solution of *p*-chloroaniline (3.1 g, 0.024 mol) in 40 ml of benzene was added. After stirring for 90 min the suspension was filtered and the solid obtained was washed with water and dried to give 4.5 g (52%) of a white solid, mp 265–267°. An analytical sample was prepared by recrystallization from ethanol, mp 265–267°, ir (Nujol) 1685, 1630 cm^{-1}.

Anal. Calcd for $C_{17}H_{17}ClN_2O_2$: C, 64.45; H, 5.41; N, 8.84. Found: C, 64.31; H, 5.40; N, 8.70.

4-Hydroxycyclopenta[*b*]-2-pyrone (17, *n* = 1).—The diketo ester (19 g), prepared in 49% crude yield from the morpholine enamine of cyclopentanone and carboethoxyacetyl chloride, was dissolved in dry dimethylformamide (100 ml). Sodium methoxide (5.4 g, 0.1 mol) was added to the solution, which was then heated for 20 hr at 75–80°. Work-up gave 0.4 g (3%) of the product: mp 188° dec (lit.[4] mp 191–195° dec); ir (Nujol) 3350, 1650, 1610 cm^{-1}; nmr (DMSO) τ 7.93 (m, 2 H, aliphatic), 7.38 (m, 4 H, allylic), 4.77 (s, 1 H, olefinic), and −1.5 (s, 1 H, hydroxyl).

4-Hydroxycyclohepta[*b*]-2-pyrone (17, *n* = 3).—The morpholine enamine of cycloheptanone (36.2 g, 0.2 mol) was dissolved in 200 ml of ether. After the solution had been cooled to −70° (Dry Ice–acetone bath), carboethoxyacetyl chloride (31 g, 0.2 mol) dissolved in 50 ml of ether was added dropwise. When addition was complete (*ca.* 30 min) the temperature of the mixture, now at −50°, was raised to room temperature. Water (200 ml) was added and the suspension was stirred for 15 min. The ethereal layer was isolated, dried ($MgSO_4$), and evaporated to afford 39 g of a yellow oil.

A solution was prepared of 39 g of the oil in 250 ml of dry dimethylformamide. When sodium methoxide (10.8 g, 0.2 mol) was added, a solid formed immediately and the suspension was heated at 80° for 5 hr. When cooled the suspension was poured into ice water (1000 ml). A light yellow solid (7 g) precipitated and was isolated. The filtrate was extracted with methylene dichloride (300 ml) and then acidified (concentrated HCl). A flocculent precipitate that formed was isolated, washed with water, and dried to give 12 g of a light yellow solid. The infrared spectra of both solids were identical. The combined solids were recrystallized from dioxane to give a white solid: 18 g (59%); mp 183–185° (lit.[4] mp 181–183°); ir (Nujol) 3350, 1650, 1610 cm^{-1}; nmr (DMSO) τ 8.33 (m, 6 H, aliphatic), 7.4 (m, 4 H, allylic), 4.67 (s, 1 H, olefinic), and −3.37 (s, 1 H, hydroxyl).

3-(Dimethylaminomethylene)-4-ketocyclohepta[*b*]-2-pyrone (18, *n* = 3).—Pyrone **17** (*n* = 3, 10.6 g, 0.04 mol) was suspended in 70 ml of anhydrous 1,4-dioxane. Following addition of the dimethyl acetal of dimethylformamide (8.8 g, 0.074 mol), the suspension was swirled until solution was complete. For 3 days the solution was let stand at room temperature. Isolation of the crystalline material and recrystallization from 2-propanol gave 4.2 g (30%) of a white solid, mp 164–166°, ir (Nujol) 1700, 1645 cm^{-1}.

Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.21; N, 5.95. Found: C, 66.23; H, 7.20; N, 5.90.

3-Carboxy-*N*-methylcyclohepta[*b*]-4-pyridone (19, *n* = 3).—Following the same procedure for the synthesis of **19** (*n* = 2), the desired product was prepared in 95% yield, mp 225–230°, as white needles after one recrystallization from methanol, ir (Nujol) 1710, 1645 cm^{-1}.

Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.33; N, 6.8. Found: C, 64.88; H, 6.32; N, 6.77.

3-(*p*-Chlorophenylcarbamoyl)-*N*-methylcyclohepta[*b*]-4-pyridone (20, *n* = 3).—Following the identical procedure for synthesis of **20** (*n* = 2), 3.5 g (0.016 mol) of 3-carboxy-*N*-methyl-1*H*-cyclohepta[*b*] 4-pyridone afforded 2.1 g (40%) of the amide **20**, mp 255–258°, as a white solid. The melting point was unchanged after one recrystallization from ethanol; ir (Nujol) 1690, 1630 cm^{-1}.

Anal. Calcd for $C_{18}H_{19}ClN_2O_2$: C, 65.35; H, 5.80; N, 8.47. Found: C, 64.95; H, 5.73; N, 8.13.

Registry No.—**1** (R = H), 33821-58-8; **1** (R = CH_3), 33821-59-9; **1** (R = *n*-C_4H_9), 33821-60-2; **7**, 33821-61-3; **8**, 33821-62-4; **18** (*n* = 2), 33821-63-5; **18** (*n* = 3), 33821-64-6; **19** (*n* = 2), 33821-65-7; **19** (*n* = 3), 33821-66-8; **20** (*n* = 2), 33821-67-9; **20** (*n* = 3), 33821-68-0.

Acknowledgment.—The authors wish to thank Mrs. Florence Burnley for recording the nmr spectra and Mr. W. David Weir for the synthesis of several intermediates.

The Photochemistry of Substituted 1,5-Hexadien-3-ones

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The effects of methyl group substitution on the photochemistry of the 1,5-hexadien-3-one system has been examined, with particular emphasis on the intramolecular cycloaddition reaction to form the bicyclo[2.1.1]hexan-2-one system. Monosubstituted compounds **12**, **13**, **15**, **17**, and **18** and disubstituted compounds **14**, **16**, and **19** were studied. These structural changes were found to have profound effects on the photochemical reactions shown by these compounds, but few general trends of reactivity with substitution could be discerned. It appears that each system is unique in its behavior. The results obtained are rationalized on the basis of present knowledge of the mechanisms of photochemical reactions.

In a previous publication we described an approach to the bergamotene sesquiterpenes starting from readily available bicyclo[3.1.1]heptane precursors.[1] Because of the nature of the method used, this synthesis was limited to the formation of representatives of the cis series, *e.g.*, *cis*-β-bergamotene (**1**). The stereospecific nature of the synthesis was useful for the establishment of the absolute stereochemistry of the cis bergamotenes,[1] but could not be used for the synthesis of members of the trans series, *e.g.*, *trans*-α-bergamotene (**2**).[1,2] A method which appeared to have promise for the simultaneous synthesis of both cis and trans material was suggested by the report that direct irradiation of myrcene (**3**) afforded β-pinene (**4**) in low yield.[3] The major product formed in this reaction is the cyclobutene **5**.

In order to avoid the formation of products such as **5**, we decided to replace the diene chromophore of **3** with the enone system. However, we found the irradiation of the three model compounds **6**, **7**, and **8** to be unsuccessful as a method for the formation of the bicyclo[3.1.1]heptan-2-one system. No evidence could be found for the formation of cyclic products of any type, a result which is substantiated by an independent study of the photochemistry of **7**.[4]

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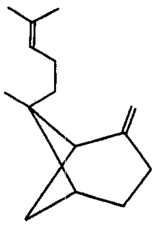
[1] T. W. Gibson and W. F. Erman, *J. Amer. Chem. Soc.*, **91**, 4771 (1969).

[2] V. Herout, V. Ruzicka, M. Vrany, and F. Sorm, *Collect. Czech. Chem. Commun.*, **15**, 373 (1950).

[3] K. J. Crowley, *Proc. Chem. Soc.*, 245 (1962).

[4] R. A. Schneider, Ph.D. Thesis, Cornell University, 1966, p 133.



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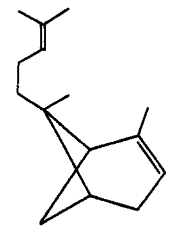

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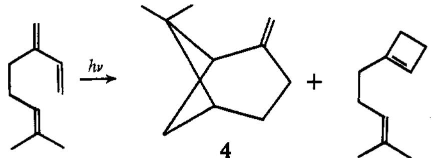
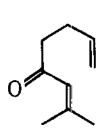


3 4 5



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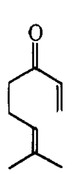
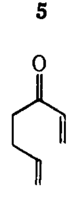
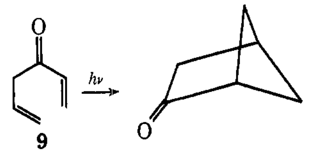


7

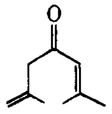


8

An alternate process was suggested by the observation that 1,5-hexadien-3-one (**9**) undergoes relatively efficient photocycloaddition to produce bicyclo[2.1.1]hexan-2-one (**10**).[5] If this reaction could be accomplished with suitably substituted derivatives of **9**, then a simple ring expansion reaction would provide access to the bicyclo[3.1.1]heptanone system. At the time this work was being contemplated, the photocycloaddition of **9** was the only known example of this reaction, and thus little information was available concerning the effects of structural variation on the course or efficiency of the process. We, and others, had observed the complete absence of cycloaddition products upon irradiation of the dienone **11**.[6,7] We decided,



9 10



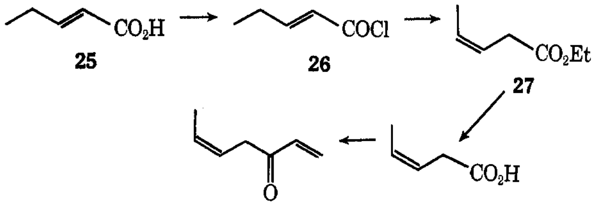
11

therefore, to begin with a thorough study of the effect of substitution on the cycloaddition process.[8]

Results

Synthesis of Dienones.—Compounds **12–17** were synthesized by the method described for the formation of 1,5-hexadien-3-one,[5] which involves addition of an allylic Grignard reagent to the appropriate aldehyde, followed by Jones oxidation[9] of the resultant alcohol to the dienone. That dienone **12** was uncontaminated with its cis isomer was shown by spectroscopic data.

Compounds **18** and **19** were synthesized by an alternate procedure, since the appropriate Grignard reactions resulted in the exclusive formation of the allylic alcohols leading to **13** and **14**, respectively. The process is exemplified by the following synthesis of **18**. The acid **25**, prepared by the condensation of malonic acid with propanal,[10] was converted to the acid chloride **26** with thionyl chloride. Deconjugation of **26** and conversion to the ester **27** was accomplished in high yield by the use of triethylamine in ethanolic acetone.[11] Hydrolysis of **27** followed by reaction of the resultant acid with vinyllithium resulted in the formation of the cis dienone **18** in good yield. The same process was



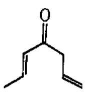
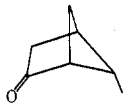
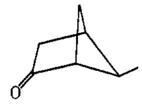
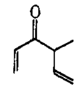
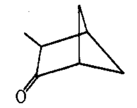
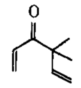
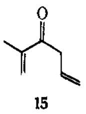
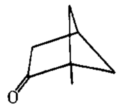
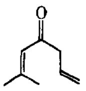
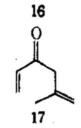
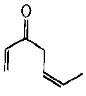
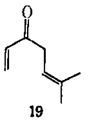
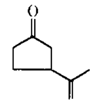
25 26 27 18

used for the synthesis of **19** starting from isobutyraldehyde.

Irradiation of Dienones.—The results of the irradiation experiments are shown in Table I.[12] Dilute solu-

TABLE I

IRRADIATION OF DIENONES IN PENTANE

Dienone		Product	Yield, %
 12	→	 20 +  21	3 (2:3)
 13	→	 22	41
 14	→	Polymer	
 15	→	 23	57
 16	→	No reaction	
 17	→	Polymer	
 18	→	20 + 21	56 (2.3:1)
 19	→	 24	10

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[5] F. T. Bond, H. L. Jones, and L. Scerbo, *Tetrahedron Lett.*, 4685 (1965).

[6] P. J. Kropp and T. W. Gibson, *J. Chem. Soc. C*, 143 (1967).

[7] K. J. Crowley, R. A. Schneider, and J. Meinwald, *ibid.*, 571 (1966).

[8] Part of this work has been presented at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970.

[9] R. G. Curtis, I. Heilbron, E. R. H. Jones, and G. F. Woods, *J. Chem. Soc.*, 457 (1953).

[10] A. A. Goldberg and R. P. Linstead, *ibid.*, 2343 (1928).

[11] T. Ozeki and M. Kusaka, *Bull. Chem. Soc. Jap.*, **39**, 1995 (1966).

[12] Results essentially identical to those reported in Table I have also been obtained in the laboratory of Professor F. T. Bond, who also studied the trans isomer of **18**. We thank Professor Bond for the communication of his results to us.

tions of the dienones in pentane were irradiated with a 450-W medium-pressure mercury lamp through Vycor or Pyrex glassware until all or most of the starting material had disappeared, as determined by gas-liquid phase chromatography (glpc). Isolation of the highly volatile products was accomplished by removal of solvent by distillation through a spinning band column, followed by distillation of the residual liquids in a microstill. Pure compounds were isolated by preparative glpc and identified by spectroscopic methods. Detailed accounts are included in the Experimental Section.

Bond reported that photocycloaddition of 1,5-hexadien-3-one occurred in 30–60% yield,[5] a result which we have confirmed. However, irradiation of **12**, which possesses a methyl group at the terminal position of the conjugated double bond, leads to very little observable cycloaddition. In fact, no evidence was found for the production of **20** or **21** unless the irradiation was carried out in the presence of excess acetophenone, which presumably serves as a photosensitizer.[13] Under all conditions studied, the initial observed reaction is isomerization of **12** to its cis isomer. In contrast, irradiation of **18**, which possesses a methyl group at the terminus of the nonconjugated double bond, results in the formation of the ketones **20** and **21** in good yield, although in a different ratio.

Irradiation of **15**, which possesses a methyl group at the *α* position of the conjugated double bond, resulted in cycloaddition to **23** in good yield. Similarly, irradiation of **13**, with a single methyl group at the saturated position, resulted in cycloaddition to **2**. However, with **14**, which possesses two methyl groups at this position, irradiation led only to rapid polymer formation. In one experiment, irradiation of **14** resulted in the isolation of a small amount of a mixture of volatile compounds. The infrared spectrum of the mixture indicated the presence of the bicyclic ketone, but none could be isolated in a pure state. The dienone **16**, which was obtained only in an impure state in low yield, did not appear to undergo any photochemical reaction.

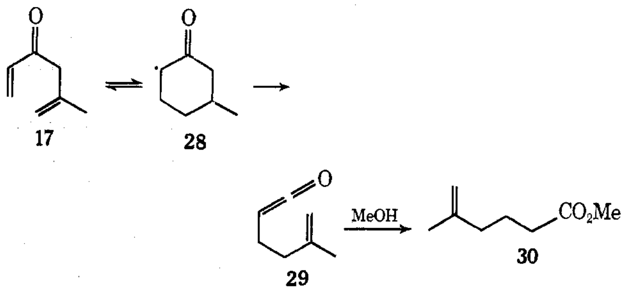
The dienone **17**, with a methyl group at the internal position of the nonconjugated double bond, also proved remarkably stable to light. On extended irradiation, the dienone slowly disappeared with no volatile products being observed.

In view of the photochemical behavior of **18**, the dienone **19** would appear to be ideal for the synthesis of 5,5-dimethylbicyclo[2.1.1]hexan-2-one. However, irradiation of **19** in pentane solution resulted in a mixture of volatile products, from which only 3-isopropenylcyclopentanone (**24**), could be isolated. Again, the infrared spectrum of the crude product indicated the presence of a trace of bicyclohexanone, but none could be isolated *via* glpc.

Discussion

Attempts to rationalize the behavior of the various dienones studied on the basis of results observed in other dienone[14] and triene[15] systems have been largely unsuccessful. In contrast to the photochemically simpler trienes studied by Liu and Hammond,[15b] the dienones examined in this work can react by a variety of processes. In addition to cycloaddition, major pathways should involve types I and II cleavage and hydrogen abstraction. In pentane solution these processes would lead to highly volatile and polymeric products, none of which were characterized. Substitution at the various positions in the system would influence the competition among these processes in different ways, through either ground state or excited state energetics. For example, the decrease in cycloaddition product observed on proceeding from **1** to **13** to **14** is probably due to increased incidence of type I cleavage brought about by increased stability of the allylic radical formed in this process.

In the dienone **17**, the presence of the methyl group at the 5 position may stabilize the six-membered ring diradical intermediate **28** at the expense of the normally preferred five-membered ring.[15] The diradical **28** can fragment either to the starting material or to the ketene **29**. In order to determine whether the ketene was being formed in the reaction, irradiation of **17** was carried out in the presence of methanol, resulting in the formation of ester **30** in 10% yield.



This result prompted us to examine the irradiation of several of the other dienones in methanol solvent. Both **13** and **15**, when irradiated in methanol, afforded only the bicyclic products **22** and **23**, respectively, in about the same yields (and at qualitatively the same rates) as were observed in pentane. Prolonged irradiation led to reaction of the bicyclic ketones to give as yet uncharacterized products.

Irradiation of **19** in methanol led, as before, to formation of **24** in about 14% yield, and also to the esters **33** and **34** in 4 and 13% yields, respectively. Initial cyclization to diradical **31** followed by hydrogen transfer provides a rationalization for the formation of **24**. However, in contrast to **28**, fragmentation of **31** can only result in return to starting material and does not explain ketene formation. The ketenes must, therefore, be formed by initial fragmentation of **19** to give acyl and allyl radicals, which can recombine in two ways to give ketenes. The minor ester **33** results from recombination at the alternate position of the allyl radical. This type of process is probably also responsible for the formation of **30** from **17**.

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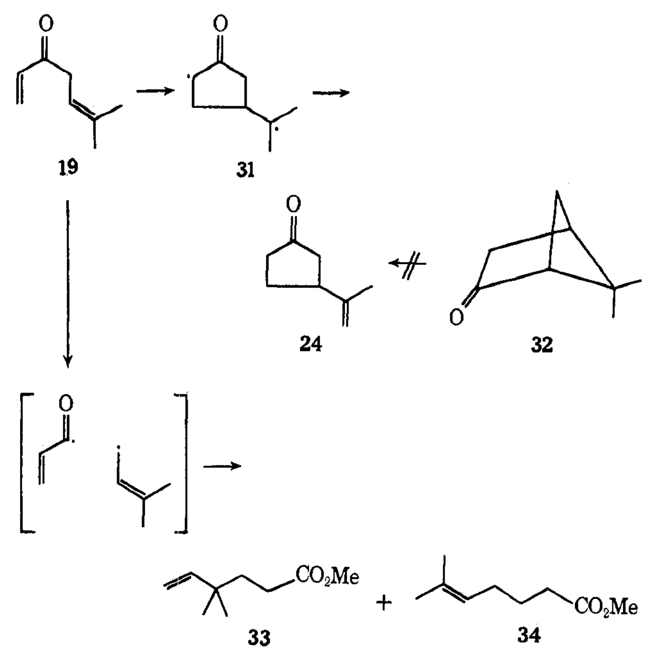
[13] In contrast to this result, Professor W. R. Roth has obtained a 25% yield of **20** and **21** (ratio 2:3) in the direct irradiation of **12** (private communication).

[14] (a) E. Y. Y. Lam, D. Valentine, and G. S. Hammond, *J. Amer. Chem. Soc.*, **89**, 3482 (1967); (b) P. DeMayo, J. P. Pete, and M. Tchir, *Can. J. Chem.*, **46**, 2535 (1968); (c) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964); (d) P. D. Bartlett, *Science*, **159**, 833 (1968).

[15] (a) R. Srinivasan and K. L. Carlaugh, *J. Amer. Chem. Soc.*, **89**, 4932 (1967); (b) R. Liu and G. Hammond, *ibid.*, **89**, 4936 (1967).



The lack of ring formation from diradical **31** contrasts strongly with the behavior of its counterpart generated from **18**. This is apparently a result of increased steric hindrance and also to an increased probability of the existence of a favorable conformation for hydrogen transfer. An alternate explanation, that bicyclic product **32** affords **24** *via* a type II photoreaction, does not appear plausible in view of the absence of this type of product in the irradiation of **18**.

It is evident from this study that many complex factors are involved in deciding the course of reaction to be taken by any one of these dienones. However, the investigation has shown that the photocycloaddition reaction is useful synthetically for the formation 1-, 3-, and 5-monosubstituted bicyclo[2.1.1]hexan-2-ones. The method is not applicable, unfortunately, to the 5,5-disubstituted system required for a synthesis of the bergamotenes, or to the 3,3-disubstituted or 4-monosubstituted compounds.[16]

Experimental Section[17]

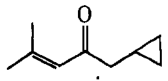
2-Methyl-2,7-octadien-4-one (6).—To 36 g of magnesium metal in 250 ml of ether in a flame-dried flask was added 60.0 g (0.60 mol) of 4-chloro-1-butene in 50 ml of ether. After reaction had started and all the chlorobutene had been added, the mixture was refluxed for 1 hr and stirred overnight under argon. The solution was filtered into a 2-l. Morton flask, and 800 ml of ether and 61 g (0.33 mol) of $CdCl_2$ were added. During the ensuing exothermic reaction, the mixture turned purple and became viscous. After refluxing for 0.5 hr, 72 g (0.61 mol) of 3-methyl-2-butenoyl chloride (prepared in 86% yield from 3-methyl-2-butenoic acid and thionyl chloride) was added, and the mixture was refluxed overnight. After cooling, 170 ml of saturated NH_4Cl solution was added and the aqueous phase was extracted twice with ether. The combined ether extracts were washed four times with saturated $NaHCO_3$, twice with water, and twice with saturated brine, and dried over $MgSO_4$. Distillation gave 43.6 g (52%) of **6**, bp 70–71° (10 mm). Glpc analysis showed the product to be composed of about 82% of one compound and 12 and 6% of two minor products. Purification of the major constituent by glpc gave material with λ_{max} 5.90 and 6.15 μ, λ_{max}^{EtOH} 237.5 mμ (ϵ 11,900), mol wt 154 (mass spectrum), and nmr signals at τ 8.14 (3 H, d, J = 1 Hz), 7.87 (3 H, d, J = 1 Hz), 7.54 (4 H, m), 5.13 (1 H, m), 4.88 (1 H, broad d, J = 5 Hz), 4.2 (1 H, m), and 3.91 (1 H, m).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.92; H, 10.05.

The 2,4-dinitrophenylhydrazone derivative had mp 57–57.5°, λ_{max}^{EtOH} 364 mμ (22,000).

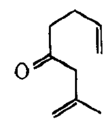
Anal. Calcd for $C_{15}H_{18}N_4O_4$: C, 56.59; H, 5.70; N, 17.60. Found: C, 56.67; H, 5.68; N, 17.62.

The more abundant minor constituent (12%) showed λ_{max} 3.20, 5.90, and 6.14 μ, λ_{max}^{EtOH} 238 mμ (ϵ 11,700), and nmr signals at τ 9.84 (2 H, m), 9.40 (2 H, m), *ca.* 9.0 (1 H, broad), 8.15 (3 H, d, J = 1 Hz), 7.85 (3 H, d, J = 1 Hz), 7.72 (2 H, d, J = 6.4 Hz), and 3.88 (1 H, m). These data suggest structure i for this compound, but this has not been proven unambiguously.



i

Irradiation of 6.—Irradiation of **6** was carried out with a variety of combinations of solvents and light sources. Only with the use of methanol as solvent were any volatile products obtained in more than trace amounts. A solution of 0.70 g of **6** in 400 ml of methanol was irradiated under argon with a 550-W mercury lamp for 12 hr. Distillation gave 0.36 g of colorless oil, bp (bath) 60–80° (25 mm). Glpc analysis on a 5-ft SF-96 column showed two main peaks in a ratio of 1:3.8. Attempted collection by preparative glpc showed the first peak to be unstable, while the major product (*ca.* 40% yield) was obtained in a state of purity sufficient for identification as ii. This ketone, the product of a simple deconjugation of **6**, showed a molecular weight of 138 (mass spectrum), λ_{max} 3.25, 5.80, 6.06, 10.0, 10.95, and 11.2 μ, and nmr signals at τ 8.28 (3 H, s), 7.72 (2 H, m), 7.51 (2 H, d, J = 6 Hz), 6.94 (2 H, s), 5.24 (1 H, s), 5.15 (2 H, s), 5.00 (1 H, d, J = 8 Hz), and 4.28 (1 H, m). Repeated attempts to obtain this compound after the photochemical reaction vessel had been washed with base were unsuccessful, suggesting that the formation of ii was catalyzed by traces of acid.



ii

7-Methyl-1,6-octadien-3-one (7).—This compound was prepared by the same method used by Schneider,[4] except that the vinyllithium was prepared from tetravinyltin and phenyllithium. Our material, purified by glpc, showed essentially the same data as those reported, except for the absence of the band at 11.22 μ in the infrared. This band was probably due to an impurity, since glpc was apparently not used in the purification of **7** by Schneider. In addition, the nmr signals for methyl groups appeared at τ 8.37 (3 H, s) and 8.32 (3 H, d, J = 1 Hz).

Irradiation of 7.—Irradiation of **7** in various solvents with medium pressure mercury lamps led to the formation of only trace amounts of volatile materials, none of which were isolated.

1,6-Heptadien-3-one (8).—To 35.6 g of magnesium shavings under 1 l. of ether was added 50.0 g of 4-bromo-1-butene at a rate sufficient to maintain reflux. A solution of 21.0 g of acrolein in ether was then added at a rate sufficient to maintain reflux, and the mixture was stirred overnight. Hydrolysis was carried out with saturated Na_2SO_4 solution, and the solution was filtered and dried over Na_2SO_4. Distillation gave 21.4 g (52%) of the desired alcohol, bp 58° (23 mm). A solution of 17.8 g of the alcohol in 250 ml of a 1:1 acetone-benzene mixture was oxidized with 46.0 ml of Jones reagent[9] at ice-bath temperature. The resulting mixture was poured into ether, extracted once with water and twice with saturated $NaHCO_3$ solution, and dried over Na_2SO_4. Removal of drying agent and distillation of sol-

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[16] A study of some ring expansion reactions of **10**, **20**, **21**, **22**, and **23** will be described soon.

[17] Melting points were determined on a micro hot stage and are corrected; boiling points are uncorrected. Infrared spectra were recorded on Perkin-Elmer 257 or 137 spectrophotometers as neat films or 5% solutions in CCl_4. Nuclear magnetic resonance spectra were obtained on a Varian Associates HA-100 spectrometer using TMS as an internal reference in $CDCl_3$. Nmr data are recorded in this order: chemical shift (integration, multiplicity where s = singlet, d = doublet, t = triplet q = quartet, m = multiplet, and coupling constant in hertz). Mass spectra were determined with an Atlas CH-4 spectrometer, or, where noted, high-resolution spectra were obtained with an Atlas SM-1 spectrometer. Microanalyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich.

vent on a spinning band column left a gelatinous mass, which was distilled *in vacuo* directly into a Dry Ice cooled trap. Redistillation of the trapped material gave 7.65 g (44%) of ketone **8**, bp 35–40° (20 mm), shown to be about 98% pure by glpc. Material collected by preparative glpc showed λ_{max} 3.26, 5.95, 6.08, 6.20, 10.05, 10.35, and 10.95 μ, mol wt 110 (mass spectrum), and nmr signals at τ 7.62 (2 H, m), 7.34 (2 H, m), 5.00 (2 H, m), 4.17 (2 H, m), and 3.77 (2 H, m).

Anal. Calcd for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 75.86; H, 9.06.

Catalytic reduction over PtO_2 gave only 3-heptanone, identified by ir and glpc comparison with an authentic sample.

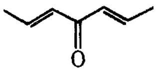
Irradiation of 8.—Irradiation of dilute solutions of **8** in pentane and methanol through Vycor glassware with a 450-W mercury lamp resulted in gradual disappearance of starting material and formation of insoluble polymeric material. Many products were formed in trace amounts in methanol solvent, but no attempt was made to identify these.

Bicyclo[2.1.1]hexan-2-one (10).—The alcohol corresponding to **9** was synthesized in 61% yield using the Grignard reaction between 3-bromo-1-propene and acrolein.[5] Oxidation ot 40.0 g of the alcohol with 25% excess Jones reagent[9] in 1:1 benzene–acetone solvent gave good conversion to the ketone **9**, which was irradiated directly in benzene with a 550-W mercury lamp for 9 hr through a Pyrex filter. Distillation gave 7.5 g of 95% pure bicyclohexanone (**10**), bp 55–57° (26 mm). Further purification could be achieved through formation of the crystalline bisulfite adduct followed by regeneration of **10** with base. The low yield (17% from **9**) is probably mainly due to the extreme volatility of both ketones. Spectroscopic data for **10** agreed well with those reported by Bond[5] and those expected for this structure.

1,5-Heptadien-4-one (12).—To 80 g of magnesium shavings in 1 l. of ether was added 100 g of 3-bromo-1-propene at a rate sufficient to maintain reflux. A solution of 50 g of crotonaldehyde in ether was added to the Grignard reagent at a rate as rapid as condensation of refluxing solvent would allow, and the mixture was allowed to stand overnight at room temperature. Hydrolysis was effected with 60 ml of saturated Na_2SO_4 solution, and the resulting mixture was filtered and dried over Na_2SO_4. Distillation gave 72.6 g (91%) of the alcohol, bp 58° (23 mm), $n^{25}D$ 1.4505 [lit.[18] bp 62° (15 mm), $n^{20}D$ 1.4533]. The alcohol, which appeared to be greater than 99% pure by glpc, showed λ_{max} 3.1, 6.12, 10.05, 10.38, and 10.98 μ, indicative of the terminal and trans double bonds as expected for this compound.

A solution of 3.0 g (26.8 mmol) of the alcohol in 100 ml of purified acetone was oxidized with 7.35 ml (80.4 mmol) of Jones reagent.[9] Normal work-up followed by distillation gave 1.32 g (45%) of **12**, bp 42–44° (16 mm). Glpc analysis revealed the presence of one major peak and two minor peaks in the range of 5–10%. Collection of the major constituent *via* preparative glpc gave material with ir λ_{max} 3.25, 5.90, 5.97, 6.12, 10.07, 10.27, and 10.9 μ, uv λ_{max}^{EtOH} 227 mμ (ϵ 10,400) and 320 (56), and nmr signals at τ 8.09 (3 H, dd, J = 6.6 and 1.4 Hz), 6.71 (2 H, dt, J = 6.6 and ~1 Hz), 4.82 (1 H, dd, J = 17 and 1 Hz), 4.80 (1 H, dd, J = 10 and 1 Hz), 4.0 (1 H, m), 3.85 (1 H, dd, J = 16 and 1.4 Hz), and 3.08 (1 H, dq, J = 16 and 6.6 Hz). The major coupling constant, 16 Hz, of the protons of the conjugated double bond and the 10.27-μ infrared band[19] indicate that the conjugated double bond is in the trans configuration. In addition, the intensity of the uv maximum and the relative intensities of the carbonyl bands suggest a preference for the s-trans conformation.[20]

The use of excess oxidant resulted in partial isomerization to the doubly conjugated compound iii, which could be prevented by the use of a benzene–acetone solvent mixture.



iii

Catalytic reduction of **12** over PtO_2 in ethyl acetate gave two saturated ketones in a ratio of 82:18. The major ketone was identified as 4-heptanone by ir and glpc comparison with an authentic sample, while the minor ketone was identified as 2-heptanone by the same method. This apparently is formed by reduction of the ketones resulting from allylic rearrangement of the alcohol during Jones oxidation.

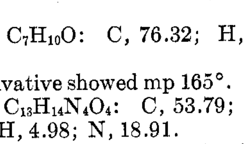
Irradiation of 1,5-heptadien-4-one (12).—A solution of 0.347 g of **12** and 1.9 g of acetophenone in 170 ml of pentane was irradiated under argon for 95 min with a 200-W mercury lamp through Vycor glassware. Distillation gave a liquid consisting mostly of acetophenone and three products in the ratio of 10:35:55. The two major product peaks were isolated *via* glpc and identified by spectroscopic comparison with the products **20** and **21** obtained from the irradiation of **18**. In the present instance, these two compounds were isolated in yields of 1.4 and 2.2%, respectively. Neither product was observed to form during irradiations carried out in the absence of acetophenone. Short-term irradiation allowed the isolation of the cis isomer of **12**, which, purified by glpc, showed ir λ_{max} 5.90, 6.17, 10.1, and 10.9 μ, uv λ_{max}^{EtOH} 227 mμ (ϵ 8600), and nmr signals at τ 7.89 (3 H, d, J = 4.8 Hz), 6.79 (2 H, d, J = 7.0 Hz), 4.82 (1 H, dd, J = 18 and 1.5 Hz), 4.79 (1 H, dd, J = 9.5 and 1.5 Hz), 4.0 (1 H, m), and 3.8 (2 H, m).

4-Methyl-1,5-hexadien-3-one (13).—The alcohol corresponding to **13** was synthesized by the reaction of the Grignard reagent from crotyl bromide with acrolein. Distillation gave a 46% yield of about 90% pure alcohol, bp 53° (18 mm), $n^{25}D$ 1.4483 [lit.[21] bp 55–56° (14 mm), $n^{22}D$ 1.4490].

A solution of 11.5 g of alcohol in 100 ml of 50:50 acetone–benzene was titrated with 30% excess Jones reagent.[9] The resultant solution was diluted with ether, washed with saturated $NaHCO_3$ solution, and dried over Na_2SO_4. Distillation gave 5.36 g (47%) of **13**, bp 54–58° (25 mm), λ_{max} 5.90, 6.09, 6.18, 10.12, 10.35, and 10.85 μ, and nmr signals at τ 8.80 (3 H, d, J = 7 Hz), 6.57 (1 H, quintet, J = 7 Hz), 4.90 (1 H, dd, J = 10 and 1 Hz), 4.88 (1 H, dd, J = 17 and 1 Hz), and 3.4–4.4 (4 H, complex).

Hydrogenation of **13** over PtO_2 gave only 4-methyl-3-hexanone, identified by ir and glpc comparison with an authentic sample.

Irradiation of 13.—A solution of 0.426 g of **13** in 450 ml of pentane was irradiated under argon with a 450-W mercury lamp through Vycor for 45 min, at which time no starting material was detectable by glpc analysis. After filtration to remove the precipitated polymer, the solvent was distilled through a spinning band column, and the residue was distilled in a Hickman flask to give 0.184 g (41%) of **22**, bp 100° (bath) (55 mm), which proved to be 94% pure by glpc analysis. Material purified by preparative glpc showed λ_{max} 5.67 μ, λ_{max}^{EtOH} 278 mμ (ϵ 21), mol wt 110 (mass spectrum), and nmr signals at τ 8.86 (3 H, d, J = 7.0 Hz), 8.43 (H_6, q, J = 9.5 and 7 Hz), 8.23 (H_4, q, J = 9.5 and 7 Hz), 7.8 (H_5, H_7, m), 7.7 (H_1), 7.44 (H_2, m), 7.21 (H_3, d of t, J = 7 and 2.5 Hz). An analysis of this spectrum using spin-spin decoupling allows the following assignment of coupling constants.



22

$$J_{2,3} = 7\ \text{Hz}, J_{2,7} = J_{2,5} = J_{3,7} = J_{3,5} = 2.5\ \text{Hz},$$
$$J_{4,6} = 9.5\ \text{Hz}, J_{6,7} = J_{4,5} = 7\ \text{Hz}$$

$J_{1,2}$ could not be determined accurately, but appears to be on the order of 2 Hz.

Anal. Calcd for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 75.65; H, 9.14.

The 2,4-DNP derivative showed mp 165°.

Anal. Calcd for $C_{13}H_{14}N_4O_4$: C, 53.79; H, 4.86; N, 19.30. Found: C, 54.13; H, 4.98; N, 18.91.

4,4-Dimethyl-1,5-hexadien-3-one (14).—The alcohol corresponding to **14** was prepared by the Grignard reaction of 3,3-dimethylallyl bromide with acrolein. The product, bp 61–63° (25 mm), obtained in about 50% yield, was contaminated with the C_{10} hydrocarbon resulting from dimerization of the Grignard reagent. Material purified by glpc showed λ_{max} 2.95, 3.27, 6.16, 10.1, and 10.9 μ, mol wt 126 (mass spectrum), and nmr signals at

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[18] H. R. Henze, B. B. Allen, and W. B. Leslie, *J. Org. Chem.*, **7**, 326 (1942).

[19] L. J. Bellamy, "The Infra-Red Spectra of Complex Molecules," Methuen, London, 1964, p 45.

[20] R. L. Erskine and E. S. Waight, *J. Chem. Soc.*, 3425 (1960).

[21] O. Kiun-Houo, *Ann. Chim.*, **13**, 175 (1940).

τ 9.01 (6 H, s), 8.34 (1 H, s), 6.26 (1 H, d, J = 6 Hz), 5.92 (4 H, m), and 5.20 (2 H, m).

A solution of 2.88 g of the alcohol in 200 ml of a 50:50 mixture of benzene and acetone was titrated with 5.4 ml of Jones reagent.[9] Normal work-up gave 1.15 g of ketone **14**, bp 62–66° (45 mm), contaminated with some starting material and the C_{10} hydrocarbon. Material collected by glpc showed λ_{max} 3.3, 5.90, 6.14, 6.22, 10.1, and 10.9 μ, and nmr signals at τ 8.75 (6 H, s), 4.88 (1 H, dd, J = 18 and 1.0 Hz), 4.86 (1 H, dd, J = 10 and 1.0 Hz), 4.42 (1 H, dd, J = 10 and 2.5 Hz), 4.10 (1 H, dd, J = 18 and 10 Hz), 3.72 (1 H, dd, J = 17 and 2.5 Hz), and 3.28 (1 H, dd, J = 17 and 10 Hz).

Irradiation of 14.—Irradiation of 0.386 g of a mixture comprised of **14** and the diene impurity in a ratio of 53:47 was carried out in pentane with a 200-W mercury lamp using a Pyrex filter. After 90 min the product was distilled to give 77.3 mg of oil, bp 50–70° (30 mm). Collection of the only new peak observed on chromatography on an SE-30 column gave 7.0 mg of material whose infrared spectrum showed a band at 5.67 μ. Rechromatography on an FFAP column revealed this to be a mixture of three compounds. The bicyclic ketone cannot be present in more than about 1% yield.

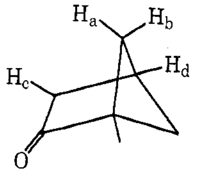
2-Methyl-1,5-hexadien-3-one (**15**).—Treatment of the Grignard reagent derived from 60 g of allyl bromide and 60 g of Mg in ether with 35 g of methacrolein gave, after normal work-up, 40.3 g (72%) of 2-methyl-1,5-hexadien-3-ol, bp 64–65° (25 mm). Material purified by glpc showed mol wt 112 (mass spectrum), λ_{max} 2.95, 6.07, 10.05, 10.95, and 11.1 μ, and nmr signals at τ 8.39 (3 H, s), 8.02 (1 H, s), 7.70 (2 H, t, J = 6.5 Hz), 5.94 (1 H, t, J = 6.0 Hz), 5.18 (1 H, broad s), 5.07 (1 H, broad s), 4.92 (2 H, m), and 4.14 (1 H, m).

A solution of 5.2 g of the alcohol in 150 ml of acetone was titrated with 17.4 ml of Jones reagent.[9] Normal work-up followed by careful distillation gave 1.87 g (38%) of yellow oil, bp 53–54° (25 mm). Glpc analysis of this material showed it to consist of >95% of a single compound. Material isolated by preparative glpc showed λ_{max}^{EtOH} 217 mμ (ϵ 7200), 320 (52), λ_{max} 3.25, 5.97, 6.14, 10.1, and 10.9 μ, mol wt 110 (mass spectrum), and nmr signals at τ 8.15 (3 H, s), 6.56 (2 H, d, J = 7 Hz), 4.88 (1 H, dd, J = 11 and 1 Hz), 4.90 (1 H, dd, J = 18 and 1 Hz), 4.24 (1 H, s), 4.06 (1 H, s), and *ca* 4.1 (1 H, m).

Hydrogenation over PtO_2 in ethyl acetate gave 2-methyl-3-hexanone, identified by comparison of the infrared spectrum and glpc retention time with those of an authentic sample.

Irradiation of 15.—A solution of 0.614 g of **15** in 150 ml of pentane was irradiated through a Pyrex filter with a 200-W mercury lamp. After 135 min, glpc analysis revealed the presence of only a trace of starting material and one major product peak. Distillation gave 0.347 g (57% of 1-methylbicyclo[2.1.1]hexan-2-one (**23**) in about 95% purity, bp 69–70° (47 mm). Material collected by glpc showed mol wt 110 (mass spectrum), λ_{max}^{EtOH} 277.5 mμ (ϵ 43), ir λ_{max} 5.67 μ, and nmr signals at τ 8.85 (3 H, s), 8.39 (2 H, dd, J = 4.5 and 2 Hz), 8.00 (2 H, m), 7.86 (2 H, m), and 7.32 (1 H, m).

Decoupling experiments showed that both protons H_b and H_c are coupled to proton H_a and to proton H_d, although the coupling constants could not be determined.



23

Anal. Calcd for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 76.13; H, 9.22.

The 2,4-DNP derivative had mp 181–182°.

Anal. Calcd for $C_{13}H_{14}N_4O_4$: C, 53.79; H, 4.86; N, 19.30. Found: C, 54.21; H, 4.86; N, 19.03.

6-Methyl-1,5-heptadien-4-one (**16**).—A Grignard reaction between allyl bromide and 3-methyl-2-butenal (prepared by MnO_2 oxidation of the corresponding alcohol) gave the alcohol 6-methyl-1,5-heptadien-4-ol in 43% yield. Material purified by glpc showed λ_{max} 3.0, 6.10, 10.1, 10.9, and 11.9 μ, and nmr signals at τ 8.32 (3 H, d, J = 1.5 Hz), 8.30 (3 H, d, J = 1.5 Hz), 7.76 (2 H, t, J = 6.5 Hz), 5.65 (1 H, m), 4.96 (2 H, m), 4.83 (1 H, m), and 4.25 (1 H, m). The OH proton signal was apparently obscured by the methyl proton signals at τ 8.3.

Oxidation of 1.37 g of the alcohol with 2.7 ml of Jones reagent[9] afforded a mixture of two compounds in low yield, bp *ca.* 65° (10 mm). The major constituent, isolated by glpc, showed data consistent with dienone **16**, with mol wt 124 (mass spectrum), λ_{max} 5.92, 6.18, 10.05, and 10.9 μ, and nmr signals at τ 8.11 (3 H, s), 7.87 (3 H, s), 6.87 (2 H, d, J = 7.0 Hz), 4.91 (2 H, AB part of normal ABC system), 4.15 (1 H, m), and 3.95 (1 H, s).

Irradiation of the crude distilled product from this reaction in pentane solution with a 450-W lamp produced no noticeable change in glpc or infrared spectrum after 1 hr. No evidence could be found for the formation of the desired bicyclic compound.

5-Methyl-1,5-hexadien-3-one (**17**).—The Grignard reaction between methallyl chloride and acrolein in ether afforded 5-methyl-1,5-hexadien-3-ol in good purity in 25% yield, bp 59–61° (25 mm). Material purified by glpc showed mol wt 112 (mass spectrum), λ_{max} 2.9, 6.06, 10.05, 10.9, and 11.2 μ, and nmr signals at τ 8.24 (3 H, s), 8.12 (1 H, s), 7.79 (2 H, d, J = 6.5 Hz), 5.78 (1 H, q, J = 6.5 Hz), 5.22 (1 H, s), 5.14 (1 H, s), 4.86 (2 H, m), and 4.14 (1 H, m).

A solution of 4.0 g of the alcohol in 200 ml of 50:50 benzene–acetone was oxidized with 14 ml of Jones reagent.[9] Normal work-up followed by distillation gave 2.2 g (56%) of ketone **17**, bp 66–68° (50 mm). Material collected by glpc showed uv λ_{max}^{EtOH} 209 mμ (ϵ 8400) and 333 (62); ir λ_{max} 3.25, 5.94, 6.05, 6.17, and 11.2 μ; mol wt 110 (mass spectrum), and nmr signals at τ 8.26 (3 H, s), 6.76 (2 H, s), 5.21 (1 H, s), 5.08 (1 H, s), 4.23 (1 H, dd, J = 9 and 2 Hz), and 3.72 (2 H, m).

Irradiation of 17. A. In Pentane.—A solution of 0.603 g of **17** in 180 ml of pentane was irradiated through a Pyrex sleeve with a 200-W mercury lamp. After 90 min, no change could be detected in the glpc analysis of the solution. The irradiation was continued in the absence of the Pyrex filter for 30 min, and some loss of starting material was noted. Acetophenone, 2.0 g, was added, and the irradiation was continued for another 2 hr, at which time no starting material could be detected, and a heavy polymer was observed in the flask. Filtration and distillation gave acetophenone with only minute traces of volatile materials.

B. In the Presence of Methanol.—A solution of 0.336 g of **17** and 1.041 g of methanol in 170 ml of pentane was irradiated through Vycor with a 200-W mercury lamp for 105 min, during which time appreciable polymer appeared and most of the starting material disappeared. Distillation gave 66 mg of colorless oil comprised of 38% of **17** and 62% of the methyl ester **30** (10% yield). Structure **30** for the product was established by spectroscopic investigation of material purified by preparative glpc, which showed λ_{max} 3.25, 5.72, 6.04, and 11.2 μ, mass spectral fragments at m/e 142 (parent ion), 43 (base peak), 111 (P − OMe), and 110 (P − MeOH), and nmr signals at τ 8.31 (3 H, s), 8.19 (2 H, m), 7.96 (2 H, t, J = 6 Hz), 7.72 (2 H, t, J = 7 Hz), 6.39 (3 H, s), and 5.36 (2 H, s).

1,5-Heptadien-3-one (**18**).—Condensation of 100 g of propanal with 100 g of malonic acid in 160 ml of pyridine and 2 ml of piperidine was carried out at room temperature in the dark for 36 hr.[10] Distillation after work-up gave 65.3 g (68%) of *trans*-2-pentenoic acid, bp 78–80° (1 mm). The trans nature of the conjugated double bond is suggested by an ir band at 10.25 μ,[19] in addition to bands at 3.4, 5.9, and 6.1 μ.

A mixture of 55.0 g of *trans*-2-pentenoic acid and 65.0 g of thionyl chloride was kept overnight at room temperature, then heated to reflux for 2 hr. Distillation gave 53.1 g (82%) of the acid chloride, bp 54–56° (23 mm), ir λ_{max} 5.67 and 6.15 μ.

A mixture of 46.0 g of triethylamine and 24.0 g of ethanol in 250 ml of purified acetone in a 500-ml flask was cooled in an ice bath. To this was added dropwise 53.0 g of the acid chloride at a rate slow enough to keep the temperature below 20°.[11] After 1 hr at room temperature, the mixture was poured into ether, washed twice with water, and dried over $MgSO_4$. Distillation gave 42.1 g (67%) of ethyl *cis*-3-pentenoate, which was >99% pure by glpc analysis. Material collected by glpc showed λ_{max} 5.72 μ and nmr signals at τ 8.73 (3 H, t, J = 7.5 Hz), 8.37 (3 H, d, J = 4 Hz), 6.91 (2 H, d, J = 5 Hz), 5.85 (2 H, q, J = 7.5 Hz), and 4.37 (2 H, m).

Hydrolysis of 41.1 g of ethyl *cis*-3-pentenoate with 16 g of NaOH in water was carried out at room temperature overnight. Distillation of the acidic product gave 28.9 g (88%) of *cis*-3-pentenoic acid, bp 54° (2 mm). The acid was converted to the lithium salt by treatment with 1 equiv of LiOMe and evaporation of solvent, followed by drying at 100°.

To a solution of 10.0 g of bromobenzene in 100 ml of ether under argon was added 1.10 g of lithium metal. After stirring at room temperature for 4.5 hr, a solution of 4.50 g of tetravinyltin in ether was added.[22] After 0.5 hr the resultant solution was filtered slowly through a sintered glass disk by means of a slight argon pressure into a slurry of 6.0 g of the lithium carboxylate salt in ether, followed by stirring at room temperature for 2 days. The solution was poured into ice water and extracted twice with ether, and the ether solution was dried with $MgSO_4$. Distillation gave 2.76 g (44%) of **18**, bp 58–60° (20 mm), greater than 95% pure by glpc. Material isolated by glpc showed λ_{max} 3.35, 5.95, 6.20, 10.1, and 10.4 μ, mass spectrum signals at *m/e* 110 (P^+) and 55 (base peak), and nmr signals at τ 8.35 (3 H, d, $J = 5.6$ Hz), 6.67 (2 H, d, $J = 6.0$ Hz), 4.41 (2 H, m), 4.21 (1 H, dd, $J = 8.4$ and 3.0 Hz), and 3.72 (2 H, m). The presence of some impurity, possibly the trans isomer, is indicated by the nmr spectrum.

Irradiation of 18.—A solution of ketone **18** (0.308 g) in 130 ml of pentane was irradiated under argon through a Pyrex filter with a 200-W mercury lamp for 3 hr. Distillation gave 0.174 g (58%), bp 60–80° (bath) (15 mm), of colorless oil. Glpc analysis showed this to consist of two peaks in a ratio of 70:30 corresponding in retention times to the products isolated from irradiation of **12**, and a small amount of bromobenzene remaining from the synthesis of **18**. Both compounds were isolated by preparative glpc and identified by spectroscopic means.

Major peak (**20**) had ir λ_{max} 5.68 μ, mass spectrum signals at *m/e* 110 (P^+) and 67 (C_5H_7, base peak), and nmr signals at τ 9.14 (3 H, d, $J = 6.0$ Hz), 8.50 (1 H, d, $J = 6.6$ Hz), 7.97 (3 H, m), 7.50 (1 H, m), and 7.34 (2 H, t, $J = 1$ Hz).

Minor peak (**21**) had ir λ_{max} 5.65 μ, mass spectrum signals at *m/e* 110 (P^+) and 68 (C_5H_8), and nmr signals at τ 8.63 (3 H, d, $J = 6.4$ Hz), 8.37 (1 H, t, $J = 7.0$ Hz), 7.80 (3 H, m), 7.48 (2 H, m), and 7.26 (1 H, m). The chemical shifts of the methyl doublet signals in these two compounds are in good accord with the assigned structures.[23]

6-Methyl-1,5-heptadien-3-one (19).—Reaction of 100 g of isobutyraldehyde with 100 g of malonic acid in pyridine–piperidine[10] afforded 4-methyl-*trans*-2-pentenoic acid in 82% yield, bp 78° (3 mm). Treatment of 40.0 g of the acid with 55.0 g of thionyl chloride gave 38.9 g (84%) of the acid chloride, bp 61–62° (25 mm), λ_{max} 5.6 and 5.7 μ.

To a solution of 81.5 g of triethylamine and 56.0 g of ethanol in 400 ml of acetone at ice bath temperature was added 97.7 g of the acid chloride to maintain reaction temperature below 20°.[11] Normal work-up followed by distillation gave ethyl 4-methyl-3-pentenoate, bp 66° (17 mm), 85.0 g (80%). Material isolated by glpc showed λ_{max} 5.70 μ and nmr signals at τ 8.72 (3 H, t, $J = 7.5$ Hz), 8.33 (3 H, broad s), 8.22 (3 H, d, $J = 2$ Hz), 6.95 (2 H, d, $J = 7.5$ Hz), 5.81 (2 H, q, $J = 7.5$ Hz), and 4.83 (1 H, broad t, $J = 7.5$ and 2 Hz).

Hydrolysis of 68.0 g of the ester with 25.0 g of NaOH in 500 ml of water at room temperature overnight gave 48.0 g (88%) of the acid, bp 65° (2 mm). The acid was converted to the lithium salt with LiOMe in methanol, and dried at 100°.

Treatment of 16.5 g of bromobenzene in ether with 4.0 g of lithium was followed by addition of 7.70 g of tetravinyltin.[22] The resulting solution was filtered under argon pressure into a slurry of 10.0 g of the lithium carboxylate salt in ether, and the mixture was stirred for 20 hr. The mixture was cooled in an ice bath and poured into water. Extraction with ether followed by drying over $MgSO_4$ gave material which was flash distilled directly into a Dry Ice trap at 1-mm pressure. This material (5.0 g, 49%) proved to be 90% pure by glpc analysis. Material collected by preparative glpc showed λ_{max} 5.94 and 6.20 μ, mass spectrum signals at 124 (P^+) and 41 (base), and nmr signals at τ 8.36 (3 H, s), 8.25 (3 H, s), 6.80 (2 H, d, $J = 6.0$ Hz), 4.72 (1 H, broad t, $J = 6.0$ Hz), 4.27 (1 H, dd, $J = 8.4$ and 3.4 Hz), and 3.76 (2 H, m).

Irradiation of 19. A. In Pentane.—A solution of 0.292 g of a mixture composed of 85% of ketone **19** and 15% of bromobenzene in 130 ml of pentane was irradiated through Pyrex with a 200-W mercury lamp for 140 min. Distillation gave 63.5 mg of oil, bp 70–90° (15 mm), which showed three peaks on glpc in the ratio of 26:30:44. Collection of these showed the first to be bromobenzene, while the second (a mixture of two unresolved compounds) showed ir absorption at 5.67 μ suggestive of a bicyclohexanone. Further attempts at separation of these compounds were unsuccessful. The last peak was identified by spectroscopic means as 3-isopropenylcyclopentanone (**24**), glpc yield 9.5%. Glpc purified material showed λ_{max} 3.25, 5.71, 6.05, and 11.2 μ, mol wt 124 (mass spectrum), and nmr signals at τ 8.24 (3 H, s), 7.5–8.2 (6 H), 7.27 (1 H, m), and 5.26 (2 H, m).

Hydrogenation of glpc-purified material over PtO_2 gave only 3-isopropylcyclopentanone, identified by ir and glpc comparison with an authentic sample prepared by similar hydrogenation of 3-isopropyl-2-cyclopentenone.[24]

B. In Methanol.—Irradiation of 0.70 g of **19** (~95% pure) in 400 ml of methanol was carried out in Vycor glassware with a 450-W mercury lamp for 30 min. Distillation gave 0.23 g of colorless oil, bp 95–105° (20 mm), which showed three major peaks in the ratio of 12:45:43 on glpc analysis (Reoplex 400 column). The latest peak (43%, 13% yield) was shown to be ketone **24** by ir and glpc comparison. The others were identified as **33** and **34** as follows.

Peak 1 (12%, 4% yield, **33**) had ir λ_{max} 3.25, 5.71, 6.07, 10.0, and 10.95 μ, mol wt 156 (mass spectrum), and nmr signals at τ 9.00 (6 H, s), 8.35 (2 H, t, $J = 8$ Hz), 7.78 (2 H, t, $J = 8$ Hz), 6.38 (3 H, s), 5.10 (2 H, AB part of ABC system), and 4.3 (1 H, m).

Peak 2 (45%, 13% yield, **34**) had ir λ_{max} 5.76, 8.05, 8.37, 8.56, and 8.80 μ, mol wt 156 (mass spectrum), and nmr signals at τ 8.45 (3 H, s), 8.36 (3 H, s), 8.2–8.5 (2 H), 8.09 (2 H, m), 7.83 (2 H, t, $J = 7$ Hz), 6.48 (3 H, s), and 4.98 (1 H, m).

Registry No.—i, 33686-88-3; ii, 33698-56-5; **6**, 33698-57-6; **6** 2,4-DNP, 33698-58-7; **7**, 24903-94-4; **8**, 33698-60-1; **10**, 5164-64-7; *cis*-**12**, 33698-62-3; *trans*-**12**, 33698-63-4; **13**, 33698-64-5; **14**, 33698-65-6; **15**, 33698-66-7; **16**, 33698-67-8; **17**, 998-83-4; **18**, 33698-68-9; **19**, 33698-69-0; **20**, 33698-70-3; **21**, 33698-71-4; **22**, 33698-72-5; **22** 2,4-DNP, 33698-73-6; **23**, 20609-40-9; **23** 2,4-DNP, 33698-75-8; **24**, 33698-76-9; **30**, 32853-30-8; **33**, 33698-78-1; **34**, 33077-53-1; 4,4-dimethyl-1,5-hexadien-3-ol, 33698-80-5; 2-methyl-1,5-hexadien-3-ol, 17123-60-3; 6-methyl-1,5-heptadien-4-ol, 33698-82-7; 5-methyl-1,5-hexadien-3-ol, 17123-61-4; *trans*-2-pentenoic acid, 13991-37-2; *trans*-2-pentenoic acid chloride, 33698-85-0; ethyl *cis*-3-pentenoate, 27829-70-5; *cis*-3-pentenoic acid, 33698-87-2; 4-methyl-*trans*-2-pentenoic acid, 16666-43-6; ethyl 4-methyl-3-pentenoate, 6849-18-9; *trans*-1,5-heptadien-4-ol, 24581-03-1.

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[22] D. Seyferth and M. A. Weiner, *J. Amer. Chem. Soc.*, **83**, 3583 (1961).

[23] T. W. Gibson and W. F. Erman, *J. Org. Chem.*, **31**, 3028 (1966).

[24] We thank Dr. Wayne Fanta for a sample of this material.