Organic and Biological Chemistry

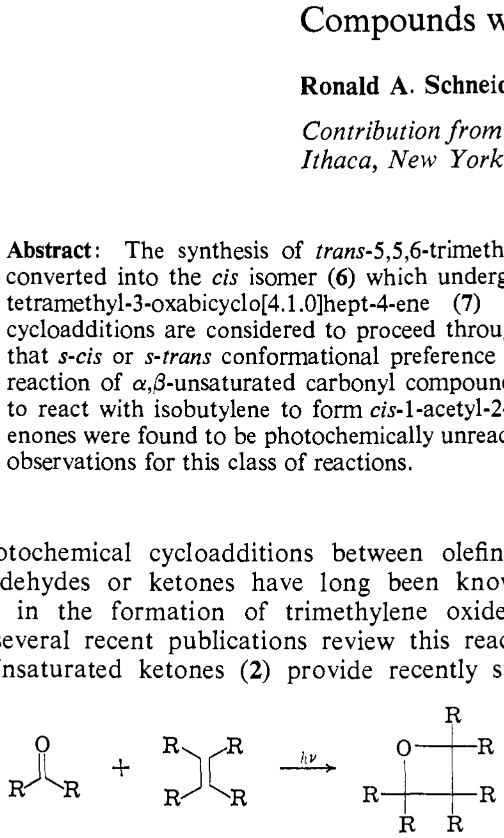
Photochemical Reactions of α,β-Unsaturated Carbonyl Compounds with Olefins[1]

Ronald A. Schneider[2] **and Jerrold Meinwald**

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. *Received August 29, 1966*

Abstract: The synthesis of *trans*-5,5,6-trimethyl-3,6-heptadien-2-one (**5**) is described. Upon irradiation, **5** is converted into the *cis* isomer (**6**) which undergoes two modes of intramolecular cycloaddition to form 1,4,7,7-tetramethyl-3-oxabicyclo[4.1.0]hept-4-ene (**7**) and 1,3,6,6-tetramethyl-2-oxabicyclo[3.1.1]hept-3-ene (**8**). The cycloadditions are considered to proceed through a diradical intermediate formed from *s-cis* **6**. It is suggested that *s-cis* or *s-trans* conformational preference may be an important factor in determining the mode of photoreaction of α,β-unsaturated carbonyl compounds with olefins. The *s-trans*-1-acetylcyclohexene (**17**) was found to react with isobutylene to form *cis*-1-acetyl-2-methylallylcyclohexane (**18**) without side reactions. Several *s-cis* enones were found to be photochemically unreactive. Some general rules are presented which summarize existing observations for this class of reactions.

Photochemical cycloadditions between olefins and aldehydes or ketones have long been known to result in the formation of trimethylene oxides (**1**), and several recent publications review this reaction.[3] γ,δ-Unsaturated ketones (**2**) provide recently studied intramolecular examples of this reaction.[4] Büchi, *et al.*,[5] suggested that the mechanism of the reaction might involve excitation of the carbonyl group to a diradical triplet state, followed by addition of one end of the excited carbonyl group to one end of the double bond in a way that would form the more stable diradical intermediates. This mechanism, which provides a rationalization of the orientation observed in these additions, has been generally accepted.[3a]



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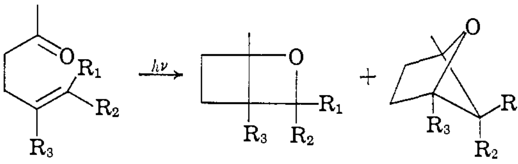
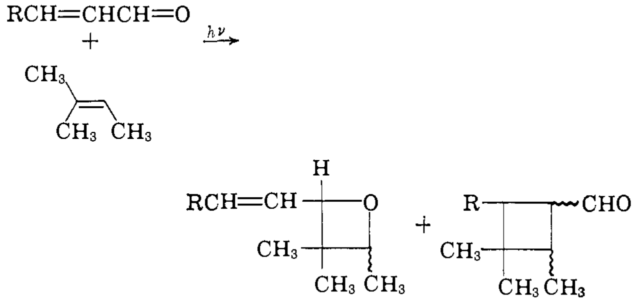


2

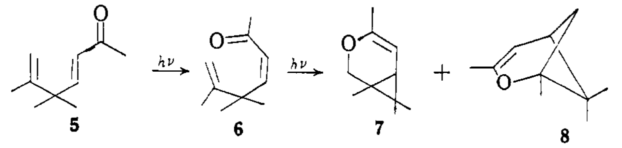
R = H or CH_3

On the basis of this mechanism, one might expect an α,β-unsaturated aldehyde or ketone to react photochemically with an olefin to form a dihydropyran as well as a trimethylene oxide. Yang,[3c] however, examined the products from the reactions of crotonaldehyde and of cinnamaldehyde with 2-methyl-2-butene, and failed to detect any dihydropyran formation, although both trimethylene oxides (**3**) and cyclobutanes (**4**) were isolated. Yang concluded from these observations that "free" radical intermediates in these reactions are unlikely.



3 **4**

In studying the irradiation of α,β-unsaturated ketones which contain an isolated double bond in the same molecule, we have encountered an intramolecular reaction (**5** → **6** → **7** + **8**) which is the converse of the reactions of crotonaldehyde and cinnamaldehyde. It results in the formation of neither trimethylene oxides nor cyclobutanes, but solely the dihydropyrans **7** and **8**. So far as we know, no dihydropyran has previously been observed as the product of a photochemical reac-



5 **6** **7** **8**

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[1] The partial support of this research by a grant from the National Science Foundation is acknowledged with pleasure.

[2] National Science Foundation Cooperative Graduate Fellow, 1962–1965; National Institutes of Health Fellow, 1965–1966.

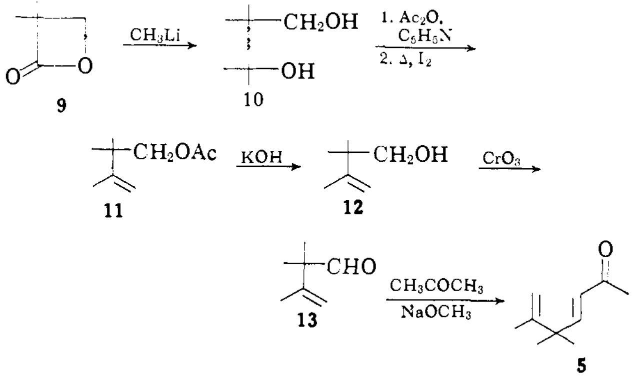
[3] See (a) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 539; (b) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 208; (c) N. C. Yang in "International Symposium on Organic Photochemistry," Butterworth and Co., Ltd., London, 1964 (*Pure Appl. Chem.*, **9**), p 591; (d) W. L. Dilling, *Chem. Rev.*, **66**, 373 (1966).

[4] N. C. Yang, M. Nussim, and D. R. Coulson, *Tetrahedron Letters*, 1525 (1965).

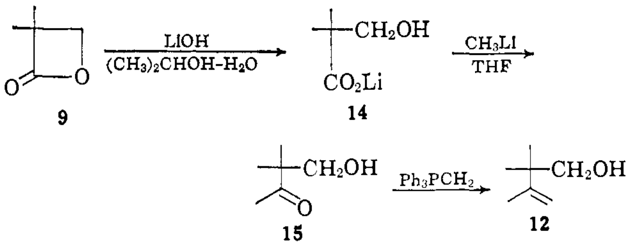
[5] G. Büchi, C. G. Inman, and E. S. Lipinsky, *J. Am. Chem. Soc.*, **76**, 4327 (1954).

tion between an α,β-unsaturated carbonyl function and an olefin function.[6]

Synthesis of 5. *trans*-5,5,6-Trimethyl-3,6-heptadien-2-one (**5**) was prepared as shown below. In this sequence, **13** and **5** appear to have been previously unknown, as were the photoproducts described in the next section. New and improved syntheses of the other intermediates in the sequence were developed in the course of this work. The oxidation of the neopentyl alcohol **12** to the corresponding aldehyde **13** could not be effected by the usual means,[7] but yields of about 25% could be obtained by adding to the alcohol under reduced pressure a solution of chromium trioxide in a mixture of propionic and acetic acids which has a boiling point between those of the alcohol and the aldehyde, and removing the aldehyde along with the acid by distillation through a fractionating column.



The unsaturated alcohol **12** was also prepared by an alternative reaction sequence. An interesting feature in this second sequence was the striking solvent dependence of the reaction of methyllithium with the lithium salt **14**. In ethyl ether, the reaction did not take place at all, but in tetrahydrofuran it proceeded readily.



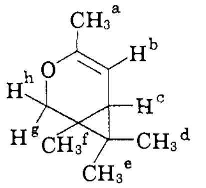
Photochemical Behavior of 5. When the *trans*-heptadienone **5** is irradiated in either methanol or pentane, and the reaction is monitored by glpc analysis, one sees first the conversion of the *trans* isomer **5** to the *cis* isomer **6**. By stopping the irradiation after a suitable time, **6** could easily be obtained by fractional distillation in yields of greater than 50%. The nmr, infrared, and ultraviolet spectra unambiguously confirm the structures and stereochemistry of these two isomers (see the Experimental Section for details).

The configurations of **5** and **6** are established by the larger coupling constant between the α and β olefinic protons in **5** (16 cps) compared to **6** (13 cps), the longer wavelength, lower intensity ultraviolet absorption of **6** [227 mμ (ϵ 7500)] compared to **5** [223 mμ (ϵ 10,900)], and the much smaller deshielding of both the α and β protons of **6** (τ 4.35 and 4.11) compared to **5** (τ 4.07 and 3.37). The latter two properties of **6** indicate that the normal *s-trans*, planar conformation of the α,β-unsaturated carbonyl chromophore (typified by **5**) has been disturbed in **6**, as one might predict on the basis of nonbonding interactions. Evidence that **6** exists in an *s-cis* conformation rather than a distorted *s-trans* one will be presented below.

As the irradiation of **5** and **6** is continued, another major volatile product **7** begins to appear. In time, **5** very nearly disappears, leaving a decreasing amount of **6** with a growing amount of **7**. Accompanying **7** at all stages of the reaction is about one-tenth that amount of **8**. Eventually, the **6** disappears, leaving **7** and **8**.

These observations indicate (but do not conclusively prove) that initially **5** is isomerized to **6**, and then **6** undergoes further intramolecular reactions to form both **7** and **8**.

The dihydropyran **7** was isolated in 45% yield by fractional distillation of the irradiated solution. The structure of **7**, which can be derived readily from **6** *via* a formal intramolecular 1,4-cycloaddition reaction, is suggested by the strong enol ether infrared absorption band at 5.96 μ, and it is supported by the elemental analytical data and by the fact that nine of the ten most abundant fragments in the mass spectrum of this product (**7**) are the same as in the mass spectrum of the *trans*-heptadienone **5**. The structure is proved by its nmr spectrum, which appears to allow only one interpretation, and is in good agreement, with regard both to predicted chemical shifts and to splitting pattern, with expectations based on the structure proposed.



7

τ

$H_a = 8.36$ (s)

$H_b = 5.38$ (d, $J_{bc} = 5.5$ cps)

$H_c = 9.38$ (d, $J_{bc} = 5.5$ cps)

H_d, H_e, H_f: 9.03 (s) (3H); 8.90 (s) (6H)

H_g, H_h: 6.11 (d, $J_{gh} = 11$ cps); 6.31 (d, $J_{gh} = 11$ cps)

The other dihydropyran (**8**) also corresponds to 1,4 addition of the isolated double bond of **6** to the α,β-unsaturated ketone function, but in the opposite sense to that which leads to **7**. Proof of the structure of **8** rests solely on its infrared and nmr spectra, for the compound is quite labile and decomposes readily to a carbonyl compound. We failed even to obtain an ade-

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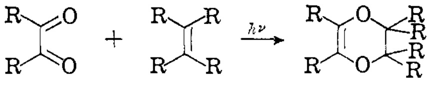
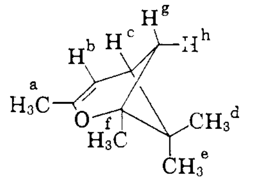
[6] Known photoreactions involving double bonds and conjugated carbonyl groups and leading to the formation of six-membered rings are (1) reversible rearrangements of 2,4-dienones to pyrans [P. de Mayo and S. T. Reid, *Quart. Rev.* (London), **15**, 393 (1961)] and (2)

"photochemical Diels-Alder" additions of olefins to α-dicarbonyl compounds (C. R. Masson, V. Boekelheide, and W. A. Noyes, Jr., in "Technique of Organic Chemistry," Vol. II, 2nd ed., A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p 257).



[7] This conversion was first attempted by Oppenauer oxidations (some of which would have led directly to **5**), a Sarett oxidation which had been reported to be effective with another neopentyl alcohol [S. Sarel and M. S. Newman, *J. Am. Chem. Soc.*, **78**, 5416 (1956)], and oxidations using dimethyl sulfoxide and either dicyclohexylcarbodiimide [K. E. Pfitzner and J. G. Moffatt, *ibid.*, **85**, 3027 (1963)] or simple anhydrides [J. D. Albright and L. Goldman, *ibid.*, **87**, 4214 (1965)]. All were unsuccessful.

quate mass spectrum. The infrared spectrum, showing enol ether absorption at 5.99 μ, greatly limits possible structures, however, and the nmr spectrum, again, appears to be open to only one interpretation.



8

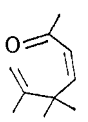
τ

$H_a = 8.28$ (s)
$H_b = 5.05$ (d, $J_{bc} = 5$ cps)
$H_c \approx 7.9$ (mult)
H_d, H_e, H_f } 9.26 (s) (3 H); 8.88 (s) (6 H)
H_g } ≈ 7.9 (mult)
H_h } ≈ 9.0 (mult)

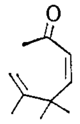
Mechanism of Formation of the Photoproducts 7 and 8. Work detailed in the Experimental Section establishes that the transformations **5** → **6** → **7** + **8** are photochemical rather than thermal reactions. They do not appear to involve preliminary formation of four-membered ring or other reasonably stable intermediates, since no trace of any intermediate other than **6** was observed when the reaction was monitored by glpc analysis.

To rationalize the production of **7** and **8**, one might consider either a radical mechanism or a photochemical Diels–Alder type mechanism.[8] Whichever mechanism is operating, one must explain the striking difference between this intramolecular reaction and the intermolecular reactions studied by Yang;[3c] *i.e.*, irradiation of **6** leads only to the two six-membered ring products **7** and **8**, and no four-membered ring products, while photocycloaddition between crotonaldehyde or cinnamaldehyde and 2-methyl-2-butene leads only to four-membered ring products (both trimethylene oxides **3** and cyclobutanes **4**), and no six-membered ring products. Other dienones have been observed to undergo intramolecular photocycloaddition to give cyclobutanes,[9] and thermal Diels–Alder reactions of crotonaldehyde or cinnamaldehyde with alkenes[8] give good yields of dihydropyrans.

A clue to a possible explanation may be obtained from an examination of molecular models of *cis*-heptadienone **6**. No radical reaction involving initial attack



s-cis **6**



s-trans **6**

by the oxygen atom on the isolated double bond is possible in any readily attainable conformation of *s-trans* **6** (or of either the *s-trans* or *s-cis* forms of **5**), and any concerted reaction is similarly impossible except for the formation of a bicyclo[2.1.0]pentane,[10] a product which was not observed. Therefore, either the photocycloaddition of **6** is a radical reaction, involving initial attack on the terminal double bond by the β-carbon atom of the enone chromophore in *s-trans* **6**, or else the reaction must proceed through *s-cis* **6**. The former possibility, in order to account for the preferential formation of **7** over **8**, would require that the β-carbon atom add to the *more* substituted end of the double bond to form a *primary* radical ten times more readily than it adds to the *less* substituted end to form a *tertiary* radical. Such behavior seems distinctly improbable.[11] It would thus appear reasonable to assume that the reaction of **6** takes place only in the *s-cis* conformation.

An independent argument leading to the conclusion that the reaction of **6** takes place in the *s-cis* conformation can be based upon the conformational preference shown by **6** in the ground state. This second argument may be generally applicable to similar cycloadditions of other enones. We will now consider the probable conformation of **6**.

Eliel[12] states as a general rule that α,β-unsaturated ketones with extinction coefficients greater than 10,000 exist in *s-trans* conformations, while those with coefficients less than 10,000 are *s-cis*. This rule, taken so simply, is not fully justified, although the generality holds fairly well.[13,14] Infrared spectral analysis appears to be a more reliable tool for assigning conformation in this case, and ultraviolet data have to be considered in conjunction with the corresponding infrared data.

Mecke and Noack, and Erskine and Waight, have amassed considerable infrared[13,15,16] and Raman[17]

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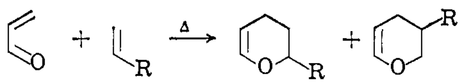
[8] The thermal Diels–Alder synthesis of dihydropyrans is a common reaction. See S. B. Needleman and M. C. Chang Kuo, *Chem. Rev.*, **62**, 405 (1962). In the reaction shown, R can be alkyl or aryl as well as alkoxyl or acyl. When R is alkyl or alkoxyl, the product is exclusively the 2-substituted dihydropyran; this mode of reaction was rationalized when discovered by postulating a diradical intermediate: C. W. Smith, D. G. Norton, and S. A. Ballard, *J. Am. Chem. Soc.*, **73**, 5267, 5273 (1951).



[9] (a) J. Meinwald and R. A. Schneider, *ibid.*, **87**, 5218 (1965); (b) P. Yates and P. Eaton, *Tetrahedron*, **12**, 13 (1961); (c) R. C. Cookson, J. Hudec, S. A. Knight, and B. R. D. Whitear, *ibid.*, **19**, 1995 (1963); (d) F. T. Bond, H. L. Jones, and L. Scerbo, *Tetrahedron Letters*, 4685 (1965); see also ref 3d.

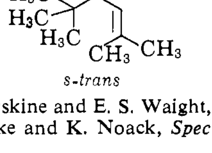
[10] In the formation of a bicyclo[2.1.0]pentane, very little π overlap could be achieved, and so no conformation appears very favorable to this mode of reaction.

[11] In all known examples of radical chain additions to olefins of the type $RCH{=}CH_2$, the point of initial attack has been observed to be exclusively at the terminal methylene group, although most studies have not been rigorous (J. I. G. Cadogan and M. J. Perkins in "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 600). For primary radical formation to be favored over tertiary radical formation would be an extraordinary result. Two cases have been reported in which 5-hexenyl radicals in solution form methylcyclopentane derivatives [R. C. Lamb, P. W. Ayers, and M. K. Toney, *J. Am. Chem. Soc.*, **85**, 3483 (1963); N. O. Brace, *ibid.*, **86**, 523 (1964)]. To explain this anomalous behavior of 5-hexenyl radicals, Lamb, Ayers, and Toney, who studied the formation of methylcyclopentane from the 5-hexenyl radical generated in toluene, suggested that rather than a cyclopentylmethyl radical being formed (the anomaly of which they discuss), an intramolecular complex is formed between the free radical site and the double bond, with subsequent donation of a hydrogen atom from the solvent to the complex. An analogous mechanism might operate in *s-cis* **6**, with the oxygen atom taking the place of the hydrogen donating solvent. No analogous mechanism could operate when **6** is in the *s-trans* conformation; an intermediate primary radical would have to be formed.

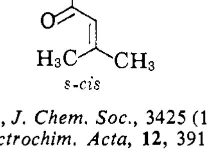
[12] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 333 ff.

[13] R. Mecke and K. Noack, *Chem. Ber.*, **93**, 210 (1960).

[14] A blatant exception is 1-isobutenyl *t*-butyl ketone (ε 10,850),[15] for which the *s-trans* conformation is sterically almost impossible. In support of the generality, see R. B. Turner and D. M. Voitle, *J. Am. Chem. Soc.*, 73, 1403 (1951).



s-trans



s-cis

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

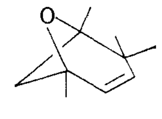
[16] R. Mecke and K. Noack, *Spectrochim. Acta*, **12**, 391 (1958).

spectral evidence to prove that, in every case examined, α,β-unsaturated methyl ketones lacking a *cis*-β substituent are *s-trans*, and those possessing a *cis*-β substituent are *s-cis*.[18] There is also evidence indicating that compounds designated as "*s-cis*" really do have this conformation and are not in nonplanar *s-trans* conformations.[13]

According to the rule just cited, the *trans*-heptadienone **5** should be *s-trans*, and the *cis* isomer **6** should be *s-cis*. The infrared absorptions of **5** (ν 1681 and 1623 cm^{-1}) and **6** (ν 1695 and 1623 cm^{-1}) are in fact in excellent agreement with the average values given[13] for *s-trans* compounds (ν 1680 and 1635 cm^{-1}) and *s-cis* compounds (ν 1692 and 1620 cm^{-1}), except for the carbon–carbon stretching frequency of the *trans* compound, which lies at the lower boundary of the range, It is also true that the ultraviolet extinction coefficient of **5** does have a value greater than 10,000 (10,900), while that of **6** is smaller (7500). Thus **6** in the ground state may be considered to exist principally in the *s-cis* conformation.

It appears plausible that the conformation of an α,β-unsaturated ketone in the photoexcited state should be the same as that in the ground state. Initially, this must be so on the basis of the Franck–Condon principle, and when the electronically excited molecule comes to vibrational equilibrium, the geometric difference between the ground state and the (n–π*) excited state (where the middle bond is shortened and the others lengthened) would not appear to lead to great changes in the nonbonding interactions which primarily determine the conformational preference. Furthermore, since the ease with which the *s-cis* and *s-trans* excited states of an α,β-unsaturated ketone add to a double bond may be expected to be roughly comparable, the preferred excited state conformation will be the one in which reaction occurs, as long as that conformation is favorable to the reaction. Therefore, one might predict not only that the photocycloaddition of **6** should take place primarily when **6** is in the *s-cis* conformation (which we have already indicated to be true on other grounds), but that other conformationally mobile α,β-unsaturated ketones with *cis*-β substituents will undergo photoreactions primarily in the *s-cis* conformation, and those ketones without *cis*-β substituents will undergo photoreactions primarily in the *s-trans* conformation.

Now with **6** in the *s-cis* conformation, it would appear from molecular models that concerted reactions leading to the dihydropyran **7** or to the trimethylene oxide **16** might take place easily. Concerted cycloaddition to form a bicyclo[2.1.0]pentane appears less facile. Finally, concerted cycloaddition to form **8** would seem to be quite difficult. Since **8** is an observed product from **6**, and **16** was not detected at all, even though trimethylene oxides are readily formed and observed in similar cases,[4] the implication is that the cycloaddition in **6** is not concerted, but proceeds by a diradical mechanism such as that suggested by Büchi[5] for the formation of trimethylene oxides from olefins and aromatic aldehydes and ketones, and that suggested by Corey[20] for the formation of cyclobutanes from olefins and cyclic α,β-unsaturated ketones. In the *s-cis* conformation of **6**, the oxygen atom occupies an ideal position from which to initiate a radical addition to the double bond; the β-carbon atom can also be imagined to initiate addition.[21]



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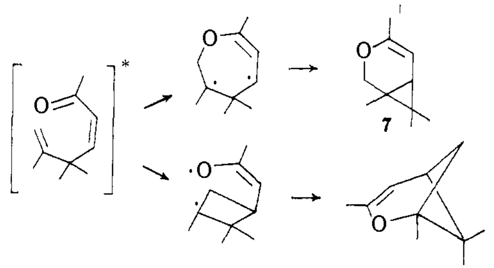
The best radical mechanism may be that shown below, in which the key feature is the derivation of the main product (**7**) from an initial attack by the carbonyl oxygen atom on the terminal olefinic carbon, while the minor product (**8**) is derived from attack of the β-carbon atom of the enone system on the same terminal olefinic site.[11,22] An alternative would be initial addition of only the carbonyl oxygen in a less selective fashion, leading to 10% primary and 90% tertiary radicals; in the formation of trimethylene oxides from aromatic ketones, where the reaction does appear to proceed by addition of the oxygen atom to the double bond to form a diradical intermediate, approximately this same degree of specificity is observed. The example given below[23] appears to be typical. There is, therefore, no



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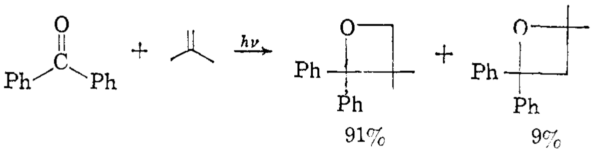

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(17) K. Noack and R. N. Jones, *Can. J. Chem.*, **39**, 2201 (1961).

(18) From this type of evidence, Mecke and Noack[13] conclude, for instance, that the favored conformation of mesityl oxide (**23**) (ϵ *ca.* 13,000; cited by Eliel[12] as *s-trans*) is in fact *s-cis*. (This conclusion was confirmed by dipole moment and ionization potential studies.[19a,b]) The ultraviolet extinction coefficient may be considered abnormally high.

(19) (a) D. Cook, *Can. J. Chem.*, **39**, 31 (1961); (b) J. B. Bentley, K. B. Everard, R. J. B. Marsden, and L. E. Sutton, *J. Chem. Soc.*, 2957 (1949). (c) Phorone, too, has been shown by independent dipole moment studies[19b] to have an *s-cis,s-cis* conformation.

(20) E. J. Corey, J. D. Bass, R. Le Mahieu, and R. B. Mitra, *J. Am. Chem. Soc.*, **86**, 5570 (1964).

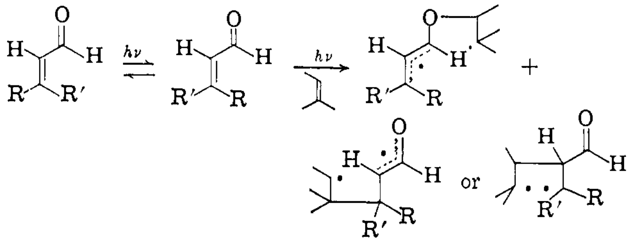
(21) Whether the reactive photoexcited state and the diradicals formed from it are singlets or triplets we cannot say. Good evidence has been amassed to show that the reactions examined by Büchi[5] and Corey[20] involve triplets, and our case might be imagined to be similar. It might be true, however, that our reaction, because it is intramolecular, takes place through singlet states before triplets have time to form. If that were true, it would provide one simple explanation of why the mode of reaction we observe is different from the mode of reaction in intermolecular cases. Nevertheless, that would not affect the other arguments and conclusions in this paper.

(22) In support of the radical mechanism drawn, some evidence does exist that an allyl radical is slightly more stable than a carbonyl-conjugated radical (C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 122). The allylic radical might be expected to form **7** much more readily than a trimethylene oxide because of the greater ease of forming a three-membered rather than a four-membered ring, and the probable greater stability of the substituted vinyl ether compared to its alternative. The other diradical should definitely prefer to form **8** rather than the highly strained bicyclo[1.1.1]pentane.

(23) D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Letters*, 1425 (1964).

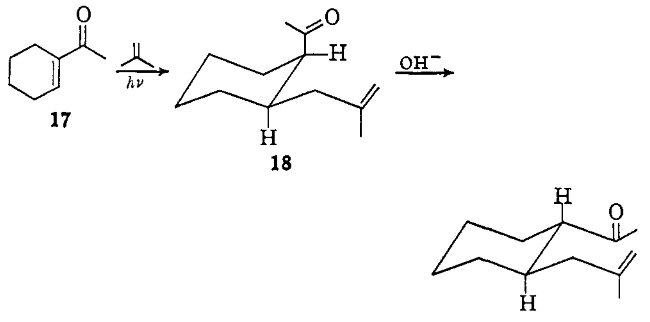
firm basis on which to choose between these closely related possibilities.

In light of the above discussion, the difference between the intramolecular cycloadditions in **6** and the intermolecular cycloadditions between α,β-unsaturated aldehydes and olefins can be explained by considering that each is a radical reaction, but realizing that the aldehydes, according to the arguments already given, react almost entirely in *s-trans* conformations, while **6** reacts in its *s-cis* conformation. In the *s-trans* conformation of any α,β-unsaturated carbonyl compound, not only is it impossible to form a six-membered ring by a concerted mechanism, but by a radical mechanism as well, for the diradical intermediates shown below[24] would have to form *trans*-dihydropyrans in coupling to form six-membered rings. Before they could isomerize, they would presumably couple to form the trimethylene oxides and cyclobutanes which Yang[3c] observed. In *s-cis* conformations, coupling to form a six- rather than a four-membered ring should be preferred on the basis of simple, steric strain consideration.



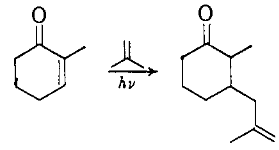
In the hope of testing the hypotheses presented here, two selected compounds, 1-acetylcyclohexene (**17**) and 2-ethylidenecyclohexanone (**21**), were irradiated in the presence of a large excess of isobutene. 1-Acetylcyclohexene, according to the arguments cited before, should exist principally in its *s-trans* conformation, and 2-ethylidenecyclohexanone must be *s-cis*. While the results obtained did not provide a definitive test of these hypotheses, they do contribute to the growing body of organic photochemistry.

The Photoproduct from 1-Acetylcyclohexene and Isobutylene. 1-Acetylcyclohexene (**17**) was found to react with isobutylene to give almost exclusively one product (**18**), which was identified by its spectra and by a base-catalyzed isomerization which gave **19**. The infrared absorption of **18** at 5.84 μ indicates a normal, nonconjugated ketone, and those at 3.23, 6.06, and 11.24 μ indicates a disubstituted terminal methylene. The nmr spectrum confirms the presence of the disubstituted terminal methylene group (τ 5.6) and reveals the allylic (τ 8.43) and acetyl (τ 8.07) methyl groups. A single proton resonance at about τ 7.6 suggests that one proton is present in the cyclohexane ring α to the carbonyl group. The presence of that proton is confirmed, and the possibility of a 1,1-disubstituted cyclohexane definitely excluded, by the observed isomerization of **18** in base to a compound of very similar glpc retention time and almost identical spectral properties. This must therefore be the more stable *trans* epimer **19**. The photoproduct **18** contains little or no **19**, but it is converted almost completely to **19** by treatment with base. The chief difference between the nmr spectra of **18** and **19** is the above-mentioned single proton resonance which appears at τ 7.6 in the case of **18**, and is lost upfield in the case of **19**, in accord with the fact that an axial cyclohexane proton in general appears significantly upfield compared to an epimeric equatorial proton.[25,26]



17 **18** **19**

The product **18** is the analog of what appears to be the major product (**20**)[27] of the reaction of 2-methylcyclohexenone with isobutene. The similarity is not surprising, since the chromophores of 1-acetylcyclohexene and 2-methylcyclohexenone are almost identical. But it does confirm that the acetyl group, which formally has freedom to rotate, does react as if it were fixed *s-trans*.



20

If one postulates that the diradical I is first formed in the reaction of **17** with isobutylene, the preferential formation of **18** is then understandable, for (1) the oxygen is inaccessible for direct coupling, (2) hydrogen abstraction involving a six-membered ring transition state is probably favored over the coupling of two tertiary radicals to form a cyclobutane,[28] and (3) the preferred

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(24) The orientation of substituents in the cyclobutane product Yang observed, and in the two corresponding diradicals drawn, is the same as that favored in the case of the cycloaddition between cyclohexenone and isobutylene. Corey[20] gives good reasons for believing that one or the other of these diradicals is involved, but which it is and what rules govern the orientation have not been adequately explained.

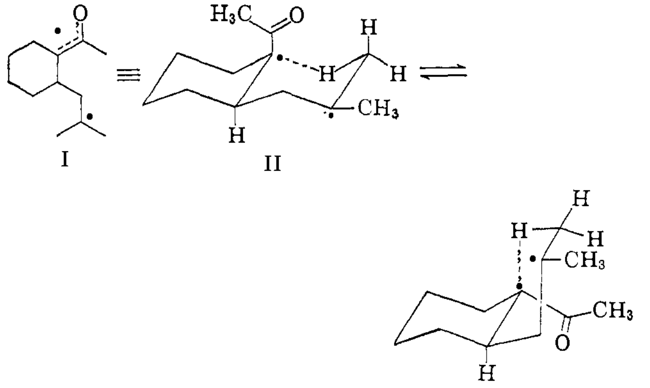
(25) N. S. Bhacca and D. H. Williams, "Applications of Nmr Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, pp 47–49.

(26) The absorption for the axial α-proton in **19** should also be broader than that of the corresponding equatorial α-proton in **18** (ref 25, pp 49–52).

(27) That **20** is the structure of this product may be deduced from the experimental data given by Corey,[20] although he does not explicitly present this conclusion. The major component made up about half of the product mixture, and was accompanied by seven other compounds. In contrast, the reaction reported here is a relatively clean one.

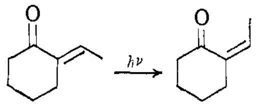
(28) 2-Methylcyclohexenone and isobutylene also give primarily the product of hydrogen atom abstraction, while cyclohexenone and isobutylene give products which correspond to both abstraction and coupling, and cyclohexenone and 2-butene give only products of coupling.[20] The implication of this series of reactions is that with diradicals of this type, coupling of two secondary radicals is considerably more facile than hydrogen abstraction, which is in turn considerably more facile than coupling of two tertiary radicals. The intramolecular photoreactions of citral[9c] also indicate that hydrogen abstraction is favored over the coupling of two tertiary radicals. It should be noted, however, that the intramolecular cycloaddition of carvone[9a] proceeds through the coupling of two tertiary radicals with no observed hydrogen atom abstraction taking place, although such abstraction would seem possible. This observation concerning carvone lends credence to the possibility that some intramolecular cycloadditions may proceed through singlet rather than triplet diradicals (see ref 21), but the correct explanation for the difference in behavior between citral and carvone is not known.

transition state ought to be the *trans*-decalin analog II rather than the corresponding *cis*-decalin analog III.

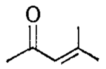

I II III

We have no certain evidence that I really is the intermediate, but it does appear likely. Why I is formed exclusively in preference to the product of addition of the α-carbon atom is a question which, in the context of the other known analogous photoadditions, still awaits adequate explanation. It is also unclear why the reaction to form **18** should be such a unidirectional one, while the reaction to form **20** is accompanied by so many side reactions.

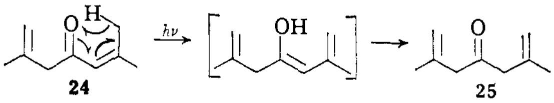
Irradiation of Other *s-cis* Enones. 2-Ethylidenecyclohexanone was irradiated in pentane and isobutylene as was 1-acetylcyclohexene. The isomerization of the *trans* **21** to the *cis* **22** was observed, but beyond that no reaction at all could be detected, even under conditions sufficient for 50% conversion of **17** to **18**, and 50% conversion of carvone to carvonecamphor.

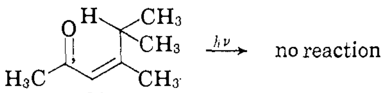

21 **22**

Mesityl oxide (**23**, shown above[18] to be *s-cis*) was similarly irradiated in the presence of isobutylene, but no reaction could be detected; even after 120 hr, the glpc peak and the infrared spectrum of an evaporated aliquot were identical with those of starting material.


23

These negative results are surprising in view of the fact that the conformations of **22** and **23** should not only be favorable for cycloaddition, but also for photoenolization and subsequent deconjugation, since most photoenolizations appear to proceed upon $n \rightarrow \pi^*$ excitation by the six-center mechanism drawn below for 2,6-dimethyl-1,5-heptadien-4-one[29,30] (**24**). Yang, also, reports that mesityl oxide and two other homologs, each with a *cis*-β-methyl substituent, fail to photoenolize "under a large variety of conditions."[29c] Similarly, *cis*-4,5-dimethyl-3-hexen-2-one (**26**) was found to be unreactive. Yet *cis*-5-methyl-3-hexen-2-one (**27**) was found to undergo facile isomerization. Yang suggested that perhaps the $(n-\pi^*)$ triplet state of **27** is of lower energy than the $(\pi-\pi^*)$ triplet state, but that for **26** this relationship is reversed because of the additional methyl substituent.


24 **25**



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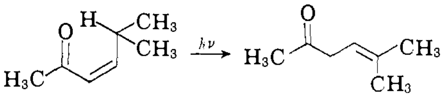
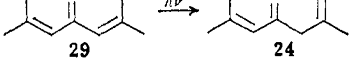

27 **28**

If Yang's explanation is correct, then the allyl substituent on the carbonyl group of compound **24** must again reverse the energy levels of the $(n-\pi^*)$ and $(\pi-\pi^*)$ states (by a narrow margin), for photoenolization does occur when **24** is irradiated through Pyrex in aqueous methanol,[34] although the conversion of **24** to **25** is very slow and probably incomplete. The reaction of **24** was observed only in methanol, however; when the reaction was attempted in pentane, it was not observed at all, although a careful comparison under controlled conditions has not been made. The energy of the $(\pi-\pi^*)$ state relative to the $(n-\pi^*)$ state should be lower in methanol than in pentane. If it were the relative energy levels that determined reactivity, one would have predicted that the reaction of **24** should have occurred in pentane but not in methanol.


29 **24**

Compound **24** can be prepared in good yield from phorone (**29**) by a rather slow photochemical reaction in either pentane or methanol.[34] (The reaction proceeds more rapidly in methanol, which appears to be generally true in all these cases and may help to explain the behavior of **24**.) Yet piperitenone (**30**), a compound which is electronically almost identical with phorone, when irradiated in methanol was observed to be unreactive. No trace of the hypothetical photoenolization

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(29) (a) Evidence for such a mechanism is provided by the isomerization of β-ionone; see P. de Mayo, J. B. Stothers, and R. W. Yip, *Can. J. Chem.*, **39**, 2135 (1961). (b) A photochemically produced enol (that from *o*-benzylbenzophenone) was first trapped by N. C. Yang and C. Rivas, *J. Am. Chem. Soc.*, **83**, 2213 (1961). Yang subsequently demonstrated that an enol is the intermediate in the photoisomerization of acyclic α,β-unsaturated ketones by converting **27** to **28** in the presence of deuteriomethanol and showing that one deuterium atom was incorporated at C-3.[29c] (c) N. C. Yang and M. J. Jorgenson, *Tetrahedron Letters*, 1203 (1964).

(30) Cases are also known of photochemical isomerization of α,β- to β,γ-unsaturated ketones when the isomerization cannot proceed through a six-center enolization step because the α,β isomers exist in a fixed configuration.[31] 1-Acetylcyclohexene (**17**, the compound which we report in this paper to be converted to **18** without interference from a side reaction of isomerization) has been reported to be such a case,[32] but the reproducibility of that observation has been questioned.[29c] So far as we know, in all cases reported of fixed *s-trans*- or *trans*-α,β-unsaturated ketones photoisomerized to the β,γ isomers, the reactions have been conducted in quartz vessels with unfiltered light. They have been postulated[33] to involve a $(\pi-\pi^*)$ excited state. The fact that we did not detect isomerization in the case of 1-acetylcyclohexene tends to support that postulate, since our irradiations through Pyrex should result only in the $n \rightarrow \pi^*$ transition.

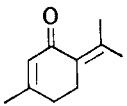
(31) H. Wehrli, R. Wenger, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **46**, 678 (1963).

(32) R. Ya. Levina, V. N. Kostin, and P. A. Gembitskii, *J. Gen. Chem. USSR*, **29**, 2421 (1959).

(33) G. S. Hammond and N. J. Turro, *Science*, **142**, 1541 (1963).

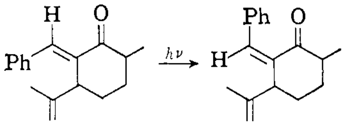
(34) K. J. Crowley, R. A. Schneider, and J. Meinwald, *J. Chem. Soc., Org.*, 571 (1966).

product or of possible photoderivatives of it could be detected (see the Experimental Section for details).



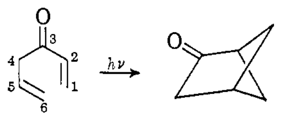
30

Another *s-cis* enone which is unreactive except for *cis–trans* isomerization is benzylidenedihydrocarvone.[32,33] Benzylidenedihydrocarvone, prepared by the condensation of benzaldehyde with dihydrocarvone as described in the Experimental Section, was found to be a mixture consisting of 94% of the *trans* isomer (**31**) and 6% of the *cis* isomer (**32**).[35] Upon irradiation, **31** was readily and completely converted to **32**, but **32** remained unchanged after 25 days of irradiation, even though intramolecular photocycloaddition to form a bicyclopentane system should have been possible.



31 **32**

One might also note that **24** fails to undergo intramolecular photocycloaddition, despite the fact that its less highly substituted homolog 1,5-hexadien-3-one (**33**) is readily converted to bicyclo[2.1.1]hexan-2-one[9d] (**34**). The difference between these two cases may well lie in the fact that **24** has an *s-cis* conformation, while **33** should have an *s-trans* conformation. If the cycloaddition in **33** starts by addition of the β-carbon atom (C_1) of the enone system to the isolated double bond, then it obviously could not start in *s-cis* **24**. If the cycloaddition proceeds by addition of the α-carbon atom (C_2), then the difference in reactivity between **24** and **33** would either reflect the much greater possible extent of π overlap between the double bonds of **33**, or would be another example of the general unreactivity of *s-cis* enones.



33 **34**

Thus the general rule appears to be that most simple *s-cis*, α,β-unsaturated ketones are unreactive when irradiated with light of wavelength longer than 300 mμ. The factors which control reactivity in these cases have yet to be explained.

An obvious choice in seeking a photoreactive *s-cis* enone is phorone[19c] (**29**), since its relative ease of photoenolization has already been established.[34] Phorone was irradiated in a 1:4 mixture of 2-ethyl-1-butene (a more convenient, higher boiling homolog of isobutylene) and ethanol for 60 hr, until about half of the phorone had been converted to **24**. By glpc analysis, no peak of higher retention time could be detected, indicating that for phorone, photoisomerization is distinctly favored over photoaddition.

Conclusion

From the facts one can formulate a series of rules which summarize existing results concerning photochemical additions between α,β-unsaturated carbonyl compounds and olefins, but the collection of observations on which they can be based is yet meager. It appears likely that all such photochemical additions (at least those which occur upon irradiation with light of wavelength longer than 300 mμ) are initiated by the (n–π^*) excited state of the enone and proceed through a diradical intermediate. When α,β-unsaturated ketones which exist in an *s-cis* conformation (*i.e.*, those of fixed conformation, and conformationally mobile enones possessing a *cis-β* substituent) are irradiated, they are likely to be unreactive; if reactive, they are likely to undergo photoenolization more readily than cycloaddition,[36a] and if cycloaddition with a double bond is favored (*e.g.*, because the reaction is intramolecular) they may react to give substituted dihydropyrans.[36b] When α,β-unsaturated ketones which exist in *s-trans* conformations (*i.e.*, those of fixed conformation and conformationally mobile ones lacking *cis-β* substituents) are irradiated, they react with olefins to form either cyclobutanes or uncyclized 3,4-addition products, depending upon the relative ease of radical coupling compared to hydrogen abstraction. α,β-Unsaturated aldehydes appear to react as do *s-trans* ketones, with the additional possibility of forming trimethylene oxides.

It will be interesting to see whether these patterns of reactivity turn out to be general.

Experimental Section

Details of apparatus and routine procedure may be found in ref 9a. All irradiations were conducted through Pyrex, and sometimes a 200-w rather than a 550-w Hanovia lamp was used, as noted.

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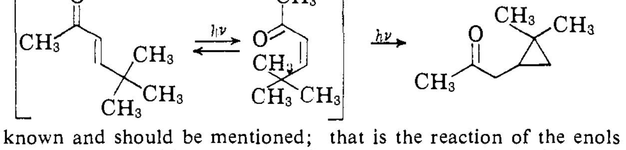
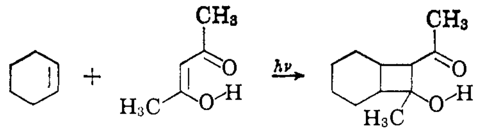
(35) The assignment of *cis* and *trans* configurations can be made by recognizing that the chromophore of the *cis* isomer will be distorted out of planarity because of nonbonding interactions. In the infrared, the *cis* isomer **32** shows shorter wavelength carbonyl absorption (5.90 *vs.* 5.93 μ) and much shorter wavelength, lower intensity carbon–carbon, double-bond absorption (6.08 *vs.* 6.20 μ), and in the ultraviolet it shows shorter wavelength, much lower intensity absorption for the extended chromophore [271 mμ (ϵ 8400) *vs.* 281 mμ (ϵ 14,700)] but not for the simple enone chromophore [222 mμ (ϵ 12,300) *vs.* 220 mμ (ϵ 7800)]. The nmr spectrum of the *cis* isomer shows a one proton singlet at τ 3.72, but in the *trans* form this proton appears under the phenyl peak (τ 2.78). All of these spectral data for the *trans* isomer (**31**) closely resemble the data for benzylidenecyclohexanone [λ_{max} 5.91 and 6.25 μ;[15] λ_{max}^{EtOH} 288 and 222 mμ (ϵ 19,000 and 7400);[15] nmr, a singlet at τ 2.60 (6 H)], known from dipole moment studies to have the *trans* configuration.[19b]

(36) (a) The possibility of forming cyclopropanes, as in the reaction below, should also be noted. See M. J. Jorgenson and N. C. Yang, *J. Am. Chem. Soc.*, **85**, 1698 (1963). (b) One other example of photocycloaddition between an *s-cis* α,β-unsaturated ketone and an olefin



is known and should be mentioned; that is the reaction of the enols of 1,3-diketones with olefins to give unstable products which are presumably cyclobutanes, as exemplified below [P. de Mayo, in "International Symposium on Organic Photochemistry," Butterworth and Co., Ltd., London, 1964 (*Pure Appl. Chem.*, **9**), p 597). The enols of 1,3-diketones are clearly a very special type of enone, but so is **6**. If intermolecular cycloadditions with ordinary α,β-unsaturated ketones could be discovered, it is difficult to predict which way they might react.



The TCEP glpc column contained 20% 1,2,3-tris(2-cyanoethoxy)-propane on 80–100 mesh Chromosorb P, and the 15% silicone analytical column contained 15% SE 30 silicone rubber gum on 80–100 mesh Chromosorb W.

Lithium Dimethylhydracrylate (14). A solution of 98.5 ml (1 mole) of pivalolactone[37] (9) in 100 ml of isopropyl alcohol was added dropwise to a stirred solution of 37.8 g (0.9 mole) of lithium hydroxide monohydrate in 400 ml of water and 200 ml of isopropyl alcohol. After the addition was complete (1 hr), 500 ml of ether was added, the aqueous phase was separated, and the aqueous solvent was removed by distillation at reduced pressure. Then 400 ml of ethanol was added to the residue, and the mixture was heated and agitated to pulverize the caked solid. After the mixture was cooled, 200 ml of ether was added and the solid was filtered, washed with ether, and dried under vacuum to give 105 g (85%) of the white lithium salt **14**.

4-Hydroxy-3,3-dimethyl-2-butanone[38] (15). To 78.6 g of lithium dimethylhydracrylate (**14**) in 750 ml of tetrahydrofuran was added 635 ml of a 2 *M* solution of methyllithium in ether.[39] The solution was distilled until most of the ether had been removed; then it was heated under reflux overnight.[40] It was cooled and poured into 300 ml of ice and water; a solution of 50 g of potassium carbonate in 50 ml of water was added, and the resulting solution was extracted with three 500-ml portions of ether. The ether solution was dried and evaporated, and the residue was distilled, yielding 29.4 g (40%) of pure **15**, bp 75° (8 mm); n^{23}D 1.4370; $\lambda_{max}^{CCl_4}$ 2.76, 5.87, 6.81, 7.12, 7.39, 7.77, 8.43, 8.92, 9.49, 9.72, 10.54, 11.03, and 11.78 μ; nmr spectrum (τ), a singlet at 8.92 (6 H), a singlet at 7.90 (3 H), and an asymmetric peak at 6.52 (3 H).

2,2,3-Trimethyl-3-buten-1-ol (12).[41] A Wittig reaction procedure based on that described by Sondheimer[42] (wherein tetrahydrofuran is used as solvent) was followed, using 14.45 g of 4-hydroxy-3,3-dimethyl-2-butanone and 2 molar equiv of methyltriphenylphosphonium bromide.[43] The product was distilled to give 2.06 g (14.5%) of **12**, bp 65° (30 mm) (lit.[41a] 152° at atmospheric pressure); n^{20}D 1.4475; $\lambda_{max}^{CCl_4}$ 2.78, 6.13, 7.20, 7.30, 9.56, and 11.12 μ; nmr spectrum (τ): a singlet at 8.97 (6 H), a singlet at 8.28 (3 H) revealing splitting at higher resolution, a singlet at 8.04 (1 H), a singlet at 6.70 (2 H), and a multiplet at 5.21 (2 H).

Anal. Calcd for $C_7H_{14}O$: C, 73.63; H, 12.36. Found: C, 73.45; H, 12.22.

2,2,3-Trimethyl-1,3-butanediol (10). A solution of 10.0 g (0.10 mole) of pivalolactone[37] (**9**) in 30 ml of ether was added dropwise, under nitrogen, to 220 ml of a stirred 1 *M* solution of methyllithium in ether[39] cooled in an ice bath. After standing overnight, the solution was poured into a mixture of 12 g of ammonium sulfate and 40 ml of ice and water. The aqueous fraction was extracted again with ether, and the combined ether extracts were evaporated, leaving 13.3 g (~100%) of a slushy solid which was recrystallized twice from pentane at Dry Ice temperatures. The white, crystalline **10** showed mp 118–128° (lit.[44] mp 127–127.5°); $\lambda_{max}^{CCl_4}$ 3.0, 8.39, 8.70, 9.49, 9.61, 10.57, and 11.33 μ.

2,2,3-Trimethyl-3-buten-1-yl Acetate (11). A solution of 57.0 g of the diol **10** and 44.0 g of acetic anhydride in 100 ml of pyridine was allowed to stand at room temperature for 24 hr, then poured into a mixture of 110 ml of concentrated hydrochloric acid and 200 ml of ice and water. The acetate was extracted with ether, and the ether solution was washed with acidic, neutral, basic, and neutral aqueous solutions and dried and evaporated. To the residue was added 50 mg of iodine, and the residue was distilled at atmospheric pressure, the bath temperature being increased gradually to 180°. The aqueous fraction of the distillate was separated and washed with ether, and the ether was added to the organic fraction, which was then dried and distilled at 28 mm to give 33.8 g (70%) of **11** boiling between 77 and 80°, and a total of 41.7 g (86%) of fairly pure **11** boiling between 70 and 83° [lit.[41a] bp 170–171° (atmospheric pressure)]; λ_{max}^{neat} 3.24, 5.75, 6.08, 7.29, 8.11, 9.63, and 11.17 μ.

Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 68.93; H, 10.49.

2,2,3-Trimethyl-3-buten-1-ol (12). To a solution of 15 g of potassium hydroxide in 75 ml of methanol was added, with cooling, 31.0 g of the unsaturated acetate **11**. After standing overnight, the solution was poured into 150 ml of water and 150 ml of ether. The water layer was separated and reextracted with ether, and the combined ether extracts were washed with water, dried, and evaporated. The residue was distilled and 20.8 g (~100%) of **12**, bp 65–67° (35 mm), was collected and found to be identical with the **12** prepared by the procedure described above.

2,2,3-Trimethyl-3-butenal (13). A solution of 100.0 g of the unsaturated alcohol **12**, 35 ml of acetic acid, and 15 ml of propionic acid was heated until distillation through a Podbielniak column commenced. Then a solution of 85 g of chromium trioxide, 15.3 ml of water, 700 ml of acetic acid, and 300 ml of propionic acid was added at a rate equal to the rate of distillation. To the distillate was added, slowly with cooling, a solution of 300 g of sodium hydroxide in 1 l. of water. The aqueous fraction was extracted with three 150-ml portions of pentane, and the combined pentane fractions were washed with sodium hydroxide solution and with water, and dried. Fractional distillation of the solution gave 27.0 g (28%) of **13**, bp 72–75° (138 mm); λ_{max}^{neat} 3.24 (w), 3.37 (m), 3.57 (w), 3.70 (w), 5.80 (s), 6.10 (m), 8.60 (w), 11.02 (s), 11.89 (m), and 13.73 (w) μ; nmr spectrum (τ): singlets at 0.85 (1 H) and 8.83 (6 H), closely split multiplets at 5.03 (1 H) and 5.16 (1 H), and a multiplet at 8.31 (3 H) resolvable into four nearly equal peaks each separated by 0.6 cps.

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.87; H, 10.91.

The residue from the distillation consisted of 39 g of the starting material (**12**) mixed with a small amount of aldehyde.

***trans*-5,5,6-Trimethyl-3,6-heptadien-2-one (5).** To a stirred solution of 1.54 g of the aldehyde **13** in 8 ml of acetone was added a solution of 750 mg of sodium methoxide in 16 ml of methanol. After the solution had stood at room temperature for 3 days, ether and acidified calcium chloride solution were added, and the ether extract was washed with water, sodium hydroxide solution, and water, and dried and evaporated. A few small crystals of iodine were added to the residue, which was then distilled to give 1.50 g (72%) of **5**, bp 95–97° (20 mm); $\lambda_{max}^{CCl_4}$ 5.95 (plus a shoulder at 5.88), 6.16, 7.26, 7.36, 7.99, 10.14, and 11.11 μ; $\lambda_{max}^{95\%\ EtOH}$ 223 mμ (ϵ 10,900) with no maximum at longer wavelength; nmr spectrum (τ): singlets at 8.79 (6 H) and 7.85 (3 H), a quadruplet at 8.30 (3 H, J = 0.8 cps), a triplet at 5.20 (2 H, J = 0.8 cps), and a pair of doublets (each 1 H, J = 16 cps) representing values calculated to be 3.37 and 4.07; glpc analysis, one single peak: T_r = 13.1 min, Carbowax, 150°; T_r = 13.2 min, silicone 86°; mass spectrum (the most intense peaks above *m/e* 50, in order of decreasing intensity): *m/e* 109, 67, 55, 137, 53, 79, 95, 81, and 152.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 79.08; H, 10.73.

Products from Irradiation of *trans*-5,5,6-Trimethyl-3,6-heptadien-2-one (5). A solution of 5.68 g of **5** in 500 ml of methanol was irradiated with the blacklights.[9a] Periodically, aliquots were withdrawn and monitored by glpc analysis. After 40 hr, most of the starting material had disappeared, leaving **6** accompanied by a lesser amount of **7**. Water (1 l.) was then added, and the solution was extracted twice with 500 ml of pentane, which in turn was water washed, dried, and evaporated. (The photoproduct decomposes in warm methanol.) The residue was distilled through a spinning-band column at 8 mm. The fractions boiling between 55 and 69° were almost entirely mixtures of **6** and **7**, amounting to a total of 3.4 g and containing about 20% of **7**. The two compounds were separated by glpc (TCEP, 100°; T_r = 3.0 and 9.4 min; upon reinjection on the same column, each component gave only a single peak). *cis*-5,5,6-Trimethyl-3,6-heptadien-2-one (**6**) showed $\lambda_{max}^{CCl_4}$ 5.90, 6.16, 7.30, 7.42, 8.55, 9.50, and 11.16 μ; λ_{max}^{MeOH} 227 mμ (ϵ

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(37) The pivalolactone was the 90% pure material obtained from Eastman Chemical Products, Inc., Kingsport, Tenn. It was used without further purification.

(38) This compound had been reported by J. É. Dubois [*Ann. Chim.* (Paris), **6**, 406 (1951)], who prepared it by base-catalyzed addition of formaldehyde to methyl isopropyl ketone. Our attempt to prepare **15** by his method led to a very impure product. Recently, however, R. Longeray and J. Dreux [*Bull. Soc. Chim. France*, 2849 (1964)] have reported an improved method of carrying out this condensation.

(39) The solution of methyllithium was obtained from Lithium Corporation of America, Bessemer City, N. C.

(40) When ethyl ether was used rather than tetrahydrofuran, and the solution was heated under reflux for 3 days, all of the dimethylhydracrylic acid was recovered unchanged after work-up.

(41) Prepared previously by different methods by (a) M. A. Courtot, *Bull. Soc. Chim. France*, **35**, 298 (1906); and (b) J. C. Munday and A. H. Matuzak, U. S. Patent 2,490,276.

(42) F. Sondheimer and R. Mechoulam, *J. Am. Chem. Soc.*, **79**, 5029 (1957).

(43) The reaction procedure used first was based on that described by R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963), wherein dimethyl sulfoxide is used as solvent. We found this technique unsuccessful when applied to **12**.

(44) R. Criegee, E. Höger, G. Huber, P. Kruck, F. Marktscheffel, and H. Schellenberger, *Ann.*, **599**, 81 (1956).

7500) with no maximum at longer wavelength; nmr spectrum (τ): singlets at 8.77 (6 H) and 7.91 (3 H), a quadruplet at 8.31 (3 H, with separations between peaks of 0.5, 0.9, and 0.5 cps), a multiplet at 5.32 (2 H), and a pair of doublets (each 1 H, J = 13 cps) representing τ values calculated to be 4.11 and 4.35.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.82; H, 10.70.

1,4,7,7-Tetramethyl-3-oxabicyclo[4.1.0]hept-4-ene (**7**) showed $\lambda_{\max}^{\mathrm{CCl_4}}$ 5.96, 6.90, 7.23, 7.71, 8.32, 8.70, 9.47, 10.54, and 11.38 μ; nmr spectrum (τ): singlets at 9.03 (3 H) and 8.90 (6 H) and an apparent singlet at 8.36 (3 H) showing barely resolvable fine structure which may be that of a doublet of J = 0.5 cps, a pair of doublets (each 1 H, J = 11 cps) representing τ values calculated to be 6.11 and 6.31, and doublets at 5.38 (1 H, J = 5.5 cps) and 9.38 (1 H, J = 5.5 cps), each showing additional fine structure; mass spectrum (the most intense peaks above m/e 50, in order of decreasing intensity): m/e 96, 95, 109, 152, 67, 81, 55, 137, 53, and 79.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.79; H, 10.70.

No change was apparent upon glpc analysis of either **6** or **7** which had been heated in a sealed ampoule at 175° for 15 min. At 275° for 15 min, both compounds polymerized and decomposed.

When the irradiation was carried to completion in methanol, the dihydropyran **7** made up about 95% of the volatile products.

When 1.15 g of **5** was irradiated with the blacklights in 80 ml of pentane, the same two products, **6** and **7**, were observed to form. After 21 hr, the ratio of **7**:**6**:**5** was 1:8:8. As time went on, **5** very nearly disappeared, leaving **6** with a growing amount of **7**. The **7** was accompanied by about 10% of an even more volatile compound which proved to be **8** (TCEP, 100°; T_r = 1.9 min for **8**, 3.3 min for **7**, and 10.0 min for **6**).

When the reaction was interrupted at this point and the solution was allowed to stand in the dark for 4 days, the chromatogram was unchanged, and it continued unchanged when the solution was heated under reflux for 12 hr. When another solution of 1.15 g of **5** was irradiated for a total of 5 days, **6** completely disappeared, leaving **7** and **8**, and a third compound which was present in even smaller amount than **8** and which had a retention time greater than that of **7**. This trace of third compound was not identified. At any stage in the reaction, the ratio of **8** to **7** appeared to be constant, but the small quantities of **8** were difficult to measure. Continued irradiation of mixtures of **7** and **8** did not change their ratio.

The product **8** did not result from a contaminant in the starting material, for the starting material was ≥99% pure according to glpc. The product **8** was found to decompose when preparative glpc was attempted, and it proved to be quite labile; distilled fractions of **8** and **7** decompose upon standing for several days at room temperature, and pure **8** in dilute solution in carbon tetrachloride is almost completely converted to a carbonyl compound ($\lambda_{\max}^{\mathrm{CCl_4}}$ 5.79 μ) even on standing under nitrogen at room temperature for a few hours.

To isolate pure **8**, a solution of 3.02 g of **5** in 400 ml of pentane was irradiated with the 200-w Hanovia lamp (see the opening paragraph of this section) until the *cis* compound (**6**) had disappeared. The time required was 35 hr. As when the blacklights were used, somewhat less than 10% of the mixture consisted of **8**. The pentane was removed rapidly by distillation through a Podbielniak column, and the residue was distilled through a spinning-band column at 9 mm, giving the following fractions, boiling points, weights, and ratios of **8** to **7**: 1, 48–50°, 61 mg, 1:1; 2, 50–51°, 89 mg, 1:1; 3, 51–53°, 156 mg, 1:3; 4, 53–55°, 193 mg, 1:5; 5, 55–57°, 1.36 g, 1:20. (Similar work-up of a blacklight experiment, in which fractions were cut differently, resulted in 15% of pure **7** (≥99%), 12% of 93% pure **7**, and 9% of 67% pure **7** (the remainder being **8**), and 8% of **7** contaminated with a few per cent of the unknown third compound.) The fractions were stored in the freezer, and the infrared spectra indicated no decomposition of **8**. Pure **8** was isolated from the first fractions by employing the microcollector of the Aerograph 660 (TCEP, 70°) and storing the product at Dry Ice temperatures until spectra were taken: $\lambda_{\max}^{\mathrm{CCl_4}}$ 5.99 (m), 6.90 (m), 7.26 (m), 7.69 (m), 8.38 (w), 8.57 (m), 8.72 (w), 9.50 (m), 9.74 (w), 10.1 (w), 10.5 (w), 10.76 (w), and 11.5 (w) μ; nmr spectrum (τ): singlets at 9.26 (3 H), 8.88 (6 H), and 8.28 (3 H; this might be a closely split doublet), a poorly defined doublet at 5.05 (1 H, J = 5 cps), a broad multiplet between 7.75 and 8.0 (2 H), and a multiplet at about 9.0 (1 H) on the edge of the methyl peak. An attempt was made to obtain a mass spectrum but the result showed no peaks of significant intensity above m/e 80, either at an ionizing voltage of 70 ev or of 16 ev. The observed spectrum consisted essentially of three peaks of approximately equal intensity at m/e 74, 59, and 43; presumably the sample decomposed in the instrument.

When the irradiation of **5** in methanol and in pentane was photosensitized with an equal weight of benzophenone, no significant change in the product ratios was observed.

Photochemical Cycloaddition between 1-Acetylcyclohexene (17) and Isobutylene. A solution of 18.6 g of 1-acetylcyclohexene[45] (**17**), 200 ml of pentane, and 150 ml of isobutylene was irradiated with the 550-w Hanovia lamp following, essentially, the procedure described by Corey[20] except that a Pyrex filter was used and the reaction was monitored continually by glpc analysis (silicone, 120°). Only one major product peak was observed (T_r = 10.8 min; T_r of starting material = 3.8 min), and it grew slowly and steadily until after 28 hr conversion was about two-thirds complete. The only other detectable peak (T_r = 6.2 min) had an area about 2% that of the major product peak and was not identified.

The solution was distilled through a spinning-band column, and after a forerun of 5.19 g, bp 60–80° (3–2 mm) (consisting mostly of starting material), 4.11 g (15%) of **18** was obtained, bp 80–83° (2 mm), and 7.1 g of nondistillable residue remained. In its infrared spectrum **18** showed $\lambda_{\max}^{\mathrm{neat}}$ 3.23 (w), 5.84 (s), 6.06 (m), 8.65 (m), and 11.24 (s) μ; nmr spectrum (τ): a multiplet at 5.6 (2 H), a broad single hump between 7.45 and 7.75 (1 H), and multiplets between 7.9 and 9.0 (17 H) including a sharp singlet at 8.07 and a less sharp singlet at 8.43, both of which appear to be methyl singlets superimposed on a background.

Anal. Calcd for $C_{12}H_{20}O$: C, 79,94; H, 11.18. Found: C, 79.85; H, 11.09.

An attempt was made to degrade **18** to the known hexahydrohomophthalic acid by ozonization followed by oxidation with sodium hypobromite, but the attempt led to no readily isolable product.

Epimerization of the Photoproduct 18. A solution of 103 mg of **18**, 200 mg of potassium hydroxide, and 4 ml of methanol was allowed to stand at room temperature. The starting **18** gave a single, symmetrical peak upon glpc analysis (silicone, 112°; T_r = 12.5 min). On standing for 15 min, the solution showed the same peak, but with a leading shoulder, which gradually grew, The solution was heated under reflux for 1 hr, whereupon it again gave one single, symmetrical peak, T_r = 11.6 min. A mixed injection confirmed these two retention times, the latter of which is ascribed to **19**. An amount of **19** present in **18** to the extent of about 10% could easily be detected by the shape of the leading edge of the peak. The photoproduct **18** gave no indication at all of **19** being present, but amounts less than 10% might not have been detectable.

Water and ether were added to the solution of **19**, and the ether extract was washed with water, dried, and evaporated, and the crude **19** was distilled in a molecular distillation apparatus at 2 mm and a bath temperature of 110°; $\lambda_{\max}^{\mathrm{neat}}$ 3.24 (w), 5.84 (s), 6.06 (m), 8.66 (m), and 11.23 (s) μ; nmr spectrum (τ): a multiplet at 5.6 (2 H), and multiplets between 7.75 and 9.1 (18 H) including a sharp singlet at 8.04 and a less sharp singlet at 8.41, both of which appear to be methyl singlets superimposed on a background.

Irradiation of Ethylidenecyclohexanone (21), Mesityl Oxide (23), and Phorone (29). Ethylidenecyclohexanone (**21**) was prepared by the condensation of acetaldehyde with cyclohexanone as reported by Dubois and Dubois.[46] Glpc analysis (silicone, 119°) revealed two peaks, T_r = 3.0 and 4.5 min, in a ratio of 1:4 [lit.[46] 1:9, assigned as *cis* (**22**) and *trans* (**21**)].

A solution of 32 g of the mixture of **21** and **22**, 500 ml of pentane, and 500 ml of isobutylene was irradiated as described for 1-acetylcyclohexene. After 2 hr, the ratio of **22** to **21** had become roughly 1:1. After 6 hr, it was 4:3. After 12 hr, it was the same, and no other peak could be detected at all. An amount of 1% or more of material of higher retention time should easily have been detectable. An aliquot was removed and evaporated. The residue gave an infrared spectrum identical with that of the starting material except that the relative intensities of the peaks were slightly different. The carbonyl peak was a single, sharp one at 5.90 μ.

Commercial mesityl oxide was purified by extraction with sodium hydroxide solution and with water, chromatography over alumina, and fractional distillation.

A solution of 18 g of purified mesityl oxide (**23**), 500 ml of pentane, and 500 ml of isobutylene was irradiated as above. After 10 hr, glpc analysis (silicone) showed only the peak due to starting material, and no other peak was detected at all. The infrared spec-

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(45) Obtained from Aldrich Chemical Co., and used directly.

(46) J. É. Dubois and M. Dubois, *Compt. Rend.*, **256**, 715 (1963).

trum of an evaporated aliquot was identical with that of starting material.

A solution of 15 g of mesityl oxide, 100 g of 2-ethyl-1-butene, and 250 ml of pentane was irradiated with the 550-w Hanovia lamp, after nitrogen had been bubbled through the solution, for 120 hr. At the end of that time, glpc analysis still showed only one peak, and the infrared spectrum was that of starting material.

The same lamp and apparatus were used to reproduce the experiment of irradiating carvone in ethanol.[9a] After 1 hr, the peak of carvonecamphor was readily detectable, and, after 20 hr, the amounts of carvone, carvonecamphor, and ethyl ester photolysis product were roughly equal, proving that the apparatus for irradiation was functioning normally.

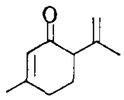
A solution of 3 g of phorone (**29**), 80 ml of 2-ethyl-1-butene, and 300 ml of ethanol was irradiated with the 550-w Hanovia lamp, after nitrogen had been bubbled through the solution, for 60 hr. At the end of that time, according to glpc analysis (silicone and Carbowax), conversion of phorone to **24** was about half complete, and no peak of longer retention time could be detected.

Piperitenone (30). Geranic acid was prepared from citral by oxidation with silver oxide.[47] Crude piperitenone was prepared from geranic acid by treatment with acetic anhydride, the method of Balant.[48] It was purified through the bisulfite adduct as described by Naves.[49]

The less expensive preparation from mesityl oxide and methyl vinyl ketone described by Wiemann[50] could not be reproduced satisfactorily. Attempts to oxidize citral to geranic acid by (1) use of the Cornforth modification of the Sarett oxidation procedure,[51] (2) use of the Jones oxidation procedure,[52] (3) silver oxide catalyzed autoxidation, and (4) oxidation with hydrogen peroxide and potassium hydroxide solution, all led to failure.

The piperitenone gave an infrared spectrum almost identical with that reported by Balant,[48] but lacking any indication of contamination by a compound with a saturated carbonyl group. It gave only one peak upon glpc analysis (Carbowax, 235°: T_r = 5.9 min; silicone, 109°: T_r = 18 min).

Irradiation of Piperitenone. Piperitenone (**30**) was irradiated in methanol solution in several different experiments, using both the blacklights and Hanovia lamps of various wattage. In all cases, the reaction was very slow. After irradiation for 20 hr with the 550-w Hanovia lamp, piperitenone comprised about 85% of the total material detectable by glpc analysis. After irradiation for 47 days with the blacklights, glpc analysis showed a peak due to piperitenone (15% silicone, 157°; T_r = 12.5 min) with an area about 20% of that of the peak of the starting solution, plus four other peaks, T_r = 5.5, 6.2, 8.0, and 9.3 min, all about the same size and none of an area greater than 10% of that of the accompanying piperitenone peak. These same four monomeric products were obtained when 1.14 g of piperitenone was irradiated in 400 ml of methanol with the 550-w Hanovia lamp for 6 days, until all the piperitenone had disappeared. The solvent was removed by distillation, and the residue was distilled at 0.7 mm to give a fraction of 50 mg of an unknown acid mixture, bp about 30°, and a fraction of 238 mg of an unknown ketone or ester mixture, bp 50–57°. In the infrared spectrum of the latter fraction, no significant peak was present in the region of 11.1–11.2 μ, indicating that the photoenolization product isopiperitenone (**35**) was absent, and no carbonyl peak was observed of wavelength shorter than 5.74 μ, indicating that the isopiperitenone analog of carvonecamphor (**36**, which might have been expected to absorb in the region 5.65–5.69 μ typical of other bicyclo[2.1.1]hexan-2-ones[9d,53]) and the other possible intramolecular cycloaddition product of isopiperitenone (**37**, a cyclobutanone) were both absent. The products were not further characterized. The remainder of the material was undistillable polymeric residue.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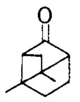
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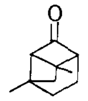
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8-*p*-Menthen-2-one (Dihydrocarvone). Dihydrocarvone was prepared following the method of Wallach[54] (the reduction of carvone with zinc dust in ethanolic potassium hydroxide solution). According to glpc analysis (silicone, 120°; T_r = 4.0 min), it contained only a trace of carvone and less than a few per cent of the only other detectable impurity (T_r = 6.9 min); λ_{max}^{neat} 5.82 (s), 6.06 (w), 6.86 (m), 7.24 (m), 7.56 (w), 8.18 (w), 8.41 (w), 8.72 (w), and 11.15 (s) μ.

***trans*-3-Benzylidene-8-*p*-menthen-2-one (31).** A solution prepared from 250 ml of absolute ethanol and 3.75 g of sodium was added under nitrogen to a stirred solution of 21.0 g of dihydrocarvone and 12.2 ml of freshly distilled benzaldehyde in 170 ml of absolute ethanol.[55] After allowing the reaction mixture to stand for 9 days, most of the ethanol was evaporated, and water and ether were added. The ether was washed once with sodium bicarbonate solution and twice with water, then dried and evaporated. The residue was distilled to give four fractions; fraction 1, bp 60–65° (0.7 mm), 9.7 g of dihydrocarvone; fraction 2, bp 65–146° (0.7 mm), 0.4 g; fraction 3, bp 146–150° (0.8 mm), 11.3 g (34%) of a pale yellow liquid; fraction 4, the remaining distillable material, 0.7 g.

Fraction 3 gave two peaks upon glpc analysis (silicone, 210°), T_r = 7.7 and 8.3 min, the first comprising about 6% of the mixture and corresponding to **32**, and the second (94%) corresponding to **31**. Constants for this mixture (*i.e.*, for nearly pure **31**) were: $n^{21}D$ 1.5706; λ_{max}^{neat} 5.93 (s), 6.07 (w), 6.20 (s), 6.69 (m), 6.90 (s), 8.47 (m), 8.67 (m), 8.83 (s), 9.89 (m), 10.66 (m), 11.11(s), 13.29 (s), and 14.36 (s) μ; λ_{max}^{MeOH} 281 μ (ϵ 14,700), λ_{min} 237 mμ (ϵ 3300), λ_{max} 220 mμ (ϵ 7800), λ_{min} 215 mμ (ϵ 7600); nmr spectrum (τ): an apparent singlet at 2.78 (6 H), closely split multiplets at 5.04 (1 H), 5.32 (1 H), and 6.40 (1 H), a complex group of multiplets between 7.3 and 8.7 (8 H, including what is probably a methyl singlet at 8.18), and a doublet centered at 8.91 (3 H, J = 6.5 cps).

Anal. Calcd for $C_{17}H_{20}O$: C, 84.95; H, 8.39. Found: C, 84.67; H, 8.45.

***cis*-3-Benzylidene-8-*p*-menthen-2-one (32).** A solution of 403 mg of the *cis–trans* mixture of benzylidene derivatives (94% **31** and 6% **32**) in 80 ml of methanol was irradiated for 17 hr with the blacklights, after which it gave only one peak, that corresponding to **32**, upon glpc analysis.

Pure **32** was obtained simply by evaporating the solvent and removing the last traces of solvent by maintaining the resulting yellow oil under vacuum: $n^{25}D$ 1.5619; λ_{max}^{neat} 5.90 (s), 6.08 (m), 6.33 (w), 6.68 (m), 6.89 (s), 7.27 (s), 8.88 (s), 9.33 (m), 9.88 (s), 10.05 (m), 10.65 (m), 11.12 (s), 13.38 (s), and 14.45 (s) μ; λ_{max}^{MeOH} 271 mμ (ϵ 8400), λ_{min} 247 mμ (ϵ 6500), λ_{max} 222 mμ (ϵ 12,300), λ_{min} 213 mμ (ϵ 10,900); nmr spectrum (τ): a multiplet at 2.8 (5 H), a singlet at 3.72 (1 H), a pair of closely split multiplets at 5.09 and 5.23 (a total of 2 H), a closely split multiplet at 6.74 (1 H), a complex group of multiplets between 7.3 and 8.7 (8 H) including what is probably a methyl singlet at 8.28, and a doublet centered at 8.99 (3 H, J = 6.5 cps).

Anal. Calcd for $C_{17}H_{20}O$: C, 84.95; H, 8.39. Found: C, 85.03; H, 8.37.

When 5.5 g of **32** in 1100 ml of methanol was irradiated with the Hanovia lamp for 25 days, it remained unchanged.

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(54) O. Wallach, *Ann.*, **279**, 377 (1894).

(55) This is essentially the method of O. Wallach, *Ann.*, **305**, 268 (1899).