

symmetrically trans doubly bridged structure **6** (D_{2h}) is only 1.9 kcal/mol higher in energy than the most stable one. The present X-ray results of **2** evidently support the trans doubly bridged structure of lithium.

Further works are in progress.

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Supplementary Material Available: Listings of atomic parameters and thermal parameters (Tables I and II), anisotropic temperature factors (Table III), distances for heavy atoms (Table IV), distances for hydrogen atoms (Table V), angles for heavy atoms (Table VI), and angles for hydrogen atoms (Table VII) (7 pages); listing of observed and calculated structure factors (Table VIII) (9 pages). Ordering information is given on any current masthead page.

Kinetics and Mechanism of the Reaction of Diphenylcarbene with [1.1.1]Propellane¹

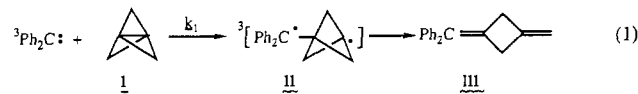
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Molecules with inverted structures at carbon are of considerable interest to theoreticians and experimentalists as a result of the unusual bonding and reactivity properties that result from these highly strained structures.²⁻⁵ [1.1.1]Propellane (**I**) is the smallest member, and perhaps one of the most interesting, of this group of substrates. **I** was first prepared by Wiberg et al. in 1982.⁶ More recently Szeimies et al. reported a more convenient synthesis, which has been employed in our work.⁷

I has been reported to react with various substrates by a presumed free-radical mechanism,^{8,9} for example, *t*-BuOCl and PhSSPh add readily across the central bond in **I**.⁸ Our own kinetic work shows that *tert*-butoxyl and thiophenoxyl radicals are scavenged by **I** with rate constants in excess of $10^6 \text{ M}^{-1} \text{ s}^{-1}$.¹⁰

Triplet carbenes add to olefins nonstereospecifically by a biradical mechanism which is believed to involve stepwise formation of the two carbon bonds.¹¹ We reasoned that reaction of diphenylcarbene with **I** could involve addition of the carbene to one of the bridge positions to yield a biradical (**II**). We report here kinetic and product studies which demonstrate that addition does occur, ultimately leading to the formation of **III**, reaction 1.



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(10) Rate constants of 2.8×10^6 and $6.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ were measured for reaction of *tert*-butoxyl and phenylthiyl radicals, respectively, with [1.1.1]-propellane. The addition of phenylthiyl is reversible at room temperature.

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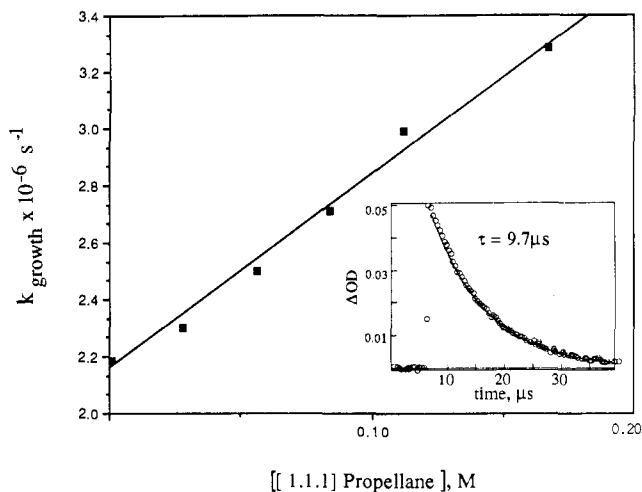


Figure 1. Plot of the growth of benzophenone oxide at 410 nm in benzene saturated with 1% oxygen in nitrogen as a function of [1.1.1]propellane concentration. Inset: decay trace for biradical **II** at 330 nm in Freon-113 under nitrogen.

Irradiation of a solution of 8.1 mM diphenyldiazomethane in benzene containing 0.28 M **I** until the characteristic color of the diazo compound had been discharged leads cleanly to a single product which was isolated and characterized as carbene/propellane adduct **III**. Both ${}^1\text{H}$ and ${}^{13}\text{C}$ NMR and GC/MS data are fully consistent with the assigned structure.¹² The NMR spectra of **III** show similar methylenecyclobutane resonances to those which we have observed in the dimer of **I**.¹³

In order to determine the kinetics of the initial step in reaction 1 (k_1) we performed a series of laser flash photolysis experiments. In principle, the carbene may be detected directly ($\lambda_{\text{max}} \sim 310 \text{ nm}$) when dilute solutions (10^{-5} – 10^{-4} M) are employed.¹⁴ Under these conditions, however, it is essential to use a flow system in order for the diazo precursor to be continuously replenished. Unfortunately, this is not a viable approach with **I** as a substrate. Even with Szeimies's improved synthesis, this volatile material can only be prepared in small amounts, requires preparative GC purification, and is not indefinitely stable.¹⁵ Quite simply, **I** is not available in the amounts required to prepare the volume of solution (usually $\geq 100 \text{ mL}$) needed for each flow experiment. In order to employ static cells, and therefore less **I**, higher concentrations of the diazo compound are required, which rendered the solutions opaque in the 310-nm region. Thus, the carbene cannot be monitored directly, and we had to resort to a probe technique using benzophenone oxide which had been employed successfully in earlier work.¹⁶ Thus, the samples were saturated with a custom mixture of 1% oxygen in nitrogen and irradiated with the pulses (337 nm) from a nitrogen laser. Benzophenone oxide, Ph_2COO , formed by reaction of the triplet carbene with oxygen, can be easily monitored at 410 nm.¹⁶ The growth traces follow clean first-order kinetics and lead to a rate constant, k_{growth} , that can be related to the rate constants of interest according to eq 2

$$k_{\text{growth}} = k_0 + k_{\text{ox}}[\text{O}_2] + k_1[\text{I}] \quad (2)$$

(12) ${}^1\text{H}$ NMR (ppm, CDCl_3 , 300 MHz) 7.25 (m, 10 H), 4.29 (pent, 2 H, $J = 2.5 \text{ Hz}$), 3.55 (t, 4 H, $J = 2.5 \text{ Hz}$); ${}^{13}\text{C}$ NMR (ppm, CDCl_3) 144.0, 140.5, 134.1, 134.0, 128.7 (CH), 128.1 (CH), 126.4 (CH), 106.4 (CH_2), 41.4 (CH_2); GC/MS m/e 232 (M^+); mp 86.0–88.5 °C.

(13) ${}^1\text{H}$ NMR (ppm, CDCl_3) 4.98 (pent, 4 H, $J = 2.1 \text{ Hz}$), 3.30 (t, 8 H, $J = 2.1 \text{ Hz}$); ${}^{13}\text{C}$ NMR (ppm) 144.5, 124.4, 106.7 (CH_2), 38.8 (CH_2); GC/MS m/e 132 (M^+).

(14) Closs, G. L.; Rabinow, B. E. *J. Am. Chem. Soc.* **1976**, *98*, 8190 or ref 16.

(15) [1.1.1]Propellane is stored at $-78 \text{ }^\circ\text{C}$ and as described in the literature. Even with these precautions, the dimer and higher oligomers are detectable by GC analysis after several days. The hydrocarbon is remarkably stable, however, in dilute solutions ($\sim 1 \text{ molar}$) at low temperature. Thus, it is usually desirable to purify propellane just prior to use in an experiment. This method can only be used for relatively small amounts (in our case $\sim 500 \text{ mg}$).

(16) Griller, D.; Majewski, M.; McGimpsey, W. G.; Nazran, A. S.; Scaiano, J. C. *J. Org. Chem.* **1988**, *53*, 1550.

where k_{ox} is the rate constant for the carbene scavenging by oxygen ($k_{ox} = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), and k_0 is the reciprocal of the carbene lifetime in the solvent used, in the absence of oxygen and of I. Since only the last term in equation 2 is a function of the concentration of I, a plot of k_{growth} vs [I] yields, from the slope, the value of k_1 . Such a plot is shown in Figure 1 and leads to $k_1 = (6.7 \pm 0.8) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. This suggests that reaction 1 is much faster than typical carbene additions to olefins, reflecting the fact that addition of the carbene to one of the bridgehead positions allows the other to acquire a more favored pyramidal conformation.

We anticipated that biradical II would be initially formed in its triplet state and would, possibly, have a sufficiently long lifetime to be detected by transient absorption techniques. In fact, 308-nm excitation of dilute solutions of diphenyldiazomethane plus 2 M propellane in Freon-113 at -2°C lead to the rapid formation of a strongly absorbing transient with λ_{max} at 330 nm (similar to diphenylmethyl radicals) and with a lifetime of $9.7 \mu\text{s}$ (see insert in Figure 1). Under these conditions the carbene lifetime (monitored at 320 nm) was 105 ns. These samples only allow for a few laser excitation shots, because of the rapid depletion of the dilute ($\sim 5 \times 10^{-5} \text{ M}$) diazo solution; fortunately, the signals are so intense that a few attenuated shots are sufficient to yield virtually noise free traces (see insert in Figure 1). Biradical II and triplet III are both possible candidates for the observed transient. However, the observation of a 124-ns lifetime for triplet III (generated by acetone sensitization in Freon-113 at room temperature) allowed us to rule out the latter possibility. Thus, we suggest that the long-lived transient is, in fact, biradical II. The unusually long lifetime for II may result from the fact that the two unpaired electrons are in orthogonal orbitals. This would be expected to substantially reduce the intersystem crossing which is generally the rate-determining step for triplet biradical decay.¹⁷ Further experiments aimed at demonstrating whether or not intersystem crossing does affect the lifetime of II will be reported in a full paper.

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A Connection between Intramolecular Long-Range Electron, Hole, and Triplet Energy Transfers

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Over the past few years there has been an active program in our laboratories on long-range intramolecular electron transfer and its dependence on energetics, solvent, distance, and stereochemistry.¹ More recently we have extended this study to include positive ions, or hole transfer,² and triplet energy transfer.³ The

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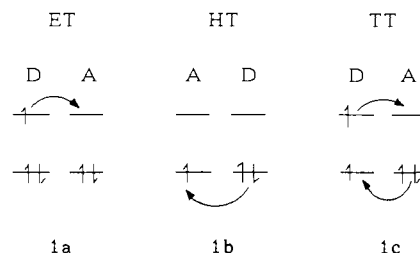


Figure 1. Frontier orbital representation of electron exchange in (1a) electron transfer, (1b) hole transfer, and (1c) triplet energy transfer by the Dexter mechanism.

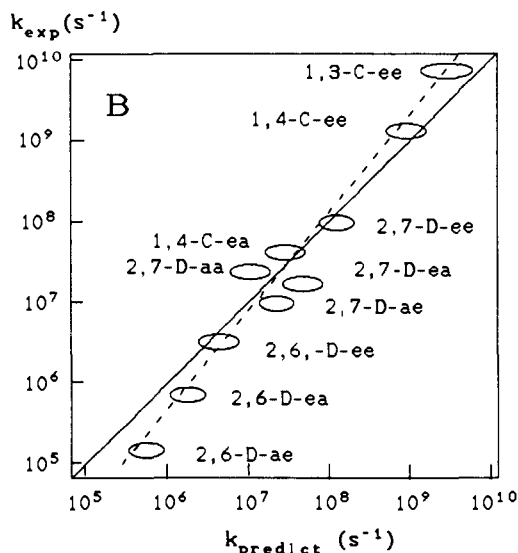
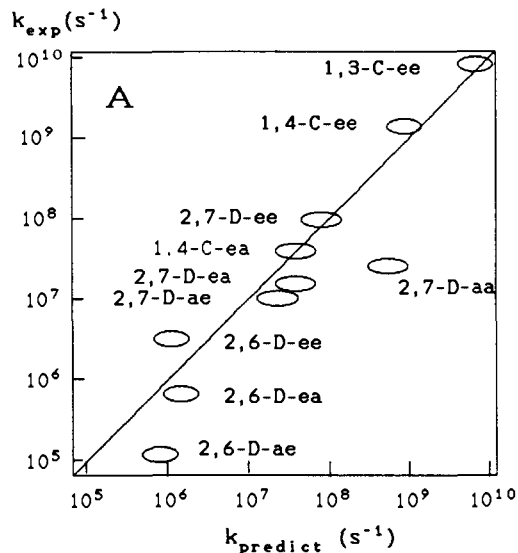
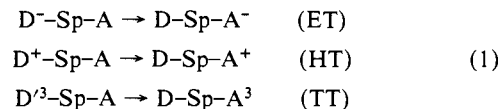


Figure 2. A. Experimental triplet transfer rate constants plotted against predicted rate constants using eq 4. B. Experimental versus predicted triplet transfer rate constants including corrections for reorganization energy changes with distance in ET and HT. Solid line: perfect fit to eq 4; dotted line: least-squares fit of points. Ellipses represent the estimated uncertainties. Note that the estimated rate constants contain the cumulative errors of two measurements.

compounds in the three studies were the same or closely related, and the processes can be summarized and designated as in (1).



In the three series A = 2-naphthyl, and D = 4-biphenyl in the ET and HT series and 4-benzophenoyl in the TT series. The