CHEMISTRY LETTERS, pp. 155-158, 1991.

Photochemical Reactions of 4-Methyl-2-quinolinecarbonitrile with Optically Active 2-Phenylpropionic Acids.
The Magnetic-Field and Solvent Effects

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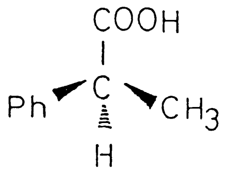
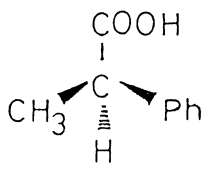
The photochemical reactions of 4-methyl-2-quinolinecarbonitrile with (S)- or (R)-2-phenylpropionic acid (PPCOOH) in benzene were investigated in the absence and in the presence of a magnetic field. The reactions were also examined in polar solvents such as dichloromethane and acetonitrile. The experimental results led to the conclusion that (S)- and (R)-forms of the 2-phenylpropionate ion ($PPCOO^{\ominus}$) differ distinctly in their chemical properties.

Until now all experiments have shown that all chemical reactions proceed symmetrically for left- and right-handed forms of chiral molecules; that is to say, enantiomers have identical chemical properties except toward optically active reagents.¹⁾ We now report that this principle is violated in the photochemical reaction of 4-methyl-2-quinolinecarbonitrile with optically active 2-phenylpropionic acid and further, a new type of magnetic field effect is observed in this reaction.

The irradiation of a benzene solution (50 cm^3) of 4-methyl-2-quinolinecarbonitrile 1 (50 mg) and (S)- or (R)-2-phenylpropionic acid PPCOOH (500 mg) afforded 2-(1-phenylethyl)-4-methylquinoline 2 in a high yield (>80%);$^{2)}$ hereafter, the photoreaction involving (S)- or (R)-PPCOOH is referred to as (S)- or (R)-reaction.

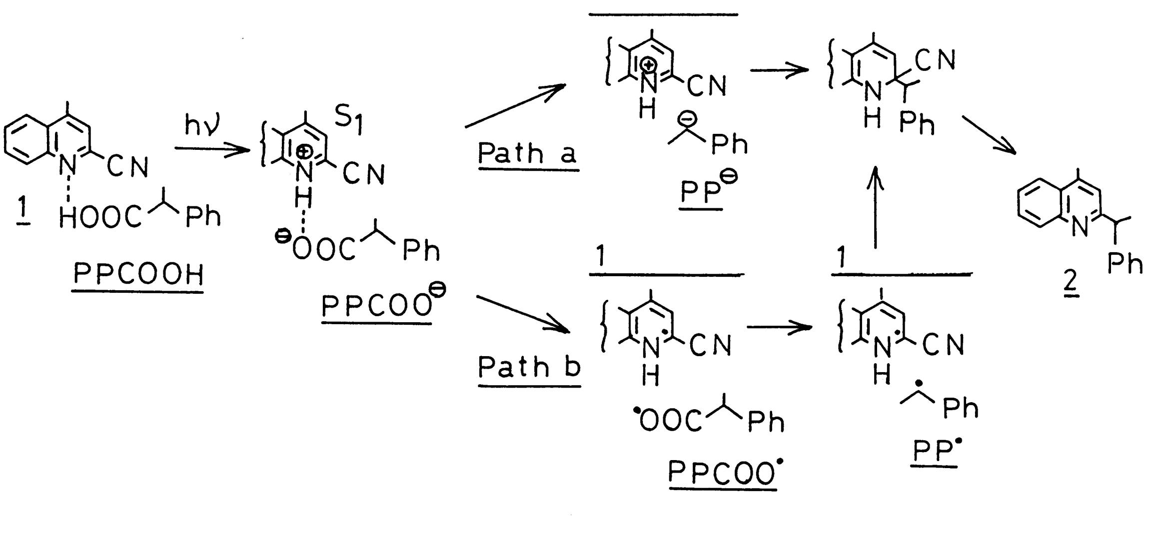


(S)-PPCOOH



(R)-PPCOOH

The photoreactions of aza-aromatic compounds such as quinoline, isoquinoline and acridine with some carboxylic acids have been extensively studied by Noyori et al. and discussed in terms of acid-base equilibrium in the S_1 state.$^{3)}$ The CIDNP studies have been also reported by Libman.$^{4)}$ According to the reaction mechanism



Scheme 1.

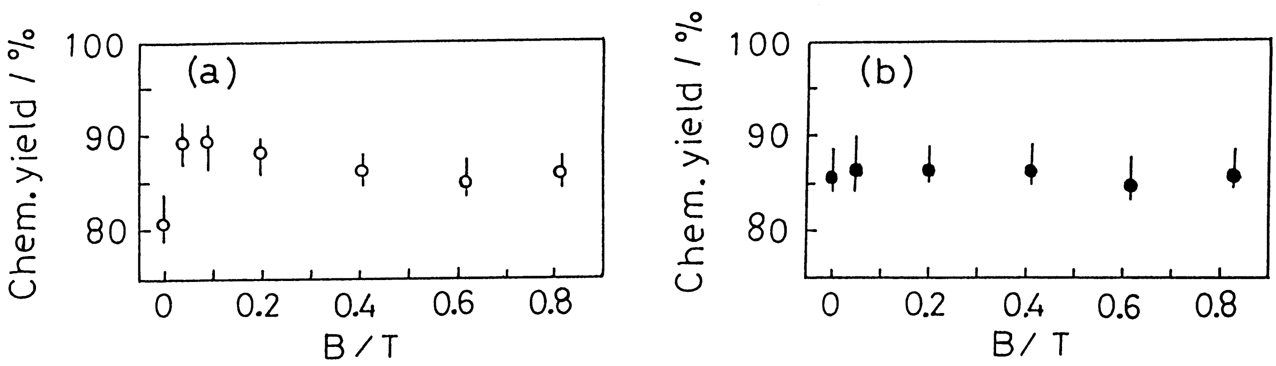


Fig.1. Chemical yield of the product 2 vs. magnetic-field strength.
(a): (R)-reaction, (b): (S)-reaction

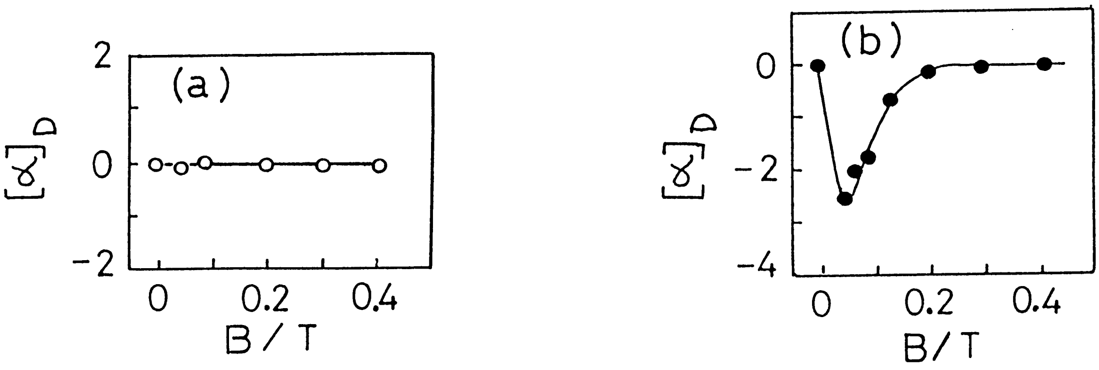


Fig.2. Specific rotation of the product 2 vs. magnetic-field strength.
(a): (R)-reaction, (b): (S)-reaction

proposed by Noyori et al.,[3)] as shown in Scheme 1, the photoreaction 1 → 2 is assumed to proceed via the S_1 state through the formation of ion-pair intermediate (Path a, ion-pair mechanism) or radical-pair intermediate (Path b, radical-pair mechanism). The photoreaction can be thus expected to show a magnetic field effect provided it proceeds via the S_1-born singlet radical-pair intermediate (Path b).[5)] For this reason, we carried out the reaction in the absence or presence of a magnetic field and determined the chemical yield and specific rotation $[\alpha]_D$ of the product 2.

(1) In the case of (R)-reaction (Fig.1a), the chemical yield of 2 was 81.2 ± 2.1% at the zero field, but it steeply increased by the application of a magnetic field of ca.45 mT to be 89.3 ± 2.3% (magnetic field effect due to HFI mechanism[5)]). In the case of (S)-reaction (Fig.1b), however, the chemical yield was nearly constant ($\approx$86%) regardless of the magnetic field. The results clearly indicate that (R)-reaction proceeds by the radical-pair mechanism (Path b), whereas (S)-reaction proceeds according to the ion-pair mechanism (Path a). (2) In the case of (S)-reaction (Fig.2b), the product 2 was optically active when the reaction was carried out at particular magnetic fields (45 mT – 0.1 T), $[\alpha]_D^{24}$ -2.5° (c 2.36, $CHCl_3$) at 45 mT;[6)] this is a new type of magnetic field effect unexpected before. The result strongly suggests that the ion-pair intermediate containing the asymmetric carbanion $PP^{\ominus}$ which has a pyramidal arrangement (Path a) is involved in (S)-reaction and that the rate of inversion of the carbanion $PP^{\ominus}$ undergoes magnetic perturbation at the particular magnetic field to be retarded although its mechanism is quite ambiguous. On the other hand, the product 2 of (R)-reaction was racemic even when the reaction was run in the presence of a magnetic field, suggesting (R)-reaction to proceed via the radical-pair intermediate containing the phenylethyl radical $PP^{\bullet}$ which has a virtually planar arrangement (Path b).

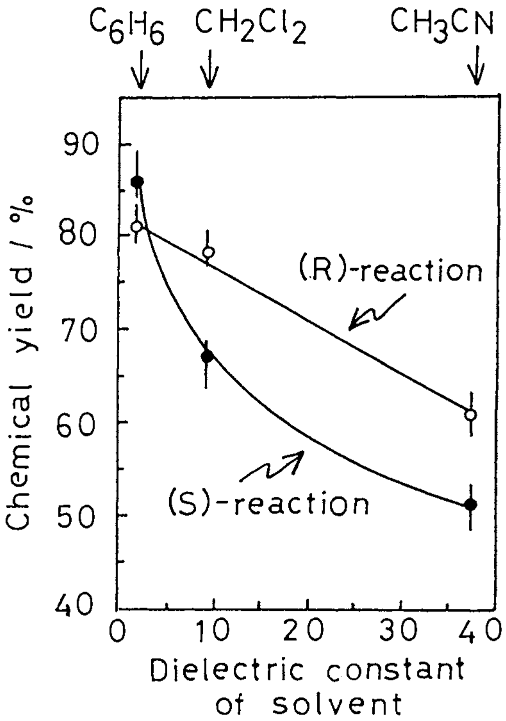


Fig.3. (S)- and (R)-reactions in benzene, dichloromethane or acetonitrile.

Next the photoreaction at the zero field was studied in polar solvents such as CH_2Cl_2 and CH_3CN. Figure 3 shows the chemical yield of 2 when the reaction was carried out in C_6H_6, CH_2Cl_2, or CH_3CN. As seen from this figure, (S)-reaction was much more subject to polar-solvent effect than (R)-reaction. Observation of such different patterns of solvent dependence provides further support for the idea that (S)- and (R)-reactions proceed by the ion-pair mechanism (Path a) and radical-pair mechanism (Path b), respectively.

In conclusion, examination of the magnetic-field and solvent effects upon the photochemical reaction 1 → 2 has revealed that (S)-reaction (Path a) proceeds by a mechanism different from that of (R)-reaction (Path b),[7] implying that (S)- and (R)-forms of the 2-phenylpropionate ion $PPCOO^{\ominus}$ differ distinctly in their chemical reactivities toward the excited quinolinium ion (Scheme 1). Further details will be reported elsewhere.

The author wishes to thank Professor H.Iwamura of the University of Tokyo for his valuable discussion.

References

1) Recently it has been pointed out that left- and right-handed chiral molecules are energetically inequivalent due to the parity-violating weak neutral current interaction between an electron and a nucleus. See R.A.Hegstrom, D.W.Rein, and P.G.Sandars, J.Chem.Phys., 73, 2329 (1980); A.J.MacDermott and G.E.Tranter, Chem.Phys.Lett., 163, 1 (1989).

2) The sample solution in a quartz vessel (44 X 45 X 25 mm^3) was irradiated with a 500W Ushio super-high-pressure Mercury Lamp (USH-500D) equipped with a Toshiba filter UV-31 at room temperature, while nitrogen was bubbled in. The unreacted 1 and product 2 were separated by means of silica-gel TLC (Merck silica-gel plate $60F_{254}$, layer thickness, 2 mm; eluent, hexane – ethyl acetate (5:1)). The amounts of 1 and 2 were determined spectrophotometrically. Analytical data of the product 2: mp 86 °C (from MeOH). MS m/z 247(M^+). ^1H-NMR($CDCl_3$) δ= 7.0–8.1(m,10H), 4.44(q,J=6.92 Hz,1H,-$\underline{H}$C(Ph)CH_3), 2.56(s,3H,-CH_3), 1.79(d,J=6.92 Hz,4H, -CH(Ph)$C\underline{H}_3$). Found: C,87.37;H,6.90;N,5.67%. Calcd for $C_{18}H_{17}N$: C,87.45;H,6.88;N,5.67%.

3) R.Noyori, M.Kato, M.Kawanishi, and H.Nozaki, Tetrahedron, 25, 1125 (1969).

4) J.Libman, J.Chem.Soc., Chem.Commun., 1976, 198.

5) Cf. Appendix in the following literature. N.Hata and N.Nishida, Bull. Chem.Soc.Jpn., 58, 3423 (1985). Recent reviews on magnetic field effects in chemical phenomena: U.E.Steiner and T.Ulrich, Chem.Rev., 89, 51 (1989).

6) $[\alpha]_D$ of the product 2 was determined with a JASCO digital polarimeter DIP-370. Solvent, $CHCl_3$; Temperature, 24 – 25 °C; c 1.9 – 2.3

7) (R)-reaction (or (S)-reaction) may proceed in part according to Path a (or Path b), but the present experimental results tell us nothing about it.

(Received September 19, 1990)