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CHEMICALLY INDUCED DYNAMIC NUCLEAR POLARIZATION IN THE CYCLOADDITION REACTION OF DISPIRO[2.2.2.2]DECA-4,9-DIENE WITH DIMETHYL TRANS,TRANS-MUCONATE

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The cycloadducts of dispiro[2.2.2.2]deca-4,9-diene I to dimethyl trans,trans-muconate II formed by way of the singlet diradical intermediate exhibited CIDNP signals in spite of the absence of diffusive separation of the correlated radicals.

The radical pair theory, proposed independently by Closs[1] and by Kaptein and Oosterhoff,[2] has been quite successful in explaining the phenomenon of the chemically induced dynamic nuclear polarization (CIDNP).[3-5] According to this theory, the electronic multiplicity-independent process competitive with the reaction of the radical pair in the cage is required to observe CIDNP effect.[1,2] For the radical pair, the diffusive separation generally provides such a process. For the diradical, however, the diffusive separation is apparently impossible. In fact, almost all observations of CIDNP reported so far were made in the radical pair reactions and, to our knowledge, only one instance of CIDNP has been known for the reaction of singlet diradical.[6,7] We report here another successful observation of CIDNP effect in the reaction products derived from the singlet diradical intermediate.

Previously we reported the cycloaddition reaction of dispiro[2.2.2.2]deca-4,9-diene I[8] with 1,3-butadienes which afforded [8]paracyclopha-4-enes.[9] In the presence of p-thiocresol the reaction afforded no cycloadducts but the hydrogen abstraction products and thus was found to proceed by way of the diradical intermediates (Scheme I). This finding and rarity of the CIDNP in the reaction of diradical prompted us to seek the effect in the cycloaddition reaction of I. An nmr tube containing the solution of I and dimethyl trans, trans-muconate II in diphenyl ether (0.5 mol/l in I and 1.0 mol/l in II) was placed in the preheated (190°C) probe of a JEOL PS-100 spectrometer and the nmr spectrum was recorded repeatedly. The observed spectrum in the region of δ 1.0 to 5.0 is shown in Fig I. The cycloaddition of I to II in benzene afforded VI and VII in 54% and 9% yields respectively. These cycloadducts exhibited the characteristic double doublets at δ 4.1 and 4.3 in their nmr spectra, which were ascribed to the olefinic protons of VI and VII shielded by the underlying aromatic ring. Presence of two double doublets in the nmr spectrum of the reaction product (Fig Ib) showed that appreciable amounts of VI and VII were also formed in diphenyl ether. Observed emission at δ 4.1 and 4.3, therefore, would certainly be due to the polarized olefinic protons of VI and VII.

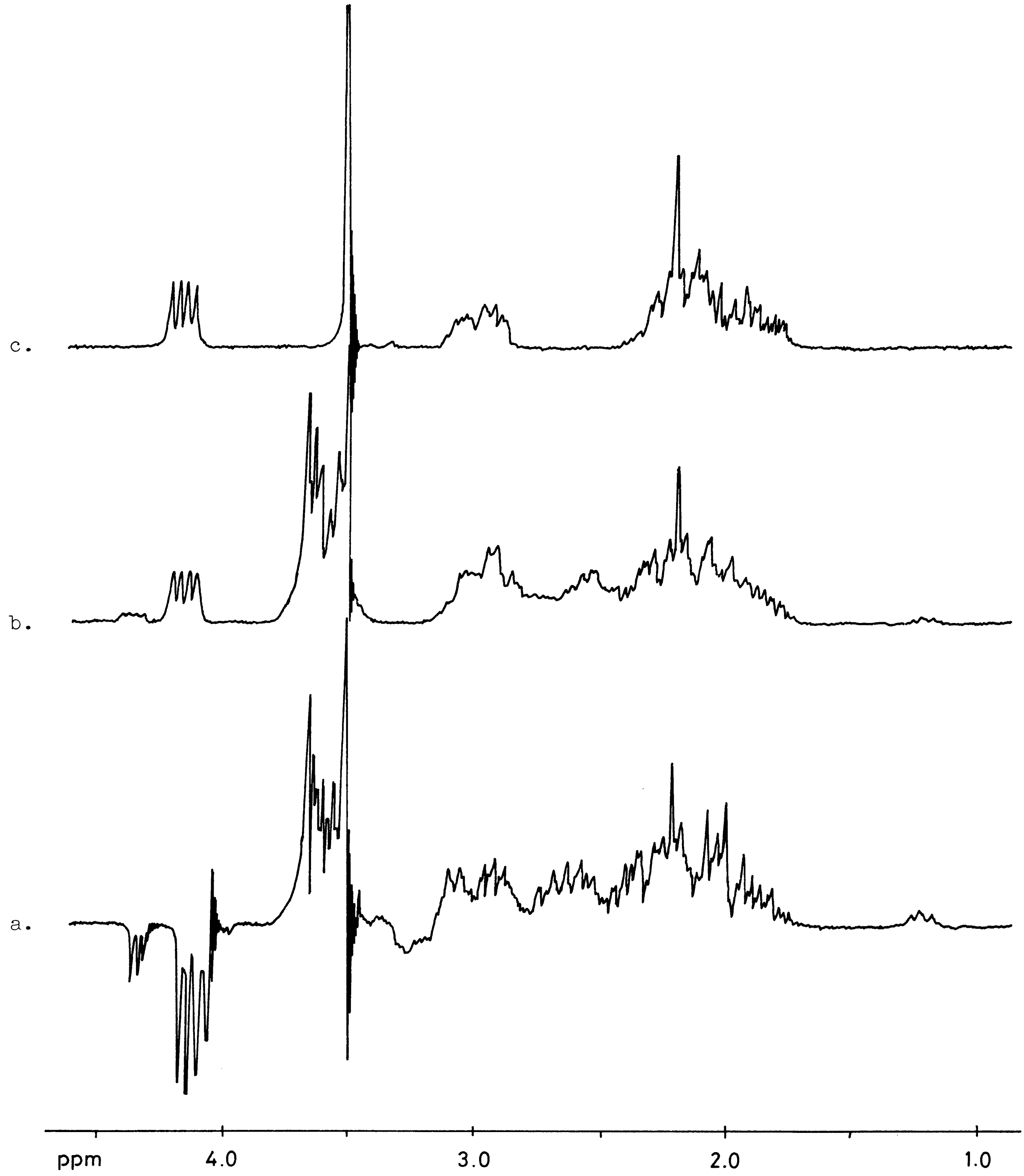


Fig I. Nmr spectra in diphenyl ether at 190°C.

a. Spectrum recorded during the reaction of dispiro[2.2.2.2]deca-4,9-diene with dimethyl trans,trans-muconate.

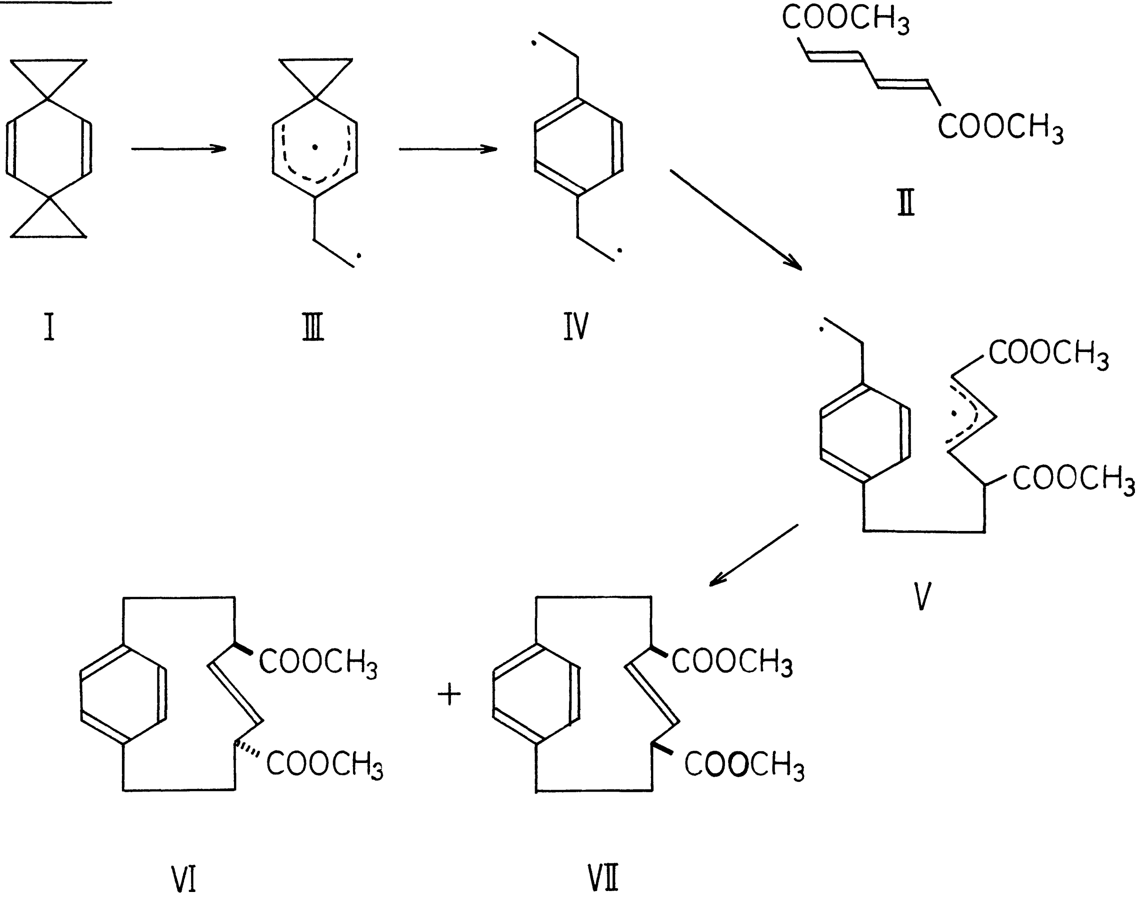
b. Spectrum after the reaction completed. Spectrum amplitude is three times that of a.

c. Spectrum of VI.

Enhanced complex absorptions observed in the region of δ 1.6 to 3.2, where the signals due to the aliphatic protons of VI and VII appeared, could not be analysed because of overlapping with the absorptions due to the by-products.

Homolytic cleavage of a cyclopropane bond initiates the reaction.[9] The radical whose odd-electron delocalized over the six-membered ring in the resulting diradical III is structurally identical with the posturated intermediate in the 1,2-aryl migration. Therefore, it will be reasonable to assume that III rearranged rapidly to IV under the reaction conditions. Thus polarization of olefinic protons would be brought about through the dynamic process of the diradical V. In allyl radical, the hyperfine coupling constant of proton on the central carbon atom is generally positive while those on the end carbon atoms are negative.[11,12] Therefore, the polarization of olefinic protons in VI and VII would be partially canceled because of the degeneracy. Cancelation, however, would not be complete since the hyperfine coupling constant of proton on the central carbon atom should be much smaller.[11-13] The singlet multiplicity of the diradical precursor (thermal reaction from ground state) led to the conclusion that $g_{-C_6H_4CH_2CH_2\cdot} > g_{-\overline{CH-\dot{C}H-CH}COOCH_3}$.

Scheme I



The present results showed that the CIDNP effect could be observed in the products derived from the reaction of singlet diradical in spite of a prediction by Closs,[1] in accord with the observation of Kaptein et al.[7] The reaction of the diradical V with another diene would provide one of the processes competitive with collapse of V to VI and VII. In the reaction of I with 1,3-butadiene, 1:2 adducts have been isolated besides 1:1 cycloadducts.[9]

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13. Presence of methoxycarbonyl group on the end carbon atom of allyl radical would not appreciably affect the distribution of the spin density of the odd-electron (therefore, hyperfine coupling constants of protons).[11]

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