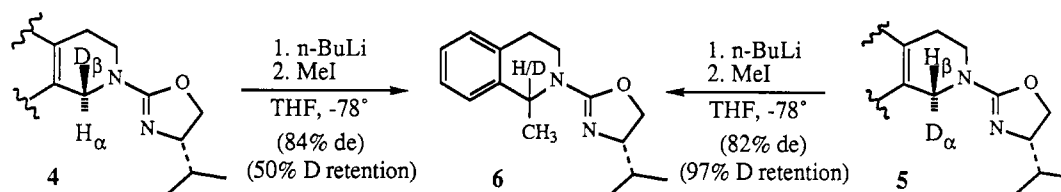


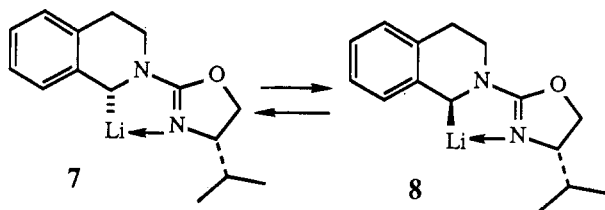
Scheme III



coordinated alkyllithium whereby the butyl group is anti to the isopropyl (Figure 1).

The stereoselectivity in the deprotonation is determined quantitatively by the relative rates of abstraction of the two protons,  $H_\alpha$  and  $H_\beta$  (Scheme II). This quantity, as well as the isotope effect, can be calculated from the ratios of  $6D/6H$  obtained from **4** and **5**.<sup>10</sup> The calculations yield a relative rate of 5.8 and an isotope effect of 5.9.<sup>11</sup> Thus, when the deuterium is up (as in **4**, Scheme III), the stereoselectivity of the deprotonation (loss of  $D_\beta$  favored) is opposed by the kinetic isotope effect, which directs the base to  $H_\alpha$ . The result is deprotonation at both sites. In contrast, when the deuterium is down (as in **5**, Scheme III), both the stereoselectivity of the deprotonation and the isotope effect work in concert, directing the base to  $H_\beta$ , and virtually complete retention of deuterium is observed.

I believe that since both deuterated epimers give the same diastereomeric product ratios while at the same time deprotonating via different mechanisms, a set of equilibrating lithiated amino-oxazolines such as **7** and **8** are implicated. It also is possible that



there are equilibrating ion-pair aggregates, but further work is required on this point. It is interesting that the stereochemical sense by which these equilibrating anions are quenched is a function of the electrophile. Most intriguing is the opposite configuration obtained when the lithiated oxazolines are quenched with  $RX$  and  $Me_2SO-d_6$ . Two possibilities seem to be the most likely explanations: (1) that the position of the equilibrium is reversed when  $Me_2SO$  is added or (2) the organolithium is quenched with retention of configuration in one case and inversion in the other. The two possibilities cannot be distinguished with the presently available data.<sup>12</sup>

These results are consistent with those reported by Meyers and Dickman in the accompanying paper.<sup>4b</sup> The difference between the formamidines and the oxazolines is the lack of an isotope effect in the deprotonation of the formamidines. A dependence of asymmetric induction on the temperature of the alkyl halide quench of lithiated formamidines has been noted,<sup>13</sup> raising the possibility of thermodynamic control of equilibrating organolithiums in that system as well. It is noteworthy that bidentate chelation of the lithium by the chiral auxiliary is not necessary

for high levels of asymmetric induction (cf., Scheme I). However, a "monodentate" formamidine derived from  $\alpha$ -methylbenzylamine gives only moderate selectivity (10–52%).<sup>13</sup> What is required for good asymmetric induction is a nonrotating bond between the ligating nitrogen and the stereocenter of the chiral auxiliary. In the oxazolines, this is provided by the ring. In the formamidines, bidentate chelation serves the same purpose.

**Summary.** The experiments described herein clearly demonstrate that the stereoselectivity which exists in the deprotonation to form dipole-stabilized anions of aminooxazolines is not the source of the stereoselectivity observed for the overall process. The relative rates of deprotonation indicate that **8** is the diastereomer formed initially, consistent with a coordinated alkyllithium base preferring to adopt a conformation anti to the isopropyl. The stereochemical sense of the reaction has the lithiated isoquinolyl-oxazolines (when drawn as in either **7** or **8**) being quenched by alkyl halides from the same side as the isopropyl but from the opposite side with  $Me_2SO$ .

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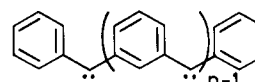
## Magnetic Interaction of Two Diphenylcarbene Units Linked with an Ethylenic Double Bond

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In 1967, Itoh and Wasserman et al. established independently that the dicarbene **1**, consisting of two phenylcarbene units attached to the meta positions of a benzene ring, had a quintet ground state.<sup>1</sup> The finding awoke both the experimental<sup>2</sup> and



1:  $n = 2$   
2:  $n = 4$

theoretical<sup>3</sup> interests in organic high-spin molecules and partic-

(10) Eliel, E. L.; Hartmann, A. A.; Abatjoglou, A. G. *J. Am. Chem. Soc.* **1974**, *96*, 1807–1816. The only assumption involved is that the isotope effect is the same for  $H_\alpha$  and  $H_\beta$ . The isotope effect is given by  $IE = (6D/6H)_4^{1/2}/(6D/6H)_5^{1/2}$  while the relative rates are given by  $k_\beta/k_\alpha = (6D/6H)_4^{1/2}/(6D/6H)_5^{1/2}$ , where  $(6D/6H)_4$  and  $(6D/6H)_5$  are the deuterium to hydrogen ratios in both stereoisomers of **6**, obtained from **4** and **5**, respectively. The actual values are  $(6D/6H)_4 = 1.01$  and  $(6D/6H)_5 = 34.5$ .

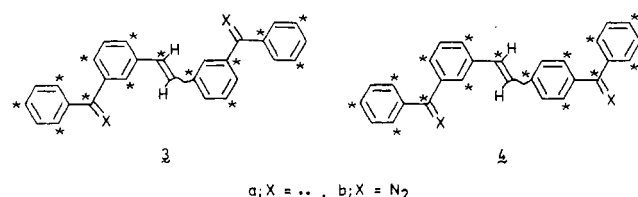
(11) The results are subject to some error due to the less than 100% stereoselectivity in the  $Me_2SO-d_6$  deuteration but clearly indicate that the kinetic isotope effect and the stereoselectivity of the deprotonation are of comparable magnitude.

(12) We have recently learned that in a related system (isoindolyl-oxazolines), the stereochemical preference for alkylation is reversed when the solvent is changed from THF to ether: Chemburkar, S., unpublished results. **Note Added in Proof.** In side-by-side experiments at -78 °C, the ratio of **2** to **3** (Scheme I) was 9/1 in THF and 2/1 in ether.

(13) Meyers, A. I.; Fuentes, L. M. *J. Am. Chem. Soc.* **1983**, *105*, 117–118.

ularly in the possibility of organic ferromagnets. Recently we have shown that the tetracarbene **2** has a nonet ground state which is the highest spin multiplicity ever reported for organic molecules.<sup>4</sup> Whereas **1**, **2**, and the homologues have the origin of the spins in the main framework of the molecules, there is another possibility of designing a series of high-spin systems in which the origin of the spins resides on the appendage of a mainframe conjugate system. To study the latter interaction, we have prepared the model systems and studied the magnetic interaction of two triplet diphenylcarbene units connected with an ethylenic double bond, which is thought to be an accessible connecting group as in polyacetylenes from a synthetic point of view.

Two regioisomeric dispositions, namely, meta,meta' isomer **3a** and meta,para' isomer **4a**, were taken into account. According



to the Longuet-Higgins' theory on  $\pi$ -nonbonding molecular orbitals (NBMO) in alternant hydrocarbons,<sup>5</sup> both **3a** and **4a** have  $N = 28$  atomic orbitals and the maximum number of double bonds occurring in any resonance structure is  $T = 13$ . The number of NBMO ( $N - 2T$ ) is therefore two. The modern theory by Borden and Davidson<sup>6</sup> differentiates **3a** and **4a** as disjoint and nondisjoint, respectively. Therefore, **3a** is predicted to have a singlet ground state. The interaction of the two carbenes is expected to be ferromagnetic in meta,para' isomer **4a** and to lead to a quintet ground state. The numbers of starred and unstarred carbon atoms are equal in **3a** and differ by two in **4a**. Therefore, the same theoretical prediction is obtained according to the valence-bond theory of Ovchinnikov<sup>3b</sup> and Klein.<sup>3d</sup> The dicarbenees were generated by irradiation ( $>380$  nm) of the corresponding bis(diazo) precursors, **3b** and **4b**, in a 2-methyltetrahydrofuran (2-MTHF) glass at 16 K. The preparations of the precursors were as follows: 3,3'- and 3,4'-dibromostilbenes were lithiated with *n*-butyllithium in ether, followed by the reaction with benzaldehyde to give the corresponding diols. These diols were oxidized to the diketones with pyridinium chlorochromate in dichloromethane. Each diketone was separated by gel permeation chromatography into the cis and trans isomers and converted separately to the corresponding hydrazone in a usual manner ( $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}/\text{EtOH}$ ) under nitrogen atmosphere, which was then oxidized with activated  $\text{MnO}_2$  in ether to the cis and trans isomers of **3b** and **4b**.

The ESR spectrum obtained by the photolysis of *cis*-**3b**<sup>7</sup> at 16 K contained a set of signals (marked \* in Figure 1) characteristic of a triplet species<sup>8</sup> and a pair of conspicuous signals (ca. 250 mT) which showed a dramatic temperature dependence. First their intensity increased as we raised the temperature, reached a

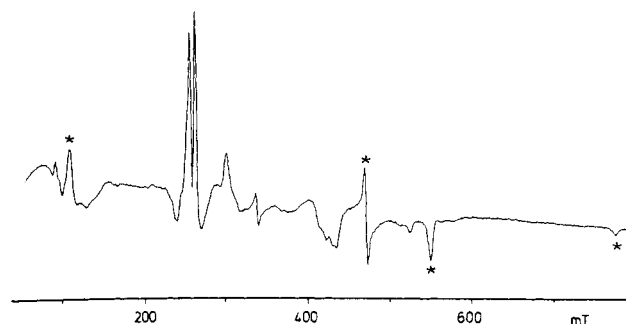


Figure 1. ESR spectrum ( $\nu_0 = 9.323$  GHz) recorded at 45 K after photolysis of *cis*-**3b** in 2-MTHF at 16 K. The starred signals are due to the triplet monocarbene.<sup>8</sup>

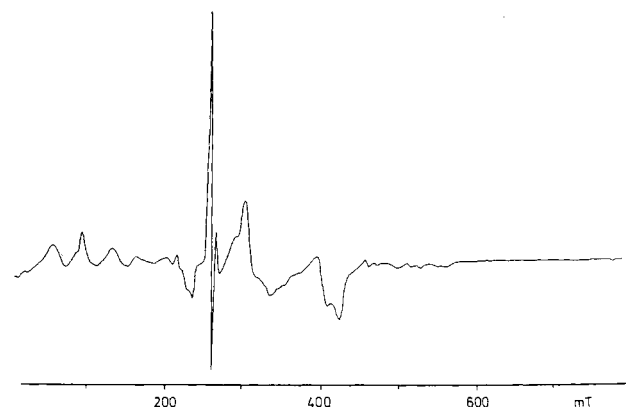


Figure 2. ESR spectrum ( $\nu_0 = 9.323$  GHz) obtained by the irradiation of *trans*-**4b** in 2-MTHF at 16 K.

maximum at 50 K, and then decreased somewhat and eventually irreversibly at above 65 K. In contrast, an intense signal at around 250 mT and some weak signals appeared from **4b** (Figure 2).<sup>7</sup> The intensity of these signals decreased linearly with the reciprocal of the temperature as dictated by Curie law.

Compared with the analyzed ESR spectra of similar quintet species in matrices,<sup>9</sup> it is reasonable to assume that the characteristic signals at around 250 mT in both isomers are derived from the dicarbenees **3a** and **4a** in the quintet states. The contrasting temperature dependence between the regioisomers seems to indicate that the dicarbene **4a** has a quintet ground state, while the quintet state of **3a** is populated thermally but lies very close to the ground state.<sup>10</sup>

It is concluded that the two remote triplet diphenylcarbene moieties linked with a carbon-carbon double bond interact sufficiently through the bonds to form a quintet state, which is likely to be a ground state in the meta,para' isomer **4a** as predicted by theory. A carbon-carbon double bond is concluded to be an effective linking group for the construction of organic molecules with high-spin multiplicities.

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(6) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587.

(7) Although the pattern of the quintet spectra was somewhat different between the cis and trans isomers, there were little differences in the temperature behaviors.

(8) The intensity of these signals decreased linearly with the reciprocal of the temperature, showing that they were due to triplet mono(diazo)monocarbene or monocarbene which were formed by the reaction of one carbene site of **3a** with the surroundings.

(9) It is known that the zfs parameters of the quintet species consisting of two weakly interacting triplet carbenes are calculated from the sum of dipolar coupling tensors of each triplet carbene.<sup>2d</sup> Our preliminary calculations show that the zfs parameters can change in a wide range ( $|D| = 0.06\text{--}0.13$  cm<sup>-1</sup>), depending on the relative orientation of the two carbene units in various conformations of **3a** and **4a**. It has been confirmed, however, that the quintet species with the above zfs parameters should show intense signals at 250–300 mT. Recently we reported the quintet dicarbenees with a [2.2]paracyclophane skeleton, the zfs parameters of which were determined by the computer-simulation technique (preliminary reports: Izuoka, A.; Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1985**, *107*, 1786).

(10) According to the theory on two weakly interacting triplet species,<sup>2d</sup> a thermally populated triplet is expected to lie between the singlet and quintet states. Since the triplet state was not found in these experiments, presumably because of the overlap with other signals, it is difficult to estimate the accurate energy gap between the singlet and quintet states. However, from the temperature dependence of the quintet state, this state is estimated to lie by ca. 200 cal/mol above the singlet ground state.