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Photochemical Solvent Addition to 2(5*H*)-Furanone. Hydrocarbon Solvents

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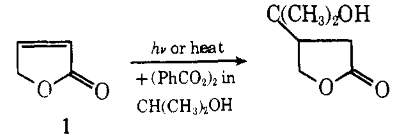
The α,β-unsaturated lactone 2(5*H*)-furanone was shown to add hydrocarbon solvent across its carbon–carbon double bond in three different ways characterized by different β/α addition product ratios. Direct irradiation with ultraviolet light or benzene sensitization afforded a $\beta/\alpha = 1$ while "chemical sensitization" using acetophenone or benzophenone gave a $\beta/\alpha \gg 1$. A benzoyl peroxide initiated reaction gave $\beta/\alpha = 2$.

Photochemical solvent additions to cyclic α,β-unsaturated carbonyl compounds have been reported by many workers.[1-8] In general, alcoholic and ether solvents have been found to add to the β position almost exclusively. In the case of 2-cyclopentenone evidence has been presented both in favor of[1] and against[2] a radical chain process. Ketone sensitizers have been discussed as energy[1-4] and hydrogen transfer[5a,9] agents.

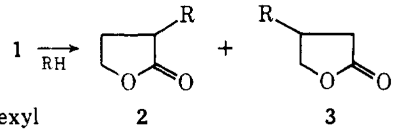
The α,β-unsaturated lactone, 2(5*H*)-furanone (**1**), has been shown to add isopropyl alcohol in a similar (β) fashion under both photochemical and free radical chain (benzoyl peroxide initiated) conditions[5b] (see eq 1). Only in the cases of 2-cyclopentenone[1,2] and **1**[5b] has evidence been gathered concerning the mechanism of the solvent addition. We wish to report our results with this lactone in which we have evidence of at least three different patterns of solvent addition.



1 (1)

Results

The lactone **1** was allowed to react with cyclohexane or toluene solvent under the following conditions: (a) direct irradiation of dilute (7 mM) deoxygenated solutions at room temperature; (b) irradiation of dilute deoxygenated solutions containing benzoyl peroxide at room temperature; (c) irradiation of dilute deoxygenated solutions containing various sensitizers at room temperature; and (d) heating of dilute deoxygenated solutions containing benzoyl peroxide at the boiling point of the solution. The products derived from **1** in cyclohexane were 3- and 4-cyclohexyldihydro-2(3*H*)-furanone (**2** and **3**, respectively) in 90 ± 10% combined yield. In toluene the products were 3- and 4-benzyldihydro-2(3*H*)-furanone (**4** and **5**) (see eq 2). The structures of these photoproducts were confirmed by comparison with samples independently prepared by previously reported methods.[10] In each case the isomeric photoproducts were separated by gas chromatography (VPC) and the relative amounts of the isomers determined. The results are summarized in Table I. The product ratio in each case provides a "fingerprint" of the mechanism(s) involved in that reaction.



(2)

R = cyclohexyl **2** **3**
R = benzyl **4** **5**

A careful examination of the ultraviolet absorption spectra of **1**, acetophenone plus **1**, and acetophenone alone in cyclohexane showed no new bands and the presence of **1** did not modify or quench phosphorescence emission from acetophenone. No phosphorescence emission from **1** could be detected. The disappearance of **1** was not quenched by 0.10 M 1,3-cyclohexadiene in a direct irradiation but **2** and **3** were not among the products formed in this reaction.

A series of Pyrex-filtered irradiations of **1** in cyclohexane containing various concentrations of acetophenone and an experiment using a moderate concentration of benzophenone were done. The results are shown in Table II.

Discussion

The ratios of the solvent adducts (β/α) for the various addition reactions fall into three categories. We believe that these categories indicate at least three different pathways for the formation of these photoproducts.

The exclusive formation of the β adduct **3** in the acetophenone and the predominant formation of **3** in the benzophenone sensitized reactions is similar to the sensitized addition of solvent to 2-cyclopentenone reported by several workers.[1,2,6] A mechanism similar to that proposed by Wagner[5a] would involve hydrogen abstraction by the n,π* triplet

Scheme I

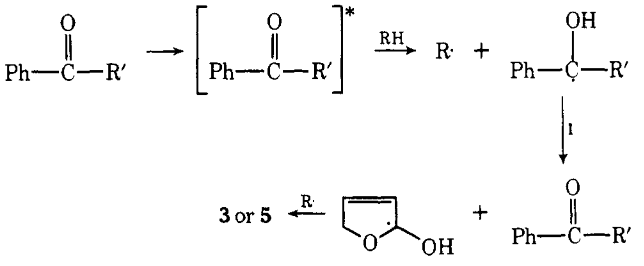


Table I. Results of the Reaction of 1[a] with Hydrocarbon Solvents

Conditions	Solvent	Sensitizer or initiator (concn)[b]	Filter[c]	Product ratio[d]
Photochemical	Cyclohexane	None	Vycor	1.2
Photochemical	Toluene	None	Corex	0.92
Photochemical	Cyclohexane	Benzene (0.30)	Vycor	0.85
Photochemical	Cyclohexane	Acetone (0.45)	Pyrex	2.0
Photochemical	Cyclohexane	Benzoyl peroxide (0.0030)	Corex	2.2
Thermal	Cyclohexane	Benzoyl peroxide (0.0030)		2.1
Thermal	Toluene	Benzoyl peroxide (0.0030)		2.0
Photochemical	Cyclohexane	Acetophenone (0.20)	Pyrex	>21

[a] 7.0 mM. [b] Molar. [c] See ref 15. [d] 3/2 or 5/4, ±10%.

Table II. Photochemical Reactions of 1 in Cyclohexane with Various Aryl Ketone Concentrations[a]

Sensitizer concn, mM	3/2[b]	Conversion, %
0[c]	1.2	40
0.36	4.0	18
0.60	4.5	22
4.0[d]	7.3	18
7.0	8.1	30
200	>21	42

[a] Standard conditions: 1 7.0 mM, Pyrex filter, 4-h irradiation. [b] ±10%. [c] Vycor filter. [d] Benzophenone as sensitizer; all others were with acetophenone.

state of the sensitizer, transfer of that hydrogen atom to either the carbonyl oxygen or (improbably) the α carbon of 1, and then collapse of this radical with a radical derived from the solvent (Scheme I). This process may represent one pathway for formation of solvent adduct. The radical apparently produced by hydrogen transfer to 1 must react slowly (if at all) with solvent. No dihydro-2(3*H*)-furanone (the product expected from such a reaction with solvent[4,7,9,11]) was detected in any of these reactions.

Several pieces of information are useful in excluding alternative explanations for the role of acetophenone in this reaction. The a priori possibility exists, for example, that acetophenone is simply transferring energy to 1. The triplet excited state of 1[12] involved in photocycloaddition reactions lies 75–80 kcal/mol above the ground state. Thus, direct energy transfer from acetophenone (E_t = 73.6 kcal/mol[13]) to 1 leading to reactions of excited 1 would be endothermic and very inefficient. Lack of simple energy transfer from acetophenone to 1 is confirmed by the fact that 1 does not quench the phosphorescence of acetophenone. The successful sensitization experiment using benzophenone (E_t = 68.5 kcal/mol[13]) certainly indicates a process other than energy transfer.

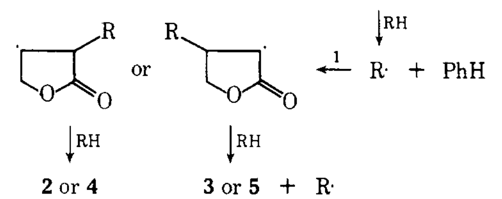
Another possibility to be considered is that the role of the acetophenone (or benzophenone) is simply to abstract a hydrogen atom[14] from cyclohexane to produce the cyclohexyl radical. The attack of the solvent-derived radicals on 1 cannot, however, account for the almost exclusive formation of the β adduct in the acetophenone or benzophenone sensitized reactions because generation of such radicals via a benzoyl peroxide initiated reaction gives a different product ratio (Table I).

The product ratio dependence on acetophenone concentration was at first interpreted as evidence for an intermediate trappable by ground-state acetophenone. However, close inspection of the ultraviolet absorption curves of acetophenone and 1 and the cutoff spectrum of the Pyrex filter used[15] showed that at low (<10 mM) acetophenone concentrations some direct light absorption by the lactone must occur. This may account for the concentration dependence. The predominance of β solvent addition (as compared with the direct irradiation results) at very low acetophenone concentrations may be due to acetophenone quenching of excited lactone. In any event, the trapping of intermediates by ground state acetophenone was shown to be either reversible or a minor process by the high yields in the acetophenone sensitized reactions (90% at 40% conversion).

The formation of equal amounts of both α and β solvent adducts in the direct irradiation of 1 in hydrocarbon solvents requires a different reaction pathway for solvent addition from that proposed in Scheme I. Certainly the lack of preference for the mode of addition (α or β) of hydrocarbon solvents to excited 1 is inconsistent with an n,π* excited state which should clearly favor hydrogen abstraction by oxygen[14] and, hence, β addition. Supporting this analysis is the β/α ratio of 7 for the photoaddition of cyclohexane to 2-cyclopentenone,[4] a compound which reacts from a predominantly n,π* excited state. A pathway for photochemical solvent addition which is decidedly different from that shown in Scheme I must exist. Although definitive information about this second pathway is not available, a reasonable suggestion is that excited 1 (presumable a π,π* state) adds solvent to its carbon–carbon double bond in a manner not greatly dependent upon substituents attached to the carbons, perhaps in a concerted fashion.[16] Benzene and acetone are both sufficiently high in excited state energy to sensitize the photochemical reactions of 1 by simple energy transfer.

A third pathway for solvent addition to 1 is dictated by differing product ratios and by different reaction conditions. The benzoyl peroxide initiated addition of cyclohexane to 1 cannot, to any major extent, be following the pathway outlined in Scheme I since the β/α ratio observed (2.1) is very different from the ratio observed (>20) in reactions following that pathway. Obviously, the peroxide decomposition cannot be following a pathway which involves an excited state of 1 (the second pathway outlined above). The logical process for the peroxide initiated reaction is the well-known free-radical addition to a double bond,[17] the third mechanism for solvent addition to 1 (Scheme II).

Scheme II



The quenching results are ambiguous. Control experiments show that 1 is stable in the presence of 1,3-cyclohexadiene in the dark. The fact that the disappearance of **1** is not quenched may indicate that the cyclohexane addition in the direct irradiation proceeds via an excited singlet state. However, the absence of **2** or **3** from the product mixture (many products were formed) may only indicate that the singlet or triplet excited state of **1** reacts with quencher in a process unrelated to the reaction occurring in the absence of the quencher.

Experimental Section

General. Proton magnetic resonance spectra were recorded on a Varian Associates T-60 instrument in deuteriochloroform with tetramethylsilane as an internal standard. Infrared spectra were determined on either a Beckman IR8 or an IR20 as thin films between salt plates. Gas chromatographic analyses were done using an Aerograph A90-P instrument with a 5 ft × 0.25 in. copper column containing 10% OV-1 on 80–100 mesh Gas-Chrom Q. Ultraviolet spectra were determined on a Cary 15 spectrometer and phosphorescence spectra on an Aminco-Bowman spectrophosphorimeter in a 2-methyltetrahydrofuran glass at liquid nitrogen temperature. The spectra of acetophenone were very similar to those reported.[13] Cyclohexane was purified by stirring it over 30% fuming sulfuric acid, washing it with dilute sodium carbonate solution, and distilling it onto sodium wire. Toluene was distilled onto sodium wire after the initial fraction was discarded.

Preparation of Photoproducts. The 3-cyclohexyldihydro-2(3*H*)-furanone (**2**) was prepared by the method of Reppe.[10a] This material (a clear oil) had these spectra: IR 2920, 2850, 1760 (C=O), 1445, 1158, 1020 cm^{-1}; NMR δ 1.0–2.66 (m, 14 H), 4.0–4.4 (m, 2 H, -OCH$_2$-). The 4-cyclohexyldihydro-2(3*H*)-furanone (**3**) was prepared by the method of Elderfield.[10b] The spectra follow: IR 2920, 2840, 1765 (C=O), 1438, 1158, and 1000 cm^{-1}; NMR δ 0.67–2.91 [m, 14 H, with a sharp singlet superimposed at 2.33, -CH$_2$C(=O)-], 3.72–4.53 (symmetrical m, 2 H, -CH$_2$O-). The 3-benzyldihydro-2(3*H*)-furanone (**4**) was prepared by the method of Reppe.[10a] It had these spectra: IR 2910, 1750 (C=O), 1680, 1470, 1360, 1190, 1120 cm^{-1}; NMR δ 1.33–3.33 (m, 5 H), 4.07–4.33 (m, 2 H, -CH$_2$O-), 7.17 (s, 5 H, aromatic). The 4-benzyldihydro-2(3*H*)-furanone (**5**) was prepared by the method of Zimmer.[10c] The spectra follow: IR 2920, 1770 (C=O), 1590, 1470, 1160, 1010 cm^{-1}; NMR δ 1.80–3.20 [m, 5 H, with a slightly broadened singlet superimposed at 2.7, -CH$_2$C(=O)-], 3.85–4.55 (symmetrical m, 2 H, -CH$_2$O-), 7.33 (br s, 5 H, aromatic).

Photochemical and Thermal Reactions. Irradiations were conducted with a 100-W Hanovia mercury vapor lamp in a quartz immersion well equipped with the appropriate filter and inserted into an irradiation flask that held a working volume of 350 ml. Solutions were deoxygenated by stirring them while bubbling nitrogen through them for 1 h before and then during the irradiation. Irradiations routinely were done for 4 h. Thermal reactions were conducted by heating and stirring 120 ml of deoxygenated solutions at reflux for 1 h. Product analyses were done in the following manner: solvent was removed from each reaction solution at aspirator pressure and room temperature to ensure that the starting lactone would remain in the mixture. NMR spectra of these mixtures at this stage indicated the presence of only **1**, the appropriate products (**2** and **3** or **4** and **5**), and, if added, sensitizer and sensitizer photoproducts. In the case of the cyclohexadiene reaction the only assignable NMR absorptions were due to **1**. In each case residual **1** and acetophenone or benzophenone, if present, were then removed at high vacuum and the resulting oil separated by VPC. Collected samples were compared to authentic materials. Relative amounts were determined from VPC peak areas. In the case of the attempted quenching, no identifiable materials could be collected from the more than 16 product peaks. The retention times of **2** and **3** were 13.0 and 16.0 min, respectively, at 200 °C with a flow rate of 60 ml/min. At 250 °C with a flow rate of 50 ml/min **4** and **5** eluted with retention times of 6.6 and 8.4 min, respectively.

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Registry No.—**1**, 497-23-4; **2**, 40541-50-2; **3**, 54996-29-1; **4**, 61129-28-0; **5**, 22530-98-9; cyclohexane, 110-82-7; toluene, 108-88-3.

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