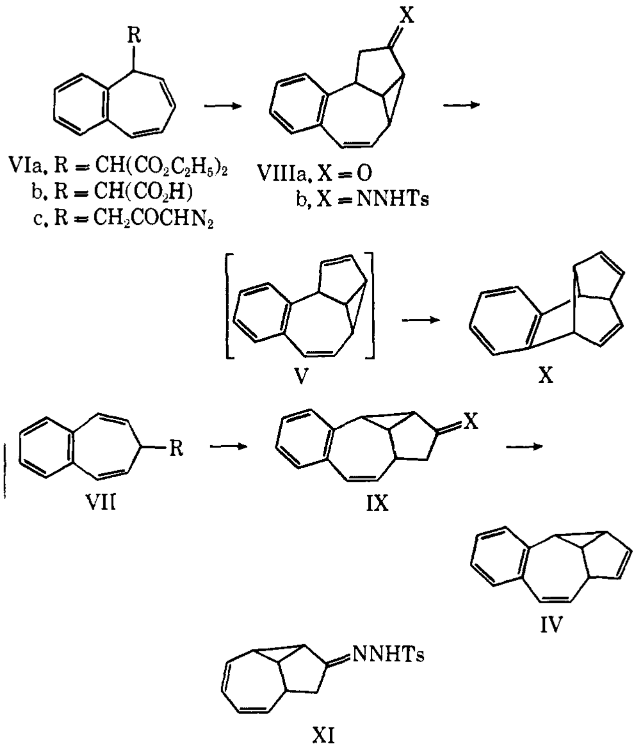
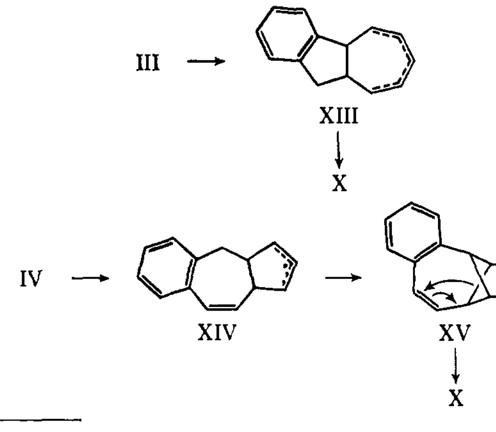
Scheme I



Extended pyrolysis of III at 450° affords phenanthrene and a mixture of 1,2- 3,4-, and 9,10-dihydrophenanthrenes. An interesting rationale for this reaction involves the unprecedented[8] ring opening to mono-*trans*-benzo[10]annulene followed by closure to 4a,10a-dihydrophenanthrene (XII). However, carefully controlled pyrolysis of III (330°, flow system) results in formation of X[9] instead of the expected XII. Surprisingly, the isomer IV also rearranges to X at 330°, although more slowly than III. The conversion of III to X can be explained by a nonconcerted 1,3 shift involving the diradical XIII, but a more elaborate sequence is necessary to account for the conversion of IV. The most stable diradical in this case, XIV, may reclose at C-8 to form the intermediate XV which may rearrange to X by a second 1,3 shift. In summary, tricyclo[5.3.0.0^{2,10}]decatrienes I and V undergo facile Cope rearrangement at 0°, while III and IV rearrange at 330° *via* diradical intermediates. As evidenced by the absence of phenanthrene derivatives, the diradicals XIII and XIV do not open to benzo[10]annulene at 330°. This behavior contrasts with the thermal reactions of various $C_{10}H_{10}$ hydrocarbons which invariably rearrange to 9,10-dihydronaphthalene or its transformation products under similar conditions.[10,11]



Acknowledgment. We thank the Wisconsin Alumni Research Foundation for support of this work.

Terrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, **23**, 3943 (1967).

(7) M. Jones, Jr., *J. Amer. Chem. Soc.*, **89**, 4236 (1967). We are grateful to Professor Jones for spectra of II.

(8) Cleavage of the 1,7 and 2,10 bonds in III to give a [10] annulene can be viewed as an allowed 2s + 6a cycloreversion which would lead to a *trans* double bond between C_1 and C_{10}: R. B. Woodward and R. Hoffman, *Accounts Chem. Res.*, **1**, 17 (1968).

(9) Pyrolysis of III (or X) in a flow system above 400° affords phenanthrene (28%), the three possible aromatized dihydrophenanthrenes (65%), and four minor products which have not been identified.

(10) W. von E. Doering and J. W. Rosenthal, *J. Amer. Chem. Soc.*, **88**, 2078 (1966); *Tetrahedron Lett.*, 349 (1967); also, ref 7.

(11) Note Added in Proof. The Cope rearrangement of I has been suggested independently as a rationale for certain $C_{10}H_{10}$ interconversions by T. J. Katz and J. J. Cheung, *J. Amer. Chem. Soc.*, **91**, 7772 (1969).

Edwin Vedejs, Robert A. Shepherd, Richard P. Steiner
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706
Received December 22, 1969

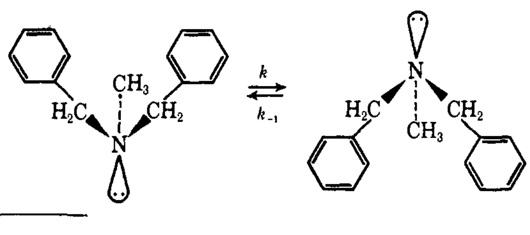
Direct Observation of Nitrogen Inversion in Free, Unprotonated Dibenzylmethylamine

Sir:

The rate of nitrogen inversion in simple amines is of considerable theoretical and practical interest in heterocyclic conformational analysis. Barriers to nitrogen inversion have been determined in certain acyclic amines possessing electronegative substituents, *e.g.*, $-OCH_3$, bonded to nitrogen.[1] Many examples of slow nitrogen inversion rates in cyclic amines are known.[2] In most instances, an electronegative substituent is bonded to nitrogen, although slow nitrogen inversion has been observed in N-alkylaziridines[3] and other aziridines.[4] Indeed, conformational isomers of various N-chloroaziridines have been separated above room temperature.[5]

The rate of inversion in dibenzylmethylamine has been estimated in aqueous acid solution by examination of the shape of proton magnetic resonances as a function of acid concentration.[6]

This report concerns the measurement of the rate of nitrogen inversion in free, unprotonated dibenzylmethylamine (eq 1) using variable temperature proton magnetic resonance (pmr) spectroscopy.



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(1) D. L. Griffith and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 4089 (1965), and references therein.

(2) J. B. Lambert and W. L. Oliver, Jr., *Tetrahedron Lett.*, 6187 (1968); J. E. Anderson and J. M. Lehn, *J. Amer. Chem. Soc.*, **89**, 81 (1967); E. L. Allred, C. L. Anderson, R. L. Miller, and A. L. Johnson, *Tetrahedron Lett.*, 525 (1967); J. E. Anderson and J. D. Roberts, *J. Amer. Chem. Soc.*, **90**, 4186 (1968).

(3) R. G. Kostyanovsky, Z. E. Samojlova, and I. I. Tchervin, *Tetrahedron Lett.*, 3025 (1968); A. Loewenstein, J. F. Neumer, and J. D. Roberts, *J. Amer. Chem. Soc.*, **82**, 3599 (1960).

(4) F. A. L. Anet, R. D. Trepka, and D. J. Cram, *ibid.*, **89**, 357 (1967), and references therein.

(5) S. J. Brois, *ibid.*, **90**, 506, 508 (1968).

(6) M. Saunders and F. Yamada, *ibid.*, **85**, 1882 (1963).

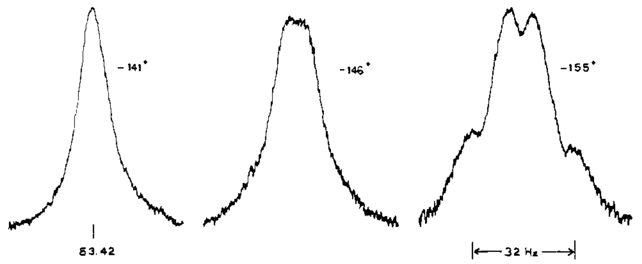

Figure 1. The pmr spectrum (60 MHz) of the N-CH$_2$ (δ 3.42) protons of dibenzylmethylamine (0.08 *M* in CH$_2$CHCl) at various temperatures.

If nitrogen inversion (eq 1) is slow on the pmr time scale, the two methylene protons of a given benzyl group of dibenzylmethylamine are in a dissymmetric environment and should be nonequivalent exhibiting a typical AB spectrum. This situation should prevail even in the event of rapid C–N bond rotation. However, rapid nitrogen inversion on the pmr time scale *plus* rapid C–N bond rotation will render the two benzylic hydrogens equivalent.

Examination of the proton magnetic resonances (60 MHz) due to the N-CH$_3$ (δ 2.08) and N-CH$_2$ (δ 3.42) groups of dibenzylmethylamine (0.08 *M* in CH$_2$CHCl) at −100° revealed two sharp singlet resonances. At temperatures below −100°, the N-CH$_3$ resonance exhibited broadening due to viscosity effects and/or quadrupole-induced ^{14}N relaxation[7] while the N-CH$_2$ peak broadened and separated in typical fashion into what is clearly an AB spectrum ($J_{AB} \cong 12$ Hz; $\Delta\nu_{AB} \cong 17$ Hz) consistent with *slow nitrogen inversion on the pmr time scale* (Figure 1). The first-order rate constant (k or k_{-1}; eq 1) was calculated to be 76 sec^{-1} at −146° using an analytic expression for the rate at coalescence of the pertinent resonances.[8] The barrier ($\Delta G^{\ddagger}$) to inversion in dibenzylmethylamine is 6.0 ± 0.5 kcal/mol at −146° assuming the transmission coefficient of the Eyring equation to be unity.[9] Although the spectral behavior reported here may also be affected by slow C–N bond rotation, the relatively low rotational barrier in trimethylamine (4.4 kcal/mol)[10] indicates that C–N bond rotation is still rapid on the pmr time scale at −146°.

Thus it is evident that inversion barriers in simple, acyclic trialkylamines can be determined using conventional variable-temperature nmr techniques and we are continuing our investigations especially with respect to steric and solvent effects on the inversion barriers.

Acknowledgment. We thank Research Corporation (Cottrell Grant) and the National Science Foundation (COSIP Grant) for support of this work and the referees for useful suggestions.

(7) J. E. Anderson, D. L. Griffith, and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 6371 (1969).

(8) S. Alexander, *J. Chem. Phys.*, **37**, 966 (1962).

(9) A total nmr line-shape analysis for dibenzylmethylamine and several other amines is in progress and the results will be reported in the full paper.

(10) D. R. Lide and D. E. Mann, *J. Chem. Phys.*, **28**, 572 (1958).

C. Hackett Bushweller, James W. O'Neil
Department of Chemistry
Worcester Polytechnic Institute
Worcester, Massachusetts 01609

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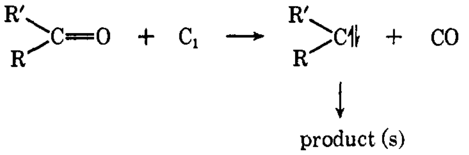
Deoxygenation by Atomic Carbon. III. Dichlorocarbene and Methoxycarbene

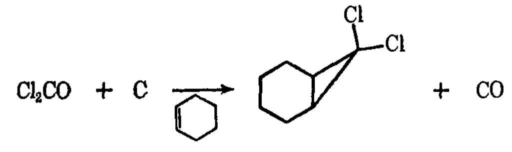
Sir:

We have reported previously[1] that ketones and aldehydes react with excited state carbon atoms (^{1}D and/or ^{1}S) during codeposition at a liquid nitrogen cooled surface to produce mono- and dialkylcarbenes and carbon monoxide. In the course of the ketone and aldehyde deoxygenation studies it was noted that product formation always occurred in an intramolecular manner and that efforts to intercept the intermediate carbenes with cyclohexene were unsuccessful. This is apparently due to a low activation energy for intramolecular carbene stabilization.



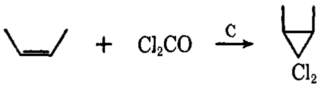
We now wish to report that when carbenes having no intramolecular mode of stabilization are generated by deoxygenation in the presence of olefins, cyclopropanes are formed.

One example of this is the deoxygenation of phosgene in the presence of cyclohexene to produce 7,7-dichloronorcarane. When a gas-phase mixture of 75% phosgene and 25% cyclohexene was added to the reaction flask[2] and codeposited at the liquid nitrogen cooled surface with carbon vapor from a 16-V a.c. arc, 7,7-dichloronorcarane, determined by comparison with an authentic sample, is the major product formed in 25% yield.[3] No detectable quantity of tetrachloroethylene was found in the reaction.



This observation is consistent with the intermediacy of free dichlorocarbene from the deoxygenation of phosgene. To determine the stereochemistry of the addition of deoxygenative dichlorocarbene to olefins and thereby its multiplicity,[4] carbon vapor was cocondensed with mixtures of *cis*- and *trans*-2-butene and phosgene.

When a gas-phase mixture of 65% phosgene and 35% *cis*-2-butene was used as the reactive matrix, 1,1-dichloro-*cis*-2,3-dimethylcyclopropane was the major product (formed in 20% yield[3]) with no peak present in the gas chromatogram which corresponded to the *trans* isomer. When a mixture of 67% phosgene and 33%



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(1) P. S. Skell and J. H. Plonka, *J. Amer. Chem. Soc.*, **92**, 836 (1970).

(2) P. S. Skell, L. Wescott, Jr., J. P. Goldstein, and R. R. Engel, *ibid.*, **87**, 2829 (1965), describes the reaction system.

(3) Based on C$_1$; assuming 40% of the carbon vaporized is monatomic. See R. F. Harris, Ph.D. Thesis, Pennsylvania State University, 1968.

(4) P. S. Skell and R. C. Woodworth, *J. Amer. Chem. Soc.*, **78**, 4496 (1956).