

Photo-CIDNP Observed in *O*-Methylbenzoin–Carbon Tetrachloride System

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Synopsis. Photo-induced decomposition of *O*-methylbenzoin in carbon tetrachloride was investigated. A reaction scheme is proposed with the aid of photo-CIDNP technique and product analysis.

Photodecomposition of benzoin and its derivatives has been investigated mainly from the standpoint as initiators of photo-polymerization.^{1a–f} By means of CIDNP photo-induced α -cleavage of benzoin has already been examined in correlation with photochemical reaction of benzaldehyde, because both processes generate common radical pair, *i.e.*, pair of benzoyl radical and α -hydroxybenzyl radical.^{2a–c} Though these studies were carried out in rather inert solvent, *e.g.*, benzene, methanol, or acetonitrile, here we investigated the photo-induced decomposition of *O*-methylbenzoin in good chlorine atom donor; carbon tetrachloride. From the viewpoint to investigate the escaping feature of the incage radical pair, carbon tetrachloride is a helpful solvent. In actual, chlorine atom and trichloromethyl radical incorporated with the photo-decomposition processes of *O*-methylbenzoin.

When a carbon tetrachloride solution of *O*-methylbenzoin **1** was deaerated and irradiated with a high pressure Hg arc lamp for 30 min, **1** decomposed completely. Benzoyl chloride **2** (94 mol%), benzaldehyde **3** (41 mol%), 1-methoxy-1-phenyl-2,2,2-trichloroethane **4** (28 mol%), an equimolar mixture of diastereomeric *O,O'*-dimethylbenzopinacol **5** (7 mol%), hexachloroethane **6** (48 mol%), and α,α,α -trichloroacetophenone **8** (a trace) were identified in the reaction mixture (yields were calculated on the basis of **1**) (Scheme 1). This

product distribution is quite different from that observed in other solvents as benzene or acetonitrile.^{1b,c,d} In the latter cases, **5** is a major product (60–70%, quantum yield; ≈ 0.35), accompanied by less amounts of benzil ($<10\%$). This fact clearly indicates participations of chlorine atom and trichloromethyl radical in the escaping process of the incage radical pair.

The CIDNP spectrum observed during the irradiation of carbon tetrachloride solution of **1** is illustrated in Fig. 1(A). Polarized emission was observed in the methine proton of the starting material **1** (signal 2). Besides the signal 2, three distinct polarized signals (indicated as signal 1, 3, and 5) were observed. In comparison of their chemical shifts with those of the authentic samples, the polarized signals 1 and 3 are assignable to the methine proton of 1-methoxy-1-phenyl-2,2,2-trichloroethane **4** (δ : 4.58 ppm) and that of α -chlorobenzyl methyl ether **7** (δ : 6.36 ppm), respectively. The polarized signal 5 is originated from the formyl proton of benzaldehyde **3**. Although the

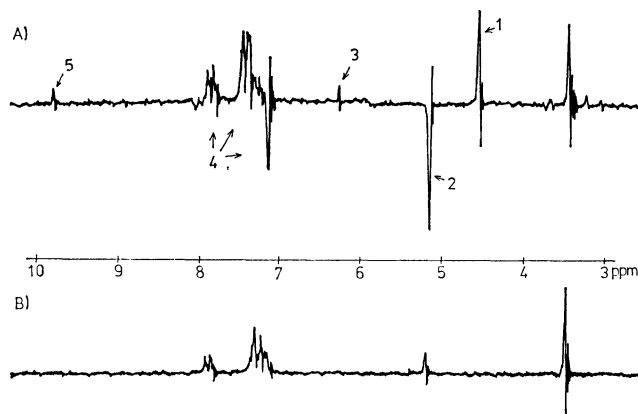
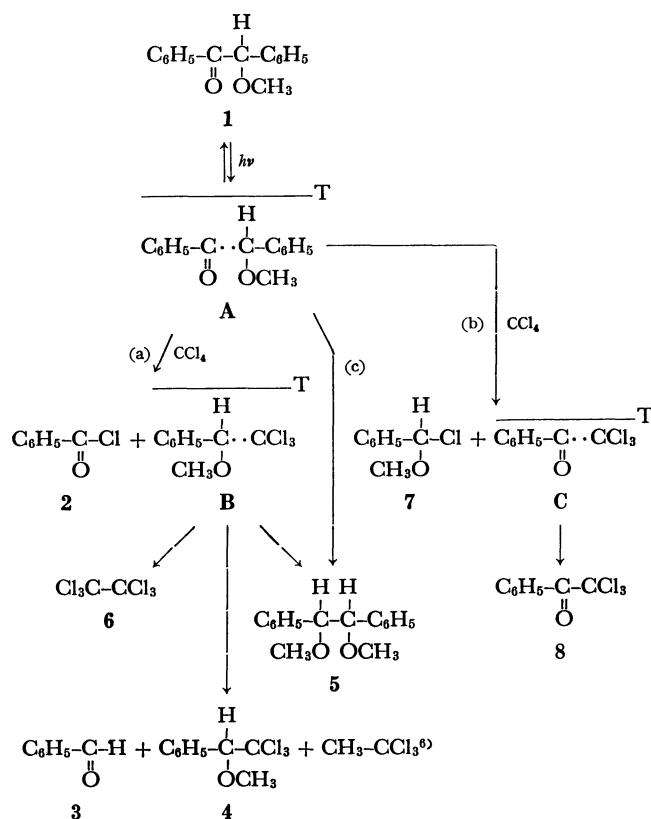
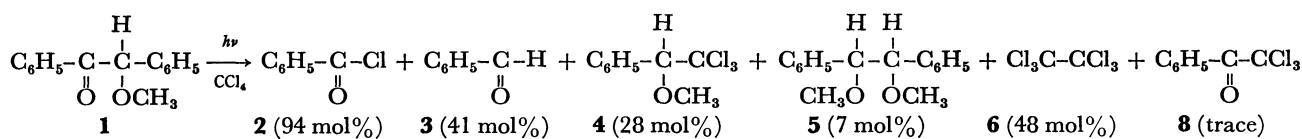


Fig. 1. Photo-CIDNP spectra of *O*-methylbenzoin in carbon tetrachloride.

A): During irradiation, B): before irradiation.



Scheme 2.



Scheme 1.

polarized signals in the region of aromatic protons cannot be assigned unambiguously, they consist of the overlapped aromatic proton signals of **1**, **2**, **3**, **4**, **7**, and **8**. The directions of the polarizations were in good agreement with the expected from the simple rule by Kaptein,³⁾ assuming the radical pair **A**, **B**,⁴⁾ and **C**⁴⁾ which have triplet multiplicity⁵⁾ (Scheme 2).

Observation of CIDNP signal due to **1** indicates the presence of the back process of α -cleavage, that is, regeneration of **1** from radical pair **A** once produced. Apart from the regeneration of **1**, the radical pair **A** could collapse *via* paths (a), (b), and (c) (Scheme 2). Almost quantitative yield of benzoyl chloride **2** (94 mol%) clearly shows that the major path is the path (a). α -Methoxybenzyl radical, the other moiety of the radical pair **A**, is also stabilized as benzaldehyde **3** (41 mol%), 1-methoxy-1-phenyl-2,2,2-trichloroethane **4** (28 mol%), and *O,O'*-dimethylbenzopinacol **5** (7 mol%). On the other hand, minor path (b) is taking place, because of detections of α -chlorobenzyl methyl ether **7** by CIDNP (signal 3) and α,α,α -trichloroacetophenone **8** by GLC.⁶⁾ Even if in part, path (b) as well as path (c) might contribute to the formation of hexachloroethane **6**. The relative intensity of polarized CIDNP signals (signal 1/signal 3) suggests again the preponderance of path (a), though the polarized intensity of CIDNP signals doesn't directly reflect the amounts of the corresponding products.

As described above photodecomposition of **1** in carbon tetrachloride takes a quite different path (path (a)) compared with those observed in other inert solvents, allowing a greater participation of carbon tetrachloride in it. This is highly suggesting that the use of carbon tetrachloride as an additive of "sensitizer," *O*-methylbenzoin, in photo-polymerization system is promising to raise the initiation rate.

Experimental

Materials. Commercially available benzaldehyde, benzoyl chloride, and hexachloroethane were used as the authentic samples without further purification. *O*-Methylbenzoin was a gift from Nippon Gosei Kagaku Co., Ltd., (Osaka, Japan) and used without further purification. 1-Methoxy-1-phenyl-2,2,2-trichloroethane,⁷⁾ *dl*- and *meso-O,O'*-dimethylbenzopinacol,⁸⁾ α -chlorobenzyl methyl ether,⁹⁾ and α,α,α -trichloroacetophenone¹⁰⁾ were synthesized according to the literatures. Carbon tetrachloride was dehydrated by

refluxing the commercially available reagent-grade of the reagent in the presence of calcium hydride and distilled under nitrogen atmosphere.

Photochemical Reaction. A carbon tetrachloride solution (15 ml) of *O*-methylbenzoin **1** (0.13 mmol) was irradiated with a high pressure Hg arc lamp (300 W) under nitrogen atmosphere at room temperature. After the complete consumption of **1**, the reaction mixture was analyzed by GLC (Silicone DC 550-column) compared with the authentic samples. Yields of the products were estimated by means of GLC.

CIDNP Measurement. The PS-100 type of NMR spectrometer manufactured by JEOL was modified for CIDNP measurement as described previously.¹¹⁾

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