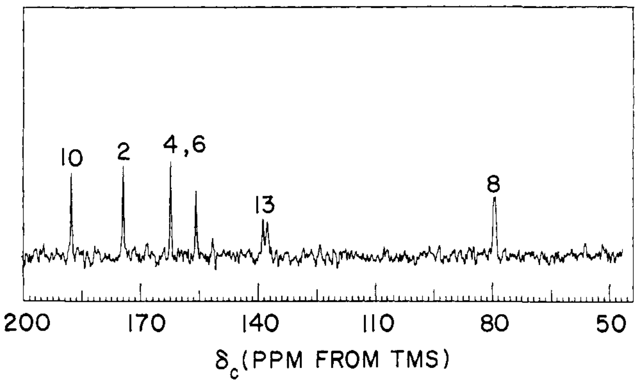

Figure 2. CW decoupled ^{13}C nmr spectrum of radicinin from $CH_3{}^{13}COONa$. Concentration same as in Figure 1b; 37 scans of 3775 Hz (150 ppm) at 50 sec/scan; lock signal DMSO; chemical shifts in δ_c.

technique was employed to obtain more information on spectrum b. Figure 2 shows the appearance of the methine carbons at C_8 and C_{13} as close-spaced doublets with the carbonyls and quaternary carbons remaining as singlets.

Nuclear Overhauser effects preclude precise calculation of incorporation yields by integration of peak areas since peak enhancements of up to 2.98 have been observed.[9] This effect may be responsible for the different spectral line intensities observed for C_4 and C_6 in Figure 1b. Incorporation yields can be approximated by relative comparison with natural abundance peaks, particularly with carbon atoms of similar substitution pattern which can undergo relaxation by similar mechanisms. Since natural abundance peaks in the labeled radicinins were not readily visible with the small number of scans employed, an incorporation yield of ~17% was determined by integration of the proton-^{13}C satellite bands of the C_{11} and C_{14} methyl groups ($J_{^{13}C-H}$ = 126 Hz) clearly evident in the proton spectrum at 60 MHz. Other $J_{^{13}C-H}$ values observed were (C_5) 172, (C_9) 148, and (C_{12}) 162 Hz. Detection and integration of ^{13}C satellite peaks serve as an alternate method of biosynthetic studies.[10]

The application of ^{13}C nmr spectroscopy to biological isotopic tracer studies offers many distinct advantages over conventional radioactive tracer methods.

Acknowledgment. Support of this work by the Public Health Service under Grant No. AI 08143 is gratefully acknowledged. We thank Professor S. Yamamura for a sample of *dl*-radicinin.

ley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, New York, N. Y., 1966, pp 1009.

(9) A. J. Jones, D. M. Grant, and K. F. Kuhlmann, *J. Amer. Chem. Soc.*, **91**, 5013 (1969).

(10) (a) M. Tanabe and G. Detre, *ibid.*, **88**, 4515 (1966); (b) D. Desaty, A. G. MacInnes, D. G. Smith, and L. C. Vining, *Can. J. Biochem.*, **46**, 1293 (1968); (c) A. G. MacInnes, O. G. Smith, L. C. Vining, and J. L. C. Wright, *Chem. Commun.*, 1669 (1968).

(11) On leave of absence from the Institute of Applied Microbiology, University of Tokyo.

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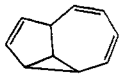
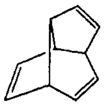
Received January 19, 1970

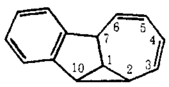
Thermal Reactions of Some Tricyclo[5.3.0.0^{2,10}]decatriene Derivatives

Sir:

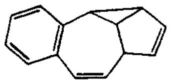
Tricyclo[5.3.0.0^{2,10}]decatriene (I) is one of the $C_{10}H_{10}$ isomers which can be related to [10]annulene by a simple valence bond reorganization. However, the isolation of I poses a difficult challenge because the molecule contains a *cis*-divinylcyclopropane unit. Thus the activation energy for the Cope rearrangement of I is expected to be less than ~23 kcal/mol[1] and any thermal process involving [10]annulene is not likely to compete with facile rearrangement to II. In order to study transformations which might lead to [10]annulenes under more favorable circumstances, we have examined the thermal behavior of the benzo derivatives III,[2] IV, and V of tricyclo[5.3.0.0^{2,10}]decatriene. Compounds III and IV are expected to resist Cope rearrangement owing to the strategic presence of a benzene ring, while V should be unstable for the same reasons as I.

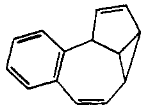

I


II



III


IV


V

A synthetic route to the hitherto unknown structures IV and V is described in Scheme I. Benzotropylium ion[3] is condensed with diethyl malonate to afford a 2:3 mixture of VIa and VIIa. The isomers are separated by crystallization of VIb and VIIb, which are then converted into the cyclopropyl ketones VIIIa and IXa *via* copper-catalyzed decomposition of the diazoketones VIc and VIIc. The desired olefin IV[4] is obtained from the tosylhydrazone IXb upon treatment with methyllithium.[5] In the case of tosylhydrazone VIIIb, however, the divinylcyclopropane V cannot be isolated under the conditions necessary for olefin formation (several hours at 0°, 10–15% yield) and the sole hydrocarbon product is the rearranged isomer X.[4] As expected, a similar rearrangement occurs when the parent tosylhydrazone XI[6] is treated with methyllithium, and II[7] is the only detectable $C_{10}H_{10}$ product at 0°.

(1) The activation energy for the rearrangement of a model compound, *endo*-6-vinylbicyclo[3.1.0]hex-2-ene, is 23 kcal/mol: J. M. Brown, *Chem. Commun.*, 227 (1965). The additional constraints present in I compared to the model are expected to lower the magnitude of $\Delta S^{\ddagger}$ but the effect on $\Delta H^{\ddagger}$ is not easily predictable. A somewhat more facile rearrangement appears likely in the case of I.

(2) E. Vedejs, *Tetrahedron Lett.*, 2633 (1968).

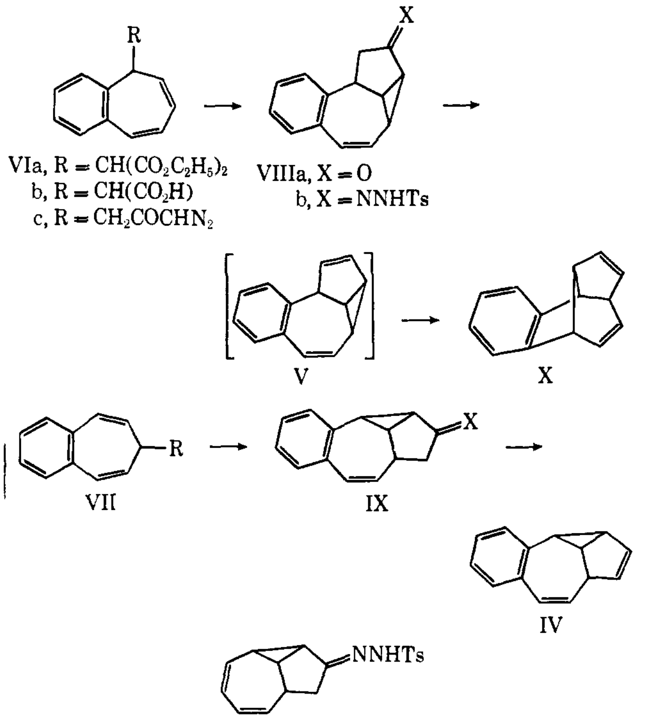
(3) Benzotropylium tetrafluoroborate is easily prepared from trityl tetrafluoroborate and benzocycloheptatriene in methylene chloride solution.

(4) Compound IV: mp 51°; λ_{max}^{EtOH} 211 nm (ϵ 24,600), 234 nm (ϵ 19,400), 262 nm (ϵ 6250); nmr ($CDCl_3$) τ 2.90 (4 H, m), 3.82 (1 H, d of d, J = 11, 1 Hz), 4.00 (1 H, d of d, J = 11, 8.5 Hz), 4.51 (1 H, m), 4.84 (1 H, m), 6.30 (1 H, m), 7.7–8.1 (3 H, m). Compound X: mp 79°; λ_{max}^{EtOH} 265 nm (ϵ 800), 272 nm (ϵ 1100), 278 nm (ϵ 1100); nmr (CCl_4) τ 3.05 (4 H, m), 3.40 (1 H, d of d, J = 3, 6 Hz), 4.37 (3 H, m), 6.41 (1 H, m), 6.59 (1 H, m), 6.99 (1, H, m), 7.46 (1, H, m).

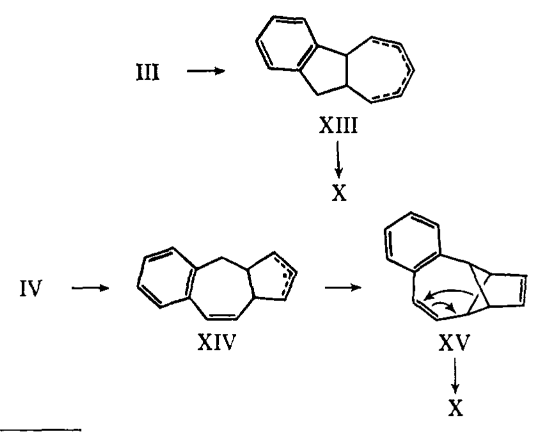
(5) R. H. Shapiro and M. J. Heath, *J. Amer. Chem. Soc.*, **89**, 5735 (1967); G. Kaufman, F. Cook, H. Shechter, J. Bayless, and L. Friedman, *ibid.*, **89**, 5736 (1967).

(6) XI is available in the usual way as a mixture of stereoisomers from tricyclo[5.3.0.0^{2,10}]deca-3,5-dien-9-one: W. von E. Doering, B. M.

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).

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Received December 22, 1969

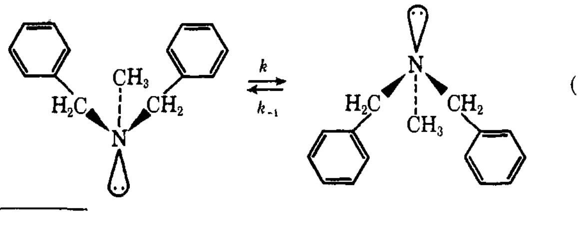
Direct Observation of Nitrogen Inversion in Free, Unprotonated Dibenzylmethylamine

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.



(1)

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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).