under which the hydrogens of **5b** are >98% relaxed giving singlets of appropriate relative intensities.

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Registry No.—**5a**, 54595-52-7; **5b**, 40755-74-6.

Supplementary Material Available. A listing of atomic coordinate positions and anisotropic thermal parameters will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JOC-75-1444.

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Photochemical Reactions of α,β-Unsaturated Acids, Esters, and Nitriles

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Cyclohexene-1-carboxylic acid, the corresponding methyl ester, and cyclohexene-1-carbonitrile undergo slow addition to electron-rich alkenes upon irradiation. Reaction occurs, very slowly, at the carbon–carbon double bond of the ester and nitrile to give [2 + 2] cycloadducts, sometimes accompanied by products of ene-like reactions. Cyclohexene-1-carboxylic acid gives ester **15** and lactone **16** via retro-type II processes.

The photochemical behavior of five- and six-membered ring conjugated enones is diverse and interesting, with reactions such as α-cleavage, oxetane formation, [2 + 2] cycloaddition to the carbon–carbon double bond, the lumirearrangement to bicyclo[3.1.0]hexanones (in certain cases), and others being observed, depending on the presence or absence of coreactants.[1] It is believed that these molecules have lowest lying n,π* and π,π* triplet states of approximately equal energies, and that the precise structural details of the compound defines which state is of lowest energy, but that reactions from either state are possible in most cases.

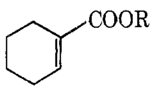
On the other hand, the photochemical behavior of α,β-unsaturated acids and their derivatives, such as esters and nitriles, has, with the exception of a few specific compounds, been much less thoroughly investigated. The structures of the several [2 + 2] photodimers produced on irradiation of cinnamic acid in the solid state have been well worked out.[2] Cinnamic esters have been reported to undergo [2 + 2] photochemical addition to olefins in solution.[3] Maleic anhydride, fumaric acid, and maleic acid, and also fumaronitriles, undergo [2 + 2] photodimerization most efficiently in the solid state.[4] Coumarin undergoes direct and sensitized dimerization and sensitized addition to olefins, the former process apparently occurring via both singlet and triplet excited states.[5a,c] α-Phenylcinnamic acids on irradiation close to β-lactones.[6] Acrylonitrile dimerizes in the [2 + 2] fashion on photosensitization, whereas 2-cyanobutadiene undergoes two types of electrocyclic ring closure,[7] just as does butadiene itself. This would imply that the reactive excited states of butadiene and the 2-cyano derivative are similar (i.e., π,π*).

In other simple α,β-unsaturated acids, esters, and nitriles which have been examined, the photochemistry which has been observed has been similar to that exhibited by acylic ketones. Both classes of compounds undergo processes such as (a) migration of the double bond to the β,γ position, probably via hydrogen abstraction by the carbonyl oxygen, as in the type II elimination (this has been observed in crotonic acid and crotonic esters);[8,9] (b) cis–trans isomerization about the double bond;[8,9] (c) occasionally, as in the case of acrylonitrile, mentioned above, [2 + 2] cyclodimerization.[7]

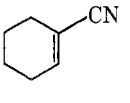
Our recent studies of the photochemical behavior of benzoic acid,[10] benzoate esters,[11] and benzonitrile[12] have shown that these benzene derivatives exhibit a varied and interesting photochemistry, undergoing reactions with alkenes at both the functional group and also ring positions, depending on the exact structure of the alkene and on reaction conditions. In order to provide a basis for comparison, it was deemed worthwhile to study the behavior of nonaromatic unsaturated acids and their derivatives which might serve as models. This report records some of our results with this class of compounds.

Attention was directed mainly at cyclohexene-1-carboxylic acid and the corresponding ester and nitrile for two reasons: (1) these are of the same ring size as the benzene derivatives previously studied, and hence strain effects will be minimized, and (2) a five- or six-membered cyclic system should be incapable of undergoing processes a or b mentioned above, which are the major processes observed in the photochemistry of acyclic aldehydes and ketones.[13] However, cyclic enones, especially those containing five- and six-membered rings, undergo cycloaddition, lumirearrangements, and other interesting and useful reactions.[1]

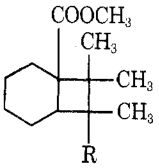
Accordingly, methyl cyclohexene-1-carboxylate (**1**) was irradiated through Vycor in the presence of excess 2,3-dimethyl-2-butene (DMB). There was formed in 38% yield (based on unrecovered **1**) a mixture of [2 + 2] cycloadduct **5** and compound **7** in a ratio of ~5:1. Their structures were apparent from their NMR and mass spectral characteristics, the two-hydrogen multiplet in the NMR and mass spectrum of **7** at τ 5.1 being especially helpful. From irradiation of ester **1** and 2-methyl-2-butene, the ene-type adduct **8** was isolated in pure form, as the sole product, unaccompanied by cycloadducts such as **6**. The reasons for the difference in reaction pathway caused by one methyl group are not clear.



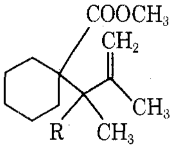
1, R = CH_3
2, R = H



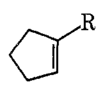
3



5, R = CH_3
6, R = H

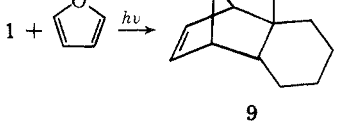


7, R = CH_3
8, R = H



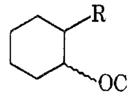
4a, R = $COOCH_3$
b, R = CN

Irradiation of **1** in excess furan led cleanly to the [4 + 2] cycloadduct, **9**, in 65% yield. The nature of adduct **9** was apparent from its NMR spectrum. The two vinyl hydrogens appear as an AB-like multiplet centered at τ 3.86; the two bridgehead hydrogens α to oxygen exhibit narrow multiplets at τ 5.37 and 5.45. The chemical shifts and general appearance of these signals are typical of [4 + 2] thermal and photochemical adducts of furan with α,β-unsaturated ketones.[14] The two vinyl hydrogens of 2,3-dihydrofurans, including [2 + 2] cycloadducts of furan, exhibit chemical shifts differing by 1.1–1.4 ppm.[14,15]

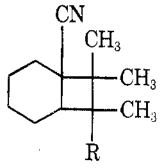


9

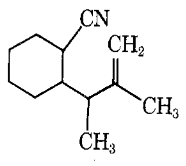
In agreement with the results of Kropp and Krauss,[9] we find that irradiation of **1** in methanol gives a modest (24%) yield of the isomeric 2-methoxycyclohexanecarboxylic esters of structure **10**.



10, R = $COOCH_3$
14, R = CN



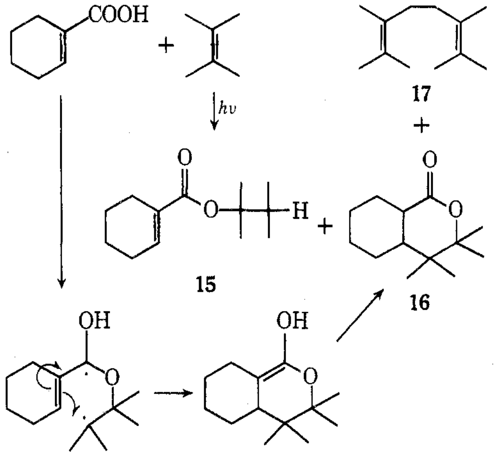
11, R = CH_3
12, R = H



13

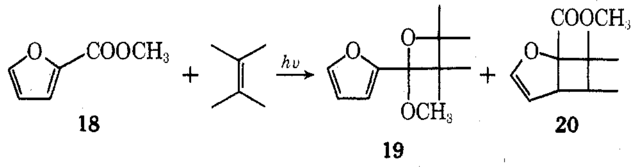
1-Cyclohexenecarbonitrile (**3**) upon irradiation in the presence of excess DMB underwent a slow but clean [2 + 2] cycloaddition to give adduct **11** in 53% yield. When 2-methyl-2-butene was employed as substrate, both cycloadduct **12** and the ene-like adduct, **13**, were observed (28 and 18%, respectively). Irradiation of **3** in methanol in the presence of xylene as sensitizer gave a modest (36%) yield of the isomeric 2-methoxycyclohexanecarbonitriles (**14**). Use of 1,1-dimethoxy-2,2-dimethylethylene as substrate with **3** gave, in addition to considerable amounts of tarry materials, low conversions of a complex mixture of products. The individual components were not separated; however, the spectral properties of the mixture indicate that it does not contain an appreciable amount of 2-azabutadienes, a type of compound previously shown to result from addition of photochemically excited benzonitrile to electron-rich alkenes such as DMB and 1,1-dimethoxy-2,2-dimethylethylene.[12] Irradiation of 1-cyclohexenecarbonitrile and excess furan led only to the rapid formation of highly colored tarry material.

The five-membered ring analog of **3**, cyclopentene-1-carbonitrile, compound **4b**, showed similar photochemical behavior, giving a mixture of [2 + 2] cycloadduct and ene-like product (2:1) on irradiation in the presence of excess DMB.



Cyclohexene-1-carboxylic acid (**2**) exhibits photochemical behavior indicative of biradical intermediates. Irradiation through Vycor of mixtures of **2** and excess DMB gave 2,3-dimethyl-2-butyl cyclohexene-1-carboxylate (**15**, 32%), lactone **16** (26%), and a mixture of C_{12} hydrocarbons, the predominant isomer being identified as 2,3,6,7-tetramethylocta-2,6-diene (**17**). The hydrocarbon has also been isolated from mixtures obtained on irradiation of benzoic acid and methyl benzoate with DMB.[10,11] Ester **15** was identified initially by its spectral properties (see Experimental Section) and later by hydrolysis to acid **2**. The structure of **16** was deduced from its various spectral parameters, including an infrared carbonyl stretching band at 1748 cm^{-1}, consistent with a δ-lactone, and a broad one-hydrogen NMR signal at τ 7.72 attributable to the hydrogen α to carbonyl. A plausible mechanism for the formation of **16** is shown above, involving the same diradical intermediate which accounts for the production of **15**. Lactone **16** most likely arises via a retro-type II elimination, as was postulated for photolysis of benzoic acid–DMB mixtures.[10]

While compound **2** reacts at the carboxylic acid function, **1**, **3**, and **4** all prefer to react with alkenes at the carbon–carbon double bond. This reluctance to react at the functional group is in contrast to the behavior which we earlier observed with the corresponding benzene derivatives.[10-12] The furan system is regarded as lying on the borderline between olefinic and aromatic character.[16] Consequently, we decided to study the behavior of a representative furan derivative, viz., methyl furoate (**18**). Interestingly, irradiation of methyl furoate (**18**) in the presence of excess DMB gave appreciable amounts of both oxetane **19** and compound **20**,



the product of [2 + 2] cycloaddition across the 1,2 positions of the furan ring (20 and 31%, respectively). The structures of these compounds were evident from their spectral parameters (see Experimental Section).

The most striking feature of the results described above is the absence of any products resulting from reaction of the unsaturated acid derivatives at the functional group itself of **1**, **3**, and **4**. A priori, one might argue that this is a reflection of the intrinsically greater reactivity of the alkenic double bonds of **1–4** as compared to that of the ring positions of the benzene derivatives previously studied.[10-12] However, the pronounced sluggishness of the presently observed reactions makes that explanation unlikely. Quantitative measurements were quite difficult to perform because of the low rates of reaction, and because the compounds **1–4** absorb light only at very short wavelengths. However, for the reaction between **1** and DMB, a quantum yield for disappearance of **1** of 0.004 is estimated. Although they are two orders of magnitude slower, the reactions of **1–4** with alkenes occur at the C=C double bond, as is the case with five- and six-membered ring cyclic unsaturated ketones.[17]

Experimental Section

Irradiations were conducted in an annular apparatus using light from a Hanovia 450-W medium-pressure mercury arc lamp, filtered through Vycor (transmits >220 nm) and cooled by ice water in an immersion well. All photochemical reaction solutions were flushed with argon for 1 hr prior to irradiation and an argon atmosphere was maintained during irradiation. NMR spectra were obtained on Varian A-60 and XL-100 instruments. Mass spectra were obtained on a Hitachi Perkin-Elmer Model RMU-6E. Gas chromatography was performed on the following columns: column A, 2 ft × 0.25 in., 10% SE-30 on Chromosorb W; column B, 2 ft × 0.25 in., 15% Carbowax 20M on Chromosorb W; column C, 6 ft × 0.25 in., 10% SE-30; column D, 6 ft × 0.25 in., 15% Carbowax 20 M; column E, 6 ft × 0.375 in., 25% SE-30; and column F, 6 ft × 0.25 in., 15% FFAP on Chromosorb W.

Photolysis of Methyl Cyclohexene-1-carboxylate (1) with Excess 2-Methyl-2-butene. A solution of ester **1** (3.0 g, 0.02 mol) and 2-methyl-2-butene (30 g) in spectrograde pentane (80 ml) was irradiated through Vycor for 36 hr. Evaporation of the solvent and excess alkene gave, after two vacuum distillations of the residue, recovered starting material (1.8 g), bp 40–44° (1 mm), and ene-like product **8**, bp 73–75° (0.5 mm) (0.72 g, 51%); ir (film) 1730 cm^{-1}; NMR (CDCl$_3$) τ 5.3 (2 H, m), 6.37, (3 H, s), 7.3–8.5 (9 H, m), 8.42 (3 H, s, br), and 9.00 (3 H, d, J = 6.7 Hz); mass spectrum m/e (rel intensity) 210 (11, P), 195 (6), 141 (100), 109 (48). Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.29; H, 10.45. Found: C, 74.16; H, 10.30.

Photochemical Reaction of Ester 1 with 2,3-Dimethyl-2-butene. A solution of ester **1** (3.0 g) and 2,3-dimethyl-2-butene (30 g) in spectrograde hexane (90 ml) was irradiated through Vycor for 42 hr. Evaporation of excess alkene and solvent gave an oily residue which was fractionally distilled. Besides unchanged **1**, bp 38–43° (1 mm) (1.8 g), there was obtained two product fractions: a, bp 76–78° (0.3 mm) (0.32 g, 22%), and b, bp 88–90° (0.3 mm) (0.36 g). Fraction a appeared to be ene-like product **7**: ir (film) 1730 cm^{-1}; NMR (CDCl$_3$) τ 5.2 (2 H, m), 6.31 (3 H, s), 7.7–8.5 (10 H, m) 8.45 (3 H, s br), and 9.02 (6 H, s); mass spectrum m/e (rel intensity) 224 (11), 209 (21), 141 (100), and 109 (56). Anal. Calcd for $C_{14}H_{24}O_2$: C, 75.04; H, 10.74. Found: C, 74.91; H, 10.60. Fraction b was assigned the [2 + 2] structure **5**: ir (film) 1732 cm^{-1}; NMR (CDCl$_3$) τ 6.33 (3 H, s), 7.7–8.7 (9 H, m), 8.71 (3 H, s), 8.77 (3 H, s), and 9.04 (6 H, s); mass spectrum m/e (rel intensity) 244 (16, P), 209 (30), 141 (46), 109 (80), and 84 (100). Anal. Found: C, 75.26; H, 10.50.

Photochemical Cycloaddition of Ester 1 to Furan. A solution of ester **1** (2.00 g, 14 mol) in furan (120 ml) was irradiated through Corex for 9 hr. Evaporation of the excess furan and vacuum distillation of the residue gave recovered **1** [0.8 g, bp 35–38° (0.8 mm)], and [4 + 2] adduct **9**: bp 82–84° (0.08 mm) (1.23 g, 68%); ir (film) 1740 cm^{-1}; NMR (CDCl$_3$) τ 3.86 (2 H, AB, J = 2.6 Hz), 5.37 (1 H, m), 5.45 (1 H, m), 6.51 (3 H, s), and 7.7–8.8 (9 H, m); mass spectrum m/e (rel intensity) 208 (12, P), 149 (23), 148 (23), 140 (60), 109 (51), 108 (58), 81 (90), and 68 (100). Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.25, H, 7.70. Found: C, 69.39; H, 7.55.

Irradiation of Ester 1 in Methanol. Photolysis of **1** (1.0 g) in methanol (125 ml) through Vycor for 30 hr gave a mixture of *cis*- and *trans*-methyl 2-methoxycylohexanecarboxylate [0.31 g, bp 52–56° (0.08 mm)] identified by comparison of the spectral with the reported parameters.[9]

Irradiation of 1-Cyclohexenecarbonitrile (3) with 2,3-Dimethyl-2-butene. A solution of nitrile **3** (2.0 g, 19 mol) and DMB (30 g) in spectrograde hexane (80 ml) was irradiated through Vycor for 60 hr. Evaporation of the solvent and excess alkene, followed by distillation of the residue, gave recovered **3** (0.6 g) and [2 + 2] cycloadduct **11**: bp 82–84° (0.1 mm) (0.78 g, 46%); ir (film) 2241 cm^{-1}; NMR (CCl$_4$) τ 7.6–8.5 (9 H, m), 8.69, 8.90, 9.01, and 9.04 (3 H each, s); mass spectrum m/e (rel intensity) 191 (28, P), 159 (17), 158 (46), 107 (100), and 84 (72). Anal. Calcd for $C_{13}H_{21}N$: C, 81.69, H, 11.00. Found: C, 81.42; H, 11.18.

Irradiation of Nitrile 3 with 2-Methyl-2-butene. A solution of nitrile **3** (2.0 g) and 2-methyl-2-butene (25 g) was made up to 140 ml with spectrograde pentane and irradiated through Vycor for 50 hr. Evaporation of the solvent and excess alkene gave a brown residue, which on distillation yielded unchanged **3** (1.0 g) and a mixture of **12** and **13**, bp 68–70° (0.1 mm). Separation on column B gave the components in 60:40 ratio. Eluted first was **12**: ir (film) 2244 cm^{-1}; NMR (CDCl$_3$) τ 7.4–8.4 (10 H, m), 8.75 (3 H, s), 8.83 (3 H, s), and 8.90 (3 H, d, J = 7 Hz); mass spectrum m/e (rel intensity) 177 (20, P), 162 (11), 107 (100), and 70 (56). Anal. Calcd for $C_{12}H_{19}N$: C, 81.37; H, 10.78. Found: C, 81.14; H, 10.70.

The second ene-like product collected, **13**, showed ir (film) 2240 cm^{-1}; NMR (CCl$_4$) τ 5.2 (2 H, br), 7.15–8.4 (9 H, m), 8.26 (3 H, s, br), and 8.78 (3 H, d, J = 7 Hz); mass spectrum m/e (rel intensity) 177 (14, P),

Irradiation of 3 with Miscellaneous Substrates. Irradiation of 1:10 mixtures of **3** and 1,1-dimethoxy-2,2-dimethylethylene gave, besides unchanged **3**, a small amount of distillate, bp 85–100° (0.1 mm), which exhibited NMR absorption in both the methoxyl (τ 6.1–6.9) and CH$_2$ (τ 7.8–8.5) regions. Analysis on several GC columns indicated the mixture to be quite complex and poorly resolved on the columns used.

Irradiation of **3** in furan at 25 and at −10° led to rapid darkening of the solution. Distillation gave only recovered **3** and a small amount of brown tarry material.

Irradiation of Cyclohexene-1-carboxylic Acid (2) and 2,3-Dimethyl-2-butene. A solution of acid **2** (3.0 g) and DMB (30 g) in spectrograde hexane (100 ml) was irradiated through Vycor for 8 hr. Evaporation of solvent and excess alkene gave a slightly yellow residue which was distilled to give two fractions: a, 1.2 g, bp 38–40° (0.01 mm), identified as **17** by comparison with authentic material,[10] and b, 2.2 g of colorless oil, bp 75–90° (0.08 mm). This latter material was dissolved in ether and washed with 5% sodium bicarbonate. Acidification of the bicarbonate extracts gave 1.1 g of recovered **2.** Redistillation of the neutral fraction gave 0.96 g of colorless oil, bp 77–80° (0.08 mm). Separation on column F at 120° gave, in order of elution, ester **15** (32% yield): ir (film) 1710 cm^{-1}; NMR ($CDCl_3$) τ 3.25 (1 H, m, br), 7.7–8.5 (9 H, m), 8.59 (6 H, s), and 9.09 (6 H, d, J = 7 Hz); mass spectrum *m/e* (rel intensity) 210 (0.2); 109 (30), 105 (100), and 84 (64). Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.31; H, 10.76. Found: C, 74.17; H, 10.52. The second peak collected was identified as lactone **16:** ir (film) 1748 cm^{-1}; NMR ($CDCl_3$) τ 7.7 (1 H, d, br, J = 7 Hz), 8.0–9.1 (9 H, m), and 8.90, 8.95, 8.98, and 9.04 (all 3 H each, s); mass spectrum *m/e* (rel intensity) 210 (P, 3), 192 (22), 177 (12), 150 (51), 122 (39), 121 (32), 109 (100), and 99 (48). Anal. Found: C, 74.55; H, 10.65.

Irradiation of Methyl 2-Furoate (18) with 2,3-Dimethyl-2-butene. A solution of **18** (3.0 g) and DMB (30 g) in spectrograde hexane was irradiated for 9 hr. Evaporation of solvent and excess alkene gave a brown oil which gave on distillation 1.0 g of recovered **18** and 1.2 of a mixture of **19** and **20.** Separation was accomplished by GC on column D to give, first, oxetane **19** [ir (film) 1100 cm^{-1} (s, br); NMR ($CDCl_3$) τ 2.62 (1 H, 2 d, J = 2.0, 0.9 Hz), 3.58 (1 H, 2d, J = 2.4, 2.0 Hz), 3.66 (1 H, m), 6.95 (3 H, s), 8.60, 8.84, 9.09, and 9.15 (all 3 H, s); mass spectrum *m/e* (rel intensity 210 (0.2, P), 195 (1.4), 126 (48), 84 (100). Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.58; H, 8.54. Found: C, 68.84; H, 8.40.] and second, [2 + 2] cycloadduct **20** [ir (film) 1732 cm^{-1}; NMR ($CDCl_3$) τ 3.67 (1 H, d, J = 28 Hz), 5.03 (1 H, t, J = 2.8 Hz), 6.62 (1 H, m), 6.97 (3 H, s), 8.75, 8.84, 8.92, and 9.10 (all 3 H, s); mass spectrum *m/e* (rel intensity) 210 (6, P), 195 (9), 151 (21), 126 (45), and 84 (100). Anal. Found: C, 68.39; H, 8.31.]

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Registry No.—**1,** 18448-47-0; **2,** 636-82-8; **3,** 1855-63-6; **5,** 54642-98-7; **7,** 54642-99-8; **8,** 54643-00-4; **9,** 54643-01-5; **11,** 54643-02-6; **12,** 54643-03-7; **13,** 54643-04-8; **15,** 54643-05-9; **16,** 54643-06-0; **17,** 18495-18-6; **18,** 611-13-2; **19,** 54643-07-1; **20,** 54643-08-2; 2-methyl-2-butene, 513-35-9; 2,3-dimethyl-2-butene, 563-79-1; furan, 110-00-9.

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Model Studies Directed toward the Total Synthesis of Vernolepin. III. Synthesis of the α-Methylene-δ-valerolactone AB Ring Model

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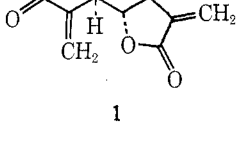
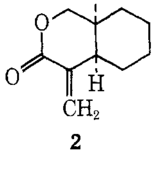
Two routes to the α-methylene-δ-valerolactone AB ring system (**2**) of vernolepin have been developed. The first approach involves a second-order Beckmann fragmentation on oxime **8**. The other approach employs an ozonolysis (reductive) of a Δ^2-enol acetate of an appropriately functionalized 3-ketodecalin. Introduction of the angular vinyl group in the latter approach is accomplished by facile elimination of the *o*-nitrophenyl selenoxide **20**. Introduction of the α-methylene unit involves α-hydroxymethylation of the enolate derived from lactone **3** followed by mesylation and β-elimination.

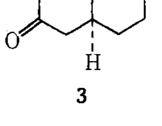
Our model studies directed toward the total synthesis of the growth-inhibitory sesquiterpene bislactone vernolepin (**1**)[3] have concentrated on the synthesis of the novel cis-fused AB ring system possessing an angular vinyl group. We wish to describe here the details of our model studies initiated a few years ago which led to the first synthesis of the vernolepin AB ring model **2**.[4] Several recent reports have described the synthesis of the δ-valerolactone system **3**[5-8] as well as its conversion to the α-methylene lactone **2**.[5]



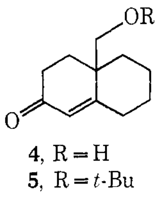
1



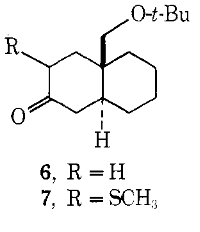
2



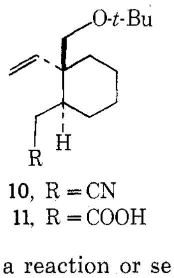
3



4, R = H
5, R = *t*-Bu



6, R = H
7, R = SCH_3



10, R = CN
11, R = COOH

Our approach (see Scheme I) required a reaction or series of reactions which would allow for the specific cleavage of the C-2–C-3 bond (steroid numbering) of a suitably functionalized *trans*-decalin system with conversion of C-1 and C-2 into an olefin or potential olefin and formation of a carboxylic acid function or its equivalent at C-3. Such a carboxylic acid would upon lactonization provide the vernolepin cis-AB ring system possessing the angular vinyl