Solution Photolysis of *cis*- and *trans*-2-Methylcyclopropyl Methyl Ketone[1]

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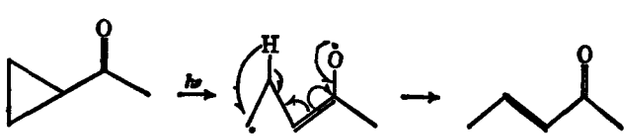
The photolysis of *cis*- (1) and *trans*-2-methylcyclopropyl methyl ketone (2) was studied in pentane and isopropyl alcohol. Irradiation of *cis* ketone 1 in either solvent yielded, exclusively, 1-hexen-5-one (3). *trans* ketone 2 slowly formed 3 in pentane, presumably through isomerization to 1, but in addition gave two saturated ketones, *n*-butyl methyl ketone (4) and isobutyl methyl ketone (5). The formation of 4 and 5 occurs *via* opening of either of the cyclopropane bonds α to the carbonyl group, followed by hydrogen abstraction from the solvent. These results show that when an intramolecular γ hydrogen abstraction (Norrish "type II") can occur, this process will prevail over any other type of hydrogen migration. In addition, the efficiency of isopropyl alcohol to trap the intermediate radicals is demonstrated.

The cleavage of the cyclopropyl ring during the irradiation of conjugated cyclopropyl ketones has been well established.[2-5] In the cases studied, one of the bonds adjacent to the carbonyl group breaks and a subsequent hydrogen migration leads to a conjugated enone.



In fused bicyclic systems,[3] geometrical factors appear to control the direction of ring opening, *i.e.*, if the cyclopropane ring is held in a rigid conformation with respect to the carbonyl π system, excitation of an electron into the π^* orbital leads to rupture of that cyclopropane bond which has greater overlap with the π electrons of the carbonyl group. When free rotation is possible and when both cyclopropane bonds are able to overlap the carbonyl π cloud, the stability of the radical formed determines the product ratio.[3,6]

In the present study, the photochemical behavior of *cis*- (1) and *trans*-2-methylcyclopropyl methyl ketone (2) has been examined in solvents which have differing abilities to donate hydrogen atoms. Three products were observed: 1 hexen-5-one (3), *n*-butyl methyl ketone (4) and isobutyl methyl ketone (5). The experimental results are summarized in Table I.

The sole product of irradiation of *cis* ketone 1 was 1-hexen-5-one (3), the structure of which was established by comparison of its ir and nmr spectra with those of an authentic sample. The formation of ketone 3 is analogous to the formation of 2-methyl-1-hexen-5-one observed in the irradiation of 2,2-dimethylcyclopropyl methyl ketone.[5,7,8] Two possible mechanisms have been proposed for such a ring opening.[5] The first mechanism follows an intramolecular Norrish "type II" process (Figure 1a), whereas the second mechanism (b) involves an initial rupture of the cyclopropane ring followed by an internal 1,4-hydrogen shift.

TABLE I

THE IRRADIATION OF *cis*- (1) AND *trans*-2-METHYLCYCLOPROPYL METHYL KETONE (2) IN PENTANE AND ISOPROPYL ALCOHOL

Compd	Solvent	Irradiation time, hr	Material in reaction mixture, % 1	2	3	4	5
1	Pentane	2	45		55		
1	Isopropyl alcohol	2	28		70		
2	Pentane	7[a]	*b*	26	23	6	9
2	Isopropyl alcohol	2.5		58		30	10

[a] Owing to the long irradiation time several over-irradiation products were observed of which acetone (14%) was identified. Acetone is a known photoproduct of ketone 4 [W. Davis, Jr., and W. A. Noyes, *J. Amer. Chem. Soc.*, 69, 2153 (1947)]. [b] *cis* ketone 1 could not be separated from ketone 4 but its presence was indicated by ir (1695 cm^{-1}) and the mass spectrum (*m/e* 98 and 83).

The study of the irradiation of *trans* ketone 2 has given more definitive information with regard to the mechanism of the photolytic process. As shown in Table I, there was a dramatic difference between the irradiation times and the products of irradiation of *cis* and *trans* isomers (1 and 2), respectively. This rules out the mechanism as depicted in Figure 1b, where *trans* ketone 2 would be expected to behave like *cis* ketone 1, because it would give the same intermediate **a**. In the "type II" process (Figure 1a) only *cis* isomer 1 can yield 1-hexen-5-one (3). It seems likely that the same mechanism (Figure 1a) applies to the irradiation of 2,2-dimethylcyclopropyl methyl ketone,[5,7,8] as the additional methyl group is not expected to cause drastic changes.

About 23% 1-hexen-5-one (3) was found in the irradiation of 2 in pentane. However, early in the irradiation a peak was observed in the vpc trace which had retention time corresponding to *cis* ketone 1 and to product 4. This material was collected from the vpc and its infrared spectrum indicated that the major component was ketone 4 (1718 cm^{-1}) and the minor component was *cis* ketone 1 (1695 cm^{-1}). Further support for the presence of *cis* ketone 1 was provided by finding the characteristic *m/e* 98 and 83 peaks in the mass spectrum.

cis ketone 1 did not build up as the irradiation of 2 in pentane proceeded. This result is expected, since 1 readily photolyzes to give ketone 3. The absence of 3 when 2 was irradiated in isopropyl alcohol as compared to its presence when 1 was treated similarly supports the hypothesis that *trans* ketone 2 is unable to form unsaturated ketone 3 directly, and the intermediate

(1) This work was supported in part by Public Health Service Grant No. 00709, National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service.

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

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

(4) L. D. Hess and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **89**, 1973 (1967).

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(6) R. E. K. Winter and F. R. Lindauer, *Tetrahedron Lett.*, 2345 (1967).

(7) R. M. Roberts and R. G. Landolt, *J. Amer. Chem. Soc.*, **87**, 2281 (1965).

(8) G. Huppi, Frl. G. Eggart, S. Iwasaki, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chem. Acta*, **49**, 1986 (1966).

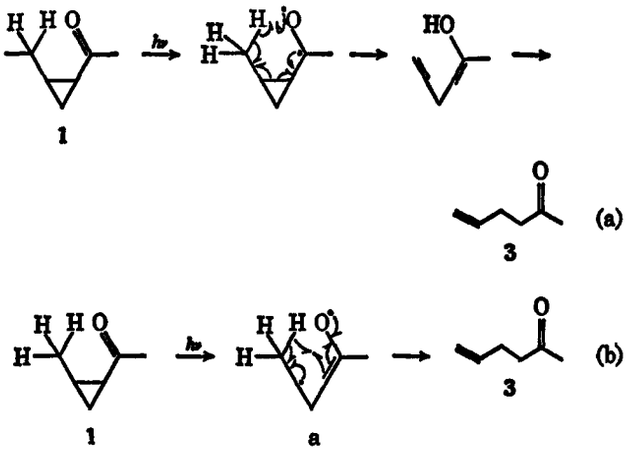

Figure 1

formation of *cis* ketone **1** *via* an isomerization step is required.

The presence of the two saturated ketones **4** and **5**, the structures of which were established by comparison of the vpc retention times and the ir and mass spectra with those of authentic samples, in the irradiation mixture of *trans* ketone **2** shows that both of the cyclopropane bonds adjacent to the carbonyl group undergo cleavage. This result might be expected, since both bonds should be able to overlap with the carbonyl π system. The intermediate radicals formed are especially well trapped in isopropyl alcohol, since no formation of ketone **3** was observed.

The reaction scheme proposed to explain the product distribution in the irradiation of *trans*-2-methylcyclopropyl methyl ketone (**2**) is depicted in Figure 2.

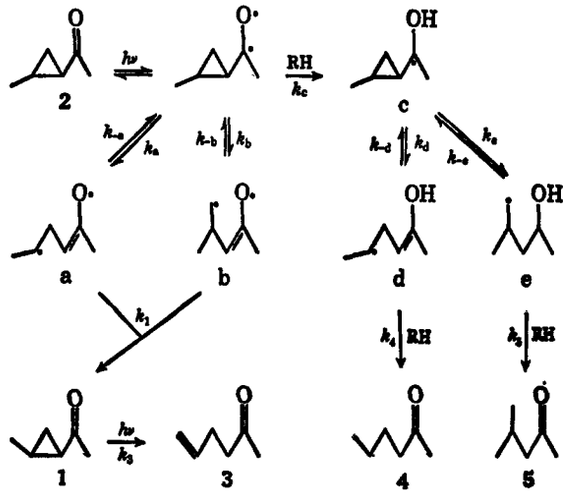

Figure 2.—In this scheme, cyclopropylhydroxycarbinyl radical c although the most likely intermediate, is not a necessary intermediate, since monoradicals d and e could be formed directly from a and b.

The initial process which is envisaged to occur is the excitation of an electron into an antibonding orbital followed by opening of the cyclopropane ring to form a and b (k_a and k_b) or by abstraction of a hydrogen atom from the solvent to form c (k_c). Inversion, rotation and closure of a or b provides *cis* ketone **1** (k_1), which rearranges readily to give ketone **3**. The independent irradiation of *cis* ketone **1** has shown that this over-irradiation process is rapid. Ring opening of monoradical species c yields d and e (k_d and k_e),[9] which abstract another hydrogen atom from the solvent to form saturated ketones **4** and **5** (k_4 and k_5).

When the photolysis of ketone **2** was conducted in isopropyl alcohol, only saturated products were observed. In addition, the irradiation time was short. This result suggests strongly that hydrogen abstraction in a good hydrogen-donating solvent is more rapid than inversion, rotation and reclosure (*i.e.*, $k_c > k_1$).

It is interesting to note that when the photolysis of **2** was conducted in isopropyl alcohol, the 3:1 product ratio of **4**:**5** reflects the relative stability of the intermediate radicals formed. Cleavage of the bond between C-1 and C-2 provides the more stable secondary radical d, whereas cleavage of the bond between C-1 and C-3 gives primary radical e (*i.e.*, $k_d > k_e$; $k_4 > k_{-d}$; $k_5 > k_{-e}$).

In pentane, the ratio of **4**:**5** was reversed, the ratio being 2:3. Since pentane is a poor hydrogen donor, abstraction is more selective than in isopropyl alcohol. The dissociation energies of primary *vs.* secondary radicals[10] indicate that primary radicals are more reactive than secondary radicals (*i.e.*, $k_5 > k_4$; $k_4 \leq k_{-d}$; $k_5 \leq k_{-e}$). The preferred formation of isobutyl methyl ketone (**5**) in pentane is in agreement with those reactivities. Also, from the long irradiation time, it can be seen that hydrogen abstraction in pentane proceeds at a slower rate than in isopropyl alcohol, and is, in fact, in competition with isomerization to *cis* compound **1**, detected as its over-irradiation product **3** (*i.e.*, $k_1 \sim k_3$). Since the conditions of irradiation in pentane and in isopropyl alcohol were similar, reclosure of the radicals formed appears to be a relatively rapid process (k_{-a} and k_{-b}).

Since no conjugated enones were found comparable to those reported in the irradiation of cyclopropyl methyl ketone in the vapor phase,[2] it may be inferred that internal hydrogen shifts, other than "type II" migrations, are less efficient than hydrogen abstraction from the solvent and *cis–trans* isomerization of the cyclopropane ring.[11]

Experimental Section

Syntheses.—*cis*- (**1**) and *trans*-2-methylcyclopropyl methyl ketone (**2**) were prepared from the corresponding *cis*- and *trans*-cyclopropylcarbinols using the Brown oxidation procedure.[12] The spectral data obtained are in agreement with those reported for these ketones.[13]

***cis*-2-Methylcyclopropylmethylcarbinol.**—The Simmons–Smith procedure[14] as modified by Dauben and Berezin[15] was employed with *cis*-3-penten-2-ol, which in turn was prepared[16,17] from 3-pentyn-2-ol.[18]

(9) Ground-state radical rearrangements of this type have been studied. See D. C. Neckers, A. Schaap, and J. Hardy, *J. Amer. Chem. Soc.*, **88**, 1265 (1966).

(10) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, p 50.

(11) In this laboratory irradiation of cyclopropyl methyl ketone in pentane (3 hr, 50% conversion) also proceeded to give predominantly the saturated analog (20% propyl methyl ketone).

(12) H. C. Brown and C. P. Gary, *J. Amer. Chem. Soc.*, **83**, 2952 (1961).

(13) R. M. Roberts, R. G. Landolt, R. N. Green, and E. W. Heyer, *J. Amer. Chem. Soc.*, **89**, 1404 (1967).

(14) See H. E. Simmons, E. P. Blanchard, and R. D. Smith, *J. Amer. Chem. Soc.*, **86**, 1347 (1964), and references cited there.

(15) W. G. Dauben and G. H. Berezin, *ibid.*, **85**, 468 (1963).

(16) The Brown[3] hydrogenation apparatus was utilized. See C. A. Brown and H. C. Brown, *J. Org. Chem.*, **31**, 3989 (1966). The authors wish to thank Dr. C. A. Brown for his assistance in this hydrogenation.

(17) For ir spectral data on *cis*- and *trans*-3-penten-2-ol, see R. Heilmann, G. De Gaudemaris, and P. Arnaud, *Bull. Soc. Chim. Fr.*, 119 (1957). The ir spectra obtained in this laboratory were in agreement with the published data.

The data obtained for *cis*-2-methylcyclopropylmethylcarbinol were bp 81–83° (93 mm); ir (CCl_4) 3600, 3360 (OH), 1075, 1030, 1010, 995, 950, 910, 880, and 850 cm^{-1}; nmr (CCl_4) δ 3.83 (s, 1, OH), 3.28 (m, 1, CHOH), 1.23 (d, 3, J = 6 Hz, CH_3CHOH), 1.03 (d, 3, J = 3 Hz, c-$C_3H_5CH_3$), 0.87–0.75 (m, 3, cyclopropyl H), 0.1 (m, 1, cyclopropyl H); mass spectrum (prominent peaks) m/e 85 (M − 15), 82 (M − 18), 71, 67, 58 (B), 45.

Anal. Calcd for $C_6H_{12}O$ (100.17): C, 71.94; H, 12.07. Found: C, 71.96; H, 12.30.

trans-2-Methylcyclopropylmethylcarbinol.—Using the same procedure as described above, *trans*-cyclopropylcarbinol was prepared from *trans*-3-penten-2-ol.[17,19] The data obtained for *trans*-2-methylcyclopropylmethylcarbinol were ir (CCl_4) 3600, 3380 (OH), 1245, 1110, 1075, 1020, 995, 960, 937, 890, and 860 cm^{-1}; nmr (CCl_4) δ 3.29 (s, 1, OH), 3.1 (m, 1, CHOH), 1.17 and 1.04 (m, 6, at 1.17 a doublet of doublets, J = 6 and 1 Hz; at 1.04 a distorted doublet), 0.52 and 0.21 (2 m, 4, cyclopropyl H).

Irradiations were conducted in 125 ml (c 0.4–0.2%) solutions with an immersed Hanovia 450-W lamp, held in a water-cooled jacket and surrounded by a Corex filter (λ >280 mμ). The solutions were degassed with helium. The reactions were followed by vpc on a 5% XF-1150 cyanosilicone column (10 ft × 0.125 in., 60°, on a F & M 5750 gas chromatograph). After irradiation the solvent was carefully distilled from the product mixture and the products were collected from a 10 ft × 0.375 in. 20% XF-1150 cyanosilicone column on an Aerograph A-90-P gas chromatograph. Analyses were conducted by the Microanalytical Laboratory, University of California, Berkeley, Calif.

Registry No.—1, 2371-81-5; 2, 2863-92-5; *cis*-2-methylcyclopropylmethylcarbinol, 19293-89-1; *trans*-2-methylcyclopropylmethylcarbinol, 19293-90-4.

(18) I. M. Heilbron, E. R. H. Jones, and R. A. Raphael, *J. Chem. Soc.*, 264 (1943).

(19) K. N. Campbell and L. T. Eby, *J. Amer. Chem. Soc.*, **63**, 2683 (1941).

Reactivity Studies in Free-Radical α Bromination of Cyclopropyl Compounds by N-Bromosuccinimide

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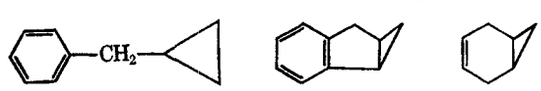
The relative reactivities of benzylcyclopropane, *trans*-1-benzyl-2-methylcyclopropane, cycloprop[2,3]indene, and bicyclo[4.1.0]hept-3-ene toward α-hydrogen abstraction in N-bromosuccinimide bromination have been determined. Rate accelerations resulting from electron release by the cyclopropyl substituents α to the incipient radical centers have been observed.

Product studies on the free-radical N-bromosuccinimide (NBS) brominations of the cyclopropyl compounds I, II, and III, which were reported earlier,[1]



I II III

showed that the reactions proceed predominantly *via* initial abstraction of hydrogen atoms from the carbons α to the cyclopropane rings. Bromide products resulting from both cyclopropylcarbinyl and rearranged allylcarbinyl radical intermediates were observed. No evidence was obtained, however, for the intermediacy of nonclassical cyclopropylcarbinyl radical species in product formation.

Various investigations[2] involving other methods for generation of cyclopropylcarbinyl radicals have also predominantly yielded either inconclusive or negative evidence for nonclassical intermediates in product formation. However, a number of examples have been reported[2e,3] in which α-cyclopropyl substituents do accelerate radical formation steps. Thus we became interested in determining whether rate acceleration also results from the presence of cyclopropyl substituents adjacent to the incipient radical centers in NBS α-bromination reactions. The model compounds, benzylcyclopropane (I), cycloprop[2,3]indene (II), and bicyclo[4.1.0]hept-3-ene (III), used for the reactivity investigation are the same as those used in the product study. Because of the difficulties involved in carrying out direct kinetic studies with heterogenous reactions, the alternate approach of investigating the relative rates of reaction of different substrates was used.

Results and Discussion

A summary of the reactivities relative to toluene toward NBS bromination at 77° in carbon tetrachloride solution for the compounds investigated is given in Table I. Literature values[4] for the relative reactivities in carbon tetrachloride solution of certain of the compounds and for several other compounds of interest are also given.

The data in Table I were obtained by successive comparisons of the relative reactivity values found for the individual competition experiments listed in Table II. Analyses of the competition product mixtures were done by quantitative nmr techniques[4a] as are described in the Experimental Section.

In most cases, hydrocarbon consumption and "normal bromide" formation per NBS reacted were approximately 90% or greater and no evidence was found in the nmr spectra of the competition product mixtures for significant side-product formation. Only in the competitions with benzylcyclopropane and *trans*-1-benzyl-2-

(1) E. C. Friedrich, *J. Org. Chem.*, **34**, 528 (1969).

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