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Photoreaction of 2,2-Diphenylvinyl Ketones

Kazuyuki MAEDA, Ichiro MORITANI, and Akio SONODA

Department of Chemistry, Faculty of Engineering Science, Osaka University, Machikaneyama, Toyonaka, Osaka 560

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Synopsis. The photoreaction of 2,2-diphenylvinyl ketones leading to 1,1,4,4-tetraphenylbutadiene, which seems to formally involve α-cleavage of vinyl ketones.

Although much attention has been paid to the photochemical dimerization of unsaturated aliphatic ketones,[1-3] and (2+2) cycloaddition to olefins,[4,5] only one case has been reported on the primary photodissociation of α,β-unsaturated ketones at elevated temperature with low efficiency.[6]

We report herewith on the photoreaction of 2,2-diphenylvinyl ketones (**1**) leading to 1,1,4,4-tetraphenylbutadiene (**2**), which formally involves α-cleavage of **1** and dimerization.

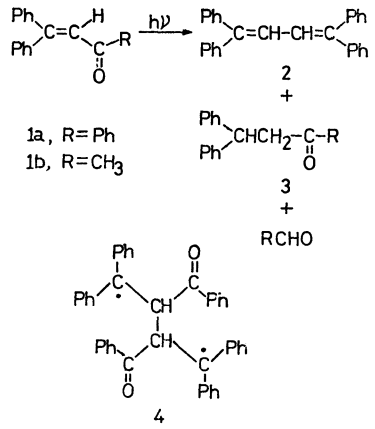

Fig. 1.

Irradiation of a solution of 1,3,3-triphenyl-2-propen-1-one (**1a**) in 2-propanol (2.9×10^{-2} mol/l) with high-pressure mercury arc was carried out for 90 hr under argon atmosphere. Removal of the resulting benzoic acid (7%) by extraction with the base followed by chromatography on Al_2O_3 gave the butadiene **2** (37%) and 1,3,3-triphenylpropan-1-one (**3a**) (27%). The structural assignment of these products was established by comparison of their spectral data with those of the authentic samples. Analogous photoreaction of 4,4-diphenyl-3-buten-2-one (**1b**) in 2-propanol afforded the butadiene **2** (18%) and 4,4-diphenylbutan-2-one (**3b**) (5%).

A probable pathway involves the initial coupling of **1** at the α-position leading to **4**, the most stable biradical of three possible intermediate species. Subsequent cleavage of Norrish Type I of **4** would lead to the butadiene **2** and two benzoyl radicals. Hydrogen abstraction of the latter followed by autoxidation during the work-up may lead to benzoic acid. Although a number of photodimers of unsaturated aliphatic ketones,[2] carboxylic acid,[1] and esters[3] have been isolated, no photodimer could be detected in this photoreaction probably because of extraordinary stability of the biradical **4**.

An alternative mechanism which includes α-cleavage of the ketones **1** affording 2,2-diphenylvinyl radical and subsequent coupling to give **2** seems unlikely, since facile hydrogen abstraction of vinyl radical can overcome the coupling reaction.[7] No product such as diphenylethylene which can be derived from hydrogen abstraction of 2,2-diphenylvinyl radical could be detected during the course of photoreaction.

Ketone **3a**, derived from photoreduction of **1a**,[8,9] could be obtained only in 2-propanol among various solvents as shown in Table 1.[10]

Table 1. Solvent effect of photoreaction of **1a** under nitrogen (30 hr)

Solvent	Conversion (%)	Yield of **2** (%)	Yield of **3a** (%)
2-Propanol	74	26	26
Cyclohexane	28	25	0
Benzene	26	17	0

Experimental

*Irradiation of 1,3,3-Triphenyl-2-propen-1-one (**1a**) in 2-Propanol.* A solution of **1a** (8.25 g), mp 87.5—88.7 °C (lit,[11] mp 84—87 °C), in 2-propanol (1000 ml) was irradiated under argon. The reaction was monitored periodically (UV analysis and tlc technique). After 90 hr irradiation, the solvent was evaporated, and the residue was dissolved in CH_2Cl_2. Extraction of the CH_2Cl_2 solution with a $NaHCO_3$ solution followed by acidification gave benzoic acid (0.20 g). The neutral products were subjected to alumina chromatography (400 g of alumina). Elution with *n*-hexane gave butadiene **2** (1.65 g, 37%), which was identified by comparison with an authentic specimen, mp 201—202 °C (lit,[12] mp 204—205 °C), Found: C, 94.04; H, 6.20%. Calcd for $C_{28}H_{22}$: C, 93.81; H, 6.19%). NMR (CCl_4, δ): 6.65 (2H, s, vinyl), 7.10 (10H, s) and 7.20—7.40 (10H, broad d). Further elution with benzene afforded a yellow oil, which upon fractional distillation under reduced pressure gave **3a** (1.93 g, 27%), bp 205—207 °C/2 mmHg, and recovered **1a** (1.22 g). The structure of **3a** was established by comparison with an authentic sample and mixed mp. Mp 92.8—93.5 °C (lit,[13] 91—92 °C). IR (nujol mull): 1670 cm^{-1} (C=O). NMR (CCl_4, δ): 3.53—3.70 (2H, d), 4.70—4.90 (1H, t) and 7.05—7.95 (15H, m). Finally, elution with ether gave a trace of a crystalline compound (mp 250—254 °C, mol wt. 554) and a tarry material.

*Irradiation of **1a** in the Presence of Oxygen.* A solution **1a** (16.50 g) in 2-propanol (1000 ml) was irradiated under a slow stream of dry air for 45 hr. The treatment as described above gave benzoic acid (0.17 g, 3%). An alumina chromatography of the neutral products gave the butadiene **2** (2.26 g, 27%), benzophenone (5.61 g, 66%), acetophenone (2.26 g, 46%), and recovered **1a** (1.10 g) in addition to tarry materials.

*Irradiation of 4,4-Dipheny-3-buten-2-one (**1b**) in 2-Propanol.* A solution of **1b** (2.96 g), bp 168—170 °C/7 mmHg, mp 33.5—34.5 °C (lit,[14] bp 195—205 °C/15 mmHg), in 2-propanol (500 ml) was irradiated for 50 hr under nitrogen. The resulting mixture was subjected to alumina chromatography. Petroleum ether–benzene eluted **2** (0.39 g, 18%). Elution with benzene gave benzoic acid (0.013 g, 1%) and the ketone **3b** (0.11 g, 5%). Mp 47.0—48.0 °C (lit,[15] mp 47.5 °C). IR (nujol mull): 1710 cm^{-1} (C=O). NMR (CS_2, δ): 1.93 (3H, s), 3.01 (2H, d, J=7.5 Hz), 4.44 (1H, t, J=7.5 Hz), 6.90—7.95 (10H, m).

References

1) J. Corse, B. J. Finkel, and R. E. Lundin, *Tetrahedron Lett.*, **1961**, 1.
2) G. Montaudo and S. Caccamese, *J. Org. Chem.*, **38**, 710 (1973); references cited therein.
3) H. Stobbe, *Ber.*, **45**, 3396 (1912).
4) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964).
5) P. E. Eaton, *Accounts Chem. Res.*, **1**, 50 (1968).
6) J. N. Pitts, Jr., and J. K. S. Wan, "The Chemistry of the Carbonyl Group," Vol. I, ed. by S. Patai, John Wiley & Sons, Inc., New York, N. Y. (1966), p. 870; references cited therein.
7) J. K. Haynes, Jr., and J. A. Kampmeire, *J. Org. Chem.*, **37**, 4167 (1972).
8) H. M. Rosenberg and P. Sarve, *J. Amer. Chem. Soc.*, **92**, 4746 (1970).
9) M. J. Jorgenson and N. C. Yang, *ibid.*, **85**, 1698 (1963); idem, *Tetrahedron Lett.*, **1203** (1964).
10) Irradiation of **1a** in 2-propanol under slow stream of oxygen gave **2** (27%), benzoic acid (3%), benzophenone (66%), and acetophenone (46%).
11) H. K. Hess W. Weltzien, *Ber.*, **54**, 2511 (1921); K. H. Meyer and K. Schuster, *ibid.*, **55**, 819 (1922).
12) G. Wittig and F. v. Lupin, *ibid.*, **61**, 1627 (1928).
13) P. R. Shildneck, "Organic Syntheses," Coll, Vol. II, p. 236 (1943).
14) W. Wilson and Zu-Young Kyi, *J. Chem. Soc.*, **1321** (1952).
15) G. G. Henderson and M. A. Parker, *ibid.*, **71**, 676 (1897).