supported in part by NSF Grant BMS74-12247. This research was supported by NSF Grant MPS74-21436.

Registry No.—**4,** 59463-14-8; **5,** 59463-15-9; **6,** 59473-88-0; **7** isomer a, 59463-16-0; **7** isomer b, 59463-17-1; **15a,** 59463-18-2; **15b,** 59463-19-3; **16,** 21170-08-1; **16** ethylene acetal, 59463-20-6; **17,** 59463-21-7.

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Photochemistry of 3-Cyano-4,4-dimethyl-2,5-cyclohexadienone. Evidence for Selectivity during the Photorearrangement of Unsymmetric Cyclohexadienones[1]

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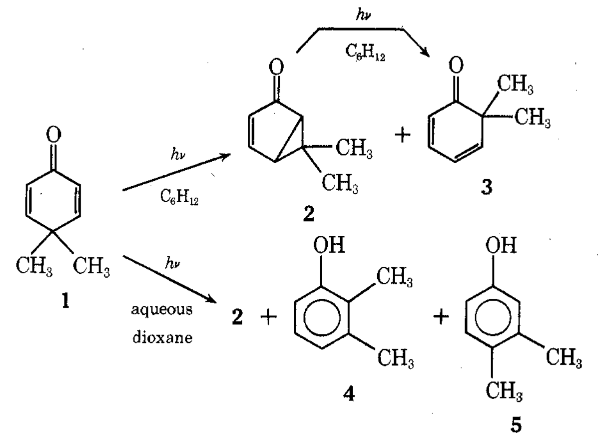
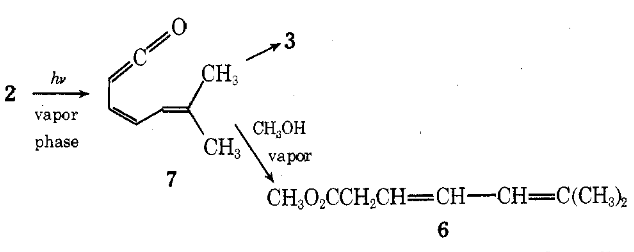
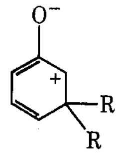
The irradiation of 3-cyano-4,4-dimethyl-2,5-cyclohexadienone (**13**) in *tert*-butyl alcohol gave *tert*-butyl 3-cyano-6-methylhepta-3,5-dienoate (**19**). Irradiation of **13** in moist *tert*-butyl alcohol yielded, in addition to **19**, (3-methyl-2-butenylidene)succinimide (**14**) and 3-carbamoyl-6-methylhepta-3,5-dienoic acid (**16**). Although no isomers resulting from photorearrangement of **13** were observed, the structures of the isolated products indicated that this process had occurred. Consistent with studies of similar systems, the results may be explained in terms of dienone rearrangement to one of two possible bicyclo[3.1.0]hexenones, which affords the observed products via a common ketene intermediate. The exclusive intermediacy of only one bicyclic ketone suggests that the photorearrangement of **13** involves excited-state diradical species.

The intramolecular photorearrangements of 2,5-cyclohexadienones in general give rise to three product types: bicyclo[3.1.0]hex-3-en-2-ones, phenols, and 2,4-cyclohexadienones, the latter resulting from recyclization of an intermediate ketene. In nucleophilic media, solvent addition to the ketene affords unsaturated acids or esters. All of these processes are well documented[2] and are typified by the photochemistry of 4,4-dimethyl-2,5-cyclohexadienone (**1**).[3] Irradiation of **1** in cyclohexane yields 6,6-dimethylbicyclo[3.1.0]hex-3-en-2-one (**2**) and 6,6-dimethyl-2,4-cyclohexadienone (**3**). Irradiation of **2** in cyclohexane affords **3**, while photolysis of **1** in aqueous dioxane gives **2** plus phenols **4** and **5**. The gas-phase irradiation of **2** likewise affords **3**, whereas addition of methanol vapor effects the formation of ester **6**. The intermediacy of a ketene (**7**) was postulated[3] to account for this behavior.

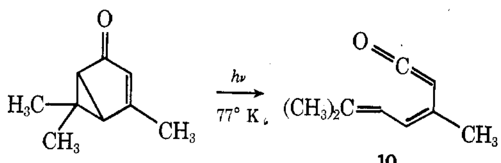




Extensive investigations of the photorearrangements of 2,5-cyclohexadienones have shown that the bicyclic ketone (e.g., **2**) is the only primary photoproduct.[2c,3] Further transformations of this intermediate are responsible for production of the other species isolated from cyclohexadienone photolysates. To some extent the stepwise nature of these photoconversions has facilitated elucidation of mechanistic details. For example, compelling evidence is available for the intermediacy of a zwitterionic species (e.g., **2a**,[3] **8**[4]) in the photoformation of phenols from bicyclic ketones, and spectroscopic



2a, R = CH_3
8, R = C_6H_5



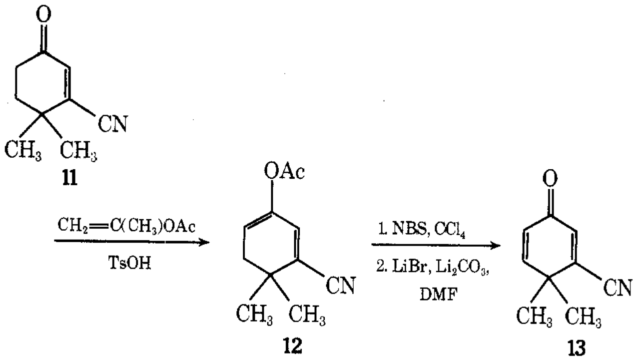
9 **10**

detection of a ketene intermediate (**10**) during low-temperature irradiation[5] of 4,6,6-trimethylbicyclo[3.1.0]hex-3-en-2-one (**9**) confirms the pathway involved in linear dienone and photoester formation.

Perhaps least well understood are the mechanistic details of the primary photoprocess, 2,5-cyclohexadienone photorearrangement. While the proposed[2c] stepwise mechanism involving 3,5 bonding followed by skeletal rearrangement has been widely applied to explain photorearrangements of this class of compounds, the electron distribution in the molecule at any given point during the transformation remains debatable. Some evidence is available that skeletal rearrangement occurs from a zwitterionic intermediate.[6] In order to probe the electronic character of the carbon skeleton during the rearrangement process, a 2,5-cyclohexadienone was synthesized with a cyano substituent at the C-3 position. This powerful electron-withdrawing group would be expected to destabilize electron-deficient species, thereby retarding rearrangement if it proceeded via a zwitterionic mechanism. On the other hand, electron-rich intermediates should be stabilized and reactivity enhanced.

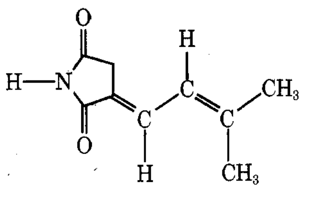
In designing a suitably substituted 2,5-cyclohexadienone, structural features which might either inhibit 3,5 bonding or induce rearrangement in an atypical fashion (as has been observed for some fused-ring dienones)[2b] were avoided. As anticipated by our previous investigation,[7] 3-cyano-4,4-dimethylcyclohex-2-en-1-one (**11**) was utilized for the synthesis of 3-cyano-4,4-dimethyl-2-cyclohexenone (**13**). A published[8] multiple-step route was utilized, with modifications, as outlined in Scheme I.

Scheme I

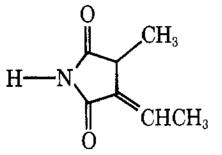


Results

Irradiation of a 10^{-2} M solution of **13** in moist[9] *tert*-butyl alcohol resulted in rapid destruction of the starting material (VPC analysis). Removal of most of the solvent caused precipitation of a tan solid; high-resolution mass spectral analysis of the purified product indicated a molecular formula equivalent to **13** plus the elements of water. The absence of nitrile and ketone functions was determined from ir and qualitative chemical analyses, which also indicated the presence of an imide moiety. A detailed analysis of the NMR and mass spectra permitted identification of the photoproduct as (3-methyl-2-butenylidene)succinimide (**14**). The ir and NMR spectral data reported[10] for methylethylidenesuccinimide (**15**) provide additional support for the correctness of structure **14**.



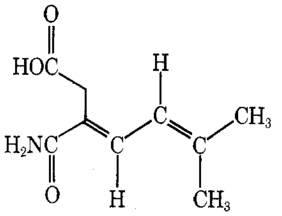
14



15

The structural assignment of compound **14** is also confirmed by its ^{13}C NMR spectrum (Table I). The observed chemical shifts are in good agreement with the predicted values,[11] based on appropriately substituted 1,3-butadienes.[12]

Low-temperature vacuum sublimation of the volatile components of the remaining photolysate afforded a solid residue. The high-resolution mass spectrum of the pure product indicated a molecular formula corresponding to **13** plus the elements of two molecules of water. The ir spectrum showed the presence of OH, C=O, and NH_2 groups, and the absence of a nitrile substituent. On the basis of additional chemical data and the similarity of its proton and ^{13}C NMR spectra (Table I) to those of **14**, this photoproduct was identified as 3-carbamoyl-6-methylhepta-3,5-dienoic acid (**16**).



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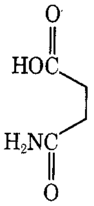

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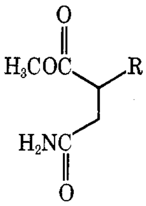


18

R = *n*-pentyl, *n*-hexyl, *n*-heptyl

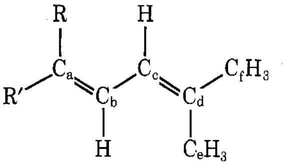
Additional supportive evidence was obtained from the ir spectra of succinamic acid (**17**)[13] and the methyl esters[14] of 2-alkylsuccinamic acids (**18**). An intense peak at *m/e* 124.0762 in the mass spectrum of **16**, corresponding to $(M - C_2H_3O_2)^+$, provided further evidence that the methylene group is situated between the carboxyl group and the olefinic chain, as shown.

The remaining volatile photolysate contained one component in addition to residual solvent and a trace of unreacted **13**. This component was isolated in good yield when **13** was irradiated in anhydrous *tert*-butyl alcohol. Chemical and spectral data suggested that this compound was a nitrile-substituted, unsaturated *tert*-butyl ester. However, the olefinic region of the NMR spectrum, which accounted for two of the 19 protons, exhibited complex coupling which could not be explained on the basis of two adjacent protons in any structure which correlated with the other available data. Spin decoupling experiments revealed that each olefinic proton resonance was in fact a pair of protons in slightly different magnetic environments. The ratio of each of the two proton pairs was approximately 40:60. These data indicated a mixture of two quite similar isomers. Although no method was found which effected complete separation of the isomers without decomposition, partial separation was achieved by column chromatography. Spectral analysis permitted their identification as a mixture of geometric isomers having the general formula **19**. The nonequivalence of the olefinic protons and previous reports[2b,15] of the isolation of cis and trans photoacids and -esters from cyclohexadienone photolysates suggest structures **19a** and **19b** for the photoesters. Additional support for structure **19** was provided by a detailed analysis of the

$$(CH_3)_2C{=}CHCH{=}C(CN)(CH_2)_xCO_2R$$

19, R = $(CH_3)_3C$; $x = 1$
20, R = C_2H_5; $x = 0$

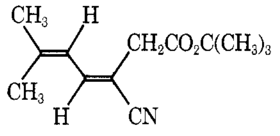
Table I. Carbon-13 Chemical Shifts for Photoproducts of 13[a]



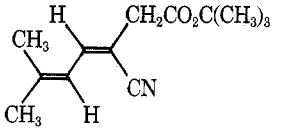
14, R, R′ = $CH_2CONHCO$
16, R = CH_2CO_2H; R′ = $CONH_2$
19a, R = $CH_2CO_2C(CH_3)_3$; R′ = CN
19b, R = CN; R′ = $CH_2CO_2C(CH_3)_3$

									t-Butyl		
Compd (solvent)	C_a	C_b	C_c	C_d	C_e	C_f	C=O	CH_2	C–O	CH_3	CN
14 ($CDCl_3$)	122.8	130.9	121.1	149.7	19.1	26.9	170.7 174.0	33.5			
16 (Me_2SO-d_6)	126.2	130.7	120.8	143.1	18.5	26.4	170.1 172.1	*b*			
19[c] ($CDCl_3$)	102.8 103.1	141.9 143.3	119.5 122.0	146.5 148.0	19.0	26.5 26.8	167.9 168.4	35.5 40.3	81.6 81.7	27.9	117.5 120.7

[a] The ^{13}C NMR spectra were obtained by the Fourier transform method at 22.63 MHz on a Bruker HFX-90 spectrometer, and chemical shifts are reported in parts per million from Me_4Si internal standard; methine, methylene, and methyl carbons were identified by single frequency off-resonance decoupling for **14** and **19**. [b] Chemical shifts of Me_2SO-d_6 solvent appeared in the region where this resonance is expected. [c] The spectrum was obtained only for a mixture of **19a** and **19b**; chemical shift values were not assigned to the individual isomers.



19a



19b

NMR spectrum of ethyl 2-cyano-5-methylhexa-2,4-dienoate (**20**)[16] (see Experimental Section).

The presence of two structurally similar isomers also follows from the ^{13}C NMR spectrum of **19** (Table I), which exhibits a pair of chemical shifts for each carbon, with the exception of the vinyl and *tert*-butyl methyl carbons which are sufficiently far from the site of geometric isomerism to be equivalent. The chemical shift difference between the two methylene carbons (4.8 ppm) further indicates that in one isomer the methylene group is cis to the isobutenyl moiety, while in the other isomer it is trans. This is also the case for the two nitrile carbons ($\Delta\delta$ 3.2 ppm).[17]

Discussion

The structural similarities in the four products obtained from the photolysis of **13** indicate that they very likely arise from a common intermediate. Ketene **21** is the likely precursor

$$(CH_3)_2C{=}CH{-}CH{=}C(CN)CH{=}C{=}O$$

21

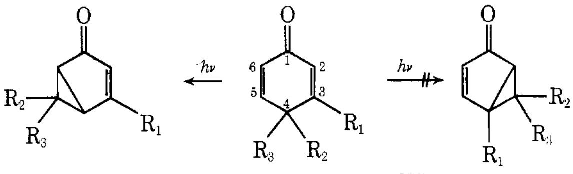
both on the basis of previous studies and structural features of the products. The ketene, in turn, doubtlessly arises either directly or indirectly from a bicyclo[3.1.0]hexenone derived from **13**.

Since it was known[3,5] that bicyclic ketones which readily afford acids or esters in nucleophilic media could be isolated from cyclohexadienone photolyses carried out in cyclohexane, **13** was irradiated in the latter solvent. Although the starting material was rapidly consumed, no low molecular weight products were formed. In another experiment, acetophenone sensitization of the photorearrangement of **13** gave the same products as direct irradiation in *tert*-butyl alcohol. Although this result suggests that the rearrangement occurs via a triplet, the intermediacy of a bicyclic ketone in the phototransformation of **13** has not been demonstrated. However, in light of previous studies and in view of the fact that ketene **21** cannot be formed from **13** by any reasonable bond alteration process not involving at least a transient bicyclic ketone species, 4-cyano-6,6-dimethylbicyclo[3.1.0]hex-3-en-2-one (**22**) is included to explain the formation of the observed products on irradiation of **13** in *tert*-butyl alcohol. Scheme II outlines the overall process.

Irradiation of **13** in *tert*-butyl alcohol results in photoexcitation to **13a**, which, whether diradical or zwitterionic, undergoes 3,5 bonding and rearrangement to give the bicyclic ketone **22**. Cleavage of the 1,2 and 5,6 bonds in **22** affords ketene **21**. Addition of water to **21** gives imide **14** and acid **16**, while *tert*-butyl alcohol addition gives ester **19a** which may partially photoisomerize to **19b**.

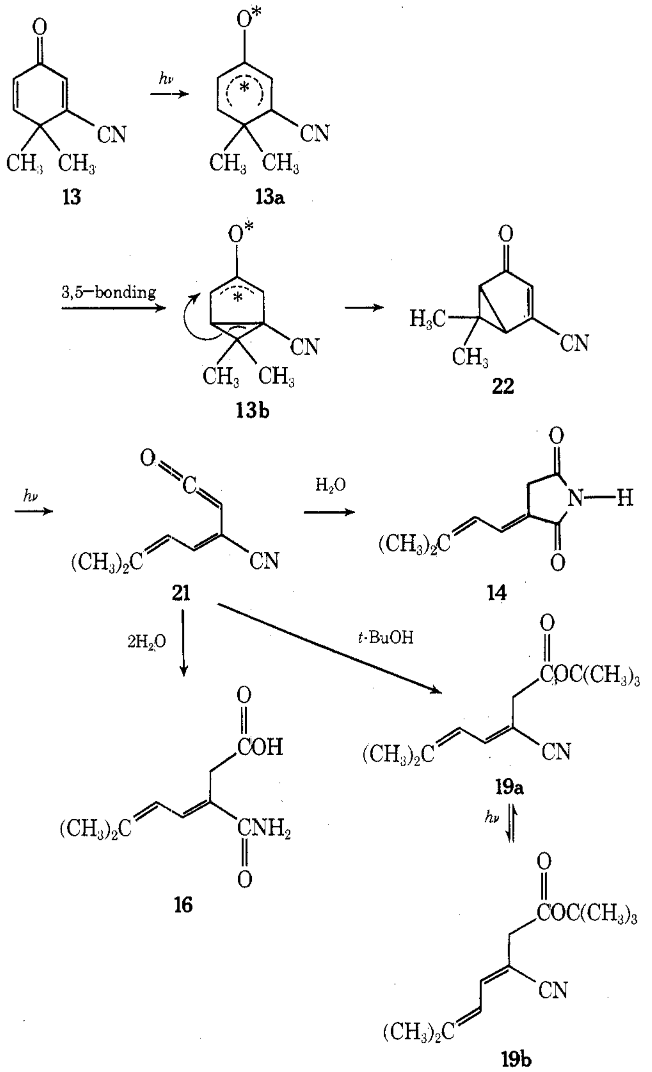
The mechanistic details of the formation of **14** and **16** from **21** were not investigated; however, addition of water to the ketene moiety of **21** would give a β-cyano acid. Addition of a second molecule of water would occur spontaneously to give amic acid **16**.[18] Although intramolecular rearrangement of the β-cyano acid could occur to give imide **14**, the sequence of water addition and ring closure to form this product is unresolved, since no precedent could be found in the literature.

Of particular interest is the indication, based on the structures of the isolated products, that the photorearrangement of **13** gives only one of the two possible bicyclic ketones. This specificity is not unique to **13**; only one bicyclic ketone was reported in each case from the photolyses of the unsymmetrical dienones **23**[5] and **24**.[19] In all of these cases[20] the C-3 substituent completely quenches skeletal rearrangement which would result in bonding between C-2 and C-4 (**26**). The preference for rearrangement to the side of the molecule not bearing the C-3 substituent can be explained in terms of a

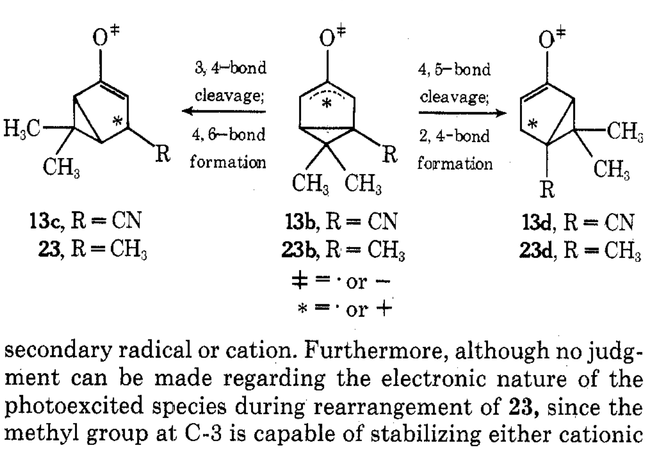


22 **13**, R_1 = CN; R_2 = R_3 = CH_3 **26**
9 **23**, R_1 = R_2 = R_3 = CH_3
25 **24**, R_1 = R_2 = CH_3; R_3 = CCl_3

Scheme II



stepwise mechanism. Following 3,5 bonding, cleavage of the 3,4 bond in **13b** or **23b** results in the formation of a tertiary radical or cation (**13c** or**23c**); on the other hand, formation of **13d** or **23d** via 4,5-bond cleavage would afford a less stable



secondary radical or cation. Furthermore, although no judgment can be made regarding the electronic nature of the photoexcited species during rearrangement of **23**, since the methyl group at C-3 is capable of stabilizing either cationic or radical character at that position (**23c**), formation of **13c** indicates that the photorearrangement of **13** proceeds via excited-state diradical intermediates, because prior demotion would lead to a zwitterionic species in which the positive charge at C-3 is destabilized by the adjacent cyano group. Indeed, if the 3,5-bonded intermediate **13b** were zwitterionic in nature, the preferred mode of rearrangement in this case would be 4,5-bond cleavage to give **13d** (* = +). This transformation does not occur, however, since no products resulting from a 2,4-bonded bicyclic ketone were present in the photolysate of **13**.[21]

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 (flame ionization); (B) 5 ft × 0.25 in. 20% SE-30 on 60–80 mesh Chromosorb W (thermal conductivity).

1-Cyano-3-acetoxy-6,6-dimethylcyclohexa-1,3-diene (12). A mixture of 30.0 g (0.20 mol) of **11**, 100 g (1.00 mol) of isopropenyl acetate, and 0.50 g (0.0026 mol) of *p*-toluenesulfonic acid monohydrate was heated at 125–130 °C with stirring. The course of the reaction was followed by VPC (column B at 150 °C), and the acetone produced was distilled as formed through a 30-cm zig-zag column maintained at 50–65 °C. After 24 h it was determined that less than 20% of the starting material had been converted; an additional 50 ml of isopropenyl acetate and 0.5 g of *p*-toluenesulfonic acid were added. After 90 h total reaction time VPC analysis showed greater than 95% conversion.

The reaction mixture was cooled and the residual isopropenyl acetate was removed under reduced pressure. The residue was taken up in 1 l. of 1:1 pentane–benzene; this solution was washed with 200 ml of 10% sodium bicarbonate solution. The residue, after solvent removal under reduced pressure, was dissolved in 1 l. of pentane. This solution was concentrated under reduced pressure until a dark polymeric material precipitated. The mixture was filtered and the solid was repeatedly extracted with hot pentane. The filtrate and pentane extracts were combined and concentrated. The residue was dissolved in methylene chloride, dried over sodium sulfate, filtered, and concentrated. Distillation of the residue yielded 33.3 g (0.174 mol, 87.2%) of **12**: bp 88–89 °C (0.4 mm); NMR (CDCl$_3$) δ 6.37 (d, 1, *J* = 1.8 Hz, CH=CCN), 5.67 (d of t, 1, *J* = 5.0 Hz, 1.8 Hz, CH$_2$ CH=COAc), 2.35 (d, 2, *J* = 5.0 Hz, CH$_2$), 2.15 (s, 3, OCOCH$_3$), and 1.22 [s, 6, C(CH$_3$)$_2$].

Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.33. Found: C, 69.00; H, 7.13; N, 7.19.

3-Cyano-4,4-dimethylcyclohexa-2,5-dienone (13). A mixture of 33.3 g (0.174 mol) of **12**, 32.5 g (0.182 mol, 5% excess) of *N*-bromosuccinimide, and 400 ml of carbon tetrachloride was heated with stirring at the reflux temperature for 7 h. The reaction mixture was cooled and the solvent was removed under reduced pressure. The residue was taken up in 125 ml of ether and filtered into a separatory funnel; the filtrate was washed with 50 ml of 10% sodium bicarbonate solution and 20 ml of water. The etherate was dried over sodium sulfate, filtered, and concentrated. The residual liquid, which showed a carbonyl peak at 1725 cm^{-1}, was dehydrobrominated without further purification.

To a solution of the above bromination product in 100 ml of *N*,*N*-dimethylformamide (DMF) were added with stirring 44.7 g (0.513 mol) of lithium bromide and 38.0 g (0.513 mol) of lithium carbonate, followed by an additional 250 ml of DMF. The mixture was stirred at the reflux temperature under nitrogen for 5 h and cooled, and the salts were removed by filtration. The filtrate was poured into 500 ml of water and extracted with four 100-ml portions of methylene chloride. The organic layer was washed with 75 ml of 10% sodium bicarbonate solution followed by 100 ml of water. The resulting mixture was dried over sodium sulfate, filtered, and concentrated. Residual DMF was distilled under aspirator pressure, leaving a black, tarry material which partially solidified upon standing.

The tarry residue was taken up in methylene chloride, and hexane was added until polymeric material precipitated. This mixture was filtered, and the solid was repeatedly extracted with hot hexane. The filtrate and hexane extracts were combined, and the solvents were removed under reduced pressure. The orange-yellow crystalline residue was sublimed twice and finally recrystallized from hexane, yielding 18.2 g (0.124 mol, 61.9%) of greenish-white crystals: mp 62–63.5 °C; ir (CCl$_4$) 1601 (C=C), 1630 (C=C), 1665 (C=O), 1730, and 2225 cm^{-1} (C≡N); NMR (CDCl$_3$)[22] δ 6.92 [d, 1, *J* = 10.0 Hz, CH=CHC(CH$_3$)$_2$], 6.72 (d, 1, *J* = 1.6 Hz, CH=CCN), 6.27 [d of d, 1, *J* = 10.0, 1.6 Hz, CH=CHC(CH$_3$)$_2$], and 1.45 (s, 6, CH$_3$); uv λ_{max}

(EtOH) 239 nm (ϵ 16 600) and 334 (39), λ_{max} (*t*-BuOH) 239 nm (ϵ 17 000) and 334 (38); mass spectrum (70 eV) *m/e* 147 (M^+).

Anal. Calcd for C_9H_9NO: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.25; H, 6.21; N, 9.63.

The 2,4-dinitrophenylhydrazone was obtained from 95% ethanol as dark orange crystals, mp 190–191.5 °C dec.

Irradiation of 13 in Anhydrous *tert*-Butyl Alcohol. A 500-ml photoreaction vessel equipped with a water-cooled internal Pyrex immersion well was dried at 110 °C for 1 h and was cooled under a nitrogen atmosphere. Into this vessel were placed 3.00 g (0.0204 mol) of **13** and a magnetic stirring bar. *tert*-Butyl alcohol was then distilled from sodium metal directly into the reactor, to a volume of 500 ml. The solution concentration was ca. 0.041 M. A sparging tube was inserted and dry helium was bubbled through the stirred solution for 12 h prior to and during irradiation with a 450-W Hg lamp.

Irradiation was terminated after 180 min. The *tert*-butyl alcohol was removed under reduced pressure at 48 °C. VPC analysis (column B at 155 °C) of the residual oil indicated the presence of one volatile component. This oil was repeatedly extracted with hexane and the combined extracts were concentrated. The residue (3.41 g) was distilled under reduced pressure to yield 2.45 g (0.111 mol, 54.3%) of a light yellow oil; bp 99.5 °C (0.05 mm); NMR ($CDCl_3$)[23] δ 1.43 [s, 9, $C(CH_3)_3$], 1.83 [m, 6, *J* = 1.5, ~0.5 Hz, $(CH_3)_2C{=}C$], 3.12 (m, 40% of 2, *J* = 1, ~0.5 Hz, CH_2CO_2), 3.18 (m, 60% of 2, *J* = 1, ~0.5 Hz, CH_2CO_2), 6.04 [d with secondary splitting, 60% of 1, *J* = 11.5, 1.5 Hz, $(CH_3)_2C{=}C\mathbf{H}$], 6.13 [d with secondary splitting, 40% of 1, *J* = 11.5, 1.5 Hz, $(CH_3)_2C{=}C\mathbf{H}$], 6.93 [d with secondary splitting, 40% of 1, *J* = 11.5, 1 Hz, $C\mathbf{H}{=}C(CN)CH_2$], and 7.06 [d with secondary splitting, 60% of 1, *J* = 11.5, 1 Hz, $C\mathbf{H}{=}C(CN)CH_2$]; ir (liquid film) 2215 ($C{\equiv}N$), 1740 ($C{=}O$), and 1642 cm^{-1} ($C{=}C$); uv λ_{max} 271 nm (ϵ 27 950); mass spectrum (70 eV) *m/e* (calcd) 221.1426 (221.1415, M^+), 165.0789 (165.0789, $M - C_4H_8$), 148.0765 (148.0762, $M - C_4H_9O$), 121.0891 (121.0891, $M - C_5H_8O_2$), 120.0817 (120.0813, $M - C_5H_9O_2$).

Anal. Calcd for $C_{13}H_{19}NO_2$: C, 70.56; H, 8.65; N, 6.33. Found: C, 70.32; H, 8.65; N, 6.41.

This oil gave a negative test with 2,4-dinitrophenylhydrazine reagent.

Double irradiation of the proton resonances in the NMR spectrum indicated the presence of two very similar isomers. No satisfactory method was found for separating these isomers without decomposition; however, partial separation was effected by column chromatography. A 40 × 1 cm column of 100–200 mesh SilicAR CC-7 was prepared and washed with AR hexane. A 0.5-g sample of the above oil was applied; elution was begun with AR hexane. Fractions 1–18 (25 ml each) were combined and concentrated. The residue was analyzed as follows: NMR ($CDCl_3$)[23] δ 1.43 (s, 9), 1.83 (m, 6, *J* = 1.5, ~0.5 Hz), 3.12 (m, 2, *J* = 1, ~0.5 Hz), 6.13 (d with secondary splitting, 1, *J* = 11.5, 1.5 Hz), 6.93 (d with secondary splitting, 1, *J* = 11.5, 1 Hz); ir (liquid film) 2216 ($C{\equiv}N$), 1738 ($C{=}O$), and 1642 cm^{-1} ($C{=}C$); uv λ_{max} 271 nm.

Elution was continued with 100 ml of hexane–ether (90:10 v/v), followed by 100 ml of 80:20 (v/v) hexane–ether. The combined fractions were concentrated and the residue was analyzed: NMR ($CDCl_3$)[23] δ 1.43 (s, 9), 1.83 (m, 6, *J* = 1.5, ~0.5 Hz), 3.18 (m, 2, *J* = 1, ~0.5 Hz), 6.04 (d with secondary splitting, 1, *J* = 11.5, 1.5 Hz), 7.06 (d with secondary splitting, *J* = 11.5, 1 Hz); ir (liquid film), 2221 ($C{\equiv}N$), 1739 ($C{=}O$), and 1641 cm^{-1} ($C{=}C$); uv λ_{max} 271 nm.

Each sample of partially purified isomer showed partial decomposition; attempts to further purify these samples resulted in increased decomposition. The NMR and ir spectra of each isomer indicated the presence of minor amounts of the other isomer.

Approximately 50 mg of a light tan solid was isolated from the pot residue of the vacuum distillation of the photolysate. This substance was identified as **14** (vide infra) on the basis of its melting point, solubility properties, and NMR spectrum. No other products were isolated.

Irradiation of 13 in Moist[9] *tert*-Butyl Alcohol. A solution of 3.00 g (0.0204 mol) of **13** in 2.0 l. of moist *tert*-butyl alcohol was placed in a cylindrical irradiation vessel equipped with a water-cooled internal Pyrex immersion well containing a 550-W Hg lamp. UHP nitrogen was bubbled through the solution for 1 h prior to and during irradiation.

Irradiation was terminated after 60 min. The uv spectrum of the photomixture was then obtained by pipetting a 1.0-ml aliquot into a 250-ml volumetric flask and diluting to volume with 95% ethanol. This spectrum showed a λ_{max} 271 nm, *A* – 1.075; no shoulders or other maxima were observed at this concentration (4.1×10^{-5} M) from 220 to 360 nm.

Most of the solvent was removed from the photolysate under reduced pressure. Upon standing, 0.37 g of tan solid separated from the residue. This material was isolated by suction filtration, washed with pentane, and air dried, mp 223–227 °C dec. Recrystallization from ethyl acetate gave white crystals: mp 225–227 °C dec; ir (KBr) 3160 (s), 3060 (s), 2930 (m), 2780 (sh, w), 1755 (m), 1695 (s), and 1618 cm^{-1} (s); NMR (Me_2SO-d_6)[23] δ 11.22 (br s, 1), 7.13 (m, 1, *J* = 12, 2.2, ~1 Hz), 5.95 (m, 1, *J* = 12, ~1 Hz), 3.30 (m, 2, *J* = 2.2, ~1 Hz), and 1.90 (m, 6, *J* = ~1 Hz); uv λ_{max} 289 nm (ϵ 20 600); mass spectrum (70 eV) *m/e* (calcd) 165.0792 (165.0789, M^+), 150 (150, $M - CH_3$), 122.0609 (122.0605, $M - C_2H_3O$), 94.0784 (94.0782, M – CONHCO), 79 [79, M – (CONHCO + CH_3)].

Table II

Irradiation time, min	Relative peak area of **13**	mmol of **13**
0	101	13.6
15	66	8.89
30	35	4.71
45	28	3.77
60	24	3.23
75	23	3.10
90	19	2.56

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.43; H, 6.71; N, 8.48. Found: C, 65.31; H, 6.86; N, 8.44.

This compound was found to be insoluble in cold 5% HCl and cold 10% $NaHCO_3$, very slightly soluble in acetone, ether, benzene, CCl_4, CH_2Cl_2, and CH_3CN, slightly soluble in cold water and cold 95% ethanol, and soluble in cold 5% NaOH and cold dimethyl sulfoxide. Negative test results were obtained with 2,4-dinitrophenylhydrazine reagent, $FeCl_3$ (in H_2O or $CHCl_3$), and benzenesulfonyl chloride, while a brown precipitate formed on addition of aqueous potassium permanganate. Based on these data, structure **14** was assigned to this compound.

Low-temperature vacuum sublimation of the filtrate effected separation of volatile and nonvolatile components. The solid residue weighed 0.47 g, mp 153.5–154.5 °C dec. Recrystallization from ethyl acetate gave white crystals: mp 155.0–155.5 ° dec; ir (KBr) 3395 (s), 3205 (s), complex series of bands 3000–2300 (m-w), 1722 (s), 1656 (s), 1638 (m), 1605 (m), and 1570 cm^{-1} (m); NMR (Me_2SO-d_6)[23] δ 12 (br s, 1), 7.17 (br s, 2), 7.16 (d, 1, *J* = 11.5 Hz), 6.07 (m, 1, *J* = 11.5, 1.0 Hz), 3.31 (br s, 2), and 1.86 (d, 6, *J* = 1.0 Hz); uv λ_{max} 278 nm (ϵ 8700); mass spectrum (70 eV) *m/e* (calcd) 183.0905 (183.0895, M^+), 168 (168, $M - CH_3$), 166 (166, M – OH), 139.0994 (139.0996, $M - CO_2$), 124.0762 (124.0762, $M - C_2H_3O_2$).

Anal. Calcd for $C_9H_{13}NO_3$: C, 59.00; H, 7.15; N, 7.65. Found: C, 58.56; H, 7.23; N, 7.64.

This compound was very slightly soluble in acetone, ether, benzene, CCl_4, CH_2Cl_2, and CH_3CN, slightly soluble in cold water, moderately soluble in cold 5% HCl and cold 95% ethanol, and soluble in cold 5% NaOH, cold 10% $NaHCO_3$, and cold dimethyl sulfoxide. Functional group tests gave negative results with 2,4-dinitrophenylhydrazine, $FeCl_3$ (in H_2O or $CHCl_3$), and benzenesulfonyl chloride, while addition of aqueous $KMnO_4$ gave a brown precipitate. On the basis of these data, this compound was assigned structure **16**.

VPC analysis (column B at 155 °C) of the volatile portion of the photolysate indicated the presence of a single component (in addition to a trace of **13**). This material was identified by its uv, ir, and NMR spectra as a mixture of **19a** and **19b**.

Irradiation of 13 in Cyclohexane. A solution of 2.00 g (0.0136 mol) of **13** in 750 ml of spectroquality cyclohexane was placed in a 750-ml photolysis vessel equipped with a water-cooled lamp well, magnetic stirring bar, and gas inlet and exit tubes. Deoxygenation was accomplished by bubbling UHP nitrogen through the stirred solution for 1 h prior to and during irradiation with the 550-W Hg arc lamp. Aliquots removed from the reaction mixture at 15-min intervals were analyzed by VPC (column A at 100 °C). The following data were obtained (Table II).

Irradiation was terminated after 1.5 h. VPC analysis (column A at 100 °C) indicated the absence of an appreciable amount of volatile components other than **13** and solvent. A film of ivory-yellow solid material coated the lamp well. This was dissolved in ether and added to the photolysate. Solvents were removed under reduced pressure, leaving 2.0 g of light yellow gummy residue. An attempt was made to partially separate the components of the mixture by precipitation of high molecular weight solids with hexane. This procedure resulted in isolation of 0.1 g of a yellow solid which, on heating, decomposed at 185–200 °C. NMR analysis (acetone-d_6) showed no olefinic absorption and suggested the presence of many types of methylene and methyl groups. Elemental analysis did not permit calculation of an empirical formula.

The remainder of the mixture was subjected to steam distillation to isolate volatile components. The steam distillate was extracted with methylene chloride and the combined extracts were dried over sodium sulfate. Filtration and concentration gave a light yellow oil which by VPC and NMR analyses was identified as unchanged **13**. No other volatile components could be isolated from the photolysate.

Ethyl 2-Cyano-5-methylhexa-2,4-dienoate (20). This compound was prepared in 15.1% yield according to a published procedure.[16] The NMR spectrum ($CDCl_3$) was interpreted in greater detail[23] than was reported in the literature:[16] δ 1.31 (t, 3, J = 7 Hz, CH_2CH_3), 2.04 [d, 6, J = 1.5 Hz, $(CH_3)_2C{=}C$], 4.28 (q, 2, J = 7 Hz, CH_2CH_3), 6.43 [d with secondary splitting, 1, J = 12, 1.5 Hz, $(CH_3)_2C{=}CH$], 8.10 [br d, J = 12 Hz, $(CH_3)_2C{=}CHCH{=}C$]. Sharpening of the doublet at δ 8.10 was observed on irradiating the peak at δ 2.04.

Irradiation of 13 in the Presence of Acetophenone. A solution of 0.524 g (0.0036 mol) of **13** and 52.8 g (0.44 mol) of acetophenone in 350 ml of *tert*-butyl alcohol was deoxygenated with UHP nitrogen for 30 min prior to irradiation through a Pyrex filter with 350-nm light. The relative concentrations were adjusted so that at this wavelength acetophenone absorbed 97% of the incident radiation.

After 1 h the irradiation was terminated and the solvents were removed under reduced pressure to give 0.48 g of an amber oil. Spectral analysis of the photolysate indicated the presence of **14** and **19**, in addition to unreacted **13**. No **22** was detected.

Registry No.—**11**, 54303-58-1; **12**, 59463-22-8; **13**, 55341-17-8; **13**, 2,4-DNPH, 59463-23-9; **14**, 59463-24-0; **16**, 59463-25-1; **19a**, 59463-26-2; **19b**, 59463-27-3; **20**, 28525-73-7; *isopropenyl acetate*, 108-22-5.

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(20) The same selectivity has been reported for two 3-methylspirodienones.[2b]

(21) Alternative mechanistic interpretations,[4b,4c] in which skeletal rearrangement and electron redistribution occur simultaneously, fail to account for the striking selectivity exhibited by 2,5-cyclohexadienones bearing C-3 substituents.

(22) Coupling constants were determined at 220 MHz.

(23) Coupling constants were determined from double irradiation experiments at 60 MHz.

Alicyclic Ring Closure. 1. Preferential Formation of Five-Membered over Seven-Membered Rings in Aldol Ring Closure Reactions

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Diones **7a**, **7b**, and **7c**, synthesized from cyclopentanone, cyclohexanone, and cycloheptanone, respectively, were subjected to base-catalyzed aldol cyclization yielding principally an α,β-unsaturated ketone **8**, along with lesser amounts of the β,γ-unsaturated isomer **9**. No seven-membered ring unsaturated ketone **10** could be detected.

The closure of six-membered alicyclic rings has long been recognized as a facile process, particularly by enolate addition to a carbonyl group as in the ring closure step of the Robinson ring annelation procedure.[1] When a five- or seven-membered ring has to be closed, the same methods which work well in closing six-membered rings are usually employed. In the case of the five-membered rings, these are often successful, although sometimes they fail. When they do fail, that fact usually rates only passing mention, making systematic search of the literature for them all but impossible. Any attempt at explanation is usually confined to an inference of adverse steric interaction and/or strain. When the enolate addition methods are used in attempts to close a seven-membered ring, they often fail, although there are successful examples in the literature. Nevertheless, a large percentage of syntheses of compounds containing seven-membered rings, e.g., the hydroazulenic sesquiterpenoids, are actually achieved by ring expansion procedures, either chemical or, more often, photochemical. Nature herself appears to make the hydroazulenic compounds by cyclization of a ten-membered ring.[2] We, therefore, were interested to examine the products obtained from molecules able to close to give a five- or a seven-membered ring, but not a six-membered one. We have examined several such cyclizations where the reaction involved was an aldol reaction performed under conditions where both enolate ion formation and the first step of the aldol were reversible.