

# Photochemistry of $\alpha'$ -Substituted $\beta,\gamma$ -Cyclopropyl Cyclic Ketones. Influence of Geometric Constraints and Substituent Effects on Competitive Norrish Type I Photoreactions

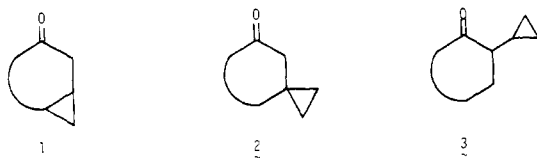
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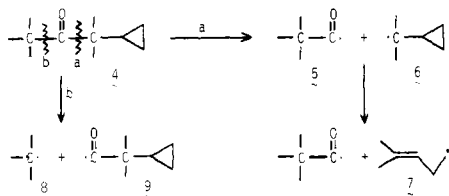
**Abstract:** The first examples of photochemical reactions of  $\beta,\gamma$ -cyclopropyl cyclic ketones that occur by Norrish type I cleavage of the carbonyl carbon to  $\alpha'$ -carbon bond (bond b) are reported. It is shown that this mode of reaction can become competitive with scission of the carbonyl carbon to  $\alpha$ -carbon bond (bond a) through geometric constraints in the cyclopropyl ketone which destabilize the cyclopropylcarbinyl radical that might be formed upon cleavage of bond a relative to the alkyl radical generated by scission of bond b. This behavior also may be attributed in part to efficient radical coupling of the diradical produced upon cleavage of bond a which effectively precludes product formation. It is also demonstrated that photocleavage of bond b can be made competitive with that of bond a by the introduction of suitable substituents at the  $\alpha'$  carbon so that the alkyl radical generated by scission of bond b is stabilized relative to the cyclopropylcarbinyl radical that might be formed by cleavage of bond a.

## Introduction

There are three possible skeletal arrangements for a  $\beta,\gamma$ -cyclopropyl cyclic ketone. The cyclopropyl moiety may have two points in common with the carbon ring containing the carbonyl functional group (**1**, bicyclic), one point in common (**2**, spiro), or no points in common (**3**, exocyclic). The photo-



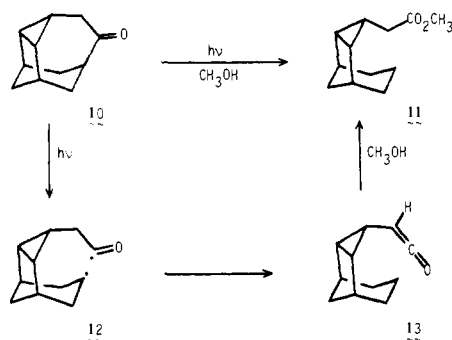
chemistry of representative examples of each of these types has been investigated.<sup>2-4</sup> Although diverse products have been obtained in these reactions, irradiation of each  $\beta,\gamma$ -cyclopropyl ketone (**4**) appears to lead to initial Norrish type I  $\alpha$ -cleavage of bond a to give acyl radical **5** and cyclopropylcarbinyl radical **6**. The latter subsequently rearranges to homoallyl radical **7** and then product formation proceeds by a variety of competitive pathways.



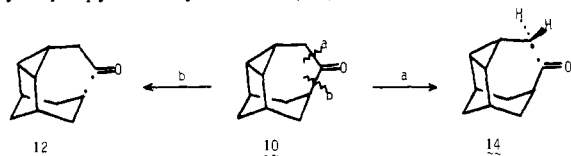
In principle, photolysis of **4** might also result in the initial scission of bond b to give alkyl radical **8** and acyl radical **9**. However, in all of the examples cited in the literature where the site of photocleavage can be deduced from the structure of the products, path a obtains. It should be possible to make photocleavage of bond b in a  $\beta,\gamma$ -cyclopropyl ketone competitive with scission of bond a either by sufficiently stabilizing alkyl radical **8** relative to cyclopropylcarbinyl radical **6** or by sufficiently destabilizing **6** relative to **8**. We now wish to report experimental demonstrations of each of these cases.

## Results and Discussion

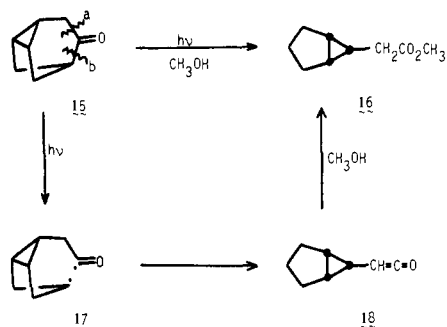
The photochemistry of 2,11-dehydro-5-homoadamantane<sup>5</sup> (**10**) stands in striking contrast to that of other  $\beta,\gamma$ -cyclopropyl cyclic ketones.<sup>2-4</sup> Irradiation of a methanol solution



of **10** through a Vycor filter provides methyl *endo*-tricyclo[3.3.1.0<sup>2,4</sup>]non-3-*syn*-ylacetate (**11**) as the only volatile photoproduct in ca. 60% yield. Consistent with the structure assignment, the infrared spectrum of ester **11** contains a carbonyl absorption at 1742  $\text{cm}^{-1}$  and the <sup>13</sup>C NMR spectrum of **11** consists of nine signals with three of the signals being twice as intense as the others. The reaction is readily accounted for by initial Norrish type I bond cleavage to give diradical **12**, followed by a hydrogen transfer to provide ketene **13**. Capture of **13** by the solvent affords **11**. It is to be emphasized that product formation must occur by initial cleavage of bond b in **10** to give an acyl radical and a secondary alkyl radical (**12**) rather than by scission of bond a to provide an acyl radical and a cyclopropylcarbinyl radical (**14**).

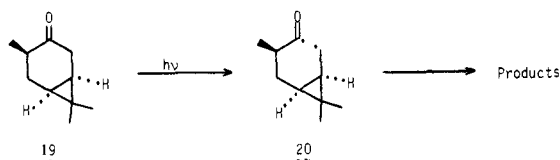


This behavior is not unique. Irradiation of a methanol solution of tricyclo[3.2.1.0<sup>2,7</sup>]octan-4-one<sup>6</sup> (**15**) under comparable conditions affords methyl bicyclo[3.1.0]hex-6-*syn*-ylacetate (**16**) in ca. 45% yield. The infrared spectrum of **16** contains a carbonyl absorption at 1744  $\text{cm}^{-1}$  and its <sup>1</sup>H NMR spectrum features a methoxy singlet at  $\delta$  3.79 and a two-proton doublet for the hydrogens  $\alpha$  to the carbonyl at  $\delta$  2.32. Consistent with the presence of a plane of symmetry in **16**, its <sup>13</sup>C NMR spectrum contains only seven signals with two of the signals being twice as intense as the others. As in the case of **10**, it is apparent that irradiation of **15** has resulted in cleavage of bond b to give secondary alkyl radical **17** which has subse-

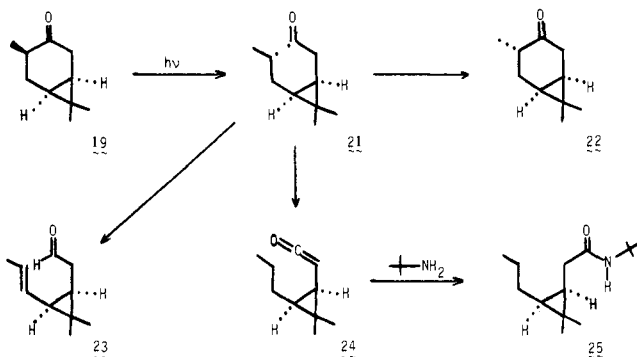


quently undergone a hydrogen transfer to provide ketene **18**. Reaction of **18** with methanol affords **16**.

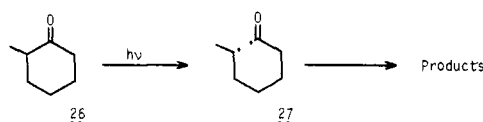
Are the photoreactions of **10** and **15** the consequence of the cleavage of bond b in these ketones being especially favored or do they follow from the scission of bond a being disfavored? An examination of the many reported photoreactions of  $\beta,\gamma$ -cyclopropyl cyclic ketones clearly shows that in the absence of unusual structural features  $\alpha$ -scission to give a cyclopropylcarbinyl radical is favored over cleavage leading to a primary alkyl radical.<sup>2-4</sup> This also appears to be the case for a secondary alkyl radical. Heckert and Kropp have found that irradiation of (-)-*cis*-4-caranone **19** under a variety of conditions provides a mixture of photoproducts that can readily be accounted for by initial  $\alpha$ -cleavage of the C-4 to C-5 bond in **19** to give diradical **20**.<sup>2c</sup> Norrish type I cleavage of bond C-3



to C-4 in **19** does not seem to be an important process. Such a scission would give diradical **21** which might be expected to undergo ring closure to give some **22** and/or hydrogen-transfer processes to provide unsaturated aldehyde **23** or ketene **24**. It



was shown that **19** does not photoepimerize to **22**, nor was **23** detected in the crude photolysate of **19**.<sup>2c</sup> However, when **19** was irradiated in the presence of *tert*-butylamine, an amide (assumed to be **25**) was found among the products, but in less than 1% yield.<sup>2c</sup> These results stand in striking contrast to the photochemistry of other 2-alkylcyclohexanones which undergo  $\alpha$ -cleavage predominantly or solely at the more substituted carbon. Thus, the photoproducts from 2-methylcyclohexanone (**26**) arise exclusively from diradical **27**.<sup>7</sup> Consequently, it can



be concluded that the unprecedented photoreactions observed for **10** and **15** are *not* determined by cleavage leading to a secondary radical being preferred over scission to give a cy-

clopropylcarbinyl radical. Rather it appears that the acylcyclopropylcarbinyl biradical **14** that might be formed from **10** by cleavage of bond a is destabilized relative to biradical **12**.

It is clear from both electron spin resonance studies<sup>8</sup> and theoretical calculations<sup>9</sup> that the stabilization provided to a radical center by a cyclopropyl substituent is geometrically dependent. Both approaches have led to the conclusion that the cyclopropylcarbinyl radical prefers the "bisected" conformation **28** to the "perpendicular" conformation **29**. The

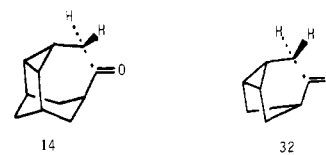


calculations show that **29** is less stable than **28** by 6.05 (INDO)<sup>9a</sup> to 1.4 (ab initio with a STO-3G Gaussian basis set)<sup>9b</sup> kcal/mol. Moreover, both computer conformational analysis calculations<sup>10</sup> and experimental evidence<sup>11</sup> suggest that at room temperature homoadamantane (**30**) possesses  $C_{2v}$



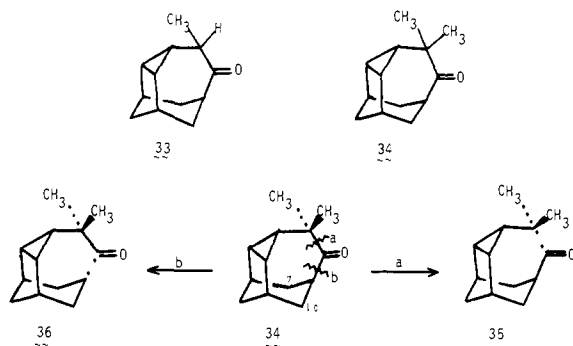
symmetry; i.e., the two-carbon bridge is not twisted. This also seems to be the case for 4-homoadamantylcarbene (**31**).<sup>12</sup> If this geometry holds for ketone **10**, then **10** contains a plane of symmetry and cleavage of bond a in **10** would lead to a cyclopropylcarbinyl radical whose initial conformation is "perpendicular", i.e., **14**. The rigid carbon skeleton of ketone **15** also requires that cleavage of bond a affords a perpendicular cyclopropylcarbinyl radical. In this geometry the cyclopropyl substituent mildly inductively destabilizes the radical center.<sup>13</sup> Thus, in effect, the alternative Norrish type I cleavages available in **10** and **15** can occur by scission of bond a to give an acyl radical and a "primary" radical or by cleavage of bond b to provide an acyl radical and a secondary radical. The photoreactions thus proceed by the more stable radicals.

On the other hand, it might be argued that photocleavage of bond a in both **10** and **15** occurs in preference to bond b, but efficient radical coupling of the resulting diradical precludes significant product formation. Product formation from **14** or **32** requires some torsion about the bond from the radical center



to the cyclopropyl moiety in order to have sufficient orbital overlap to generate the corresponding homoallyl radical. The carbon skeleton of **14** holds the two radical centers in close proximity. It is possible that coupling of the radicals in **14** to regenerate **10** may occur much faster than rearrangement of the cyclopropylcarbinyl radical and thus product formation from **14** may not take place. Although **32** is potentially more flexible than **14**, an analogous rationale may account for the photochemistry of **15**.

In order to investigate these ideas, we have examined the photochemical consequences of alkyl substitution at the  $\alpha$  carbon in ketone **10**. Treatment of **10** with 1 equiv of lithium *N*-cyclohexyl-*N*-isopropylamide at  $-70$  °C, followed by the addition of an excess of methyl iodide, provides a mixture of 4-methyl-2,11-dehydro-5-homoadamantanone (**33**) and 4,4-dimethyl-2,11-dehydro-5-homoadamantanone (**34**) in yields of 45 and 4.5%, respectively. Prolonged irradiation of a methanol solution of **34** only results in a small amount of photodegradation and no detectable product formation. Photocleavage of bonds a and b in **34** would lead to diradicals **35**



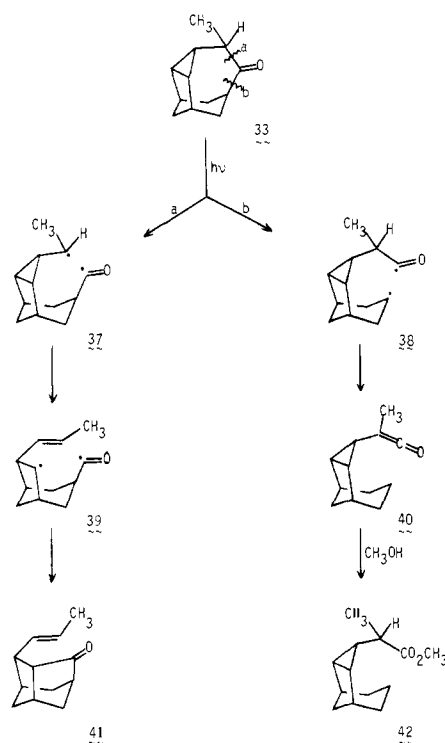
and **36**, respectively. In this case path a should be favored since scission of bond a would give a tertiary radical, whereas scission of bond b would provide a secondary radical. An examination of molecular models of **34** does not show any significant interactions between the methyl substituents and the endo hydrogens at C-7 and C-10. Consequently, the molecular geometry of **34** would be expected to resemble that of **10**. Thus, cleavage of bond a in **34** would give a cyclopropylcarbiny radical **35** with a perpendicular conformation and rotation about the bond from the radical center to the cyclopropyl group would be required in order to give a homoallyl radical. Since irradiation of **34** leads to no net reaction, it appears that radical coupling in **35** to regenerate **34** proceeds significantly faster than rearrangement of the cyclopropylcarbiny radical. This behavior is reminiscent of the remarkable photostability of adamantanone.<sup>14</sup>

These constraints to product formation are removed in the case of ketone **33**. Here competitive Norrish type I photocleavages at bonds a and b each must lead to an acyl radical and a secondary alkyl radical (Scheme I). A hydrogen is present at C-4 in **33** and so ketene formation from **38** is possible. However, of greatest interest is the presence of a single substituent at C-4 which, by a simple symmetry argument, must induce some degree of torsion in the two-carbon bridge relative to **10**. This means that cleavage of bond a in **33** must lead to cyclopropylcarbiny radical **37** which is not in a perpendicular conformation. In accord with these considerations, irradiation of a methanol solution of **33** gives two primary photoproducts. The major product was obtained in 65% yield and has been identified as methyl *endo*-tricyclo[3.3.1.0<sup>2,4</sup>]-non-3'-*syn*-yl-2-propionate (**42**). Ester **42** shows a carbonyl absorption at 1739 cm<sup>-1</sup> in its infrared spectrum and the <sup>1</sup>H NMR spectrum of **42** contains a methoxy singlet at  $\delta$  3.67, a one-proton multiplet for the hydrogen  $\alpha$  to the carbonyl at  $\delta$  3.30-2.90, and a methyl doublet at  $\delta$  1.30. The minor product was obtained in 5% yield and characterized as 4-*endo*-[1-(*E*)-propenyl]-2-noradamantanone (**41**). The infrared spectrum of **41** contains a characteristic cyclopentanone carbonyl absorption at 1749 cm<sup>-1</sup> and shows a strong trans olefinic C-H bending vibration at 965 cm<sup>-1</sup>.

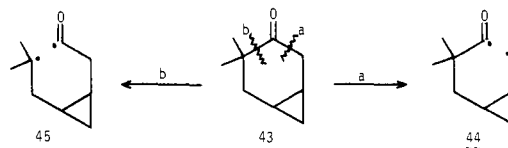
The formation of **41** and **42** from **33** is consistent with the competitive photocleavage of bonds a and b in **33** (Scheme I). Scission of bond a in **33** provides diradical **37**, which rearranges to homoallyl radical **39**. Ring closure of **39** gives **41**. Cleavage of bond b in **33** affords diradical **38**, which undergoes hydrogen transfer to provide ketene **40**. Reaction of **40** with methanol gives **42**. Since **41** is photolabile under the reaction conditions, the chemical yields of **41** and **42** do not reflect the relative propensities for the photocleavage of bonds a and b in **33**. However, the relative product yields do suggest that bond b is cleaved in preference to bond a. This may be deceiving for it is possible that diradical **37** may be ring closing to regenerate **33** more efficiently than it is rearranging to **39**.

In all of these studies the photocleavage of bond b in  $\beta,\gamma$ -cyclopropyl cyclic ketones has been made competitive with the scission of bond a by effectively disfavoring the cleavage

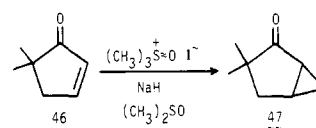
Scheme I



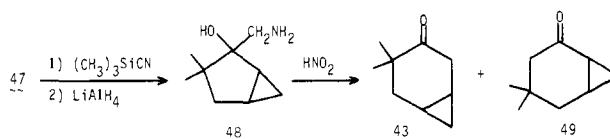
of bond a and/or by hindering product formation upon cleavage of bond a. In principle, the preferential scission of bond b also could be accomplished by making the cleavage of bond b especially favored through sufficiently stabilizing alkyl radical **8** relative to cyclopropylcarbiny radical **6**. To test this alternative we have examined the photochemistry of 4,4-dimethylbicyclo[4.1.0]heptan-3-one (**43**). In this ketone scission of bond a would lead to an acyl radical and a cyclopropylcarbiny radical (**44**), whereas cleavage of bond b would give an acyl radical and a tertiary alkyl radical (**45**).



Ketone **43** was prepared from 5,5-dimethyl-2-cyclopentenone<sup>15</sup> (**46**). Treatment of **46** with dimethylloxosulfonium methylide<sup>16</sup> provides 3,3-dimethylbicyclo[3.1.0]hexan-2-one (**47**). This compound previously was obtained in a mixture of



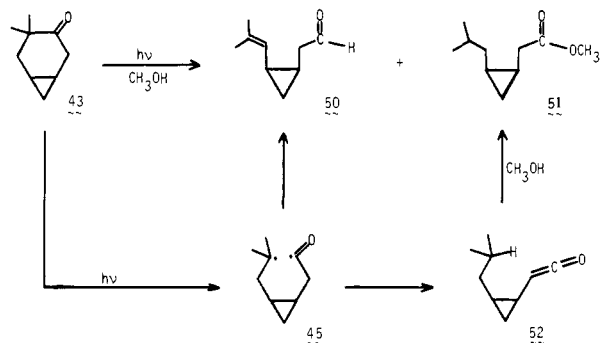
products resulting from the deamination of 6,6-dimethyl-2-aminocyclohexanone.<sup>17</sup> Ketone **43** was then generated from **47** by Tiffeneau-Demjanov ring expansion. Reaction of **47** with trimethylsilyl cyanide,<sup>18</sup> followed by reduction of the resulting trimethylsilyl cyanohydrin ether with lithium aluminum hydride, gives  $\beta$ -amino alcohol **48**. Treatment of **48**



with nitrous acid provides a mixture of **43** and 4,4-dimethylbicyclo[4.1.0]heptan-2-one (**49**) in yields of 37 and 12%, respectively. The infrared spectrum of **43** contains an absorption

for the nonconjugated carbonyl at  $1711\text{ cm}^{-1}$ , whereas the conjugated carbonyl in **49** appears at  $1695\text{ cm}^{-1}$ .

Irradiation of a methanol solution of **43** through a Vycor filter gives a mixture of 2-*cis*-isobutenylcyclopropylacetaldehyde (**50**) and methyl 2-*cis*-isobutenylcyclopropylacetate (**51**)



in yields of 25 and 12%, respectively. The infrared spectrum of the major product shows absorptions at  $2720$  and  $1730\text{ cm}^{-1}$  for the aldehyde functional group, while the  $^1\text{H NMR}$  spectrum of **50** contains a signal for the aldehyde proton at  $\delta$  9.87–9.69 and a multiplet at  $\delta$  4.97–4.60 for the olefinic proton. The infrared spectrum of ester **51** contains a carbonyl absorption at  $1744\text{ cm}^{-1}$  and its  $^1\text{H NMR}$  spectrum features a methoxy singlet at  $\delta$  3.64, a two-proton doublet for the hydrogens  $\alpha$  to the carbonyl at  $\delta$  2.22, and a six-proton doublet for the *gem*-dimethyls at  $\delta$  0.93. These products can only be accounted for by initial Norrish type I cleavage of bond b in **43** to give diradical **45**. Competitive hydrogen transfers in **45** provide aldehyde **50** and ketene **52**. Capture of **52** by the solvent affords ester **51**. Thus, it appears that photocleavage in **43** to give a tertiary radical is preferred over generation of a cyclopropylcarbinyl radical. This suggests that, in contrast to the photochemical behavior of **19**, preferential photocleavage of bond b in other mono- $\alpha'$ -substituted  $\beta,\gamma$ -cyclopropyl cyclic ketones might be achieved by having one exceptionally good radical stabilizing group, e.g., phenyl, present at the  $\alpha'$  carbon.

## Experimental Section

Melting points were obtained in sealed capillary tubes using a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were obtained on Perkin-Elmer 180 or 337 spectrophotometers. Proton magnetic resonance spectra were recorded with a Perkin-Elmer R-12B 60-MHz spectrometer and are referenced to an internal standard of tetramethylsilane. Apparent splittings are reported in all cases. Carbon magnetic resonance spectra were taken at an operating frequency of 22.63 MHz on a Bruker HFX-90 spectrometer equipped for Fourier transform pulsed NMR with a Nicolet 1085 data acquisition system and are referenced to an internal standard of tetramethylsilane. Electron-impact mass spectra were obtained with a Du Pont CEC 21-110B mass spectrometer. Unless noted otherwise, yields were obtained by integration of appropriate signals in the  $^1\text{H NMR}$  spectrum of the product(s) vs. the signal of a predetermined amount of an added standard (generally chloroform or trichloroethylene) and are regarded as being accurate to ca.  $\pm 10\%$ . Elemental analyses were performed by Micro-Analysis, Inc., Wilmington, Del.

**Photolysis of 2,11-Dehydro-5-homoadamantanone (10).** A nitrogen-purged solution of **10**<sup>5</sup> (94 mg, 0.58 mmol) in methanol (10 mL) was irradiated through a Vycor filter with a Hanovia L 450-W high-pressure mercury lamp. Monitoring the photolysis by GLC (10 ft  $\times$  0.25 in. SE-30 column, 200  $^\circ\text{C}$ ) showed a gradual disappearance of **10** and the concomitant appearance of a single photoproduct. The reaction was essentially complete after irradiation for 6 h. Evaporation of the solvent at reduced pressure gave an oil. Analysis of the residue by  $^1\text{H NMR}$  indicated that the product was obtained in ca. 60% yield. Purification by GLC (above conditions) provided methyl *endo*-tricyclo[3.3.1.0<sup>2,4</sup>]non-3-*syn*-ylacetate (**11**) as a colorless oil:  $^1\text{H NMR}$   $\delta$  (CCl<sub>4</sub>) 3.67 (s, 3 H, OCH<sub>3</sub>), 3.02–2.79 (m, 2 H, CH<sub>2</sub>CO), 2.72–1.16

(complex m, 13 H);  $^{13}\text{C NMR}$   $\delta$  (CDCl<sub>3</sub>) 174.6 (C=O), 51.5, 45.8, 33.1, 33.0, 30.1, 28.2, 24.1, 13.0 in the ratio of 1:1:1:1:2:1:2:2:1, respectively; IR  $\nu$  (CCl<sub>4</sub>) 3010, 2940, 2880, 1742, 1490, 1465, 1435, 1320, 1300, 1265, 1165, 1050, 1040, 1010  $\text{cm}^{-1}$ .

Anal. Calcd for C<sub>12</sub>H<sub>18</sub>O<sub>2</sub>: C, 74.19; H, 9.34. Found: C, 74.21; H, 9.20.

**Photolysis of Tricyclo[3.2.1.0<sup>2,7</sup>]octan-4-one (15).** A nitrogen-purged solution of **15**<sup>6</sup> (320 mg, 2.6 mmol) in methanol (30 mL) was irradiated through a Vycor filter with a Hanovia L 450-W high-pressure mercury lamp. Monitoring the photolysis by GLC (10 ft  $\times$  0.25 in. DC-550 column, 165  $^\circ\text{C}$ ) showed a gradual disappearance of **15** with the concomitant formation of a major photoproduct and trace amounts of several minor photoproducts. The reaction was terminated after irradiation for 6 h and the solvent was evaporated at reduced pressure. Analysis of the oily residue by  $^1\text{H NMR}$  showed that the major product was obtained in ca. 45% yield. Purification by GLC (above conditions) gave methyl bicyclo[3.1.0]hex-6-*syn*-ylacetate (**16**) as a colorless oil:  $^1\text{H NMR}$   $\delta$  (CDCl<sub>3</sub>) 3.79 (s, 3 H, OCH<sub>3</sub>), 2.32 (d,  $J = 6.7$  Hz, 2 H, CH<sub>2</sub>CO), 2.64–1.0 (br m, 9 H);  $^{13}\text{C NMR}$   $\delta$  (CDCl<sub>3</sub>) tentative assignments 172.3 (C=O), 49.4 (OCH<sub>3</sub>), 27.1 (CH<sub>2</sub>CO), 24.3 (C-3), 22.8 (C-2 and C-4), 20.1 (C-1 and C-5), 15.0 (C-6); IR  $\nu$  (CCl<sub>4</sub>) 3030, 2955, 2870, 1744, 1440, 1365, 1315, 1260, 1190, 1165  $\text{cm}^{-1}$ .

Anal. Calcd for C<sub>9</sub>H<sub>14</sub>O<sub>2</sub>: C, 70.10; H, 9.15. Found: C, 70.39; H, 8.90.

**4-Methyl-2,11-dehydro-5-homoadamantanone (33) and 4,4-Dimethyl-2,11-dehydro-5-homoadamantanone (34).** A stirred solution of *N*-isopropylcyclohexylamine (240 mg, 1.7 mmol) in anhydrous tetrahydrofuran (5 mL) which was maintained under nitrogen was cooled to  $-70\text{ }^\circ\text{C}$  and treated dropwise with *n*-butyllithium (0.73 mL of a 2.2 M hexane solution, ca. 1.6 mmol). After the reaction mixture had been stirred for 15 min at  $-70\text{ }^\circ\text{C}$ , a solution of **10** (250 mg, 1.54 mmol) in anhydrous tetrahydrofuran (3 mL) was added and the resulting solution was stirred at  $-70\text{ }^\circ\text{C}$  for 30 min. At this point the reaction mixture was stirred vigorously and methyl iodide (2.2 g, 15.4 mmol) was added rapidly. The reaction mixture was stirred overnight, during which time it was allowed to slowly warm to room temperature. Ether (25 mL) was then added and the solution was poured into 10% aqueous hydrochloric acid. The resulting aqueous layer was separated and further extracted with ether (2  $\times$  25 mL). The organics were combined and washed sequentially with 10% aqueous sodium bisulfite (2  $\times$  15 mL), 10% aqueous hydrochloric acid (10 mL), saturated aqueous sodium bicarbonate (2  $\times$  10 mL), and brine (10 mL) and then dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure provided an oil which was column chromatographed on silica gel with hexane as eluent. Initially, 13 mg (4.5% yield) of **34** was obtained. Final purification of **34** via GLC (10 ft  $\times$  0.25 in. DC-550 column, 215  $^\circ\text{C}$ ) gave a colorless solid: mp 44.5–46  $^\circ\text{C}$ ;  $^1\text{H NMR}$   $\delta$  (CCl<sub>4</sub>) 2.8–2.3 (br m, 4 H), 2.17–1.17 (br m, 14 H, containing the *gem*-dimethyl singlet at  $\delta$  1.38); IR  $\nu$  (CCl<sub>4</sub>) 3020, 2940, 2865, 1700, 1470, 1450, 1375, 1360, 1355, 1340, 1310, 1250, 1160, 1120, 1080, 1065, 1035  $\text{cm}^{-1}$ . Exact mass: calcd for C<sub>13</sub>H<sub>18</sub>O, 190.136; found, 190.137. Continued elution with hexane provided 122 mg (45% yield) of **33** as an oil:  $^1\text{H NMR}$   $\delta$  (CCl<sub>4</sub>) 3.29 (doublet of quartets,  $J_1 = 7.4$ ,  $J_2 = 2.8$  Hz, 1 H, CH<sub>3</sub>CHCO-), 2.82–1.12 (br m, 15 H, containing a methyl doublet,  $J = 7.4$  Hz, at  $\delta$  1.39); IR  $\nu$  (CCl<sub>4</sub>) 2935, 2865, 1703, 1460, 1450, 1255, 1160  $\text{cm}^{-1}$ . Exact mass: calcd for C<sub>12</sub>H<sub>16</sub>O, 176.120; found, 176.120.

**Photolysis of 33.** A nitrogen-purged solution of **33** (50 mg, 0.28 mmol) in methanol (4 mL) was irradiated through a Vycor filter with a Hanovia L 450-W high-pressure mercury lamp. Monitoring the photolysis by GLC (10 ft  $\times$  0.25 in. DC-550 column, 215  $^\circ\text{C}$ ) showed a gradual disappearance of **33** and the concomitant appearance of a major and a minor photoproduct. The reaction was essentially complete after irradiation for 50 min. Evaporation of the solvent at reduced pressure gave an oil. Purification of the photoproducts by GLC (above conditions) provided methyl *endo*-tricyclo[3.3.1.0<sup>2,4</sup>]non-3'-*syn*-yl-2-propionate (**42**) as a colorless oil [ $^1\text{H NMR}$   $\delta$  (CCl<sub>4</sub>) 3.67 (s, 3 H, OCH<sub>3</sub>), 3.30–2.90 (m, 1 H, -CHCO<sub>2</sub>CH<sub>3</sub>), 2.71–0.96 (br m, 16 H, containing a methyl doublet,  $J = 6.7$  Hz, at  $\delta$  1.30)]; IR  $\nu$  (CCl<sub>4</sub>) 3005, 2940, 2880, 1739, 1480, 1460, 1435, 1375, 1335, 1250, 1190, 1160, 1125, 1070  $\text{cm}^{-1}$ . Anal. Calcd for C<sub>13</sub>H<sub>20</sub>O<sub>2</sub>: C, 74.96; H, 9.63. Found: C, 75.14; H, 9.55] and 4-*endo*-[1-(*E*)-propenyl]-2-noradamantanone (**41**) as a colorless oil [ $^1\text{H NMR}$   $\delta$  (CCl<sub>4</sub>) 5.80–5.45 (br m, 2 H, -CH=CH-), 3.3–1.1 (complex m, 14 H, containing a poorly resolved methyl doublet at  $\delta$  1.85)]; IR  $\nu$  (CCl<sub>4</sub>) 2940, 2870, 1749,

1475, 1450, 1380, 1175, 1065  $\text{cm}^{-1}$ . Exact mass: calcd for  $\text{C}_{12}\text{H}_{16}\text{O}$ , 176.120; found, 176.119].

Analysis of the crude photolysate by  $^1\text{H}$  NMR showed that **42** and **41** were obtained in yields of ca. 65 and 5%, respectively. Although **42** proved to be stable under the photolysis conditions, further irradiation of the crude photolysate led to the disappearance of **41**.

**3,3-Dimethylbicyclo[3.1.0]hexan-2-one (47)**. Dimethyl sulfoxide (60 mL, freshly distilled from calcium hydride) was added under nitrogen to a mixture of sodium hydride (54 mmol, washed several times with hexane) and trimethylsulfoxonium iodide (12 g, 54 mmol) in a flame-dried flask. Vigorous gas evolution ensued which led to a milky-white solution of dimethylsulfoxonium methylide. To this stirred solution was added dropwise a solution of 5,5-dimethyl-2-cyclopentenone<sup>15</sup> (5.4 g, 48.9 mmol) in anhydrous dimethyl sulfoxide (12 mL). An exothermic reaction occurred to yield a clear red solution. After stirring for 6 h at room temperature, the mixture was poured into water (500 mL) and then extracted with ether (3  $\times$  50 mL). The combined ether extracts were washed successively with saturated aqueous sodium bicarbonate (20 mL), water (20 mL), and brine (20 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure (100 mmHg, 25  $^{\circ}\text{C}$ ) gave crude **47** which was column chromatographed on silica gel with 0.5% ether-pentane as eluent. This provided 1.17 g (19% yield) of **47**. Final purification via GLC (10 ft  $\times$  0.25 in. DC-550 column, 120  $^{\circ}\text{C}$ ) afforded **47** as a colorless oil:  $^1\text{H}$  NMR  $\delta$  ( $\text{CCl}_4$ ) 2.18–1.62 (m, 4 H), 1.43–0.67 (m, 8 H, containing methyl singlets at  $\delta$  1.03 and 0.99); IR  $\nu$  ( $\text{CCl}_4$ ) 3050, 3015, 2970, 2945, 2880, 1725, 1470, 1450, 1385, 1360, 1310, 1300, 1205, 1170, 1135, 1050, 1030, 1010, 980  $\text{cm}^{-1}$ . These spectroscopic data compare well with those previously reported for **47**.<sup>17</sup>

**4,4-Dimethylbicyclo[4.1.0]heptan-3-one (43) and 4,4-Dimethylbicyclo[4.1.0]heptan-2-one (49)**. Zinc iodide (5 mg) was added to a solution of **47** (810 mg, 6.5 mmol) in freshly distilled trimethylsilyl cyanide (1.56 g, 15.8 mmol) which was maintained at ca. 5  $^{\circ}\text{C}$  under nitrogen. The resulting solution was allowed to warm to room temperature and then was stirred at this temperature under nitrogen for 48 h. At this point the excess trimethylsilyl cyanide that was present was removed from the reaction mixture by evaporation at reduced pressure to give a viscous oil which showed no carbonyl absorption in the infrared. The resulting unpurified  $\alpha$ -siloxy nitrile was dissolved in anhydrous ether (10 mL) and the solution was added dropwise under nitrogen to a stirred slurry of lithium aluminum hydride (2.5 g, 65 mmol) in anhydrous ether (70 mL). After the addition had been completed, the reaction mixture was stirred for 12 h at room temperature. The excess lithium aluminum hydride present was then destroyed by the dropwise addition of 2.5 mL of water, followed by 2.5 mL of 15% sodium hydroxide and 7.5 mL of water. Stirring was continued until a granular white precipitate formed which was filtered and washed with methylene chloride. The filtrates were combined and the solvent was evaporated at reduced pressure to provide crude amino alcohol **48** as a pale yellow oil.

A solution of sodium nitrite (700 mg, 10.0 mmol) in water (4 mL) was added dropwise to a stirred solution of crude **48** in acetic acid (2 mL) and water (11 mL) which was maintained at 0  $^{\circ}\text{C}$ . The resulting reaction mixture was allowed to warm slowly to room temperature and then was stirred at this temperature for 10 h. The reaction mixture was diluted with brine (50 mL) and extracted with ether (3  $\times$  25 mL). The combined ether extracts were washed with saturated aqueous sodium bicarbonate (4  $\times$  10 mL) and brine (10 mL) and then dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure gave an oil which was Kugelrohr distilled to provide 440 mg (49% overall yield) of a mixture of **43** and **49**. Column chromatography of this material on silica gel with pentane as eluent afforded 328 mg of **43** as an oil:  $^1\text{H}$  NMR  $\delta$  ( $\text{CCl}_4$ ) 2.92–1.81 (complex m, 4 H), 1.66–0.80 (m, 10 H, containing methyl singlets at  $\delta$  1.20 and 0.91); IR  $\nu$  ( $\text{CCl}_4$ ) 3060, 3020, 2970, 2920, 2855, 1711, 1470, 1460, 1420, 1385, 1365, 1110, 1090, 1080, 1030  $\text{cm}^{-1}$ .

Anal. Calcd for  $\text{C}_9\text{H}_{14}\text{O}$ : C, 78.21; H, 10.21. Found: C, 78.08; H, 10.07.

Continued elution with 1% ether-pentane provided 110 mg of **49** as an oil:  $^1\text{H}$  NMR  $\delta$  ( $\text{CCl}_4$ ) 2.21–0.56 (complex m containing a sin-

glet at  $\delta$  0.93),  $\delta$  ( $\text{C}_6\text{D}_6$ ) 2.27–0.56 [complex m, containing a broad singlet at  $\delta$  1.69 ( $-\text{CH}_2\text{CO}-$ ) and methyl singlets at  $\delta$  0.80 and 0.63]; IR  $\nu$  ( $\text{CCl}_4$ ) 3075, 3005, 2950, 2925, 2870, 1695, 1465, 1355, 1285, 1245, 1190, 1085, 1045, 1025  $\text{cm}^{-1}$ .

Anal. Calcd for  $\text{C}_9\text{H}_{14}\text{O}$ : C, 78.21; H, 10.21. Found: C, 78.33; H, 10.07.

**Photolysis of 43**. A nitrogen-purged solution of **43** (150 mg, 1.1 mmol) in methanol (13 mL) was irradiated through a Pyrex filter with a Hanovia L 450-W high-pressure mercury lamp. Monitoring the photolysis by GLC (10 ft  $\times$  0.25 in. DC-550 column, 150  $^{\circ}\text{C}$ ) showed a gradual disappearance of **43** and the concomitant formation of two photoproducts. The reaction was terminated after 58 h of irradiation when the photolability of the primary photoproducts became apparent. Evaporation of the solvent at reduced pressure gave an oil. Purification of the photoproducts by GLC (above conditions) provided **2-cis-isobutenylcyclopropylacetaldehyde (50)** as a colorless oil [ $^1\text{H}$  NMR  $\delta$  ( $\text{CCl}_4$ ) 9.87–9.69 (m, 1 H,  $-\text{CHO}$ ), 4.97–4.60 (m, 1 H,  $(\text{CH}_3)_2\text{C}=\text{CH}-$ ), 2.94–0.78 (m, 12 H, containing the methyls at ca.  $\delta$  1.71)]; IR  $\nu$  ( $\text{CCl}_4$ ) 3070, 2975, 2925, 2820, 2720, 1730, 1460, 1370, 1250  $\text{cm}^{-1}$ . Exact mass: calcd for  $\text{C}_9\text{H}_{14}\text{O}$ , 138.104; found, 138.105] and **methyl 2-cis-isobutylcyclopropylacetate (51)** as a colorless oil [ $^1\text{H}$  NMR  $\delta$  ( $\text{CCl}_4$ ) 3.64 (s, 3 H,  $-\text{OCH}_3$ ), 2.22 (d,  $J = 6.7$  Hz, 2 H,  $-\text{CH}_2\text{CO}_2\text{CH}_3$ ), 2.0–0.6 (m, 13 H, containing a doublet,  $J = 5.7$  Hz, at  $\delta$  0.93 for  $(\text{CH}_3)_2\text{CH}-$ ); IR  $\nu$  ( $\text{CCl}_4$ ) 3060, 2995, 2950, 2870, 1744, 1470, 1440, 1380, 1365, 1315, 1260, 1185, 1165, 1020  $\text{cm}^{-1}$ . Exact mass: calcd for  $\text{C}_{10}\text{H}_{18}\text{O}_2$ , 170.131; found, 170.131]. Analysis of the crude photolysate by  $^1\text{H}$  NMR showed that **50** and **51** were obtained in yields of ca. 25 and 12%, respectively.

## References and Notes

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