) + R^2H \qquad (11)$$

$$2\ R^{2\cdot} \longrightarrow (2) \qquad (12)$$

Upon irradiation of ketones in propan-2-ol, the formation of a number of products proceeds *via* the $R^1R^2\dot{C}OH$ radicals as intermediate.[7] The occurrence of the $R^1\dot{C}HOH$ radicals in the present systems could not be established using $CCl_4$ as radical scavenger because of the instability of the resulting geminal chlorohydroxy-compound [steps (13) and (14)]. Evidence in favour of this radical as intermediate is the presence of the $R^1HOHC$-group in a number of products [(5a), (7a), and (8a)] for cyclopropanecarbaldehyde, and for cyclobutanecarbaldehyde (5b), (7b), (8b), (11b), (11c), and (13b). In the presence of a sufficient concentration of Q only (8a) [and possibly some (8b)] is formed. Apparently step (5) then dominates over step (6).

$$R^1\dot{C}HOH + CCl_4 \longrightarrow R^1CClHOH + Cl_3C\cdot \qquad (13)$$

$$R^1CClHOH \longrightarrow A + HCl \qquad (14)$$

*Cyclopropanecarbaldehyde*.—The formation of butanal, (4a), (5a), and (9) obtained in the case of cyclopropanecarbaldehyde may be explained by reactions (15)—(22).

$$\text{cyclo-}C_3H_5\dot{C}HOH + A \longrightarrow (7a) + \text{cyclo-}C_3H_5\dot{C}O \qquad (15)$$

$$\text{cyclo-}C_3H_5\dot{C}HOH + \text{cyclo-}C_3H_5\dot{C}O \longrightarrow (5a) \qquad (16)$$

$$2\ \text{cyclo-}C_3H_5\dot{C}O \longrightarrow (4a) \qquad (17)$$

$$\text{cyclo-}C_3H_5\dot{C}HOH \xrightarrow{\circ} \cdot CH_2CH_2CH{=}CHOH \qquad (18)$$

$$\cdot CH_2CH_2CH{=}CHOH \xrightarrow{\circ} \cdot(CH_2)_3CHO \qquad (19)$$

$$\cdot(CH_2)_3CHO + R^2H \longrightarrow \text{butanal} + R^{2\cdot} \qquad (20)$$

$$\cdot(CH_2)_3CHO + A \longrightarrow \text{butanal} + \text{cyclo-}C_3H_5\dot{C}O \qquad (21)$$

$$\text{cyclo-}C_3H_5\dot{C}O + \cdot(CH_2)_3CHO \longrightarrow (9) \qquad (22)$$

The occurrence of the cyclo-$C_3H_5\dot{C}O$ and $\cdot(CH_2)_3CHO$ radicals in the system is supported by the formation of the corresponding isopropyl ester and chloride when the photolysis is performed in the absence and presence of $CCl_4$ respectively. In the presence of this radical scavenger reactions (23)—(30) take place instead of (8)—(12), (15)—(17), and (20)—(22). In this reasoning it is assumed that the formation of the cyclo-$C_3H_5\dot{C}O$ and $\cdot(CH_2)_3CHO$ radicals is not induced by the presence of carbon tetrachloride.[8] The intermediacy of the cyclopropanecarbonyl chloride in the formation of the isopropyl ester [steps (23) and (24)] is supported by the observation that the carbonyl chloride is a major product upon irradiation of the aldehyde in neat carbon tetrachloride.[9] The occurrence of acetone (1) and chloroform as the main products indicates the occurrence of a chain process. It is proposed that the propagating steps are (26) and (28). The resulting 2-chloro-2-hydroxypropane is unstable [10] and decomposes according to (29).

$$\text{cyclo-}C_3H_5\dot{C}O + CCl_4 \longrightarrow \text{cyclo-}C_3H_5COCl + Cl_3C\cdot \qquad (23)$$

$$\text{cyclo-}C_3H_5COCl + R^2H \longrightarrow \text{cyclo-}C_3H_5CO_2CHMe_2 + HCl \qquad (24)$$

$$\cdot(CH_2)_3CHO + CCl_4 \longrightarrow Cl(CH_2)_3CHO + Cl_3C\cdot \qquad (25)$$

$$Cl_3C\cdot + R^2H \longrightarrow HCCl_3 + R^{2\cdot} \qquad (26)$$

$$Cl_3C\cdot + A \longrightarrow HCCl_3 + \text{cyclo-}C_3H_5\dot{C}O \qquad (27)$$

$$R^{2\cdot} + CCl_4 \longrightarrow R^2Cl + Cl_3C\cdot \qquad (28)$$

$$R^2Cl \longrightarrow (1) + HCl \qquad (29)$$

$$2\ Cl_3C\cdot \longrightarrow C_2Cl_6 \qquad (30)$$

The formation of cyclopropylmethanol (7a) from the 1-hydroxy-1-cyclopropylmethyl radical may proceed either by disproportionation of the initially formed $\overline{\text{cyclo-}C_3H_5\dot{C}HOH\ Me_2\dot{C}OH}$ radical pair, or by hydrogen abstraction by the escaped cyclo-$C_3H_5\dot{C}HOH$ radical from propan-2-ol and the aldehyde [steps (9) and (15) respectively]. Using *O*-deuteriopropan-2-ol as solvent, deuterium transfer from $(CH_3)_2\dot{C}OD$ to cyclo-$C_3H_5\dot{C}HOH$ would yield cyclo-$C_3H_5CDHOH$, whereas hydrogen transfer from this radical to cyclo-$C_3H_5\dot{C}HOH$ would yield $CH_3COCH_2D$ (*via* $CH_3COD{=}CH_2$). In fact, none of the photoproducts contained carbon-bonded deuterium. Accordingly cyclopropylmethanol is not formed by disproportionation of the two fragments of the radical pair.

The presence of products containing the cyclopropylcarbonyl group [(4a)—(6a) and (9)] indicates that hydrogen abstraction from the aldehyde takes place, probably mainly by the $Me_2\dot{C}HOH$ radicals [step (31)]. On the basis of bond dissociation energies [$\Delta H$(H − $CMe_2OH$) 91 and $\Delta H$(H−COMe) 86 kcal $mol^{-1}$][11] step (31) is expected to be exothermic.

$$A + R^{2\cdot} \longrightarrow \text{cyclo-}C_3H_5\dot{C}O + R^2H \qquad (31)$$

Cyclopropylcarbonyl is a σ type of radical.[12] It is

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[7] S. A. Weiner, *J. Amer. Chem. Soc.*, 1971, **93**, 425.

[8] J. O. Pavlik, P. I. Plooard, A. C. Somersall, and J. Guillet, *Canad. J. Chem.*, 1973, **51**, 1435.

[9] C. W. Funke, J. A. J. Geenevasen, J. L. M. de Boer, and H. Cerfontain, *J.C.S. Perkin II*, in the press.

[10] P. Salomee, in ' The Chemistry of the Carbonyl Groups,' ed. S. Patai, Interscience, New York, 1966, p. 178.

[11] ' Handbook of Chemistry and Physics,' Chemical Rubber Co., Cleveland, 1972—1973, 53 edn., p. F189; J. A. Kerr, *Chem. Rev.*, 1966, **66**, 465.

[12] H. Fischer, in ' Free radicals,' ed. J. K. Kochi, Interscience, New York, 1973, vol. II, p. 435.

remarkably stable[13] towards ring opening and decarbonylation, probably as a result of conjugation between the carbonyl and cyclopropyl group, just as in the parent aldehyde.[14] It is also practically inert towards hydrogen abstraction from $R^2H$, because of the endothermicity of this reaction. Therefore the cyclopropylcarbonyl radicals will only combine with (i) one another [step (17)], (ii) 1-hydroxy-1-cyclopropylmethyl radicals [step (16)], and (iii) 4-oxobutyl radicals [step (22)] to yield (4a), (5a), and (9) respectively.

At −90° the amount of 5-cyclopropyl-5-oxopentanal far exceeds that of butanal. The preferred recombination (22) and the absence of *e.g.* 5-hydroxy-5-methylhexanal strongly indicates that the rearrangement [(18) and (19)] proceeds at that temperature mainly within the triplet radical pair, resulting from hydrogen abstraction by $^3A$ from A [step (32)]. The formation of the trimeric

$$^3A + A \longrightarrow \overline{\text{cyclo-}C_3H_5\dot{C}HOH\ \text{cyclo-}C_3H_5\dot{C}O}^{\,3} \tag{32}$$

product 1,2,3-tricyclopropyl-2-hydroxypropane-1,3-dione (6a) is remarkable, especially since it is formed in very substantial amounts. It's special mode of formation from 1,2-dicyclopropylethanedione and cyclopropanecarbaldehyde will be discussed elsewhere.[15]

TABLE 2

Major products in the photoreduction of cyclobutanecarbaldehyde

| Hydrogen donor $R^3H$ | Product composition [a] | | | | | | |
|---|---|---|---|---|---|---|---|
| | cyclo-$C_4H_8$ | cyclo-$C_4H_7CH_2OH$ | cyclo-$C_4H_7CHOHR^2$ | $R^3{}_2$ | Carbonyl compound [b] | (5b) | (13b) |
| $Me_2CHOH$ | 0.5 | 1 | 1 | <0.1 | 1.8 | 0 | 0 |
| $Ph_2CHOH$ | 0.3 | 1 | | + | 0.1 | 0 | 0 |
| $PhCH_2OH$ | | 0 | 1 | 0.3 | 0 | 0 | 0 |
| $PhCHMe_2$ | 0.25 | 1 | | 0 | | | |
| $PhCH_3$ | + | 0 | 1 | 0.3 | | 0.7 | 0.3 |

[a] Amounts, expressed relative to cyclo-$C_4H_7CH_2OH$ (7b) or cyclo-$C_4H_7CHOHR^3$ for the experimental conditions described in the Results section. [b] Derived from $R^3$ by loss of the hydroxy hydrogen atom.

*Cyclobutanecarbaldehyde.*—The photoproducts (1), (2), (7b), and (8b) formed from this aldehyde in propan-2-ol may be explained in terms of the steps (1), possibly (2) and (3), and (4)—(12). This differs from the sequence proposed for cyclopropanecarbaldehyde only in so far that (8b) is now (predominantly if not only) a triplet state product, whereas (8a) was a singlet state product. In the presence of $CCl_4$, the HCl formed *via* step (13) strongly accelerates the thermal formation of (12) which is in fact the only product.

There is no indication for ring opening of the 1-hydroxy-1-cyclobutylmethyl radicals, as observed with the cyclopropyl analogue [step (18)]. Such a ring opening has been observed for some cyclobutylmethyl radicals.[16] Apparently steps (3), (8), (9), and (10) are fast relative to this isomerization.

Another difference between the two aldehyde systems is the absence of products containing the cycloalkylcarbonyl group in the case of cyclobutanecarbaldehyde. Possibly hydrogen abstraction of the acyl hydrogen is easier from cyclopropane- than from cyclobutanecarbaldehyde. Another reason may be the relatively efficient decarbonylation at 20° of the cyclobutylcarbonyl radical to yield cyclobutyl radicals[6] which may then abstract hydrogen to yield cyclobutane. Other routes to cyclobutane are *via* initial α-cleavage of triplet excited aldehyde [steps (33)—(36)].

$$^3A \longrightarrow \text{cyclo-}C_4H_7\cdot + H\dot{C}O \tag{33}$$

$$\text{cyclo-}C_4H_7\cdot + H\dot{C}O \longrightarrow \text{cyclo-}C_4H_8 + CO \tag{34}$$

$$\text{cyclo-}C_4H_7\cdot + R^2H \longrightarrow \text{cyclo-}C_4H_8 + R^2\cdot \tag{35}$$

$$\text{cyclo-}C_4H_7\cdot + A \longrightarrow \text{cyclo-}C_4H_8 + \text{cyclo-}C_4H_7\dot{C}O \tag{36}$$

The following aspects of the photochemistry of cyclobutanecarbaldehyde in the presence of the other hydrogen donors seem to merit discussion. First, 1,2-dicyclobutylmethanol and 1,2-dicyclobutyl-1-hydroxyethanone are only formed as major products in toluene as solvent. Further they are also major products in non-hydrogen donating solvents like hexane.[6] Despite a 180-fold excess of the benzylic hydrogens of toluene, the hydrogen abstraction from toluene [$\Delta H(PhCH_2–H)$ 85 kcal mol$^{-1}$][11] and from the aldehyde [$\Delta H(MeCO–H)$ 86 kcal mol$^{-1}$][11] is of about equal importance (Table 2). This may be explained in terms of association of the polar aldehyde molecules in the non-polar toluene solvent. For then it may be expected that the excited aldehyde molecule has a greater chance to abstract hydrogen from the adjacent ground state aldehyde than from toluene. That toluene is a relatively poor hydrogen donor for $n$–$\pi^*$ carbonyl excited triplet states has also been observed with benzophenone, its photoreduction being slower in toluene and cumene than in propan-2-ol or the presence of diphenylmethanol.[17]

Secondly, the nature of the products and their relative amounts depend strongly on the hydrogen donor employed (Table 2). The products mainly arise *via* initial hydrogen abstraction of the excited aldehyde from the hydrogen donor $R^3H$. The fate

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of the resulting radicals will then be at least in part

$$A^* + R^3H \longrightarrow \text{cyclo-}C_4H_7\dot{C}HOH + R^{3}\cdot \quad (37)$$

determined by the steric properties of $R^3\cdot$. Combination of cyclo-$C_4H_7\dot{C}HOH$ and $R^3\cdot$ occurs efficiently (since no disproportionation products are found) with the apparently easily accessible α-hydroxybenzyl and benzyl radicals. Combination with the 1-hydroxy-1-methylethyl radical is sterically less easy and now both the combination product (8b) *and* cyclobutylmethanol (7b) are formed. The even more bulky cumyl and α-hydroxy-α-phenylbenzyl radicals do not combine with cyclo-$C_4H_7$-$\dot{C}HOH$, but yield cyclobutylmethanol by hydrogen abstraction from *e.g.* the $R^3\cdot$ radical (disproportionation) or the solvent.

TABLE 3

G.l.c. columns and conditions

| | Brass column | | | Adsorbent | | Solid support | | |
|---|---|---|---|---|---|---|---|---|
| Starting mixture | No. | length (m) | Diameter (mm) | Compound | % | Material | Particle size (mesh) | Temp. (°C) |
| A, B | I | 1.8 | 6 | DNP | 20 | Chromosorb-P | 100—120 | 50—150 |
| A, C | II | 1.8 | 6 | SE-30 | 20 | Chromosorb-W | 60—80 | 50—230 |
| A | III | 6 | 2 | SE-30 | 5 | Chromosorb-W | 100—120 | 50—220 |
| D, E | IV | 1.3 | 6 | QF-1 | 7 | Chromosorb-W-NAW | 100—120 | 50—220 |
| D, F, G | V | 1.8 | 6 | SE-30 | 3 | Varaport-30 | 80—100 | 50—200 |
| E, F, G | VI | 1.3 | 6 | Carbowax-20M | 7 | Chromosorb-A | 45—60 | 50—200 |
| E, F | VII | 1.8 | 6 | SE-30 | 20 | Chromosorb-W | 60—80 | 50—250 |

A = cyclo-$C_3H_5CHO$ + $Me_2CHOH$; B = cyclo-$C_4H_7CHO$ + $Me_2CHOH$; C = cyclo-$C_3H_5CHO$ + $Me_2CHOH$ + $CCl_4$; D = cyclo-$C_4H_7CHO$ + cumene; E = cyclo-$C_4H_7CHO$ + toluene; F = cyclo-$C_4H_7CHO$ + diphenylmethane + benzene; G = cyclo-$C_4H_7CHO$ + benzyl alcohol.

Thirdly, with benzyl alcohol and toluene as hydrogen donors the symmetrical recombination products 1,2-dihydroxy-1,2-diphenylethane and bibenzyl are formed. Their formation implies the presence of free α-hydroxybenzyl and benzyl radicals, formed by escape from the primary formed radical pairs. It is remarkable that the concomitantly resulting free 1-hydroxy-1-cyclobutylmethyl radicals do not abstract hydrogen from the solvent. Apparently the latter radicals only combine with the benzylic radicals with formation of (11c) and (13e) respectively.

## EXPERIMENTAL

*Materials.*—Cyclopropanecarbaldehyde, $\lambda_{max.}$ (cyclohexane) 286 nm (ε 20 l $mol^{-1}$ $cm^{-1}$); $\lambda_{max.}$ (ethanol) 279 nm (ε 20 l $mol^{-1}$ $cm^{-1}$),[18] was prepared by reduction of cyclopropyl cyanide with $LiAlH_4$ at −40° and subsequent hydrolysis,[19] and purified by distillation and preparative g.l.c. Cyclobutanecarbaldehyde, $\lambda_{max.}$ (cyclohexane) 297 nm (ε 25 l $mol^{-1}$ $cm^{-1}$); $\lambda_{max.}$ (ethanol) 293 nm [ε (equilibrium composition) 6 l $mol^{-1}$ $cm^{-1}$)], was prepared from the corresponding acid according to two methods, *via* the imidazolyl ketone ρ[20] or through the cyanide,[21] and subsequent $LiAlH_4$ reduction.[19]

(*Z*)-Penta-1,3-diene and cumene (Fluka) were distilled from $LiAlH_4$ to remove any peroxides if present. Other chemicals were commercial and used without further purification.

*Irradiation and Analysis.*—Room and elevated temperature irradiations were performed in a Rayonet photochemical reactor, model RPR-208, equipped with 300 nm lamps. Low temperature irradiations were carried out using an immersion Hanovia medium pressure mercury lamp. In both cases the radiation with λ < 300 nm was cut off by using Pyrex irradiation vessels. The progress of the photoreactions was monitored by g.l.c. analysis. The products were isolated by preparative g.l.c., using the analytical columns (Table 3).

*Identification.*—The products were identified on the basis of (i) their g.l.c. retention times on at least two columns by comparison with those of authentic samples [compounds (2), benzophenone, chloroform, and hexachloroethane], (ii) the mass spectrum after conversion into the corresponding 2,4-dinitrophenylhydrazone [(1)], (iii) their i.r. spectra by comparison with authentic samples [(3) and hexachloroethane], (iv) their mass spectra [(4) and (5)], (v) their i.r. and $^1H$ n.m.r. spectra [(6)], or (vi) their i.r., $^1H$ n.m.r., and mass spectra (the remaining products). All the spectral data have been reported elsewhere.[22] We thank Mr. J. A. J. Geenevasen for experimental assistance. This investigation was carried out under the auspices of the Netherlands Foundation for Chemical Research (S.O.N.) with financial support from the Netherlands Organization for Advancement of Pure Research (Z.W.O.).

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