Photochemical Behavior of 1,4-Diphenyl-4-penten-1-ol. A Hydrocarbon Analog of the Type II Photoelimination of Ketones

Sir:

Among the most common photochemical reactions of the carbonyl group are those initiated by hydrogen abstraction by the oxygen of the excited carbonyl. These include the photoreduction[1] of ketones in solvents with abstractable hydrogens and the type II reaction[1,2] of ketones possessing γ-hydrogens. Although hydrogen abstraction reactions of excited acyclic alkenes are less common, a recent report[3] of the photoreduction of 1,1-diphenylethylene in isopropyl alcohol demonstrates that such processes do occur. Intramolecular hydrogen abstractions by carbon have also been observed in the photochemistry of α,β-unsaturated enones.[4] We wish to report our studies of the photochemical behavior of 1,4-diphenyl-4-penten-1-ol, (1), which provide the first example of a type II reaction of an alkene.

Alcohol 1[5] was prepared by a Wittig reaction of 1,4-diphenyl-4-hydroxy-1-butanone[6] with excess methylenetriphenylphosphorane. The photochemical behavior of 1 was dependent on both the solvent and the
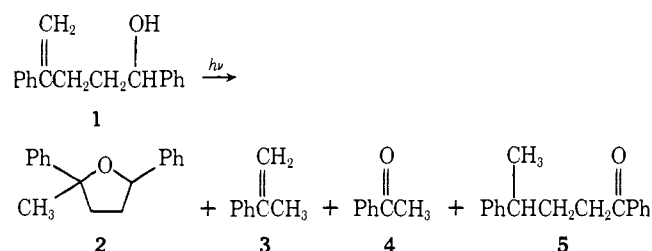
multiplicity of the reacting state (see Table I). Upon direct irradiation[7] in either hexane or benzene, 1 produced 2-methyl-2,5-diphenyltetrahydrofuran (2),[5] obtained as a mixture of diastereomers, as the major volatile product. In addition, small amounts of α-methylstyrene (3), acetophenone (4), and an unidentified component were produced. Tetrahydrofuran derivative 2 was identified by comparison of its spectral properties with those of an authentic sample prepared by acid catalyzed cyclization of 1. Direct irradiation of 1 in *tert*-butyl alcohol, however, provided a marked

(1) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967, Chapter 6.

(2) (a) P. J. Wagner, *Accounts Chem. Res.*, 4, 168 (1971); (b) N. J. Turro, *et al., Accounts Chem. Res.*, 5, 92 (1972).

(3) H. M. Rosenberg and P. Serve, *J. Amer. Chem. Soc.*, 95, 4746 (1970). For related examples see P. Serve, H. M. Rosenberg, and R. Rondeau, *Can. J. Chem.*, 47, 4295 (1969); J. Nasielski, M. Janquet, E. Vander Donckt, and A. Van Sinoy, *Tetrahedron Lett.*, 4859 (1969); H. M. Rosenberg and M. P. Serve, *J. Org. Chem.*, 37, 141 (1972); H. E. Zimmerman and J. A. Pincock, *J. Amer. Chem. Soc.*, 95, 3246 (1973).

(4) A. B. Smith, III, and W. C. Agosta, *J. Amer. Chem. Soc.*, 95, 1961 (1973), and references contained therein; W. Herz and M. G. Nair, *ibid.*, 89, 5474 (1967); D. Bellus, D. R. Kearns, and K. Shaffner, *Helv. Chim. Acta*, 52, 971 (1969); R. Reinfried, D. Bellus, and K. Shaffner, *ibid.*, 54, 1517 (1971).

(5) Satisfactory analytical and spectral data have been obtained for all new compounds.

(6) R. E. Lutz and J. S. Gillespie, Jr., *J. Amer. Chem. Soc.*, 72, 2002 (1950).

(7) Preparative irradiations were conducted through quartz, Vycor, or Pyrex with oxygen-free nitrogen[8] purged solutions using a Hanovia 450-W high pressure lamp. Analytical irradiations employed a merry-go-round apparatus with the same light source. Appropriate control experiments assured that light was necessary in each reaction.

(8) L. Meites and T. Meites, *Anal. Chem.*, 20, 984 (1948).

Table I. Photoproducts of 1,4-Diphenyl-4-penten-1-ol

Solvent	% conversion	—Percentage of products—			
		2	3	4	5
Hexane	13	58	*a*	*a*	
Hexane	81	25	*a*	2	
Benzene	34	31	2	2	
Benzene[b]	40		21	19	5
tert-butyl alcohol	48	7	3	12	
tert-butyl alcohol[b]	79		7	29	

[a] Less than 1%. [b] Containing benzophenone as photosensitizer.

change in the product distribution, producing larger amounts of 3 and 4 while the amount of 2 decreased substantially.[9]

Sensitized irradiation of 1 in either benzene or *tert*-butyl alcohol produced 3 and 4 as major products. In neither case was any 2 detected. A small amount of an additional product was observed in benzene. This material was identified as 1,4-diphenyl-1-pentanone[5] (5), by comparison of its gc retention times on three different columns with those of an authentic sample (prepared by alkylation of ethyl benzoylacetate with 1-bromo-2-phenylpropane followed by acid cleavage of the β-ketoester). The observation that 2 was not quenched by 10^{-3} M cyclohexadiene while 3 and 4 were partially quenched confirmed that 2 is a product of the singlet excited state[10] while 3 and 4 arise from the triplet.

We propose a mechanism analogous to that accepted[1,2] for the type II reaction of ketones to account for the formation of acetophenone and α-methylstyrene upon irradiation of 1. Thus, carbon 5 of the triplet excited state of 1 abstracts the hydrogen from carbon 1, *via* a cyclic, six-membered transition state, to produce a 1,4-biradical 6 (see Chart I). Biradical 6 would be expected[1,2] to fragment to produce 3 and the enol tautomer of 4. Such biradicals are often observed to produce cyclobutanols in addition to fragmentation products.[1,2] However, irradiation of ketone 5, which also produces biradical 6, gave a nearly quantitative yield of 3 and 4, with only a small amount (*ca.* 2%) of a material which could be the expected cyclobutanol. Further support for the proposed mechanism was provided by the formation of 5 from the irradiation of 1 in benzene, but not in *tert*-butyl alcohol. Exactly such behavior has been observed[12] for biradicals similar to 6 when generated from ketone precursors and has been postulated to be the result of hydrogen bonding by the hydroxy biradical to solvent, which inhibits disproportionation.

Deuterium labeling studies provided definitive evidence for the proposed mechanism. Oxidation of 1a with chromium trioxide–pyridine complex[13] followed by reduction with lithium aluminum deuteride gave 1b. Irradiation of this material revealed a substantial deuterium isotope effect on the production of both 3

(9) We are presently investigating this interesting solvent effect.

(10) Several examples of the photochemical addition of alcohols to acyclic alkenes have recently been reported.[11] The formation of ether 2 can be represented as an intramolecular example of these apparently ionic processes.

(11) E. J. Reardon, Jr., and P. J. Kropp, *J. Amer. Chem. Soc.*, 93, 5593 (1971); P. J. Kropp, *et al., ibid.*, 95, 7058 (1973); S. S. Hixson, *ibid.*, 94, 2505 (1972); *Tetrahedron Lett.*, 4211 (1971).

(12) P. J. Wagner, *J. Amer. Chem. Soc.*, 89, 5898 (1967).

(13) R. Ratcliffe and R. Rodehorst, *J. Org. Chem.*, 35, 4000 (1970).

Communications to the Editor

Chart I
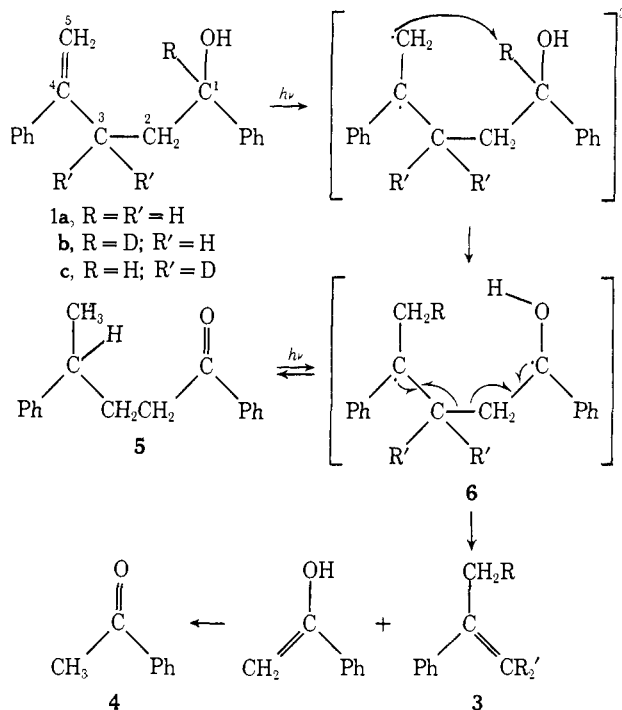
and 4 (Φ_H/Φ_D = 5.5 ± 2).[14] Analysis of the α-methylstyrene produced, by gc–mass spectroscopy, indicated the presence of one deterium per molecule (parent at 119). A strong peak at 103 (P — 16, loss of monodeuteriomethyl) suggests the location of the deuterium as in **3b**. This was confirmed and carbon **5** was demonstrated to have become the methyl carbon of **3** through the use of **1c** (prepared by a Wittig reaction of α-dideuterated ketone precursor). Analysis by nmr of the α-methylstyrene produced upon irradiation of **1c** revealed the deuterium to be entirely in the vinyl positions, as in **3c**. All of these observations are uniquely consistent with the mechanism outlined in Chart I.

Acknowledgment. The donors of the Petroleum Research Fund, administered by the American Chemical Society, are gratefully acknowledged for support of this research.

(14) Two Pyrex tubes, the first containing **1a** and the second containing **1b**, in equimolar amount, and both containing equimolar amounts of sensitizer (benzophenone), were irradiated in a merry-go-round apparatus to ensure equal absorption of light, then analyzed for the amount of **3** and **4** produced. The low yield of the products and their instability to the reaction conditions limit the accuracy of this experiment.

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Highly Stereoselective Total Syntheses of Prostaglandins via Stereospecific Sulfenate–Sulfoxide Transformations. 13-cis-15β-Prostaglandins E₁ to Prostaglandins E₁[1]

Sir:

Recently, we reported highly stereoselective syntheses of 13-*cis*-prostaglandins resulting from the conjugate addition of the *cis*-divinylcuprate (**1**) to the

(1) Publication No. 443 from the Institute of Organic Chemistry. Studies in Prostaglandins No. 40.

enones (**3a**) and (**3b**).[2] The advantages of using the cis reagent (**1**) over the corresponding trans reagent (**2**)[3] were: (a) higher yields of the addition and (b) the remarkably high degree of stereoselectivity of the reaction (>97%), which led to 13-*cis*-15β-isomers of natural 13-*trans*-15α-prostaglandins. If the 13-*cis*-15β-PGE₁'s (**4**) could be converted stereospecifically into PGE₁'s, an efficient, nearly stereospecific total synthesis of prostaglandins (E₁, F₁α, A₁, and B₁) would be achieved.
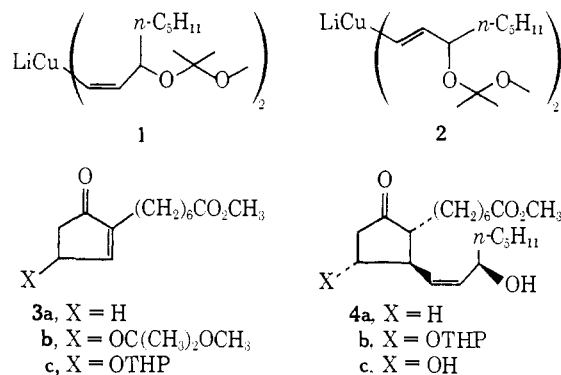
We now wish to report that the desired transformation of both the chiral and geometric centers can be accomplished concomitantly *via* the sulfenate esters (**5**), which undergo [2,3]sigmatropic rearrangements,[4] giving the sulfoxides (**6**). Treatment of the sulfoxides (**6**) with trimethylphosphite provides the prostaglandins of natural configuration (**7**).[5] The anticipated result of this transformation sequence was based on the prediction that the [2,3]sigmatropic rearrangement of the sulfenate ester (**5**) would be stereospecific with regard to carbon chirality[6] by proceeding through the thermodynamically more stable transition state, which resembles conformer **5a** more than **5** and, thus, would provide the desired geometric and chiral inversions.
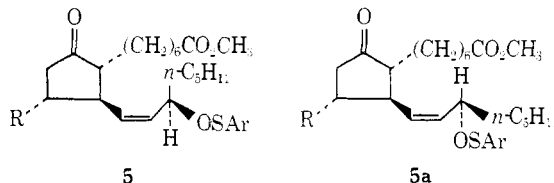
Treatment of ketol ester (*dl*-**4a**) in ether with *n*-butyllithium (1 equiv) in hexane at −78°, followed by addition of *p*-toluenesulfenyl chloride gave the *trans*-13α-sulfoxide (*dl*-**6a**): mp 51–52°;[7] ir (KBr) 1730, 1035 (SO), 965 (*trans*-HC=CH) cm⁻¹; uv (MeOH) 250 nm

(2) A. F. Kluge, K. G. Untch, and J. H. Fried, *J. Amer. Chem. Soc.,* **94**, 9256 (1972).

(3) A. F. Kluge, K. G. Untch, and J. H. Fried, *J. Amer. Chem. Soc.,* **94**, 7827 (1972).

(4) (a) P. Bickart, F. W. Carson, J. Jacobus, E. G. Miller, and K. Mislow, *J. Amer. Chem. Soc.,* **90**, 4869 (1968); (b) J. E. Baldwin, R. E. Hackler, and D. P. Kelly, *Chem. Commun.,* 538 (1968).

(5) Interceptive cleavage of sulfenate esters to allylic alcohols has been reported by D. J. Abbott and C. J. M. Stirling, *J. Chem. Soc. C,* 818 (1969), using piperidine and, more recently, using other thiophiles, including phosphite, by D. A. Evans, G. C. Andrews, and C. L. Sims, *J. Amer. Chem. Soc.,* **93**, 4956 (1971) and D. A. Evans and G. C. Andrews, *ibid.,* **94**, 3672 (1972). For a recent comprehensive review of the sulfenate–sulfoxide rearrangement, see D. A. Evans and G. C. Andrews, *Accounts Chem. Res.,* **7**, 147 (1974).

(6) In this paper we exclude chiral sulfur when using the term stereospecific. All the sulfoxides reported here are diastereomeric due to chirality of the sulfur. All the prostaglandin-like compounds here are epimerically homogeneous at C-15. Both diastereomers of each sulfoxide undergo the [2,3]sigmatropic rearrangement to achiral sulfur sulfenates, which are cleaved.