Photocycloaddition Reactions of 3-Isopropyl-6-methyl-2-cyclohexenone and 3-*tert*-Butyl-2-cyclohexenone

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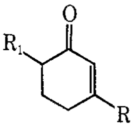
3-Isopropyl-6-methyl-2-cyclohexenone (1) has been observed to undergo cycloaddition reactions with cyclohexene, cycloocta-1,5-diene, ethoxyethylene, 1,1-dimethoxyethylene, dimethyl maleate, and dimethyl acetylenedicarboxylate under the influence of ultraviolet light. The structure and stereochemistry of these adducts have been proven by physical and chemical methods. The orientational specificity observed in the photoadducts of 1 to electron-rich olefins, ethoxyethylene, and 1,1-dimethoxyethylene, and the stereochemistry of its dimethyl maleate adduct are explained on the basis of a 1,4-diradical intermediate which closes to a cyclobutane ring. The 3-*tert*-butyl-2-cyclohexenone (2) is also found to give 1:1 photoadducts with cyclohexene. Stereochemistry of the cyclobutane–cyclohexanone ring junction in the adducts has been found to be predominantly cis.

The photocycloaddition of α,β-unsaturated ketones to carbon–carbon multiple bonds to give cyclobutane derivatives has been of considerable recent interest,[2] and the cycloaddition reactions have been fruitfully used for the preparation of key intermediates in total syntheses of natural products[3] and cage compounds.[4] In addition, the conjugated ketones have been reported to undergo molecular rearrangements,[5] dimerization,[6] solvent addition,[7] and reduction[8] in the presence of ultraviolet light. Recently, Dauben and coworkers reported the effect of alkylsubstituents on the photochemistry of 2-cyclohexenones[9] and reported that whereas the 3-alkylcyclohexen-1-ones underwent dimerization easily the 3-isopropyl-6-methyl-2-cyclohexenone (carvenone, 1) and 3-*tert*-butyl-2-cyclohexenone (2), were stable to light under normal conditions. They concluded that in these cases the excessive steric hinderance either slows the reaction to the point where demotion from the triplet to the ground state is the only efficient process open to the molecule; or, less likely, decreases the efficiency of S_1–T_1 intersystem crossing. As it is generally agreed, on the basis of experiments involving sensitizers and quenchers, and on the study of emission spectra, that the reactive excited states in dimerization and crossed cycloadditions of 2-cyclohexenones are n–π^* triplets,[10] we thought it of interest to see if 3-alkyl-2-cyclohexenones, sterically hindered for dimerization, could be added photochemically to olefins.[11] A qualitative comparison of the steric requirements for photocycloaddition and photodimerization reactions of cyclic α,β-unsaturated ketones could also prove interesting.

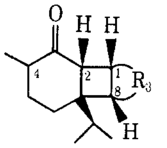
Results

Described below are the photochemical cycloaddition reactions of 3-isopropyl-6-methyl-2-cyclohexenone (carvenone, 1) to cyclohexene, cycloocta-1,5-diene, ethoxyethylene, 1,1-dimethoxyethylene, dimethyl maleate, and dimethyl acetylenedicarboxylate, and of 3-*tert*-butyl-2-cyclohexenone (2), to cyclohexene. Unless stated otherwise, all the photochemical reactions were carried out with a 250-W medium-pressure mercury lamp through a Pyrex filter.

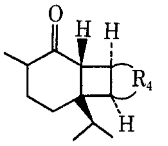
A. Products from Carvenone.—Irradiation of carvenone (1) and cyclohexene in benzene for 20 hr afforded the photoadducts **3a** and **4a** in excellent yield (90%), in relative ratio of 2:1, respectively, and were separated by preparative glpc. Both of these compounds, analyzed for $C_{16}H_{26}O$, had their molecular ion corresponding to the 1:1 adduct in the mass spectra, showed the presence of saturated carbonyl and isopropyl groups in their ir, and demonstrated the absence of vinylic protons in the nmr spectra. Based on these analytical and spectral data, the major and the minor fractions are assigned structures **3a** and **4a**, respectively. Both of these adducts could be chromatographed unchanged on basic alumina and were found to be stable to refluxing sodium methoxide in methanol, showing, therefore, that in both the isomers the cyclobutane–cyclohexanone ring junction is cis and the C-4 methyl group is, probably, equatorial. The nmr spectrum of **3a** showed the C-2 methine proton as a doublet at δ 2.39 (J = 9 Hz), while the same proton in **4a** appeared as a broad singlet at δ 2.6. The large coupling



1, R_1 = Me; R_2 = *i*-Pr
2, R_1 = H; R_2 = *tert*-Bu



3a, $R_1 = -(CH_2)_4-$
b, $R_3 = -(CH_2)_2CH$ ‖ $-(CH_2)_2CH$



4a, $R_4 = -(CH_2)_4-$
b, $R_4 = -(CH_2)_2CH$ ‖ $-(CH_2)_2CH$

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[1] Synvar Research Institute, Palo Alto, Calif. 94304.

[2] (a) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964); (b) P. E. Eaton, *Accounts Chem. Res.*, **1**, 50 (1968); (c) T. S. Cantrell, W. S. Haller, and J. C. Williams, *J. Org. Chem.*, **34**, 509 (1969); (d) P. G. Bauslaugh, *Syn.*, 287 (1970); (e) P. Boyle, J. A. Edwards, and J. H. Fried, *J. Org. Chem.*, **35**, 2560 (1970); (f) A. I. Meyers and P. Singh, *ibid.*, **35**, 3022 (1970); (g) W. C. Agosta and W. W. Lowrance, Jr., *ibid.*, **35**, 3851 (1970).

[3] P. G. Sammes, *Quart. Rev., Chem. Soc.*, 47 (1970), and references cited therein.

[4] (a) P. E. Eaton and T. W. Cole, *J. Amer. Chem. Soc.*, **86**, 962 (1964); (b) R. C. Cookson, E. Crundwell, R. R. Hill, and J. Hudec, *J. Chem. Soc.*, 3043 (1964); (c) R. C. Cookson, R. R. Hill, and J. Hudec, *ibid.*, 3062 (1964).

[5] O. L. Chapman, *Advan. Photochem.*, **1**, 323 (1963).

[6] (a) O. L. Chapman, P. J. Nelson, R. W. King, D. J. Trecker, and A. A. Griswold, *Recl. Chem. Progr.*, **28**, 167 (1967); (b) P. Yates, S. N. Eğe, G. Büchi, and D. Knutsen, *Can. J. Chem.*, **45**, 2927 (1967).

[7] B. J. Ramey and P. D. Gardner, *J. Amer. Chem. Soc.*, **89**, 3949 (1967).

[8] H. Koller, G. P. Rabold, K. Weiss, and T. K. Makherjee, *Proc. Chem. Soc.*, 332 (1964).

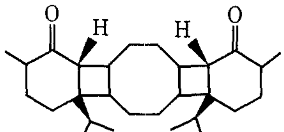
[9] W. G. Dauben, G. W. Shaffer, and N. D. Vietmeyer, *J. Org. Chem.*, **33**, 4060 (1968).

[10] (a) J. L. Ruhlen and P. A. Leermakers, *J. Amer. Chem. Soc.*, **88**, 5671 (1966); (b) P. E. Eaton and W. S. Hurt, *ibid.*, **88**, 5038 (1966); (c) J. L. Ruhlen and P. A. Leermakers, *ibid.*, **89**, 4944 (1967); (d) E. Y. Lam, D. Valentine, and G. S. Hammond, *ibid.*, **89**, 3482 (1967); (e) P. DeMayo, P. J. Pete, and M. F. Tchir, *Can. J. Chem.*, **46**, 2535 (1968); (f) P. DeMayo, A. A. Nicholson, and M. F. Tchir, *ibid.*, **48**, 225 (1970).

[11] A part of this work was published as a preliminary communication: P. Singh, *Tetrahedron Lett.*, 4089 (1970).

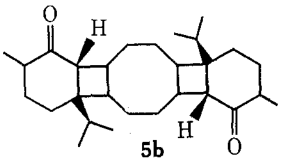
constant obtained for the cyclobutane protons in **3a** requires that they have the syn relationship as shown, and the value is in agreement with those reported in the literature.[12-14] The compound **4a** with a small coupling constant has, therefore, the C-1 and C-2 bridgehead protons anti to each other. Although the stereochemistry at C-8 in both these isomers could not be determined conclusively from the available data, it is very probably cis.

The photocycloaddition of carvenone (**1**) to cycloocta-1,5-diene was relatively slower and gave a 1:1 photoadduct in *ca.* 60% yield after 30 hr of irradiation. This material showed a single spot, in various solvent systems, on a silica tlc plate and gave a sharp-melting 2,4-dinitrophenylhydrazone, mp 165-165.5°. Even though the derivative had a sharp melting point and the adduct showed a single tlc spot, nevertheless, the product was found to be a mixture of two isomers by glpc. The mixture could not be separated by repeated column chromatography on alumina, silica, and Florisil, and by preparative glpc. The mixture was found stable to sodium methoxide in methanol and the two isomers, therefore, represent the photoadducts **3b** and **4b**. In principle, the photoaddition of carvenone to cycloocta-1,5-diene could give a 2:1 photoadduct. Indeed, a minor product, **5**, was obtained by careful chromatography of the crude reaction mixture on basic alumina. From analytical data and molecular weight determination this compound is formulated as $C_{28}H_{44}O_2$. It showed saturated carbonyl and isopropyl absorption bands in the ir spectrum and demonstrated the absence of vinylic protons in its nmr spectrum. The compound **5** could be obtained by further irradiation of the mixture of **3b** and **4b** with carvenone. The minor adduct is thus assigned structure **5** with either the head-to-head (**a**) or the head-to-tail (**b**) orientation of carvenone moieties. The cis fusion of the six- and the four-membered rings is in agreement with the stability of this adduct to basic alumina.



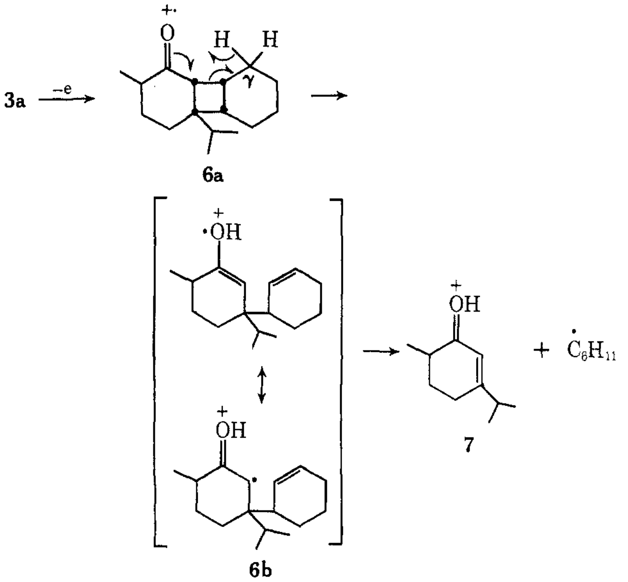
5a

or

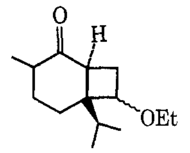


5b

The 70-eV mass spectrum of the tricyclic ketone **3a** showed a weak molecular ion peak at *m/e* 234 (1%) and low intensity peaks corresponding to the ions resulting from cleavage of the cyclobutane ring at *m/e* 152 (10%) and 82 (8%). In contrast, a strong peak at *m/e* 153, as the base peak, was observed. In general the cyclobutane derivatives are known to give a strong fragment resulting from cleavage of the cyclobutane ring.[15] We attribute the observed fragmentation pattern to the molecule preferentially undergoing McLafferty rearrangement, by transfer of one of the γ hydrogens, to give **6b** over cleavage of the cyclobutane ring. The molecular ion **6b** could readily cleave to give **7**, *m/e* 153. This argument is supported by the observation that the ketone **4a** as well as the mixture of the tricyclic ketones **3b** and **4b** also showed its base peak at *m/e* 153,[16,17] while the bicyclic ketones **9**, **14**, and **15** (see below), devoid of suitably positioned γ protons, exhibited normal cyclobutane cleavage to give an abundant fragment at *m/e* 152.



The photoaddition of 3-isopropyl-8-methyl-2-cyclohexenone (**1**) to ethoxyethylene afforded 1:1 photoadducts in nearly quantitative yield after 6 hr of exposure to a 450-W Hanovia lamp. Analysis of the crude reaction mixture by glpc showed the presence of three compounds in relative ratio of 2:7:1. The two isomers, obtained in the relative ratio of 2:7, are regarded as having trans and cis stereochemistry, respectively, at the ring junction as the former, **8**, could be isomerized to the latter, **9**, by exposure to basic alumina.[2a] The nmr spectrum of the major product showed its bridgehead C-1 methine proton as a pair of doublets (J_1 = 9 and J_2 = 1.5 Hz), which is in accord with the ethoxy group at C-7 rather than at C-8 position. The position of the ethoxy group was secured by chemical means; for example, treatment of the isomerized photoproduct with sodium methoxide in methanol neither led to replacement of the ethoxy by methoxy group (nmr and glpc analysis) nor accomplished elimination of the ethoxy group to form an unsaturated ketone.[2a] The minor adduct **10** had its spectral data similar to that of the compound **9** and is believed to be the isomer of **9** differing in stereochemistry of the ethoxy group at C-7.



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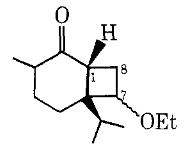

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The photochemical reaction of carvenone with 1,1-dimethoxyethylene was also investigated. Under the

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[12] I. Fleming and D. H. Williams, *Tetrahedron*, 2747 (1967).

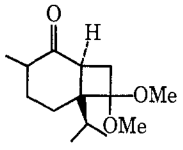
[13] J. W. Hanifin and E. Cohen, *J. Amer. Chem. Soc.*, **91**, 4494 (1969).

[14] L. Paolillo, H. Ziffer, and O. Buchardt, *J. Org. Chem.*, **35**, 38 (1970).

[15] (a) G. Sugowdz, P. J. Collin, and W. H. F. Sasse, *Tetrahedron Lett.*, 3843 (1969); (b) M. L. Gross and C. L. Wilkins, *ibid.*, 3875 (1969); (c) N. Sugiyama, Y. Sato, and C. Kashima, *Bull. Chem. Soc. Jap.*, **43**, 3205 (1970).

[16] The γ hydrogens in the cis-anti-cis ketone **4a** are not so close to the carbonyl group as in its cis-syn-cis isomer **3a**. However, a slight distortion of the molecule **4a**, conceivably undergoing rapidly at such a high energy as 70 eV, could suitably place these protons for an efficient intramolecular hydrogen transfer. The 15-eV mass spectrum of **4a** indeed showed a strong peak resulting from cleavage of the cyclobutane ring at *m/e* 152 (45%).

[17] P. Singh, *Tetrahedron Lett.*, 1071 (1971).



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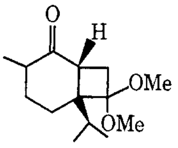

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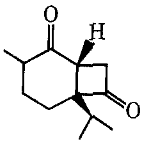

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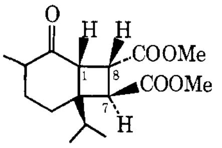
standard conditions the reaction proceeded readily and afforded two products **11** and **12** in 20 and 80% yield, respectively (overall yield 80%). The former could be isomerized to the latter by basic alumina and must be the trans isomer of **12**. That the methoxyls are at C-7 rather than C-8 was shown by stability of the adduct **12** to sodium ethoxide in ethanol and its acid hydrolysis to the γ diketone **13** (ir spectrum and negative ferric chloride test).

Photocycloaddition of **1** to dimethyl maleate, the electron-poor olefin, was rather sluggish and gave a complex mixture from which the bicycloadduct **14** could be isolated in poor yield (12%). The adduct was stable to basic alumina, supporting cis fusion of the rings. The nmr spectrum (60 MHz), in carbon tetrachloride, showed the bridgehead methine proton as a broad doublet (J = 10 Hz). The large coupling constant is in agreement with the cis relationship of C-1 and C-8 cyclobutyl protons; the broadening of the signal is, presumably, due to long-range coupling with the C-7 proton.[12] The 100-MHz spectrum of the diester **14**, in deuteriochloroform, was very revealing and showed the bridgehead C-1 methine proton as a sharp doublet at δ 2.8 (J = 10 Hz), while the C-7 proton appeared as a doublet at δ 3.52 (J = 3.5 Hz) showing trans relationship of the C-7 and C-8 protons. The trans relationship of the ester groups was further secured by the stability of **14** to sodium methoxide in methanol and to boiling pyridine.



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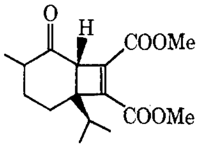

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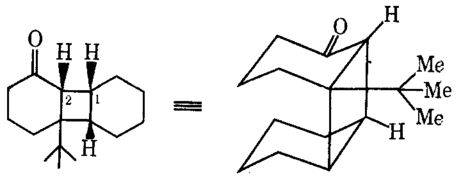
Carvenone (**1**) was also found to add to acetylenes; thus, irradiation with dimethyl acetylenedicarboxylate afforded 1:1 adduct **15** and the structure is in agreement with its spectral data (see Experimental Section). No other product arising from photorearrangement of the unsaturated diester **15** could be detected.[18] The cycloadduct **15** was stable to basic alumina and pyridine; on this basis the cis fusion shown is assigned.

B. Products from 3-*tert*-Butyl-2-cyclohexenone.— In order to study the effect of a sterically bulkier and electron-donating group at the β carbon of 2-cyclohexenones on photocycloaddition reactions, 3-*tert*-butyl-2-cyclohexenone (**2**) was irradiated with excess cyclohexene. Usual work-up after 30 hr gave a mixture of photoadducts **16** and **17** in moderate yield (37%), in relative ratio of 5:1, respectively. The mixture was stable to basic alumina and boiling pyridine, demonstrating the cis fusion of cyclobutane–cyclohexanone rings in both these isomers. The isomers **16** and **17** were separated by preparative glpc. These compounds, analyzed for $C_{16}H_{26}O$, showed the presence of a saturated carbonyl group in their ir, and demonstrated the absence of vinylic protons in the nmr spectra. Based on the analytical and spectral data, the major and the minor isomers are assigned structures **16** and **17**. Examination of molecular models indicated a severe nonbonded interaction of the *tert*-butyl group with the cyclohexyl protons in the cis–anti–cis adduct **17**, while the same interaction in the cis–syn–cis adduct **16** was relatively less pronounced. Based on this, the major and the minor isomers are assigned structures **16** and **17**, respectively. This is further substantiated by the 100-MHz nmr spectrum of these stereoisomers.



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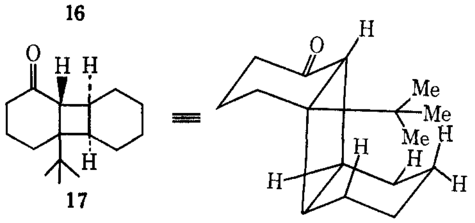

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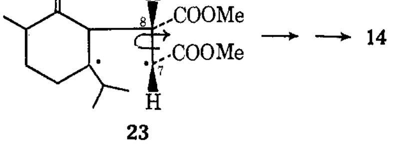
Thus, the major isomer **16** showed its C-2 bridgehead methine proton as a doublet with a large coupling constant (J = 9 Hz) as compared to the doublet (J = 2.5 Hz) of the same proton in its stereoisomer **17**.

Discussion of Results

Although a complete product analysis was not undertaken, the present results are consistant with those of the previous workers who have studied the photochemical addition of alkenes to α,β-unsaturated ketones. Thus, the orientational specificity observed in formation of the adducts **8**–**12** is in agreement with Corey's proposal that the complex **18** collapses to give the more stable 1,4 diradical **19**, which recombines to give the products observed.[2a] The diradical **19** should be fairly shortlived, collapsing to cyclobutane products as soon as it is formed, as a relatively long-lived radical **19** could give the unsaturated compound **22** by either of two routes: (a) by intramolecular hydrogen transfer followed by recombination of the diradical thus formed, and (b) by loss of the hydrogen atom to give the radical **21** which could give **22**. Neither the unsaturated compound nor a dimer of **21** could be detected. In fact, carvenone added to ethoxyethylene to give the cyclobutane adducts **8**–**10** in nearly quantitative yield. See Scheme I.

The trans configuration of the methyl ester groups in **14** is also compatible with the diradical mechanism. Rotation about the C-7,C-8 bond in the corresponding diradical **23**, before recombination, would result in the



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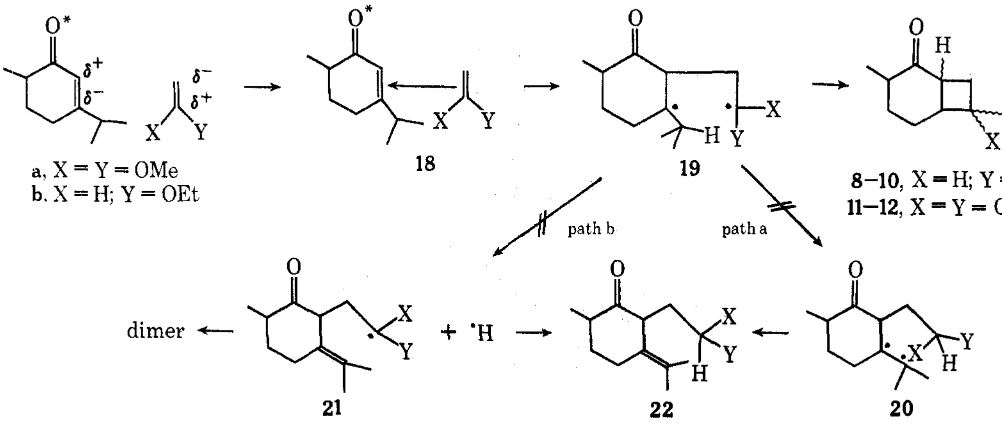
[18] (a) J. Ipaktschi, *Tetrahedron Lett.*, 3179 (1970); (b) W. Kothe, *ibid.*, 5201 (1969); (c) G. Büchi and E. M. Burgess, *J. Amer. Chem. Soc.*, **82**, 4333 (1960).

Scheme I



formation of thermodynamically more stable product **14**. The poor yield obtained in the photoaddition of dimethyl maleate (and dimethyl acetylenedicarboxylate) to carvenone (**1**), substantiates Corey's observation that substitution of olefins with electron-withdrawing groups is deterious to photocycloaddition reactions.

It might be of interest to note the predominance of cis fusion at the cyclobutane–cyclohexanone ring junction in the photoadducts. Only in the case of electron-rich olefins, ethoxyethylene and 1,1-dimethoxyethylene, did the carvenone give a small amount of the trans-fused adducts. The trans-fused ring junction is normally formed when a 2-cyclohexenone is irradiated with olefins.[2a–d] The reason for this deviation from the normal behavior is still obscure, but our observation has ample precedence in the literature; for example, 3-phenyl-2-cyclohexenone and chromones gave only the cis-fused cyclobutane products when irradiated with various olefins.[2c,13]

In conclusion, it is quite clear that 2-cyclohexenones having sterically bulkier substituents react quite efficiently with olefins under the influence of ultraviolet light. This knowledge extends considerably the synthetic utility of such photocyclizations. These results also indicate that compared to photodimerization the photocycloaddition of 2-cyclohexenone is less sensitive to steric effects.

Experimental Section

Melting points and boiling points are uncorrected. Ir spectra were recorded on a Unicam SP 200 spectrometer. Unless stated otherwise, nmr spectra were recorded on a Varian A-60 spectrometer; the values are given in δ parts per million downfield from tetramethylsilane as internal standard. Mass spectra were recorded on an MS-12 instrument and glpc was run on a Perkin-Elmer F-11 chromatograph using silicone gum rubber (SE-304) as an analytical column. Preparative gas chromatographic separations were accomplished using a 5 ft × $^3/_8$ in. 15% silicone rubber SE-30 on Chromosorb. The general procedure used for irradiation is outlined below.

The apparatus consisted of a cylindrical Pyrex irradiation vessel fitted with a quartz immersion well, a reflux condenser, and a nitrogen inlet. The reactants, with or without a solvent, were thoroughly flushed with nitrogen. The solutions were irradiated, through a Pyrex filter, with a 250-W Hanovia lamp, and a slow stream of nitrogen was kept bubbling through the reaction mixture during the course of irradiation. The progress of the reaction was monitored by drawing aliquots and examining by tlc on silica plates.

3-Isopropyl-6-methyl-2-cyclohexenone (Carvenone, 1).—This terpenoid ketone was obtained as a mobile liquid by a modified procedure of Whiting and coworkers.[19]

A mixture of camphor (304 g, 2 mol) and concentrated sulfuric acid (1.6 kg) was stirred at 110° for 1 hr. The reaction mixture was cooled, diluted carefully with cold water (2 l.), and steam distilled. The steam distillate was extracted with ether. The extracts were washed with a saturated aqueous solution of sodium bicarbonate and with water. The organic layer was dried ($MgSO_4$) and concentrated to give a yellow oil (136 g). Phenol (96 g) was added and fractionation through a 2-ft long vacuum jacketed column gave a mixture of camphor with excess phenol, bp 80–90° (10 mm), followed by carvenone, bp 98–102° (10 mm). The carvenone fraction, containing traces of phenol, was dissolved in ether and washed with 5% aqueous, cold sodium hydroxide and with water. The ethereal layer was dried ($MgSO_4$) and concentrated and distillation on a spinning-band column gave pure carvenone (**1**, 85 g): bp 80–82° (3 mm) [lit.[9] bp 80–81° (3.5 mm)]; ir (neat) 1670, 1630, 1210, and 885 cm^{-1}; nmr (CCl_4) δ 1.26 (d, J = 6 Hz, ring methyl), 1.27 (d, J = 7 Hz, isopropyl methyls) (total 9 H), 1.8–2.5 (m, 6 H, methylene and methine protons), and 5.86 (br, s, 1 H, vinyl proton).

3-*tert*-Butyl-2-cyclohexenone (2).—From 1-*tert*-butylcyclohexene (14.1 g, 0.102 mol), using the procedure of Rao and Dev,[20] there was obtained the title compound **2** (2.7 g, 18%) as a mobile liquid: bp 70–72° (3 mm) [lit.[9] bp 80–81° (4 mm)]; nmr (CCl_4) δ 1.25 (s, 9 H), 1.8–2.5 (m, 6 H), 5.74 (br, s, 1 H).

Photoaddition of Carvenone (1) to Cyclohexene. Formation of 3a and 4a.—A solution of carvenone (4.0 g, 0.026 mol) and cyclohexene (20.5 g, 0.25 mol) in benzene (60 ml) was irradiated for 20 hr. Removal of the solvent and the excess olefin under reduced pressure afforded a mobile liquid, which showed two glpc peaks. The liquid was chromatographed on neutral alumina and elution with *n*-hexane gave **3a** + **4a** as a colorless liquid (5 g, 91%). Although tlc showed only one spot in various solvent systems, glpc showed the presence of two compounds, with the same retention times as for the crude reaction mixture, in relative ratio of 2:1. These compounds were separated by preparative glpc.

The major fraction **3a**, with shorter retention time, was a colorless crystalline solid: mp 52–54° (short-path distillation at 0.5 mm in an oil bath at 80°); ir (CCl_4) 1698, 1383, and 1372 cm^{-1}; nmr ($CDCl_3$) δ 0.77 (d, J = 7 Hz), 0.83 (d, J = 7 Hz), 1.02 (d, J = 6.5 Hz) (total 9 H), 1.13–2.13 (m, 15 H), 2.3–2.8 (m, COCHMe), and 2.39 (d, J = 9 Hz, bridgehead C-2 methine proton) (total 2H); mass spectrum (70 eV) m/e (rel intensity) 234 (1, M^+), 191 (3), 153 (100), 152 (10), 110 (25), 67 (22), 43 (15), and 41 (31).

Anal. Calcd for $C_{16}H_{26}O$: C, 82.05; H, 11.11. Found: C, 81.82; H, 10.91.

The 2,4-dinitrophenylhydrazone was obtained as a deep yellow solid: mp 156–157° (crystallized from methanol); uv max (95% EtOH) 365 nm (ε 25,000), 269 (13,500), and 234 (8000).

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[19] C. A. R. Baxter, G. C. Forward, and D. A. Whitting, *J. Chem. Soc. C*, 1162 (1968).

[20] G. S. K. Rao and S. Dev, *J. Indian Chem. Soc.*, **33**, 539 (1956).

Anal. Calcd for $C_{22}H_{30}N_4O_4$: C, 63.75; H, 7.30; N, 13.52. Found: C, 63.68; H, 7.52; N, 13.59.

The minor fraction **4a**, with longer retention time, was obtained as a thick liquid: ir ($CHCl_3$) 1690, 1385, and 1379 cm^{-1}; nmr ($CDCl_3$) δ 0.73 (d, J = 6.5 Hz), 0.77 (d, J = 7 Hz), 1.02 (d, J = 6.5 Hz) (total 9 H), 1.1–2.4 (m, 15 H), 2.6 (br, s, bridgehead C-2 methine proton), and 2.5–2.8 (m) (total 2 H); mass spectrum (70 eV) m/e (rel intensity) 234 (1.5, M^+), 191 (2.5), 153 (100), 152 (7.5), 110 (35), 67 (20), 43 (27), and 41 (20).

Anal. Calcd for $C_{16}H_{26}O$: C, 82.05; H, 11.11. Found: C, 81.76; H, 11.31.

The 2,4-dinitrophenylhydrazone, obtained as deep yellow crystals, had mp 171–172°; uv max (95% EtOH) 366 nm (ϵ 20,000), 265 (9500), and 234 (14,500).

To determine the stereochemistry of the cyclohexanone–cyclobutane ring junction rigorously, the mixture of **3a** and **4a** (107 mg) was refluxed with sodium methoxide (30 mg) in methanol (10 ml), under nitrogen, for 24 hr. The solution was cooled, neutralized with dilute hydrochloric acid, and diluted with water (40 ml). The organic layer was extracted with chloroform and removal of the solvent from the dried ($MgSO_4$) extract gave a colorless liquid. Analysis by glpc showed only **3a** and **4a** and their relative ratio was unchanged.

Photoaddition of 1 to Cycloocta-1,5-diene. Formation of 3b, 4b, and 5.—A solution of carvenone (4.0 g, 0.026 mol) and cycloocta-1,5-diene (9.0 g, 0.082 mol) in benzene (80 ml) was irradiated for 30 hr. Removal of the solvent and the excess diene gave a thick oil, which was chromatographed on an alumina (neutral) column. Earlier eluents with *n*-hexane–diethyl ether (95:5) gave a mixture of **3b** and **4b** as a colorless, mobile liquid (4.2 g, 60%) and later eluents with *n*-hexane–diethyl ether (50:50) gave the adduct **5** as a thick oil (300 mg). The mixture of **3b** and **4b** had ir (neat) 1695 (C=O), 1656 (C=C), 1471, 1397, 1381, and 735 cm^{-1}; nmr ($CDCl_3$) δ 0.7–1.2 (m, 9 H, Me groups of both the isomers), 1.3–2.4 (m, 17 H), and 5.6 (br, t, 2 H, J = 5 Hz, vinylic protons); mass spectrum (70 eV) m/e (rel intensity) 260 (10, M^+), 217 (7), 183 (10), 182 (29), 154 (26), 153 (100), 152 (27), 110 (27), 96 (33), 95 (33), 79 (30), 67 (40), 55 (27), 44 (68), 43 (35), 41 (66), and 39 (37).

The 2,4-dinitrophenylhydrazone, obtained as yellow crystals from hexane–benzene, had mp 165–165.5°.

Anal. Calcd for $C_{24}H_{32}N_4O_4$: C, 65.43; H, 7.32; N, 12.72. Found: C, 65.49; H, 7.52; N, 12.67.

Even though the 2,4-dinitrophenylhydrazone had a sharp melting point and the oil obtained above showed a single tlc spot, nevertheless, the product was found to be a mixture of two compounds, **3b** and **4b**, by glpc. The mixture could not be separated into its components by repeated column chromatography on alumina, silica, or forisil, and by preparative glpc. The mixture underwent no change on refluxing for 24 hr with sodium in methanol.

The crude adduct **5** obtained above, rechromatographed on an alumina column, could be crystallized with difficulty from *n*-hexane. Two more crystallizations from the same solvent afforded pure **5**: mp 61–63°; ir ($CHCl_3$) 1690, 1380, and 1370 cm^{-1}. The nmr spectrum showed the absence of a vinylic proton in the compound.

Anal. Calcd for $C_{28}H_{44}O_2$: C, 81.50; H, 10.72; mol wt, 412. Found: C, 81.78; H, 10.46; mol wt, 408.[21]

The deep orange crystalline bis-2,4-dinitrophenylhydrazone had mp 234–236° and showed the absence of a carbonyl band in its ir spectrum.

Anal. Calcd for $C_{40}H_{52}N_8O_8$: C, 62.16; H, 6.78; N, 14.50. Found: C, 62.43; H, 6.93; N, 14.72.

The compound **5** could also be obtained in *ca.* 25% yield when the mixture of tricyclic ketones **3b** and **4b** was further irradiated with carvenone (**1**) for 15 hr.

Photoaddition of Carvenone (1) to Ethoxyethylene. Formation of the Adducts 8, 9, and 10.—Carvenone (**1**, 525 mg) and ethoxyethylene (2 g) in benzene (5 ml) were irradiated in a Pyrex tube with a 450-W Hanovia lamp. After 6 hr the irradiation was stopped; removal of the solvent and the excess olefin gave the 1:1 photoadduct as a light yellow mobile liquid (775 mg, 97%). Analysis by glpc showed three compounds, **8–10** (retention times 12, 14, and 18 min at 108°), in relative ratio of 2:7:1, respectively. The light yellow liquid was chromatographed on basic alumina and analysis by glpc showed the adducts **9** and **10** in a relative ratio of 9:1. The photolysis mixture was separated by preparative glpc. The major component **9** was obtained as a colorless mobile liquid: ir (neat) 1700, 1385, 1375, and 1130 cm^{-1}; nmr (CCl_4) showed the bridgehead C-1 methine proton as a pair of doublets at δ 2.87 (J_1 = 9 and J_2 = 1.5 Hz, 1 H); mass spectrum (70 eV) m/e (rel intensity) 224 (2, M^+), 181 (20), 153 (2.7), 152 (23), 136 (85), 110 (55), 81 (60), 72 (91), 69 (25), 43 (100), and 41 (6).

Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.75; H, 10.95.

The adduct **8** was also obtained as a liquid. This compound showed the following spectral data: ir (neat) 1703, 1385, 1370, and 1145 cm^{-1}; nmr (CCl_4) showed the C-1 proton at δ 2.95 (doublet of a doublet, J_1 = 8.5 and J_2 = 1.0 Hz, 1 H).

Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 75.13; H, 10.85.

The compound **8** was quantitatively isomerized to **9** when passed through an alumina column.

The minor fraction **10**, obtained as an oil, showed bands in its ir spectrum (CCl_4) at 1700, 1380, 1367, and 1170 cm^{-1} and exhibited its C-1 proton as a pair of doublets at δ 2.89 (J_1 = 8.5 and J_2 = 1.5 Hz).

Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.32; H, 10.53.

In order to determine position of the ethoxy group in the adducts, 100 mg of the isomerized photoproducts **9** + **10** was stirred, at room temperature and under nitrogen, with sodium (70 mg) in methanol (5 ml) for 4 hr. Solid carbon dioxide (excess) was added to decompose sodium methoxide, and the product was extracted with a hexane–ether (1:1) mixture. The extract was dried and removal of the solvents gave an oil (80 mg). This was examined by ir, nmr and glpc and was found to be the completely unchanged starting material.

Photoaddition of Carvenone (1) to 1,1-Dimethoxyethylene. Formation of 11 and 12.—A solution of carvenone (500 mg) and 1,1-dimethoxyethylene (5 ml) in benzene (5 ml) was irradiated in a Pyrex tube for 10 hr. Removal of the solvent and the excess of olefin gave a light yellow liquid. Analysis by glpc showed two compounds, **11** and **12**, in relative ratio of 1:4, respectively. The liquid was chromatographed on basic alumina and elution with benzene gave **12** as a colorless oil (600 mg, 75%), which showed a single glpc peak. The oil was further purified by distillation, under reduced pressure, in a short-path distillation apparatus: ir (neat) 1685 cm^{-1}; nmr ($CDCl_3$) showed the bridgehead C-1 methine proton as a pair of doublets at δ 2.92 (J_1 = 8.5 and J_2 = 1 Hz, 1 H) and the methoxyl protons as a broad singlet at δ 4.1 (6 H).

Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.07. Found: C, 69.68; H, 10.22.

Hydrolysis of the Bicyclic Ketone 12 to Diketone 13.—A 100-mg portion of the ketone **12** in 1.5 ml of methanol was stirred, under nitrogen with 4 drops of concentrated hydrochloric acid in water (5 ml). After 2 days the reaction mixture was neutralized and extracted with chloroform to give **13** as a light yellow oil (70 mg, 88%). The infrared spectrum showed very strong absorption bands at 1780 (cyclobutanone) and 1710 cm^{-1} (cyclohexanone). The oil in methanol gave a negative ferric chloride test.

Photoaddition of Dimethyl Maleate to Carvenone. Formation of Diester 14.—A solution of carvenone (4 g, 0.027 mol) and dimethyl maleate (4 g, 0.027 mol) in diethyl ether (90 ml) was irradiated; the irradiation was stopped from time to time and ether was added to maintain the volume of the solution. After 30 hr the irradiation was stopped. Removal of the solvent under reduced pressure gave a colorless liquid, which showed on a tlc plate only one new spot, R_f 0.5 (hexane–ethyl acetate, 2:1), although glpc showed it to be a complex mixture. Repeated column chromatography on silica gave **14** as a thick liquid (800 mg, 10%): ir (neat) 1725 (ester C=O), 1705 (cyclohexyl C=O), 1387 and 1365 (isopropyl); nmr (CCl_4, 60 MHz) δ 0.7–1.4 (m, 11 H), 1.6–2.3 (m, 4 H), 2.8 (br, d, J = 10 Hz, 1 H, bridgehead cyclobutyl methine proton), 3.0–3.4 (m, 2 H), and 3.7 (s, 6 H); the 100-MHz nmr spectrum ($CDCl_3$) showed the bridgehead C-1 methine proton as a sharp doublet at δ 2.88 (J = 10 Hz), C-7 cyclobutyl proton as a sharp doublet at δ 3.52 (J = 3.5 Hz), C-8 methine proton as a multiplet at δ 3.2–3.5, and the methyl esters as a pair of singlets at δ 3.64 and 3.68; mass spectrum (70 eV) m/e (rel intensity) 296 (10, M^+, $C_{16}H_{24}O_5$ requires M^+, 296), 265 (20), 264 (32), 253 (5.6), 204 (40), 153 (16), 152 (94), 151 (24), 110 (100), 109 (26), 57 (17), 43 (28), and 41 (50).

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[21] Determined with a Macrolab vapor pressure osmometer.

For analysis, the diester **14** was purified by preparative glpc.

Anal. Calcd for $C_{16}H_{24}O_5$: C, 64.87; H, 8.11. Found: C, 64.71; H, 8.34.

When the adduct **14** was heated under reflux with pyridine for 8 hr, only the starting material could be recovered (ir, nmr, and glpc analysis), showing the trans relationship of the ester groups and the cis fusion of the rings. The diester **14** was also recovered unchanged when allowed to stand in methanol containing sodium.

Photoaddition of Dimethyl Acetylenedicarboxylate to Carvenone. Formation of Diester 15.—The mixture of carvenone (3 g, 0.02 mol) and dimethyl acetylenedicarboxylate (5 g, 0.032 mol) was irradiated in a Pyrex tube for 30 hr. Analysis by tlc on silica (hexane–ethyl acetate, 2:1) as also by glpc showed the formation of only one product. The mixture was chromatographed on basic alumina and elution with benzene afforded the adduct **15** as a pale yellow liquid (750 mg, 12%): ir (neat) 1720 (ester C=O) and 1650 cm^{-1} (C=C); nmr ($CDCl_3$, 100 MHz) δ 0.94 (d, $J = 6$ Hz), 0.96 (d, $J = 6$ Hz), 1.1 (d, $J = 7$ Hz) (total 9 H), 1.46–2.6 (m, 6 H), 3.26 (s, 1 H, bridgehead methine proton), 3.74 (s) and 3.80 (s) (total 6 H); mass spectrum (70 eV) m/e (rel abundance) 294 (14, M$^+$, $C_{16}H_{22}O_5$ requires M$^+$, 294), 263 (17), 262 (23), 234 (30), 204 (67), 202 (25), 193 (20), 192 (46), 191 (33), 189 (24), 177 (25), 175 (26), 164 (33), 153 (11), 152 (40), 110 (50), 59 (55), 43 (43), and 41 (100). The analytical sample was obtained by further purification of **15** by preparative glpc.

Anal. Calcd for $C_{16}H_{22}O_5$: C, 65.31; H, 7.48. Found: C, 65.60; H, 7.63.

The unsaturated diester **15** was recovered unchanged when stirred with pyridine for 6 hr.

Photoaddition of 3-*tert*-Butyl-2-cyclohexenone (2) to Cyclohexene. Formation of 16 and 17.—A solution of 3-*tert*-butyl-2-cyclohexenone (2 g) and cyclohexene (5 ml) in benzene (5 ml) was irradiated in a Pyrex tube for 30 hr. Removal of the solvent and excess olefin under reduced pressure afforded a liquid, which showed two new glpc peaks. The liquid was chromatographed on neutral alumina and elution with *n*-hexane–benzene (1:1) gave **16** + **17** as a pale yellow liquid (1.15 g, 37%), with the same glpc retention times as in the crude photolysis mixture. The relative ratio of **16** and **17**, as found by glpc, was 5:1, respectively. The analytical sample was obtained as a thick, colorless liquid by distillation of the pale yellow liquid (short-path distillation at 0.05 mm in an oil bath at 80°).

Anal. Calcd for $C_{16}H_{26}O$ (mixture): C, 82.05; H, 11.11. Found: C, 82.22; H, 11.42.

The mixture was separated by preparative glpc. The major component **16** was a crystalline solid: mp 59–61°; ir (CCl_4) 1700, 1385, and 1360 cm^{-1}; nmr ($CDCl_3$, 100 MHz) δ 0.77 (s, 9 H), 1.2–2.2 (m, 16 H), and 2.42 (d, $J = 9$ Hz, 1 H, bridgehead C-2 methine proton).

The minor fraction **17** was obtained as a thick liquid: ir (CCl_4) 1695, 1388, and 1365 cm^{-1}; nmr ($CDCl_3$, 100 MHz) δ 0.75 (s, 9 H), 1.1–2.2 (m, 16 H), and 2.53 (d, $J = 2.5$ Hz, 1 H, bridgehead C-2 methine proton). The photoadducts were recovered unchanged when refluxed for 8 hr with pyridine.

Registry No.—**1,** 499-74-1; **2,** 17299-35-3; **3a,** 30462-49-8; **3a** 2,4-DNPH, 30462-50-1; **3b,** 31444-44-7; **3b** 2,4-DNPH, 31444-45-8; **4a,** 30462-51-2; **4a** 2,4-DNPH, 30462-52-3; **4b,** 31444-48-1; **4b** 2,4-DNPH, 31444-49-2; **5a,** 31444-50-5; **5a** bis-2,4-DNPH, 31489-90-4; **5b,** 31444-51-6; **5b** bis-2,4-DNPH, 31442-94-1; **8,** 31442-95-2; **9,** 31442-96-3; **10,** 31442-97-4; **12,** 31442-98-5; **13,** 31442-99-6; **14,** 31443-00-2; **15,** 31443-01-3; **16,** 31443-02-4; **17,** 31443-03-5.

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Concerning the Reaction of 1,3,5-Cyclooctatrien-7-yne at Various Temperatures

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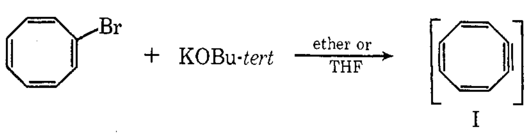
1,3,5-Cyclooctatrien-7-yne (dehydrocyclooctatetraene) has been reported to be best prepared in ether at room temperature to afford the highest yield of adduct with a trapping agent. We now report on how the yields of product from the reaction of this species with a trapping agent vary depending upon (a) when the trapping agent is added and (b) the temperature employed. Our results indicate that, contrary to previous indicated reports, dehydrocyclooctatetraene is best prepared and allowed to react at temperatures other than room temperature.

The recently[1,2] prepared 1,3,5-cyclooctatrien-7-yne (dehydrocyclooctatetraene, I) has been reported[2] to be best prepared in ether at room temperature to afford the highest yield of adduct with a trapping agent. We now report on how the yields of product, from the reaction of this species with a trapping agent, vary depending upon (a) when the trapping agent is added and (b) the temperature employed. Our results indicate that, contrary to previous indicated reports, I is best prepared and allowed to react at temperatures other than room temperature.

The method used[1,2] to prepare I is treatment of bromocyclooctatetraene with potassium *tert*-butoxide at room temperature in ether or tetrahydrofuran (THF). In the absence of any trapping agent, I has been observed[1,2] to react with the base to yield *tert*-butoxycyclooctatetraene or to dimerize to cycloocta[*b*]naphthalene. The intermediate I may, however, be trapped with a variety of trapping agents (*e.g.*, 1,3-diphenylisobenzofuran,[1,2] phenyl azide,[1,2] 1-diethylaminobutadiene,[1,2] and furan[3]), but tetraphenylcyclopentadienone (tetracyclone) was chosen for this study because of its availability and because of the high



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