solute in the excited state tends to affect the transition probability such that $\alpha$ is smaller in the polar media, its value being greater than one in all the media studied. An increase in $\tau_{0m}$ as a function of polarity of the medium was also observed for $\alpha$-naphthylamine and 5-dimethylaminonaphthalene-1-sulfonamide (DNSA).

The dependence of $\tau_{0m}$ on the solvent leads to an interesting temperature dependence. For DNSA in ethanol the radiative lifetime increases from a low value of 20 nsec at 77°K to a higher limiting value of 34.4 nsec at temperatures above 190°K. At low temperatures when the solvent cage reorientation cannot occur during the lifetime of the excited state, emission arises from a Franck–Condon state which has an equilibrium configuration similar to that of the ground state. Under these conditions it is expected that $\tau_{0m}$ is smaller and the emission blue shifted compared to results at room temperature, as has been observed for DNSA.

(8) On leave from Monash University, Clayton, Victoria, Australia.

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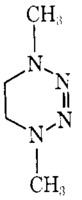
*Received December 4, 1969*

## 1,4,7,10-Tetramethyl-1,2,3,4,7,8,9,10-octaazacyclododeca-2,8-diene. A Cyclic Bis-2-tetrazene

*Sir:*

Our interest in 2-tetrazenes[1,2] led us to attempt preparation of the cyclic-2-tetrazene **1**, for comparison of its properties with *trans* analogs, such as tetramethyl-2-tetrazene (**2**). The oxidation of **3**[3] with potassium bromate[4] gave moderate yields (17–29%) of a solid, which was purified by alumina chromatography and crystallization from pentane (dec 123–123.5° with gas evolution).



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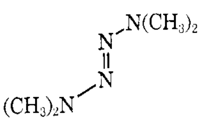

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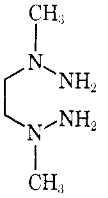

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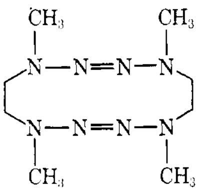

**4**

Several spectral properties indicated that this material was a 2-tetrazene. The uv spectrum ((heptane) $\lambda_{max}$ 241 ($\epsilon$ 4.4 × $10^3$), 258 (6.0 × $10^3$), 267 (9.0 × $10^3$), 276 (9.3 × $10^3$), 300 nm shoulder (1.6 × $10^3$)) is qualitatively similar to that of **2**, $\lambda_{max}$ 250 and 277 nm.[5] The ir spectrum is also consistent with a 2-tetrazene structure (6.80, 7.01, 7.34, 7.70, 7.90, 9.28, 9.63, 10.04 $\mu$) and the analysis[6] fits **1** (Calcd for $C_4H_{10}N_4$: C, 42.07; H, 8.83; N, 49.10. Found: C, 41.97; H, 8.81; N, 49.22); the nmr shows the expected two singlets ($CDCl_3$) at $\delta$ 2.83 and 3.67, 3:2 intensity ratio. The mass spectrum showed, however, that the solid was a dimer of **1**; at 70 eV (AEI MS 9 spectrometer, direct inlet), the parent at $m/e$ 228 was 40% of the intensity of the base peak at 42, and 6.9 times as intense as the 114 peak. In carbon tetrachloride, observed osmometric molecular weights were 229 (0.091 *M*), 227 (0.046), 225 (0.019).

The data require structure **4** for the isolated oxidation product of **3**. The formation of the twelve-membered ring dimer in preference to a six-membered ring is quite surprising.

The thermal stability of **4** is inconveniently great for accurate measurement of its decomposition rate by our nitrogen evolution apparatus,[1] but five runs at 159 ± 1° in tetralin gave times for half-decomposition in the range 138 ± 12 min (5 × $10^{-3}$ *M* initial concentration). Curvature was evident in first-order plots, which might be expected from the bistetrazene structure, since concerted cleavage of both nitrogens is not likely. Clearly **4** is somewhat stabler than **2**, which has an extrapolated half-life of 91 min at 159° (vapor phase);[7] the only reported decomposition rate in solution corresponds to a half-life of 206 min at 145° (cumene),[8] at which temperature the vapor phase half-life is about 340 min. Since it is apparent[9] that a *cis*-azo linkage in an azoalkane lowers the activation energy for decomposition by approximately 10 kcal/mol over that for a *trans*-azoalkane (in the absence of strain, which lowers the activation energy even more[10]), the thermal stability of **4** is most consistent with it possessing *trans*-2-tetrazene groups.

The nmr spectrum of **4** is temperature dependent; the methylene absorption is noticeably broadened even at room temperature, and at −45° appears as a double doublet, $\nu_{ab}$ = 57, $J_{ab}$ = 11.3 Hz; the methyl absorption remains sharp. The coalescence temperature for the methylene absorption is about +5°, giving an apparent $\Delta G^*$ for interconversion of the methylene hydrogens of about 13.5 kcal/mol. This free energy of activation is remarkably high for a twelve-membered ring, and actually is somewhat above values observed for several saturated azamethyl cyclohexyl systems.[11] *trans*-Azo linkages would seem necessary to give sufficient rigidity to the ring system to observe the slow interconversion of the methylene hydrogens. Whether additional rigidity is imparted by significant hindered rotation about the four amino nitrogen–azo nitrogen bonds must remain an open question without further data, but no temperature dependence has proved observable in the nmr spectrum of **2**.[12]

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(1) S. F. Nelsen, R. B. Metzler, and M. Iwamura, *J. Amer. Chem. Soc.*, **91**, 5103 (1969).

(2) S. F. Nelsen and D. H. Heath, *ibid.*, **91**, 6452 (1969).

(3) Prepared by lithium aluminum hydride reduction of bisnitroso-N,N′-dimethylethylenediamine, bp 66–67° (2.7 mm), characterized as the bisoxalate, mp 178–179°, which gave the expected analysis and spectral properties.

(4) W. R. McBride and H. W. Kruse, *J. Amer. Chem. Soc.*, **79**, 572 (1957).

(5) W. E. Bull, J. A. Seaton, and L. F. Audrieth, *ibid.*, **80**, 2516 (1958). Their contention that the 250-nm peak corresponds to protonated **2** is untenable, since the ratio $\epsilon$ 277/$\epsilon$ 250 only varies from 2.01 to 1.22 in going from cyclohexane to water.

(6) Spang Microanalytical Laboratories, Ann Arbor, Mich.

(7) B. G. Gowenlock, P. P. Jones, and D. R. Snelling, *Can. J. Chem.*, 41, 1911 (1903).

(8) B. L. Erusalimksy, B. A. Dolgoplosk, and A. P. Kavunenko, *J. Gen. Chem. USSR*, 27, 301 (1957).

(9) For example, *trans*-2,2′-azoisobutane has an activation energy of 42.8 kcal/mol, while the closest known *cis* analog, *meso*-3,6-dimethyl-3,6-diethylpiperidazene, has an activation energy of 34.3 kcal/mol: Thesis of N. A. Porter, Harvard University, Boston, Mass., 1969, p 40.

(10) T. Mill and R. S. Stringham, *Tetrahedron Lett.*, 1853 (1969).

(11) (a) R. K. Harris and R. A. Spragg, *Chem. Commun.*, 313 (1966); (b) F. G. Riddell, *J. Chem. Soc.*, *B*, 570 (1967); (c) J. M. Lehm, F. G. Riddell, B. J. Price, and I. O. Sutherland, *ibid.*, 387 (1967); (d) J. E. Anderson and J. D. Roberts, *J. Amer. Chem. Soc.*, **90**, 4186 (1968).

(12) W. M. Tolles, D. W. Moore, and W. E. Thun, *ibid.*, **88**, 3476 (1966).

The uv spectrum, thermal stability, and nmr spectrum of **4** all seem most consistent with *trans*-2-tetrazene groups; in the absence of *cis*-tetraalkyl-2-tetrazenes as models, however, this point remains possibly ambiguous. Further attempts at synthesis of *cis*-tetraalkyl-2-tetrazenes are continuing in these laboratories.

**Acknowledgment.** We thank the Wisconsin Alumnae Research Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for support of this work. We thank Professor P. D. Bartlett for making the data from N. A. Porter's thesis available

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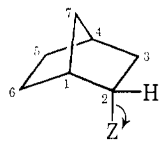
## Ring Contraction in Solvolysis of a Norbornyl System[1]

*Sir:*

A characteristic of Wagner-Meerwein rearrangements in 2-substituted bicyclo[2.2.1]heptyl (norbornyl) systems is that they involve migration of the $C_1$–$C_6$ bond whether the departing group at C-2 is initially *exo* or *endo*.[2] For *exo* groups the shift of C-6 is understandable on geometric grounds whether the first intermediate is viewed as a (nonclassical) bridged cation or as a classical cation shielded on the *exo* side by the departing species. Failure to observe migration of C-7 (**1** → **2** → **3**) in ionization of *endo* groups might be rationalized in terms of a distorted initial geometry for backside participation and/or of an increase in skeletal strain that would presumably accompany a ring contraction.[2,3] Conceivably these unfavorable features might be mitigated if the stability of the rearranged ion were substantially enhanced by appropriate substitution and if C-7 became involved before the ionization site lost its *endo* identity.[4] We now report that solvolysis of 1-methoxy-2-*endo*-norbornyl brosylate (**6b**) produces a product with a bicyclo[3.1.1]heptyl skeleton and thus provides the first example of a ring contraction in solvolysis of a norbornyl system.[5]

In our synthetic work, 1-methoxynorbornan-2-one (**4**)[6] was reduced with $LiAlH_4$ to a mixture of C-2 epimeric liquid alcohols, which were separated by preparative glpc. The *exo* alcohol (**5a**, $C_8H_{14}O_2$)[7] and its *endo* epimer (**6a**, $C_8H_{14}O_2$) were individually converted to the corresponding *p*-bromobenzenesulfonates and acetates by treatment, in pyridine, with brosyl chloride and with acetic anhydride, respectively. The 1-methoxy-*exo*-2-norbornyl brosylate (**5b**, $C_{14}H_{17}O_4$-BrS; mp 69–69.5° from ether–hexane) showed four groups of proton signals ($CCl_4$) at $\delta$ 7.75 (q, 4, aromatic), 4.58 (m, 1, C-2), 3.14 (s, 3, $OCH_3$), and 2.3–0.8 (m, 9). The corresponding 2-*exo*-acetate (**5c**, $C_{10}H_{16}O_3$; ir 2838, 1740 $cm^{-1}$) also showed four groups of nmr signals: $\delta$ 4.86 (d, $J$ = 7 Hz, C-2), 3.21 (s, 3, $OCH_3$), 1.97 (s, 3, $COCH_3$), 2.4–0.7 (m, 9). The 1-methoxy-*endo*-2-norbornyl brosylate (**6b**, $C_{14}H_{17}O_4BrS$) had mp 65–67° (ether–hexane); $\delta$ 7.75 (q, 4, aromatic), 4.82 (d, $J$ = 9 Hz, 1, C-2), 3.11 (s, 3, $OCH_3$), 2.5–1.0 (m, 9). The 2-*endo*-acetate **6c** ($C_{10}H_{16}O_3$, $\nu$ 2833, 1740 $cm^{-1}$) had $\delta$ 5.07 (d, $J$ = 10 Hz, 1, C-2), 3.26 (s, 3, $OCH_3$), 2.00 (s, 3, $COCH_3$), 2.7–0.8 (m, 9).[8]



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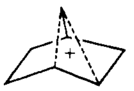

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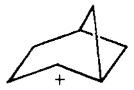

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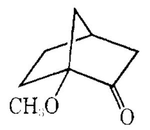

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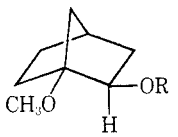

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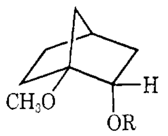
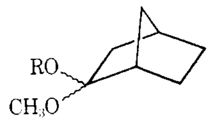


**6**

**a**, R = H
**b**, R = Bs
**c**, C = Ac



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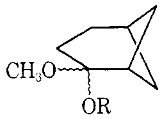

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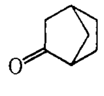

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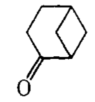

**10**

Acetolysis of the *exo*-brosylate **5b** at 50° (HOAc–KOAc) followed by aqueous work-up gave only one product, norbornan-2-one (**9**, >99.9% by glpc) identified by infrared comparison with an authentic sample. With nortricyclanone[9] as an internal glpc standard the conversion appeared virtually quantitative. In contrast, acetolysis of *endo*-brosylate **6b** gave norbornan-2-one (**9**), 1-methoxy-2-*exo*-norbornyl acetate (**5c**), and bicyclo[3.1.1]heptan-2-one (**10**), whose glpc ratios are summarized in Table I. The ring-contracted ketone **10** was also formed when the solvolysis was conducted in trifluoroacetic acid and in 60% aqueous acetone. The products were separated by preparative glpc[10] and

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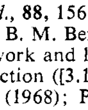
(1) This work was supported by the National Science Foundation.

(2) For recent reviews see: (a) G. D. Sargent, *Quart. Rev. Chem. Soc.*, **20**, 301 (1966); (b) G. E. Greame, *Rev. Pure Appl. Chem.*, **16**, 25 (1966); (c) H. C. Brown, *Chem. Brit.*, **2**, 199 (1966); *Chem. Eng. News*, **45** (7), 86 (1967); (d) J. A. Berson, "Molecular Rearrangements," P. de Mayo, Ed., Interscience, New York, N. Y., 1963, Chapter 3; (e) B. Capon, M. J. Perkins, and C. W. Rees, "Organic Reaction Mechanisms-1955," Interscience, New York, N. Y., 1966, Chapter 1.

(3) F. R. Jensen and B. E. Smart, *J. Amer. Chem. Soc.*, **91**, 5688 (1969).

(4) The isolation of products containing the tricyclic system i in solvolysis of *anti*-7-norbornenyl substrates shows that the geometry for bonding of C-7 simultaneously to C-1 and C-2 is attainable: H. Tanida, T. Tsuji, and T. Irie, *ibid.*, **88**, 864 (1966); A. Diaz, M. Brook-Hart, and S. Winstein, *ibid.*, **88**, 3133 (1966).



**i**

(5) For an authentic example in a diazoketone rearrangement see P. Yates and R. J. Crawford, *ibid.*, **88**, 1561 (1966), and in a deamination see C. J. Collins, V. F. Raaen, B. M. Benjamin, and I. T. Glover, *ibid.*, **89**, 3940 (1967). For recent work and leading references on solvolytic rearrangements in reverse direction ([3.1.1] → [2.2.1]) see: W. Kirmse and R. Siegfried, *ibid.*, **90**, 6564 (1968); P. von R. Schleyer, W. E. Watts, and C. Cupas, *ibid.*, **86**, 2722 (1964); E. C. Friedrich and S. Winstein, *ibid.*, **86**, 2721 (1964).

(6) (a) A. Nickon, T. Nishida, and Y-i Lin, *ibid.*, **91**, 6860 (1969); (b) A. Nickon and Y-i Lin, *ibid.*, **91**, 6861 (1969).

(7) Satisfactory carbon and hydrogen analyses were obtained for all new compounds whose empirical formulas are given.

(8) The nmr characteristics of the C-2 proton in **5** and **6** (*e.g.*, doublets are broadened) are consistant with our stereochemical assignments. For extensive literature references see: P. Laszlo and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964).

(9) W. G. Dauben, Ed., *Org. Syn.*, **45**, 77 (1965).

(10) The *exo*- and *endo*-acetates **5c** and **6c** were not resolved under our glpc conditions whereas the alcohols **5a** and **6a** were. We showed