Photochemistry of the *cis*- and *trans*-Bicyclo[6.1.0]nonan-2-ones[1]

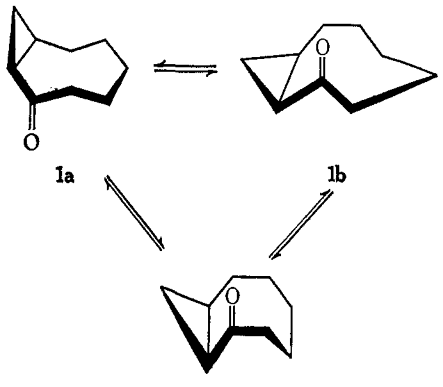
Leo A. Paquette and Richard F. Eizember

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received June 25, 1969*

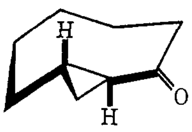
Abstract: The photochemical behavior of *cis*- and *trans*-bicyclo[6.1.0]nonan-2-ones has been found to differ significantly and to be quite solvent dependent. The *cis* isomer (**1**) was seen to undergo photoreduction in diethyl ether solution to give cyclononanone and 3-methylcyclooctanone in a ratio of 2:1. In sharp contrast, irradiation of **1** in *t*-butyl alcohol afforded 4,8-nonadienal, 2-(4-pentenyl)cyclopropanecarboxaldehyde, and *trans*-bicyclo[6.1.0]nonan-2-one (**2**). The structures of these products were established by chemical correlations. The photolysis of **2** in ether slowly gave rise to polymer; no volatile product was seen. In *t*-butyl alcohol solution, however, *t*-butyl *trans*-2-(*n*-pentyl)cyclopropanecarboxylate was produced in 50% yield. Attempts were made to determine the multiplicities of these photochemical transformations and the results are summarized. The possible role of geometric and conformational factors in controlling the differing excited state behavior of **1** and **2**, the simplest known pair of geometrically isomeric bicyclo[*n*.1.0]alkan-2-ones, is discussed.

The principal consequence of photoexcitation of cyclic conjugated cyclopropyl ketones is conversion to α,β-unsaturated ketones.[2] Studies on both the gas and liquid phase photochemistry of such cyclic ketones have indicated that, in each example of enone formation, the cyclopropyl bond which best overlaps with the carbonyl π-lobes undergoes homolytic cleavage, frequently in highly specific fashion. In their examination of the photoisomerization of bicyclo[4.1.0]heptan-2-ones, Dauben and Shaffer[2f] have noted further that α-cleavage at C_2–C_3 also can compete with cyclopropyl ring opening when C_3 is alkyl substituted. The present investigation has concerned itself with an analysis of the influence of geometric factors on the excited state properties of representative cyclic conjugated cyclopropyl ketones. We wish now to report that *cis*- (**1**) and *trans*-bicyclo[6.1.0]nonan-2-ones (**2**), the simplest known pair of geometrically isomeric bicyclo[*n*.1.0]alkan-2-ones,[3,4] exhibit significantly different photochemical behavior.

Examination of molecular models of **1** suggests that the cyclooctyl ring in this structure is conformationally mobile; however, evaluation of bond angle deformations and nonbonded steric interactions has led us to the conclusion that conformations **1a–c** are likely preferred. Similar structural considerations have shown that **2** is appreciably strained[5] and significantly more rigid. It is apparent from models of this ketone that the minimum in the potential functions for this molecule is best represented by conformer **2**. In **2**, the internal C_1–C_8 cyclopropyl bond is most suitably aligned for overlap with the π^* orbital of the carbonyl group. However, since the geometry of the reactive n → π^* excited keto group deviates only slightly, if at all, from a planar arrangement[6] and because the rigidly enforced internal angle of the C_1–C_8 and C=O bonds approaches 120°, maximization of the extent of overlap is not geometrically possible. In contrast, overlap between the carbonyl π^* orbital and a vicinal cyclopropyl bond in **1** is maximizable, but is a function of the particular conformation (**1a**–**1c**). For example, in **1a** the internal C_1–C_8 cyclopropyl bond is ideally positioned for stereoelectronic involvement with the carbonyl system; on the other hand, in **1b** and **1c** the external C_1–C_9 bond is best situated for maximum overlap with the π^* orbital. Accordingly, examination of the photochemistry of **1** and **2** was expected to permit assessment of the relative importance of these criteria.



1a **1b** **1c**



2

Photolysis of *cis*-Bicyclo[6.1.0]nonan-2-one (1). Irradiation of **1**[7] in dilute ether solution using a 450-W Hanovia lamp and Corex (absolute cutoff at 2580 Å) or Pyrex filters (absolute cutoff at 2800 Å) was followed by withdrawal of small aliquots at periodic intervals and quantitative analysis of these by vapor phase chromatography (vpc). After 2 hr, cyclononanone (**3**, 21%) and 3-methylcyclooctanone (**4**, 10%) were produced, the remainder consisting of unreacted **1** (41%) and residual polymer (~28%). The volatile products were

---

[1] The support of this research by grants from the Army Research Office (Durham) and the Petroleum Research Fund, administered by the American Chemical Society, is acknowledged with pleasure.

[2] (a) O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton, and P. Fitton, *Tetrahedron Lett.*, 2049 (1963); (b) R. Beugelmans, *Bull. Soc. Chim. France*, 3087 (1965); (c) C. H. Robinson, O. Gnoj, and F. E. Carlon, *Tetrahedron*, 21, 2509 (1965); (d) L. D. Hess and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **89**, 1973 (1967); (e) R. E. K. Winter and R. F. Lindauer, *Tetrahedron Lett.*, 2345 (1967); (f) W. G. Dauben and G. W. Shaffer, *ibid.*, 4415 (1967).

[3] C. H. DePuy and J. L. Marshall, *J. Org. Chem.*, **33**, 3326 (1968).

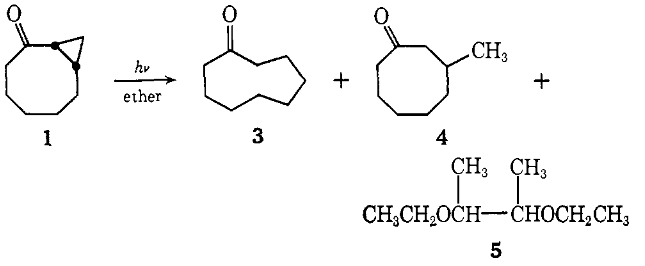
[4] K. B. Wiberg and A. deMeijere, *Tetrahedron Lett.*, 59 (1969).

[5] Wiberg and deMeijere have estimated that an enthalpy difference of 3.5 kcal/mole separates **1** from **2**.[4]

[6] E. W. Abrahamson, J. G. F. Littler, and K.-P. Vo, *J. Chem. Phys.*, 44, 4082 (1966), and references cited therein.

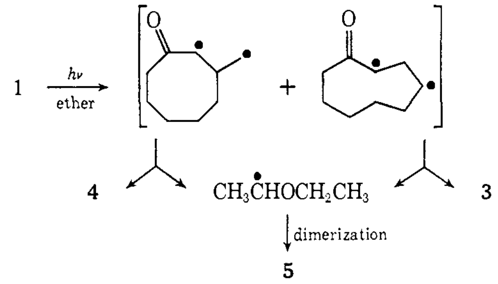
[7] The n → π^* band of 1 (hexane) is seen at 293 nm (ϵ 36).

isolated by preparative scale vpc and shown to be identical with authentic samples. Careful examination of the solvent fraction revealed the presence of **5**, in agreement with the fact that **3** and **4** are reduction products of **1**.



Evidence for the multiplicity of the rearranging species was sought in the following manner. A solution of **1** and benzophenone (E_T = 68.5 kcal/mole)[8,9] in ether was prepared in which the concentration of the sensitizer was such that it absorbed >95% of the incident radiation. Exposure of this solution to the identical light source for 5 hr resulted in the disappearance of only minor amounts of **1**: no new volatile products were detected. A like result was obtained with acetone (E_T = $\sim$80 kcal/mole)[9,10] as sensitizer. These observations suggest that either the triplet excitation energy of **1** is of the same order of magnitude as a normal aliphatic ketone ($\sim$80 kcal/mole) or the photorearrangement occurs *via* the singlet manifold of this ketone. Since measurement of the triplet energy of a typical conjugated cyclopropyl ketone has not yet been reported,[11a] the effect of such conjugation on the singlet and triplet levels of the $n \rightarrow \pi^*$ carbonyl band can only be surmised. In view of their ultraviolet spectra,[11b] however, the expectancy is that lowering of the triplet level should obtain, as seen with α,β-unsaturated ketones. Nevertheless, this conclusion is highly tentative. The photolysis of **1** was quenched by the addition of 1,3-pentadiene, but concentrations of 0.05 M or higher were required. Unfortunately, at these concentrations there existed substantial competition by the diene for the incident light under the conditions employed. Thus, it is not clear from these experiments whether singlet or triplet **1** was being quenched, particularly since quenching by high concentrations of dienes can no longer be accepted as uniquely sufficient evidence for a triplet reaction.[12] From the foregoing data the nature of the excited state species in this photoreaction does not appear subject to ready elucidation, particularly since the "fingerprint method" [13] of analysis is not applicable.

Irrespective of this fact, the mechanism of the formation of **3–5** is thought to be as shown below. Thus, both the internal and proximate external cyclopropyl bonds in **1** are cleaved, with the first pathway being preferred by a factor approximating 2:1.

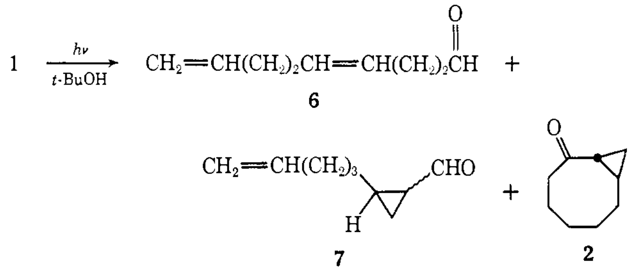


Interestingly, irradiation of **1** in dilute *t*-butyl alcohol solution takes an entirely different course to give three new products (Table I). This mixture could be separated with difficulty by preparative vpc. The products were identified in their order of elution as 4,8-nonadienal (**6**), 2-(4-pentenyl)cyclopropane carboxaldehyde (**7**), and *trans*-bicyclo[6.1.0]nonan-2-one (**2**).

Table I. Percentage Composition Ratios for the Irradiation of *cis*-Bicyclo[6.1.0]nonan-2-one (**1**) in *t*-Butyl Alcohol (Corex Optics)

	Composition, %[a]			
Time, hr	1	2	6	7
0	100			
2	79	6	Trace	4
4	60	8	2	5
6	47	10	4	4
8	41	12[b]	5	4

[a] Cyclooctane was employed as the internal standard. [b] Trace amounts of **16** began to appear after 6–8 hr irradiation (see below).



The elemental analysis of the first component indicated that this substance was isomeric with **1**. The colorless liquid exhibited pertinent infrared bands at 2710 (aldehyde CH stretch), 1735 ($>C{=}O$), and 1645 cm^{-1} ($>C{=}C<$); its ultraviolet spectrum was devoid of peaks, except for end absorption. Its nmr spectrum revealed several important points; specifically, the presence of (a) an aldehyde proton necessarily spin coupled to two α-hydrogens, (b) a terminal vinyl group in addition to two other vinyl protons, and (c) only -CH$_2$C(=O)- and allylic protons in the remainder of the structure (absence of absorption above δ 2.0) was clearly indicated. These spectral features were uniquely congruent with the 4,8-nonadienal assignment (**6**). This conclusion was reinforced by catalytic hydrogenation of **6** over 5% Pd–C which proceeded with the uptake of 2 molar equiv of hydrogen to give nonanal.

---

(8) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964); G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *ibid.*, **86**, 3197 (1964).

(9) (a) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, p 298; (b) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 132–179.

(10) R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, 44, 945 (1966).

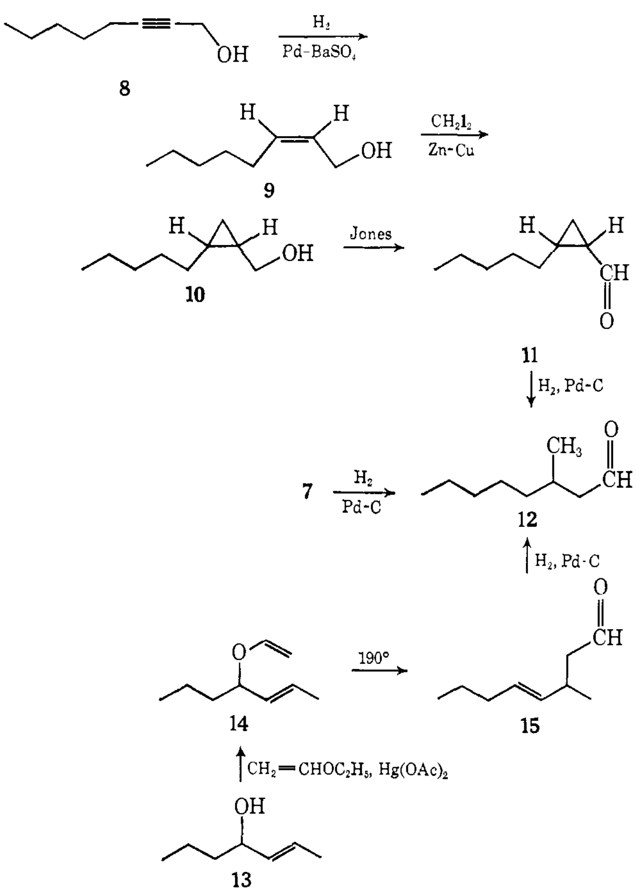
(11) (a) Some indication that the triplet energy of dicyclopropyl ketone is quite high is available from the work of D. Scharf and F. Korte [*Tetrahedron Lett.*, 821 (1963)], who report that this ketone sensitizes norbornene dimerization rather than producing an oxetane; (b) W. G. Dauben and G. H. Berezin, *J. Am. Chem. Soc.*, **89**, 3449 (1967).

(12) L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *ibid.*, **88**, 3665 (1966).

(13) H. E. Zimmerman and R. L. Morse, *ibid.*, **90**, 954 (1968).

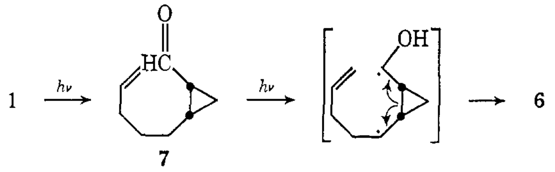
The second photoproduct was also an unsaturated aldehyde since it likewise exhibited characteristic infrared bands at 2830, 2720, 1710, and 1645 cm^{-1}. The nmr spectrum denoted that the cyclopropane ring was intact; additionally, the aldehyde proton appeared as a doublet indicating the presence of only one α-hydrogen, whereas the three vinyl protons displayed the spin–spin pattern typical of a terminal vinyl group. Catalytic hydrogenation of this colorless liquid did not give nonanal, but rather a new aldehyde which was assigned the structure 3-methyloctanal (**12**) on the basis of infrared and nmr evidence (see Experimental Section). From these considerations, it seemed that this photoproduct was cyclopropylaldehyde **7** and this structural assignment was confirmed in the manner outlined in the following scheme.

Careful catalytic reduction of 2-octynol (**8**) over 5% Pd–BaSO$_4$ with 1 mole of hydrogen afforded *cis*-2-octenol (**9**) which, under Simmons–Smith conditions, was stereospecifically[14] cyclopropanated to give alcohol **10**. Mild oxidation of **10** with Jones reagent in the cold yielded *cis*-2-*n*-pentylcyclopropanecarboxaldehyde (**11**) which upon catalytic hydrogenation afforded a product identical in all respects with that which resulted from reduction of **7**. In order to establish that this substance was indeed 3-methyloctanal (**12**), 2-hepten-4-ol (**13**) was vinylated in the presence of ethyl vinyl ether and mercuric acetate and the resulting allyl vinyl ether (**14**) was subjected to Claisen rearrangement by pyrolysis at 190°. The 3-methyl-4-octenal (**15**) so produced was hydrogenated to give authentic 3-methyloctanal (**12**) which proved to be identical in all respects with the samples isolated earlier.



The formation of *trans*-bicyclo[6.1.0]nonan-2-one (**2**) is theoretically interesting. Although *cis–trans* photoisomerization of *acyclic* cyclopropyl ketones has been noted previously,[15] the conversion of **1** to **2** is the first example to be encountered in a bicyclo[*n*.1.0]alkan-2-one. The production of **2** is necessarily a consequence either of homolytic rupture of cyclopropyl bonds C$_1$–C$_8$ or C$_1$–C$_9$, or acyl cleavage in the C$_1$–C$_2$ direction, and subsequent rebonding to produce the less stable isomer. That **2** can be isolated from this photolysis is a reflection of its slower rate of reaction under these conditions (see below).

The formation of **7** is viewed as arising from the well-known type I reaction[16] of cyclic ketones. Dienealdehyde **6** appears to be the result of a type II reaction[16] involving **7**, and finds analogy in the photoconversion of 3-methylbicyclo[4.1.0]heptan-2-one to 4,6-octadienal.[2f] In contrast to the smaller bicyclo[*n*.1.0]alkan-2-ones, therefore, α-cleavage of the C$_2$–C$_3$ bond occurs in **1** even though C$_3$ is unsubstituted.



As before, the photoreactions which take place in *t*-butyl alcohol could not be sensitized and quenching was achieved only with higher concentrations of 1,3-pentadiene. Finally, it should be mentioned that the photochemically induced transformations of **1** are very sensitive to solvent. For example, irradiation of **1** in methanol or pentane results uniquely in polymer formation; no volatile products could be detected at any stage of the irradiations.

Photolysis of *trans*-Bicyclo[6.1.0]nonan-2-one (2). It was observed that photolysis of **2**[17] in *t*-butyl alcohol with ultraviolet light of wavelength above 260 nm proceeded with less facility than **1**, but afforded a single product in 50% yield after 12 hr. The colorless liquid analyzed correctly for $C_{13}H_{24}O_2$, thus indicating that a molecule of solvent has been incorporated. On the basis of its infrared carbonyl absorption at 1715 cm^{-1} and its nmr spectrum which displayed simply a broad 15-proton multiplet at δ 0.6–1.5 and a 9-proton singlet at δ 1.45, the photoproduct was tentatively defined as the *t*-butyl ester **16**. To confirm this structural assignment, and particularly to establish the *trans* nature of the substitution on the cyclopropane ring, 1-heptene (**17**) was heated at 90° with ethyl diazoacetate in the presence of copper powder, and the resulting mixture of esters (**18**) was simultaneously equilibrated and hydrolyzed with sodium hydroxide in methanol. Exposure of this carboxylic acid to isobutylene in the presence of a small

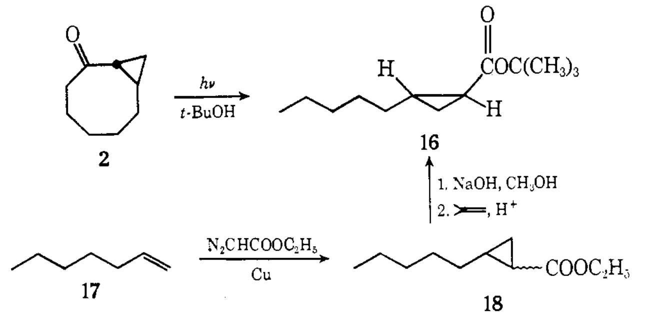
---

[14] L. A. Paquette and O. Cox, *J. Am. Chem. Soc.*, **89**, 5633 (1967); J. H.-H. Chan and B. Rickborn, *ibid.*, **90**, 6406 (1968); R. Wiechert, O. Engelfried, V. Kerb, H. Laurent, H. Miller, and G. Schultz, *Ber.*, **99**, 1118 (1966); W. G. Dauben and A. C. Ashcraft, *J. Am. Chem. Soc.*, **85**, 3673 (1963); W. G. Dauben and G. H. Berezin, *ibid.*, **85**, 968 (1963); S. Winstein and J. Sonneberg, *ibid.*, **83**, 3235 (1961).

[15] G. W. Griffin, E. J. O'Connell, and H. A. Hammond, *ibid.*, **85**, 1001 (1963); (b) H. E. Zimmerman and J. W. Wilson, *ibid.*, **86**, 4036 (1964); 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.*, 144 (1964); W. G. Brown and J. F. Neumer, *Tetrahedron*, **22**, 473 (1966).

[16] Reference 9a, pp 368–427.

[17] The n → π^* band of **2** (hexane) is seen at 286 nm (ϵ 51).



amount of sulfuric acid yielded *t*-butyl *trans*-2-(*n*-pentyl)cyclopropanecarboxylate (**16**), identical in all respects with the photoproduct.

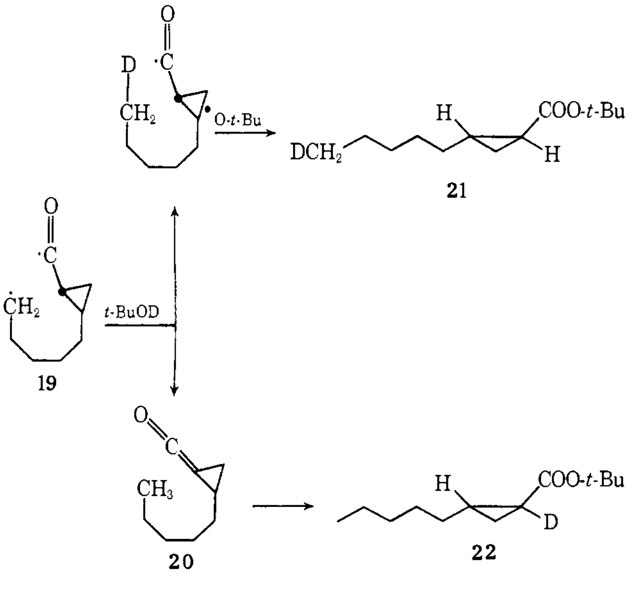
Again in this instance, the effect of 1,3-pentadiene as a possible quencher was examined. In contrast to the results obtained with **1**, however, no quenching of the formation of **16** was seen over a 20-fold concentration range (Table II). This result, in conjunction with the observation that acetone sensitization experiments were unsuccessful, suggests that a singlet mechanism is operative.

Table II. Percentage Composition Ratios for the Irradiation of *trans*-Bicyclo[6.1.0]nonan-2-one (**2**) in *t*-Butyl Alcohol (Corex Optics)

	Composition, %^{a}					
	No 1,3-pentadiene added		0.01 *M* in 1,3-pentadiene		0.2 *M* in 1,3-pentadiene	
Time, hr	**2**	**16**	**2**	**16**	**2**	**16**
0	100		100		100	
4	65	20	68	18	72	15
8	44	38	45	35	50	31
12	33	50	35	44	39	40

^{a} Cyclooctane was employed as the internal standard.

The question of the origin of **16** was investigated by photolysis of **2** in *t*-BuOD. The formation of **16** obviously necessitates α-cleavage of the C_2–C_3 bond; however, *t*-butyl ester **16** could be produced by two different reactions of the resulting diradical (**19**), one of which involves the interesting cyclopropylketene **20**. The question is whether the terminal methylene group abstracts a proton from solvent or from the remote (eight-membered transition state) α-carbonyl position. In *t*-BuOD, the two pathways would give **21** and **22**, respectively. The position of deuterium incorporation was determined in this instance by nmr spectroscopy which indicated the product to be **22**. Therefore, diradical **19** is converted to **20** despite the medium-sized nature of the requisite transition state, presumably through the operation of a solvent cage effect.



Irradiation of an ether solution of **2** in an entirely analogous manner resulted in the gradual disappearance of **2**, but only polymer was produced. Analogous observations were made in methanol and pentane solutions. Thus, the photochemical behavior of **2** is even more solvent dependent than that of **1**.

Discussion

The above experiments clearly establish that the photochemical behavior of bicyclo[6.1.0]nonan-2-ones is highly dependent on the stereochemistry of the two ketones. Furthermore, both **1** and **2** are seen to react quite differently from smaller bicyclo[*n*.1.0]alkan-2-ones, all of which have the common structural feature of an α,β-cyclopropyl carbonyl moiety.

That the conversion of **2** to **16**, an α-cleavage of the C_2–C_3 bond proceeds to the exclusion of other possible photochemical pathways is indicated by the fact that no 3-methylcyclooctanone (**4**), cyclononanone (**3**), *cis*-bicyclo[6.1.0]nonan-2-one (**2**), or lumiproducts of the latter ketone (*i.e.*, **6** and **7**) could be detected under conditions where <0.5% concentration levels could be readily observed. Therefore, we conclude that **2** shows no tendency to proceed to the less strained *cis* isomer (**1**) by a C_1–C_2, C_1–C_8, or C_1–C_9 bond rupture–recombination pathway. In contrast, *cis*-**1** does produce significant amounts of *trans*-**2** under the same conditions. Additionally, the formation of **6** and **7**, but no *t*-butyl ester comparable to **16**, reveals that **1** prefers a type I cleavage of the C_2–C_3 bond over the C_1–C_2 bond. This widely differing reactivity may be the exclusive result of conformational consequences; however, the role of geometric effects must not be underestimated. Until more data are obtained on *cis*–*trans* pairs of this type, it is perhaps most reasonable to attribute these significant differences to the combined influence of both factors.

This line of reasoning brings us to a more general point. Specifically, since it has been often demonstrated in conformationally rigid conjugated cyclopropyl ketones that π-assisted cyclopropane opening is ideally operative when a bent bond of the three-membered ring overlaps the π system of the carbonyl group, can the product distribution derived from **1** in ether solution be employed as a probe of the excited state conformations of this ketone? Unfortunately, an evaluation of this relationship is presently impeded by the paucity of examples and by the absence of sufficient information on the singlet and triplet energy levels of the compounds involved, and the like. It is important to note, however, that such considerations might in fact provide a means by which examination of excited-state conformations of medium-ring ketones could be made possible.

Experimental Section[18]

Irradiation of 1 in Ether. A solution of 2 g of **1**[3] in 450 ml of anhydrous ether was irradiated with a 450-W Hanovia mercury-vapor lamp in an immersion-well apparatus fitted with a Corex filter. The progress of the reaction was followed by withdrawal of small aliquots at periodic intervals and analysis of these by vapor phase chromatography. For quantitative work, carefully weighed amounts of **1** and cyclooctane were dissolved in ether and this solution was partitioned into several quartz test tubes which were affixed in vertical array around the immersion well. Each tube was then tightly stoppered with a serum cap which permitted the withdrawal of aliquot samples with a microsyringe.

Upon termination of the irradiation (2 hr), the solution was carefully concentrated, and the residual oil was subjected to preparative scale vpc (6 ft × 0.25 in an Al column packed with 5% SF-96 on Chromosorb G). The second substance to be eluted proved to be cyclononanone (**3**) by comparison with physical and spectral data of an authentic sample.

The first component was identified as 3-methylcyclooctanone (**4**). This ketone was synthesized independently by the addition of methylmagnesium bromide to 2-cyclooctenone in the presence of cuprous chloride.[19]

When the solvent fraction was examined gas chromatographically, the presence of **5** was detected. A small amount of this volatile substance was isolated by preparative vpc, $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 3.15–3.72 (multiplet, 6 H, >C*H*O– protons) and 1.0–1.3 (multiplet, 12 H, methyl groups).

Irradiation of 1 in *t*-Butyl Alcohol. The *cis*-ketone **1** was similarly irradiated in *t*-butyl alcohol solution. After approximately 8 hr, the solvent was carefully removed by fractional distillation, and the residual liquid was subjected to preparative scale vpc separation as above.

The first photoproduct to be eluted was subsequently shown to be 4,8-nonadienal (**6**): $\nu_{\max}^{\mathrm{neat}}$ 2710, 1735, and 1645 cm^{-1}; $\lambda_{\max}^{\mathrm{C_2H_5OH}}$ only end absorption; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 9.36 (triplet, J = ~1 Hz, aldehyde proton), 4.8–5.65 (multiplet, 5 H, vinyl protons), and 2.0–2.65 (two broad peaks, 10 H, allylic and α-carbonyl protons).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.50; H, 10.44.

The second component was subsequently shown to be 2-(4-pentenyl)cyclopropanecarboxaldehyde (**7**): $\nu_{\max}^{\mathrm{neat}}$ 2830, 2720, 1710, and 1645 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 8.95 (doublet, J = 5.0 Hz, aldehyde proton), 4.8–6.18 (multiplet, 3 H, terminal vinyl group[20]), and 1 0–1.55 (broad absorption, 11 H, methylene, allyl, and cyclopropyl protons). The 2,4-dinitrophenylhydrazone of **7** had mp 102–104°.

Anal. Calcd for $C_{15}H_{20}N_4O_4$: C, 56.24; H, 5.92. Found: C, 56.05; H, 5.92.

The third and major photoproduct proved to be identical in all respects with an authentic sample of *trans*-bicyclo[6.1.0]nonan-2-one (**2**).

***cis*-2-Octenol (9).** A solution of 1.26 g of 2-octynol (**8**) in 25 ml of hexane containing 5% palladium on barium sulfate was hydrogenated at atmospheric pressure and room temperature. After the consumption of 1 mole of hydrogen, the catalyst was removed by filtration, and the filtrate was concentrated to give 1.26 g of **9**. A pure sample of **9** was obtained by preparative vpc, $\nu_{\max}^{\mathrm{neat}}$ 3250 cm^{-1} (–OH).

Anal. Calcd for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.77; H, 12.55.

***cis*-1-Hydroxymethyl-2-*n*-pentylcyclopropane (10).** To a stirred mixture of 5 g of zinc–copper couple freshly prepared by the Shank–Shechter method,[21] 0.02 g of iodine, and 100 ml of anhydrous ether was added 8.7 g (0.05 mole) of methylene iodide. The flask was heated in the absence of atmospheric moisture until a spontaneous reaction began as evidenced by continued refluxing of the ether when the heat source was removed. Upon completion of the exothermic reaction, the mixture was refluxed for 30 min. The heat was removed and to this mixture there was added a solution of 5.42 g (0.04 mole) of **9** in 10 ml of anhydrous ether at a rate sufficient to maintain constant reflux. When the addition was completed, the mixture was refluxed for 3 hr. The flask was cooled and the mixture was filtered; the filtrate was washed with cold dilute hydrochloric acid and saturated sodium bicarbonate solution, dried, and evaporated. A pure sample of **10** was obtained by preparative vpc (5 ft × 0.25 in. Al column packed with 5% SF-96 on 60/80 Chromosorb G); $\nu_{\max}^{\mathrm{neat}}$ 3275 cm^{-1} (–OH).

Anal. Calcd for $C_9H_{18}O$: C, 75.99; H, 12.76. Found: C, 76.21; H, 13.06.

***cis*-2-Pentylcyclopropanecarboxaldehyde (11).** A solution of 256 mg (0.002 mole) of **10** in 20 ml of acetone was cooled to 0° in an ice–salt bath. To this stirred solution was added slowly 0.0022 mole of Jones reagent.[22] Upon completion of the addition, the solution was filtered and carefully concentrated; ether was added and this solution was washed with sodium bicarbonate solution, dried, and evaporated. Preparative vpc of the residue gave 100 mg (55%) of **11**, $\nu_{\max}^{\mathrm{neat}}$ 1710 cm^{-1}.

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.68; H, 11.36.

Vinylation of 2-Hepten-4-ol (13). A solution of 1.14 (0.01 mole) of **13** and 1.0 g of mercuric acetate in 60 ml of vinyl ether was heated at reflux under nitrogen for 16 hr. After cooling, the mixture was treated with 0.1 g of glacial acetic acid, stirred for 3 hr at room temperature, and diluted with an equal volume of pentane. This solution was washed with 5 ml of 5% sodium hydroxide solution, dried over anhydrous potassium carbonate, and evaporated *in vacuo*. The residual oil (1.20 g, 95%) was shown to be >95% homogeneous by vpc. A pure sample of **14** was obtained by preparative scale vpc (6 ft × 0.25 in. Al column packed with 5% Carbowax 2000M on 60/80 mesh Chromosorb G); $\nu_{\max}^{\mathrm{neat}}$ 1640 and 1190 cm^{-1}.

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.62; H, 11.82.

Claisen Rearrangement of 14. 3-Methyl-4-octenal (15). A 200-mg sample of **14** was sealed into a thick-walled Pyrex tube under a nitrogen atmosphere and the tube was heated at 180° for 3 hr. The resulting brown viscous liquid was purified by preparative vpc (6 ft × 0.25 in. Al column packed with 5% SF-96 on 60/80 mesh Chromosorb G) to give 165 mg (93%) of **15**: $\nu_{\max}^{\mathrm{neat}}$ 1715 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 9.75 (triplet, J = 2.4 Hz, 1 H, aldehyde proton), 5.35–5.6 (multiplet, 2 H, vinyl protons), and 0.80–3.0 (multiplet, 13 H, remaining protons).

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.37; H, 11.74.

3-Methyloctanal (12). A. Hydrogenation of 11. A solution of 140 mg of **11** in 25 ml of hexane was hydrogenated at atmospheric pressure over 5% palladium on charcoal. Isolation of the major component by preparative vpc (60 mg, 40%) showed this substance to be identical with 3-methyloctanal (**12**, see C).

B. Hydrogenation of 7. A solution of 40 mg (0.3 mmole) of **7** in 25 ml of purified hexane was hydrogenated as above. Work-up gave 38 mg which when purified by preparative vpc on the 5% SF-96 column afforded 26 mg (67%) of 3-methyloctanal (**12**, see C).

C. Hydrogenation of 15. A solution of 42 mg (0.3 mmole) of of **15** in 25 ml of purified hexane was hydrogenated as above. Work-up gave 38 mg (98%) of **12**: $\nu_{\max}^{\mathrm{neat}}$ 1750 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 9.80 (triplet, J = ~1 Hz, aldehyde proton), 1.8–2.4 (multiplet, 2 H, $-CH_2C(=O)-$), and 0.85–1.5 (multiplet, 15 H, remaining protons).

Anal. Calcd for $C_9H_{18}O$: C, 75.99; H, 12.76. Found: C, 76.25; H, 12.77.

Irradiation of 2 in *t*-Butyl Alcohol. A solution of 1.38 g (0.01 mole) of **2**[3] in 450 ml of dry *t*-butyl alcohol was irradiated through Corex optics in the above manner. After 12 hr, the solution was carefully concentrated and the lone photoproduct (**16**) was isolated by preparative vpc (6 ft × 0.25 in. Al column packed with 5% Carbowax 200 M on 60/80 mesh Chromosorb G): $\nu_{\max}^{\mathrm{neat}}$ 1715 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 1.45 (singlet, 9 H) and two broad multiplets centered at 1.32 and 0.88 (peak at 0.88 represents central band of methyl absorption).

Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.53; H, 11.39. Found: C, 73.70; H, 11.31.

For the deuterium labelling studies, the following analytical procedure was employed. That the protons in heavy type appeared at lower field in the δ 1.32 envelope was established by comparison with spectra of simpler model compounds. The remaining protons appear in the upfield envelope (δ 0.88). The ratio of the two sets of protons is 3:1, and this value is clearly revealed by the spectrum of the unlabeled material. Should a deuterium atom be acquired

---

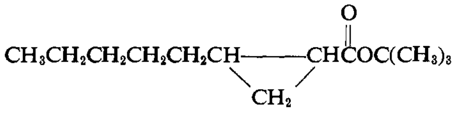
[18] The microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. The nmr spectra were recorded with Varian A-60 and A-60A spectrometers purchased with funds made available through the National Science Foundation.

[19] A. C. Cope and G. L. Woo, *J. Am. Chem. Soc.*, **85**, 3601 (1963).

[20] For representative spectra of compounds containing a terminal vinyl group, see Varian Associates, "NMR Spectra Catalog," spectra no. 134 and 298.

[21] R. S. Shank and H. Shechter, *J. Org. Chem.*, 24, 1825 (1959).

[22] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).



in the terminal methyl group, the absorption of that substituent at δ 0.88 should be greatly altered and the proton ratio should increase to 3.6:1. This was not the case. Rather, the methyl absorption was not perceptibly changed in the deuterated isomer and the proton ratio dropped to 2.7:1, in excellent agreement with the theoretical value of 2.8:1 demanded by structure **22.**

***t*-Butyl *trans*-2-(*n*-Pentyl)cyclopropanecarboxylate (16).** Ethyl diazoacetate (11.4 g, 0.1 mole) was added slowly under nitrogen to a vigorously stirred slurry of 1-heptene (14.7 g, 0.15 mole) and powdered copper metal (1.0 g, 0.015 g-atom) heated to 90°. The addition required 1.5 hr. The mixture was cooled, filtered, and fractionated. In addition to 4.1 g of recovered 1-heptene, bp 30–35° (200 mm), there was obtained 9.0 g of a clear liquid, bp 105–109° (20 mm). Vpc analysis indicated that three products had been formed, one of which predominated to the extent of 60%. This major product was secured by preparative vpc and shown to be **18**, $\nu_{\max}^{\text{neat}}$ 1715 cm^{-1}.

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.55; H, 11.03.

This crude mixture of esters (1.84 g) was added dropwise to a solution of 4 g of sodium hydroxide dissolved in 25 ml of methanol. A vigorous exothermic reaction was observed together with a color change to yellow. After stirring for 3 hr at 40°, the reaction mixture was poured onto ice-sulfuric acid and the product was extracted with ether. The combined organic layers were dried and placed in a pressure bottle. After the addition of 11 ml (*ca.* 0.2 mole) of isobutylene and 1 ml of sulfuric acid, the bottle was tightly stoppered and shaken for 12 hr at room temperature. The reaction mixture was poured into an ice-cold sodium hydroxide solution and extracted with ether. The combined organic layers were dried and evaporated. Vpc analysis indicated the presence of three components in yields of 25, 35, and 20%, respectively. The first two components proved to be unsaturated esters which were not further characterized. The third component gave spectral characteristics in excellent agreement with those expected for **16** (see above).

Quenching of Biacetyl Fluorescence and Phosphorescence[1]

Nicholas J. Turro and Robert Engel

Contribution from the Department of Chemistry, Columbia University, New York, New York 10027. *Received May 24, 1969*

Abstract: The quenching of biacetyl fluorescence and phosphorescence by alcohols, tri-*n*-butylstannane, aryl- and alkylamines, phenols, and aryl alkyl ethers has been studied in benzene and other solvents. Irreversible hydrogen abstraction appears to be the mechanism for quenching of biacetyl phosphorescence by alcohols and stannane, neither of which measurably quenches biacetyl fluorescence. Phenols quench both biacetyl fluorescence and phosphorescence but aryl alkyl ethers quench only biacetyl phosphorescence (at a rate 10^3 times slower than analogous phosphorescence quenching by phenols). Aryl- and alkylamines quench both biacetyl fluorescence and phosphorescence. The rates of phenol quenching are slower in solvents which are polar or hydrogen bonding, while the rates of quenching by amines are enhanced by increasing solvent polarity. Pyrene and acridine quench biacetyl phosphorescence (but not biacetyl fluorescence) by physical energy transfer. Mechanisms consistent with these results are discussed.

All of the previously reported photoreactions of biacetyl **1**, in solution are thought to have originated from the triplet state.[2–8] Theoretical evidence exists[9,10] and in some cases, experiments have shown[11–14] that n,π* singlet and triplet states of ketones have similar reactivities and are probably electronically similar. In the case of acetone, however, the n,π* triplet is apparently ~10^2 times more reactive toward intermolecular hydrogen abstraction from tri-*n*-butylstannane than the n,π* singlet.[15] Biacetyl, because of its relatively unique property of exhibiting phosphorescence as well as fluorescence in fluid solution at room temperature, allows the observation of both singlet and triplet quenching and direct determination and comparison of the reactivities of these two excited states. We have studied several types of quenchers and now report the quenching of biacetyl phosphorescence and fluorescence.

Experimental Section

The procedures for degassing and obtaining spectra on an Aminco–Bowman spectrophotofluorometer have been reported previously.[16] The rate constants for quenching were obtained by

---

[1] (a) Molecular Photochemistry. XVI. For paper XV, see N. J. Turro, E. Lee-Ruff, D. R. Morton, and J. M. Conia, *Tetrahedron Lett.*, 2991 (1969); we gratefully acknowledge the generous financial support of the Air Force Office of Scientific Research (Grants AFOSR-66-1000 and AFOSR-68-1381) and the National Science Foundation (Grant NSF-GP-4280). R. E. would like to thank the National Institutes of Health for a predoctoral fellowship (F1-GM-32,589). (b) For preliminary communications of this work, see N. J. Turro and R. Engel, *Mol. Photochem.*, **1**, 143, 235 (1969).

[2] H. L. J. Backstrom and K. Sandros, *Acta Chem. Scand.*, **12**, 823 (1958).

[3] K. Sandros and H. L. J. Backstrom, *ibid.*, **16**, 958 (1962); K. Sandros, *ibid.*, **18**, 2355 (1964).

[4] W. A. Urry and D. J. Trecker, *J. Amer. Chem. Soc.*, **84**, 118 (1962).

[5] P. W. Jolly and P. De Mayo, *Can. J. Chem.*, **42**, 170 (1964).

[6] J. Lemaire, *J. Phys. Chem.*, **71**, 2653 (1967); *Compt. Rend.*, *C* **267**, 33 (1968).

[7] J. Barltrop and J. A. Smith, *J. Chem. Soc.*, *B*, 227 (1968).

[8] W. G. Bentrude and K. R. Darnall, *Chem. Commun.*, 810 (1968).

[9] J. T. DuBois and H. Berens, *J. Chem. Phys.*, **48**, 2647 (1968).

[10] (a) G. W. Robinson and V. E. DiGiorgio, *Can. J. Chem.*, **36**, 31 (1958); (b) J. W. Sidman and D. S. McClure, *J. Amer. Chem. Soc.*, **77**, 6461, 6471 (1955).

[11] N. J. Turro and P. A. Wriede, *ibid.*, **90**, 6863 (1968).

[12] P. J. Wagner and G. S. Hammond, *ibid.*, **88**, 1245 (1966).

[13] N. C. Yang and S. P. Elliott, *ibid.*, **90**, 4194 (1968).

[14] J. A. Barltrop and J. D. Coyle, *Tetrahedron Lett.*, 3235 (1968).

[15] (a) P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 2503 (1967); (b) P. J. Wagner, *J. Chem. Phys.*, **45**, 2335 (1966); (c) For other examples of inertness of ketone singlets toward TBS see: K. Schaffner, *Pure Appl. Chem.*, **16**, 80 (1968).

[16] (a) N. J. Turro and R. Engel, *Mol. Photochem.*, in press; (b) N. J. Turro and R. Engel, *J. Amer. Chem. Soc.*, **90**, 2989 (1968).