2,3,4-Trimethylcyclohex-2-en-1-ol. This alcohol was prepared by reducing 2,3,4-trimethylcyclohex-2-en-1-one[30] with lithium aluminum hydride in ether, bp 84–85° (9 mm). Nmr analysis showed τ 6.18 (1 H, very broad and unresolved), 7.29 (1 H, broad and unresolved), 8.38 (6 H), 8.98 (3 H, d, J = 6.8), and a very complex region from 7.9 to 9.0 for the methylene protons.

1,2,3,4-Tetramethylcyclohex-2-en-1-ol. This alcohol was kindly supplied by Mr. K. A. Ananthanarayan of this department.

4,6-Dimethylhepta-1,5-dien-4-ol. The preparation of this alcohol has been reported.[31]

1-Isopropyl-2,3-dimethylcyclopent-2-en-1-ol. A solution of 1.281 g (0.0116 mol) of 2,3-dimethylcyclopent-2-en-1-one[32] in 10 ml of pentane was added to a stirred, ice-cold solution of isopropyllithium (8–9 ml of 1.8 M in pentane). The reaction was worked up in the usual manner[33] and the residue was dissolved in pentane and added to a second portion of isopropyllithium (8–9 ml). The reaction was again worked up and distillation of the residue gave 1.01 g (56%) of product, bp 36–40° (0.15 mm). As usual with these alcohols, some dehydration occurred during the distillation (nmr analysis) and a satisfactory C, H analysis was not obtained. This dehydration product yields the same carbonium ion as the alcohol and is of no consequence. Nmr analysis showed a complex region from τ 7.0 to 8.5 for the methylene and methine protons, 8.40 (3 H, broad), 8.49 (3 H, t, J = 1.8), 8.85 (1 H, OH), 9.08 and 9.37 (6 H, both d, J = 7.0).

5-Carbethoxy-2,2-dimethyloctane-3,6-dione. A solution of the sodium enolate of ethyl 3-oxopentanoate[34] was prepared in the usual order of addition from 36 g (0.25 mol) of ethyl 3-oxopentanoate, 200 ml of absolute ethanol, and 6.25 g-atoms (0.272 mol) of sodium. This solution was heated to reflux and 60 g (0.335 mol) of 1-bromo-3,3-dimethylbutan-2-one[35] was added dropwise over a period of 2 hr. The solution was refluxed a further 3 hr and cooled. Water was added to dissolve the precipitated salt and most of the ethanol removed on a rotary evaporator. The resulting mixture was extracted with three 300-ml portions of ether and the ether dried over magnesium sulfate. Removal of the ether gave a residue (63.5 g). Distillation gave a considerable forerun of the unreacted bromo ketone and then a main product: bp 134–135° (8 mm), yield 35.0 g (60%). *Anal.* Calcd for $C_{13}H_{22}O_4$: C, 64.43; H, 9.15. Found: C, 64.42; H, 8.89. Nmr analysis showed τ 5.88 (2 H, quart., J = 7.2), 6.07 and 6.20 (1 H, both d, J = 6.2), 6.91, 7.03, 7.13, (2 H, AB part of ABX system), 7.37 (2 H, quart., J = 7.2), 8.73 (3 H, t, J = 7.2), 8.87 (9 H), 8.95 (3 H, t, J = 7.2).

3-*tert*-Butyl-2-methylcyclopent-2-en-1-one. A solution of 32.5 g (0.135 mol) of 5-carboethoxy-2,2-dimethyloctane-3,6-dione in 150 ml of methanol, 100 ml of water, and 25.0 g of sodium hydroxide was heated to reflux. After a few minutes, sodium carbonate begins to precipitate (bumping!). After 2 hr, the solution was cooled and the salt removed by filtration and washed with 50 ml of methanol. An additional 50 g of sodium hydroxide was added to the filtrate together with a further 100 ml of water and the mixture was refluxed for 40 hr in a closed atmosphere. Water (500 ml) was then added and the cold mixture extracted twice with two 250-ml portions of ether. The wet ether layer was evaporated on a rotary evaporator and the residue treated with 100 ml of water and 200 ml of ether. The ether layer was again separated and washed with 100 ml of water, back-extracting the wash layer with an additional 100 ml of ether. The combined ether extracts were dried over magnesium sulfate. Removal of the ether gave 18.5 g of residue which was distilled through a spinning band column to give a main fraction, bp 96° (8 mm), yield 11.0 g (54%), of the title compound. The rest of the crude material remains as a high boiling residue. *Anal.* Calcd for $C_{10}H_{16}O_2$: C, 78.83; H, 10.59. Found: C, 78.96; H, 10.08. Nmr analysis showed τ 7.33–7.97 (4 H, complex series of peaks), 8.23 (3 H, t, J = 1.8), 8.76 (9 H).

3-*tert*-Butyl-2-methylcyclopent-2-en-1-ol. Prepared in 80% yield from 1.0 g (0.0066 mol) of the above ketone and 0.2 g of lithium aluminum hydride (0.006 mol) in ether; bp 94–95° (8 mm). *Anal.* Calcd for $C_{10}H_{18}O$: C, 77.89; H, 11.74. Found: C, 77.95; H, 12.37. Nmr analysis showed τ 5.5–5.7 (1 H, broad and unresolved); 7.6–8.0 (4 H, broad and unresolved); 8.21 (3 H, broad, partially resolved triplet), 8.88 (9 H).

1,3,5-Trimethylcyclohex-2-en-1-ol. This alcohol was prepared in 70% yield from 0.6 g (0.005 mol) of 3,5-dimethylcyclohex-2-en-1-one and 3 ml of 2.16 M methyllithium (0.0065 mol) solution, in ether solvent, bp 81° (8 mm).

Acknowledgments. The authors wish to thank the National Research Council of Canada for generous support.

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Cyclopropane in Photochemistry. I. Photochemistry of 4,4-Dicyclopropylcyclohexenone

Roger C. Hahn* and Gerald W. Jones[1]

Contribution from the Department of Chemistry, Syracuse University, Syracuse, New York 13210. *Received November 5, 1970*

Abstract: Irradiation of 4,4-dicyclopropylcyclohexenone (**5**) in *tert*-butyl alcohol affords only 6,6-dicyclopropylbicyclo[3.1.0]hexan-2-one (**6**) and 3-(dicyclopropylmethyl)-2-cyclopentenone (**10**). The absence of detectable amounts of cyclopropyl migration products is rationalized most readily in terms of a reacting excited state having radical character.

One of the more pronounced mechanistic dichotomies in photochemistry is the behavior of 4,4-dimethylcyclohexenone (**1**) and 4,4-diphenylcyclohexenone (**3**) on irradiation. Whereas **1** reacts predominantly *via* breakage of the 4,5 bond and rebonding of the 2,4 and 3,5 carbon atoms, respectively,[2] **3** undergoes predominant 4,3-phenyl migration, without attendant skeletal rearrangement.[4]

(1) National Science Foundation Trainee, 1965–1968.
(2) O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton, and P. Fitton, *Tetrahedron Lett.*, 2049 (1963). The general transformation of 4-substituted cyclohexenones and cyclohexadienones to 6-substituted bicyclo[3.1.0] systems, in which C-3 and C-4 appear to exchange places, has been termed a type A rearrangement.[3]
(3) H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. Staley, and M. Semmelhack, *J. Amer. Chem. Soc.*, **88**, 1965 (1966).
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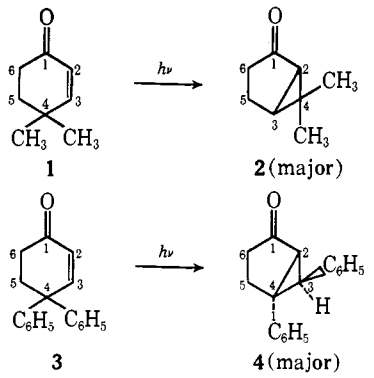
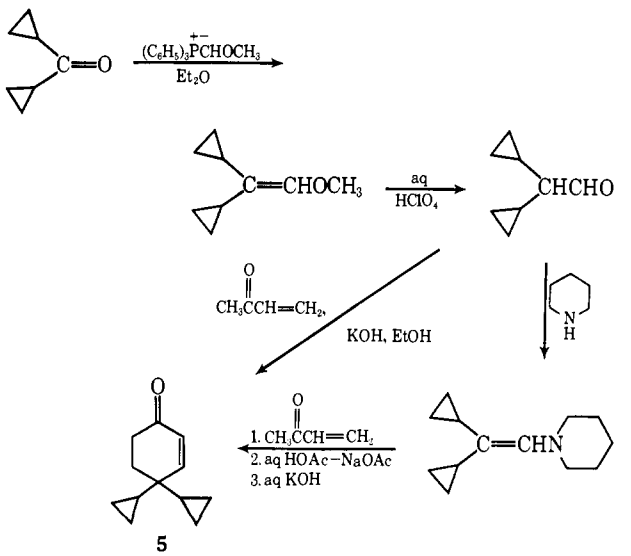


1 2 (major) 3 4 (major)

These dramatic substituent effects on photochemical reactivity may be viewed as consequences of the differences in migration aptitudes of the phenyl and methyl groups. Thus it seemed of intrinsic interest and potential utility in further exploration of cyclohexenone photochemistry to study a cyclohexenone system having substituents with chemical properties intermediate between those of vinyl (aryl) and alkyl (methyl) groups. Such a group is cyclopropyl; in ground-state solution chemistry, the relative aptitude of the cyclopropyl group in migration to an electron-deficient center is between those of phenyl and methyl groups;[5] a cyclopropyl–methyl migration aptitude ratio of 56:1 has been reported.[6]

However, extrapolation of such ground-state behavior to all photochemical reactions of α,β-unsaturated ketones is questionable. Although many results of irradiation of α,β-unsaturated ketones are consistent with formation of a "polar state" intermediate ($^{+}C-C=C-O^{-}$) having carbonium ion character "on the carbon atom β to the carbonyl group in the product controlling state,"[7] the photochemical aryl migration reactions of some 4,4-diarylcyclohexenones, designed specifically to probe the character of the β carbon in the reacting species,[8] are consistent only with a radical mechanism. Examples of alkyl (or cyclopropyl) radical migration are unknown in ground-state (mono)radical systems,[9] rare in excited state (di)radical systems,[10,11a] and seldom documented in ketone "ionic type" photochemical rearrangements such as the cyclohexenone type A rearrangement.[2,11] It appeared possible, therefore, that the photochemical behavior of a 4-cyclopropyl-substituted cyclohexenone would provide another point of view of the question of the nature of the excited state(s) and reacting species in α,β-unsaturated ketones.[11] Consequently, a study was undertaken of the photochemical behavior of 4,4-dicyclopropylcyclohexenone (**5**). Synthesis of **5** is outlined in Chart I.

Chart I



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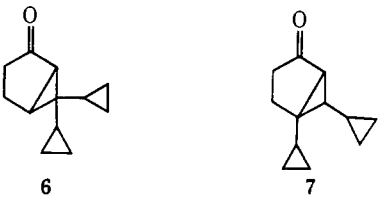
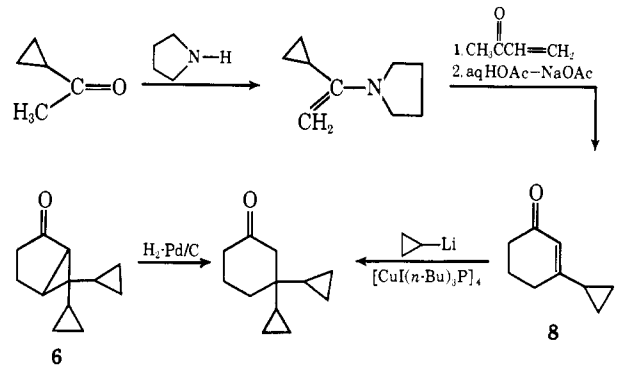
Photolysis. Irradiation of **5** in *tert*-butyl alcohol caused slow conversion to two volatile photoproducts (vpc analysis), which accounted for 85% of consumed starting material. The major photoproduct, *ca.* 93% of the product mixture, was isomeric with **5** but contained no carbon–carbon double bonds; infrared absorption (C=O at 5.83 mμ) was consistent with a bicyclo[3.1.0] structure[12] such as **6** or **7**.



6 **7**

This product was identified as 6,6-dicyclopropylbicyclo[3.1.0]hexan-2-one (**6**) by catalytic hydrogenation of **6** to independently synthesized 3,3-dicyclopropylcyclohexanone (Chart II). The β cyclopropylation of

Chart II



6 **8**

3-cyclopropyl-2-cyclohexenone (**8**) is believed to be a novel extension of the process previously used to add a methyl, ethyl, or phenyl group to the β position of an α,β-unsaturated ketone.[13]

The infrared spectrum of the minor photoproduct shows carbonyl bands at 5.88 and 5.98 μ and a C=C

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(10) H. E. Zimmerman and A. C. Pratt, *J. Amer. Chem. Soc.*, 92, 1407, 6259 (1970).
(11) (a) M. H. Fisch and J. H. Richards, *ibid.*, 90, 1547 (1968), and references therein. The possible nature of ketone excited states and reaction intermediates is discussed in detail in this paper. (b) D. I. Schuster and D. F. Brizzolara, *ibid.*, 92, 4357 (1970).
(12) *Cf.* H. E. Zimmerman, R. D. Rieke, and J. R. Scheffer, *ibid.*, 89, 2033 (1967), and references therein.
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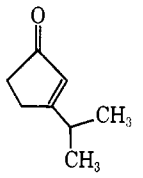
stretching band at 6.19 μ. A maximum in the ultraviolet spectrum (95% ethanol) appears at 229.5 nm (ϵ 14,300). These spectral characteristics are very similar to those reported[14] for 3-isopropyl-2-cyclopentenone (**9**) (ir C=O at 5.82 and 5.93 μ, C=C at 6.19 μ; uv $\lambda_{max}^{CCl_4}$ at 227 nm (ϵ 14,300)), and with the nmr spectrum of the photoproduct (vinyl singlet at τ 3.94, 1 H) suggested assignment as 3-(dicyclopropylmethyl)-2-cyclopentenone (**10**).



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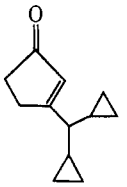

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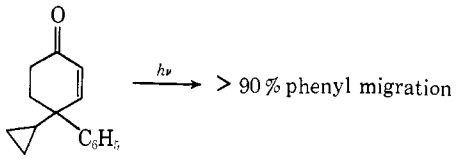
There is ample precedent for formation of 3-substituted cyclopentenones such as **10**;[15] *e.g.*, hexenone **1**[2] in *tert*-butyl alcohol is photochemically converted to a mixture of **2** and **9** in about the same ratio as found for the present cyclopropyl analogs. It was not established whether **10** is produced by direct rearrangement of **5** or *via* secondary photochemical or thermal reaction of **6**; both processes have been detected in analogous systems.[2,15]

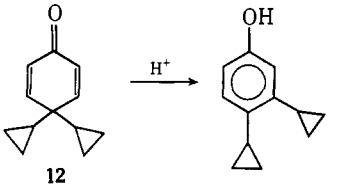
Though it is possible that small amounts of cyclopropyl migration product(s) are formed on irradiation of **5**, none were detected; it is clear that the type A rearrangement[3] (lumirearrangement[15]) predominates in this system. Zimmerman has accumulated evidence[16] consistent with the suggestion that the type A rearrangement is preferred over *aryl* migration (from C-4 to C-3) when stabilization by the group not migrating is insufficient, *i.e.*, when the nonmigrating group is not aryl. If this were the only condition for migration of any group, the present results might be taken to indicate that cyclopropyl is much less efficient than is phenyl in providing such stabilization. However, irradiation of 4-cyclopropyl-4-phenylcyclohexenone (**11**)



11

affords predominantly products of phenyl migration.[17] Stabilization at C-4 by cyclopropyl should not be any more significant for **11** than it is for **5**, and so it is concluded that the identity of the migrating group is more important than that of the nonmigrating group, and that cyclopropyl simply does not have as great a migration aptitude as does phenyl toward the type of migration terminus generated on irradiation. In the absence of quantum yields and rate data for reactions of **11** and **5**, these conclusions remain tentative; *i.e.*, it is possible (though not indicated by qualitative observations of reactivity) that the type A rearrangement of **5** is faster and more efficient than the phenyl migration processes of **11**. The absence of cyclopropyl migration in **5** then would be no indication of relative cyclopropyl migration aptitude. This possibility appears unlikely, however, in view of data showing phenyl migration to be orders of magnitude faster than type A rearrangement in comparable systems.[8]

The electronic character at C-3 (the potential migration terminus) in the reacting excited state of cyclohexenone **5** remains debatable. In addition to the previously noted examples of cyclopropyl migration to an electron-deficient center,[5,6] 4,4-dicyclopropylcyclohexadienone (**12**) undergoes facile acid-catalyzed rearrangement to 3,4-dicyclopropylphenol.[18] In **5** and



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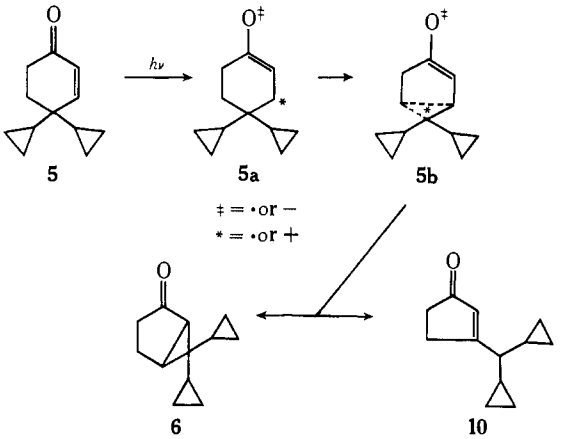
12, C-3, C-4, and the groups bonded to the latter effectively comprise a neopentyl system which should not differ greatly, sterically, from the neopentyl carbonium ion system reported to give facile cyclopropyl migration.[6] If **5a** had cationic character at C-3, a



5 **5a** **5b** **6** **10**

cyclopropyl group might be expected to have an appreciable tendency to migrate to that terminus. The absence or paucity of authenticated reports of alkyl (or cyclopropyl) migration to a radical center in ground-state and excited-state chemistry[9-11] and the absence of cyclopropyl migration products in the photochemistry of **5** therefore may be viewed as indicating generation of radical rather than cationic character at C-3 in the reacting state of **5**, in keeping with the conclusions of Zimmerman and coworkers with respect to cyclohexenone aryl migration reactions.[8]

However, with respect to the cyclohexenone type A reaction, the question remains, why does an *alkyl* group (the C-5,C-6-dimethylene group in **5**) migrate to C-3 (*i.e.*, undergo the type A rearrangement) in total preference to cyclopropyl migration? It is suggested only that factors affecting cyclohexenone photochemistry remain incompletely elucidated.

A final observation on the photolysis of **5** concerns temperature effects. In photoreactions continued to

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(18) G. W. Jones, Ph.D. Dissertation, Syracuse University, 1970.

essentially complete disappearance of **5**, the temperature of the reaction vessel varied in different runs by as much as 25°. The time required for complete photolysis of **5** (*tert*-butyl alcohol) varied from 15 to 45 hr, and was inversely related to the temperature of the reaction vessel. It was reported recently that 4,4-diphenylcyclohexenone shows an energy barrier (~10 kcal/mol) to photochemical rearrangement;[19] an increase of 50° in the reaction temperature increased the quantum yield sixfold. Although the possibility of a similar energy barrier was not further explored with **5**, the existence of such a barrier would account for the observed temperature effects.

Experimental Section

Infrared spectra were obtained with a Perkin-Elmer 137 Infracord, and ultraviolet spectra with a Perkin-Elmer 202 spectrometer. Nmr spectra were obtained with a Varian A-60 using tetramethylsilane or dichloromethane as an internal standard. Melting points were taken on a Fisher-Johns apparatus and are corrected; boiling points are uncorrected. Elemental analyses were performed by Micro Analytical Laboratories, Herlev, Denmark.

Analytical vapor phase chromatography (vpc) was performed on an Aerograph Hi-Fi 600-C using 15% Carbowax 20M or 10% QF-1 (5 ft × 1/8 in. column) on 60–80 acid-washed Chromosorb W. Preparative vpc separations were accomplished with an Aerograph Autoprep A-700 using 15% XF-1150 (5 ft × 1/4 in. column) on 60–80 Chromosorb W or 10% QF-1 (10 ft × 3/8 in. column) on 20–30 Chromosorb A. Column chromatography was monitored by passing the eluate into a flow-through cell in the beam of a uv spectrophotometer set at an appropriate wavelength.

1,1-Dicyclopropyl-2-methoxyethylene. To a thoroughly dried 2000-ml flask was added 1000 ml of sodium-dried ether and 170 g (0.494 mol) of finely pulverized methoxymethyltriphenylphosphonium chloride.[20] The flask was cooled in an ice bath and an equimolar quantity of *n*-butyllithium (250 ml of 29.1 wt % in hexane) was added with stirring over a 10-min period. The resulting red solution was allowed to warm up slightly without an ice bath for 10 min. To this well-stirred solution was added 54 g (0.49 mol) of dicyclopropyl ketone at a rate fast enough to cause refluxing. The pink suspension then was refluxed 1 hr. The precipitate was filtered and the ether layer was washed with water, separated, and dried over magnesium sulfate. The dark red solution was concentrated *in vacuo* and distilled to yield 48.2 g (70.5%) of 1,1-dicyclopropyl-2-methoxyethylene: bp 48–56° (3.7 mm); ir (NaCl) 6.05, 8.30, 8.90, and 10.27 μ; nmr (neat) τ 4.32 (singlet, 1 H, vinyl), 6.62 (singlet, 3 H, methoxy), 8.1–8.6 (multiplet, 2 H, methine), 9.08–10.00 (multiplet, 8 H, cyclopropyl).

Dicyclopropylacetaldehyde.[21] To 2 l. of ether was added 92.6 g (0.67 mol) of 1,1-dicyclopropyl-2-methoxyethylene, 83 ml of water, and 54 ml of 70% perchloric acid. The solution was stirred at reflux for 23 hr and then neutralized with aqueous sodium carbonate. The layers were separated and the ether layer was washed with one 100-ml portion of water and dried over magnesium sulfate. The solution was concentrated *in vacuo* and distilled to yield 57.3 g (69%) of dicyclopropylacetaldehyde: bp 56–62° (7.5 mm); ir (NaCl) 3.29, 3.35, 3.58, 3.70, 5.80, 9.80, and 12.20 μ; nmr (neat) τ 0.50 (doublet, 1 H, aldehyde), 8.84–10.00 (multiplet, 11 H).

Dicyclopropylacetaldehyde semicarbazone, mp 147–148°, was analyzed.

Anal. Calcd for $C_9H_{15}N_3O$: C, 59.64; H, 8.34; N, 23.19. Found: C, 59.88; H, 8.40; N, 22.88.

2,2-Dicyclopropylacetaldehyde Piperidine Enamine.[22] To 200 ml of benzene was added 57.3 g (0.462 mol) of 1,1-dicyclopropylacetaldehyde and 85 g (1 mol) of piperidine. The solution was stirred at reflux for 15 hr; 8.3 ml of water collected in the Dean-Stark separator. The liquid was distilled to yield 76.4 g (87%) of 2,2-dicyclopropylacetaldehyde piperidine enamine: bp 72–75° (0.4 mm); ir (NaCl) 3.30, 3.38, 3.45, 3.54, 3.61, 6.08, 7.30, 8.50, and 9.18 μ; nmr (CCl_4) τ 4.67 (singlet, 1 H, vinyl), 7.17–7.51, (multiplet, 4 H, methylene), 8.03–8.67 (multiplet, 7 H, 6 methylene and one cyclopropyl methine), 8.95–9.88 (multiplet, 9 H, cyclopropyl).

4,4-Dicyclopropylcyclohex-2-en-1-one (5). To a 5-l. round-bottomed flask equipped with a condenser, stirrer, and nitrogen inlet tube was introduced 2.5 l. of absolute ethanol (dried over molecular sieves), 76.4 g (0.40 mol) of 2,2-dicyclopropylacetaldehyde piperidine enamine, and 28.7 g (0.41 mol) of freshly distilled methyl vinyl ketone. The mixture was refluxed 23 hr; 170 ml of water, 126 ml of glacial acetic acid, and 67.5 g of sodium acetate then were added. Reflux was continued for 15 hr; aqueous potassium hydroxide was added until pH 9 was attained and the solution was refluxed 24 hr more. Water was added and the solution was ether extracted, layers were separated, and the organic layer was dried over magnesium sulfate. After concentration *in vacuo*, the liquid was distilled to yield 41.6 g of impure product, bp 74–97° (0.1 mm). Spinning band fractionation gave 28.6 g (40.7%) of 4,4-dicyclopropylcyclohex-2-en-1-one: bp 79° (0.6 mm); ir (NaCl) 3.28, 3.35, 3.43, 3.50, 5.94, 7.24, 8.08, 9.82, 10.45, 13.05, and 13.31 μ; nmr ($CHCl_3$) τ 3.53–4.25 (quartet, 2 H, vinyl), 7.33–7.68 (quartet, 2 H, methylene), 7.93–8.27 (quartet, 2 H, methylene), 8.80–9.80 (multiplet, 10 H, cyclopropyl); uv (95% EtOH) λ_{max} 228 nm (ϵ 8300), 322 nm (ϵ 34); mass spectrum *m/e* 176 (parent).

The semicarbazone, mp 199–200°, was analyzed.

Anal. Calcd for $C_{13}H_{20}N_3O$: C, 66.90; H, 8.21; N, 18.02. Found: C, 66.44; H, 8.23; N, 17.71.

Photolysis of 5. A typical experiment is described. A stirred solution of 5.00 g (28 mmol) of **5** in 130 ml of *tert*-butyl alcohol (dried over molecular sieves) was purged with oxygen-free nitrogen for 15 min before and during irradiation. The irradiation was carried out using a 450-W Hanovia medium-pressure lamp with a Pyrex filter. The lamp was cooled by recirculating water at 40–45°. The progress of the reaction was monitored by vpc analysis of aliquots. After 41 hr[23] of irradiation only traces of **5** remained, and two new vpc peaks had appeared. These products, identified as 6,6-dicyclopropylbicyclo[3.1.0]hexan-2-one (**6**) and 3-(dicyclopropylmethyl)-2-cyclopentenone (**10**), had relative peak areas of 90:95 and 5:8, respectively. Removal of solvent and distillation of the residue gave 4.3 g (86%) of this mixture, bp 80–87° (0.05 mm). The mixture was put on a silica gel column (Will grade 950, 60–200 mesh), and eluted with 10% ether–hexane. 4,4-Dicyclopropylcyclohexenone was eluted first, followed by **6**; **10** was eluted with 15% ether–hexane. The spectral data for **6** include: ir (NaCl) 3.29, 3.36, 3.43, 3.50, 5.83 (C=O), 8.41, 9.83, and 11.41 μ; nmr (neat) τ 7.80 (singlet, 4 H, methylene), 8.00–8.34 (multiplet, 1 H, cyclopropylmethine), 8.40–8.60 (doublet, 1 H, cyclopropylmethine), 8.67–10.25 (multiplet, 10 H, cyclopropyl).

Spectral data for **10** include: ir (NaCl) 3.38, 5.88, 5.98, 6.22, 8.47, 10.77, and 11.00 μ; nmr ($CDCl_3$) τ 3.94 (narrow multiplet, 1 H, vinyl), 7.08–7.41 (multiplet, 2 H, methylene), 7.42–7.70 (multiplet, 2 H, methylene), 8.67–10.00 (multiplet, 11 H, 10 cyclopropyl and one methine); uv (95% EtOH) λ_{max} 229.5 nm (ϵ 14,300).

Instability of 10. A sample of ketone **6** containing 7.7% of the cyclopentenone **10** according to vpc analysis (XF-1150) was injected into the same column with the injection port temperature raised from 200 to 300°; the indicated percentage of **10** increased to 16.2%.

A portion of the same mixture was allowed to stand 19 hr on a silica gel column packed with 5% ether–hexane. The sample was flushed off with 95% ethanol; vpc analysis at the lower injection port temperature showed that the mixture now contained 14% of **10**. A similar increase in the proportion of **10** was noted on exposure of the original mixture to a silica gel column impregnated with silver nitrate. Ketone **6** thus is capable of nonphotochemical rearrangement to **10**; however, from nmr and ir spectra of crude photolysate and careful vpc analysis, a maximum of 8% of **10** is formed during irradiation of **5**.

Preparation of the Benzylidene Derivative of 6. Freshly distilled benzaldehyde, 1.3 g (12 mmol), was added to 805 mg (4.55 mmol) of **6** in 10 ml of 95% ethanol. Aqueous sodium hydroxide, 0.5 ml (5 *N*), was added and the solution was permitted to stand 12 hr. Ice-bath cooling and filtration isolated a crude solid. Recrystallization (four times) from 95% ethanol gave 583 mg of colorless

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(21) The procedure used is a modification of that of D. M. Jones and N. F. Wood, *J. Chem. Soc.*, 5400 (1964).

(22) For a general preparation and reactions of enamines see G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 207 (1963).

(23) Other runs made with recirculating water 25–30° warmer needed as little as 15 hr of irradiation for essentially complete reaction of **5**.

solid: mp 124–125°; ir (KBr) 3.29, 3.35, 3.46, 5.91, 6.16, 8.39, 9.81, 11.49, 13.02, and 14.03 μ; nmr ($CDCl_3$) τ 2.25–2.85 (multiplet, 6 H, 5 aromatic and one vinyl), 6.84 (slightly split singlet, 2 H, methylene), 8.13 (slightly split singlet, 2 H, cyclopropyl methine), 8.79–10.07 (multiplet, 10 H, cyclopropyl); mass spectrum *m/e* 264 (parent).

Anal. Calcd for $C_{19}H_{26}O$: C, 86.32; H, 7.63. Found: C, 86.11; H, 7.50.

Hydrogenation of 6. The hydrogenation was done in a Brown[24] apparatus at atmospheric pressure.

To 30 mg of prehydrogenated 10% palladium on carbon suspended in 20 ml of 95% ethanol was added, *via* syringe, 315 mg (1.79 mmol) of **6** in 5 ml of 95% ethanol. After 52 hr of vigorous stirring, 42 ml of hydrogen had reacted (96.5% of theory). The catalyst was filtered out and the solution was concentrated *in vacuo* to yield 312 mg of a colorless liquid. The liquid was placed on a silica gel column (Will grade 950, 60–200 mesh) packed with hexane and eluted with increasing amounts of ether in hexane (0–10%). Six fractions were collected: fraction 1, 26 mg; 2, 140 mg; 3, 113 mg; 4, 24 mg; 5, 48 mg; and 6, 51 mg. Fraction 1 contained a compound which had a strong ir C=O stretch at 5.73 μ, characteristic of cyclopentanones. Fraction 2 had weak absorption at 5.73 and a strong band at 5.88; the latter indicated a cyclohexanone structure. Fractions 3–5 were mainly unreacted **6**; fraction 6 was not identified. Fraction 2 was distilled to yield 76 mg of material, bp *ca.* 70° (external bath temperature; 0.1 mm), identified as mostly 3,3-dicyclopropylcyclohexanone. This product afforded 35 mg of pure ketone on preparative vpc (15% XF-1150).

Spectral data include: ir (NaCl) 3.30, 3.39, 3.45, 3.51, 5.88, 8.15, 9.85, 11.15, and 12.11 μ; nmr ($CDCl_3$) τ 7.50–8.67 (multiplet, 8 H, methylene), 9.17–9.94 (multiplet, 10 H, cyclopropyl).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.93; H, 10.22.

Synthesis of 3,3-Dicyclopropylcyclohexanone. Methyl Cyclopropyl Ketone Pyrrolidine Enamine. To 150 ml of dry benzene was added 5 g (59.5 mmol) of methyl cyclopropyl ketone and 10 g (141 mmol) of pyrrolidine. The apparatus was equipped with a thimble extractor charged with molecular sieves. After refluxing for 18 hr the reaction mixture was distilled to yield 2.1 g (26%) of methyl cyclopropyl ketone pyrrolidine enamine: bp 27–30° (0.05 mm); ir (NaCl) 3.31, 3.43, 3.55, 3.60, 6.21, 7.11, 7.45, 7.71, 9.81, 10.70, and 13.35 μ; nmr (neat) τ 6.50–6.90 (multiplet, 6 H, 4 methylene and 2 vinyl), 7.84–8.89 (multiplet, 5 H, 4 methylene and cyclopropyl methine), 9.0–9.67 (multiplet, 4 H, cyclopropyl $-CH_2-$).

3-Cyclopropylcyclohex-2-en-1-one. To a 50-ml flask equipped with a nitrogen inlet, condenser, drying tube, and stirrer was added 12 ml of dry benzene and 2 g (14.6 mmol) of methyl cyclopropyl ketone pyrrolidine enamine. When the methyl vinyl ketone (1.02 g, 14.6 mmol) was added, the mixture became hot and boiled vigorously. The solution was refluxed for 20 hr; 2.5 ml of glacial acetic acid, 2.5 ml of water, and 1.25 g of sodium acetate then were added and the mixture was refluxed an additional 6 hr. The layers were separated, the aqueous phase was washed once with benzene, and the benzene portions were combined and washed with 30 ml of 10% hydrochloric acid, followed by washing with aqueous sodium bicarbonate and drying over magnesium sulfate. Distillation afforded 0.713 g (36%) of 3-cyclopropylcyclohex-2-en-1-one, bp 60–68° (0.1 mm), mp 12°. The product was further purified by recrystallizing from a pentane–ether solution in Dry Ice–acetone.

The ketone spectral data include: ir (NaCl) 3.30, 3.38, 3.43, 3.52, 6.05, 6.20, 8.00, 8.43, 9.91, and 10.95 μ; nmr ($CDCl_3$) τ 4.19 (singlet, 1 H, vinyl), 7.50–9.34 (multiplet, 11 H, 6 methylene and 5 cyclopropyl); mass spectrum *m/e* 136 (parent).

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.22; H, 8.87.

3,3-Dicyclopropylcyclohexanone. Into a three-necked, 50-ml, round-bottomed flask equipped with a nitrogen inlet, stirrer, drying tube, and condenser was placed 5.13 g (18.4 mmol) of tetrakis[iodo(tri-*n*-butylphosphine)copper(I)][25] in 15 ml of anhydrous ether. The solution was placed in an ice bath and 20 ml of a previously prepared cyclopropyllithium solution[26] (from 258 mg of lithium metal (0.0368 g-atom) and 2.23 g (18.4 mmol) of cyclopropyl bromide in 18 ml of ether) was syringed into the funnel under 5 ml of absolute ether. The cyclopropyllithium solution was added in less than 5 min to the phosphine complex. The color immediately became a deep orange, then a light green, and finally a deep brown. The solution was stirred for 30 min in the ice bath; then 713 mg (5.24 mmol) of 3-cyclopropylcyclohex-2-en-1-one in ether was added rapidly. The reaction was stirred 30 min in the ice bath and poured into aqueous ammonium chloride, layers were separated, and the ether layer was dried over magnesium sulfate. After concentration of the solution *in vacuo*, the residue was placed on a silica gel column (Will grade 950, 60–200 mesh) packed with hexane and eluted with 1% ether–hexane until all the tri-*n*-butylphosphine had come off. Further elution with 5% ether–hexane gave 286 mg (30.5%) of 3,3-dicyclopropylcyclohexanone, followed by 310 mg of recovered starting material.

The 3,3-dicyclopropylcyclohexanone was identical in infrared, nmr, and vpc retention time with the compound obtained from catalytic reduction of 6,6-dicyclopropylbicyclo[3.1.0]hexan-2-one (**6**).

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