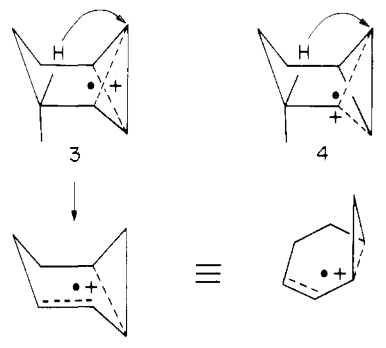
conditions, i.e., with acetone-d_6 as solvent. Under these reaction conditions, very little polarization is generated for the reactant hydrocarbon, but strong CIDNP effects are observed for a bicyclic isomer, norcar-2-ene (**6**). Significantly, these effects (Figure 1d) are identical with those generated in the reaction of **6** with CA. Obviously, a rapid rearrangement, either of the reactant in the dark, or of a radical cation immediately after its generation, is occurring. Although Moore's hydrocarbon is known to suffer rapid acid-catalyzed rearrangement to **6**,[4] this conversion cannot explain the current results. Simple NMR experiments indicate that **1a** does not rearrange at sufficiently fast rates under the reaction conditions. Accordingly, there is little doubt that the rearrangement of **1a** is a consequence of the photoreaction with CA.

The observed results are most readily explained by invoking a different radical cation, such as **3** or **4**, an efficient 1,3-hydrogen migration, which would convert this intermediate to the radical cation **5**, and geminate electron return, which would generate the isomeric hydrocarbon **6**.



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The involvement of a different radical cation under only slightly different conditions requires a relatively delicate balance between the two radical cations; such a situation is not without precedent. For example, we have found evidence that two different cations are derived from hexamethyl(Dewar benzene)[3b] and likewise, from methylenebicyclo[2.2.0]hexene.[3c] Similarly, two types of radical cations are derived from cyclopropane and several examples are known for each structure type.[3a,5] These provide an even closer analogue to the proposed balance between **2** and **3** or **4**.

The mono- and dimethyl derivatives of Moore's hydrocarbon, **1b** and **1c**, respectively, also give rise to CIDNP effects upon reaction with photoexcited CA. These spectra are dominated by strong emission singlets representing the methyl groups. In addition, the broad resonance of the single C7 proton of **1b** appears in enhanced absorption, whereas the remaining signals of **1b** and **1c** show emission. These results can be interpreted on the basis of the same mechanistic scheme discussed for the reaction of the parent compound with 1-CN*.

Given this mechanism, the results indicate that, in the radical cations derived from **1b** and **1c**, the methyl groups and the single proton on C1 and C7 are attached to centers of positive spin density. This identifies the radical cations as species in which the the C1-C7 bond is broken or weakened, that is as in **2b** and **2c**. The results obtained in acetonitrile-d_3 and acetone-d_6 are quite similar. Obviously the introduction of one or two methyl groups has suppressed the propensity for rearrangement, which is so pronounced for the reaction of **1a** with CA in acetone.

The divergent results observed for the reaction of **1a** with CA in two different solvents suggest the involvement of two different high-energy occupied MO's. We are continuing our studies in an effort to identify factors influencing the relative energies of these occupied MO's and to elucidate the nature of the rearrangement.

Acknowledgment. We thank the National Science Foundation for a grant to P.G.G., which partially supported this investigation.

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[5] (a) Roth, H. D., Schilling, M. L. M. *J. Am. Chem. Soc.* **1980**, *102*, 7956-7958; (b) *Ibid.* **1983**, *105*, 6805-6808.

Trapping of a Stable Complex in the Reaction between $C(^3P)$ and Trimethylamine

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We recently reported a combined theoretical and experimental study of the reaction between $C(^1D)$ and ammonia which indicated that an initial complex between these two species was not an energy minimum but rapidly cleaved an N-H bond to generate products.[1] We now report calculations and experiments which indicate that the triplet complex between $C(^3P)$ and amines is an intermediate that can be trapped in some cases.

Ab initio calculations at the UMP3/6-31G** level[2] indicate that complex **1a** is an energy minimum that lies 20.1 kcal/mol lower in energy than $C(^3P) + NH_3$. The lowest energy reaction for **1a** is calculated to be the cleavage in eq 1 (ΔH = 30.4

$$C(^3P) + NR_2R' \rightarrow \overset{-}{C}\text{—}\overset{+}{N}R_2R' \rightarrow \cdot\overset{-}{C}\text{=}\overset{+}{N}R_2 + \cdot R' \quad (1)$$

1a, R = R′ = H
1b, R = CH_3; R′ = H
1c, R = R′ = CH_3

kcal/mol). If **1** has the ylid structure shown in eq 1, it is expected that the addition of methyl groups as in **1b** and **1c** will stabilize the positive charge on nitrogen and increase the stability of **1b** and **1c** relative to **1a**. Not surprisingly, the calculations indicate this to be true. Although the number of atoms in **1b** and **1c** preclude UMP3/6-31G** calculations, we have approximated [UMP3/6-31G*] calculations for **1b** by combining 6-31G* and UMP3/6-31G calculations.[3] This approximation leads to the conclusion that **1b** is 24.7 kcal/mol more stable than methylamine and $C(^3P)$ and has a barrier of 22.3 kcal/mol to the methyl cleavage shown in eq 1. The energy of **1c** was calculated at the UMP2/6-31G level and indicates that **1c** is 30.9 kcal/mol more stable than trimethylamine and $C(^3P)$ with a barrier to methyl cleavage of 30.5 kcal/mol.[4] In order to compare the relative stabilities of **1a-c**, the energy of each species relative to that of reactants and the barrier to cleavage of R′ was calculated at the UMP2/6-31G level. The results of these calculations, shown in Table I, indicate that these amine adducts of $C(^3P)$ lie in relatively deep energy wells and are potentially trappable.

Since these complexes are calculated to be triplets and $C(^3P)$ itself has been observed to react rapidly with oxygen to generate carbon monoxide, trapping with oxygen was attempted. In these studies carbon atoms were generated in a carbon arc under high dynamic vacuum and cocondensed with substrate at 77 K.[5,6] After

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[1] McPherson, D. W.; McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1983**, *105*, 6493.

[2] (a) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. "GAUSSIAN80" QCPE 406, Indiana University. The version used here has been developed in other laboratories to run on an IBM machine. (b) The correlation treatment follows that presented by: Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem., Symp.* **1976**, *10*, 1. (c) All geometries were optimized at the 3-21G level. (d) Geometries of NH_3, $CHNH_2$, and CH_3NH_2 at the 3-21G level were taken from: Whiteside, R. A.; Frisch, M. J.; Binkley, J. S.; DeFrees, D. J.; Schlegel, H. B.; Raghavachari, K.; Pople, J. A. "Carnegie-Mellon Quantum Chemistry Archive", 2nd ed.; Carnegie-Mellon University: Pittsburgh, 1981. (e) For basis set description, see: Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. For UMP3 treatment, see: Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem., Symp.* **1976**, *10*, 1.

[3] (a) Additivity has been demonstrated to be accurate to within 1-4 kcal/mol of the full calculation. We would like to suggest that calculations that use additivity enclose the appropriate basis set in brackets.[3b,c] (b) McKee, M. L.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1981**, *103*, 4673. (c) Nobes, R. H.; Bouma, W. J.; Radom, L. *Chem. Phys. Lett.* **1982**, *89*, 497.

[4] The true barrier is likely to be 5-15 kcal/mol lower as inclusion of the point energy correction and additional correlation should preferntially stabilize the transition state.

[5] The carbon atom reactor is based on that described by: Skell, P. S.; Wescott, L., Jr.; Goldstein, J.-P.; Engel, R. R. *J. Am. Chem. Soc.* **1965**, *87*, 2829.

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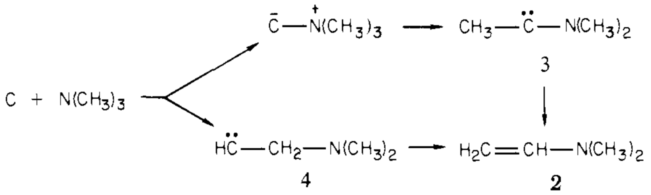
Table I. Energies of Complex 1 and Barriers to Cleavage of R' Calculated at the UMP2/6-31G Level

reactants	energy of complex,[a] kcal/mol	barrier to cleavage of R', kcal/mol
$C(^3P) + NH_3$	−21.4	+33.7
$C(^3P) + NH_2CH_3$	−25.8	+25.8
$C(^3P) + N(CH_3)_3$	−30.9	+30.5

[a] Energies are tabulated relative to that of reactants in each case.

deposition of carbon and substrate, the reactor was sealed off and oxygen gas was admitted at 77 K. The reactor was then allowed to warm to room temperature, and the contents were pumped out and analyzed for carbon monoxide. When this experiment was carried out using ammonia and dimethylamine as substrates, no carbon monoxide was observed among the volatile products. However, the cocondensation of carbon (82.2 mmol) with trimethylamine (86.1 mmol) followed by the addition of oxygen (21.8 mmol) gave carbon monoxide (6.4×10^{-2} mmol). Other volatile products observed were methane (8.1×10^{-2} mmol), *N*,*N*-dimethylvinylamine (**2**, 1.2 mmol), and methylisocyanide (2.7×10^{-1} mmol). The formation of **2**, which need not be a product of triplet carbon, may be rationalized as occurring during cocondensation via either carbene **3** or **4**. Likewise, methylisocyanide could be the result of cleavage during condensation or could result directly from the radical pair in eq 1. However, the carbon monoxide and methane must be generated after condensation as there is no source of oxygen until this time and any methane formed during the reaction would be pumped out.[7]

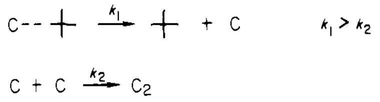


The fact that carbon monoxide is observed under these conditions constitutes strong evidence for the trapping of either triplet complex **1c** or $C(^3P)$ itself. These results are reminiscent of an earlier reaction reported by Skell and Engel[8] in which it was stated that $C(^3P)$ could be stabilized on a neopentane matrix at 77 K. Although Skell and Engel did not report the reaction of this $C(^3P)$ with oxygen, we have now observed this reaction, which confirms their postulate of the existance of $C(^3P)$ under these conditions. Thus, cocondensation of carbon (76.4 mmol) with neopentane (82.5 mmol) followed by the addition of oxygen (20.9 mmol) gave, upon warming to room temperature, carbon monoxide (4.9×10^{-2} mmol) and acetylene (1.8 mmol).

If we assume that the triplet species generated in both of these systems react quantitatively with excess oxygen to generate carbon monoxide, the amount of carbon monoxide generated should be a measure of the amount of triplet species present at any time. Thus, oxygen may be used as a titrant to measure the concentration of triplet species as a function of time. We have used this method to measure the rate of decomposition of the complex of $C(^3P)$ with both trimehtylamine and neopentane. In order to do this, carbon was condensed with substrate and the matrix was allowed to age for periods of 0, 5, 7.5, 10, and 12.5 s before adding the oxygen. The yield of carbon monoxide after each of these intervals was taken as a measure of the concentration of triplet species at that time. In both systems, the concentration of triplet species remained approximately constant over the first 5 s. This fact may be due to decay of metastable carbon species to the ground-state triplet during this time. However, the rate of decay of triplet species after this initial period revealed a significant difference between the trimethylamine and neopentane complexes of $C(^3P)$.

In the case of the carbon–trimethylamine reaction, the complex was observed to decay by clean first-order kinetics with $k = 6.3 \times 10^{-1}$ s^{-1} (correlation coefficient = 0.987). However, the decay of the complex between carbon and neopentane was observed to follow second-order kinetics with $k = 6.3 \times 10^{-1}$ mmol^{-1} s^{-1} (correlation coefficient = 0.975). Fitting the decay of **1c** to second-order kinetics and that of the neopentane complex to first-order kinetics was less satisfactory with correlation coefficients of 0.970 and 0.899, respectively. Thus, the complex between $C(^3P)$ and trimethylamine appears to decay by what is predominantly a first-order process which is most likely the cleavage of a methyl group shown in eq 1. The methyl radical generated in this reaction then abstracts a hydrogen from trimethylamine to generate the observed methane. The use of [UMP3/6-31G*] calculations revealed no lower energy reaction pathways for **1b** than cleavage. Thus, methyl migration to generate carbene **3** has a barrier of 50.8 kcal/mol while insertion of the carbon into an adjacent C–H bond in **1b** has a barrier of 40.8 kcal/mol.

The fact that $C(^3P)$ on neopentane disappears by a second-order process may be rationalized by assuming a very loose complex that decays by rate-determining dimerization of the carbon atom as shown in eq 2. We are currently investigating the additional chemistry of both of these interesting triplet species.



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Rates of Reversible Bond Switch with Participation of π-Bonded S^{IV} in a Protonated Thiadiazole Ring System

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The unsymmetrical nature of thiathiophthenes (**1**) and their analogues in solid state has been established by X-ray crystallographic analyses,[1] but neither the unsymmetrical nature nor any kinetic evidence of ring transformation of analogues of **1** in solution has been found in spite of a careful ^{1}H NMR study.[2] In a recent

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