Photochemical Studies on Spiro[2.4]heptan-4-one and Spiro[2.5]octan-4-one[1a]

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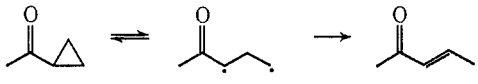
The photochemically induced reactions of the title ketones have been examined. The photoproducts observed do not result from isomerization of the cyclopropyl ring, but rather from α cleavage at the opposite side of the carbonyl group. Spiro[2.4]heptan-4-one yields 1-allylcyclopropylcarboxaldehyde, the corresponding methyl acetal, and cyclic acetal **5** in methanol as solvent. In cyclohexane, only the first product is formed unless oxygen is present, in which case lactone **6** is also found. Spiro[2.5]octan-4-one gives 1-(3-butenyl)cyclopropanecarboxaldehyde as the only primary photoproduct in either of the above solvents. Further conversion of this photoproduct leads to its acetal in methanol solvent; *cis*-1-(2-butenyl)cyclopropanecarboxaldehyde and cyclobutanol **11** are observed as secondary products in either solvent.

Subsequent to the initial report on the photochemical conversion of methyl cyclopropyl ketone to methyl propenyl ketone in 1954,[2] a number of additional simple cyclopropyl ketones have been observed to behave similarly.[3-6] Photoepimerization of cyclopropyl substituents is also a well established process.[4,7] These transformations are nicely accommodated mechanistically by invoking a biradical intermediate as illustrated below. This species can reclose to a cyclopropane with or without inversion of configuration at the radical centers or it can undergo 1,2-hydrogen migration to give the conjugated acyclic ketone. In-

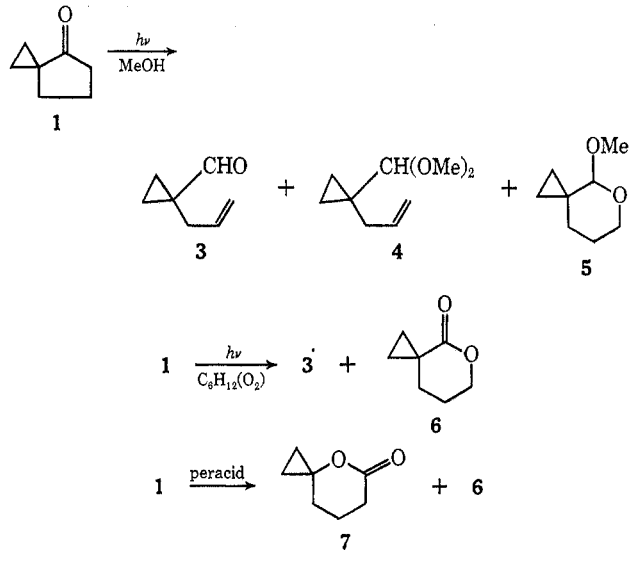


corporation of the basic chromophore into a bicyclic system does not appear to greatly change the situation, except that there is a stereochemical preference for cleavage of the cyclopropyl bond which overlaps best with the π orbital of the carbonyl group.[4,6] Substitution at the α carbon on the other side of the carbonyl, however, does promote competitive operation of the normal cycloalkanone–unsaturated aldehyde isomerization.[8]

In the present study we have examined the photochemistry of the spiro cyclopropyl ketones **1** and **2**, compounds whose geometries might be expected to be optimal for communication between the two chromophoric moieties.[9]

Results

Irradiation of a dilute solution of **1** in methanol with the 3100-Å lamps of a Rayonet photochemical reactor effected clean conversion into three products, subsequently identified as aldehyde **3** (32%), the related acetal **4** (6%), and the unusual cyclic acetal **5** (57%). Specified yields were determined against an internal glpc standard. Control experiments demonstrated that acetal **4** was derived from aldehyde **3** under the experimental conditions.



1-Allylcyclopropanecarboxaldehyde (**3**) was identified on the basis of its characteristic spectral properties as detailed in the Experimental Section. A comparison sample was secured by selective lithium aluminum hydride reduction of the corresponding nitrile, which was prepared by allyl bromide alkylation of the lithium salt of cyclopropyl nitrile. *In situ* generation of this anion by reaction of γ-chlorobutyronitrile with 2 equiv of lithium diethylamide proved to be expedient. Acetal **4** displays definitive spectral properties.

The structure of cyclic acetal **5** rests on its spectral characterization. The infrared spectrum shows the group of characteristic acetal bands in the 8–10-μ region. The nmr shows a single methoxyl group (τ 6.76), retention of the cyclopropyl ring (τ 9.7), and three protons in a complex multiplet at τ 6.2 appropriate for hydrogens adjacent to the ring oxygen. The four remaining protons are found in multiplets centered at τ 8.3 and 9.2 in a 3:1 ratio. The upfield position of the single hydrogen is rationalized by assigning it as the methylene proton adjacent to the cyclopropyl group which conformationally spends most of its time in the shielding region above the plane of the cyclopropane.[10]

(1) (a) This work was supported by the National Science Foundation; (b) Alfred P. Sloan Research Fellow 1968–1970; (c) National Science Foundation Trainee 1966–1967.

(2) J. N. Pitts and I. Norman, *J. Amer. Chem. Soc.*, **76**, 4815 (1954); see also L. D. Hess, J. L. Jacobson, K. Schaffner, and J. N. Pitts, *ibid.*, **89**, 3684 (1967).

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

(4) H. E. Zimmerman, K. G. Hancock, and G. C. Licke, *ibid.*, **90**, 4892 (1968).

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

(6) W. G. Dauben and G. W. Schaffer, *ibid.*, 4415 (1967), and references therein.

(7) G. W. Griffin, E. J. O'Connell, and H. A. Hammond, *J. Amer. Chem. Soc.*, **85**, 1001 (1963); G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *ibid.*, **87**, 1410 (1965); R. C. Cookson, M. J. Nye, and G. Subrahmanyam, *Proc. Chem. Soc.* (London), 144 (1964); W. G. Brown and J. F. Neumer, *Tetrahedron*, **22**, 473 (1966).

(8) For a brief review, see R. O. Kan, "Organic Photochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, pp 71–93.

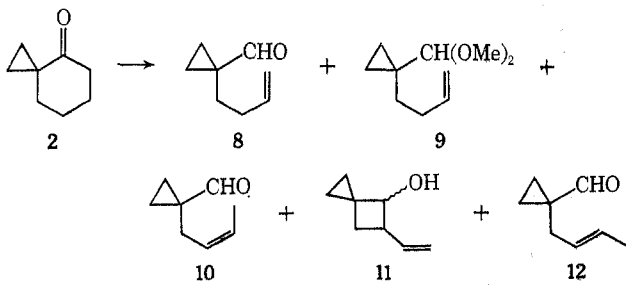
(9) W. G. Dauben and G. H. Berezin, *J. Amer. Chem. Soc.*, **89**, 3449 (1967).

(10) D. J. Patel, M. E. H. Howden, and J. D. Roberts, *ibid.*, **85**, 3218 (1963).

Photolysis of **1** in cyclohexane gave **3** in 26% yield. The lower material recovery in this reaction undoubtedly reflects the instability of the aldehyde to light, since an independent experiment demonstrated that **3** disappears rapidly without the production of observable products. (The products expected from normal photodecomposition of **3** would not have been visible under the glpc conditions utilized.) Inadvertant irradiation of **1** in cyclohexane under an oxygen-containing atmosphere led to the isolation of a second product. Spectral examination of this material suggested lactone **6** as its structure. Chemical confirmation of this assignment was provided by an alternate synthesis involving monopermaleic acid oxidation of ketone **1**. The major lactone obtained from this reaction, however, was **7**, which predominated over **6** by a ratio of 9:1.

Spirooctanone **2** gave four identifiable products and three unknown minor compounds amounting to *ca.* 1% each upon irradiation in methanol. After 76% consumption of **2** the following were present: aldehyde **8** (7%), its acetal **9** (49%), isomeric aldehyde **10** (1%), and cyclobutanol (**11**) (1%). The ratio of **8**/**9** was variable in other experiments depending upon solvent source and photolysis conditions. Acid hydrolysis of the photolysate demonstrated that **9** could be reconverted into **8**. Irradiation of aldehyde **8** effected conversion into **9**, **10**, and **11**. In cyclohexane as solvent, ketone **2** yielded 20% **8**, 3% **10**, and 1% **11**.

Characteristic spectral parameters detailed elsewhere provide the basis for assignments to **8** and **9**. Compound **10** was likewise shown to be an aldehyde which retained the cyclopropyl moiety but with a methyl-substituted *cis* double bond (nmr τ 8.38; ir 5.8 and 14.7 μ). These data suggested structure **10**, which was unequivocally demonstrated when an authentic sample of **10** was obtained by the procedure described above for the synthesis of **3**, except that crotyl chloride was the alkylating agent. The major aldehyde derived from this reaction was the *trans* isomer **12**. With the *trans* aldehyde in hand, it was possible to show by capillary glpc that a small amount of **12** (<1%) contributed to the peak for **8** in the usual glpc analysis. The structure of cyclobutanol (**11**) is based on its formation from **8** and its spectroscopic characterization, which indicates a secondary alcohol, a terminal vinyl group, and an intact cyclopropane. The stereochemistry of this product was not further investigated.



Discussion

The most striking aspect of this investigation is the total lack of participation of the cyclopropyl unit in the photochemical transformations of **1** and **2**, at least insofar as product formation is concerned. This result is in opposition to our *a priori* considerations based on the evidence for strong interaction between the carbonyl and cyclopropyl functions. Ultraviolet studies[9] of π–π^* absorption at *ca.* 200 nm suggest that the required geometry for **1** (carbonyl plane perpendicular to and bisecting the cyclopropyl ring) results in maximum conjugation. The preferred conformation of **2** retains the favorable orthogonality of the carbonyl and cyclopropyl planes, but the torsional angle is modified such that the π system overlaps with only one of the radial cyclopropyl bonds.

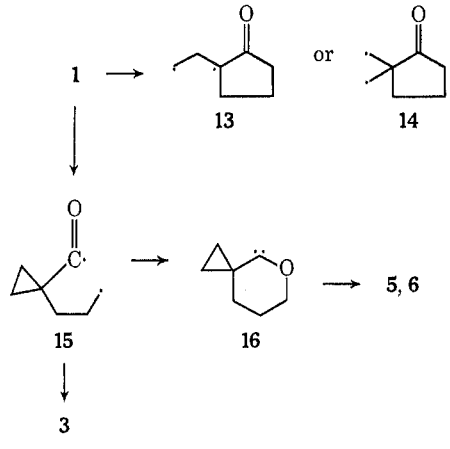
One of the important observations from the work on methyl cyclopropyl ketone was that this compound was unusually stable toward the normal fission of the C–C bond α to the carbonyl.[2] However, Dauben's studies[6] on bicyclo[4.1.0]heptan-2-ones demonstrated that α cleavage away from the cyclopropyl group could be important in product formation when stabilizing substituents were present at the α carbon, although information on the efficiency of these reactions is not available. One rule that does appear to be general is that the carbonyl–cyclopropane bond remains intact. Spiro ketones **1** and **2** obey this restriction. However, the cyclopropane is retained in all of the products and the transformations of these ketones are best described in terms of initial α cleavage of the alternate bond.

For the moment, the absence of products derived from cyclopropyl bond rupture lacks a satisfactory explanation. It is possible that the cyclopropyl group is important in the chemistry of the majority of molecules that are excited, but through either chemical or physical processes the excitation energy is dissipated without chemical consequence. For example, excited ketone **1** may isomerize to biradical **13** by breaking a radial cyclopropyl bond (or to **14** by cleavage of a peripheral bond), but this species might not be efficient in product formation for some reason and return to starting ketone. The epimerization studies[4,7] demonstrate the potential reversibility of the ring breakage step and provide the basis for such a proposal. Efficiency studies and stereochemical probing for intermediates **13** and/or **14** should provide information regarding this possible rationalization for the apparent resistance of the cyclopropyl ketone units to photochemical transformation.

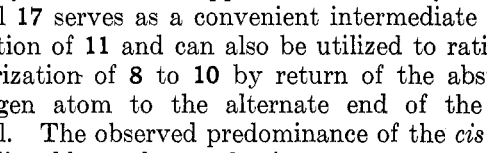
Aldehyde **3** (and its acetal in methanol solvent) represents the product of the usual decomposition of a biradical such as **15**, namely intramolecular disproportionation. The formation of cyclic acetal **5** finds analogy in a number of previous observations which have been summarized by Yates.[11] The usual rationalization for this type of reaction postulates recyclization of biradical **15** to yield intermediate carbene **16** which then adds methanol nucleophilically. This reaction is most prevalent for cyclobutanones where the disproportionation step is likely to be less facile, since it involves a four-center transition state while the carbene route forms a five-membered ring. Ordinarily cyclopentanones do not manifest such behavior, but several examples are available in which polycyclic cyclopentanones give analogous reactions, presumably because of the effects of strain and geometrical restriction upon the relative efficiences of the competing processes. Lactone **6** also appears to be a product of carbene **16** by combination with molecular oxygen.[11]

(11) P. Yates, *Pure Appl. Chem.*, **16**, 93 (1968).

A point of considerable synthetic importance concerns the better yields of products found with methanol as the photolysis solvent. This is a general observation in these laboratories and appears to be a result of hemiacetal formation by the aldehyde photoproduct.[12] The light stability of this species preserves the aldehyde against the further photodegradation that it suffers in inert solvents. This solvent is highly recommended for synthetic reactions. Acetal formation of aldehydes under photochemical conditions in methanol has been recorded recently in the literature by others.[11,13,14] This seems not to be directly related to photochemical processes but rather to arise from catalysis by acidic impurities.



In the case of 2 the corresponding aldehyde **8** is the only significant photoproduct. The absence of cyclopropyl isomerization here is particularly surprising in view of the fact that several polycyclic steroid analogs of 2 are reported to undergo this reaction without complications.[15,16] The other products identified from the reaction of 2 are secondary photoproducts derived from photolysis of **8**. The cyclobutanol-type product frequently accompanies the Norrish type II fragmentation[17] of acyclic carbonyl compounds, which is probably the major mode of disappearance of aldehyde **8**. Biradical **17** serves as a convenient intermediate for the formation of **11** and can also be utilized to rationalize isomerization of **8** to **10** by return of the abstracted hydrogen atom to the alternate end of the allylic radical. The observed predominance of the *cis* isomer is predicted by such a mechanism.



Experimental Section

General.—Nuclear magnetic resonance (nmr) spectra were recorded with Varian A-60 and HR-100 spectrometers in carbon tetrachloride with tetramethylsilane as an internal standard. Mass spectra were obtained with an AEI MS-9 mass spectrometer at 70 eV. Analytical gas chromatography (glpc) was performed on a Varian Aerograph Model 1200 (hydrogen flame detector) chromatograph utilizing a 10 ft × 1/8 in. 15% Carbowax 20M on 60–80 Chromosorb W column. Preparative columns utilized were a 5 ft × 3/8 in. 15% Carbowax 20M on 60–80 Chromosorb W, a 10 ft × 3/8 in. 30% FFAP on 60–80 Chromosorb W, a 20 ft × 3/8 in. 30% Carbowax 20M on 60–80 Chromosorb W, and a 5 ft × 1/4 in. 20% SE 30 on 60–80 Chromosorb W. The capillary column used was 250 ft × 1/100 in. of Ucon Polar.

General Photolysis Procedure. A.—Analytical irradiations were carried out in Pyrex test tubes in a Rayonet photochemical reactor equipped with 3100-Å lamps. Photolyses were performed in a cold room at 1°. All solvents were reagent grade and were used without further purification. The concentration of photolysis solutions was approximately 1% (w/v). The photolyses were monitored by periodically removing aliquots and analyzing by glpc. Percentage composition data were calculated by integrated peak areas relative to an internal standard and are uncorrected for detector response.

B.—Preparative irradiations were performed with a 450-W Hanovia Type L (Lamp No. 679A-36) high-pressure quartz mercury-vapor lamp, using a water-cooled quartz immersion well equipped with a Vycor filter. The concentration of all photolysis solutions was approximately 1% (w/v). All solutions were degassed and maintained under a positive nitrogen atmosphere.

Spiro[2.4]heptan-4-one (1).—To a solution of 46 g of potassium hydroxide in 12 ml of water and 225 ml of 95% ethanol, stirred in a methanol–ice bath, was added 129 g of 2-carbethoxycyclopentanone (commercial material contains the methyl ester) over 3 min. After 2 min, 40 ml of ether was added while the reaction temperature was maintained below 20°. The pasty white precipitate was suction filtered immediately, washed with a small amount of cold ethanol, then with ether. The potassium salt was dried for 8 hr at 55° to yield 118 g (73%).

To 118 g of the potassium salt in 950 ml of dimethyl sulfoxide[18] was added dropwise 160 g of 1,2-dibromoethane. The resulting mixture was allowed to stir at room temperature under nitrogen for 11 hr, poured into water, and extracted with ether. The ethereal extract was washed with water, dried, and concentrated. Distillation of the residue yielded 70 g (44%) of a mixture of alkylated methyl and ethyl esters: bp 127–128° (2 mm).

This mixture was refluxed vigorously with 250 ml of 40% hydrobromic acid and 5 g of finely pulverized clay for 1.5 hr.[19] The resulting solution was cooled, poured into water, and extracted with three 200-ml portions of ether. The ether solution was washed with saturated sodium bicarbonate and water. The ethereal extract was dried and concentrated to yield crude 2-(2-bromoethyl)cyclopentanone: ir 5.78 μ.

This crude product was refluxed with 200 ml of 30% alcoholic potassium hydroxide for 1.5 hr; the resulting mixture was cooled, poured into water, and extracted with ether. The ether solution was washed with saturated sodium bicarbonate and brine. The ethereal extract was dried and concentrated, and the residue was distilled to give 19.6 g (22% overall) of 1: bp 61–62° (20 mm); uv max (isooctane) 292.5 nm (ε 24) and (methanol) 280 (29);[20] ir 3.22, 3.31, and 5.78 μ; nmr τ 7.7–8.1 (m, 6) and 9.10 (AA'BB' m, 4, cyclopropane); mass spectrum *m/e* (rel intensity), 110 (100), 109 (35), 95 (20), 82 (36), 68 (25), 67 (50), 55 (43), 54 (58), 41 (20), and 39 (36).

Spiro[2.5]octan-4-one (2).—To a well-stirred solution of 45 g of 58% sodium hydride in mineral oil in 350 ml of dimethylformamide was added dropwise 170 g of 2-carbethoxycyclohexanone. The resulting solution was warmed to ensure that all hydrogen evolution had occurred. To this solution was rapidly added 376 g of 1,2-dibromoethane, and the resulting solution was refluxed for 7 hr. After cooling and diluting with water, the solution was extracted with ether. The ether solution was washed with saturated sodium bicarbonate and water. The ethereal solution was dried and concentrated to yield a mixture of esters.

This material was refluxed vigorously with 250 ml of 40% hydrobromic acid and 5 g of finely pulverized clay for 1.5 hr. After cooling and diluting with water, the solution was extracted with ether. The ether solution was washed with saturated

(12) Experimental evidence establishing this point has been secured for other aldehydes under study in this laboratory.

(13) J. Meinwald and R. A. Chapman, *J. Amer. Chem. Soc.*, **90**, 3218 (1968).

(14) W. C. Agosta and D. K. Herron, *ibid.*, **90**, 7025 (1968).

(15) C. H. Robinson, O. Gnou, and F. E. Carlon, *Tetrahedron*, **21**, 2509 (1965).

(16) R. Beugelmans, *Bull Soc. Chim. Fr.*, 244 (1967).

(17) Reference 8, pp 71–74.

(18) D. M. Pond and R. L. Cargill, *J. Org. Chem.*, **32**, 4064 (1967).

(19) R. Mayer in "Newer Methods of Preparative Organic Chemistry," Vol. 2, W. Foerst, Ed., Academic Press, New York, N. Y., 1963, pp 122–123.

(20) E. M. Kosower and M. Ito, *Proc. Chem. Soc.*, 25 (1962).

sodium bicarbonate and water. The ethereal solution was dried and concentrated to give crude 2-(2-bromoethyl)cyclohexanone.

This material was refluxed with 200 ml of 30% alcoholic potassium hydroxide for 1.5 hr, cooled, diluted with water, and extracted with ether. The ether solution was washed with saturated sodium bicarbonate and brine. The ethereal extract was dried and concentrated, and the residue was distilled to give 10.8 g (9% overall) of **2**: bp 82–84° (24 mm); uv max (isooctane) 290 nm (ϵ 29)[21] and (methanol) 282.5 (35); ir 3.21, 3.3, and 5.88 μ; nmr τ 7.55–8.4 (m, 8) and 9.21 (AA'BB' m, 4, cyclopropane); mass spectrum *m/e* (rel intensity), 124 (66), 123 (22), 96 (100), 68 (23), 67 (30), and 39 (24).

Photolysis of 1 in Cyclohexane. A. Analytical.—A solution of 27 mg of **1** and 10 mg of *n*-propyl heptanoate (internal standard) in 2.5 ml of cyclohexane was irradiated for 6 hr. Glpc analysis indicated the presence of **3** (26%) and 2% **1**. Compound **3** underwent slow decomposition without formation of observable products when photolyzed under the same conditions.

B. Preparative.—A solution of 4 g of **1** in 440 ml of cyclohexane was irradiated for 5 hr. The cyclohexane was distilled through a Vigreux column, and the residue was vacuum transferred (0.5 mm) to give 1.2 g of volatile material. Preparative glpc gave pure **3**, which had spectral properties identical with those of a synthetic sample.

Photolysis of 1 in Methanol. A. Analytical.—A solution of 35 mg of **1** and 17 mg of *n*-propyl heptanoate in 2.5 ml of methanol was photolyzed for 6 hr. Glpc analysis showed **3** (32%), **4** (6%), **5** (57%), and **1** (3%). Irradiation for another 18 hr showed almost complete disappearance of **3** with a corresponding increase of **4**. A similar photolysis of **3** in methanol slowly converted it to **4**.

B. Preparative.—A solution of 1.2 g of **1** in 110 ml of methanol was irradiated for 1 hr. The methanol was removed through a Vigreux column, and the residue was vacuum transferred (0.5 mm) to give 0.95 g of volatile material. The products were separated by preparative glpc. The first compound eluted was identified as **3** by comparison of its spectral properties with a synthetic sample. The second product was characterized as **4**: ir (CCl_4) 3.22, 3.31, 3.51, 6.09, 7.25, 8.4, 9.02, and 9.42 μ; nmr τ 4.2 (m, 1, $CH{=}CH_2$), 5.0 (m, 2, $CH{=}CH_2$), 5.68 (s, 1), 6.73 (s, 6), 7.9 (broad d, 2, J = 7.0 Hz, CH_2), and 9.6 (AA'BB' m, 4, cyclopropane); mass spectrum *m/e* (rel intensity), 156 (1), 128 (24), 125 (12), 97 (28), 93 (22), 75 (100), 67 (25), 41 (33), and 39 (26). The major product was identified as **5**: ir 3.22 and 3.31 (cyclopropane), 3.51, 8.4, 8.8, 9.05, 9.32, and 9.52 μ; nmr τ 6.3 (m, 3, OCH_2 and OCH), 6.76 (s, 3, OCH_3), 7.8–8.7 and 9.2 (m, 3, and m, 1), and 9.7 (AA'BB' m, 4, cyclopropane); mass spectrum *m/e* (rel intensity), 142 (2), 141 (3), 114 (100), 112 (32), 99 (29), 84 (63), 67 (25), 55 (48), 54 (29), 41 (47), and 39 (33).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.89; H, 9.90.

Photolysis of 1 in the Presence of Oxygen.—A solution of 2.4 g of **1** in 110 ml of cyclohexane was prebubbled with oxygen and then photolyzed for 1.5 hr under a positive oxygen pressure. Glpc analysis showed **3** (67%), **6** (10%), and **1** (23%). The cyclohexane was removed through a Vigreux column, and the residue was vacuum transferred (5 mm) to give 0.71 g of volatile material. Preparative glpc gave pure **6**. The spectral properties of **6** were identical with a synthetic sample.

1-Allylcyclopropanecarbonitrile.—To an ice-cold stirred solution of 62 ml of diethylamine in 80 ml of ether was added 443 ml of commercial 15% *n*-butyllithium in hexane under nitrogen. After 20 min a solution of 31 g of γ-chlorobutyronitrile[22] in 225 ml of ether was added with cooling over 1 hr. The resulting solution was stirred at room temperature for 4 hr. To the solution of the lithium derivative of cyclopropanecarbonitrile, cooled in a methanol–ice bath, was added dropwise 36 g of allyl bromide in 35 ml of ether. After stirring for 30 min at room temperature and 45 min under reflux, the solution was cooled, poured into water, and extracted with ether. The ether solution was washed with 1 *N* hydrochloric acid, saturated sodium bicarbonate, and water. The ethereal extract was dried and concentrated, and the residue was distilled to give 9 g (28%) of 1-allylcyclopropanecarbonitrile: bp 78–82° (29 mm); ir 3.23, 3.32, 4.45, 6.09, 10.1, and 10.9 μ; nmr τ 4.2 (m, 1, $CH{=}CH_2$), 4.8 (m, 2, $CH{=}CH_2$), 7.85 (broadened d, 2, J = 6.5 Hz, CH_2), and 9.02 (AA'BB' m, 4, cyclopropane).

Anal. Calcd for C_7H_9N: C, 78.46; H, 8.47. Found: C, 78.65; H, 8.25.

1-Allylcyclopropanecarboxaldehyde (3).—To 0.77 g of 1-allylcyclopropanecarbonitrile in 10 ml of ether, cooled in a methanol–ice bath under nitrogen, was added 0.20 g of lithium aluminum hydride in 15 ml of ether. The solution was stirred for 60 min at 0° and 30 min at room temperature. After addition of 12 ml of 5 *N* sulfuric acid, the resulting solution was extracted with three 10-ml portions of ether. The ethereal extract was washed with saturated sodium bicarbonate and water and dried. The ether was removed by flash evaporation to give 0.28 g of crude product shown by glpc analysis to contain one major product. Preparative glpc gave pure **3**: ir (CCl_4) 3.22, 3.30, 3.33, 3.64, 5.82, 6.08, 10.0, and 11.0 μ; nmr τ 1.33 (s, 1), 4.1 (m, 1, $CH{=}CH_2$), 5.0 (m, 2, $CH{=}CH_2$), 7.65 (broadened d, 2, J = 6.5 Hz, CH_2), and 8.99 (AA'BB' m, 4, cyclopropane); mass spectrum *m/e* (rel intensity), 110 (17), 109 (37), 95 (74), 82 (39), 81 (72), 79 (50), 67 (70), 55 (35), 54 (48), 53 (68), 41 (100), and 39 (81). A precise mass spectrometric determination on the molecular ion of **3** gave *m/e* 110.0723 (calcd for $C_7H_{10}O$: 110.0731).

Baeyer–Villiger Reaction of 1.—To an ice-cold stirred solution of 1.15 ml of 90% hydrogen peroxide and 21 ml of methylene chloride was added 5.35 g of freshly pulverized maleic anhydride.[23] The resulting solution was heated to reflux, and 3 g of **1** in 5 ml of methylene chloride was added. After refluxing vigorously for 24 hr, the solution was cooled and filtered to remove maleic acid. The filtrate was washed with two 20-ml portions of 10% aqueous sodium carbonate, one 20-ml portion of 10% aqueous sodium bisulfite, and two 20-ml portions of water. The methylene chloride solution was dried and concentrated, and the residue was vacuum transferred (0.5 mm) to give 1.5 g of volatile product. Two compounds were isolated by glpc as 89% and 11% of the volatile reaction mixture.

The minor product was identified as **6**: ir (CCl_4) 5.76, 8.78, and 9.3 μ; nmr τ 5.7 (broadened t, J = 5.7 Hz, 2, CH_2O), 7.9–8.4 (m, 4), and 8.98 (AA'BB' m, 4, cyclopropane); mass spectrum *m/e* (rel intensity), 126 (100), 125 (91), 99 (79), 97 (32), 81 (71), 79 (30), 69 (38), 68 (61), 67 (72), 57 (32), 55 (47), 54 (45), 53 (48), 44 (74), 43 (31), and 40 (61).

Anal. Calcd for $C_7H_{10}O_2$: C, 66.65; H, 7.99. Found: C, 66.77; H, 8.10.

The 89% component was identified as the isomeric lactone **7**: ir (CCl_4) 5.75, 8.2, and 8.8 μ; nmr τ 7.4–8.5 (m, 6) and 9.25 (AA'BB' m, 4, cyclopropane); mass spectrum *m/e* (rel intensity), 126 (6), 98 (84), 97 (28), 83 (34), 57 (22), 56 (47), 55 (100), 42 (84), and 41 (33).

Anal. Calcd for $C_7H_{10}O_2$: C, 66.65; H, 7.99. Found: C, 66.70; H, 7.99.

Photolysis of 2 in Cyclohexane.—A solution of 33 mg of **2** and 20 mg of cyclododecane (internal standard) in 2.5 ml of cyclohexane was photolyzed for 6 hr. Glpc analysis showed **8** (20%), **10** (3%), **11** (1%), **2** (25%), and two unidentified components, each amounting to approximately 1%. Resolution by capillary column of the glpc peak attributed to **8** indicated a small component, half as great as **10**, with a retention time identical with that of a synthetic sample of *trans*-1-(2-butenyl)cyclopropanecarboxaldehyde (**12**).

Photolysis of 2 in Methanol. A. Analytical.—A solution of 34 mg of **2** and 15 mg of cyclododecane (internal standard) in 2.5 ml of methanol was photolyzed for 6 hr. Glpc analysis showed **8** (7%), **9** (49%), **10** (1%), **11** (1%), **2** (24%), and three unidentified components, each amounting to approximately 1%.

B. Preparative.—A solution of 4 g of **2** in 440 ml of methanol was irradiated for 75 min. Glpc analysis showed **8** (49%), **9** (13%), **10** (6%), **11** (3%), **2** (29%), and one unidentified component (<1%). The methanol was removed through a Vigreux column, and the resulting solution was stirred for 20 min with 20 ml of 2% hydrochloric acid to hydrolyze **9**. After extraction into ether and washing with saturated aqueous sodium bicarbonate, the ethereal extract was concentrated, and the residue was vacuum transferred (0.4 mm) to give 2.5 g (61%) of volatile material.

The first product was identified as 1-(3-butenyl)cyclopropanecarboxaldehyde (**8**): ir (CCl_4) 3.22, 3.30, 3.33, 3.65, 5.82, 6.08, 10.5, and 11.0 μ; nmr τ 1.47 (s, 1), 4.3 (m, 1, $CH{=}CH_2$), 5.1 (m, 2, $CH{=}CH_2$), 7.9 (m, 2, $CH_2CH{=}CH_2$), 8.4 (m, 2, CH_2), and 9.03 AA'BB' m, 4, cyclopropane); mass spectrum *m/e* (rel

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intensity), 124 (4), 109 (34), 96 (98), 95 (31), 81 (30), 80 (25), 79 (26), 70 (23), 67 (42), 55 (100), 54 (30), 53 (35), 41 (67), and 39 (76).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.05; H, 9.66.

The second product was identified as *cis*-1-(2-butenyl)cyclopropanecarboxaldehyde (**10**). Its spectral properties were identical with those of a synthetic sample.

The third photoproduct was characterized as 5-vinylspiro[2.3]-hexan-4-ol (**11**): ir (CCl_4) 2.75, 2.98, 3.22, 3.31, 6.1, 10.1, and 10.95 μ; nmr τ 4.1 (m, 1, CH=CH_2), 5.0 (m, 2, CH=CH_2), 5.65 (broad s, 1, OH), 6.08 (d, 1, J = 7.0 Hz, OCH), 7.15 (broad quintet, 1, CH), 8.2 (d, 2, J = 9.0 Hz, CH_2), and 9.0–9.9 (m, 4, cyclopropane); mass spectrum *m/e* (rel intensity), 124 (0.3), 96 (13), 58 (46), 43 (100), and 41 (10).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.19; H, 9.87.

Photolysis of 8 in Methanol.—A solution of 27 mg of **8** was photolyzed in 2.5 ml of methanol. Glpc analysis indicated the formation of **9**, **10**, **11**, and at least one of the unidentified products observed in the photolysis of **2**. Irradiation of **8** in cyclohexane gave similar results except for the absence of **9**.

1-(2-Butenyl)cyclopropanecarbonitrile.—To an ice-cold stirred solution of 62 ml of diethylamine in 80 ml of ether was added 375 ml of commercial 15% *n*-butyllithium in hexane under nitrogen. After 20 min a solution of 31 g of γ-chlorobutyronitrile in 225 ml of ether was added with cooling over 1 hr. The resulting solution was stirred at room temperature for 4 hr. To the solution of the lithium derivative of cyclopropanecarbonitrile, cooled in a methanol–ice bath, was added dropwise 181 g of crotyl chloride in 100 ml of ether. After stirring for 30 min at room temperature and 45 min under reflux, the solution was cooled, poured into water, and extracted with ether. The ether solution was washed with 1 *N* hydrochloric acid, saturated sodium bicarbonate, and water. The ethereal extract was dried and concentrated, and the residue was distilled to give 4.5 g (13%) of 1-(2-butenyl)-cyclopropanecarbonitrile: bp 73–74° (10 mm). Glpc analysis indicated two components in a 6:1 ratio.

The major component was identified as the *trans* isomer: ir 3.31, 4.50, 5.99 (*trans* RCH=CHR), 7.25, and 10.4 μ (*trans* RCH=CHR); nmr τ 4.52 (m, 2), 7.89 (broadened d, 2, J = 4.5 Hz, CH_2), 8.28 (broadened d, 3, J = 4.5 Hz, CH_3), and 9.05 (AA'BB' m, 4, cyclopropane). The second component was identified as the *cis* isomer: ir 3.31, 4.50, 6.03 (*cis* RCH=CHR), 7.30, and 13.6 μ (*cis* RCH=CHR). A microanalysis of the mixture was obtained.

Anal. Calcd for $C_8H_{11}N$: C, 79.29; H, 9.15. Found: C, 79.44; H, 9.29.

1-(2-Butenyl)cyclopropanecarboxaldehyde.—To 1.3 g of 1-(2-butenyl)cyclopropanecarbonitrile in 10 ml of ether, cooled in a methanol–ice bath under nitrogen, was added 0.34 g of lithium aluminum hydride in 30 ml of ether. The resulting solution was stirred at 5–10° for 1 hr and at room temperature for 30 min. After addition of 20 ml of 5 *N* sulfuric acid, the solution was extracted with ether. The ethereal extract was washed with two portions each of saturated sodium bicarbonate and water and dried. The ether was removed by flash evaporation to give 0.48 g of crude product. Two compounds were isolated by glpc as 82% and 18% of the reaction mixture.

The minor product was identified as *cis*-1-(2-butenyl)cyclopropanecarboxaldehyde (**10**): ir (CCl_4) 3.22, 3.29, 3.65, 5.83, 7.29 (w), and 14.7 μ (*cis* RCH=CHR); nmr τ 1.32 (s, 1), 4.7 (m, 2), 7.63 (broadened d, 2, J = 6.0 Hz, CH_2), 8.38 (broadened d, 3, J = 5.5 Hz, CH_3), and 9.05 (AA'BB' m, 4, cyclopropane); mass spectrum *m/e* (rel intensity), 124 (11), 109 (100), 95 (29), 81 (57), 67 (41), 55 (51), 54 (32), 53 (34), 41 (47), and 39 (55).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.42; H, 9.90.

The major component was identified as *trans*-1-(2-butenyl)-cyclopropanecarboxaldehyde (**12**): ir (CCl_4) 3.22, 3.31, 5.83, 7.25, and 10.3 μ (*trans* RCH=CHR); nmr τ 1.27 (s, 1), 4.60 (m, 2), 7.72 (m, 2, CH_2), 8.35 (m, 3, CH_3), and 9.05 (AA'BB' m, 4, cyclopropane); mass spectrum *m/e* (rel intensity), 124 (13), 109 (100), 95 (29), 81 (60), 79 (23), 55 (56), 54 (32), 53 (33), and 41 (33). A microanalysis of the semicarbazone derivative (mp 120–121°) of **12** prepared from the mixture of aldehydes **10** and **12** was obtained.

Anal. Calcd for $C_9H_{15}ON_3$: C, 59.65; H, 8.34; N, 23.18. Found: C, 59.63; H, 8.16; N, 22.90.

Registry No.—**1**, 5771-32-4; **2**, 2205-98-3; **3**, 22566-27-4; **4**, 22566-29-6; **5**, 22566-30-9; **6**, 22566-31-0; **7**, 22566-32-1; **8**, 22566-33-2; **10**, 22565-64-6; **11**, 22566-34-3; **12**, 22565-65-7; 1-allylcyclopropanecarbonitrile, 22566-35-4; 1-(2-butenyl)cyclopropanecarbonitrile (*trans*), 22565-66-8; 1-(2-butenyl)cyclopropanecarbonitrile (*cis*), 22576-96-1; **12** (semicarbazone), 22565-67-9.

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