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REACTION OF PHENYLCHLOROCARBENE WITH [1.1.1] PROPELLANE: ABSOLUTE RATE CONSTANTS AND MECHANISM

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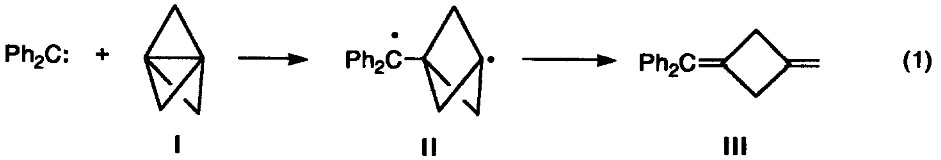
Abstract: Phenylchlorocarbene adds to [1.1.1] propellane with rate constants of 6.1 x 10^7 and 8.8 x 10^6 $M^{-1}s^{-1}$ in cyclohexane and acetonitrile respectively to produce adduct **V** in good yields. No evidence for a biradical intermediate was obtained.

The reactions of arylhalocarbenes have been recently reviewed by Moss and Turro.[1] These carbenes normally have a singlet ground states which add readily to olefins. In particular the unusual temperature dependence of those reactions have been the subject of numerous studies. [1.1.1] Propellane has an inverted structure at the two bridgehead carbon atoms.[2] This characteristic gives this molecule a high reactivity when compared with other saturated carbon compounds. For example, a variety of free radical precursors add across the central bond in [1.1.1]propellane to yield derivatives of bicyclo[1.1.1]pentane.[3] Radicals such as *tert* -butoxyl and triethylsilyl add with rate constants of 2.8 x 10^6 $M^{-1}s^{-1}$ and 6.0 x 10^8 $M^{-1}s^{-1}$, respectively.[4,5]

Diphenylcarbene adds to [1.1.1]propellane in a stepwise process, according to reaction 1.[6]



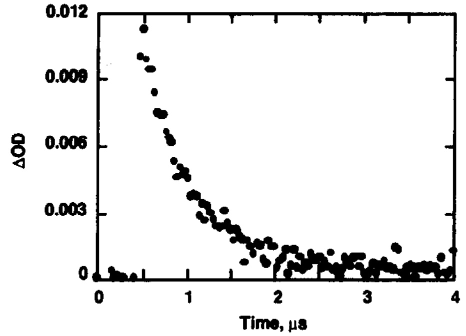
Reaction 1 occurs with a rate constant of 6.7 x 10^6 $M^{-1}s^{-1}$ and involves the intermediacy of a long lived biradical (**II**).[6] No other examples have been reported of additions of carbenes to [1.1.1]propellane, although Jones et al.[7-11] examined the addition of halocarbenes to small bicyclic systems and proposed a mechanism involving a concerted two-bond cleavage process, and Belzner and Szeimies[12] examined reactions of Cl_2C: and Br_2C: with a [1.1.1]propellane derivative.

In this letter we have examined the addition of phenylchlorocarbene (**IV**) to **I**. We report on the products of the reaction, as well as on the kinetics of the process studied by laser flash photolysis.

Results and discussion

Phenylchlorocarbene (**IV**), which can be readily prepared by photodecomposition of the diazirine precursor, has a λ_{max} at 310 nm.[13,14] Typical solution lifetimes are in the microsecond time scale, and **IV** is not quenched readily by oxygen, as expected for a singlet carbene.[1] In our case we found it convenient to monitor the carbene at

320 nm following 337 nm excitation with the pulses from a nitrogen laser. A representative decay trace is illustrated in Figure 1.



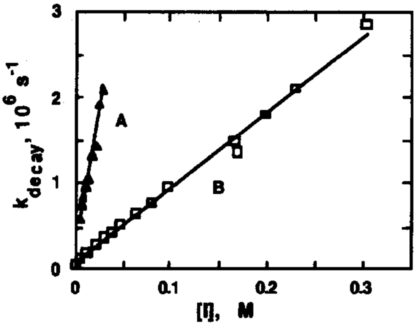


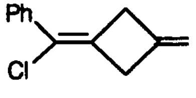
Figure 1 (left): Decay profile for IV in aerated cyclohexane in the presence of 22 mM I.
Figure 2 (right): Scavenging of IV by I in cyclohexane (A) and in acetonitrile (B).

Addition of I leads to an increase in the rate of decay of IV; even very modest concentrations of I are sufficient for IV to decay by clean first order kinetics. The first order rate constants (k_{decay}) depend on the concentration of I according to Equation 2.

$$k_{decay} = k_0 + k_r[I] \qquad (2)$$

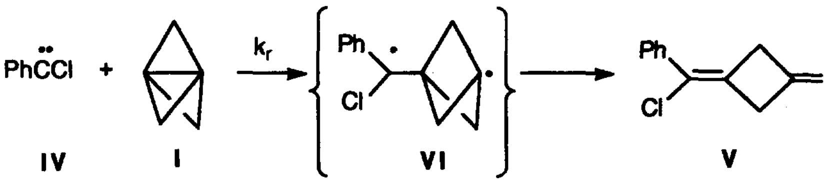
where k_0 is the rate constant for carbene decay in the absence of I and may incorporate reaction with the solvent, and k_r is the bimolecular rate constant for the reaction of I with the carbene. Figure 2 illustrates plots of the data obtained in cyclohexane and in acetonitrile, where the rate constants are $(6.1 \pm 0.3) \times 10^7$ and $(8.8 \pm 0.3) \times 10^6$ M^{-1} s^{-1}, respectively, at 21°C. The higher reactivity in non-polar solvents appears to be common for IV, which adds to tetramethylethylene with rate constants of 2.8×10^8 and 1.1×10^8 $M^{-1}s^{-1}$ in isooctane and acetonitrile, respectively.[1] The increased selectivity in the case of the slower reaction of IV with I is not uncommon in chemical kinetics. The origin of the solvent effect is not entirely clear, although it is possible that carbene complexation through ylide-like reversible interactions decrease its reactivity in acetonitrile. The formation of acetonitrile ylides is well established for many other carbenes.[15,16] The rate constant of 6.7×10^7 $M^{-1}s^{-1}$ in cyclohexane should be compared with a value of 6.7×10^6 $M^{-1}s^{-1}$ for diphenylcarbene in benzene.[6]

The products from the photolysis of phenylchlorodiazirine in the presence of I were characterized following 350 nm lamp irradiation of a solution of the reactants in Freon-113. NMR revealed that the product formed in 66% yield is V. Thus the final products are analogous to those formed in the case of diphenyldiazomethane.[6]



V

While the reaction may yield similar products, the mechanism does not need to be identical to that observed for diphenylcarbene. Thus, one may tentatively write the mechanism of reaction 3.



(3)

Biradical VI would be expected to be strongly absorbing in the 320 nm region, where benzylic radical centers typically absorb. However, all our attemps to detect this absorption were unsuccessful. We are therefore forced to conclude that if VI is formed at all, its lifetime must be less than 30ns. Thus, our data would be consistent with a concerted mechanism, although it should be noted that a short lifetime would not be unexpected for a singlet-derived biradical with no spin restrictions preventing its very rapid decay to the final products.

Finally, we note that the bridgehead position in VI would be expected to abstract hydrogen from suitable donors readily. Experiments in cyclohexane did not yield any evidence for the products anticipated from hydrogen abstraction by VI, an observation that is also consistent with the laser results discussed above.

Experimental

[1.1.1]Propellane was prepared by the method of Szeimies et al.[17] and purified by gas chromatography. Phenylchlorodiazirine, the precursor for phenylchlorocarbene (IV) was prepared by a literature procedure.[18]

Laser photolysis experiments were carried out using a 337 nm nitrogen laser (~8ns, ≤ 8mJ/pulse) for excitation. The details of the experimental set up can be found in earlier reports from our group.

Preparative photolyses were carried out in a Rayonet reactor equipped with 350 nm lamps. An aerated solution of IV (25mg) and I (~0.5ml) in Freon-113 was irradiated for 28 minutes, when the UV-VIS spectrum indicated that all the diazirine had been consumed. The solvent was removed and the resulting yellow oil was passed over a silica gel plug with the aid of 1:1 ethylacetate/hexane to give a front running fraction which contained 20 mg of nearly pure (2-chloro-2-phenylmethylene)methylenecyclobutylidene (66%) ^{1}H-NMR (ppm $CDCl_3$, 300MHz) 7.40 (m, 5H), 5.01 (pent, 2H, J = 2.0 Hz), 3.57 (t, 4H, J = 2.2 Hz); ^{13}C-NMR (ppm, $CDCl_3$) 141.6, 136.4, 133.7, 133.6, 131.1 (CH), 130.1 (CH), 127.4 (CH), 107.7 (CH_2), 47.1 (CH_2); GC/MS m/e 190 (M^+). No evidence for propellane oligomers was detected. Similar results were obtained when cyclohexane was used as the solvent.

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