# The Photochemistry of Some Cycloalkanecarbaldehydes in Inert Solvents

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The photochemistry of the first four members of the series of cycloalkanecarbaldehydes in inert solvents with λ *ca.* 300 nm has been studied. The photochemistry of cyclopropanecarbaldehyde differs from those of the other cycloalkanecarbaldehydes. All aldehydes exhibit two primary processes, *viz.* α-cleavage which is a $T_1$ process, and intermolecular hydrogen abstraction, which proceeds by both the $S_1$ and $T_1$ states of the aldehyde. Hydrogen abstraction by the cycloalkyl radical from the formyl radical then yields cycloalkane and CO. With cyclopropanecarbaldehyde, the resulting α-hydroxycyclopropylmethyl radicals rearrange to yield 3-formylpropyl and (*Z*)-but-1-enyloxyl radicals. The concommittantly formed cyclopropylcarbonyl radical does not decarbonylate due to conjugative stabilization of the cyclopropyl–carbonyl bond. For the same reason, cyclopropanecarbaldehyde gives only little α-cleavage. The cycloalkanecarbonyl radical formed with the other three aldehydes easily decarbonylates to yield the cycloalkyl radical. Combination of the radical pairs yield 1,2-dicycloalkyl-2-hydroxyethanone (2) and dicycloalkylmethanol (13). In a subsequent reaction, triplet excited cycloalkanecarbaldehyde abstracts the α-hydroxymethine hydrogen of (2) and disproportionation of the radical pair thus formed yields cycloalkylmethanol (12) and dicycloalkylethanedione (3). No products resulting from a Norrish type II process could be detected. The proposed mechanisms for the formation of the photoproducts are based on triplet quenching, radical scavenging, and CIDNP experiments.

THE photoreduction of cyclopropane- and cyclobutanecarbaldehyde in propan-2-ol has recently been studied.[1] We now report on the photochemistry of some cycloalkanecarbaldehydes $[CH_2]_nCHCHO$ ($n = 2$—5) in inert solvents. Cyclobutanecarbaldehyde is the smallest cyclic aldehyde with γ-hydrogen atoms, and which therefore would allow a Norrish type II process. However, no products resulting from such a process could be detected for this aldehyde and the two higher homologues.

A preliminary account of the results obtained with cyclobutanecarbaldehyde has been given.[2]

## RESULTS

*Cyclopropanecarbaldehyde.*—Irradiation of cyclopropanecarbaldehyde (1M) in inert solvents (benzene, neopentane, and neohexane) with λ 300 nm yields carbon monoxide, ethene, cyclopropane (1a), butanal, 1,2-dicyclopropyl-2-hydroxyethanone (2a), 1,2-dicyclopropylethanedione (3a), 1,2,3-tricyclopropyl-2-hydroxypropane-1,3-dione (4a), 1-cyclopropylbutan-1-one (5), (*Z*)-but-1-enyl cyclopropanecarboxylate (6), 1-cyclopropyl-2-hydroxypentan-1-one (7), 1-cyclopropyl-3-hydroxypentan-1-one (8), 3-cyclopropyl-3-hydroxypropanal (9), together with small amounts of nine other non-identified products.† Major products are carbon monoxide, (1a), butanal, and (2a)—(4a), minor ones ethene and (5)—(9). *E.g.* irradiation of a 0.7M-aldehyde solution in neopentane at −10° for 40 h with λ 300 nm leads to an aldehyde conversion of only 7 ± 2% and a product ratio (1a) : butanal : (2a) : (3a) : (4a) : (5) : (6) : (7) : (8) : (9) = 26 : 40 : 52 : 34 : 24 : 10 : 10 : 2 : 1 : 1.

Carbon monoxide, (1a), butanal, (2a), and (3a) are formed from the very beginning of the irradiation. The trimer (4a) is formed after an induction period and at the expense of (3a). Ethene is a primary product, but its rate of formation increases with increasing irradiation time; apparently it also results from a secondary reaction.

The initial ratio of butanal : (2a) : (3a) varies greatly with temperature (from 1 : 2 : 1 at −30° to 2 : 1 : 2 at ⩾5°). Irradiation of cyclopropanecarbaldehyde (1M) in $CCl_4$ as radical scavenger at 25° with λ 300 nm yielded chloroform, cyclopropanecarbonyl chloride, 4-chlorobutanal, and hexachloroethane in a ratio of 10 : 10 : 1 : 5.

Cyclopropanecarbaldehyde (1M) in benzene was irradiated at 25° with λ 300 nm in the presence of either (*Z*)-penta-1,3-diene (1M) or biphenyl (1M) as triplet quencher. In both cases, the formation of (1a), butanal, and (4a) was quenched completely, that of (3a) only by 80%. The formation of ethene was not at all quenched for short irradiation times, but in part for longer irradiation times, whereas the formation of (2a) was not quenched at all [no analyses were made for carbon monoxide and (5)—(9)]. The structure of compound (7) suggests that it is formed in a secondary photoreaction from butanal and cyclopropanecarbaldehyde. This was proven by irradiating with λ 300 nm a mixture of these two aldehydes (both 0.9M, and absorbing about equal amounts of radiation) in neohexane at 25°. The products detected were (2a), (7), 5-hydroxyoctan-4-one (10), and 1-cyclopropyl-1-hydroxypentan-2-one (11), formed in the ratio of 1 : 5 : 3 : 1. Irradiation of the same mixture of the two aldehydes in neohexane in the presence of biphenyl (0.2M) yielded the same products (2a) : [(7) + (11)] : (10) = 1 : 4 : 2. These results indicate that (7) is formed by reaction of a singlet excited aldehyde molecule.

*Cyclobutanecarbaldehyde.*—Irradiation with λ 300 nm of cyclobutanecarbaldehyde (0.3M) in inert solvents (neopentane, neohexane, benzene, or acetonitrile) yielded as identified products carbon monoxide, cyclobutane (1b), cyclobutylmethanol (12b), dicyclobutylmethanol (13b), 1,2-dicyclobutyl-2-hydroxyethanone (2b), dicyclobutylethanedione (3b), and 1,2,3-tricyclobutyl-2-hydroxypropane-1,3-dione (4b). No evidence was obtained for the formation of the Norrish type II product pent-4-enal and bicyclo[1.1.1]pentan-2-ol. The dependence of the amounts of (12b), (13b), (2b), and (3b) on the irradiation time for 0 and 40° has been reported.[2] There is an induction period for the formation of (3b), (4b), and (12b) which are formed at the expense of (2b). The product distribution is strongly temperature dependent,[2] as is further shown in Table 1.

Irradiation of cyclobutanecarbaldehyde (0.5M) in carbon tetrachloride as radical scavenger at 25° with λ 300 nm yields cyclobutane, (2b), (3b), (12b), and (13b) as major

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† Compounds (1a), butanal, (2a), and (3a) have also been reported as photoproducts.[3]

[1] C. W. Funke and H. Cerfontain, *J.C.S. Perkin II*, in the press.

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

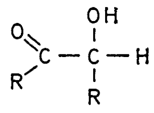
[3] J. J. I. Overwater, Thesis (in English), University of Amsterdam, 1969, (*a*) pp. 82—84; (*b*) p. 28.

products in about the same amounts as in inert solvents [no analysis was made for CO and (4b)]. It may thus be concluded that these products do not arise *via free* radical intermediates. CIDNP Measurements further showed the formation of some trichloroethanal and chloroform.

Upon irradiation of cyclobutanecarbaldehyde (0.8M) in benzene in the presence of either (*Z*)-penta-1,3-diene or naphthalene (each 0.1M) as a triplet quencher at 30° with λ 300 nm *only* (2b) is formed in a yield which is 70% of that in the unquenched reaction. With (*Z*)-penta-1,3-diene, small amounts of oxetans are formed. The oxetan formation probably proceeds *via* the excited singlet state of the aldehyde.[4] Naphthalene absorbs in the 300 nm region. The singlet energy transfer from singlet excited naphthalene to ground state cyclobutanecarbaldehyde is very efficient.* Accordingly, the absorbed radiation will eventially produce mainly singlet excited cyclobutanecarbaldehyde. From the quenching experiments it follows that CO, cyclobutane, (3b), (4b), (12b), and (13b) are formed from the excited triplet state. Taking into account the small losses of singlet excited aldehyde due to oxetan formation with (*Z*)-penta-1,3-diene and the absorption of 300 nm radiation by naphthalene, it follows that (2b) is formed in at least 70% yield from the excited singlet state and at a maximum 30% yield from the excited triplet state.

RH

(1)



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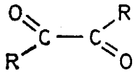

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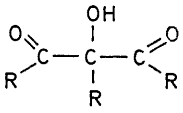
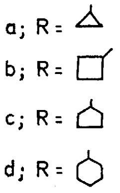


(4)

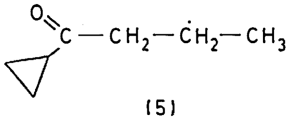


$RCH_2OH$

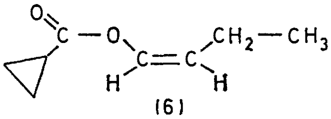
(12)

$R_2CHOH$

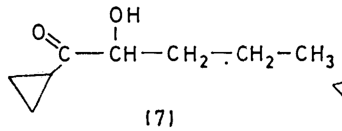
(13)



(5)



(6)



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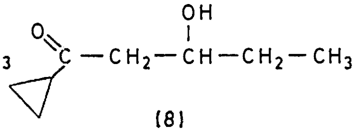
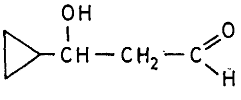
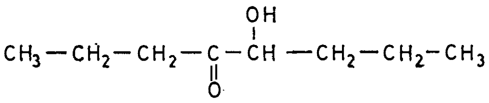


(8)

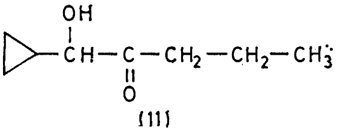


(9)



$CH_3-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-\overset{\overset{OH}{|}}{CH}-CH_2-CH_2-CH_3$

(10)



(11)

*Cyclopentane- and Cyclohexane-carbaldehyde*.—Irradiation of cyclopentanecarbaldehyde (1.5M) in neohexane at 30° with λ 300 nm yielded as identified non-gaseous products (2c), (12c) (the major product), (13c), and small amounts of (3c), bicyclopentyl, and dicyclopentyl ketone.

Irradiation of cyclohexanecarbaldehyde (0.8M) in neohexane at 30° with λ 300 nm yielded as identified products (1d), (2d), and (12d) (major product). There is an induction period for the formation of (12d). The identified products using benzene as solvent at 70° were (1d), cyclohexylbenzene, and (12d). The first two compounds are formed in a

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* Wagner recommends 1-methylnaphthalene as a combined singlet sensitizer and triplet quencher for several ketones.[5] This compound proved, however, to be unstable upon irradiation with λ 300 nm in the presence of cyclobutanecarbaldehyde, possibly on account of hydrogen abstraction from the methyl group.

[4] C. W. Funke and H. Cerfontain, *J.C.S. Perkin II*, in the press.

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

ratio of 5 : 1. Upon irradiation at room temperature no cyclohexylbenzene was formed.

*Triplet Lifetime Determination.*—Information on the triplet lifetimes of cyclopropane- and cyclobutane-carbaldehyde was obtained by irradiation of one of the aldehydes (0.8M) in benzene at 25° in the presence of various concentrations of (*Z*)-penta-1,3-diene. The plots of $\phi_0/\phi$ for the formation of cycloalkane *versus* the quencher concentration were linear. The triplet lifetime in the absence of quencher was calculated from the slopes of the Stern–Volmer plots with a value of $5.0 \times 10^9$ l $mol^{-1}$ $s^{-1}$ for the bimolecular quenching rate constant in benzene, *i.e.* on the assumption that the quenching is diffusion controlled.[6] The results are given in Table 2.

TABLE 1

Irradiation of cyclobutanecarbaldehyde; product ratio and quantum yield for low substrate conversion

| | Relative amounts [a] | | | |
|---|---|---|---|---|
| Product | −60° | 30° | 60° | $\phi$ (30°) |
| Cyclobutane | 0 | 1 | 2 | 0.06 |
| (2b) | 25 | 0.5 | 0.2 | 0.03 |
| (13b) | 1 | 1 | 1 | 0.06 |

[a] Expressed relative to (13b) as reference.

TABLE 2

Triplet lifetimes of carbonyl compounds in benzene as solvent at 25°

| Carbonyl compound | Molarity | $\tau$/ns |
|---|---|---|
| c-$C_3H_5CHO$ | 0.8 | 27 |
| c-$C_4H_7CHO$ | 0.8 | 70 |
| Butanal | 0.1—0.2 | 35 [a] |
| 4-Methylpentanal | 0.1—0.2 | 1.4 [a] |
| Hexanal | 0.1—0.2 | 6.2 [a] |

[a] Ref. 25.

*CIDNP Experiments.*—Irradiation of cyclobutanecarbaldehyde (0.3M) in hexadeuteriobenzene in the probe of the n.m.r. spectrometer led to the following deviations from the normal $^1H$ n.m.r. spectrum: (i) a doublet ($J < 2$ Hz) at $\delta$ 9.7 (c-$C_4H_7C\mathit{H}O$) in enhanced absorption, (ii) a doublet ($J$ *ca.* 4 Hz) at $\delta$ 3.9 in emission [(c-$C_4H_7$)$C\mathit{H}OH$-CO(c-$C_4H_7$)] [upon irradiation of the same solution in the presence of the triplet quencher (*Z*)-penta-1,3-diene, this signal exhibits enhanced absorption], (iii) a multiplet at $\delta$ 2.9—3.3 in emission (c-$C_3H_6C\mathit{H}CHO$), and (iv) a singlet at $\delta$ 1.9 in emission (cyclobutane).

Upon irradiation of cyclobutanecarbaldehyde (0.3M) in carbon tetrachloride the signals of the hydrogens of $CCl_3C\mathit{H}O$ and $C\mathit{H}Cl_3$ are both in emission.

## DISCUSSION

The formation of the photoproducts CO, (1)—(3), (12), and (13) in the photolysis of cyclobutanecarbaldehyde and the higher homologues in inert solvents and the influence of triplet quenchers on their formation may be explained by steps (1)—(13). A, R, And Q stand for aldehyde, cycloalkyl, and quencher respectively; the superscripts 1 and 3 denote the multiplicity of either the electronic excited state, or the intimate radical pair. Product formation in steps (7), (9), (11), and (13) requires spin inversion. The irradiation of cyclobutanecarbaldehyde in the presence of triplet quenchers yields

$$A + h\nu \longrightarrow {}^1A \tag{1}$$

$${}^1A + A \longrightarrow {}^1\overline{R\dot{C}HOH\ R\dot{C}O} \tag{2}$$

$${}^1\overline{R\dot{C}HOH\ R\dot{C}O} \longrightarrow (2) \tag{3}$$

$${}^1A \longrightarrow {}^3A \tag{4}$$

$${}^3A + Q \longrightarrow A + {}^3Q \tag{5}$$

$${}^3A \longrightarrow {}^3\overline{R\cdot\quad \cdot CHO} \tag{6}$$

$${}^3\overline{R\cdot\quad \cdot CHO} \longrightarrow (1) + CO \tag{7}$$

$${}^3A + A \longrightarrow {}^3\overline{R\dot{C}HOH\ R\dot{C}O} \tag{8}$$

$${}^3\overline{R\dot{C}HOH\ R\dot{C}O} \longrightarrow (2) \tag{9}$$

$${}^3\overline{R\dot{C}HOH\ R\dot{C}O} \longrightarrow {}^3\overline{R\dot{C}HOH\ R\cdot} + CO \tag{10}$$

$${}^3\overline{R\dot{C}HOH\ R\cdot} \longrightarrow (13) \tag{11}$$

$${}^3A + (2) \longrightarrow {}^3\overline{R\dot{C}HOH\ R\dot{C}OHCOR} \tag{12}$$

$${}^3\overline{R\dot{C}HOH\ R\dot{C}OHCOR} \longrightarrow (12) + (3) \tag{13}$$

only (2b) in a relative yield of 70%. Accordingly steps (6), (8), and (12) do not occur, apparently because of the much higher rate of step (5).

The scavenging experiments with $CCl_4$ showed that the above products are mainly formed by a route other than *via* free radical intermediates. Evidence for the occurrence of radical pair intermediates comes from the CIDNP[7] studies with cyclobutanecarbaldehyde. By application of Kaptein's rules[8] the CIDNP results can be explained as follows.* Escape of the c-$C_4H_9\dot{C}HOH$ radical from the initially formed triplet radical pair formed in step (8), followed by hydrogen transfer [step (14)] yields polarized cyclobutanecarbaldehyde with the formyl hydrogen in enhanced absorption ($\Gamma_n = \mu\varepsilon\Delta g A_i$[8] $= + - + - = +$) and the methine hydrogen in emission ($\Gamma_n = + - + + = -$). Polarized (2b) is formed *via* step (9) ($\Gamma_n = + + + - = -$).

The reversal of the signal of the carbon bonded hydrogen (2b) to enhanced absorption upon irradiation of the aldehyde in the presence of (*Z*)-penta-1,3-diene is due to the occurrence of step (3) ($\Gamma_n = - + + - = +$). The formation of polarized cyclobutane may be explained in terms of reactions (7) and (15). In the case of (15) we expect enhanced absorption for the $\alpha$-hydrogen ($\Gamma_n = + + - - = +$) † and emission for the $\beta$-hydrogen

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* A more extensive description is given elsewhere.[9a]

† In this case we have neglected the influence of the hydroxy-hydrogen which is transferred to the cyclobutyl radical, since this hydrogen is only weakly coupled with the electron spin in the 1-hydroxycyclobutylmethyl radical precursor.[10]

[6] P. J. Wagner and A. E. Kamppainen, *J. Amer. Chem. Soc.*, 1968, **90**, 5898.

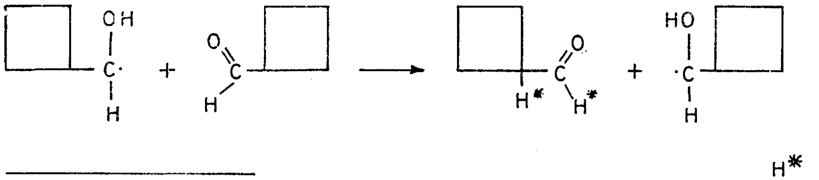
[7] H. R. Ward, *Accounts Chem. Res.*, 1972, **5**, 18; R. G. Lawler, *ibid.*, p. 25; S. H. Pine, *J. Chem. Educ.*, 1972, **49**, 662.

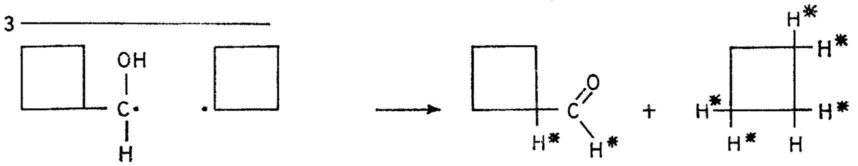
[8] R. Kaptein, *Chem. Comm.*, 1971, 732.

[9] C. W. Funke, Thesis (in English), University of Amsterdam, 1975, (*a*) pp. 26—28; (*b*) chs. III and V.

[10] H. Fischer, in 'Free Radicals,' ed. J. K. Kochi, Wiley, New York, 1973, vol. II, p. 435.

($\Gamma_n = + + - + = -$) of cyclobutane, and since $A_{\alpha\text{-H}} = -21.20$ and $A_{\beta\text{-H}} = 36.66$ G,[11] *i.e.* $|A_{\alpha\text{-H}}| < |A_{\beta\text{-H}}|$, the effect of the four β-hydrogen atoms dominates. It can be calculated that the cyclobutanecarbaldehyde formed simultaneously in (15) has an emitting formyl hydrogen ($\Gamma_n = + + + - = -$) and the methine hydrogen in enhanced absorption ($\Gamma_n = + + + + = +$). This is opposite to both the experimental observations and the calculated polarization of the cyclobutanecarbaldehyde formed in step (14). Accordingly step (15) is at most of minor importance relative to step (14).


(14)


(15)

If step (7) is responsible for the cyclobutane emission, then the emission expected for both the transferred formyl hydrogen with its large hyperfine splitting ($\Gamma_n = + + - + = -$), and the original α-hydrogen ($\Gamma_n = + + + - = -$) has to dominate over the enhanced absorption expected for the β-hydrogens ($\Gamma_n = + + + + = +$).

Additional evidence for the α-cleavage (6) comes from the observation that the resonance lines of trichloroethanol and chloroform formed upon irradiation of cyclobutanecarbaldehyde in neat carbon tetrachloride are both in emission. The emission lines for the two compounds can be explained by their formation *via* the radical pairs $^{F}\overline{Cl_3C\cdot\ \ \cdot CHO}$ by (16) and (17), in which the index F signifies a radical pair formed from free radicals, *i.e.* no appreciable interaction exists between the unpaired electrons before the radical pair is formed. The (small amounts of) $Cl_3C\cdot$ radicals may be formed by steps (18)—(20), or by a singlet excited aldehyde-induced $CCl_4$ dissociation, as proposed to explain the photochemistry of ketones in $CCl_4$.[12]

$$^{F}\overline{Cl_3C\cdot\ \ \cdot CHO} \longrightarrow CCl_3CH^{*}O \qquad (16)$$

$$^{F}\overline{Cl_3C\cdot\ \ \cdot CHO} \longrightarrow CH^{*}Cl_3 + CO \qquad (17)$$

$$CCl_4 + c\text{-}C_4H_7\dot{C}O \longrightarrow Cl_3C\cdot + c\text{-}C_4H_7COCl \qquad (18)$$

$$\begin{array}{l} CCl_4 + c\text{-}C_4H_7\dot{C}HOH \longrightarrow \\ \qquad Cl_3C\cdot + [c\text{-}C_4H_7CHClOH] \qquad (19) \\ \qquad\qquad\qquad \big\downarrow \\ \qquad\qquad c\text{-}C_4H_7CHO + HCl \end{array}$$

$$CCl_4 + c\text{-}C_4H_7\cdot \longrightarrow Cl_3C\cdot + c\text{-}C_4H_7Cl \qquad (20)$$

The present CIDNP results are similar to those obtained with propanal.[13]

Compounds (3) and (5) are thought to arise as secondary products from the primary product (2), and this explains the induction period for (3) and (5). The concentration ratio of A and (2) just after the induction period is *ca.* 400 at 0 and 800 at 40°.[2] The occurrence of (12) then illustrates that $k_{12} \gg k_8$, probably as a result of the formation of the relatively stable semidione radical.[14]

The rate of (9) will be much smaller than that of (3) because of the required spin inversion. Accordingly the lifetime will be greater for the triplet than the singlet radical pair $\overline{R\dot{C}HOH\ \ R\dot{C}O}$. In fact, decarbonylation can only compete with the radical recombination in the former case since (13b) was found to be a triplet product only. The temperature dependence of the ratio of the primary products (2b) and (13b) is ascribed to the temperature dependence of the decarbonylation of the cyclobutylcarbonyl system in the radical pair (10).

The observation that cyclobutane is the major photoproduct of cyclobutanecarbaldehyde at 60°, whereas it could not even be detected upon irradiation at −60° (Table 1), illustrates that the ratio of α-cleavage (6) to (intermolecular) hydrogen abstraction (2) + (8) increases with increasing temperature, as has been observed for ketones.[15]

The ratio of (the secondary products) (12b) and (3b) increases significantly with increasing irradiation time both at 0 and 40°.[2] This may be explained by the formation of the tertiary product (4b) from (3b) and $^1$A. This reaction has been discussed in detail elsewhere.[16]

There is no evidence for intramolecular γ-hydrogen abstraction, neither in the case of the thoroughly studied cyclobutanecarbaldehyde, nor with the far less extensively studied two higher homologues. This may be explained in terms of the conformations of the three excited cycloalkanecarbaldehydes. *E.g.* the cyclobutane ring is puckered by *ca.* 30°.[17] Accordingly, (excited)

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[11] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2147.

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

[13] H. E. Chen, S. P. Vaish, and M. Cocivera, *J. Amer. Chem. Soc.*, 1973, **95**, 7586.

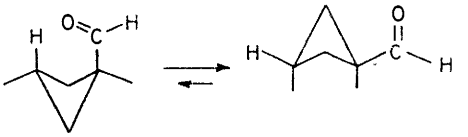
[14] (*a*) D. M. Camaioni, H. F. Walter, J. E. Jordan, and D. W. Pratt, *J. Amer. Chem. Soc.*, 1973, **95**, 7978; T. Foster, D. Klapstein, and P. R. West, *Canad. J. Chem.*, 1974, **52**, 524; (*b*) J. Kelder and H. Cerfontain, *Tetrahedron Letters*, 1972, 1307.

[15] H. Paul and H. Fischer, *Helv. Chim. Acta*, 1973, **56**, 1575.

[16] C. W. Funke and H. Cerfontain, *Tetrahedron Letters*, 1975, 406.

[17] S. Meiboom and L. C. Snijder, *J. Chem. Phys.*, 1970, **52**, 3857.

cyclobutanecarbaldehyde can exist in two conformations A and B. The former conformation in which $\gamma$-hydrogen



A B

abstraction could proceed *via* a favourable six-membered transition state, will be present only in a relatively small amount, because of intramolecular steric repulsion. In fact, the rate constant of $\gamma$-hydrogen abstraction is very much smaller for cyclobutyl phenyl ketone ($5.5 \times 10^3$ $s^{-1}$ [18]) than for hexan-2-one ($1.0 \times 10^8$ $s^{-1}$ [19]) or *exo*-5-benzoylbicyclo[2.1.1]hexane which has a locked A conformation ($3.9 \times 10^8$ $s^{-1}$ [20]). The absence of $\gamma$-hydrogen abstraction also explains the observation that the triplet lifetime of cyclobutanecarbaldehyde is significantly greater than that of hexanal (*cf.* Table 2).

The absence of the Norrish type II products with cyclopentane- and cyclohexane-carbaldehyde can be explained similarly in terms of a strong preference for the conformation in which the formyl group has the equatorial orientation (for the orientation of five-membered rings, see ref. 21).

The formation of dicyclopentyl ketone may be explained by steps (21) and (22). The formation of cyclohexylbenzene upon irradiation of cyclohexanecarbaldehyde in benzene at 70° may be explained by decarbonylation of the cyclohexylcarbonyl radicals which process is apparently temperature dependent (see Results section) and subsequent alkylation of the benzene solvent by the resulting cyclohexyl radicals.

$$\text{c-}C_5H_{11}CHO^* + (\text{c-}C_5H_{11})_2CHOH \longrightarrow \overline{\text{c-}C_5H_{11}\dot{C}HOH\ (\text{c-}C_5H_{11})_2\dot{C}OH} \qquad (21)$$

$$\overline{\text{c-}C_5H_{11}\dot{C}HOH\ (\text{c-}C_5H_{11})_2\dot{C}OH} \longrightarrow \text{c-}C_5H_{11}CH_2OH + (\text{c-}C_5H_{11})_2CO \qquad (22)$$

*Cyclopropanecarbaldehyde*.—As may be concluded from the triplet quenching experiments, the formation of the photoproduct (2a) proceeds only by the steps (1)—(3), that of cyclopropane by (6) and (7).

The formation of ethene as a primary photoproduct may be explained by step (23); the concommittantly formed keten could, however, not be detected. Overwater observed that ethene formation in the gas-phase photolysis of cyclopropanecarbaldehyde is only important for the $\lambda$ 254 nm radiation.[22] He suggested that the ethene is formed from a vibrationally excited singlet state of the aldehyde. Such a 'hot' singlet excited state should have an extremely short life time in the present solution system.[23] Accordingly, in order to be effective, the rate of step (6) must be very high.* The formation of ethene as a secondary product is easily explained, as it is known to be a photoproduct of butanal.[25]

$$^1\text{c-}C_3H_5CHO \longrightarrow C_2H_4 + CH_2CO \qquad (23)$$

The combination of the radical pair $\overline{\text{c-}C_3H_5\dot{C}HOH\ \text{c-}C_3H_5\dot{C}O}$ will be slower for the triplet than the singlet state because of the required spin inversion in the former case. Separation of the paired radicals, leading to free cyclopropylcarbonyl and cyclopropylhydroxymethyl radicals [step (24)] can now compete with their combination (9). The cyclopropylhydroxymethyl radical rearranges rapidly to the 3-formylpropyl radical [steps (25) and (26)]. This radical has been scavenged with carbon tetrachloride to yield 4-chlorobutanal (27).

$$^3\overline{\text{c-}C_3H_5\dot{C}HOH\ \text{c-}C_3H_5\dot{C}O} \longrightarrow \text{c-}C_3H_5\dot{C}HOH + \text{c-}C_3H_5\dot{C}O \qquad (24)$$

$$\text{c-}C_3H_5\dot{C}HOH \xrightarrow{R} \cdot CH_2CH_2CH{=}CHOH \qquad (25)$$

$$\cdot CH_2CH_2CH{=}CHOH \xrightarrow{R} \cdot CH_2CH_2CH_2CHO \qquad (26)$$

$$\cdot CH_2CH_2CH_2CHO + CCl_4 \longrightarrow Cl(CH_2)_3CHO + Cl_3C\cdot \qquad (27)$$

$$\cdot CH_2CH_2CH_2CHO + \text{c-}C_3H_5CHO \longrightarrow CH_3(CH_2)_2CHO + \text{c-}C_3H_5\dot{C}O \qquad (28)$$

$$2\ \text{c-}C_3H_5\dot{C}O \longrightarrow (3a) \qquad (29)$$

$$\text{c-}C_3H_5\dot{C}O + CCl_4 \longrightarrow \text{c-}C_3H_5COCl + Cl_3C\cdot \qquad (30)$$

In the absence of this scavenger the 3-formylpropyl radical abstracts hydrogen from cyclopropanecarbaldehyde with formation of a new cyclopropylcarbonyl radical [step (28)]. The remarkable stability of the cyclopropylcarbonyl radical towards decarbonylation and ring opening has been discussed.[1,9b] Since hydrogen abstraction from the parent aldehyde is a non-productive reaction, these radicals only dimerize to yield (3a) [step (29)]. In carbon tetrachloride, however, these radicals only abstract chlorine [step (30)].

The trimer (4a) is also a major photoproduct in propan-2-ol as solvent. Its special route of formation from $^1$A and (3a) has been discussed elsewhere.[16]

Let us now consider the formation of the minor photoproducts (5)—(7). That of (6) may be explained in

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* Ethene formation from cyclopropanecarbaldehyde is an important process under conditions of electron impact.[24]

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terms of the steps (31)—(33). The cyclopropylhydroxymethyl radical can occur in two relatively stable conformations, *viz.* a cisoid and a transoid one, in which the

$$ {}^3\overline{\text{cisoid-c-}C_3H_5\dot{C}HOH\ C_3H_5\dot{C}O} \xrightarrow{R} {}^3\overline{(Z)\text{-}\dot{C}H_2CH_2CH{=}CHOH\ \text{c-}C_3H_5\dot{C}O} \quad (31)$$

$$ {}^3\overline{(Z)\text{-}\dot{C}H_2CH_2CH{=}CHOH\ C_3H_5\dot{C}O} \longrightarrow {}^3\overline{(Z)\text{-}CH_3CH_2CH{=}CHO\cdot\ \text{c-}C_3H_5\dot{C}O} \quad (32)$$

$$ {}^3\overline{(Z)\text{-}CH_3CH_2CH{=}CHO\cdot\ \text{c-}C_3H_5\dot{C}O} \longrightarrow (6) \quad (33)$$

plane through the OCC bonds bisects the cyclopropyl ring.[26] Ring opening of the cisoid conformation leads to the (*Z*)-4-hydroxybut-3-enyl radical [step (31)]. Subsequent isomerization of this radical by a [1,5] hydrogen shift (*via* a favourable six-membered cyclic transition state) yields the (*Z*)-but-1-enyloxyl radical [step (32)].* Recombination with the other radical fragment of the radical pair then yields (6) [step (33)].†

The transoid cyclopropylhydroxymethyl radical upon ring opening will yield the (*E*)-4-hydroxybut-3-enyl radical, which can only react as in (26).

As shown in the Results section, (7) is formed by a photoreaction of cyclopropanecarbaldehyde and butanal.

$$\text{Pr}^{n}CHO + h\nu \longrightarrow {}^1\text{Pr}^{n}CHO \quad (34)$$

$$\text{c-}C_3H_5CHO + h\nu \longrightarrow {}^1\text{c-}C_3H_5CHO \quad (35)$$

$${}^1\text{c-}C_3H_5CHO + \text{Pr}^{n}CHO \longrightarrow \text{c-}C_3H_5CHO + {}^1\text{Pr}^{n}CHO \quad (36)$$

$${}^1\text{Pr}^{n}CHO + \text{c-}C_3H_5CHO \longrightarrow \overline{{}^1\text{Pr}^{n}\dot{C}HOH + \text{c-}C_3H_5\dot{C}O} \quad (37)$$

$$\overline{{}^1\text{Pr}^{n}\dot{C}HOH + \text{c-}C_3H_5\dot{C}O} \longrightarrow (7) \quad (38)$$

Accordingly, its formation may be explained in terms of the steps (34)—(38).‡

## EXPERIMENTAL

*Materials.*—The preparation of cyclopropane- and cyclobutane-carbaldehyde has been described.[1] Cyclopentanecarbaldehyde was prepared from the corresponding carboxylic acid.[29] Cyclohexanecarbaldehyde was obtained from Fluka. The aldehydes were purified by preparative g.l.c.

*Irradiations.*—The irradiation procedures have been described.[1] For the quantum yield determination hexan-2-one [30] and potassium ferrioxalate [31] were used as actinometer using the merry-go-round attachment (MGR-100) in the Rayonet photochemical reactor.

*CIDNP.*—60 MHz Spectra were obtained during irradiation with an Osram HBO 1 000 W high pressure mercury arc in the modified probe of a Varian DA-60 n.m.r. spectrometer.

*Analysis, Product Isolation, and Identification.*—The progress of the photoreactions was monitored by g.l.c. The product yields were determined from the relative g.l.c. peak area relative to that of chlorobenzene which was used as internal standard.[32] The products were isolated by preparative g.l.c. They were identified by means of their i.r., $^1H$ n.m.r., and mass spectra, except for the gaseous products which were identified on the basis of their g.l.c. retention times, and compounds (8) and (9) for which only mass spectra were obtained using an Aerograph-Varian A-90 gas chromatograph coupled *via* a Varian Biemann–Watson two stage separator with a G.E.C.–A.E.I. MS902 mass spectrometer.

All spectral data of the photoproducts obtained from cyclopropane- and cyclobutane-carbaldehyde, as well as the spectrometers and the g.l.c. columns employed have been described elsewhere.[9b]

*Cyclopentylmethanol.*—This had $\nu_{\text{max.}}$ (liquid capillary) 3 500ms (O–H), 2 970s, 2 880s, 1 435w, 1 430w, 1 390w, 1 220w, 1 080ms, 1 020s (C–O), and 930ms cm$^{-1}$, $\delta$($CCl_4$) 1.1—2.0br (9 H, m, cyclopentyl-H), 2.38 (1 H, s, O*H*), and 3.47 (2 H, d, *J* 7 Hz, C*H*$_2$OH), *m/e* (70 eV) 82 ($M^+ - H_2O$), 69, 68, 67, 57, 55, 54, 53, 44, 42, and 41, $M^+$ not detectable.

*Bicyclopentyl.*—This had $\delta$ 1.5—2.2, *m/e* 138 ($M^+$), 110, 109, 96, 95, 82, 81, 69, 68, 67, 55, 44, and 41.

*Dicyclopentyl Ketone.*—This had $\delta$ 1.5—2.1 [m, $(CH_2)_4$] and 2.75—3.13 (m, COC*H*), *m/e* 166 ($M^+$), 125, 97, 81, 69, 67, 57, 55, and 41.

*Dicyclopentylmethanol.*—This had $\nu_{\text{max.}}$ 3 500w (O–H), 2 980w, 2 880s, 1 455w, and 1 020w cm$^{-1}$, $\delta$ 1.1—2.5 (18 H, cyclopentyl) and 3.35 (1 H, t, *J* 5 Hz, C*H*OH), *m/e* 168 ($M^+$), 166, 99, and 81.

*Dicyclopentylethanedione.*—This had $\nu_{\text{max.}}$ 2 980, 2 880, and 1 700 (C=O) cm$^{-1}$, $\delta$ 1.4—2.1 (m, cyclopentyl $CH_2$) and 3.3—3.7 (m, CHCO).

1,2-*Dicyclopentyl*-2-*hydroxyethanone.*—This had $\nu_{\text{max.}}$ 3 500ms (O–H), 3 050ms, 2 980s, 2 880s, 1 700s (C=O), 1 455ms, 1 400w, 1 360ms, 1 240ms, 1 180ms, and 1 020ms cm$^{-1}$, $\delta$ 1.1—2.2 [m, $(CH_2)_4$], 2.2—2.6 [1 H, m, COHC*H*-$(CH_2)_4$], 2.9—3.2 [1 H, m, COC*H*$(CH_2)_4$], and 4.26 (1 H, d, *J* 3 Hz, C*H*OH), *m/e* 196 ($M^+$), 194, 99, 97, 81, 69, 67, and 41.

*Cyclohexylmethanol.*—This had $\nu_{\text{max.}}$ 3 300ms (O–H) cm$^{-1}$, $\delta$ 0.2—2.0 (22 H, m, cyclohexyl H), 3.1 (1 H, s, OH), 3.34 (2 H, d, *J* 7 Hz, C*H*$_2$OH).

1,2-*Dicyclohexyl*-2-*hydroxyethanone.*—This had $\nu_{\text{max.}}$ 3 460ms (O–H) and 1 700s (C=O) cm$^{-1}$, $\delta$ 1.1—1.9 (m, cyclohexyl $CH_2$), 2.55 (1 H, m, COHC*H*), 3.18 (1 H, m, COCH), and 4.02 (1 H, s, C*H*OH), *m/e* 224 ($M^+$), 206, and 111.

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* The occurrence of the [1,5] hydrogen shift is probably the result of an enhanced (conjugative) stabilization of the resulting radical [14a] and the preceding transition state, since without such stabilization, the [1,5] hydrogen shift would be endothermic by *ca.* 6 kcal mol$^{-1}$ [$D(CH_3CH_2CH_2\text{–}H)$ 98 and $D(C_2H_5O\text{–}H)$ 104 kcal mol$^{-1}$ [27]].

† In the (*Z*)-but-1-enyloxyl radical 85% of the free electron spin density is on C-2.[14a] The product expected from combination of c-$C_3H_5\dot{C}O$ with this position has not been detected. However, product (5) may have been formed (in part) by photodecarbonylation of this recombination product.

‡ The *n*-$\pi$* $\lambda_{\text{max.}}$ of cyclopropanecarbaldehyde and butanal in the gas phase are at 286 [3b] and 290 nm [28] respectively. Thus the energy of singlet excited cyclopropanecarbaldehyde will be somewhat greater than that of singlet excited butanal.

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*Phenylcyclohexane*.—This had δ 1.1—2.7 (11 H, m, cyclohexyl H) and 7.13 (5 H, s, Ph), *m/e* 160 ($M^+$), 117, 104, 91, and 44.

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