

Run VI-6. *cis*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-¹⁴C (101.5 mg, 408.8 μ mol) and 4.197 g of 2,5-dimethyl-2,4-hexadiene (0.0381 mol, 1.003 *M*) irradiated at 313 m μ (1.5-m μ band width), 3.91 μ E.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (412.8 mg, 1663 μ mol) plus ¹⁴C mixture (12.2 mg, 49.1 μ mol): 4, 106 mg, 116.0–118.0°, 345.9 \pm 1.1; 412.0 μ mol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (501.8 mg, 2021 μ mol) plus ¹⁴C mixture (89.3 mg, 359.7 μ mol): 5, 56 mg, 76.0–77.0°, 1.882 \pm 0.007; 0.362 μ mole produced; ϕ = 0.086 \pm 0.009.

Run VI-7. *cis*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-¹⁴C (156.7 mg, 631.1 μ mol) and 4.166 g of 2,5-dimethyl-2,4-hexadiene (0.0378 mol, 1.399 *M*) in 27.0 ml of benzene, 194 μ E.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (432.6 mg, 1742 μ mol) plus ¹⁴C mixture (31.3 mg, 126.2 μ mol): 4, 74 mg, 116.0–118.0°, 787.4 \pm 2.5; 613.4 μ mol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (559.7 mg, 2254 μ mol) plus ¹⁴C mixture (31.3 mg, 126.2 μ mol): 4, 52 mg, 76.0–77.0°, 19.86 \pm 0.07; 18.72 μ mol produced; ϕ = 0.0966 \pm 0.0097.

3,4-Diphenylcyclohex-2-en-1-one (622.6 mg, 2507 μ mol) plus

¹⁴C mixture (94.0 mg, 378.7 μ mol): 6, 78 mg, 99.0–100.0°, 1.161 \pm 0.008; 0.430 μ mol produced; ϕ = 2.2 (\pm 0.5) \times 10⁻³.

Run VI-8. *cis*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-¹⁴C (107.7 mg, 433.8 μ mol) and 5.531 g of 1,3-cyclohexadiene (0.0691 mol, 1.816 *M*), 75.4 μ E.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (373.5 mg, 1504 μ mol) plus ¹⁴C mixture (21.5 mg, 86.8 μ mol): 4, 100 mg, 116.0–118.0°, 642.8 \pm 2.1; 426.6 μ mol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (469.0 mg, 1889 μ mol) plus ¹⁴C mixture (21.5 mg, 86.8 μ mol): 5, 26 mg, 76.0–77.0°, 8.998 \pm 0.039; 7.10 μ mol produced; ϕ = 0.0942 \pm 0.0095.

3,4-Diphenylcyclohex-2-en-1-one (451.4 mg, 1818 μ mol) plus ¹⁴C mixture (64.6 mg, 260.3 μ mol): 5, 42 mg, 99.0–100.0°, 1.028 \pm 0.008; 0.260 μ mol produced; ϕ = 3.5 (\pm 0.9) \times 10⁻³.

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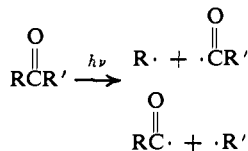
The Photochemistry of the β,γ -Cyclopropyl Ketones (-)-*cis*- and -*trans*-4-Caranone

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Contribution from the Procter & Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45239. Received January 22, 1968

Abstract: On irradiation under a variety of conditions the β,γ -cyclopropyl ketone (-)-*cis*-4-caranone (**9**) was found to undergo facile rearrangement, affording principally an approximately 3:1 mixture of cyclopentanone (**10**) and cyclobutanone (**11**) photoproducts. The cyclopentanone appeared to be a single epimer and was assigned the *trans* structure **10b**, whereas two epimeric cyclobutanones were obtained, which were assigned the *cis* and *trans* structures **11a** and **11b**, respectively. Analogous behavior was exhibited by (-)-*trans*-4-caranone (**22**). In neither case was there any detectable interconversion of the *cis* and *trans* epimers **9** and **22** during irradiation, in contrast to the previously observed photochemical epimerization of 2-methylcyclohexanones. In the presence of *t*-butylamine, an amide, assumed to be **24**, was also obtained, but in less than 1% yield. Hence the presence of the cyclopropane ring at the β,γ position facilitates type-I cleavage of the 4,5 bond to afford a cyclopropylcarbiny radical (*cf.* **12**) at the expense of cleavage toward the more highly alkyl-substituted C-3 position (*cf.* **20**). Further mechanistic implications are discussed.

One of the principal consequences of photoexcitation of aliphatic ketones is the familiar Norrish type-I homolytic cleavage of the bonds joining the carbonyl group and the α -carbon atoms.¹



Studies on both the gas and liquid phase photochemistry of bicyclic β,γ -cyclopropyl ketones, though limited in number, have indicated that in each case the major mode of decomposition is a double α cleavage leading to decarbonylation.²⁻⁴ This is il-

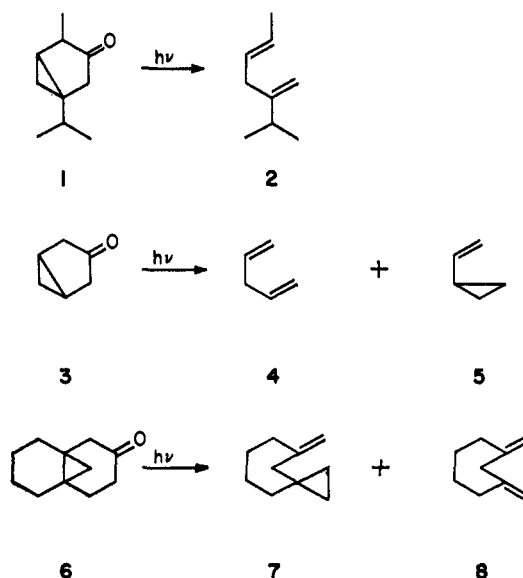
(1) See, for example, J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, pp 379–381.

(2) R. H. Eastman, J. E. Starr, R. St. Martin, and M. K. Sakata, *J. Org. Chem.*, **28**, 2162 (1963).

(3) L. D. Hess, Ph.D. Dissertation, University of California, Riverside, Calif., 1966 [*Dissertation Abstr.*, **B27**, 433 (1966)]; L. D. Hess and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **89**, 1973 (1967); see also ref 1, p 412.

(4) J. E. Starr and R. H. Eastman, *J. Org. Chem.*, **31**, 1393 (1966).

Chart I



lustrated in Chart I with the bicyclo[3.1.0]hexan-3-ones

1² and 3³ as well as the bicyclo[4.1.0]heptan-3-one 6.⁴ In the latter case decarbonylation, yielding 7, was accompanied by the apparent loss of ketene, affording 8. No product still retaining the carbonyl portion was isolated in any of these cases,⁵ suggesting that cleavage on one side of the carbonyl group is either accompanied or rapidly followed by cleavage on the other side in these systems. We wish now to report that (–)-*cis*-4-caranone (9), an analogous bicyclo[4.1.0]heptan-3-one, exhibits a significantly different pattern of photochemical behavior.

Results

As shown in Table I, irradiation of (–)-*cis*-4-caranone (9)^{6,7} under a wide variety of conditions proceeded cleanly and rapidly to give a mixture of three photoproducts which could easily be separated from unchanged *cis*-4-caranone (9) by distillation, but which could not conveniently be further separated into individual components by either distillation or gas chromatography. The rearrangement was insensitive to change of solvent and gave the same products in a similar ratio with ultraviolet sources emitting at 2537 or 3100–4100 Å or with the broad spectrum of a medium-pressure mercury lamp.

Table I. Irradiation of (–)-*cis*-4-Caranone (9)^a

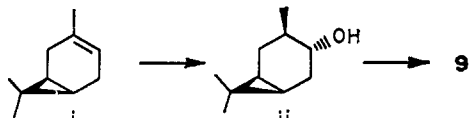
Reaction vessel	Solvent	Uv source	Yield, %	
			10b, 11a, 11b	9
Vycor	C ₆ H ₆	200 W ^b	52	17
Vycor	<i>n</i> -C ₆ H ₁₄	200 W	43	17
Vycor	CH ₃ COCH ₃	200 W	9	85
			22 ^c	65 ^c
Vycor	<i>n</i> -C ₆ H ₁₄	200 W	38	13 ^d
	<i>t</i> -C ₄ H ₉ NH ₂			
Quartz	C ₆ H ₆	2537 Å ^e	26	62
			43 ^c	36 ^c
Quartz	<i>n</i> -C ₆ H ₁₄	2537 Å	34	53
			46 ^c	27 ^c
Quartz	<i>t</i> -C ₄ H ₉ OH	2537 Å	19	60
Pyrex	C ₆ H ₆	3500 Å ^f	17 ^g	74 ^g

^a One-hour irradiation period. The exact conditions for these irradiations can be found in the Experimental Section. ^b Hanovia S-654A lamp. ^c Two-hour irradiation period. ^d Under these conditions, less than 1% of the amide 24 was formed. ^e Circular array of 16 Rayonet RPR 2537 lamps. ^f Circular array of 16 Rayonet RPR 3500 lamps emitting at 3100–4100 Å. ^g Ten-hour irradiation period.

Elemental and mass spectral analyses of the mixture showed the products to be isomeric with *cis*-4-caranone (9), but the nmr spectrum suggested that the cyclopropane ring was no longer present. The appearance of a three-proton ABX pattern in the vinyl

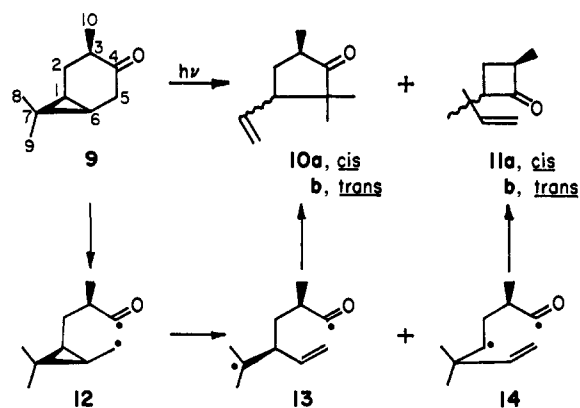
(5) However, it is reported that an infrared spectrum of the crude photoproduct from 6 suggested the presence of an unidentified and unisolated cyclobutanone.⁴

(6) Prepared by the hydroboration of (+)-3-carene (i) followed by Jones oxidation⁷ of the resulting (–)-*cis*-4 α -caranol (ii) as described by (a) W. Cocker, P. V. R. Shannon, and P. A. Staniland, *J. Chem. Soc.*, C, 485 (1967), and references contained therein, as well as (b) H. C. Brown and A. Suzuki, *J. Amer. Chem. Soc.*, **89**, 1933 (1967).



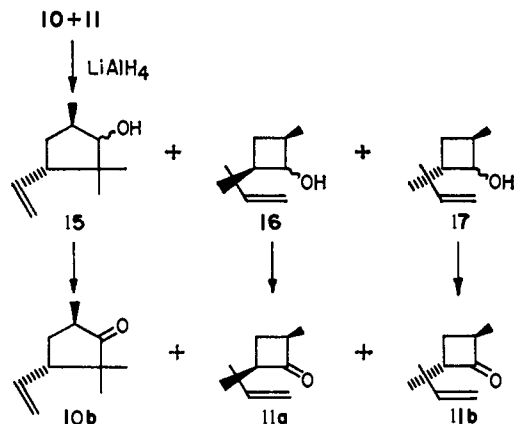
(7) K. Bowden, I. M. Heilbron, E. H. R. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

region (τ 4–5) clearly indicated the presence of a monosubstituted double bond, a fact corroborated by the absorption of 1 molar equiv of hydrogen on catalytic hydrogenation. The infrared spectrum of the mixture showed absorptions at 5.62 and 5.74 μ , which are characteristic of cyclobutanone and cyclopentanone chromophores, respectively.



On the basis of the mechanistic reasoning outlined below, several modes of rearrangement might be expected for *cis*-4-caranone (9). Homolytic cleavage of the bond "allylic" to the cyclopropane ring would produce the diradical 12, which could further rearrange to either of the two homoallylic species 13 and 14 as illustrated, depending upon which cyclopropyl bond participated. Ring closure of the diradicals would give the structures 10 and 11, which are completely consistent with the spectral data of the observed mixture of photoproducts.

Since the mixture of photoproducts could not easily be resolved by gas chromatography, separation was facilitated *via* lithium aluminum hydride reduction to the corresponding alcohols, which were readily separated by preparative gas chromatography into three components. Isolation of the principal component followed by oxidation according to the Jones procedure⁷ afforded one pure ketone isomeric with 9 and having a cyclopentanone absorption at 5.74 μ . As was observed for the unresolved mixture of photoproducts, the nmr spectrum of the cyclopentanone

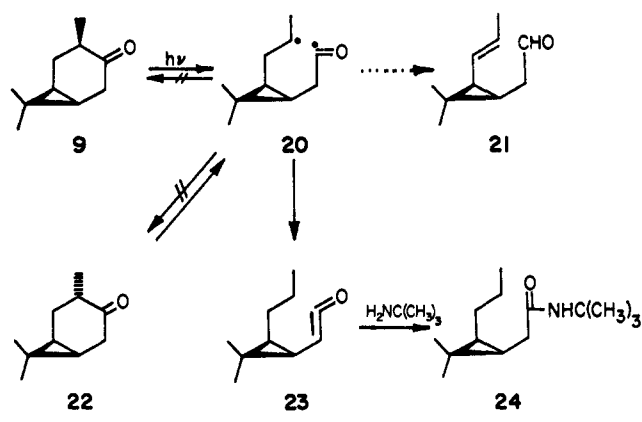


showed a three-proton ABX pattern in the vinyl region (τ 4–5) with the low-field proton being further coupled as expected for the partial structure $>CHCH=CH_2$. Also observed were two methyl singlets at τ 9.00 and 9.18 and one methyl doublet ($J = 8$ Hz) centered at τ 8.91. The assignment of the structure 2,2,5-tri-

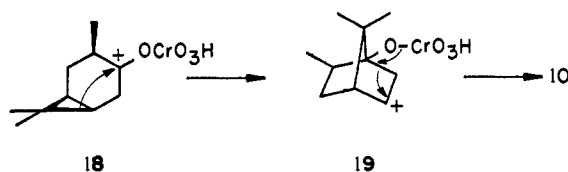
methyl-3-vinylcyclopentanone (**10**) to the major photoproduct is completely consistent with these data. Since there is no stereochemical change involved at either C-1 or -3 in the formation of the diradical **13**, closure should lead only to the *trans* epimer **10b**.⁸

The two minor components from the lithium aluminum hydride reduction of the photoproduct mixture were the cyclobutanols **16** and **17**, as shown by their reversion to two different cyclobutanones on oxidation. On the basis of the mechanistic reasoning outlined above, these cyclobutanones should have the structures **11a** and **b**. Support for these structural assignments can be found in the infrared spectra, which exhibited the characteristic cyclobutanone absorption at 5.62 μ , and in the nmr spectra. In both cyclobutanones a clean ABX pattern in the vinyl region (τ 4-5) of the nmr spectrum indicated the presence of a $-\text{CR}_2\text{CH}=\text{CH}_2$ grouping. At high field both compounds showed two methyl singlets and one methyl doublet. Unfortunately the couplings of the ring protons were sufficiently complex that unequivocal *cis* and *trans* assignments were precluded. However, since rearrangement through **14** involves a loss in stereochemical integrity at C-1, but not C-3, it can be expected that both the *cis* and *trans* isomers **11a** and **b** would be generated. This is consistent with the formation of two cyclobutanone photoproducts.

A second Norrish type-I cleavage toward the more highly substituted position, leading to the diradical **20**,



(8) It is interesting to note that in the preparation of *cis*-4-caranone (**9**) as described in ref 6, oxidation of *cis*-4 α -caranol (ii) afforded, in addition to **9**, a cyclopentanone in 0-7% yield which had a retention time on several gas chromatographic columns and infrared and nmr spectra identical with those of the major photoproduct **10b**, with the exception that the C-5 methyl appeared in the nmr spectrum as a pair of doublets. These data suggested the presence of a 1:4 mixture of the *cis* and *trans* epimers **10a** and **10b**. The cyclopentanone is apparently formed during the oxidation process, since there was no detectable amount of the cyclopentanol **15** present in the hydroboration product. Attempts to generate **10** by oxidation of *cis*-4 α -caranol (ii) with chromium trioxide-pyridine⁹ or by treatment of *cis*-4-caranone (**9**) with acid were fruitless. The mechanism of the formation of **10** is not clear, although one possibility is that illustrated below. It is possible that both the



cyclopentanone **10b** and the cyclobutanone **11a** could be formed photochemically by a somewhat similar rearrangement; however, this would not account for the formation of the *trans*-cyclobutanone **11b**.

(9) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Amer. Chem. Soc.*, **75**, 422 (1953).

might also be expected in the photochemistry of **9**. Such cleavages of α -substituted cycloalkanones are usually reversible and lead to epimerization at the α position,¹⁰ which in the case of **9** would afford the *trans* isomer **22**. Usually competing with epimerization are two hydrogen-transfer processes leading, on one hand, to an unsaturated aldehyde (*cf.* **21**) and, on the other, to a ketene (*cf.* **23**).¹¹ In actual fact, no evidence for epimerization to **22** or formation of aldehyde **21** could be found.

Irradiation of *cis*-4-caranone (**9**) in the presence of *t*-butylamine until one-half of **9** had been consumed afforded a crude product for which the infrared spectrum revealed the presence of unchanged **9**, the ketones **10b**, **11a**, and **11b**, and an amide exhibiting an absorption at 6.05 μ . Gas chromatography showed that the mixture was composed of about 30% of the photoproducts **10** and **11** and 50% of unchanged **9**. There was no evidence for *trans*-4-caranone (**22**) which could have been detected in <2% yield. To show that a photoequilibrium between **9** and **22** which highly favored **9** did not exist, the pure *trans* epimer **22**¹² was irradiated under identical conditions. Only the *trans* epimer, along with the photoproducts **10a**¹³ and **11** and an amide, was detected in the reaction mixture. Once again neither **21** nor any other aldehydic product could be detected.

The amide formed in the above irradiations was recovered in less than 1% yield by preparative gas chromatography. The structure **24** is tentatively assigned on the basis of the infrared spectrum, λ_{max} 2.98 and 6.05 μ , and the mass spectrum (m/e 225.2093, indicative of a $\text{C}_{14}\text{H}_{27}\text{ON}$ composition, combined with the characteristic amide fragmentation pattern).

Quenching and Sensitization Studies. As can be seen in Table I, the rearrangement of *cis*-4-caranone (**9**) using the broad emission of a 200-W mercury lamp proceeded with approximately equal facility in either benzene or hexane. Rearrangement on irradiation with a 2537- \AA mercury lamp also proceeded at nearly equal rates in benzene or hexane. Under these latter conditions 4-caranone is calculated to absorb less than 0.01% of the incident light in benzene solutions, suggesting that the reaction proceeds in this case *via* a transfer of energy from benzene to 4-caranone. However, since benzene has low-lying singlet and triplet states at 112 and 85 kcal/mol, respectively, and alicyclic ketones normally have singlet and triplet levels at approximately 102 and 79 kcal/mol, respectively, it is not immediately obvious whether singlet or triplet energy transfer has occurred.

In order to delineate further the multiplicity of the rearrangement, quenching experiments were devised (Table II). Rearrangement was quenched by the addition of 1,3-pentadiene, but concentrations of 20% (w/v) or higher were required. Irradiation of 4-

(10) R. L. Alumbaugh, G. O. Pritchard, and B. Rickborn, *J. Phys. Chem.*, **69**, 3225 (1965).

(11) See ref 1, pp 389-391.

(12) Pure *trans*-4-caranone (**22**) was isolated by preparative gas chromatography from the mixture of epimers obtained by the method of P. J. Kropp, *J. Amer. Chem. Soc.*, **88**, 4926 (1966).

(13) Although physical data indicated that epimeric cyclopentanone photoproducts **10** were obtained from *cis*- and *trans*-4-caranone, the *trans* (**10b**) and *cis* (**10a**) assignments, respectively, are based purely on mechanistic arguments. Attempts to establish these assignments chemically were thwarted by the difficulty in separating the cyclobutanone and cyclopentanone photoproducts.

caranone with similar concentrations of 1,3-cyclohexadiene¹⁴ quenched the rearrangement with concomitant formation of cyclohexadiene dimers.¹⁵ This latter result indicates that a triplet mechanism is involved.¹⁶

Table II. Quenching and Sensitization Studies^a

Re-action vessel	Uv source	Solvent	Time, hr	Sensitizer (quencher)	Yield, %	
					10b, 11a, 11b	9
Pyrex	3500 Å ^b	C ₆ H ₆	10	...	17	74
Pyrex	3500 Å	C ₆ H ₆	10	Acetophenone	5 ^c	90
Pyrex	3500 Å	C ₆ H ₆	10	Xanthone	0 ^d	100
Quartz	2537 Å ^e	C ₆ H ₆	2	C ₆ H ₆	43	36
Quartz	2537 Å	<i>n</i> -C ₆ H ₁₄	2	...	46	27
Vycor	200 W ^f	<i>n</i> -C ₆ H ₁₄	1	1,3-Pentadiene ^g	19	60
Corex	200 W	<i>n</i> -C ₆ H ₁₄	10	1,3-Cyclohexadiene ^h	0	100

^a The exact conditions for these irradiations can be found in the Experimental Section. ^b A circular array of 16 Rayonet RPR lamps emitting at 3100–4100 Å. ^c This rearrangement apparently reflects the absorption of up to 20% of the incident radiation in the 3500-Å region by 4-caranone. ^d Under these conditions xanthone absorbs greater than 99% of the incident radiation. ^e A circular array of 16 Rayonet RPR 2537 lamps. ^f Hanovia S-654 lamp. ^g 200 mol %. ^h 20% by weight; under these conditions the cyclohexadiene dimers were formed.

Attempts to promote the rearrangement with sensitizers having triplet excitation energies lower than benzene, such as xanthone and acetophenone ($E_T = 74$ kcal/mol¹⁷) were unsuccessful (see Table II). This suggests that the triplet energy of *cis*-4-caranone (**9**) is of the same order of magnitude as a normal aliphatic ketone (~79 kcal/mol). This result combined with the normal n, π^* absorption by *cis*-4-caranone (λ_{max} 288 $m\mu$, ϵ 24) provides no evidence for homoconjugation of the ketone and cyclopropyl moieties.¹⁸

Discussion

From the foregoing data it is clear that the photochemical behavior of *cis*- and *trans*-4-caranone is quite different from that previously observed for other β, γ -cyclopropyl ketones or 1-methylcyclohexanones, the two structural moieties of which **9** and **22** are constructed. Contrary to the previously observed pattern for the β, γ -cyclopropyl ketones **2–4** is the failure of decarbonylation to play a significant role, if indeed it occurs at all. Likewise, the failure of **9** and **22** to undergo epimerization at C-3 indicates that type-I cleavage of the C₃–C₄ bond either does not occur or

(14) Under these conditions the 4-caranone absorbed 50–75% of the incident radiation between 3000 and 3500 Å.

(15) D. Valentine, N. J. Turro, Jr., and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 5202 (1964).

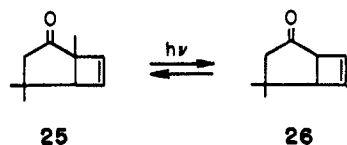
(16) Although the dimer formation at low concentrations of 1,3-cyclohexadiene is apparently specific for triplet quenching, it is not clear from these experiments whether or not singlet 4-caranone is also being quenched. Hammond has shown that singlet quenching of aromatic hydrocarbons can occur with high concentrations of added dienes: see L. M. Stevenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *ibid.*, **88**, 3665 (1966).

(17) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *ibid.*, **86**, 4537 (1964).

(18) This is in contrast to the recent conclusion of Brown and Suzuki, who interpreted the ORD spectra of (–)-*cis*- and (–)-*trans*-4-caranone in terms of homoconjugation of the cyclopropyl and carbonyl moieties.¹⁸

does so irreversibly. The formation of amide **24** indicates that this type of cleavage does in fact occur, but the low yield of amide and the lack of other detectable products such as the aldehyde **21** suggest that this is not an important mode of reaction.

In a formal sense, the photochemical behavior of the 4-caranones more closely resembles the allylic rearrangement of bicyclic β, γ -unsaturated ketones which was first noted by Büchi and Burgess¹⁹ in the rearrangement of **25** to **26** and has since been encountered in numerous other systems.²⁰ It is, to the best of our



knowledge, the first example involving a cyclopropyl analog. However, in the case of β, γ -unsaturated ketones the reaction is reversible, and a photostationary equilibrium is established, whereas with the 4-caranones rearrangement to **10** and **11** is apparently irreversible since prolonged irradiation of **10b** produced neither **9** nor **11**.

In a manner analogous to the β, γ -unsaturated ketone photolyses, the direction of α cleavage is affected by the cyclopropane ring, apparently by a weakening of the 4,5 bond "allylic" to the cyclopropane moiety by either conjugative or inductive effects.²¹ Participation of either the 1,6 or the 6,7 bond of the cyclopropane ring follows, favoring cleavage of the more highly substituted 6,7 bond. The observed 3:1 ratio of cyclopentanone to cyclobutanones apparently reflects this ease of cleavage of the more highly substituted bond and the inherent stability of the resulting tertiary and secondary radicals, respectively.

In the case of β, γ -unsaturated ketones it has been proposed that the rearrangement is a concerted process.¹⁹ That the conversion of the 4-caranones to **10** and **11** cannot be an over-all concerted process, at least in the case of the cyclobutanone products, is indicated by the formation of the two epimeric cyclobutanones **11a** and **11b**. In order for both *cis* and *trans* isomers to arise in the cyclobutanone photoproduct, the development of radical character at C-1 in the intermediate **14** must occur to such a degree that this center loses its asymmetry. The diradical **13**, on the other hand, retains asymmetry at C-1 and can lead only to the *trans*-cyclopentanone **10b**.²²

(19) G. Büchi and E. M. Burgess, *ibid.*, **82**, 4333 (1960).

(20) See for example (a) D. I. Schuster, M. Axelrod, and J. Auerbach, *Tetrahedron Lett.*, 1911 (1963); (b) R. Criegee and H. Furrer, *Chem. Ber.*, **97**, 2949 (1964); (c) P. E. Eaton, *Tetrahedron Lett.*, 3695 (1964); (d) D. I. Schuster, F. H. Lee, A. Padwa, and P. G. Gassman, *J. Org. Chem.*, **30**, 3647 (1965); (e) D. E. Bays and R. C. Cookson, *J. Chem. Soc., B*, 226 (1967); (f) J. Ciabattini, J. E. Crowley, and A. S. Kende, *J. Amer. Chem. Soc.*, **89**, 2778 (1967); (g) W. F. Ergan and H. C. Kretschmar, *ibid.*, **89**, 3842 (1967); (h) L. A. Paquette and R. F. Eizember, *ibid.*, **89**, 6205 (1967); (i) J. K. Crandall, J. P. Arrington, and J. Hen, *ibid.*, **89**, 6208 (1967); (j) R. G. Carlson and J. H. Bateman, *Tetrahedron Lett.*, 4151 (1967).

(21) See, for example, W. G. Dauben and G. H. Berezin, *J. Amer. Chem. Soc.*, **89**, 3449 (1967), and references contained therein.

(22) It is conceivable that with loss of asymmetry at C-1, the diradical **14** could reversibly form **iii** which could, in turn, either close to give (+)-*trans*-4-caranone (iv) or, through v, lead to the *cis*-cyclopentanone **10a**. The fact that only one cyclopentanone is formed, combined with the absence of epimerized 4-caranone in the irradiation mixtures,

Although the rearrangement of the 4-caranones to **10** and **11** bears a formal analogy to the behavior of β,γ -unsaturated ketones as exemplified by **25** \rightleftharpoons **26**, a number of important mechanistic differences between the two reactions are apparent. A number of questions also remain concerning both the generality of this type of behavior for β,γ -cyclopropyl ketones and the possible effects of geometry and degree of substitution of the cyclopropyl ring on the rearrangement. The answers to these questions must await further study.

Experimental Section²³

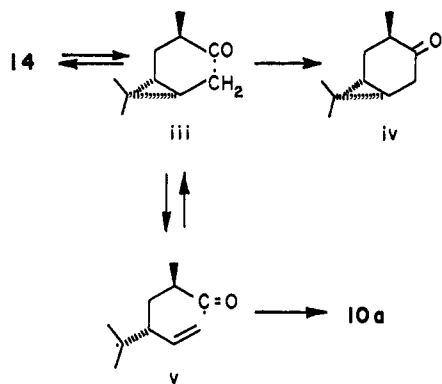
Irradiation of (-)-cis-4-Caranone (9). **A. In Benzene with a Broad Spectrum Lamp.** A solution containing 5.01 g of (-)-*cis*-4-caranone (**9**)⁶ in 150 ml of benzene was placed in a previously described Vycor photochemical reaction vessel²⁴ of 150-ml capacity. The solution was agitated by means of a continuous nitrogen flush and irradiated for 2.25 hr with a Hanovia 200-W high-pressure mercury arc lamp. The benzene was then removed by distillation at atmospheric pressure, and the residue was fractionated on a 12-in. spinning-band column to yield 2.62 g (52%) of a mixture of three ketones isomeric with 4-caranone, bp 75–80° (9.5 mm). Further purification by preparative gas chromatography and short-path distillation gave a mixture of the ketones **10b**, **11a**, and **11b**: bp 50° (0.6 mm); λ_{\max} 3.17, 5.62, 5.74, and 6.10 μ ; nmr spectrum, τ 4.0–4.4 (m, 1, vinyl CH) and 4.8–5.0 (m, 2, vinyl CH₂).²⁵
Anal. Calcd for C₁₀H₁₆O: C, 78.89; H, 10.59. Found: C, 78.79; H, 10.77.

A second fraction of the initial distillation yielded 0.87 g (17%) of a colorless liquid, bp 81–86° (7.6 mm), which had nmr and infrared spectra identical with that of authentic (-)-*cis*-4-caranone (**9**). Using gas chromatography conditions under which (-)-*trans*-4-caranone (**22**) could have been detected in less than 2% yield, the product was completely homogeneous, showing no indication of the other isomer of 4-caranone.

B. Irradiation in Acetone with a Broad Spectrum Lamp. A solution of 1.01 g of (-)-*cis*-4-caranone (**9**) in 150 ml of acetone was irradiated as in A. After 1 and 2 hr, aliquots were withdrawn and shown by quantitative gas chromatography to contain, respectively, 9 and 22% of the photoproducts **10b**, **11a**, and **11b** and 65% of **9**.

C. Irradiation in *n*-Hexane with a Broad Spectrum Lamp. A solution of 1.00 g of (-)-*cis*-4-caranone (**9**) in 150 ml of *n*-hexane

suggests that the opening of the cyclopropane ring to form **14** is an irreversible process and that iii and v are not produced.



(23) Optical rotations were measured in absolute ethanol, and infrared spectra were obtained on neat samples with a Perkin-Elmer Infracord spectrophotometer. Gas chromatographic analyses were performed on an Aerograph Model 202B or A-90P instrument using 10 ft \times 0.25 in. columns packed with 20% diethylene glycol succinate or 20% Carbowax 20M on 60–80 mesh Chromosorb W. Nuclear magnetic resonance spectra were determined in deuterated chloroform solution with a Varian Model HA-100 spectrometer, using tetramethylsilane as an internal standard. Mass spectra were determined using an Atlas Model CH-4 or SM-1 spectrometer. Microanalyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich.

(24) P. J. Kropp and W. F. Erman, *J. Amer. Chem. Soc.*, **85**, 2456 (1963).

(25) Indicates multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; and m, multiplet), integration, coupling constant if appropriate, and assignment.

was irradiated as in A. After 1 hr the solution was shown by quantitative gas chromatography to contain 43% of the mixture **10b**, **11a**, and **11b** and 17% of unchanged **9**.

D. Irradiation in *n*-Hexane at 2537 Å. A solution of 0.50 g of (-)-*cis*-4-caranone (**9**) in 75 ml of *n*-hexane was irradiated in a quartz flask with a circular array of 16 Rayonet RPR 2537 lamps. After 1 and 2 hr, aliquots were removed and were shown by quantitative gas chromatography to contain, respectively, 34 and 46% of the photoproducts **10b**, **11a**, and **11b** and 53 and 27% of **9**.

E. Irradiation in *t*-Butyl Alcohol at 2537 Å. A solution of 0.51 g of **9** in 75 ml of *t*-butyl alcohol was irradiated as in D for 1 hr. Quantitative gas chromatography of the resulting product showed it to be composed of 19% of the photoproducts **10**, **11a**, and **11b** and 60% of recovered **9**.

F. Irradiation in Benzene at 2537 Å. A solution containing 1.00 g of (-)-*cis*-4-caranone (**9**) in 150 ml of benzene was irradiated in a quartz flask placed in the center of a circular array of 16 Rayonet RPR 2537 lamps. After 1 and 2 hr, aliquots were taken and shown by quantitative gas chromatography to contain 26 and 43% of the mixture of **10b**, **11a**, and **11b**, and 62 and 36% of recovered **9**, respectively.

G. Irradiation in Benzene at 3500 Å. A solution containing 0.41 g of **9**, in 120 ml of benzene was irradiated in a Pyrex flask placed in the center of a circular array of Rayonet 3500 lamps, which emit in the 3100–4100-Å region. After 10 hr the solvent was removed and the remaining oil was shown by gas chromatography to contain 17% of the mixture of **10b**, **11a**, and **11b**, and 74% of **9**.

H. Irradiation with Added Acetophenone at 3500 Å. A solution of 0.51 g of (-)-*cis*-4-caranone (**9**) and 0.06 g of acetophenone in 120 ml of benzene was irradiated for 10 hr as described above in C. Gas chromatographic analysis of the product showed 5% of the mixture of **10b**, **11a**, and **11b** along with 90% of unchanged **9**.

I. Irradiation with Added Xanthone at 3500 Å. A solution of 0.50 g of **9** and 0.06 g of xanthone in 150 ml of benzene was irradiated as described above in C. After an irradiation period of 10 hr, gas chromatography showed the product to be composed solely of unchanged **9**.

J. Irradiation in Vycor with Added 1,3-Pentadiene. A solution of 1.00 g of **9** and 0.89 g of 1,3-pentadiene in 120 ml of *n*-hexane was irradiated in a Vycor vessel for 1 hr with a 200-W Hanovia S-654A lamp. Gas chromatographic analysis of the solution showed 19% of the ketones **10b**, **11a**, and **11b**, and 60% of recovered **9**.

K. Irradiation in Corex with Added 1,3-Cyclohexadiene. A solution of 0.51 g of **9** and 4.25 g of 1,3-cyclohexadiene in 20 ml of *n*-hexane was placed in a quartz flask and suspended 3 in. from a 200-W Hanovia S-654A lamp fitted with a Corex filter. Under these conditions, the *cis*-4-caranone absorbed 50–75% of the incident radiation between 3000 and 3500 Å. The solution was irradiated for 10 hr and the solvent was removed. Gas chromatographic analysis of the product showed only unchanged **9** and the cyclohexadiene dimers.¹⁶ Under identical conditions, but without the cyclohexadiene, **9** was rearranged with the formation of 20% of the photoproducts **10b**, **11a**, **11b**.

L. Irradiation with Added *t*-Butylamine. A solution of 1.01 g of **9** and 2.66 g of *t*-butylamine in 150 ml of *n*-hexane was irradiated in a Vycor vessel using a 200-W Hanovia S-654A lamp. After 1 hr the solvent was removed and the remaining oil was shown by gas chromatography to contain 38% of the mixture of ketones **10b**, **11a**, and **11b**, and 13% of unchanged **9**. The products from a number of such runs were combined and the ketones **10b**, **11a**, and **11b** and **9** were removed by distillation at reduced pressure. The residue was chromatographed on a 2 ft \times 0.25 in. column containing 1% SE-30–1% XE-60 on 60–80 Chromosorb W to yield less than 1% of an amide tentatively assigned the structure **24**, λ_{\max} 2.98 and 6.05 μ ; *m/e* 225.2092 (calcd for C₁₄H₂₇NO: 225–2093), 210, 196, 182, 168, 152, and 137.

M. Control Run. Cyclopentanone 10. A solution containing 528 mg of cyclopentanone **10** (obtained from oxidation of (-)-4-caranol by the Jones procedure as described below) in 150 ml of benzene was irradiated for 1 hr in a Vycor apparatus with a 200-W mercury lamp as described above in A. Infrared and gas chromatographic analysis of the colorless liquid obtained by removal of the solvent indicated that no change had occurred; there was no detectable amount of *cis*- or *trans*-4-caranone or of the cyclobutanones **11**.

Hydrogenation of the Mixture of Ketones 10 and 11. A solution containing 61 mg of the mixture of ketones **10** and **11** obtained by irradiation of (-)-*cis*-4-caranone (**9**) as described in A above was

stirred over 10 mg of 10% palladium on charcoal in an atmosphere of hydrogen. Absorption ceased with 1.1 mol equiv. Filtration followed by removal of the solvent by distillation afforded 68 mg of a colorless liquid. Further purification by gas chromatography followed by short-path distillation at 78° (5.0 mm) afforded the mixture of dihydro derivatives as a colorless liquid, λ_{\max} 5.66 (m) and 5.76 μ (s).

Anal. Calcd for $C_{10}H_{16}O$: C, 77.86; H, 11.76. Found: C, 77.71; H, 11.76.

Reduction of Photoproduct Mixture. To 1.40 g of lithium aluminum hydride in 60 ml of anhydrous ether was added 1.87 g of the mixture of ketones obtained from the irradiation of **9**. The mixture was stirred overnight at 25°. After the dropwise addition of 5.6 ml of water, the mixture was stirred for 0.5 hr, and filtered, and the inorganic solids were washed with several 50-ml portions of ether. The filtrate was dried over anhydrous magnesium sulfate and distilled to yield 1.73 g (91%) of a clear liquid, bp 81–89° (10 mm). Gas chromatography showed the mixture to be composed of three components present to the extent of 9, 15, and 75%, respectively.

Isolation of the first component by gas chromatography followed by short-path distillation gave one epimer of the cyclobutanol (**16** or **17**): bp 60–62° (1.5 mm); $[\alpha]^{27D} -17^\circ$ (*c* 1.29); λ_{\max} 2.82, 3.23, and 6.11 μ ; nmr spectrum, τ 3.87 (q, 1, *J* = 11 and 18 Hz, CH-3'), 5.00 (m, 2, CH-4'), 5.64 (m, 1, CH-1), 8.91 and 9.01 (2s, 6, 2CH₃-2'), and 9.05 (d, 3, *J* = 6 Hz, CH₃-4).

Anal. Calcd for $C_{10}H_{16}O$: C, 77.86; H, 11.76. Found: C, 77.64; H, 11.81.

Gas chromatographic separation of the second peak followed by short-path distillation yielded a second cyclobutanol epimer (**16** or **17**): bp 67–71° (2.1 mm); $[\alpha]^{27D} -32^\circ$ (*c* 1.54); λ_{\max} 2.88, 3.21, and 6.11 μ ; nmr spectrum, τ 3.86 (q, 1, *J* = 10.5 and 17.5 Hz, CH-3'), 4.95 (m, 2, CH₂-4'), 6.05 (t, 1, *J* = 7 Hz, CH-1), 8.84 and 8.93 (2s, 6, 2CH₃-2'), and ~9.0 (d, obscured by the two 2' methyls, CH₃-1).

Anal. Calcd for $C_{10}H_{16}O$: C, 77.86; H, 11.76. Found: C, 77.78; H, 11.68.

Purification of the last peak by preparative gas chromatography followed by short-path distillation yielded 2,2,5-trimethyl-3-vinylcyclopentanol (**15**): bp 73° (2.1 mm); $[\alpha]^{27D} -23^\circ$ (*c* 1.28); λ_{\max} 2.94, 3.23, and 6.11 μ ; nmr spectrum, τ 4.28 (m, 1, CH-1'), 5.07 (m, 2, CH₂-2'), 6.88 (d, 1, *J* = 8 Hz, CH-1), 8.90 (d, 3, *J* = 6 Hz, CH₃-5), and 9.05 and 9.30 (2s, 6, 2CH₃-2).

Anal. Calcd for $C_{10}H_{16}O$: C, 77.86; H, 11.76. Found: C, 77.56; H, 11.81.

Oxidation of alcohols **15**, **16**, and **17** was carried out in each case by dissolving the alcohol in 20 times its weight of acetone and cooling the solution to 0°. Chromic acid (4 *N*, 1 equiv) prepared according to the method of Jones⁷ was added dropwise to the stirred solution. The resulting mixture was diluted to twice its volume with ether, decanted from the inorganic residues, and dried over magnesium sulfate. The solvent was removed at atmospheric pressure leaving a colorless liquid. In each case only one component was present in the oxidation product.

Oxidation of the first cyclobutanol according to the above method, purification of the resulting oil by preparative gas chromatography, and short-path distillation yielded **11a** (or **b**) as a colorless liquid: bp 71–72° (8 mm); $[\alpha]^{27D} +97^\circ$ (*c* 1.65); λ_{\max} 5.62 and 6.10 μ ; nmr spectrum, τ 4.2 (q, 1, *J* = 10 and 17 Hz, CH-3'), 5.0 (m, 2, CH₂-4'), 8.81 (d, 3, partially obscured by the

C-2 methyls, CH₃-5), and 8.84 and 8.86 (2s, 6, 2CH₃-2'); *m/e* 152, 137, 124, 110, 95, 83, and 82.

Oxidation of the second cyclobutanol **16** or **17** in a similar fashion followed by purification by gas chromatography yielded a colorless oil: λ_{\max} 5.62 μ ; nmr spectrum, τ 4.2 (q, 1, *J* = 10 and 18 Hz, CH₃-3'), 5.0 (m, 2, CH₂-4'), ~8.85 (d, 3, *J* = 7 Hz, CH₃-4), and 8.82 and 8.86 (2s, 6, 2CH₃-2').

Oxidation of the cyclopentanol fraction (**15**) by the above procedure, purification by preparative gas chromatography, and short-path distillation yielded **10b** as a colorless liquid: bp 68° (6 mm); $[\alpha]^{27D} +36^\circ$ (*c* 1.48); λ_{\max} 3.23, 5.74, and 6.11 μ ; nmr spectrum, τ 4.26 (m, 1, CH-1'), 4.89 (m, 2, CH₂-2'), 8.91 (d, 3, *J* = 8 Hz, CH₃-5), and 9.00 and 9.18 (2s, 6, 2CH₃-2).

Irradiation of (–)-trans-4-Caranone **22.** A solution containing 40 mg of **22** and 100 mg of *n*-butylamine in 9 ml of *n*-hexane was irradiated in a quartz flask as described above for **9** and 1,3-cyclohexadiene. After 1.5 hr the solvent was carefully removed by distillation. An infrared spectrum of the residue showed peaks at 5.62, 5.74, 5.85, and 6.05 μ indicating the presence of a cyclobutanone, a cyclopentanone, unchanged **22**, and the amide **24**, respectively. Gas chromatography of the residue showed 31% of the mixture of cyclopentanone and cyclobutanones and 18% of unchanged **22**. Retention times on several columns indicated that this cyclopentanone was different from that obtained from (–)-*cis*-4-caranone.

Oxidation of (–)-cis-4 α -Caranol. A solution of 31.40 g of (–)-*cis*-4 α -caranol in 400 ml of acetone was stirred and cooled to 0°. A total of 51 ml of 4 *N* chromic acid solution was added dropwise over 1 hr. To the solution was added 100 ml of saturated sodium chloride solution followed by 15 ml of saturated sodium bicarbonate solution. The upper layer was separated and the lower layer was extracted with several portions of ether. The combined organic layers were dried over magnesium sulfate and distilled on a 12-in. spinning-band column to yield two fractions. The first fraction contained 1.59 g (5.1%) of a colorless oil, bp 64–72° (6.5 mm), which was shown by gas chromatography to consist of approximately 15% (–)-*cis*-4-caranone (**9**)⁶ and 85% of a compound of shorter retention time.

The second fraction, 23.82 g (78.0%), bp 73–75° (6.7 mm), consisted of (–)-*cis*-4-caranone (**9**) which was homogeneous to gas chromatography.

Isolation of the major component of the first fraction by preparative gas chromatography followed by short-path distillation yielded a mixture of **10a** and **b** as a colorless oil: bp 50–51° (4 mm); $[\alpha]^{27D} +19.3^\circ$ (*c* 1.50); λ_{\max} 3.23, 5.74, and 6.11 μ ; nmr spectrum, τ 4.26 (m, 1, CH-1'), 4.89 (m, 2, CH₂-2'), 8.87 (d, 3, *J* = 6.5 Hz, CH₃-*cis*-5), 8.91 (d, 3, *J* = 8 Hz, CH₃-*trans*-5),²⁶ and 9.00 and 9.18 (2s, 6, 2CH₃-2); *m/e* 152, 137, 123, 119, 110, 109, 96, 95, 82, and 81.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 79.17; H, 10.64.

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(26) This pair of doublets has been assigned to the epimeric C-5 methyl groups of the mixture of **10a** and **10b** and appears in a ratio of approximately 1:4.