CHEMISTRY LETTERS, pp. 631-634, 1977. Published by the Chemical Society of Japan

REINVESTIGATION ON THE CIDNP IN THE THERMOLYSIS OF DISPIRO[2.2.2.2]DECA-4,9-DIENE

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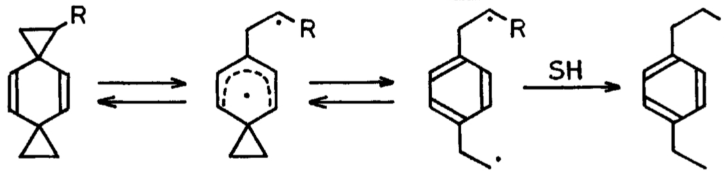
CIDNP in the thermolysis of dispiro[2.2.2.2]deca-4,9-diene and its derivative is reinvestigated and is found to be better explained in terms of S-T_- mixing in the singlet biradical 3 rather than S-T_0 mixing in 2 originally proposed.

We have previously reported that dispiro[2.2.2.2]deca-4,9-diene 1a shows CIDNP in the thermolysis, for which S-T_0 mixing in the biradical 2a has been proposed as the dominant process.[1] In the course of our continuing study on the CIDNP in 1a and its derivatives, it was revealed later that characteristics observed in the CIDNP signals of the aliphatic protons in 1 were compatible with the S-T_- mixing in the biradical 3 rather than the S-T_0 mixing in 2 as the polarization pathway.[2] Polarization in the olefinic protons (emission), however, remained unaccounted for, since S-T_- CIDNP derived from singlet biradical should appear as pure enhanced absorption.[3] Recently Closs and Czeropski have reported that the polarization in the olefinic protons in 1a could be explained in terms of nuclear Overhauser effect,[4] which has prompted us to report our results of reinvestigation on the CIDNP observed during the thermolysis of 1a and its derivative 1b.



1 2 3 4

a: R=H
b: R=$CH_2O_2CC_6H_5$

Since the NMR spectrum of the highly symmetrical 1a consists of the only two sharp singlets and there was no way to observe the informative multiplet effect but the net effect in the CIDNP in 1a, 1b was prepared[5]; NMR (CCl_4): δ 0.73 (4H, s, C_7-H and C_8-H), 0.8-1.1 (2H, m, C_2-H), 1.2-1.6 (1H, m, C_1-H), 4.32 (2H, d, J=8 Hz,

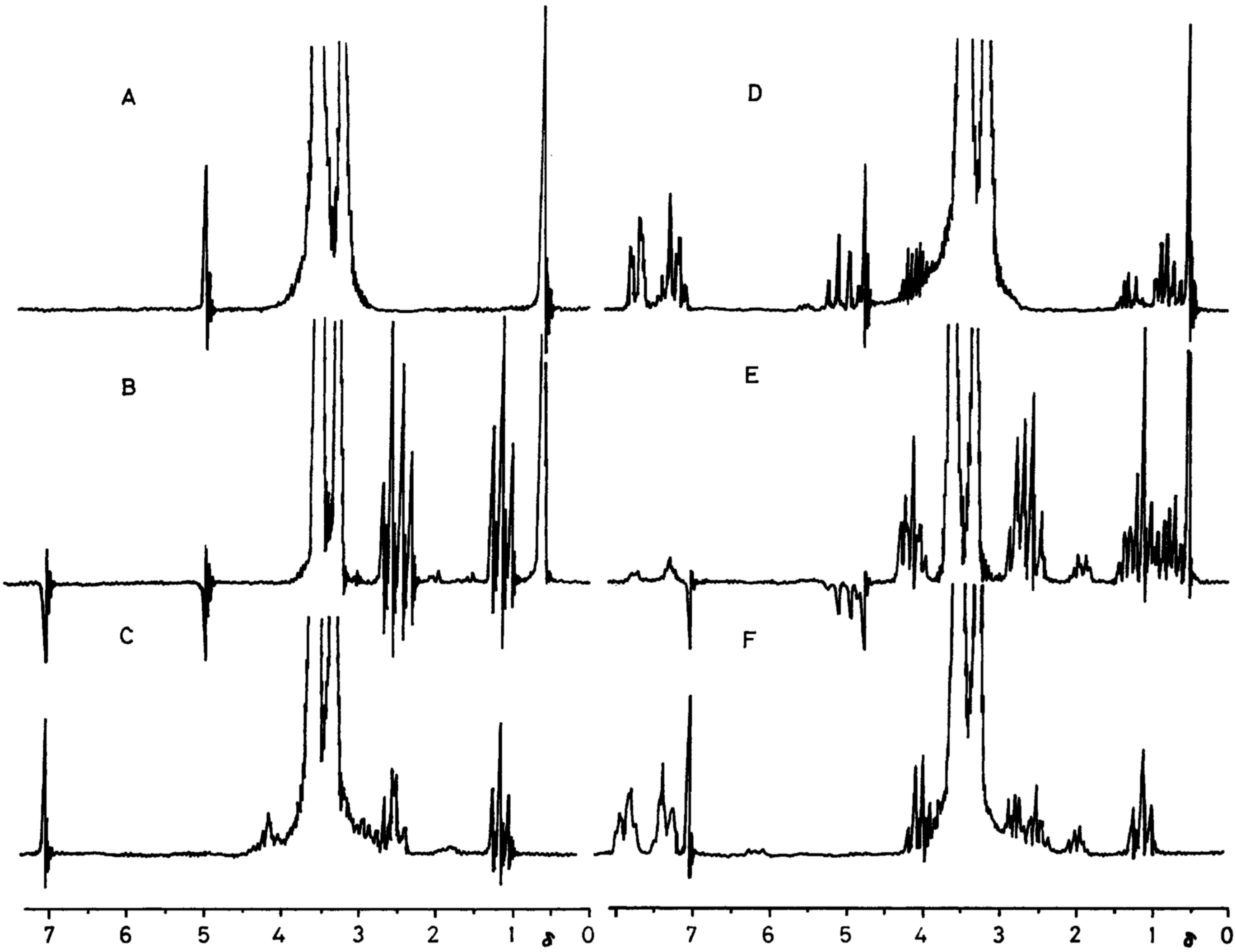
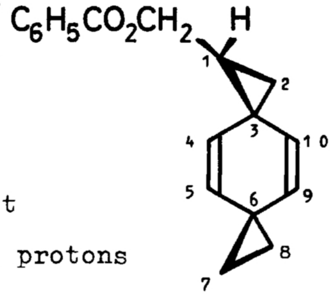


Fig.I (A) Spectrum of <u>1a</u> at 23°C. (B) Spectrum obtained during the thermolysis of <u>1a</u> at 193°C. (C) Spectrum taken after the thermolysis of <u>1a</u> completed. (D) Spectrum of <u>1b</u> at 23°C. (E) Spectrum obtained during the thermolysis of <u>1b</u> at 180°C. (F) Spectrum taken after the thermolysis of <u>1b</u> completed. All the spectra were taken in triglyme on a JEOL PS-100 spectrometer at 100 MHz. Strong absorption at δ 3-4 is due to the solvent. Spectrum amplitudes of (A) and (C) are approximately four times that of (B) and those of (D) and (F) are also approximately four times that of (E).

CH_2-protons of benzoyloxymethyl group),[6] 4.88 (2H, s, C_9-H and C_{10}-H), 4.95-5.3 (2H, AB quart, J=10 Hz, C_4-H and C_5-H), 7.2-7.5 and 7.9-8.05 (5H, two m, aromatic protons). The 100 MHz NMR spectra recorded during the thermolysis of <u>1a</u> and <u>1b</u> in triglyme are shown in Fig. I together with the spectra of <u>1a</u> and <u>1b</u>[6], and of their decomposition products. Some characteristics in the CIDNP signals of the aliphatic

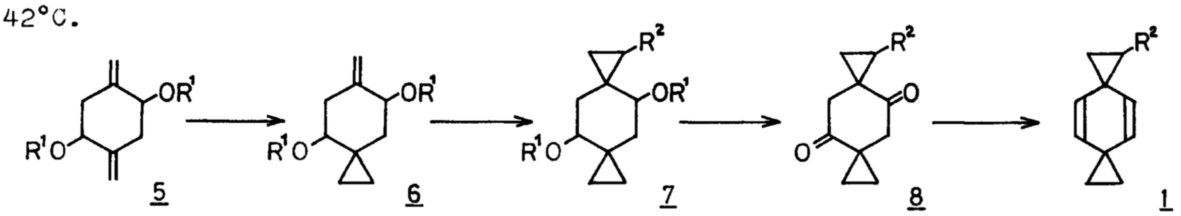


protons are readily recognized. i) Polarization in α-protons occurs with the same sign as that in β-protons; all the C_1-H, C_2-H and methylene protons of the benzoyloxymethyl group in 1b exhibit enhanced absorption. ii) Polarization in the recombination product has the same sign as that in the product resulting from the solvent transfer reaction; the cyclopropyl protons in 1a and both the methyl and methylene protons in p-diethylbenzene 4a show enhanced absorption.[7] iii) No multiplet effect is detected notwithstanding with the expectation that there will not be significant difference between the g-values of the two radical centers in both the biradicals 2 and 3. These results are incompatible with the S-T_0 CIDNP[8] and better accomodated by the S-T_- CIDNP in which all the CIDNP signals should occur in pure enhanced absorption when the biradical is generated from singlet precursor.[3] Of the two possible biradical intermediates 2 and 3, the former would not be responsible for the polarization since S-T_- mixing in 2, contrary to the experimental observation, should give rise to enhanced absorption in the olefinic proton signals. S-T_- mixing in 3, in which hyperfine coupling on the aromatic protons is insignificantly small,[9] accounts satisfactorily for the polarization in the aliphatic protons. As shown in Fig. I, the olefinic protons appear as emission. When the cyclopropyl protons were saturated with the strong H_2 field during the CIDNP measurement, polarization in the olefinic protons disappeared as has been reported by Closs and Czeropski.[4] Another emission signal at δ 7.10 also disappeared when the polarized benzyl protons in the decomposition product 4 at δ 2.6 were subjected to the strong H_2 field. Therefore the observed emission signals of the olefinic and aromatic protons probably result from the nuclear Overhauser effect in 1 and 4, respectively, polarized through the S-T_- transition in 3, but not from CIDNP.

The present results show that S-T_- CIDNP can be observed in the product resulting from singlet biradical at ordinary NMR field strength, provided that the biradical has a length to allow S-T_- transition via hyperfine interactions[3b] and the intermolecular reaction path, independent of the electronic multiplicity of the biradical, is available.[10, 11]

REFERENCES AND NOTES

1) T. Tsuji and S. Nishida, J. Am. Chem. Soc., 96, 3649 (1974).
2) T. Tsuji and S. Nishida, presented at the 15th Symposium on Organic Free-Radical Reactions, Tokyo, Oct 1974.
3) a) G. L. Closs, J. Am. Chem. Soc., 93, 1546 (1971).
   b) G. L. Closs and C. E. Doubleday, ibid., 94, 9248 (1972); 95, 2735 (1973).
4) G. L. Closs and M. S. Czeropski, Chem. Phys. Lett., 45, 115 (1977).
5) The dispiro compound 1b was prepared as follows. The bis-trimethylsilyl ether 5d was mono-cyclopropanated with CH_2I_2 and Zn(Cu) to 6d, which was subsequently treated with ethyl diazoacetate in the presence of Cu powder. The resulting ester 7de was reduced with $LiAlH_4$ to the alcohol 7df. After acetylation, 7dg was hydrolyzed to 7cg. The oxidation of 7cg with the Jones reagent and the subsequent hydrolysis afforded the diketone 8f, bis-tosylhydrazone of which was treated with n-BuLi in THF to give 1f. Mp 48.5-49.5°C. Benzoate 1b, mp 41-42°C.



5 6 7 8 1

a, R^2=H; b, R^2=$CH_2O_2CC_6H_5$; c, R^1=H; d, R^1=$Si(CH_3)_3$; e, R^2=$CO_2C_2H_5$;
f, R^2=CH_2OH; g, R^2=$CH_2O_2CCH_3$.

6) Methylene protons of benzoyloxymethyl group appear as two quartets in triglyme.
7) p-Diethylbenzene was obtained in 75% yield in the thermal decomposition of 1a in diglyme.
8) H. R. Ward, Accounts Chem. Res., 5, 18 (1972): R. Kaptein, J. Am. Chem. Soc., 94, 6251 (1972).
9) J. K. Kochi and P. J. Krusic, ibid., 91, 3940 (1969).
10) Since intramolecular reaction in T_- state is improbable, even though sufficient S-T_- mixing occurs, no net intersystem crossing take place in the reaction of singlet biradical unless electronic multiplicity-independent intermolecular reaction pathway is available. In the present reaction, hydrogen abstraction reaction from the solvent molecule probably served as such a pathway.
11) There was no precedent of the S-T_- CIDNP derived from singlet biradical until recently Kaptein et al.[12] reported the S-T_- CIDNP from thermally-generated biradical in low magnetic field. The thermal decomposition reaction of 1, to our knowledge, is the first to exhibit the S-T_- CIDNP from the singlet biradical at typical NMR field strength.
12) R. Kaptein, P. W. N. M. Van Leeuwen, and R. Huis, Chem. Phys. Lett., 41, 264 (1976).

(Received March 14, 1977)