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CIDNP IN THE STEVENS REARRANGEMENT OF A SULFONIUM YLIDE

Hiizu Iwamura, Michiko Iwamura[*], Toshiaki Nishida[**],
Masayuki Yoshida and Juzo Nakayama

Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo, [*]Department of Chemistry, Faculty of Science, Toho University, Narashino-shi, [**]Application Laboratory of Nippon Electric Varian, Ltd., Azabu, Tokyo, Japan

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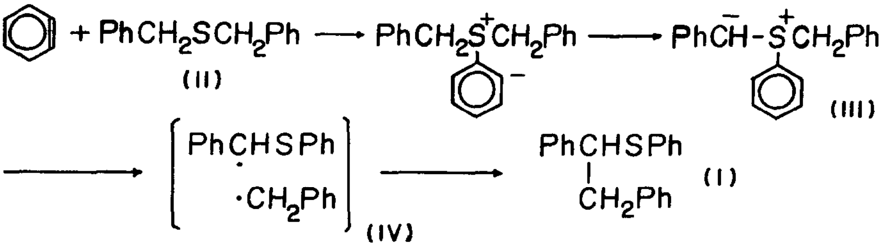
We would like to report the observation of nuclear spin polarization in 1,2-diphenylethyl phenyl sulfide (I) formed by action of benzyne on dibenzyl sulfide (II). When a solution of 1-(2-carboxyphenyl)-3,3-dimethyltetrazene [1] in II was heated at 190° in the nmr cavity of a Varian HA 100 D spectrometer (100 MHz), a series of strongly polarized signals were observed as shown in Figure 1a. After 600 sec the reaction was complete and the spectrum reproduced in Figure 1b was obtained. By comparison with the spectrum (Figure 1c) of the authentic sample of I dissolved in II, the major peaks in Figure 1b except the one at δ 3.68 ppm of the excess II were assigned the $>CH-CH_2-$ part of I, the parameters characteristic of the AB_2 spin system being $\Delta\nu_{AB} = 118$ Hz and $J_{AB} = 7.6$ Hz. Thus it is evident that the low field methine proton signals are of



enhanced absorptions in Figure 1a, while the high field CH_2 signals are emitting. Since the sulfonium ylide (III) can be considered as the intermediate of the reaction[2], the present findings of the nuclear spin polarization in I demonstrate the free radical dissociation-recombination mechanism of the rearrangement to give I. The S_Ni or the tight ion pair mechanisms had been proposed for the rearrangement.[3] The intermediacy of the radical pair (IV) was further confirmed semiquantitatively by applying the Closs mechanism which attributes development of nuclear spin polarization to singlet-triplet mixing in the radical pair by the g shift and hyperfine coupling.[4] The calculated spectrum (Figure 1d) obtained on the assumption of the following parameters is in good agreement with the observed one (Figure 1a). $A_1 = -2.3 \times 10^8$, $A_2 = -2.9 \times 10^8$, $J = 10^8$ radian.sec^{-1}, $\tau = 10^{-9}$ sec, $w_{er} > 50\, w_j$, $\Delta g = 10^{-3}$, where the subscripts 1 and 2 refer to the α-phenylthiobenzyl and benzyl radicals, respectively.

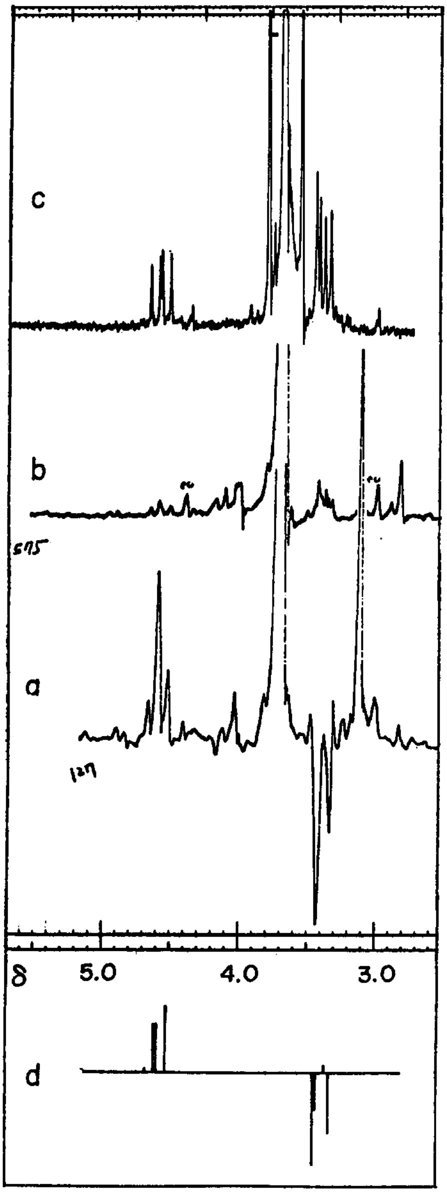


Figure 1. The nmr spectra of I ; (a) during the reaction, (b) after the reaction, (c) the authentic sample, and (d) the calculated polarization.

Recently it has been reported that the similar 1,2-rearrangements of nitrogen[5] and sulfur[6] ylides exhibit CIDNP when carried out in the nmr cavity. The second purpose of this communication is to point out the general trends that successful detection of CIDNP in the intramolecular rearrangements is so far limited only to those in which a concerted path is forbidden by formal application of the orbital symmetry rule.[7] Other examples are the Meisenheimer rearrangement,[8] the Wittig rearrangement,[9] and the 1,3-sigmatropic shifts in the exo-methylenecyclohexadiene system.[10] Application of the Woodward-Hoffmann rule to the heteroatomic systems is not straightforward twofolds. It is generally difficult to define the stereochemistry of the migrating termini and, secondly, since the bonds to be formed and to be broken are considerably different in character, the reaction can be more subject to thermodynamic factors than to orbital symmetry. Yet attempts at observing any polarization in the intramolecular rearrangement in which the cyclic array of the atomic orbitals in the transition state contains $4N+2$ electrons have all been unsuccessful. These include the 2,3-sigmatropic rearrangements of allylsulfonium ylides[6,11] and allylammonium ylides[12], 1,4-sigmatropy of the sulfonium ylide derived from benzyl allyl sulfonium salts[13], and the thermal N-nitroaniline rearrangement.[13]

Thus it is concluded that CIDNP serves as another operational test for the radical pair and biradical mechanisms of a given cyclic reaction.

References

(1) J. Nakayama, Y. Yoshida and O. Simamura, Chem. Commun., 1222 (1970).

(2) H. Hellmann and D. Eberle, Liebigs Ann., 662, 188 (1963).

(3) D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, N. Y., Chapt. 6 (1965).

(4) G. L. Closs, J. Am. Chem. Soc., **91**, 4552 (1969); G. L. Closs and A. D. Trifunac, ibid., **91**, 4554 (1969); **92**, 2183, 2186 (1970); G. L. Closs, C. E. Doubleday and D. R. Paulson, ibid., **92**, 2185 (1970).

(5) A. R. Lepley, J. Am. Chem. Soc., **91**, 1237 (1969); Chem. Commun, 1460 (1969).

(6) J. E. Baldwin, W. F. Erickson, R. E. Hackler and R. M. Scott, *Chem. Commun.*, 576 (1970); V. Schollkopf, G. Ostermann and J. Schossig, *Tetrahedron Letters*, 2619 (1969).

(7) R. B. Woodward and R. Hoffmann, "Conservation of Orbital Symmetry", Verlag Chemie, GmbH, Weinheim (1970).

(8) A. R. Lepley, P. M. Cook and G. F. Willard, *J. Am. Chem. Soc.*, **92**, 1101 (1970).

(9) P. Lansbury, unpublished but referred in F. Gerhart, *Tetrahedron Letters*, 5061 (1969).

(10) J. E. Baldwin and J. E. Brown, *J. Am. Chem. Soc.*, **91**, 3647 (1969); D. G. Morris, *Chem. Commun.*, 1345 (1969).

(11) R. W. C. Cose, A. M. Davies, W. D. Ollis, C. Smith and I. O. Sutherland, *ibid.*, 293 (1969); J. E. Baldwin, R. E. Hackler and D. P. Kelly, *ibid.*, 583 (1968).

(12) R. W. Jemison and W. D. Ollis, *Chem. Commun.*, 294 (1969).

(13) H. Iwamura, unpublished.