BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 3602—3603 (1973)

Photochemical Behavior of 1,1-Diphenylethylene in Polychloroalkane Solvents: Preferential Abstraction of Chlorine Atom[1]

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(Received February 16, 1973)

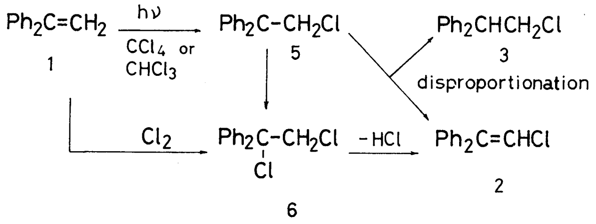
Kinetic evidence indicates that 1,1-diphenylethylene (**1**) in the triplet excited state behaves to some extent like a biradical species.[2] Irradiation of **1** induced abstraction of hydrogen atom from 2-propanol in a radical fashion.[3] We have investigated the photochemical reactions of **1** in several polychloroalkanes and chloroalkenes and found that the chlorine atom was abstracted by **1** in the triplet excited state.[4]

When a carbon tetrachloride solution of **1** was irradiated under nitrogen by means of a medium pressure mercury arc at room temperature for 140 hr, glc analysis of the reaction mixture showed the presence of two products. The residue of the distillation was chromatographed on a silica-gel column to give 2-chloro-1,1-diphenylethylene[5] (**2**) (92% based on the starting material consumed) and 2-chloro-1,1-diphenylethane[6] (**3**) (trace). Hydrogen chloride was found in the reaction mixture. The structures of the photoproducts were confirmed by direct comparison with authentic samples. It is of interest that no hexachloroethane which would result from trichloromethyl radical was detected in the reaction mixture.

Irradiation of a chloroform solution of **1** for 180 hr gave **2** (74%), **3** (trace), and HCl. Neither 1,1-diphenylethane (**4**) which is expected to be produced by hydrogen abstraction, nor products derived from trichloromethyl radical were found. Photolysis of a solution of **1** in dichloromethane for 180 hr gave **2** (6%), **3** (3%) together with only a trace amount of **4**. Photoreactions of **1** in 1,2-dichloroethane, *t*-butyl chloride, cyclohexyl chloride, and 3-chlorocyclohexene were sluggish, only a trace of **4** being detected in each reaction mixture even after prolonged irradiation. These facts suggest that the preferential mode of photochemical reaction of **1** in polychloroalkanes appears to be the abstraction of chlorine atom rather than that of hydrogen atom.

In chloroform molecule C–H bond fission usually occurs under radical reaction conditions[7] or by irradiation in nitrogen or argon matrix.[8] In the present investigation, however, only chlorine abstraction was observed. The cause is still open to discussion and the fate of the residual radical from the solvents remains unclarified.

In order to obtain information on the reactive excited species involved in the reaction between **1** and carbon tetrachloride, quenching and sensitization experiments were performed. Irradiation reaction (>330 nm) conducted in a Pyrex vessel was successfully sensitized by triphenylene, and the product distribution was not affected. The unsensitized reaction did not occur upon photolysis at this wavelength region. It was also found that the reaction could be quenched by the addition of piperylene. Since carbon tetrachloride itself absorbs light in this wavelength region[9] the possibility of the primary dissociation of the photoexcited carbon tetrachloride to give reactive species cannot be ruled out. Actually, however, light which passes a carbon tetrachloride filter induces the reaction. This indicates that at least the excited triplet state of **1** was involved in the photochemical reaction of **1** in carbon tetrachloride.



One might explain the formation of **2** and **3** by assuming intermediacy of radical species **5** which could undergo disproportionation and chlorine-abstraction (Scheme). Facile elimination of hydrogen chloride from a dichloroethane derivative (**6**) will give the final product **2** in a larger amount. An attempted chlorination of **2** by molecular chlorine[5] to obtain **6** resulted in the formation of **2** as the only isolable product. The result suggests the reaction pathway *via* **6** which, once formed, turns into **2** by ready loss of hydrogen chloride.

Experimental

All temperatures are uncorrected. Microanalyses were performed by Mrs. Kiyoko Fujimoto. The spectra were recorded in neat liquid films on a Shimadzu IR-27C spectrometer. The NMR spectra were determined on a JOEL C-60-H spectrometer using TMS as an internal standard and CCl_4 as solvent. The mass spectra were recorded with

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a Hitachi RMS-4 mass spectrometer at 70 eV. The UV spectra were obtained in ethanol solutions on a Shimadzu MPS-50L spectrophotometer.

Reagents. 1,1-Diphenylethylene (**1**) was prepared by the method of Allen and Converse,[10] bp 143—145 °C/20 mmHg (lit,[10] bp 156 °C/25 mmHg). Carbon tetrachloride,[11] chloroform,[12] dichloromethane,[13] 1,2-dichloroethane,[14] *t*-butyl chloride,[15] cyclohexyl chloride,[16] and 3-chlorocyclohexene[17] were prepared and/or purified by published methods.

General Irradiation Procedure. After a solution of **1** (0.035 M) in the solvents was bubbled with commercial nitrogen for 1 hr, it was irradiated in a quartz tube by a Haros PIH-300 medium pressure mercury arc at room temperature for specified periods. The progress of the photoreaction was monitored by glc. After irradiation the solution was washed with an aqueous NaOH solution, the latter being then titrated with an aqueous HCl solution. The excess solvent was distilled off and the distillate was carefully checked by glc to scrutinize low boiling materials. The residue was chromatographed on silica gel to give the starting material, 2-chloro-1,1-diphenylethylene (**2**),[5] 2-chloro-1,1-diphenylethane (**3**),[6] and 1,1-diphenylethane (**4**)[18] which were further purified by glc to obtain analytical samples.

Sensitization with Triphenylene. A solution of **1** (36 mg, 0.2 mmol) in carbon tetrachloride (10 ml) was divided into two equal portions after bubbling with nitrogen. Triphenylene (23 mg, 0.1 mmol) was added to one portion, and the two solutions were irradiated (>330 nm) in Pyrex tubes through a filter of NaBr–$Hg(NO_3)_2$ solution[19] for 40 hr. The progress of the reaction was monitored by glc. The reaction with added triphenylene proceeded to almost 100% completion, whereas the unsensitized reaction showed the formation of only traces of the products.

Quenching with Piperylene. A solution of **1** (90 mg, 0.5 mmol) in carbon tetrachloride (10 ml) was divided into two equal portions after bubbling with nitrogen. Piperylene (170 mg, 2.5 mmol) was added to one portion and the two solutions were irradiated in quartz vessels with a medium pressure mercury arc for several hours. Glc monitoring of the progress of the reaction showed that the unquenched reaction was about 8 times as rapid as the quenched one.

Our thanks are due to Professor Hitosi Nozaki for his help and encouragment.

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