Investigations into Possible Intermediates in the Photoreduction of Conjugated Cyclopropyl Ketones in 2-Propanol[1]

WILLIAM G. DAUBEN, LEONARD SCHUTTE, RICHARD E. WOLF, AND E. JOHN DEVINY

Department of Chemistry, University of California, Berkeley, California 94720

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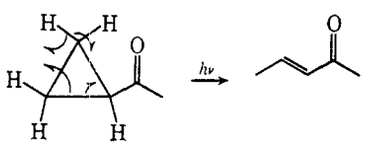
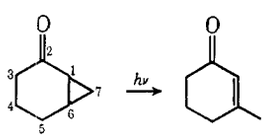
The photoreductions of a series of bicyclo[4.1.0]- and bicyclo[3.1.0]alkan-2-ones (1) in 2-propanol and the ground-state radical rearrangements of the corresponding bicyclo[4.1.0]- and bicyclo[3.1.0]alkan-2-ols (6) (using di-*t*-butyl peroxide as initiator) were compared. The product ratios, in either the photoreductive process or the radical rearrangement, change markedly with temperature. The similarity in product distributions of the two processes at different temperatures indicates that a common intermediate is involved, *i.e.*, the α-hydroxycyclopropylcarbinyl radical **7**. Overlap between the p orbital of the radical and the outside cyclopropane bond leads to selective cleavage of this bond at room temperature. However, at elevated temperatues appreciable amounts of the product originating from inside bond opening may be found, provided that in this cleavage a thermodynamically preferred species is formed. The similarity of specific ring opening of the outside bond of the cyclopropane ring in photoisomerization and photoreduction stems from the energy features of the ring system rather than a common intermediate. Initial studies on the rearrangement of the related carbonium ion are given for comparison.

It is well known that in the irradiation of conjugated cyclopropyl ketones in the vapor phase or in inert solvents a cyclopropane bond adjacent to the carbonyl group is cleaved, followed by a hydrogen migration and formation of a conjugated enone.[2-4] In the bicyclo-

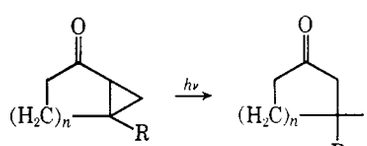


[4.1.0]heptane-2-one series, the two adjacent cyclopropyl bonds have a different geometry with respect to the carbonyl group, and in these cases photochemical ring opening appears to be selective. It is found that the C-1–C-7 bond, which has better overlap with the carbonyl π electrons, cleaves and cyclohexenones are formed.



This photoisomerization of the cyclopropylcarbonyl chromophore is highly dependent upon the substitution pattern of the system. For example, a methyl group at C-6 inhibits photoisomerization.[4] Various reasons can be postulated for the cause of this substituent effect; and, to obtain further information on the initial stage of the reaction, it was desired to learn if in all cases stereospecific opening of the cyclopropane did occur first and the fate of this first intermediate determined the ultimate over-all reaction pathway. For example, the photostability of 6-methylbicyclo[4.1.0]heptan-2-one might be due either to the photo-opening of the C-1–C-6 bond, yielding an intermediate which rapidly recloses to re-form starting material, or to the lack of migration of a methyl group if the better overlapped bond is broken. To evaluate these concepts, the photoreaction was conducted in the presence of a good hydrogen donor in order to trap any intermediate radicals; *i.e.*, in the irradiation of 6-methylbicyclo[4.1.0]heptan-2-one, if the latter route were followed, photochemical reduction would be expected to lead to 3,3-dimethylcyclohexanone.

Preliminary experiments in this laboratory indicated that photoreductive ring opening in bicyclic cyclopropyl ketones are selective.[5] Furthermore, 2-propanol appeared to be a far better hydrogen donor than methanol or pentane.[5-7] A further advantage for the use of 2-propanol in the photoreduction studies is the resemblance of the conditions to those of the photoisomerizations which were conducted in 2-methyl-2-propanol.[4] Table I summarizes the results of the photoreductions of a series of bicyclo[4.1.0]heptan-2-ones and bicyclo[3.1.0]hexan-2-ones (**1**). In no case could the product expected to be formed by cleavage of the inside bond be detected, even though such a product was shown to be stable to the reaction conditions. The low total recovery in the case of bicyclo[3.1.0]hexan-2-one (**1**, n = 1, R = H) was due to the photoreactivity of the 3-methylcyclopentanone formed.



1 **2**

TABLE I

PHOTOCHEMICAL REDUCTIONS OF SOME BICYCLO[4.1.0]- AND BICYCLO[3.1.0]ALKAN-2-ONES (1) IN 2-PROPANOL

Ketone 1	Irradiation time, hr	Starting material, %	Product 2, %
n = 2; R = H	4	30	60
n = 2; R = CH_3	0.5	63	32
n = 1; R = H	2	39	28
n = 1; R = CH_3	2.5	38	51

The results obtained from photoisomerization[4] and photoreduction in the bicyclo[4.1.0]heptan-2-one series suggest the involvement of a common intermediate

(1) This work was supported in part by National Institutes of Arthritis and Metabolic Diseases, PHS Grant AM-00709, U. S. Public Health Services.

(2) J. N. Pitts, Jr., and I. Norman, *J. Amer. Chem. Soc.*, **76**, 4815 (1954).

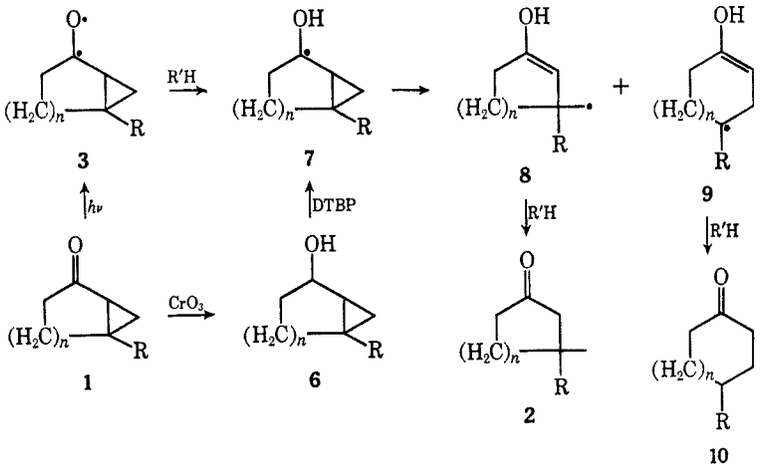
(3) L. D. Hess and J. N. Pitts, Jr., *ibid.*, **89**, 1973 (1967).

(4) W. G. Dauben and G. W. Shaffer, *Tetrahedron Lett.*, 4415 (1967).

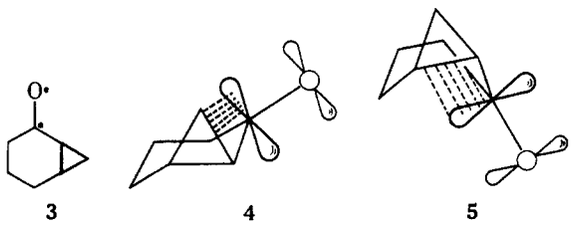
(5) E. J. Deviny, Ph.D. Thesis, University of California, Berkeley, 1965.

(6) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, p 533.

(7) W. G. Dauben, L. Schutte, and R. E. Wolf, *J. Org. Chem.*, **34**, 1849 (1969).



during the cleavage of the cyclopropane ring. That one such an intermediate could be the triplet state **3**, resulting from the known highly efficient singlet–triplet intersystem crossing in ketones, was shown by quenching and sensitization experiments. This triplet might better be represented as having the electrons delocalized, as in **4**, since such delocalization is known to occur



in the excited singlet state. Alternatively, the triplet could also adopt another extreme geometry shown in **5**, when the preferred orbital overlap occurs with the C-1–C-6 bond. In the isomerization reaction, the opening of the cyclopropane bond should proceed with continuous overlap of the carbonyl group; and, if this is the case, the reaction from conformation **4** would be favored, since overlap as in **5** demands a boatlike conformation. This feature must be more important than the relative stabilities of the potential ring-opened intermediates arising from the two conformations. In the photochemical reductions of bicyclo[3.1.0]hexan-2-ones, this preferred opening from a conformation related to **4** is also found. In these opening processes, internal hydrogen migrations would yield a conjugated enone, and hydrogen abstraction from 2-propanol would give the saturated cyclic ketone **2**. Thus, the photostability of 6-methylbicyclo[4.1.0]heptan-2-one to rearrangement would appear to be due to the inability of the methyl group to migrate and not to an inhibition of the opening of the cyclopropane ring.

From the above conclusion, it follows that opening of the cyclopropane ring has begun in the triplet state for both photorearrangement and photoreduction and that a homoallyl species would be formed directly. In the presence of a good hydrogen donor, however, the carbonyl triplet normally abstracts a hydrogen with high efficiency to yield a hydroxycarbinyl radical. Therefore, an alternative to the suggestion of a common mechanism is that there is no mechanistic relationship between the two photoreactions and that any similarity in results stems solely from the basic energy features of the ring systems involved. For example, in the presence of a good hydrogen donor, the carbonyl triplet could abstract a hydrogen to yield directly the hydroxycyclopropylcarbinyl radical **7**; and the reactions of this radical could be controlled by steric rather than by thermodynamic features to yield the reduction products. To evaluate the possible involvement of the α-hydroxycyclopropylcarbinyl radical **7**, its independent formation by peroxide-induced hydrogen abstraction[8] from the corresponding alcohol **6** and comparison of the product distribution in this ground-state reaction with that in the photoreductions was undertaken.

A series of bicyclo[4.1.0]heptan- and bicyclo[3.1.0]-hexan-2-ols (**6**),[9] corresponding to the series of bicyclic ketones photoreduced previously, were mixed with di-*t*-butyl peroxide (DTBP) and heated at 130° for 24 hr to generate the α-hydroxycyclopropylcarbinyl radical. The results are summarized in Table II.

TABLE II

RADICAL REARRANGEMENTS OF SOME BICYCLO[4.1.0]- AND BICYCLO[3.1.0]ALKAN-2-OLS (6) WITH DI-*t*-BUTYL PEROXIDE AT 130°

Alcohol 6	DTBP, mol equiv	Starting material, %	Products 10 + 2, %	Ratio, 10:2
n = 2; R = H	0.1	63	24	<0.2:10
	0.2	44	40	<0.2:10
n = 2; R = CH_3	0.1	34	63	0.5:9.5
	0.3	14	76	0.5:9.5
n = 1; R = H	0.1	60	36	2:8
	0.3	20	70	2:8
n = 1; R = CH_3	0.1	41	46	4.5:5.5
	0.4	28	71	4.5:5.5

The opening of the cyclopropane ring in the radical rearrangement reactions of cyclopropyl carbinols at 130° (Table II) does not show the same specificity as the photoreductions of cyclopropyl ketones. However, the radical generated by DTBP still gave a far greater amount of the product corresponding to outside bond opening of the cyclopropyl group (**2**) than can be accounted for on the basis of thermodynamic stabilities of the intermediates **8** and **9** formed. Two factors can be considered in determining the over-all thermodynamic stabilities of these intermediates: the stability of the

(8) D. C. Neckers, A. Schaap, and J. Hardy, *J. Amer. Chem. Soc.*, **88**, 1265 (1966).

(9) The *cis* bicyclic alcohols **6** were employed in this series. Rearrangements with a *cis–trans* (30:70) mixture of **6** (n = 2; R = H) showed that the *trans* isomer behaved in a similar fashion.

radicals[10] generated (primary *vs.* secondary or tertiary), and the stability of the ring system found as based on strain energy considerations of a cycloalkene.[11] When $n = 2$ and R = CH_3, the over-all stability favors the opening of the inside bond to yield **9** and, when R = H, a slight preference for opening of the outside bond to yield **8** is indicated. When $n = 1$, regardless of the degree of substitution, the opening of the inside bond to yield the six-membered ring compound **9** is strongly favored.

The selectivity of the ring opening could be accounted for on the basis of better overlap between the outer cyclopropane bond and the adjacent carbonyl center. However, selective product formation would also result if the reactivity of a primary radical is a predominant factor and if the secondary and tertiary radicals, though also formed, reclose to **7**, rather than abstract a hydrogen atom from the solvent. To evaluate this possibility the radical rearrangement was performed with an optically active alcohol **6** and the photochemical reduction was carried out with an optically active ketone **1**. The results of these experiments are summarized in Table III.

TABLE III

PHOTOCHEMICAL REDUCTION AND RADICAL REARRANGEMENT OF OPTICALLY ACTIVE BICYCLO[4.1.0]HEPTANE COMPOUNDS ($n = 2$, R = H)

Starting material	Type of reaction	$[\alpha]_D$ of starting material	$[\alpha]_D$ of recovered starting material	$[\alpha]_D$ of product **2**
1[a]	$h\nu$ in 2-propanol	−2.0	−2.1	−0.8[b]
6	130° with DTBP	5.2	5.2	−0.9

[a] The optically active ketone **1** was obtained by Jones oxidation of alcohol **6** and should have the same optical purity. [b] Reduction of **1** with lithium in liquid ammonia yielded ketone **2**, possessing this same optical activity (see ref 19); all optical activities were taken with vpc collected material and are accurate to ±0.1°.

Complete retention of optical activity of the starting material was observed under conditions of both rearrangement and irradiation; in addition, the product **2** obtained by either procedure was optically active to the same extent. These findings indicate that no equilibrium exists between the radical species **7** and **9**, since the absence of an asymmetric center in **9** would lead to racemization.[12]

Before using the data, summarized in Table I and II, pertaining to the difference in selectivity in photoreductions of cyclopropyl ketones **1** and in radical rearrangement of cyclopropyl carbinols **6** for mechanistic evaluation, it was essential to investigate the temperature dependence of the reactions, since room temperature was used for the former reaction and 130° for the latter. Thus, 5-methylbicyclo[3.1.0]hexan-2-ol (**6**, $n = 1$, R = CH_3), in which the difference in product distribution for the thermal and the photochemical reactions was greatest, was allowed to react at room temperature with DTBP, using filtered light as the radical initiator. In addition, the corresponding ketone (**1**, $n = 1$, R = CH_3) was irradiated at elevated temperatures. In the photolytic experiments at high temperature, some difficulties in product determination were encountered, as many by-products were observed, owing to instability of the primary products in uv light at 130°. These complications were minimized by using short irradiation times. Table IV summarizes the results of these experiments.

TABLE IV

RADICAL REARRANGEMENT AND PHOTOREDUCTION AT VARIOUS TEMPERATURES OF 5-METHYLBICYCLO[3.1.0]HEXANE COMPOUNDS ($n = 1$, R = CH_3)

Type of reaction	Temp, °C	Time, hr	Starting material, %	Products **10** + **2**, %	Ratio, **10**:**2**[a]
6 in DTBP + $h\nu$	25	24	87	13	0.5:9.5
		42	76	23	0.5:9.5
6 in DTBP	130	24	28	71	4.5:5.5
1 + $h\nu$ in *i*-PrOH	25	0.5	82	12	1:9
		1	69	23	1:9
	80	0.5	80	15	4:6
		0.8	69	18	3.5:6.5
	130	0.5	82	12	5:5
		2	60	7	5:5

[a] Irradiation of a mixture of **10** and **2** at elevated temperatures showed that both products disappear at approximately the same rate.

The radical rearrangement of the cyclopropyl alcohol investigated (**6**, $n = 1$, R = CH_3), when carried out at room temperature, showed the same selectivity of product formation as the photoreduction of the corresponding ketone (**1**, $n = 1$, R = CH_3). In both cases, 3,3-dimethylcyclopentanone (**2**, $n = 1$, R = CH_3) was formed almost exclusively. In addition, the photoreduction of the cyclopropyl ketone at elevated temperatures appeared to be much less selective than at room temperature. In fact, the similarity of the temperature dependence of product distribution in both types of reactions is remarkable. When bicyclo[4.1.0]-heptan-2-one (**1**, $n = 2$, R = H) was irradiated in 2-propanol at 130°, again only the formation of 3-methylcyclohexanone (**2**, $n = 2$, R = H) was observed. For this compound, change in temperature does not result in a diminished selectivity of ring opening, a result anticipated since the 130° radical rearrangement of the corresponding alcohol also showed a similar selectivity.

The striking similarity of temperature dependence on product formation in the two cases studied strongly suggests that photoreduction of conjugated cyclopropyl ketones **1** and radical rearrangements of the corresponding alcohols **6** proceed through the same intermediate; the α-hydroxycyclopropylcarbinyl radical **7**. Both processes are highly selective at room temperature, giving cleavage of the cyclopropane bond that overlaps best with the radical at C-2, but this selectivity can be severely affected by raising the temperature.

In the irradiation of 5-methylbicyclo[3.1.0]hexan-2-one (**1**, $n = 1$, R = CH_3) at elevated temperatures, the

(10) It is assumed that the tertiary radical is 4 kcal/mol more stable than the secondary radical, which, in turn, is 4 kcal/mol more stable than a primary radical (see C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, p 50).

(11) It is assumed that cyclohexane is 6.3 kcal/mol more stable than cycloheptane and 6.5 kcal/mol more stable than cyclopentane (see summary of values in J. D. Roberts and M. C. Casserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 112) and that the heat of hydrogenation of cyclohexene is 1.2 kcal/mol larger than that of cycloheptene and 1.4 kcal/mol larger than that of cyclopentene [see R. B. Turner and R. R. Meador, *J. Amer. Chem. Soc.*, **79**, 4133 (1957)].

(12) If reclosure of the inside bond was faster than inversion and rotation to the optical enantiomer, optical purity could be retained. From an operational viewpoint, however, such a process appears unlikely.

formation of small amounts of the alcohol **6** (about 5%) was indicated, but, in the irradiation of bicyclo[4.1.0]-heptan-2-one (**1**, $n = 2$, R = H) at 130°, no alcohol **6** could be detected. This is consistent with the previous observation that the corresponding optically active alcohol did not racemize during radical rearrangement at 130° (Table III), implying that in the latter case the α-hydroxycyclopropylcarbinyl radical does not abstract hydrogen to generate the alcohol.

In the presence of a triplet quencher (oxygen or isoprene), no photoreduction of bicyclo[4.1.0]heptan-2-one (**1**, $n = 2$, R = H) was observed. Benzene, acetone, or fluorene sensitized the reaction, but it was remarkable that the rate of overirradiation, leading to 3-methylcyclohexanol, increased more than that of the primary photoreduction step. These experiments leave little doubt that the excited species involved is in the triplet state.

The findings of the present work indicate that the photoreduction of ketone **1** and the ground-state radical rearrangement of alcohol **6** both go through the same intermediate radical **7**. The following mechanism may be considered for these reactions (see Figure 1). After excitation of **1**, a triplet species **3** is formed. This species abstracts a hydrogen atom from 2-propanol, and during this process it cascades down to the ground-state radical **7**. When $n = 1$, the thermodynamically controlled process leads to the more stable radical **9**, especially when R = CH_3 and a tertiary radical is formed. However, the pathway leading to a primary radical **8** has a lower energy of activation, since **2** is the preferred product when the reactions are run at room temperature. The lower energy of the transition state between **7** and **8** compared with that between **7** and **9** may be explained by overlap between the outer cyclopropane bond and the p orbital of the radical at C-2. The inner cyclopropane bond and the p orbital at C-2 are orthogonal, and the molecule must be twisted to form the transition state leading to opening of that bond.

When $n = 2$, an analogous conflict between kinetically and thermodynamically controlled product formation does not exist, owing to the stability of the six-membered ring in **8**.

It should be exphasized that the mechanism proposed is only applicable when a good hydrogen-donating solvent is present. In poor hydrogen donors, hydrogen abstraction is not important, and the triplet, in addition to returning to the ground state (**1**), may rearrange, the rearrangement proceeding *via* the more preferred triplet **4**.

The present study has illustrated the selectivity of bond cleavage in the photochemical reduction of conjugated cyclopropyl ketones in 2-propanol. In all cases examined, the bond that has better overlap with the carbonyl π system is preferentially cleaved. It is remarkable that the specificity of bond breaking is temperature dependent. However, this temperature dependence is not due to the photochemical process, but rather to subsequent ground-state radical reactions, as is indicated by the parallel rearrangements of the ground-state generated species.

It is interesting to compare the results of the radical rearrangements, which are largely governed by steric factors, with those of the rearrangement of the related α-hydroxycyclopropylcarbinyl carbonium ion **11**.

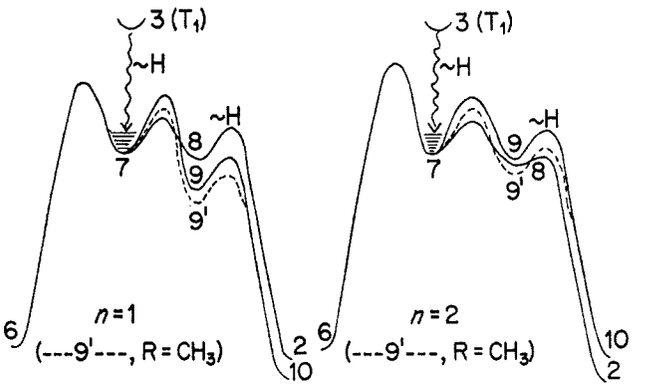
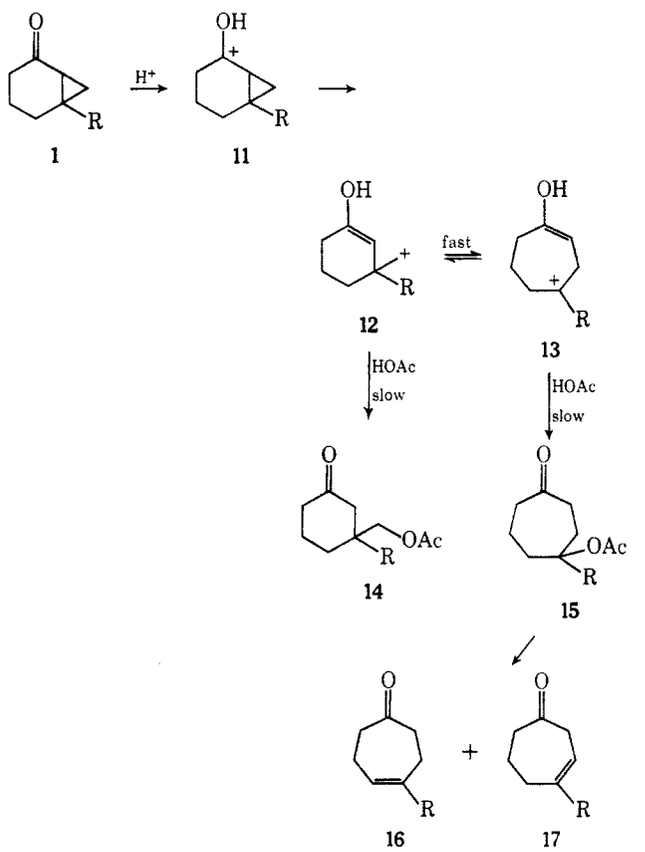


Figure 1.



For this purpose, the bicyclic ketones **1** ($n = 2$, R = H and CH_3) were allowed to react with acetic acid, using perchloric acid as a catalyst. The results of these reactions are summarized in Table V.

TABLE V

ACID-CATALYZED REARRANGEMENT OF BICYCLO[4.1.0]HEPTAN-2-ONE AND 6-METHYLBICYCLO[4.1.0]HEPTAN-2-ONE IN ACETIC ACID WITH 0.1 *M* $HClO_4$

Compd	Temp, °C	Time, hr	Starting material, %	Products **14** + **15**, %	Ratio, **15**:**14**
1, R = H	27	57	11	86	3.5:6.5
1, R = H	33	6	35	62	3.5:6.5
1, R = H	68	2.5	0	89	4:6
1, R = H	72	2	0	97	4:6
1, R = H	140	0.5	0	80	4:6
1, R = CH_3	70	0.5	0	96[a]	8.5:1.5

[a] Instead of **15**, the elimination products **16** and **17** were found in a 1:1 ratio.

The ratio of the products formed and the small effect of temperature in this reaction show that product formation follows closely the thermodynamic stabilities of the intermediate carbonium ions **12** and **13**. Although the difference in stability of these ions is difficult to evaluate because of solvation effects, they should be of the same order of magnitude as or larger than the radical stabilities. Since the ionic reaction may be reversible, it is necessary to study the process in greater detail before a direct comparison with the radical process can be achieved.

If the same type of reaction is conducted with HCl in dry chloroform, the chloride analog of **14** is formed almost exclusively. Further work is needed to decide whether this is due to the enhanced nucleophilicity of chloride compared with acetate or to less stabilization of the carbonium ions in a less polar solvent, thus causing the acid addition step to become faster than the rearrangement equilibrium under these conditions.

Experimental Section

The syntheses of the bicyclic ketones and alcohols for $n = 2$, R = H, CH_3, and for $n = 1$, R = H, have been described.[13]

5-Methylbicyclo[3.1.0]hexan-2-one was prepared by Dr. G. W. Shaffer[14] of this laboratory from 3-methyl-2-cyclopentenone[15] and dimethyloxosulfonium ylide according to the procedure described by Corey and Chaykovsky[16] in 51% yield. The following data were observed: bp 64–65° (13 mm); ir (CCl_4) 3058 (>CH), 1727 (C=O), 1175, 933, 897, 856 cm^{-1}; uv λ_{max} (95% C_2H_5OH) 194 (ϵ 3710), 280 mμ (ϵ 56).

Anal. Calcd for $C_7H_{10}O$: C, 76.33; H, 9.15. Found: C, 76.14; H, 8.92.

cis-**5-Methylbicyclo[3.1.0]hexan-2-ol** was prepared according to the procedure of Dauben and Berezin[13] from 3-methyl-2-cyclopentenol, which, in turn, was prepared by reduction of 3-methyl-2-cyclopentenone[15] following a procedure described by Davidson and coworkers.[17] The bicyclic alcohol was characterized by the following data: bp 76° (18 mm); ir (CCl_4) 3600, 3360 (OH), 1055, 1025, 1000 cm^{-1}; nmr (CCl_4) δ 4.38 (m, 1, CHOH), 3.43 (s, 1, OH), 1.63 (m, 4, ring CH_2), 1.13 (s, 3, CH_3), 0.7 and 0.2 ppm (m, 3, >CH); mass spectrum (70 eV) *m/e* 112, 111, 97, 94, 79, 70, 68 (B), 67, 55.

The optically active materials were prepared by asymmetric induction, converting cyclohexene to 2-cyclohexenol[18] ($[\alpha]_D$ 7.0°), followed by a Simmons–Smith[19] reaction to the *cis*-bicyclo[4.1.0]-heptan-2-ol[20] ($[\alpha]_D$ 5.2°) and Jones[21] oxidation to the bicyclo[4.1.0]heptan-2-one ($[\alpha]_D$ −2.0°). Optical rotations were measured in chloroform on a Zeiss polarimeter LEP A2.

Irradiation Procedures.—The irradiations described in Table I were conducted with 0.4% solutions in 125 ml of 2-propanol by Corex filtered light of an immersed Hanovia 450-W lamp. The radical rearrangements (Table II) were carried out by heating various portions of DTBP with the bicyclic alcohol at 130° for 24 hr in a sealed tube. The products of irradiation and of rearrangement were both independently collected from a preparative vpc column (Wilkens Aerograph A-90-P gas chromatograph, 10 ft × 0.375 in., 10% Carbowax 20M–10% KOH column at 160°) and were identified by ir, nmr, and mass spectra.

The irradiations at elevated temperatures were conducted in sealed Pyrex tubes in the vapor of refluxing 2-methyl-2-pentanol (bp 130°) or of refluxing 2-propanol (bp 80°) using a Hanovia 450-W lamp. Because of sample size (3-ml solutions), the product assignments were based on comparison of vpc retention times with those of authentic samples on two different analytical columns (5% XF-1150 Cyanosilicone, 10 ft × 0.125 in., 100°; 20% Carbowax 20 M–10% KOH, 10 ft × 0.125 in., 150°: Hewlett–Packard F & M 5751 gas chromatograph). Solutions of the starting materials and products were stable at 130°. The radical rearrangements, initiated by photodecomposition of DTBP (Table V), were conducted at room temperature employing a UVS-11 mineral light lamp filtered with a Vycor filter (λ >240 mμ).

Procedures in Acid-Catalyzed Rearrangements.—The perchloric acid catalyzed reaction with acetic acid was run with 1 g of the bicyclic ketone in 77 ml of glacial acetic acid and 2.2 ml of acetic anhydride containing 0.725 ml of 70% perchloric acid under magnetic stirring and in a nitrogen atmosphere. To terminate the reaction, the solution was neutralized with 95 ml of concentrated ammonium hydroxide and extracted with chloroform. The solution was washed and dried, the chloroform was evaporated, and the resulting oil was molecularly distilled. The amounts of volatile products formed were calculated from vpc traces of this distillate. The products were collected from a 20% DFGS-preparation vpc column.

Identification of Reaction Products.—Authentic samples were available of cycloheptanone, 3-methylcyclohexanone, cyclohexanone, and 4-methylcyclohexanone. The vpc retention times and spectral data of the products were in agreement with those of the authentic samples. The structures of the other products were assigned based on the following data.

4-Methylcycloheptanone: ir (CCl_4) 1705 (C=O), 1449 cm^{-1}; nmr (CCl_4) δ 2.35 (m, 4, CH_2, $COCH_2$), 1.68 (m, 7, ring protons), and 0.94 ppm (m, 3, CH_3); mass spectrum (prominent peaks) *m/e* 126, 111, 98, 97, 83 (B), 82, 70, 69, 56, 55.

3,3-Dimethylcyclohexanone: ir (CCl_4) 1715 (C=O), 1460, 1422, 1387, 1366 cm^{-1}; nmr (CCl_4) δ 2.7 (m over s, 4, CH_2, $COCH_2$), 1.7 (m, 4, ring protons), 0.97 [s, 6, $(CH_3)_2$]; mass spectrum (prominent peaks) *m/e* 176, 111, 83 (B), 69, 56, 55.

3-Methylcyclopentanone: ir (CCl_4) 1750 (C=O), 1455, 1410, 1050 cm^{-1}; nmr (CCl_4) δ 2.1 (m, 4, CH_2COCH_2), 2.0–1.2 (m, 3, ring protons), and 1.13 ppm (d, 3, J = 6 Hz, CH_3CH); mass spectrum (prominent peaks) *m/e* 98, 83, 70, 69 (B), 56, 55, 42.

3,3-Dimethylcyclopentanone: ir (CCl_4) 1745 (C=O), 1458, 1399, 1379, 1364, 1260, 1135 cm^{-1}; nmr (CCl_4) δ 2.1 (d, 2, J = 7 Hz, CH_2CH_2CO), 1.92 (s, 2, CCH_2CO), 1.90 (d, 2, J = 7 Hz, ring CH_2), 1.1 [s, 6 $(CH_3)_2C$]; mass spectrum (prominent peaks) *m/e* 112 (p), 97, 83, 69, 56 (B).

4-Acetoxycycloheptanone: ir (CCl_4) 1739, 1706, 1242, 1028 cm^{-1}; nmr (CCl_4) δ 4.57 (m, 1, CHOAc), 2.43 (m, 4, α-CH_2), 2.00 (s, 3, CH_3), and 1.88 ppm (m, 6, ring protons).

Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.63; H, 8.06.

3-Acetoxymethylcyclohexanone: ir (CCl_4) 1742, 1718, 1231, 1047 cm^{-1}; nmr (CCl_4) δ 3.88 (d, J = 3.5 Hz, 2, CH_2OAc), 2.13 (m, 4, α-CH_2), 1.96 (s, 3, CH_3), 1.92 (m, 5).

Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.29; H, 8.09.

4-Methyl-4-cycloheptenone: ir (CCl_4) 1706, 1230, 1214, 1091, 880, 823 cm^{-1}; nmr (CCl_4) δ 5.62 (m, 1, HC=C), 2.44 (m, 8, ring protons), 1.77 (s, 3, CH_3).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.16; H, 9.91.

4-Methyl-3-cycloheptenone: ir (CCl_4) 1712, 1667, 1285, 1244, 1212, 1122, 1072, 936, 891, 827 cm^{-1}; nmr (CCl_4) δ 5.36 (split t, J = 6 Hz, 1, CH=C), 3.11 (split d, J = 6 Hz, 2, α-CH_2), 2.50, 2.42, 2.22 (m, 6, ring protons), and 1.76 ppm (s, 3, CH_3).

Anal. Calcd for $C_8H_{12}O$: C, 77.83; H, 9.74. Found: C, 77.44; H, 9.63.

Registry No.—2-Propane, 67-63-0; 4-methylcycloheptanone, 5452-36-8; 3,3-dimethylcyclohexanone, 2979-19-3; 3-methylcyclopentanone, 1757-42-2; 3,3-dimethylcyclopentanone, 20500-49-6; 4-acetoxycyclo-

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heptanone, 18341-63-4; 3-acetoxymethylcyclohexanone, 20500-51-0; 4-methyl-4-cycloheptenone, 13015-11-7; 4-methyl-3-cycloheptenone, 20500-53-2; **1**, $n = 2$, R = H, 5771-58-4; **1**, $n = 2$, R = CH_3, 14845-41-1; **1**, $n = 1$, R = H, 4160-49-0; **1**, $n = 1$, R = CH_3, 14845-46-6.

Anomalous Low Solvolytic Reactivity of 2,2-Dichlorocyclopropylcarbinyl Chlorides

G. C. Robinson

Ethyl Corporation, Baton Rouge, Louisiana 70821

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The solvolyses (50 vol % aqueous ethanol, 100°) of 2,2-dichlorocyclopropylcarbinyl chloride, 1-methyl-2,2-dichlorocyclopropylcarbinyl chloride, and *trans*-3-methyl-2,2-dichlorocyclopropylcarbinyl chloride have been studied as to rate and products. The absence of rearranged solvolysis products suggests that the cyclopropyl group is not interacting with the carbinyl carbon during solvolysis. In agreement with the product picture the solvolysis rates are substantially normal for a primary alkyl chloride and are at least 10^3 slower than is suggested by a σ^+ correlation of literature data on methyl- and ethoxy-substituted cyclopropylcarbinyl systems. The solvolysis rate of cyclopropylcarbinyl chlorides is, therefore, unexpectedly sensitive to electron-withdrawing substituents on the cyclopropane ring.

The most striking special features of cyclopropylcarbinyl systems in solvolysis are greatly enhanced solvolysis rates and formation of rearranged products having allylcarbinyl and cyclobutyl structures. The effect of methyl, phenyl, and ethoxy substituents on solvolysis rates have been studied.[1] However, no systematic study has been made of the effect of deactivating substituents such as chlorine on solvolysis in cyclopropylcarbinyl systems.

We have been interested[2] in the reactions of the *gem*-dichlorocyclopropyl functional group and have now studied its behavior as part of a cyclopropylcarbinyl solvolytic system. We report in this paper solvolysis rates (50% aqueous ethanol, 100°) and products for 2,2-dichloro-1-chloromethylcyclopropane, 2,2-dichloro-1-methyl-1-chloromethylcyclopropane, and *trans*-2,2-dichloro-3-methyl-1-chloromethylcyclopropane. The results are surprising in that participation of the cyclopropane ring appears to be completely suppressed.

Experimental Section

General.—The nmr data were obtained on a Varian A-60; chemical shifts and J values are reported in cycles per second (cps) relative to tetramethylsilane. The glpc unit was fitted unless otherwise stated with a 2-ft Carbowax 20M column. Distillations were normally through an 18-in. spinning-band column. The chemicals were obtained from laboratory supply houses except for acrolein dimethyl acetal which was furnished by Shell Chemical Co.

Kinetic Runs.—Solutions were prepared by dilution of a weighed sample of dichlorocyclopropylcarbinyl chloride to volume with 50% (v/v) aqueous ethanol. The initial run was made using a standard sealed ampoule technique titrating 5-ml aliquot portions with standard base (phenolphthalein indicator, calculated infinity). Subsequent runs were carried out using duplicate glpc analyses of 10-μl portions (2-ft Carbowax 20M, programmed from 50° at 11°/min) of 30-μl aliquots sealed in Kimax capillaries. First-order rate constants were calculated using the area of the dichlorocyclopropylcarbinyl chloride peak *vs.* an internal standard (2,5-dimethoxytoluene or *o*-diethoxybenzene). Material balances were run on the high-conversion points. Identity of the products was verified by comparison with authentic samples on the Carbowax 20M column and on an SE 30 column. The constant-temperature bath was a steam chamber.

1,1-Dichloro-2-chloromethylcyclopropane.—Into a 200-ml three-necked creased flask fitted with a Stir-O-Vac[3] high shear stirrer and an ice condenser was put allyl chloride (20.3 ml, 0.25 mol), chloroform (20 ml, 0.25 mol), sodium hydroxide pellets (40 g, 1.00 mol), and tetraglyme (25 ml). The mixture was stirred and the temperature was increased first to 80° during 1.5 hr and then to 98° for 2 hr more. Work-up by water dilution, ether extraction, and distillation of the dried ether extract gave 1,1-dichloro-2-chloromethylcyclopropane [9.1 g, 23%, bp 72–74° (46 mm), lit.[4] 56° (17 mm)]: infrared 3096 (cyclopropyl CH_2), 1372 (CH_2Cl), 1029 (cyclopropane ring), and 755 and 709 cm^{-1} (CCl_2 group in cyclopropane ring).

1,1-Dichloro-2-dimethoxymethylcyclopropane.—Into the usual apparatus was put acrolein dimethyl acetal (30 ml, 0.25 mol), chloroform (20 ml, 0.25 mol), sodium hydroxide pellets (60 g, 1.5 mol), and tetraglyme (25 ml). The mixture was stirred vigorously 3 hr at 25–40° and the evolved gas (1.6 l., 0.064 mol as carbon monoxide) was measured. The reaction mixture was diluted with water, the organic products were ether extracted, and the ether extracts were dried and fractionally distilled yielding 1,1-dicloro-2-dimethoxymethylcyclopropane [12.2 g, 26%, bp 92–93° (35 mm)]: nmr 198 and 203 (methoxy groups, three protons each, peak separation was temperature independent to 140°, split by adjacent asymmetric center), 72–132 (cyclopropyl H, complex, three protons), and 254 cps (tertiary acetal H, one-proton doublet, $J = 6$). A mixture of 1,1-dichloro-2-dimethoxymethylcyclopropane (10 g, 54 mmol), *p* toluenesulfonylhydrazine (10.1 g, 54 mmol), and hydrochloric acid (1 ml of concentrated acid in 40 ml of 50% aqueous ethanol) was heated on a steam bath 1.5 hr yielding crude *p*-toluenesulfonylhydrazone (17.1 g). A 2 g sample was recrystallized (50 ml of 50% aqueous ethanol) giving pure *p*-toluenesulfonylhydrazone derivative (1.5 g, indicated yield 77%, mp 134–137° dec).

2,2-Dichlorocyclopropylcarboxaldehyde.—A mixture of the 1,1-dichloro-2-dimethoxymethylcyclopropane (44.3 g, 0.24 mol), water (200 ml), concentrated sulfuric acid (5 ml), and tetraglyme (10 ml) was stirred at 25–30° for 30 hr. Examination (glpc) of the mixture indicated about 80% conversion to aldehyde. The crude product was extracted with ether and the extract was washed (water), dried (sodium sulfate), and distilled giving 2,2-dichlorocyclopropylcarboxaldehyde [8.3 g, 30%, bp 70–71° (25 mm)]: nmr 100–170 (three-proton multiplet, cyclopropyl H) and 559 cps (one-proton doublet, aldehyde, $J = 4$); 2,4-dinitro-

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