Cyclohexenone Photochemistry. Photogeneration of Methyl Radicals from *tert*-Butyl Alcohol during Photolysis of 3-Cyano-4,4-dimethylcyclohex-2-en-1-one[1]

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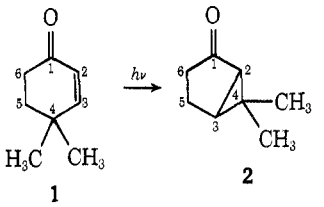
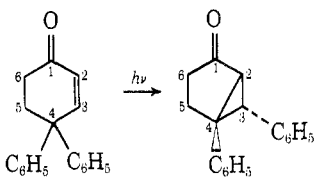
The irradiation of 3-cyano-4,4-dimethylcyclohex-2-en-1-one (**10**) in *tert*-butyl alcohol under conditions favoring intramolecular photorearrangement afforded no rearranged product. Instead, a novel methyl radical substitution reaction occurred to give 3-cyano-2,4,4-trimethylcyclohex-2-en-1-one (**11**). Formation of 3-cyano-2-perdeuteriomethyl-4,4-dimethylcyclohex-2-en-1-one (**12**) on irradiation of **10** in *tert*-butyl alcohol-d_9 showed the source of the incorporated methyl group to be *tert*-butyl alcohol. These observations necessitate qualification of assumptions regarding the suitability of *tert*-butyl alcohol as an inert solvent for photochemical studies of α,β-unsaturated ketones. The role of *tert*-butyl alcohol was confirmed by effecting the substitution reaction thermally using di-*tert*-butyl peroxide as the methyl radical source.

The intramolecular photorearrangements of 2-cyclohexenones show a striking dependence on the type and position of the ring substituents. The two most common types of phototransformations, skeletal rearrangement and aryl group migration, are exemplified by 4,4-dimethyl-2-cyclohexenone (**1**)[2] and 4,4-diphenyl-2-cyclohexenone (**3**),[3] respectively. Whereas the rearrangement of **1** to **2** involves 4,5-bond cleavage with 3,5- and 2,4-bond formation, **3** rearranges to **4** via 4,3-phenyl migration and direct 2,4 bonding without skeletal rearrangement.



1 **2**

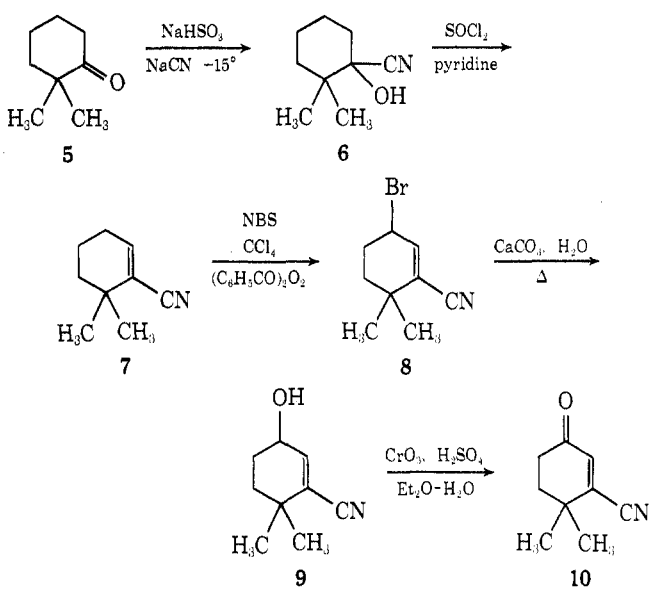


3 **4**

A major point of mechanistic interest regarding the above transformations is the electronic character at the β carbon of the excited-state cyclohexenone. The results of numerous investigations of both the rearrangement and migration processes[4] leave controversy regarding the dipolar or diradical nature of the rearranging species. Although the photochemical aryl migration reactions of systems specifically designed to test the electronic character of the β carbon[5] suggest that this process occurs via a photoexcited diradical species, the validity of conclusions regarding the electronic nature of C-3 during skeletal rearrangement based on the results of aryl migration studies is at best tenuous, particularly in view of recent evidence[6,7] that these two processes occur from different excited states whose electronic distributions are quite possibly dissimilar.

The above questions regarding the mechanism involved in cyclohexenone photorearrangements suggested the introduction of a substituent at C-3 of the enone moiety which would be sensitive to the electronic character of this position upon photoexcitation. The cyano group seemed well suited for this purpose. This group is generally recognized as a powerful electron-withdrawing substituent,[8] both by inductive and resonance mechanisms. In reactions

Scheme I



5 **6** **7** **8** **9** **10**

which proceed via a carbonium ion, such as electrophilic aromatic substitution, a cyano substituent retards the rate of attack by an electrophile and destabilizes positive charge developed in the transition state. The opposite effect is to be expected for cyano-substituted molecules undergoing carbanionic or radical reactions, in which an electron-rich transition state (or intermediate) is involved. It was thus anticipated that the cyano group would influence the course of the photorearrangement in a manner indicative of the electronic nature of the rearranging species.

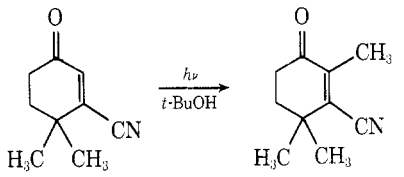
A comprehensive study[9] of the alkyl substituent requirements for intramolecular photorearrangement of 2-cyclohexenones has shown that the fourth carbon atom of the cyclohexenone ring must be fully alkyl substituted. As discussed above, aryl substituents at this position result in 4,3 migration with no skeletal rearrangement. With this knowledge in hand, a procedure was developed for the synthesis of 3-cyano-4,4-dimethylcyclohex-2-en-1-one (**10**) from 2,2-dimethylcyclohexanone (**5**). The multiple-step route is outlined in Scheme I.

Results

Irradiation of **10** in *tert*-butyl alcohol afforded a product mixture which contained one volatile photoproduct in 15% yield (VPC analysis). A comparison of the NMR spectra of

10 and the photoproduct indicated that the olefinic proton of 10 had been replaced by a methyl group. Since the chemical shift positions, multiplicities, and peak areas of all other protons in both spectra were identical, it was concluded that skeletal rearrangement had not occurred. On the basis of additional spectral and elemental analyses the photoproduct was identified as 3-cyano-2,4,4-trimethylcyclohex-2-en-1-one (11). The presence of a methyl group at C-2 in 11 is further indicated by the red shift of 11 nm in the π,π^* absorption maximum in the uv spectrum of 11 relative to that of 10.

In addition, careful VPC and mass spectral analyses of 10 showed that it contained virtually no 11 before irradiation, and the NMR spectrum of the crude photolysate after solvent removal but before steam distillation or VPC analysis contained all peaks which appeared in the product NMR spectra after separation and purification. Thus 11 is a true photoproduct of 10 under these irradiation conditions.

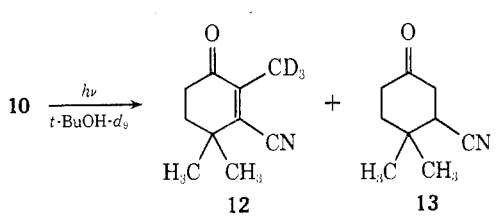


10 11

Since there is no precedent in the literature for the occurrence of this type of alkyl substitution reaction during photolysis of a 2-cyclohexenone, the source and mechanism of incorporation of the C-2 methyl group in 11 remained open to question. The combined amounts of 10 and 11 recovered from the photolysate were less than 50% of the original charge of 10. There are thus two possible sources of methyl groups: degraded molecules of 10 or the solvent, *tert*-butyl alcohol.

Irradiation of a solution of 10 in cyclohexane resulted in rapid destruction of starting material (VPC analysis); however, no volatile photoproducts were produced. This result indicated that formation of 11 quite likely involves *tert*-butyl alcohol, and it further showed that photorearrangement of 10 does not occur under conditions employing two quite different solvent media.

A more definitive test to determine the origin of the C-2 methyl group involved the use of *tert*-butyl alcohol-d_9. Irradiation of 10, in this solvent afforded one new volatile component whose VPC retention time corresponded to that of 11. This component was isolated by preparative VPC and identified by high-resolution mass spectrometry as 3-cyano-2-perdeuteriomethyl-4,4-dimethylcyclohex-2-en-1-one (12). The mass spectrum of 12 also exhibited an

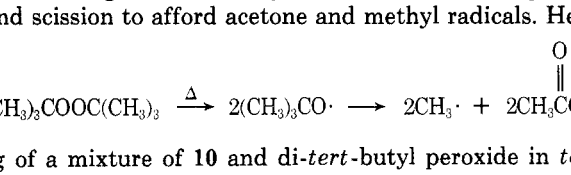


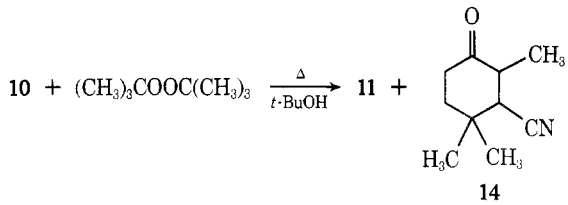
12 13

intense peak at *m/e* 151.0997, which does not correspond to $(M - CH_3)^+$ (see Experimental Section); rather, this peak indicated an ion having the formula $C_9H_{13}NO$. In light of the starting material employed in this reaction and previous examples of similar systems in which hydrogen abstraction produces the saturated analogue of the cyclohexenone employed,[9] the most reasonable structure corresponding to $C_9H_{13}NO$ would be 3-cyano-4,4-dimethylcyclohexanone (13). Further evidence that the *m/e* 151 peak results from a molecular ion was provided by field ionization mass spectral analysis of the component containing 12. VPC studies utilizing independently synthesized 13 confirmed the possibility that this compound would have eluted simultaneously with 12 under the conditions employed for isolation of the latter compound.

The results obtained show that *tert*-butyl alcohol is indeed the source of the methyl group which replaces the C-2 hydrogen of 10 in its photoconversion to 11. The probable presence of 13 in the product mixture further suggests that 10 may be involved in hydrogen abstraction from the solvent and/or the intermediate involved in the formation of 11. The mechanistic implications of these results will be discussed later.

Since it appeared that formation of 11 results from attack of 10 by photochemically generated methyl radicals, the possibility that the same result could be effected with thermally generated methyl radicals was explored. Di-*tert*-butyl peroxide is known[10] to decompose at elevated temperature to give *tert*-butoxy radicals which undergo C–C bond scission to afford acetone and methyl radicals. Heating of a mixture of 10 and di-*tert*-butyl peroxide in *tert*-butyl alcohol gave 11 in 46% yield plus 8% of a compound whose mass and NMR spectra were consistent with the structure 3-cyano-2,4,4-trimethylcyclohexanone (14), the saturated analogue of 11.





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Discussion

The results obtained from the photolysis of 10 in *tert*-butyl alcohol are consistent with the stepwise mechanism outlined in Scheme II. Hydrogen abstraction by excited-state 10 produces a *tert*-butoxy radical which decomposes to give acetone[11] and a methyl radical (step 1). The role of 10 in this process is supported by the formation of undeuterated 13 during irradiation of 10 in *tert*-butyl alcohol-d_9 and by the lack of previous reports of unimolecular photodecomposition of *tert*-butyl alcohol during irradiation at >290 nm.

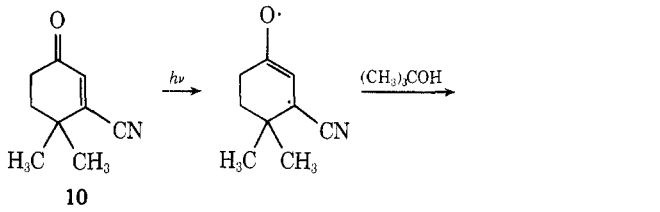
The next step in this sequence is attack at the C-2 position of 10 by methyl radical to give the α-cyano radical, 16. The facile formation 11 during thermolysis of di-*tert*-butyl peroxide provides substantial evidence for the occurrence of this process. In the particular case of 10 this step is promoted by the cyano group at C-3, since cyano-substituted olefins are greatly activated for donor (e.g., alkyl) radical attack,[12] and the resulting radical (16) would be stabilized by delocalization involving the cyano substituent.

Abstraction of the C-2 hydrogen of 16 is the necessary third and final step for the formation of 11. The process by which this occurs remains debatable since no one species has been identified as the abstracting agent. Inclusion of intermediate 15 as shown in Scheme II accounts for the formation of 13 during photolysis of 10 in *tert*-butyl alcohol-d_9.

In the absence of quantum yield and reaction rate data for the conversion of 10 to 11 the relative efficiencies of methyl radical substitution in 10 vs. skeletal rearrangement

Scheme II

Step 1



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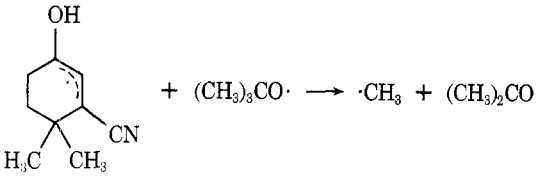

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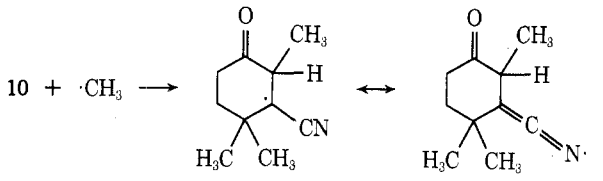
Step 2



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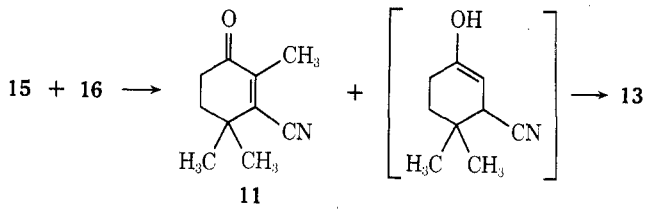
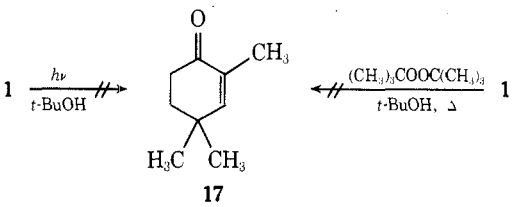
Step 3



11

in cyclohexenones such as 1 cannot be determined. It is clear, however, that any preference for methyl radical attack of **10** does not control the mode of reaction, since **10** does not photorearrange in cyclohexane, a medium in which methyl substitution does not occur. The cyano substituent in **10** thus effectively quenches skeletal rearrangement. At the same time it is obvious that the cyano group is directly responsible for methyl radical substitution in **10**, since analogous compounds such as 1 do not form substitution products [e.g., 2,4,4-trimethylcyclohex-2-en-1-one (**17**)] during irradiation[2,13] in *tert*-butyl alcohol or when heated with di-*tert*-butyl peroxide in *tert*-butyl alcohol (see Experimental Section).



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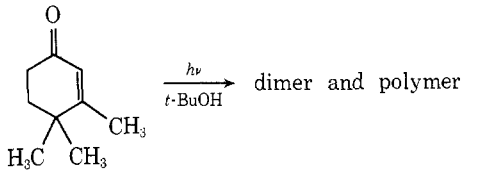
Steric inhibition toward photorearrangement resulting from the relatively small, cylindrical cyano group is not likely to be significant. A more pronounced effect is to be expected from the electronic influences of this group on the photoexcited species. In the case of **10**, quenching of skeletal rearrangement does not provide a clue to the electronic nature of C-3 after photoexcitation. While the failure of excited-state **10** to undergo rearrangement may suggest destabilization of positive character at C-3 by the cyano substituent, the behavior of 3,4,4-trimethylcyclohex-2-en-1-one (**18**), which gives only dimer and polymer upon photolysis,[9] does not support this argument, since the methyl group at C-3 of **18** would be capable of stabilizing cationic character at that position.



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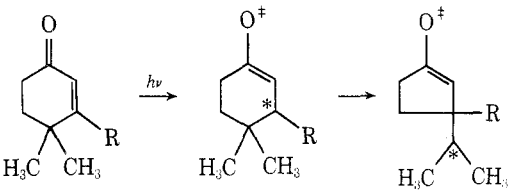
The inertness of both **10** and **18** toward photorearrangement may be explained in terms of the relative energies of the reactive intermediates, regardless of electronic distribution. Excitation of **10** or **18** would afford **19**, which contains a tertiary cationic or radical moiety at C-3. Rearrangement to **20** would create another tertiary cation or radical; no increased stability would obtain from this isom-

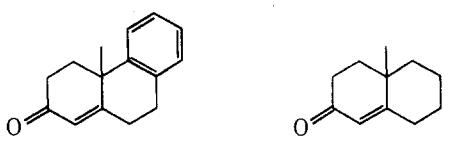


1, R = H
10, R = CN
18, R = CH_3

19 20

‡ = · or −
* = · or +

erization. On the other hand, in cyclohexenones such as 1 this rearrangement step may find its driving force in the conversion of a secondary cation or radical to a more stable tertiary cation or radical. Unfortunately, the facile photorearrangement of 3,4,4-trisubstituted fused-ring enones such as **21**[14] and **22**[15] to bicyclic products is inconsistent with this picture.



21 22

Conclusion

Although the photochemistry of **10** does not allow a choice to be made regarding the mechanism of cyclohexenone photorearrangement, the photoinitiated methyl substitution of **10** represents a previously unobserved radical substitution reaction of α,β-unsaturated ketones. It is evident that radical attack is promoted by the electron-withdrawing cyano substituent which also serves to stabilize the intermediate α-cyano radical through induction and resonance involving the cyano group directly. The role of *tert*-butyl alcohol as the source of methyl radicals also points out the need for reassessment of assumptions[4b,16] regarding the inertness and consequent suitability of this solvent for studies of α,β-unsaturated ketone photochemistry.

Experimental Section

Instruments and Methods. All melting points are corrected. NMR spectra were measured on Varian A-60, Hitachi Perkin-Elmer RE-20, and Varian HR-220 spectrometers. Ultraviolet spectra were recorded on a Beckman DK-2A spectrophotometer and, unless otherwise noted, were obtained in 95% ethanol. Mass spectra were measured at 70 eV on CEC 21-103C, CEC 21-110B, Hitachi Perkin-Elmer RMU-6, and Finnigan Model 3000 spectrometers. VPC analyses were performed on Varian Model 202b, 1525c, 90P-3, and 1400 instruments. Separations were effected with the following columns: (A) 5 ft × 0.125 in. 3% SE-30 on 100–120 mesh

Aeropak 30; (B) 5 ft × 0.25 in. 20% SE-30 on 60–80 mesh Chromosorb W; (C) 20 ft × 0.375 in. 15% SE-30 on preparative grade Chromosorb W; (D) 6 ft × 0.25 in. 5% LAC-446 on 80–100 mesh Chromosorb P; (E) 5 ft × 0.125 in. 3% OV-1 on 60–80 mesh Gas-Chrom Q. Flame ionization was employed for analyses with column A; column E was used only in conjunction with the Finnigan Model 3000 mass spectrometer; thermal conductivity was used with all other columns.

2,2-Dimethylcyclohexanone (5). Conversion of 2-methylcyclohexanone to **5** was carried out according to published procedures.[17] Purification was accomplished by distillation through a 1-m annular Teflon spinning band still.

1-Cyano-6,6-dimethylcyclohexene (7). A mixture of 148 g (1.17 mol) of **5** and 114.7 g (2.34 mol, 100% excess) of sodium cyanide in 300 ml of water was stirred at −15° (ice–salt bath). A solution of 226.7 g (2.18 mol) of sodium bisulfite in 500 ml of water was added slowly and the mixture was vigorously stirred for an additional 4 hr. The mixture was then filtered, and the filtrate was extracted with four 300-ml portions of ether. The etherate was dried over magnesium sulfate and filtered, and the ether was distilled under reduced pressure. The solid crude **6** weighed 174.5 g (1.14 mol, 97.5%).

To a solution of the crude **6** in 225 ml of pyridine and 200 ml of dry, reagent-grade benzene stirred at −15° was added a solution of 259.5 g (2.18 mol) of thionyl chloride in 200 ml of dry benzene at a rate which maintained the temperature at 10°. After addition was complete the mixture was slowly warmed and finally stirred at the reflux temperature for 1 hr.

The cooled mixture was poured onto 1 l. of cracked ice. The resulting mixture was divided into two equal portions, and each portion was extracted with four 250-ml portions of ether. The combined extracts were washed with dilute hydrochloric acid, 5% sodium carbonate solution, and finally water.

After drying over sodium sulfate, the etherate was filtered and the solution was concentrated. Distillation of the residue under reduced pressure afforded 135.9 g (1.01 mol, 86.1%) of **7**: bp 59–60° (2.2 mm) [lit.[18] 102–104° (26 mm)]; ir (neat) 1635 (C=C) and 2260 cm^{-1} (C≡N); NMR (CCl_4) δ 6.37 (t, 1, J = 5 Hz, C=CH), 2.13 (m, 2, C=CHCH_2), 1.88–1.50 (m, 4), and 1.15 (s, 6, CH_3).

Anal. Calcd for $C_9H_{13}N$: C, 79.95; H, 9.69; N, 10.36. Found: C, 80.03; H, 9.70; N, 10.53.

1-Cyano-3-bromo-6,6-dimethylcyclohexene (8). A mixture of 135 g (1.00 mol) of **7**, 195.8 g (1.10 mol) of *N*-bromosuccinimide, 0.25 g of benzoyl peroxide, and 1.0 l. of reagent-grade carbon tetrachloride was stirred at the reflux temperature for 12 hr. The mixture was then cooled in an ice bath; the succinimide was removed by filtration, and the filtrate was concentrated. Reduced-pressure distillation of the residue through a 10-cm Vigreux column gave 177.4 g (0.83 mol, 83%) of **8**: bp 83° (0.60 mm); ir (neat) 1625 (C=C) and 2230 cm^{-1} (C≡N); NMR (neat) δ 6.53 (d, 1, J = 4.5 Hz), 4.80 (m, 1), 1.45–2.32 (m, 4), 1.20 (s, 3), and 1.12 (s, 3). This compound was insufficiently stable for microanalysis even when stored under nitrogen at 0°.

3-Cyano-4,4-dimethylcyclohex-2-en-1-ol (9). A mixture of 177.4 g (0.83 mol) of **8**, 91 g (0.91 mol, 10% excess) of calcium carbonate, and 900 ml of water was stirred at the reflux temperature for 24 hr. The cooled mixture was filtered into a separatory funnel and the solid material was washed with water and ether. The combined filtrate and washings were extracted with three 300-ml portions of ether. The combined ether extracts were dried over sodium sulfate, filtered to remove drying agent, and concentrated. Distillation of the residue yielded 102.9 g (0.681 mol, 82%) of **9**: bp 89–91° (0.225 mm); ir (neat) 3500 (OH), 2227 (C≡N), and 1635 cm^{-1} (C=C); NMR ($CDCl_3$) δ 6.46 (d, 1, J = 3.0 Hz, C=CH), 4.23 (br m, 1, HCOH), 2.65 (s, 1, OH), 1.40–2.17 (m, 4, CH_2CH_2), 1.20 (s, 3, CH_3), and 1.18 (s, 3, CH_3).

Anal. Calcd for $C_9H_{13}NO$: C, 71.49; H, 8.66; N, 9.27. Found: C, 71.05; H, 8.74; N, 9.53.

3-Cyano-4,4-dimethylcyclohex-2-en-1-one (10). A solution of 116.9 g (0.39 mol) of sodium dichromate dihydrate in 65 ml (1.22 mol) of 96% sulfuric acid diluted to 500 ml was added over a period of 4 hr to a stirred solution of 102.9 g (0.681 mol) of **9** in 300 ml of ether. During the addition the mixture was maintained at <10°; the mixture was then allowed to stir at room temperature for 2 hr.

The aqueous and organic layers were then separated; the aqueous layer was extracted with three 250-ml portions of ether. The organic portion and the ether extracts were combined and washed with 250 ml of 10% potassium bicarbonate solution and water and dried over magnesium sulfate. The etherate was filtered and the filtrate was concentrated. Distillation of the residue afforded 82.8 g (0.556 mol, 81.6%) of **10**: bp 64–66° (0.45 mm); ir (CCl_4) 1600 (C=C), 1688 (C=O), and 2220 cm^{-1} (C≡N); NMR ($CDCl_3$) δ 6.38 (s, 1, C=CH), 2.55 (m, 2, CH_2CH_2CO), 1.95 (m, 2, CH_2CH_2CO), and 1.35 (s, 6, CH_3); uv λ_{max} 237 nm (ε 13600), 350.5 (28); mass spectrum (70 eV) m/e 149 (M^+).

Anal. Calcd for $C_9H_{11}NO$: C, 72.45; H, 7.43; N, 9.39. Found: C, 72.33; H, 7.73; N, 9.61.

When cooled to 0°, **10** solidified as greenish-white crystals, mp 25.5–27.0°. The 2,4-dinitrophenylhydrazone was obtained from a 95% ethanol solution as canary yellow crystals, mp 219–221° (slight dec).

3-Cyano-4,4-dimethylcyclohexanone (13). **13** was prepared according to a published procedure[19] for the preparation of 3-cyanocyclohexanone from 2-cyclohexenone. From 68.9 g (0.556 mol) of **1**[13] was obtained 43.5 g (0.288 mol, 51.8%) of **13**, bp 120–122° (0.20 mm), mp 80–81.5°. The white, crystalline product was sublimed at 55° (0.13 mm): mp 84.0–84.5°; ir (CCl_4) 1725 (C=O) and 2245 cm^{-1} (C≡N); NMR (CCl_4) δ 2.18–3.00 (m, 5), 1.55–1.90 (m, 2), 1.28 (s, 3, CH_3), and 1.23 (s, 3, CH_3); mass spectrum (70 eV) m/e 151 (M^+), 136 [$(M - CH_3)^+$], 123 [$(M - CO)^+$], and 108 [$(123 - CH_3)^+$].

Anal. Calcd for $C_9H_{13}NO$: C, 71.49; H, 8.66; N, 9.27. Found: C, 71.60; H, 8.76; N, 9.15.

Irradiation of 10 in *tert*-Butyl Alcohol. The apparatus consisted of a 2.0-l. cylindrical irradiation vessel equipped with a water-cooled internal Pyrex immersion well containing a 550-W uv lamp and fitted with provisions for maintaining a slow stream of nitrogen through the solution, and for magnetic stirring. In a typical run, 3.00 g (0.0201 mol) of **10** and 2.0 l. of *tert*-butyl alcohol freshly distilled from potassium metal were placed in the vessel. Deoxygenation was accomplished by bubbling nitrogen through the stirred solution for 1.5 hr prior to commencing the irradiation (commercial tank nitrogen was prepurified by passage through three wash bottles of Fieser's solution,[20] one bottle of saturated lead acetate solution, and finally a drying tower containing anhydrous calcium sulfate). Nitrogen was slowly bubbled through the solution during the irradiation.

Irradiation was terminated after 100 hr. The *tert*-butyl alcohol was distilled under reduced pressure, leaving 3.8 g of an amber-colored viscous oil. VPC analysis of this oil revealed the presence of a trace of residual solvent, as well as two volatile components. The volatile components were separated from the total mixture by steam distillation. The aqueous distillate was extracted with four 125-ml portions of ether. The combined ether extracts were washed with water and dried over sodium sulfate. Filtation and distillation of solvent under reduced pressure yielded 1.38 g of bright yellow oil. Analysis of the oil by VPC (column D at 135°) showed the presence of two components in a ratio of 36:64. Both components were isolated by preparative scale VPC (column C at 160°). The major component (64%) was shown by NMR and ir analyses to be unchanged **10** (29.4% recovery). Based on spectral and elemental analyses, the other component was assigned structure **11**: yield 9.50 g (0.0030 mol, 14.9% based on initial **10**; 21.1% conversion from **10**); ir (CCl_4) 1608 (C=C), 1689 (C=O), and 2212 cm^{-1} (C≡N); NMR ($CDCl_3$) δ 2.55 (m, 2, CH_2CH_2CO), 2.04 [s, 3, $C(CH_3)$=C], 1.93 (m, 2, CH_2CH_2CO), 1.33 [s, 6, $C(CH_3)_2$]; uv λ_{max} 248 nm (ε 13500), 323 (28), and 348 (sh, 25); mass spectrum (70 eV) m/e 163 (M^+).

Anal. Calcd for $C_{10}H_{13}NO$: C, 73.59; H, 8.03; N, 8.58. Found: C, 73.58; H, 8.10; N, 8.56.

Determination of the Purity of the Stock Sample of 10. VPC Analysis. A sample of **10** was analyzed by VPC (column B at 140°); the highest detector sensitivity was used. No peaks other than that corresponding to **10** were observed. A 9:1 (v/v) mixture of **10** and **11** was prepared. Analysis of this mixture under conditions identical with those used for the pure sample showed the presence of two peaks, corresponding to **10** and **11**, in a ratio of 8.9:1.1.

Mass Spectral Analysis. A sample of **10** was analyzed by mass spectrometry. The relative intensities of the molecular ion peaks of **10** and **11** were 1254.3 and 2.0 units, respectively. Assuming equal mass spectrometer sensitivities for both compounds and comparable intensities for the molecular ions, the amount of **11** in the stock sample of **10** is no greater than 0.16%.

Irradiation of 10 in *tert*-Butyl Alcohol-d_9. A mixture of 69.6 mg (0.467 mmol) of **10** and 4.28 g of *tert*-butyl alcohol-d_9 was placed in a 15 × 75 mm Pyrex tube to which a ⅋ 14/20 outer joint was sealed. The contents were deoxygenated with ultrahigh purity nitrogen for 5 min, after which the tube was tightly capped with a ⅋ 14/20 stopper. The tube was clamped against the outer surface

of a vertical Pyrex cooling well containing the 550-W Hg lamp. The sample was irradiated for 143.5 hr. VPC analysis (column A at 105°) of the crude photolysate showed, in addition to solvent, the presence of two major peaks. After distillation of the *tert*-butyl alcohol-d_9 at atmospheric pressure, the two volatile components were isolated by preparative VPC (column C at 162°). High-resolution mass spectral analysis of the component corresponding to **10** showed a molecular ion at *m/e* 149.0842 (M^+ calcd for **10**: *m/e* 149.0840). The major fragment ions at *m/e* 134, 121, 107, and 79 are also consistent with the structure of **10**. Analysis by high-resolution mass spectrometry of the other component (whose VPC retention time corresponded to that of **11**) showed a molecular ion at *m/e* 166.1185 (M^+ calcd for $C_{10}H_{10}D_3NO$: *m/e* 166.1186) as well as peaks at *m/e* 165.1128 (calcd for $C_{10}H_{11}D_2NO$: *m/e* 165.1123) and 163.0997 (calcd for $C_{10}H_{13}NO$: *m/e* 163.0996). This component was assigned structure **12**.

The above spectrum also exhibits an intense peak at *m/e* 151.0997, which does not correspond to $(M - CH_3)^+$ for **12** (calcd for $C_9H_7D_3NO$: *m/e* 151.0951). Rather, this peak corresponds to $C_9H_{13}NO$ (calcd *m/e* 151.0996). Analysis by field ionization mass spectrometry also showed an intense *m/e* 151 peak, suggesting a molecular ion. Under the conditions employed for VPC isolation of **12**, any **13** present in the reaction mixture could have eluted simultaneously.

Irradiation of 10 in Cyclohexane. A solution of 2.0 g (0.013 mol) of **10** in 750 ml of cyclohexane (Matheson Spectroquality) was placed in an apparatus similar to that described for the irradiation of **10** in *tert*-butyl alcohol. Deoxygenation was effected by bubbling nitrogen through the solution for 3 hr prior to and during the irradiation. The reaction was monitored by VPC (column A at 98°); 80% of the initial **10** had been consumed after 4.5 hr. Prolonged irradiation (44.5 hr) did not result in further destruction of starting material. Inspection of the solution surface of the lamp well revealed the presence of a coating of ivory-colored solid (accounting for the lack of complete destruction of **10**); this solid was non-VPC volatile. VPC analysis (column A at 98°) of the crude photolysate did not indicate the presence of any components which were not present in the initial mixture. Distillation of the solvent under reduced pressure afforded a residue of extremely viscous, honey-colored syrup; repeated extraction of this material with hexane and reduced-pressure distillation of hexane from the combined extracts resulted in isolation of a very small amount of **10**. No other low molecular weight compounds could be isolated.

Reaction of 10 with Di-*tert*-butyl Peroxide in *tert*-Butyl Alcohol. To a solution of 5.0 g (0.034 mol) of **10** in 1.0 l. of *tert*-butyl alcohol contained in a 2-l. glass-lined autoclave was added 4.96 g (0.034 mol) of di-*tert*-butyl peroxide. The autoclave was purged with nitrogen and sealed, and the contents were heated at 120° for 65 hr, during which an internal pressure of 70 psig was observed.

After distillation of solvent from the cooled reaction mixture under reduced pressure there remained a dark yellow oil. VPC analysis of this oil (column A at 100°) showed the presence of 14 components (in addition to residual di-*tert*-butyl peroxide), of which six accounted for greater than 98% of the total peak area. No absorption below δ 4.0 was detected in the NMR spectrum ($CDCl_3$) of this mixture, although a strong singlet absorption at δ 2.0 indicated the possible presence of **11** as a major component of the mixture. The complexity of the δ 0.7–1.6 region indicated the presence of an appreciable amount of polymeric material. The volatile components were removed from this mixture by steam distillation. The aqueous distillate was extracted with chloroform and the combined extracts were dried over magnesium sulfate. Filtration and removal of solvent under reduced pressure yielded 3.31 g of a light yellow oil which by VPC analysis (column B at 130°) was found to contain six components. The mass spectra of these components were determined by eluting the separated components from the VPC (column E, programmed from 80 to 120° at 6°/min) into the mass spectrometer. The data obtained are given in Table I. The mass spectrum of component A exhibited gradually decreasing peak intensities up to about *m/e* 180; no discrete molecular ion or fragmentation pattern was observed. The fragmentation pattern of component B was essentially identical with that of **10**, as was the VPC retention time. This component thus corresponds to unreacted **10**. Component C was isolated by preparative VPC (column B at 130°). The mass, ir, and NMR spectra were identical with those of **11**. The mass spectrum of component D indicated a molecular weight of 165, with major fragments at *m/e* 150 $[(M - CH_3)^+]$, 137 $[(M - CO)^+]$, and 122 $[(150 - CO)^+]$; this spectrum has the same general appearance as the mass spectrum of **13**. The NMR spectrum exhibited complex multiplets at δ 2.15–2.90, 1.45–2.10, and 1.09–1.43. The sharp singlet at δ 2.04 corresponding to $CH_3C{=}C$ in **11** was not present in this spectrum. The above data suggest that component D is **14**. This compound was not analyzed further. The fragmentation pattern in the mass spectrum of component E (M^+ 179) is identical with that of D, with all *m/e* values 14 units higher. Further analyses of components E and F were not carried out.

Table I

Component	Retention time, min[a]	Parent ion, *m/e*	mmol	% yield[b]
A	4.5	[c]		
B (**10**)	5.6	149	0.44	1.3[d]
C (**11**)	6.8	163	15.29	45.6
D	8.2	165	2.69	8.0
E	9.8	179	0.92	2.8
F	14.4	[c]	0.40	1.2

[a] Column B at 130°. [b] Based on initial moles of **10**. [c] Uncertain. [d] Unreacted **10**.

Heating of 1 with Di-*tert*-butyl Peroxide in *tert*-Butyl Alcohol. To a solution of 1.00 g (8.1 mmol) of **1** in 650 ml of *tert*-butyl alcohol contained in a 2-l. glass-lined autoclave was added 1.18 g (8.1 mmol) of di-*tert*-butyl peroxide. The solution was purged with ultrahigh purity nitrogen and the autoclave was immediately sealed. The contents were heated at 120° for 60 hr.

Analysis of the cooled mixture by VPC (column B at 120°) revealed that no new components were present in the mixture. Removal of solvent under reduced pressure yielded a light yellow oil which by VPC and NMR analyses was shown to be unreacted **1** contaminated with a small amount (<10%) of nonolefinic polymeric material. This oil was not analyzed further.

Heating of 10 with *tert*-Butyl Alcohol in the Absence of Di-*tert*-butyl Peroxide. A solution of 1.0 g (6.7 mmol) of **10** in 600 ml of *tert*-butyl alcohol was heated for 60 hr under conditions identical with those described above for **1**, except that no di-*tert*-butyl peroxide was added. The cooled solution was distilled under reduced pressure to remove solvent. Analysis of the residual yellow oil by VPC (column A at 104°) revealed that no new monomeric material had been formed. No further analyses were performed.

Registry No.—**1**, 1073-13-8; **5**, 1193-47-1; **7**, 56830-35-4; **8**, 56830-36-5; **9**, 56830-37-6; **10**, 54303-58-1; **10** 2,4-DNP, 56830-38-7; **11**, 56830-39-8; **12**, 56830-40-1; **13**, 56830-41-2; sodium cyanide, 143-33-9; *N*-bromosuccinimide, 128-08-5; *tert*-butyl alcohol, 75-65-0; *tert*-butyl alcohol-d_9, 25725-11-5.

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Synthesis, Photooxygenation, and Diels–Alder Reactions of 1-Methyl-4a,5,6,7,8,8a-*trans*-hexahydronaphthalene and 1,4a-Dimethyl-4a,5,6,7,8,8a-*trans*-hexahydronaphthalene

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The model dienes 1,4a-dimethyl-4a,5,6,7,8,8a-*trans*-hexahydronaphthalene (**1b**) and 1-methyl-4a,5,6,7,8,8a-*trans*-hexahydronaphthalene (**1a**) were synthesized. The intermediate, 2-bromo-*trans*-4,10-dimethyl-*trans*-3-decalone (**5b**), was prepared by bromination of the corresponding decalone, whereas 2-bromo-4-methyl-*trans*-3-decalone (**5a**) was made by a method involving the bromination of the kinetically produced 1-methyl-2-trimethylsilyl enol ether 1,4,4a,5,6,7,8,8a-*trans*-octahydronaphthalene (**4**). Dehydrobromination, followed by reduction, and then alumina dehydration, yielded the dienes **1a** and **1b**. Dye-sensitized photooxygenation of **1a** yielded as the major product the peroxide adduct. Dye-sensitized photooxygenation of **1b** gave products derived exclusively from an "ene" allylic hydrogen abstraction and shift of double bond. Reaction of the dienophile 4-phenyl-1,2,4-triazoline-2,5-dione with **1a** yielded exclusively the Diels–Alder adduct, while reaction with **1b** afforded a mixture of Diels–Alder adduct and product derived from allylic hydrogen abstraction and shift of double bond.

The study of the steric effects of axial, angular methyl groups on ring A of sesquiterpenes and related compounds led us to synthesize model compounds **1a** and **1b**. The route chosen for the synthesis was designed to serve as a model for the reexamination of 3-keto steroid bromination. The position of bromination of these steroids is determined by the stereochemistry of the A–B ring junction, and by the presence of α substituents.[1] Earlier attempts by Gunstone[2] and Yanagita[3] to brominate **3b** yielded a mixture of nonisolable products, and it was concluded, on the basis of their dehydrobromination, that the chief product was the 4-bromo derivative. Corey's bromination of tetrahydrosantonin[4] gave the 2-bromide.

Decalones **3a** and **3b** are obtained, respectively, from the reduction of octalones **2a**[5] and **2b**[6] (Scheme I). Bromination of **3b** at 0° yields exclusively 2α-bromo-*trans*-3-decalone **5b** as a white solid. The assignment of the bromine to the 2α position, on the basis of its NMR, is consistent with published results ($J_{ax,ax}$ = 13, $J_{ax,eq}$ = 6 Hz, similar to coupling constants for 2α-bromocholestanone).[7] Attempts at direct bromination of decalone **3a** gave poor yields (less than 6%) of the 2-bromo analog. The 4-bromide is the major product, indicating the important steric effects of the angular methyl group. Bromination of **3a** to yield the 2-bromide is obtained in good yield from the silyl enol ether **4**.[8] Dehydrobromination with lithium carbonate in dimethylformamide, followed by reduction of the resulting unsaturated ketone with aluminum isopropoxide, gives the respective epimeric alcohols **7a** and **7b**. Dehydration of **7b** yields only one diene, **1b**; dehydration of **7a** gives two products, separable by vapor gas chromatography. The major product (85%) is the desired diene **1a** (Scheme I). Structure proof of **1a** was accomplished by conversion of its photooxygenation products to known derivatives.

Photooxygenation.[9] The photooxygenation of dienes **1a** and **1b** yields differing results.

With diene **1b**, the crude product obtained is identified as the mixture of hydroperoxides **9** and **10**. The lack of peroxide formation, which would have resulted from the Diels–Alder type, [4 + 2] addition, is based upon the following observations: first, the NMR of the crude product shows the angular methyl group shifted downfield to δ 1.05, as the geometry of the molecule forces it into the deshielding region of the π system of the cross-conjugated double bonds in compound **9**; second, the NMR does not reveal any peaks in the region where the "expected" peroxide should occur [cf. NMR of ascaridole (Varian, spectrum 276)]; and finally, the conversion of the crude product to a known derivative. In **9** and **10** it is assumed that, because of steric hindrance, oxygen has approached from below the plane of the molecule, justifying the stereochemistry as shown. The results of photooxygenation of **1b**, and proof of structure, are shown in Scheme II.

Attempts at product separation by column chromatography failed, perhaps owing to the thermal instability of the hydroperoxides and to their ease of dehydration and/or rearrangement. The hydroperoxide mixture is oxidized with the Sarett[10,11] reagent to yield ketones **11** and **12**, which are easily separable by vapor phase chromatography. The major product **11** (85–90%) is identical with an authentic sample prepared by an alternative method.[12] Thus, the photooxygenation of **1b** proceeds exclusively by the "ene" path, abstracting a hydrogen with a shift of a double bond.

Photooxygenation of **1a** yields a mixture of products separable by silica gel column chromatography. Scheme III shows the various products formed, and proof of their structure.

On the reasonable assumption that **13** and **16** are derived from peroxide **14**, it can be seen that photooxygenation of **1a** yields at least 80% of the [4 + 2] adduct. Since there is no steric restriction to the approach of oxygen from either side, a mixture of two diastereomeric peroxides is obtained. Mild reduction of **14** yields the diastereomeric dialcohols **17**; oxidation with the Sarett reagent affords the keto alcohol **16**, which is also obtained from the rearrangement of **14** on basic alumina. Final proof is confirmed by aromatizing the keto alcohol to the naphthol derivative **18**. This also indicates that the starting diene is **1a**, rather than **8**, its iso-

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