upon solubility and/or reactivity of the alkyl iodide but there was always maintained at least a tenfold excess of iodo compound to PAT. The sealed ampoules were wrapped in aluminum foil to exclude light and placed in an oil bath maintained at 60.0 ± 0.1° for 4 hr, after which time the ampoules were removed and opened, and an appropriate external standard for glpc analysis was added.

The yields of iodobenzene and bromobenzene were determined by glpc employing a Hewlett-Packard F&M Model 700-231 gas chromatograph equipped with thermal conductivity detectors. The analyses were conducted utilizing 6 ft × $^{1}/_{4}$ in. columns with liquid-phase packing of SE-30, Carbowax 20M, or FFAP on Chromosorb W, 60–80 mesh. Areas under the peaks were determined by tracing with a planimeter and a correction was applied to the areas obtained to account for the difference in detector sensitivity to iodobenzene and bromobenzene. The relative rates were calculated from eq 3 and reported in Table I.

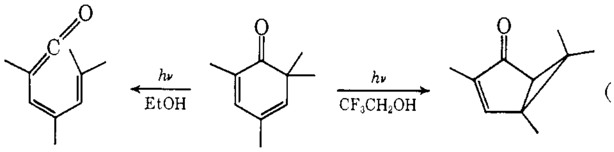
Irradiation of Eucarvone in Polar Media

Harold Hart* and Toshio Takino

Contribution from the Chemistry Department, Michigan State University, East Lansing, Michigan 48823. *Received June 16, 1970*

Abstract: The present study extends to a 2,4-cycloheptadienone a polar medium effect previously observed with 2,4-cyclohexadienones. The λ_{max} of eucarvone (**1**) is bathochromically shifted in highly polar media, from 303 nm in ethanol to 310 nm in trifluoroethanol (TFE) to 318 nm when adsorbed on silica gel suspended in cyclohexane (SGC). Irradiation through Pyrex of **1** on SGC is rapid compared with similar irradiation in cyclohexane solution. In addition to previously observed photoproducts of **1**, two new compounds were observed: 3,7,7-trimethylbicyclo[4.1.0]hept-2-en-4-one (**5**) and 1,4,4-trimethylbicyclo[3.2.0]hept-2-en-7-one (**6**). Two photoisomers of **1**, the Büchi isomer 1,4,4-trimethylbicyclo[3.2.0]hept-6-en-2-one (**2a**, major product) and compound **5** (minor product, up to 20% of the photolysis mixture), are produced initially. These photoisomerize further, as confirmed by separate irradiations. Compound **5** undergoes a photochemical vinylcyclopropane–cyclopentene rearrangement to **6** and dehydrocamphor (**4**), whereas **2a** undergoes the familiar 1,3-acyl migration (to 4,4,6-trimethylbicyclo[3.2.0]hept-6-en-2-one (**2b**)) very slowly in highly polar media. Similar results were obtained by irradiating **1** in TFE solution. The formation of **4–6** in TFE was not quenched by piperylene or 1,3-cyclohexadiene. Silica gel and TFE do not seem to be functioning simply as proton donors, since only traces of 1,5,5-trimethyl-2-norbornen-7-one (**3**), an acid-catalyzed photoproduct of **1**, were obtained in these irradiations; furthermore, only **2a** and **3** were produced when **1** was irradiated in dioxane containing sulfuric acid; compounds **4–6** were not formed. The particular excited states of **1** which give rise to **2a** and **5** remain to be firmly identified, but they are predominantly singlet states.

Highly polar media alter the spectra and normal photoisomerization path of 2,4-cyclohexadienones.[1] Most conjugated cyclohexadienones show weak n–π^* absorption at about 350 nm and a much more intense π–π^* band at about 290–310 nm; when irradiated in ether, hexane, methanol, or other common solvents they produce ketenes,[2,3] probably from the n–π^* singlet state.[3] Dissolution of the dienones in trifluoroethanol or adsorption on silica gel causes a large (10–40 nm, depending on substituents) bathochromic shift of the π–π^* band. The band also broadens considerably, and because of its greater intensity it usually completely obscures the n–π^* absorption band. When the dienones are irradiated under these conditions, they isomerize directly to bicyclo[3.1.0]hexenones rather than to ketenes; an example is shown in eq 1.



(1)

At least two explanations for this phenomenon are plausible. Since the π–π^* state is more polar than the ground state, whereas the reverse is true for the n–π^* state, polar solvents lower the energy of the former and raise that of the latter.[4] Exceedingly polar solvents such as CF_3CH_2OH or the silica gel surface may reverse the relative energies of the two states. Whereas ring opening to a ketene occurs from the n–π^* state,[3] isomerization to the bicyclo[3.1.0]hexenone may be a π–π^* singlet reaction of the dienone. If the n–π^* and π–π^* states of a molecule are not too far apart in energy (say 50 nm), such reversals by highly polar media may be general, and useful in altering the customary photochemistry of such molecules.

Alternatively, trifluoroethanol or silica gel may be functioning as proton donors, and one may be witnessing a π–π^* photoisomerization of the protonated dienone (a hydroxybenzenonium ion). Low-temperature irradiations of such ions are now well established,[5] and would lead to intermediates which, by cyclopropylcarbinyl-type rearrangement,[6] would give the observed products (eq 2).

The present work, which involves the irradiation of eucarvone (**1**) adsorbed on silica gel or in trifluoro-

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(1) J. Griffiths and H. Hart, *J. Amer. Chem. Soc.*, 90, 5296 (1968).

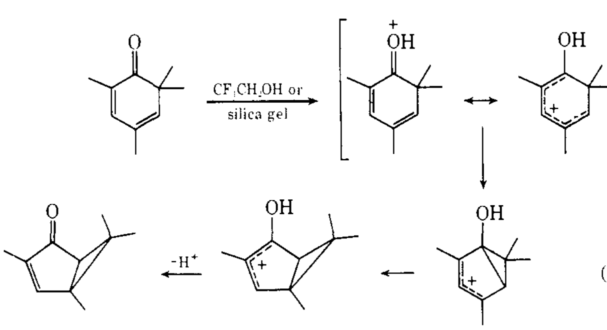
(2) G. Quinkert, *Photochem. Photobiol.*, 7, 783 (1968); O. L. Chapman and J. D. Lassila, *J. Amer. Chem. Soc.*, 90, 2449 (1968).

(3) J. Griffiths and H. Hart, *ibid.*, 90, 3297 (1968).

(4) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, pp 186–195.

(5) R. F. Childs, M. Sakai, and S. Winstein, *J. Amer. Chem. Soc.*, 90, 7144 (1968); R. F. Childs and S. Winstein, *ibid.*, 90, 7146 (1968); R. F. Childs, Abstracts of Papers, Chemical Institute of Canada and American Chemical Society Joint Conference, Toronto, May 1970, ORGN No. 63.

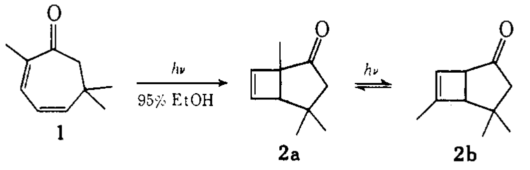
(6) D. W. Swatton and H. Hart, *J. Amer. Chem. Soc.*, 89, 5075 (1967); H. Hart, T. R. Rodgers, and J. Griffiths, *ibid.*, 91, 754 (1969).



(2)

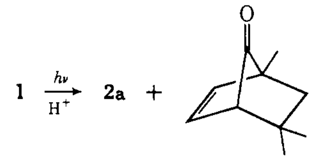
ethanol solution, was undertaken with two purposes. First, we wished to determine whether our results with 2,4-cyclohexadienones[3] could be extended to 2,4-cycloheptadienones, which are also expected to have first (mainly n–π*) and second (mainly π–π*) excited states that are rather close in energy. Second, irradiation of eucarvone in acid gives[7,8] a photoproduct normally not observed in neutral solution (*vide infra*). We thought that a determination of whether or not this product is also formed when eucarvone is irradiated on silica gel or in trifluoroethanol solution might help decide between the two interpretations of the polar media effects described above.

Eucarvone is a readily available 2,4-cycloheptadienone.[9] Its photoisomerization, studied initially by Büchi and Burgess,[10] is historically important because it exposed the first example of photolytic 1,3-acyl migration in β,γ-unsaturated ketones (**2a** ⇌ **2b**).[11] Recent quantitative studies[12] show that in benzene solution the conversion **1** → **2a** is rather inefficient (Φ = 0.0025) and may involve both singlet (60%) and triplet excited states of **1**.

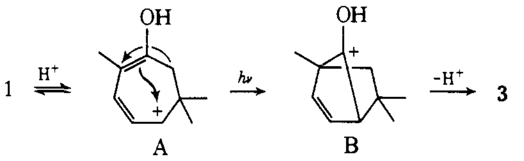


1 **2a** **2b** (3)

Hurst and Whitham reported[7] that **2a** and a third photoproduct **3** were obtained by irradiating **1** in sunlight for 4 weeks, either in 40% aqueous acetic acid or in aqueous dioxane which contained 1% sulfuric acid. This result was confirmed by Schuster, *et al.*,[8] who obtained **3** in 1–20% yield after 7–10 days irradiation of acidified **1** (Pyrex, 450-W lamp). The suggested[7] mechanism (eq 5) involves a 7-norbornenyl cation (B) in which the positive charge is stabilized in part by the 2,3-double bond.

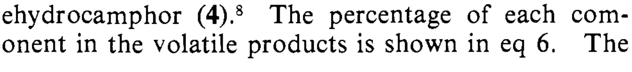


3 (4)

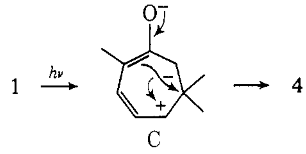


(5)

Still a fourth photoproduct from **1** was identified as dehydrocamphor (**4**).[8] The percentage of each component in the volatile products is shown in eq 6. The bond changes which lead from **1** to **4** are depicted in C, though the limitations of this representation were clearly recognized.[8]



4 10–20% (6)



C (7)

We have found two additional photoproducts from eucarvone, and wish to describe here the evidence for their structures, as well as some experiments which help clarify the relationship between all these photoproducts.[13]

Results

Spectra and Irradiation of Eucarvone (1). Eucarvone has a broad, intense absorption band with a λ_{max}^{EtOH} 303 nm (log ε 3.83).[14] The band tails off, with no clear-cut additional long-wavelength maximum being discernible. From its position, intensity, and solvent behavior we believe this is largely a π–π* band which, because of its breadth, masks any weak n–π* band expected in the vicinity of 350 nm. The λ_{max} is shifted bathochromically, without appreciable intensity change, to 310 nm in CF_3CH_2OH (hereafter, TFE) and to 318 nm when the eucarvone is adsorbed on silica gel suspended in cyclohexane (hereafter, SGC).[15]

Irradiation of **1** in SGC through Pyrex for 6 hr with a Hanovia 450-W lamp gave only 11.6% recovered **1**. All previously reported[7,8,10] photoproducts were observed (42.8% **2a**, 17.1% **2b**, a trace of **3**, and 6.9% **4**), together with two new photoproducts, assigned structures **5** (8.8%) and **6** (12.7%). Control experiments showed that **1** is recovered unchanged even after 10 hr reflux in SGC, and that the photoproducts were inert to SGC at room temperature (12 hr) and were unaltered by the vpc conditions used to collect them.

The same photoproducts were also obtained when 0.2–1.2% solutions of **1** in TFE were similarly irradiated. A discussion of yield variation with irradiation conditions is deferred until after the structural evidence for **5** and **6** is presented.

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(7) J. J. Hurst and G. H. Whitham, *J. Chem. Soc.*, 710 (1963).

(8) D. I. Schuster, M. J. Nash, and M. L. Kantor, *Tetrahedron Lett.*, 1375 (1964).

(9) E. J. Corey and H. J. Burke, *J. Amer. Chem. Soc.*, **78**, 174 (1956).

(10) G. Büchi and E. M. Burgess, *ibid.*, **82**, 433 (1960).

(11) For a recent mechanistic study and references, see E. Baggiolini, K. Schaffner, and O. Jeger, *Chem. Commun.*, 1103 (1969).

(12) D. H. Sussman, Ph.D. Thesis, New York University, 1968; D. I. Schuster and D. H. Sussman, *Tetrahedron Lett.*, in press. We are indebted to Professor Schuster for this information in advance of publication.

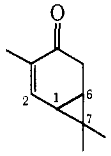
(13) For a preliminary account, see T. Takino and H. Hart, *Chem. Commun.*, 450 (1970).

(14) R. A. Barnes and W. J. Houlihan, *J. Org. Chem.*, **26**, 1609 (1961).

(15) Spectral examination of the supernatant liquid in these suspensions showed that >99% of the eucarvone was adsorbed on the silica gel.

Structures of the New Photoproducts. Compound **5** had the longest vpc retention time of all the photoproducts, including unconverted **1**. The mass spectrum (M = 150) showed that **5** was an isomer of **1**. The ir spectrum (1660 and 1640 cm^{-1}) suggested an α,β-unsaturated ketone, but the uv spectrum ($\lambda_{max}^{cyclohexane}$ 260 nm, log ϵ 3.78) indicated additional conjugation with a cyclopropane ring.[16]

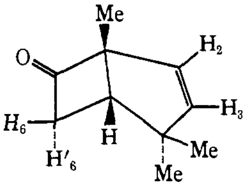
The nmr spectrum of **5** showed one vinyl proton (τ 3.35), probably adjacent to an allylic methyl group (τ 8.27, d, J = 1.5 Hz), two aliphatic methyl singlets at τ 8.78 and 9.15, and four additional protons as complex multiplets at τ 7.51 and 8.7–8.8. These data suggested that **5** was 3,7,7-trimethylbicyclo[4.1.0]hept-2-en-4-one.[17]



5

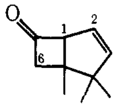
Compound **5** has been obtained recently from a natural product.[19] Our ir and uv spectra are essentially identical with those reported (no nmr data were given). On the basis of these spectral data, and photochemical conversions to be described below, structure **5** seems secure.

Compound **6** was collected as the third vpc peak (of 7); it appeared between **2a** and **4**. It is considered to be 1,4,4-trimethylbicyclo[3.2.0]hept-2-en-7-one (**6**) on the following spectral evidence. The mass spectrum (M = 150) confirmed that **6** was an isomer of **1**. Carbonyl absorption at 1770 cm^{-1} was typical for a cyclobutanone.[20] The nmr spectrum showed three aliphatic methyl singlets (τ 8.87, 8.85, and 8.75) and two vinyl protons (H_2 and H_3) as an AB quartet at τ 4.47 and 4.70, J = 5.5 Hz. In addition there were, at 60 MHz, peaks for three protons between τ 6.8 and 8.0. These were nicely resolved in a 100-MHz spectrum to two mutually coupled doublets of doublets at τ 7.33 and 6.92 (J = 18.0 Hz), each separately coupled (J = 8.0 and 7.0 Hz, respectively) with a third doublet of doublets at τ 7.92. We attribute these signals to H_6', H_6, and H_5, respectively.[21]

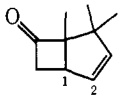


6

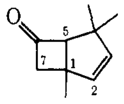
Alternative cyclobutanone structures which were considered are **6a–c**. Of these, **6a** is known[22] and can be eliminated because its nmr spectrum (particularly, the chemical shifts of the methyl and vinyl protons) differs from that observed for **6**. Some similarities in the spectra do, however, lend support to the structural assignment of **6**. For example, the C-6 protons in **6a** are mutually coupled, J = 18.0 Hz, identical with **6**, and the *endo*-H_6 of **6a** appears at higher field than the *exo*-H_6. A small coupling (J = 2.1 Hz) was observed between H_1 and H_2 of **6a**. Since no such coupling with one of the vinyl protons was observed in the nmr spectrum of the photoproduct, this observation also eliminates structure **6b**, which would be expected to show a similar small coupling. Finally, in **6a**, H_1 is coupled to one of the H_6 protons by 4.5 Hz. A similar coupling would be expected between H_5 and H_7 in **6c**, whereas in fact the observed coupling between the bridgehead proton and both methylene protons was much larger than this (7 and 8 Hz). Through these arguments, the nmr spectrum of the photoproduct strongly supports structure **6** in preference to **6a–c**.



6a



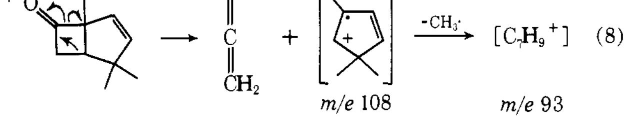
6b



6c

The uv spectrum of **6** shows the enhanced absorption characteristic of β,γ-unsaturated ketones with the appropriate geometry for overlap of the C=C and C=O orbitals.[22,23] Its $\lambda_{max}^{cyclohexane}$ 307 nm (ϵ 253) compares well with that reported[22] for **6a** (307 nm, ϵ 190) and may be inconsistent with γ,δ-unsaturated structures **6b** and **6c**, in which the orbital overlap necessary to such enhanced absorption seems unlikely.

The mass spectrum fragmentation pattern also supports structure **6** (but not in preference to **6a–c**). The dominant peaks, which appear at *m/e* 108 and 93 (relative intensities 99 and 100, compared with 7 for the parent peak), can be accounted for as in eq 8.[24]



Mechanistic Experiments. Eucarvone on SGC was irradiated through either Pyrex or quartz in a "merry-go-round" apparatus using a Hanovia 450-W lamp. Samples withdrawn at various time intervals were

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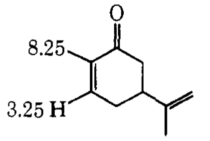
(16) Compare, for example, the umbellulone which has the O=CC=C-*c*-C_3 chromophore and a λ_{max}^{EtOH} 265 nm (log ϵ 3.5). Solvent correction for **5** would bring its λ_{max} to 266–267 nm in ethanol.

(17) The chemical shifts of the allylic methyl and vinyl protons compare favorably with those of carvone.[18] The high-field aliphatic



methyl (τ 9.15) is presumably the *endo*-C-7 methyl, shielded by the π system in the six-membered ring.

(18) Varian Associates NMR Spectra Catalog, Spectrum 271.

(19) A. Zabza and H. Kvezynski, *Rocz. Chem.*, **40**, 463 (1966).

(20) The bridged ketone **3** also possesses a strained carbonyl group, ν 1782 cm^{-1}; structure **3** was quickly eliminated by comparison with an authentic sample.

(21) The large coupling constant typical for a cyclobutanone methylene group readily distinguishes H_6 and H_6' from H_5. The chemical shift of τ 6.92 is unusually low for a proton α to a carbonyl group. Examination of a molecular model shows that H_6 lies nearly in the nodal plane of the double bond, which may cause it to be deshielded; the distinction between H_6 and H_6' is made on these grounds, and is tentative.

(22) D. E. Bays and R. C. Cookson, *J. Chem. Soc. B*, 226 (1967).

(23) R. C. Cookson and N. S. Wariyar, *ibid.*, 2302 (1956); D. E. Bays, R. C. Cookson, and S. MacKenzie, *ibid.*, *B*, 215 (1967).

(24) The major peaks in the mass spectrum of **5** also appear at *m/e* 108 (46) and 93 (100), which suggests that **5** may rearrange to **6** and **4**[8] on electron impact.

analyzed by vpc. The results of typical experiments are depicted in Figure 1. Results with Pyrex and quartz were identical within experimental error.

Although it may be difficult to interpret prolonged photolyses which yield several photoproducts, because the absorbing species change with time, some conclusions can be drawn from the results expressed in Figure 1. The earlier observations[8,10] that **2a** is the major product are confirmed. Since **2b** is formed from **2a**, its yield curve is sigmoidal.

The most significant observation is that the fraction of **5** present attains a maximum (about 20%), then decreases sharply.[25] This indicates that **5** is produced from **1**, but as it begins to absorb an appreciable fraction of the light, it photoisomerizes to other products. The likely products of this secondary reaction would be **4** and **6**.

To test this, a 0.03 M solution of **5** on SGC was irradiated for 6 hr through Pyrex using a Hanovia 450-W lamp. After that time only a trace of **5** remained, and the products were cleanly **4** (35%) and **6** (65%). This ratio is essentially the same as that observed after 3–6 hr direct irradiation of **1**.[26]

Similar irradiation of **2a** on SGC gave, after 6 hr, only **2b** (20.4%) and recovered **2a** (79.6%); no **4**, **5**, or **6** were formed.

Irradiations of **1** in trifluoroethanol solution were similar to but somewhat slower than those on SGC. After 4 hr (0.076 M, Pyrex, 450 W) 47.4% **1** remained unchanged, compared with 15% in an identical run with SGC. The other components of the photolysis mixture were **2a** (37.8%), **4** (2.2%), **5** (11.1%), and **6** (1.5%). No **2b** was present. This is due to the exceedingly slow conversion of **2a** $\rightarrow$ **2b** in TFE.[27]

Several quenching experiments were done in TFE. Eucarvone was irradiated (0.076 M TFE) with various concentrations (0.1–0.5 M) of piperylene or 1,3-cyclohexadiene. Although the precision of the analytical method could not detect slight differences, there was no systematic or major change (more than a few per cent) in the yields of any of the photoproducts.

Photolyses of **1** on SGC or in TFE appear to be much faster than identical irradiations in cyclohexane solution. Under identical conditions, irradiation of **1** in cyclohexane (1% solution) for 6 hr through Pyrex gave 89.0% unchanged **1** (compared with 11.6% on SGC) and 11.0% **2a**. The cyclohexane reaction was faster in quartz (only 42.1% recovered **1**); the products were **2a** (31.8%), **2b** (25.3%), and perhaps a trace of **6** (0.1%). In contrast, the SGC runs were not affected by the change from Pyrex to quartz (Figure 1).

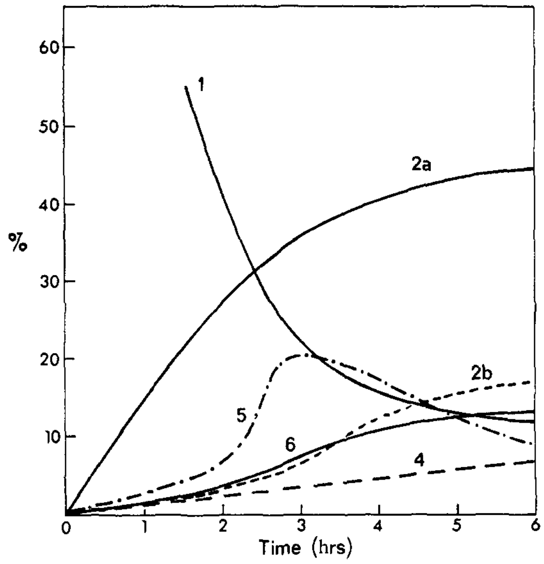


Figure 1. Irradiation of eucarvone on silica gel–cyclohexane. Product distribution as a function of time. Compounds are numbered as in the text.

The photoisomerization of **1** in acidic media was cursorily reexamined, to determine whether **4**–**6** are produced under these conditions. Irradiation of **1** in 95% aqueous dioxane containing 1% sulfuric acid (Pyrex, 450-W Hanovia lamp) proceeded very slowly indeed. After 7 days, 60.1% **1** was recovered; the only products were **2a** (30.3%) and **3** (9.6%).

Discussion

It seems clear that irradiation of eucarvone on silica gel–cyclohexane or in trifluoroethanol solution leads to two sets of products (eq 9). Separate irradiation of **2a**

$$\begin{tikzcd} & \mathbf{2a} \arrow[r, shift left, "h\nu"] & \mathbf{2b} \arrow[l, shift left] & \text{(major path)} \\ \mathbf{1} \arrow[ur, "h\nu"] \arrow[dr, "\text{SGC}"'] & & & \\ & \mathbf{5} \arrow[r, "h\nu", "\text{SGC}"'] & \mathbf{4} + \mathbf{6} & \text{(minor path)} \end{tikzcd} \qquad (9)$$

or **2b** produces only the other isomer, and separate irradiation of **5** gives only **4** and **6**. Thus, the formation of **2a** and **5** from **1** appears to be irreversible, and there is no other crossover point in the two product manifolds (*i.e.*, **2a** $\not\rightleftharpoons$ **5**, etc.).

In trifluoroethanol, neither set of products is appreciably quenched by dienes. It seems likely that the products arise predominantly or solely from a singlet state(s) of **1**. Compounds **2a** and **5** may arise from the same excited state of **1** or from two different states, close in energy. No data are yet available which provide a choice between these alternatives.

As discussed in the introduction, two explanations have been seriously considered to explain the effect of highly polar media on dienone photochemistry; either they invert the relative energies of the $n-\pi^*$ and $\pi-\pi^*$ excited states, or they act as proton donors, and reaction occurs through the $\pi-\pi^*$ state of the protonated dienone. The latter explanation seems untenable in

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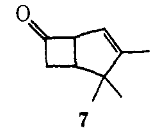
[25] No particular significance is at present attached to the shape of the initial part of the curve for **5**. This compound has the longest retention time by far of the components in the mixture, and since it follows **1** on the vpc, it is difficult to analyze for accurately in the early part of a run, when the amount of unconverted **1** is still large.

[26] Similar irradiation of **5** in cyclohexane solution, without silica gel, also gave **4** (3.2%) and **6** (49.6%), but in addition gave **2a** (10.4%), **2b** (5.6%), and a new product **7** (31.2%).[22] These three products



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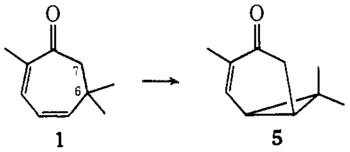
arise from photoisomerization of **4**, as shown by separate irradiation of the latter (6 hr, cyclohexane, Pyrex, 450 W), which gave 3.3% recovered **4**, as well as **2a** (36.1%), **2b** (8.2%), and **7** (47.6%). Thus **4** is photolabile in nonpolar solvents such as cyclohexane, but is photochemically relatively inert when adsorbed on silica gel.

[27] Separate irradiation of **2a** in TFE as above gave only 20% **2b** after 90 hr and 36.7% **2b** after 220 hr. The reverse reaction (**2b** $\rightarrow$ **2a**), however, is faster in TFE than in cyclohexane. Irradiation of **2b** as above gave the following percentages of **2a** in 1, 4, and 28 hr: (TFE) 33, 55, 57; (cyclohexane) 15, 23, 38. From these preliminary results it is clear that the interconversion of **2a** and **2b** as a function of solvent polarity warrants detailed study.

the case of eucarvone, for if it were correct one would expect to obtain **5** (also **4** and **6**) by irradiating **1** in acid. But a repetition of the earlier[7] irradiation of **1** in acidic dioxane gave no trace of **4**–**6**. Only the previously reported[7,8] **2a** and **3** were observed, and these were produced at an inexorably slow rate compared with the rapid formation of **4**–**6** from **1** in SGC or TFE.

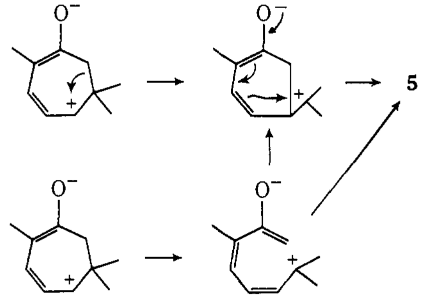
Eucarvone photoisomerizes faster in SGC or TFE than it does in nonpolar solvents such as cyclohexane. This is especially striking for irradiations through Pyrex, and may be due in part to the fact that the uv maximum of **1** in cyclohexane solution is at the edge of Pyrex transmittance; the maximum is bathochromically shifted in TFE or SGC, and the greater isomerization rate may be because more energy is available to the system. Consistent with this, eucarvone photoisomerizes much faster when irradiated through quartz rather than Pyrex (whereas irradiations on SGC were unaffected by this change). However, even through quartz the reaction was faster in SGC or TFE; quantitative measurements are required before the rate effect can be fully understood.

To produce **5** from **1** one must formally break the C_6–C_7 bond in **1** and add it to the C_4–C_5 double bond.



1 **5**

The reaction can be regarded as a photochemically allowed $\sigma 2a + \pi 2a$ process.[28,29] Although the reaction may be concerted, the transition state may develop appreciable ionic (dipolar) character, since only in polar media does the formation of **5** become competitive with the formation of **2a**. Alternatively, one may formulate the process in several stepwise fashions, such as



At present little else can be said about the mechanism by which **5** is formed from **1**, except that the *gem*-dimethyl group at C-6 is probably an important structural feature which weakens the C_6–C_7 bond or stabilizes a partial positive charge. The importance of substituent effects on this reaction remains to be investigated.

The photoisomerization of **5** to **4** and **6** affords two additional examples of the photochemical vinylcyclopropane–cyclopentene rearrangement.[30]

Experimental Section

Eucarvone (**1**) was prepared from carvone:[9] bp 54–55° (1.4 mm); uv max (cyclohexane) 298 nm (ϵ 6600), (95% ethanol) 302 nm (ϵ 6500), (trifluoroethanol) 310 nm (ϵ 8600). The position of the uv maximum on silica gel–cyclohexane varied slightly with the grade of silica gel [Davidson 62, 314 nm; Davidson 950, 320 nm; Davidson 12, 320 nm]; ir (CCl_4) 3050, 2980, 1660, 1460, 1395, 1370, 1320, 1245, 1095, and 740 cm^{-1}. The nmr spectrum agreed with that recently reported.[31]

Irradiations on Silica Gel–Cyclohexane (SGC). This procedure for eucarvone (**1**) is typical of preparative runs. Silica gel (Davidson or Fisher chromatographic grade 950, 60–200 mesh) was activated at 150° for 10 hr. Silica gel (7 g) was added to a solution of **1** (0.5 g) in cyclohexane (50 ml), and the suspension was thoroughly flushed with N_2 and capped. Eight Pyrex test tubes prepared as described were simultaneously irradiated for 6 hr using a Hanovia 679 A-36 450-W lamp. The tube contents were combined, filtered, and the silica gel was slurried with portions of methylene chloride (total 1 l.) and filtered. Combined organic layers were evaporated and the residual yellow oil was subjected to preparative vpc (20 ft × 0.25 in. column, 20% Carbowax 20M on Chromosorb W, 180°, He flow rate 75 ml/min). Under these conditions, typical retention times (min) were: **3** (9.0), **2a** (10.4), **6** (15.1), **4** (22.0), **2b** (25.1), **1** (30.0), and **5** (45.0).

Irradiations of **2a** and **5** on SGC were carried out similarly, but on a smaller scale.

Product Identification. Compound 2a. The uv spectrum (95% EtOH) and principal ir bands were identical with those reported,[10] uv (CF_3CH_2OH) 297 nm (ϵ 207). The nmr spectrum showed some differences from those previously reported.[8,10] We confirm the chemical shifts reported by Schuster[8] but have also located the C-5 bridgehead proton: nmr (CCl_4) τ 9.03, 8.90, 8.76 (s, 3 each, CH_3), 8.23 (d, 1, $J = 17.5$ Hz, *endo*-methylene proton), 7.40 (s, 1, bridgehead H), 7.16 (d, 1, $J = 17.5$ Hz, *exo*-methylene proton), 3.88 (d, 1, $J = 2.8$ Hz, $=CH$ at C-6), 3.67 (d, 1, $J = 2.8$ Hz, $=CH$ at C-7). **Compound 2b.** The uv spectrum (95% EtOH) and principal ir bands were identical with those reported,[10] uv (CF_3CH_2OH) 221 nm (ϵ 1100), 296 nm (ϵ 305). The nmr spectrum (CCl_4) agrees with those fragments of the spectrum which were previously described:[10] τ 9.03, 8.80 (s, 3 each, $C(CH_3)_2$), 8.12 (br d, 3, $=CCH_3$), 6.8–7.5 (m, 4, CH_2 and bridgehead protons), and 4.12 (m, 1, $=CH$). **Compound 3** was obtained in only trace amounts from these irradiations; it was identified by its distinctive ir carbonyl frequency[7] and by its short retention time.[12] **Compound 4.** The uv, ir, and nmr spectra were identical with those described.[8] **Compound 5.** The ir spectrum was identical with the published spectrum:[19] uv (cyclohexane) 260 nm (ϵ 6025), (silica gel–cyclohexane) 283 nm; nmr (CCl_4) τ 9.15, 8.78 (s, 3 each, $C(CH_3)_2$), 8.70–8.78 (m, 2), 8.27 (d, 3, $J = 1.5$ Hz, $=CCH_3$), 7.51 (m, 2), 3.35 (m, 1, $=CH$); mass spectrum, 70 eV, *m/e* (relative intensity) 150 (21), 108 (46), 93 (100), 91 (30), 79 (24), 39 (25). **Compound 6** showed uv (cyclohexane) 316 nm, (sh, ϵ 187), 307 (253), 298 (228); ir (CCl_4) 3070, 2980, 2890, 1770, 1730, 1640 cm^{-1}; nmr (CCl_4) τ 8.87, 8.85, 8.75 (s, 3 each, CH_3's), 7.92 (d × d, 1, $J = 7.0, 8.0$ Hz, methine), 7.33 (d × d, 1, $J = 8.0, 18.0$ Hz, *endo*-H of methylene), 6.92 (d × d, 1, $J = 7.0, 18.0$ Hz, *exo*-H of methylene), 4.70 and 4.47 (d, 1 each, $J = 5.5$ Hz, $=CH$); mass spectrum 70 eV, *m/e* (relative intensity) 150 (7), 135 (6), 108 (99), 107 (51), 93 (100), 91 (52), 79 (25), 77 (27), 65 (13), 53 (12), 40 (32).

Product Ratios as a Function of Time. A solution of eucarvone (1.041 g) in cyclohexane (250 ml) was divided into five aliquots, to each of which was added 0.7 g of activated no. 950 silica gel. These suspensions were irradiated, either through Pyrex or quartz, in a "merry-go-round" apparatus using a Hanovia 679 A-36 450-W lamp. Tubes were removed periodically and the products were extracted from the silica gel with methylene chloride and analyzed by vpc. Typical results are summarized in Figure 1.

Control Reactions. A suspension of 7–10 g of activated no. 950 silica gel in a solution of 1.5 g of eucarvone in 50 ml of cyclohexane was refluxed for 10 hr. The mixture was treated with 300 ml of methylene chloride. Work-up gave 95% recovery of eucarvone; no other volatile products were detected by vpc.

Compounds **2a**, **2b**, **4**, **5**, and **6** were recovered unchanged after 12 hr at room temperature in cyclohexane or silica gel–cyclohexane. Compound **3** was not tested. Vpc-collected samples of **1**–**6**, when

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[28] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, pp 65–73, 89–100.

[29] The alternative allowed process, $\sigma 2_s + \pi 2_s$, leads to a trans ring juncture and is not observed.

[30] For other examples and leading references, see P. H. Mazzocchi and R. C. Ladenson, *Chem. Commun.*, 469 (1970).

[31] A. A. Bothner-by and E. Moser, *J. Amer. Chem. Soc.*, 90, 2347 (1968).

resubjected to vpc, gave only one peak (*i.e.*, no thermal decomposition or rearrangement occurred).

General Irradiation Procedure in Solution. Irradiations in trifluoroethanol used 0.01–0.08 *M* solutions, a Hanovia 679 A-36 450-W lamp, and Pyrex or quartz as stated in the text, and were followed by vpc or uv methods. Quenching experiments were done similarly and analyzed by vpc after 0.5, 2, and 4 hr (approximately 7, 25, and 50% conversion of **1**).

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Photochemical Reactions of 1,8-Divinylnaphthalene and 1,8-Distyrylnaphthalene[1,2]

Jerrold Meinwald* and James W. Young

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850.

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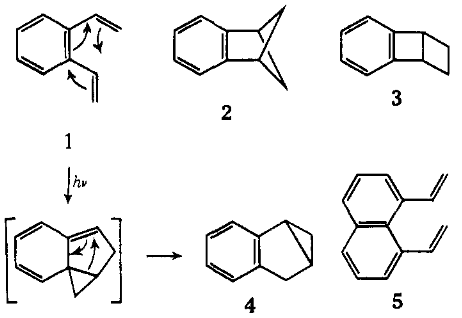
Abstract: Ultraviolet irradiation of 1,8-divinylnaphthalene (**5**) gives *peri*-naphthobicyclo[3.1.1]heptene (**6**) and *peri*-naphthobicyclo[3.2.0]heptene (**7**) in a ratio of *ca.* 10 : 1. The high-melting photoproduct derived from 1,8-distyrylnaphthalene (**11**) is shown to be dimer **14a**, rather than the previously reported head-to-head monomer **12**. In dilute solution, three monomeric photoisomers of **11** can be characterized. The two major products, **23** and **24**, are formed *via* head-to-tail cyclizations; a minor product (**12a**) results from head-to-head cyclization. Overall, the favored products correspond to expectations based on a consideration of the preferred ground-state conformations of the starting materials.

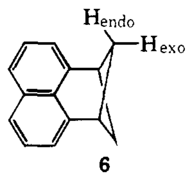
The photochemical [2 + 2] cycloaddition reaction has a long history[3] and its utility in the construction of four-membered rings has been amply demonstrated.[4] Recently, the photochemistry of *o*-divinylbenzene (**1**) was studied, in part with the thought that if it would undergo intramolecular cycloaddition of this type, it might provide entry into the then unknown benzobicyclo[2.1.1]hexene ring system (**2**).[5] The reaction in fact yielded neither **2** nor its head-to-head cycloaddition isomer **3**, but rather benzobicyclo[3.1.0]hexene (**4**). This transformation, which finds precedence in the photochemistry of 1,3,5-hexatriene,[6] requires the participation of two of the benzene π electrons. An analogous pathway is not open to 1,8-divinylnaphthalene (**5**) so that in this case 2π + 2π cycloadditions leading to some novel cyclobutanes might be realized. We wish to report the results of a study of the photochemistry of **5** and of the closely related diene **11**, which was carried out in pursuit of our interest in photochemical isomerizations leading to novel, small-ring compounds.



1 2 3 4 5

Discussion and Results

Photochemistry of 1,8-Divinylnaphthalene. Irradiation of **5** (0.002 *M* in cyclohexane) with a light source whose principal emission is at 254 nm gave a 40–50% yield of two products isomeric with the starting material, along with a comparable amount of polymer. The two monomeric isomers were formed in approximately equal amounts, and could be separated by careful column chromatography on alumina. They are assigned structures **6** and **7** on the basis of spectral and chemical evidence as described below. When the irradiation was carried out at the same concentration but with a medium-pressure mercury vapor lamp (Hanovia) through a Pyrex filter, very little polymer was formed, and products **6** and **7** were obtained in 80–95% yield. Under these conditions, the ratio of **6**:**7** is about 10:1. While the overall yield of monomeric products was found to be slightly dependent upon the solvent under both sets of reaction conditions, the two products were formed in the same relative amounts in each of the three



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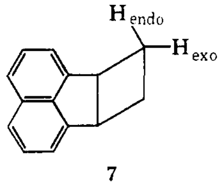

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* Address correspondence to this author.

[1] We acknowledge with thanks the partial support of this work by the National Science Foundation (GP-13085).

[2] These results are given in part in Abstracts, 21st National Organic Chemistry Symposium, Salt Lake City, Utah, 1969, pp 62–70, and were presented in part at the 3rd IUPAC Symposium on Photochemistry, St. Moritz, 1970.

[3] For some important early work and leading references, see G. Ciamician and P. Silber, *Ber.*, **35**, 4128 (1902).

[4] There are several recent reviews. Among them are: (a) A. Schönberg, "Preparative Organic Photochemistry," 2nd ed, Springer-Verlag, Berlin, 1968, Chapters 1 and 8; (b) P. E. Eaton, *Accounts Chem. Res.*, **1**, 50 (1968); (c) W. L. Dilling, *Chem. Rev.*, **66**, 373 (1966); *ibid.*, **69**, 845 (1969); (d) R. N. Warrener and J. B. Bremner, *Rev. Pure Appl. Chem.*, **16**, 117 (1966).

[5] (a) M. Pomerantz, *J. Amer. Chem. Soc.*, **89**, 694 (1967); (b) J. Meinwald and P. H. Mazzocchi, *ibid.*, **89**, 696 (1967).

[6] J. Meinwald and P. H. Mazzocchi, *ibid.*, **88**, 2850 (1966).