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PHOTOCHEMICAL REACTION OF 2-CYCLOPENTENONE WITH ETHERS

THE MECHANISM OF SOLVENT ADDITION

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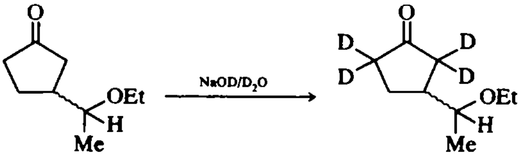
Abstract—Photochemical addition of several ethers to 2-cyclopentenone has been studied under various conditions, especially in the presence of a few aromatic ketones. The mechanism of the ether addition is suggested to be via direct abstraction of hydrogen by excited 2-cyclopentenone rather than due to a chemical process involving aromatic ketyl radicals.

Photochemical reactions of simple α,β-unsaturated cyclic ketones result in their dimerization or in the formation of cyclobutane derivatives with various olefins.[1] These cycloadditions have extensively been studied from mechanistic points of view.[2] Especially the cycloaddition of 2-cyclopentenone in various solvents has been investigated,[3–6] but the addition of solvents to cyclopentenone has received less attention. Irradiation of cyclopentenone in isopropyl alcohol in the presence of benzophenone was previously found to give an adduct 3,[7] whilst direct irradiation was reported to result mainly in dimerization and partly in formation of 3.[5,8] In dimerization of cyclopentenone in cyclohexane, a similar adduct 4 was assumed to be a by-product.[4] In contrast to the cycloaddition, the mechanism of solvent addition has scarcely been described. The photochemical reaction of 2-cyclopentenone with several ether solvents has been studied under a variety of conditions.

RESULTS

Irradiation of a solution of cyclopentenone in ethyl ether gave mainly three products. Two of them were stereoisomeric dimers of cyclopentenone (1 and 2) by comparison with authentic samples. The other product isolated after preparative VPC was a diastereomeric mixture of 3-(1-ethoxyethyl)-cyclopentanone (5) on the basis of spectroscopic data. Whether the ethoxyethyl group had added to α- or to β-position of the enone was determined by means of the NMR spectra. On treating with deutrated alkali in methanol-d_4, four deuterium incorporation was observed. This result shows that the ketone possesses four exchangeable α-hydrogens.



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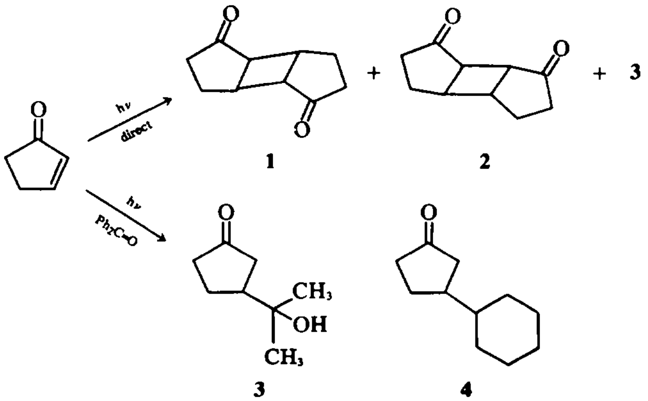
Similar results were obtained with isopropyl ether and tetrahydrofuran. The tendency to form an ether adduct was found to decrease in the order ethyl ether, tetrahydrofuran and isopropyl ether.

The photochemical reactions in ethyl ether were carried out with various concentrations of the enone and the ratio of dimers to ether adduct ((1 + 2)/5) is illustrated in Fig 1. This shows that the solvent addition gets more predominant with decreasing enone concentration, although the ratio of dimers to ether adduct does not change linearly. At this time the ratio of head-to-head to head-to-tail dimer



1
2
3
4

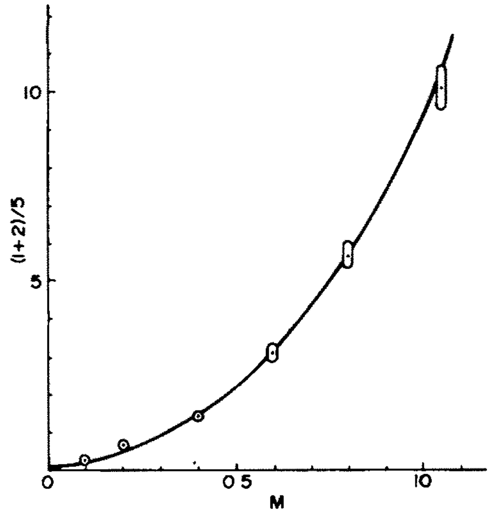


Fig 1. Effect on the ratio of dimers to ethyl ether adduct.

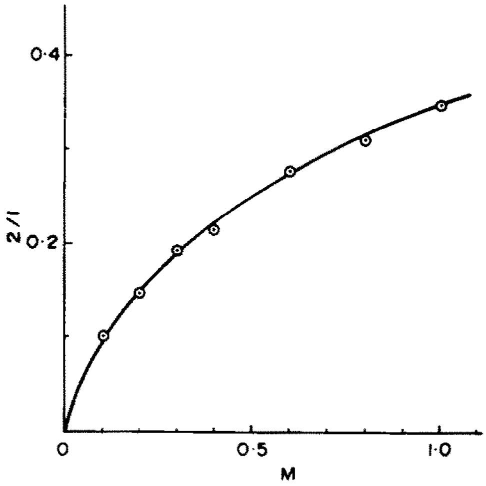
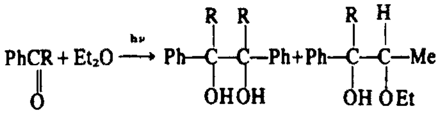


Fig 2. Effect on the formation ratio of head-to head to head-to-tail dimer.

(2/1) was also dependent on enone concentration as seen in Fig 2, which is consistent with the previous observation in less polar solvents such as benzene[3] and cyclohexane.[4]

Attempts to sensitize the ethyl ether addition were carried out with benzophenone and other sensitizers. Sunlight irradiation to a solution of benzophenone in ethyl ether has been reported to afford benzopinacol, one-to-one adduct of benzophenone and ethyl ether and polymeric substance.[9] As a result of reexamination of this reaction under UV irradiation we obtained benzopinacol in 38 per cent yield, and 1,1-diphenyl-1-hydroxy-2-ethoxypropane 7, the product previously assumed,[9] in 53 per cent yield. Acetophenone was also found to undergo the corresponding reaction, in accord with recent observation by Challand.[10] However, 2-acetonaphthone was quantitatively recovered even after longer irradiation in ethyl ether. Irradiation to a soln of cyclopentenone and benzophenone in ethyl ether through naphthalene-benzene filter ($\lambda > 340$ nm) was found to give only one product 5 ascertained by VPC and spectroscopic data, and to cause no consumption of benzophenone. Furthermore, any attempts to detect 6 or 7 were in vain. These results suggest that benzophenone did not abstract a H atom from the ether. A similar attempt with acetophenone resulted in both dimerization of the enone and solvent addition. Neither 8 nor 9 could be detected by means of VPC. In contrast, the attempt to sensitize the solvent addition with 2-acetonaphthone did not induce any reaction. These results are summarized in Table 1 accompanied by reported triplet energies (E_T) of sensitizers.



$$\mathrm{Ph}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{R} + \mathrm{Et_2O} \xrightarrow{h\nu} \mathrm{Ph}-\overset{\mathrm{R}}{\underset{\mathrm{OH}}{\mathrm{C}}}-\overset{\mathrm{R}}{\underset{\mathrm{OH}}{\mathrm{C}}}-\mathrm{Ph} + \mathrm{Ph}-\overset{\mathrm{R}}{\underset{\mathrm{OH}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{OEt}}{\mathrm{C}}}-\mathrm{Me}$$

6: R=Ph 7: R=Ph
8: R=Me 9: R=Me

DISCUSSION

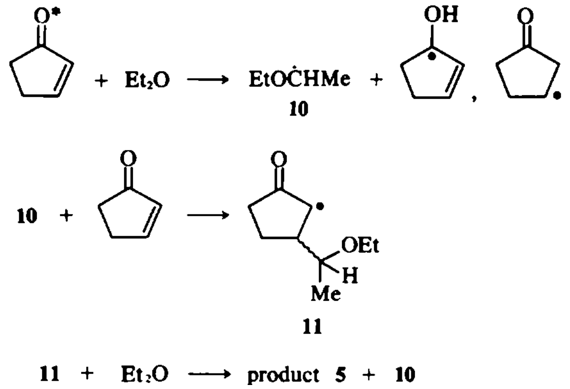
Photoaddition of cyclic ethers to 1-octene[11] and photoaddition of tetrahydrofuran to 7,7,8,8-tetracyanoquinodimethane or tetracyanoethylene[12] have been reported, the mechanism of which has been assumed to be a radical chain type. In regard to the formation of 3, de Mayo pointed out possible incursion of the radical chain process.[5] In order to test the radical chain mechanism for the present system, irradiation was carried out in the presence of cumene which is able to transfer its H atom to radical 10 and 11 to give a more stable cumyl radical,

Table 1. Sensitization of 2-cyclopentenone in ethyl ether

Sensitizer (E_T kcal/mole)[a]	Photoreduction (in ethyl ether)	Sensitizer[b] absorption (%)	Product
Acetophenone (73·6)	Yes	69	3, 4 and 5
Benzophenone (68·5)	Yes	95	only 5
2-Acetonaphthone (59·3)	No	100	none

[a] The 0–0 band of the phosphorescence measured in hydrocarbon glass at 77°K, W. G. Herkstroeter, A. A. Lamola and G. S. Hammond, *J. Am. Chem. Soc.* 86, 4537 (1964)

[b] Cyclopentenone 0·40 M, sensitizer 0·20 M, under naphthalene-benzene filter.



SCHEME 1

assuming that **10** and **11** could diffuse out of solvent cage (Scheme 1).

The results of direct and benzophenone-sensitised irradiation are illustrated in Fig 3, where ϕ_q and ϕ denote the yield of **5** with or without cumene, respectively. Since curves in both cases do not cut the zero line in reciprocal of concentration of cumene far away from one, it may be concluded that the contribution of the radical chain mechanism is not important for the present system.

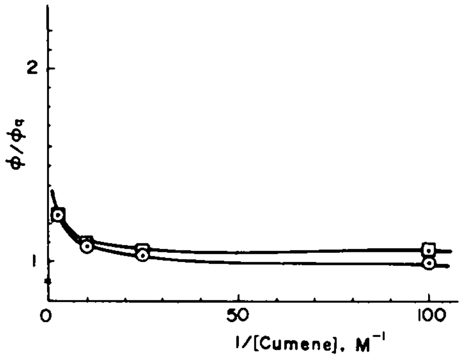
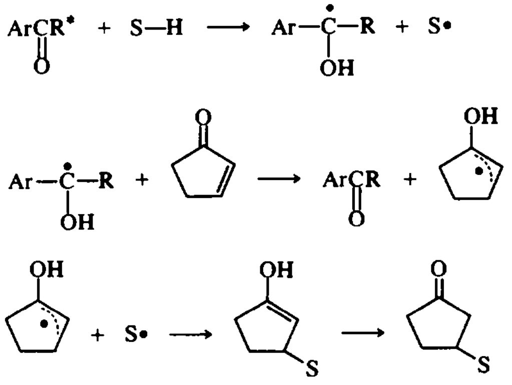


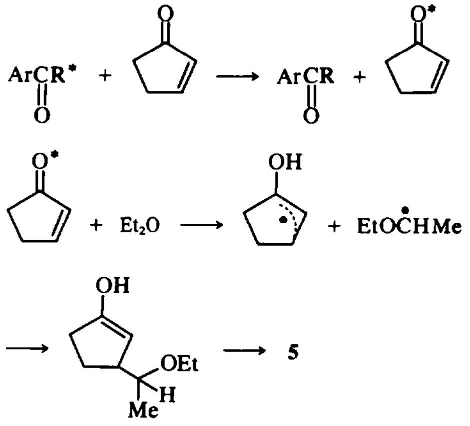
Fig 3. Direct and sensitised irradiation of cyclopentenone in the presence of cumene. ⊙ Direct irradiation; ⊡ Sensitization by benzophenone.

It is believed that the cycloaddition of cyclopentenone takes place through its triplet state, E_T of which is estimated to be about 73 kcal/mole.[2] De Mayo has concluded that the cycloaddition proceeds through a higher triplet ($E_T \simeq 73$ kcal/mole) and that the lowest triplet lies near 61 or 66 kcal/mole in energy.[5] The evidence depended on (a) the fact that benzophenone ($E_T \simeq$ 69 kcal/mole) did not sensitize the dimerization or the cycloaddition with olefins, whilst cyclopentenone *did* effectively quench the photoreduction of benzophenone in isopropyl alcohol,[5] and (b) the indication by photostationary state technique of piperylene that the triplet energy of cyclopentenone is 61 ± 1 kcal/mole.[4] Recently, Wagner has cast doubt on the existence of an energy level lower than 70 kcal/mole based on kinetic analysis of dimerizations of 2-cyclopentenone and 2-cyclohexenone, and other aspects.[6] He took the effective sensitization for the formation of **3** or **4** to be due to intervention of benzophenone ketyl radical as shown in Scheme 2. Such a hydrogen transfer process has recently been proposed in the photoreduction of camphorquinone[13] or in the photoreduction of dibenzoylethylene.[14] Our results in Table 1 seem to show good agreement with Wagner's suggestion, because only sensitizers which undergo photoreduction sensitize the solvent addition. However, our observation that irradiation of 2-cyclopentenone with benzophenone gave no detectable amount of **6** or **7** is indicative of involvement of an energy transfer process (Scheme 3) rather than a chemical process intervening kethyl radical such as Scheme 2.



SCHEME 2

Recently cyclopentenone has been reported to quench phosphorescence of benzophenone in carbon tetrachloride, though the process is less effective in the rate.[15] The excited triplet cyclopentenone responsible for hydrogen abstraction must be different from the triplet ($E_T \simeq 73$ kcal/mole) for dimerization or cycloaddition with olefins, otherwise in Fig 1 the ratio of dimers to ether adduct would vary linearly. Recently Agosta *et al.* have found that intramolecular hydrogen abstraction by β-carbon atom in more refined cyclopentenones is inclined



SCHEME 3

to be due to a $\pi\pi^*$ triplet state ($E_T \simeq 73$ kcal/mole).[16] However, the present hydrogen abstraction of 2-cyclopentenone may be ascribed to a $n\pi^*$ triplet rather than to a $\pi\pi^*$ triplet which lie close each other. In this regard additional research programs are now under way.

EXPERIMENTAL

Materials. 2-Cyclopentenone[17] which was contaminated with 1 ~ 2 per cent of a hydroxylic substance was warmed with α-naphthyl isocyanate for several hours, distilled under reduced pressure and stored over Na_2SO_4 in a refrigerator. Commercially available ethers were refluxed over Na and distilled before use. Benzophenone (guaranted grade) and 2-acetonaphthone (guaranted grade) were used with further treatment. Acetophenone was distilled before use. Cumene was washed with conc H_2SO_4, refluxed over Na and followed by distillation.

Instrumentation. VPC analyses were carried out with a Yanaco Model 550 T fitted with a 2·5 m silicon DC-550 column and a 2·0 m silicon SE-30 column under helium flow. A Varian T-60 NMR spectrometer was used to obtain NMR spectra in $CDCl_3$ or MeOH-d_4. IR spectra were obtained on a Hitachi grating IR spectrophotometer.

Irradiation procedures. Irradiations were carried out in two fashions; (A) Internal irradiations were carried out in an irradiation vessel (Pyrex glass) equipped with a 100 W high-pressure mercury lamp under N_2 bubbling and water cooling, (B) external irradiations were done in 20 ml test tubes (equally qualified Pyrex glass) on a merry-go-round apparatus using a 200 W high-pressure mercury lamp coated by a Pyrex filter and a soln filter system (0·5 cm cell-path).

Direct irradiation. Preliminarily irradiation of solns in ethyl ether, isopropyl ether and tetrahydrofuran (each 0·5 M) was carried out on apparatus B without any soln filter. Resulting mixtures were concentrated and analysed by VPC at 190°. In each case major products were dimers of cyclopentenone (**1** and **2**) which were identified on the basis of superposition in VPC retention-time and in IR spectrum on those of the compounds from relevant synthesis.[3] Each ether adduct was isolated from preparative VPC. Apparent tendency to form the adduct was deduced from their peak areas relative to those of dimers.

Adduct of ethyl ether to cyclopentenone (**5**). Large-scale irradiations were carried out on apparatus A, and **5** was isolated by fractionation (b.p. 125–126°/44 mm). VPC of the isolated product indicated that this product contained a trace of the dimers **1** and **2**. After further purification by preparative VPC gave **5**: *m/e* 156 (M^+); IR (neat) 1740 cm^{-1} ($\nu_{C=O}$), 1160, 1100; NMR ($CDCl_3$) τ 6·2–6·8 (m, 3H), 7·3–8·5 (m, 7H), 8·9 (d, J = 6·0 Hz, 3H), 8·9 (t, J = 6·0 Hz, 3H). The semicarbazone, crystallized from EtOH, had m.p. 209–210° (dec). (Found: C, 56·08; H, 9·00; N, 19·76; O, 15·25. Calc. for $C_{10}H_{19}O_2N_3$: C, 56·31; H, 8·98; N, 19·70; O, 15·00%). The NMR spectrum was also measured in MeOH-d_4. The relative intensity of the band at τ 7·3–8·5 was decreased to 3H on treatment with NaOD in D_2O.

Adduct of isopropyl ether to cyclopentenone. The product from the preliminary irradiation was purified from preparative VPC at 180°; *m/e* 184 (M^+); IR (neat) 1740 cm^{-1} ($\nu_{C=O}$), 1160, 1100, 1000; NMR ($CDCl_3$) τ 6·22 (heptet, J = 6·0 Hz, 1H), 7·5–8·3 (m, 7H), 8·9 (s, 6H), 8·9 (d, J = 6·0 Hz, 6H). The semicarbazone, crystallized from EtOH, had m.p. 188–189° (dec). (Found: C, 59·53; H, 9·47; N, 17·48. Calcd. for $C_{12}H_{23}O_2N_3$: C, 59·72; H, 9·61; N, 17·41%).

Adduct of tetrahydrofuran to cyclopentenone. The product from the preliminary irradiation was purified from preparative VPC at 180°: *m/e* 154; IR (neat) 1740 cm^{-1} ($\nu_{C=O}$), 1160, 1055; NMR ($CDCl_3$) a 6·0–6·3 (m, 3H), 7·0–8·5 (m, 11H). The ketone did not form the semicarbazone and purification for analysis was repeated on preperative VPC. (Found: C, 69·89; H, 9·07. Calcd. for $C_9H_{14}O_2$: C, 70·10; H, 9·15%).

Irradiation of cyclopentenone in ethyl ether. Irradiation of various concentrations of cyclopentenone in ethyl ether (0·05–1·0 M) was carried out with apparatus B. The reaction was monitored by VPC at 170° or 210° using cyclooctane as internal standard from time to time. The ratio of dimers to ether adduct ((**1** + **2**)/**5**) and the ratio of head-to-head to head-to-tail dimer (**2**/**1**) was estimated from the relative peak areas at low conversion of starting cyclopentenone, and are illustrated in Figs 1 and 2, respectively.

Photoreduction of benzophenone with ethyl ether. A 0·5 M soln of benzophenone (9·11 g) in ethyl ether was irradiated in apparatus A for 12 hr. The solvent was removed and 50 ml EtOH was added to the residue. The insoluble solid isolated after filtering was ascertained to be **6** by comparison of the IR spectrum with that of the authentic sample.[18] The mother liquor was concentrated, distilled under reduced pressure. The distillate (b.p. 130–135°/5 mm) was analysed with VPC at 200°. The distillate consisted of a small amount of unreacted benzophenone and **7b** which was purified with preparative VPC. Preparative yield was determined from three runs; **6** 38% and **7** 53%. **7**: *m/e* 256 (M^+); IR (neat) 3500 cm^{-1}, 1600, 1495, 1100; NMR ($CDCl_3$) τ 2·3–2·9 (m, 10H), 5·60 (q, J = 6·0 Hz, 1H), 6·50 (q, J = 7·0 Hz, 2H), 7·20 (broads, 1H), 8·90 (t, J = 7·0 Hz, 3H) 8·95 (d, J = 6·0 Hz, 3H). On treatment with D_2O, the band at τ 7·20 disappeared.

Photoreduction of acetophenone with ethyl ether. A 0·5 M soln of acetophenone (6·0 g) in ethyl ether was irradiated on apparatus A for *ca* 20 hr. After evaporating the solvent, the residue was distilled to collect the first distillate (b.p. 120–125°/4 mm 4·2 g) which was indicated to be **9** from VPC analysis at 170°. The **9** purified from preparative VPC was a mixture of *threo*- and *eryhro*-type isomers (nearly 1 : 1), as was shown by NMR analysis and in accord with the lit.[10] The distillation residue was shown to contain mainly **8** (probably a mixture of *meso*- and *dl*-isomers) based on comparison with the authentic sample in respect to IR characteristic band.[19]

Irradiation of 2-acetonaphthone in ethyl ether. A 0·2 M soln of 2-acetonaphthone (3·4 g) was irradiated on apparatus A for 3 days. From time to time, the mixture was analysed by VPC at 180°, but no consumption of the ketone was observed. After evaporating the solvent, 2-acetonaphthone was recovered without loss.

Sensitised irradiation. An irradiation of solns of cyclopentenone (0·40 M) and sensitizer (0·20 M) in ethyl ether was carried out on apparatus B using a soln of naphthalene (0·02 M) in benzene as filter for 3 days. From time to time, aliquoits were taken for analysis. Sensitiser absorptions in Table 1 were calculated on the basis of molar absorption coefficient at 363 nm.

Irradiation in the presence of benzophenone. To an aliquoit of the mixture, cyclooctane was added as external standard and the resulting mixture was carefully analysed by VPC at 180°. Under low conversion of cyclopentenone each remaining amount of benzophenone was essentially equal to the amount before irradiation. **5** was the only product and any appreciable peak due to **1**, **2** and **7** could not be observed. The aliquoit was concentrated and developed on TLC (Silica–Gel) with methylene chloride and n-pentane (1:9), but **6** could not be detected.

Irradiation in the presence of acetophenone. A mixture treated as above was analysed by VPC at 180°. Three products were identified as **5**, **1** and **2** in the course of VPC retention time. At low consumption of cyclopentenone acetophenone was not consumed and no indication of **8** nor **9** was obtained, but at longer irradiation considerable amounts of acetophenone were consumed.

Irradiation in the presence of 2-acetonaphthone. VPC analysis showed that amounts of cyclopentenone and 2-acetonaphthone were constant during the irradiation.

Direct and sensitized reaction of cyclopentenone in the presence of cumene. An ethyl ether soln of cyclopentenone (0·40 M) and an ethyl ether soln of cyclopentenone (0·40 M) and benzophenone (0·20 M) to which were added various amounts of cumene were irradiated on apparatus B using the soln filter of naphthalene in benzene for 2 days. The resulting mixtures after adding cyclooctane as external standard were analysed by VPC at 180° and the results are illustrated in Fig 3.

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