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# PHOTOCHEMICAL REACTIONS OF DIPHENYLKETENE IN SOLUTION[1]

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**Abstract**—Diphenylketene (I) dissolved in certain organic solvents was photolysed by means of a 200 W high pressure mercury lamp in a quartz immersion tube and the products separated and identified. Cyclohexene, toluene, diethyl ether or benzyl methyl ether as a solvent gave diphenylmethylated derivatives (VI) in fair yields, while in tetrahydrofuran, surprisingly, a diphenylacetylated product (IVa) was obtained. 1,1,2,2-Tetraphenylethane (VII) and coupling products of solvent radicals (VIII) were also produced. 1,1-Diphenylethylene as a solvent gave an adduct, 1,1,2,2-tetraphenylcyclopropane. In anisole, benzene or carbon tetrachloride solution the only photolysis product identified was benzophenone. Some of these products could be accounted for by assuming the formation of diphenylmethylene (II), which is a typical triplet. The formation of crossed dimerization products (VI) and of acylated products (IV), however, requires another mechanism which would supposedly involve the intermediacy of radical pairs III or V.

METHYLENE or carbene formation by vapour phase photolysis of ketenes[2,3] is well known, while little information about the photochemical behaviour of ketenes in solution is available. Zimmerman and Paskovich[4] reported recently photolysis of dimesitylketene with a low pressure mercury arc in a hydrocarbon solution to give tetramesitylethylene in 19·4% yield. The intermediacy of ketenes in the photochemical rearrangements of cyclic ketones was described by several authors.[5] In these cases, ketene itself was trapped by reactive alcohols or amines. Isolation of *cis*-octahydroindene and cyclononene in photolysis of bicyclo(5.2.1)decan-10-one[6] is the only known example of decarbonylation of an intermediate ketene in solution. In continuation of the work on phenylated carbenes[7] the photolysis of diphenylketene (I) dissolved in certain organic solvents has now been examined in hopes of observing the behaviour of dipenylmethylene (II) which would be produced in this way. The product analyses, however, have indicated the whole reaction can not be satisfactorily interpreted by simply assuming the intermediacy of diphenylmethylene (II) alone.

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[1] Partly presented at the 18th Annual Meeting of the Chemical Society of Japan, Ôsaka, April 2, 1965.

[2] S. Ho, I. Unger and W. A. Noyes, Jr., *J. Amer. Chem. Soc.* **87**, 2297 (1965); J. Chanmugam and M. Burton, *Ibid.* **78**, 509 (1956); G. B. Kistiakowsky and W. L. Marshall, *Ibid.* **74**, 88 (1952).

[3] R. A. Holroyd and F. E. Blacet, *J. Amer. Chem. Soc.* **79**, 4830 (1957); G. B. Kistiakowsky and B. H. Mahan, *Ibid.* **79**, 2412 (1957).

[4] H. E. Zimmerman and D. H. Paskovich, *J. Amer. Chem. Soc.* **86**, 2149 (1964).

[5] O. L. Chapman, *Advances in Photochemistry* (Edited by W. A. Noyes, Jr., G. S. Hammond and J. N. Pitts, Jr.) Vol. I; p. 345. Interscience, New York (1963); P. de Mayo, *Advances in Organic Chemistry* (Edited by R. A. Raphael, E. C. Taylor and H. Wynberg) Vol. II; p. 393. Interscience, New York (1960).

[6] C. D. Gutsche and J. W. Baum, *Tetrahedron Letters* 2301 (1965).

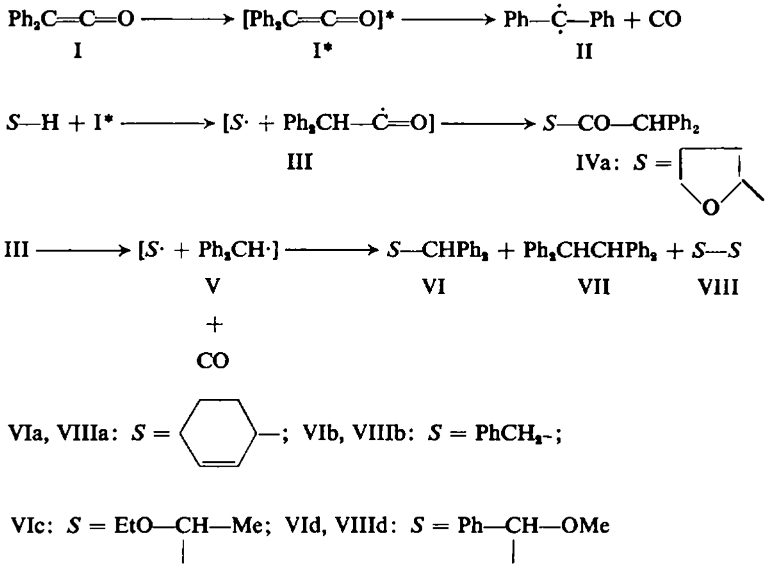
[7] H. Nozaki, R. Noyori and K. Sisido, *Tetrahedron* **20**, 1125 (1964); H. Nozaki, M. Yamabe and R. Noyori, *Ibid.* **21**, 1657 (1965).

Solutions of diphenylketene (I) were irradiated with a 200 W high pressure mercury vapour lamp in a quartz immersion tube at room temp. After removing the unchanged solvent, the products were isolated by recrystallization, distillation *in vacuo* and/or elution chromatography on a silica gel column. The characterization was mostly established by comparison with authentic samples.

Irradiation of a 0·18 molar cyclohexene solution for 60 hr resulted in evolution of ca. 80–90% calculated amount of carbon monoxide. From the nonvolatile part of the reaction mixture 3-benzhydrylcyclohexene (VIa), 1,1,2,2-tetraphenylethane (VII) and bi-2-cyclohexen-1-yl (VIIIa) were isolated in 16, 22 and 58% yields,[8] respectively. No cycloadduct of diphenylmethylene could be isolated.

Irradiation of a 0·08 molar toluene solution for 60 hr gave similarly 1,1,2-triphenylethane (VIb),[9] VII and bibenzyl (VIIIb) in 14, 16 and 14% yields, respectively. Unchanged ketene (I) or any products originating therefrom could not be obtained.

Pyrolysis and photolysis of diphenyldiazomethane in cyclohexene or toluene have been recorded[10] to afford VII and VIIIa, but the crossed dimerization products (VIa or VIb) were not isolated in the diazomethane reaction.[11]



$$\underset{\text{I}}{Ph_2C{=}C{=}O} \longrightarrow \underset{\text{I}^*}{[Ph_2C{=}C{=}O]^*} \longrightarrow \underset{\text{II}}{Ph\!-\!\ddot{C}\!-\!Ph} + CO$$

$$S\!-\!H + I^* \longrightarrow \underset{\text{III}}{[S\cdot + Ph_2CH\!-\!\dot{C}{=}O]} \longrightarrow S\!-\!CO\!-\!CHPh_2$$

IVa: $S =$

$$\text{III} \longrightarrow \underset{\text{V} + \text{CO}}{[S\cdot + Ph_2CH\cdot]} \longrightarrow \underset{\text{VI}}{S\!-\!CHPh_2} + \underset{\text{VII}}{Ph_2CHCHPh_2} + \underset{\text{VIII}}{S\!-\!S}$$

VIa, VIIIa: $S =$ —; VIb, VIIIb: $S = PhCH_2$–;

VIc: $S = EtO\!-\!CH\!-\!Me$; VId, VIIId: $S = Ph\!-\!CH\!-\!OMe$

Photolysis of a 0·88 molar solution of I in 1,1-diphenylethylene gave 1,1,2,2-tetraphenylcyclopropane[12] in 54% yield after 72 hr irradiation, unchanged I (28%) being recovered as diphenylacetic acid. The same product (in about 40% yield) has

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[8] All yields are given based on the consumed I, unless otherwise stated.

[9] A. Klages and S. Heilmann, *Ber. Dtsch. Chem. Ges.* 37, 1455 (1904).

[10] [a] W. Kirmse, L. Horner and H. Hoffmann, *Liebigs Ann.* 614, 19 (1958); [b] V. Franzen and H. I. Joschek, *Liebigs Ann.* 633, 7 (1960).

[11] Kirmse[10a] ascribed the failure of obtaining crossed dimerization products to the different stabilities of benzhydryl and solvent radicals. Bethell *et al.*, however, claim to have detected the presence of 1,1,2-triphenylethane (VIb) among the thermal decomposition products of the diazo compound in toluene by NMR Spectroscopy. See D. Bethell, D. Whittaker and J. D. Callister, *J. Chem. Soc.* 2466 (1965).

been obtained by the photolysis or pyrolysis of diphenyldiazomethane in 1,1-diphenylethylene.[12] The possibility of the initial cycloaddition of I affording 2,2,3,3-tetraphenylcyclobutanone which is then photolysed to the cyclopropane appears to be excluded. Irradiation of 2,2,3-triphenylcyclobutanone[13] obtained by the cycloaddition of I to styrene did nct give any appreciable amount of 1,1,2-triphenylcyclopropane. Examination of the IR spectrum of a mixture of I and 1,1-diphenylethylene in the dark showed no evidences for the formation of a cycloadduct. Thermal reaction of I with 1,l-diphenylethylene[14] in a sealed tube is known to give 2,2,4,4,5,5-hexaphenylcyclohexane-1,3-dione. Irradiation of this cyclic diketone in diphenylethylene did not afford the tetraphenylcyclopropane. The cyclopropane must therefore, be formed by the direct interaction of excited ketene (I*) and the ethylene.

Upon irradiation of a 0·08 molar ethereal solution the gas evolution was slower, 15 hr irradiation giving only 40% calculated amount of carbon monoxide. The isolated products were VII (36% yield), α-benzhydrylethyl ethyl ether (VIc, 2% yield) and benzophenone (18% yield). The benzhydrylated product (VIc) was independently prepared by the Williamson reaction of 1,1-diphenyl-2-propanol[15] with ethyl bromide in the presence of sodium hydride in 60% yield. No acylated product such as IV could be isolated with ether as solvent.

Irradiation of 0·13 molar tetrahydrofuran solution for 15 hr yielded 21% calculated amount of carbon monoxide. Working up the reaction mixture gave 2-diphenylacetyltetrahydrofuran (IVa)[16] in 42% yield besides benzophenone and VII in 15 and 23% yields, respectively. The acylated product (IVa) was characterized by IR and NMR spectra as well as by elemental analyses. IR spectrum indicated typical absorptions due to carbonyl and cyclic ether bondings at 1710 and 1070 $\text{cm}^{-1}$, respectively. NMR signals (given in the order of chemical shift (ppm) with splitting pattern and weight in parentheses) at 1·80 (multiplet, 4H), 3·73 (triplet, 2H) and 4·45 (triplet, 1H) also support this structure. Upon exposure in moist air IVa decomposed gradually to afford diphenylacetic acid. No alkylation product such as VIc could be isolated in the tetrahydrofuran reaction.

Benzyl methyl ether as a solvent gave under similar conditions 1,2,2-triphenylethyl methyl ether (VId),[17] *meso*-α,α′-dimethoxybibenzyl (VIIId)[18] and VII in 24, 23 and 29% yields, respectively. Irradiation of a 0·13 molar solution of I in dioxan for 20 hr resulted in VII in 50% yield as a sole product. Anisole, benzene and carbon tetrachloride were found to be inert to I and photochemically derived species from I, the only product isolated being benzophenone in 24, 56 and 67% yields, respectively. The rather high yields of benzophenone are puzzling, as the photolysis was carried out under cylinder nitrogen atmosphere.

Summarizing these observations, we may conclude that some of the reaction products such as benzophenone or 1,1,2,2-tetraphenyl-cyclopropane would reasonably be assumed to originate from diphenylmethylene (II). The formation of VI,

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[12] J. E. Hodgkins and M. P. Huges, *J. Org. Chem.* **27**, 4187 (1962).

[13] E. Bergmann and O. B. Bergmann, *J. Chem. Soc.* 727 (1938).

[14] M. O. Farooq and N. A. Abraham, *Bull. Soc. Chim. Fr.* 832 (1958).

[15] W. J. Bailey and C. King, *J. Org. Chem.* **21**, 858 (1956).

[16] Acylation of ethers on their α-position with photochemically generated acyl radicals is reported recently (U. Schmidt, *Angew. Chem.* **77**, 216 (1965)).

[17] M. S. Newman and A. Kutner, *J. Amer. Chem. Soc.* **73**, 4199 (1951).

[18] W. R. Bamford and T. S. Stevens, *J. Chem. Soc.* 4675 (1952).

VII and VIII could be explained on this basis, but the formation of the acylation product (IVa) requires another mechanism. The plausible hypothesis at present would probably involve the intermediacy of the radical pairs III and V, both being produced by the photochemically excited, polar ketene molecule (I*) and the reactive solvents (*S*–H).

## EXPERIMENTAL

All temps were uncorrected. Elemental analyses were performed at the Elemental Analyses Centre of Kyôto University.

*Starting materials.* Diphenylketene was prepared essentially according to the Staudinger's methods.[19] Irradiation solvents were thoroughly dried and freshly distilled immediately before use.

*Irradiation of diphenylketene* (I) *in cyclohexene.* A solution of I (5·5 g, 0·028 mole) in cyclohexene (160 ml) was irradiated at 15° under $N_2$ atm. Evolution of CO (80–90%) subsided at the end of 60 hr irradiation. The solid which remained upon evaporation of the solvent was recrystallized from benzene to yield VII (1·0 g, 22%). Its IR spectrum was identical with that of an authentic sample. The mother liquor of recrystallization was concentrated and distilled to give VIIIa (1·3 g, 58%), b.p. 58–59°/1 mm, which was identified as the tetrabromide, m.p. 158° (reported[10b] m.p. 158°). The distillation residue was subjected to chromatography on a silica column. Elution with n-hexane–benzene (9:1) afforded 3-*benzhydrylcyclohexene* (VIa) (1·15 g, 16%) as a heavy viscous oil. (Found: C, 91·79; H, 8·18. $C_{19}H_{20}$ requires: C, 91·88; H, 8·12%.) The IR spectrum (neat) showed an intensive absorption at 1650 $cm^{-1}$ due to olefinic bond. The NMR spectrum (in $CCl_4$) showed signals at $\delta$ 1·55 (4H, multiplet, $C_4$ and $C_5$ methylene protons), 1·95 (3H, multiplet, $C_6$ methylene and $C_3$ methine protons), 3·60 (1H, doublet, benzhydrylmethine proton), 5·67 (2H, multiplet, $C_1$ and $C_2$ protons) and 7·27 ppm (10 H, singlet, phenyl protons).

*Irradiation of diphenylketene* (I) *in toluene.* A solution of I (4·4 g, 0·023 mole) in toluene (300 ml) was irradiated during 60 hr under conditions similar to those as described above and the solvent was distilled off *in vacuo*. The residue was washed with pet. ether (b.p. 35–45°). Recrystallization of the insoluble solid from benzene gave VII (0·6 g, 16%). The soluble portion obtained by treatment with pet. ether was fractionally distilled yielding fraction I, b.p. 75–76°/1 mm, and fraction II, b.p. 135–137°/1 mm. Both distillates solidified gradually on standing. On recrystallization from MeOHaq, fraction I gave VIIIb (0·3 g, 14%), m.p. and m.m.p. 50–51°, and fraction II gave VIb (0·8 g, 14%), m.p. 52–53° (reported[9] m.p. 54°).

*Irradiation of diphenylketene* (I) *in* 1,1-*diphenylethylene.* A solution of I (7·5 g, 0·039 mole) dissolved in 1,1-diphenylethylene (44 ml) was sealed in a Vycor tube, attached to the lamp and irradiated for 72 hr. Vacuum distillation gave the excess ethylene and unchanged I, the latter being recovered as diphenylacetic acid (2·3 g, 28% recovery) from the distillate. Recrystallization of the residue from absolute EtOH produced a pure sample of 1,1,2,2-tetraphenylcyclopropane (5·2 g), m.p. 165–166° (reported[12] m.p. 165–165·5°). The yield was 54% based on the consumed I.

A 0·5 molar solution of I in 1,1-diphenylethylene was kept in the dark at room temp. No change was observed in the IR spectrum of this mixture after 3 days. Irradiation of a solution of 2,2,3-triphenylcyclobutanone[13] (0·4 g) or 2,2,4,4,5,5-hexaphenylcyclohexane-1,3-dione[14] (0·5 g) dissolved in diphenylethylene (10 ml) resulted in the formation of nondistillable tarry products, from which no cyclopropane derivative could be isolated. As the IR spectra of these mixtures did not show any absorption in the region 1000–1100 $cm^{-1}$ due to the cyclopropane ring, the possibility of tri- or tetraphenylcyclopropane formation under these conditions could be excluded.

*Irradiation of diphenylketene* (I) *in ethyl ether.* A solution of I (3·8 g, 0·020 mole) in ether (250 ml) was irradiated for 15 hr, 40% of the calculated amount of CO being evolved during this period. Evaporation of the solvent and filtration of the residue gave VII (1·17 g, 36%). The filtrate was chromatographed on a silica gel column. Elution with n-hexane–benzene (4:1) afforded *α-benzhydrylethyl ethyl ether* (VIc; 0·12 g, 2%), which was identified by superimposing its IR spectrum onto that of an authentic sample prepared as below. The NMR (in $CDCl_3$) exhibited the presence of ethyl protons centered at $\delta$ 1·03 (3H, triplet) and 3·42 (2H, quartet) and methyl protons at 1·12 ppm (3H, doublet). Further elution with benzene gave benzophenone (0·63 g, 18%), which was characterized as 2,4-dinitrophenylhydrazone.

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[19] H. Staudinger, *Liebigs Ann.* 356, 51 (1908); H. Staudinger, *Ber Dtsch. Chem. Ges.* 44, 1619 (1911).

*α-Benzhydrylethyl ethyl ether* (VIc). A mixture of 1,1-diphenyl-2-propanol[15] (7 g) and NaH (0·9 g) in dry benzene (20 ml) was stirred and refluxed during 4 hr. EtBr (4 g) dissolved in dry benzene (10 ml) was added dropwise and the reaction mixture refluxed overnight. Removal of the solvent and distillation of the residual oil afforded VIc (3·8 g, 60%), b.p. 110–111°/1 mm. (Found: C, 85·48; H, 8·25. $C_{17}H_{20}O$ requires: C, 84·95; H, 8·39%).

*Irradiation of diphenylketene* (I) *in tetrahydrofuran.* A solution of I (6·3 g, 0·033 mole) in tetrahydrofuran (250 ml) was irradiated for 15 hr, 21% of the calculated amount of CO being evolved during this period. After separating VII (1·23 g, 23%) by filtration, benzophenone (0·9 g, 15%), b.p. 115–120°/0·4 mm, and 2-*diphenylacetyltetrahydrofuran* (IVa; 3·6 g, 42%), b.p. 155–157°/0·4 mm, were obtained by distillation of the filtrate. The structure of the latter compound was established on the basis of the following information: (1) mass spectrum (m/e): 266 (parent peak), 167 and 71 (base peak), (2) elemental analyses: (Found: C, 80·87; H, 7·07. $C_{18}H_{18}O_2$ requires: C, 81·17; H, (6·81%); (3) IR absorptions (neat): $\nu_{C=O}$ 1710 and $\nu_{C-O-C}$ 1070 cm$^{-1}$, and (4) NMR spectrum (in $CDCl_3$): $\delta$ 1·80 (4H, multiplet, $C_3$ and $C_4$ methylene protons), 3·73 (2H, triplet, $C_5$ methylene proton), 4·45 (1H, triplet, $C_2$ methine proton), 5·60 (1H, singlet, benzhydrylmethine proton) and 7·22 ppm (10H, singlet, phenyl protons). The ketone IVa was very unstable and decomposed to diphenylacetic acid, m.p. 144·5–146°, upon exposure in moist air.

*Irradiation of diphenylketene* (I) *in benzyl methyl ether.* A solution of I (2·1 g, 0·011 mole) in benzyl methyl ether (60 ml) was irradiated through Vycor filter during 72 hr. Removal of the solvent and recrystallization of the residual solid from chloroform–n-hexane (1:4) afforded VII (0·52 g, 29%). Concentration of the mother liquor and repeated recrystallization from dry MeOH gave VIIId (0·3 g, 23%), m.p. 141·5–142·5° (reported[18] m.p. 140°). Residual oil recovered from mother liquor of the recrystallization was chromatographed on silica using n-hexane–benzene (4:1) as eluant yielding 1,2,2,-triphenylethyl methyl ether[17] (0·73 g, 24%), which was identified by comparison of its IR spectrum with that of an authentic sample.

*Irradiation of diphenylketene* (I) *in dioxan.* A solution of I (4·6 g, 0·024 mole) in dioxan (180 ml) was irradiated during 20 hr yielding VII (2·3 g, 50%) from the photolysis residue. Chromatography of the residual oil obtained from the filtrate of VII afforded unidentified tarry substances.

*Irradiation of diphenylketene* (I) *in anisole, benzene or carbon tetrachloride.* A solution of I (3·1 g, (0·016 mole) in anisole (150 ml), benzene (150 ml) or $CCl_4$ (150 ml) was irradiated during 25 hr. Elution of the photolysis residue on silica afforded benzophenone as an only isolable product in 24, 56 and 67% yields, respectively, based on the consumed I. Unchanged I was recovered as diphenylacetic acid or its anhydride.

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