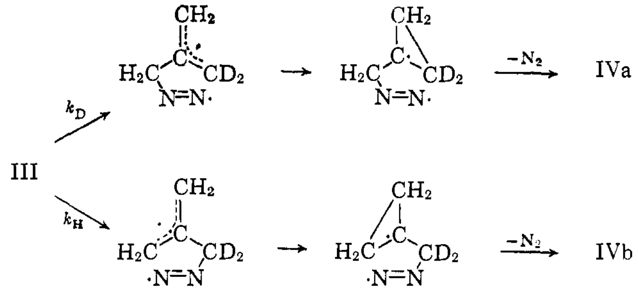
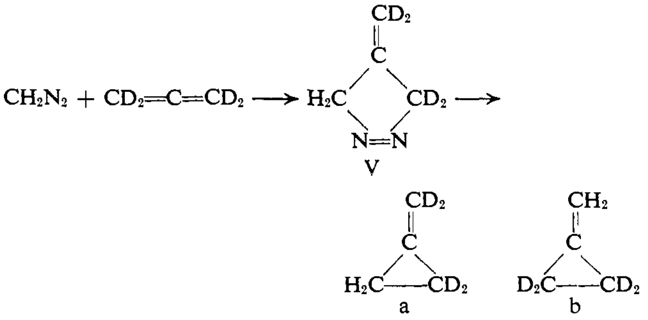
then a k_H/k_D value of 1.37 ± 0.05 is derived from the values observed in the above experiment. Mechanism B consists of the breaking of carbon–nitrogen bonds in an unsymmetrical fashion and of a secondary kinetic isotope effect of 1.47 ± 0.06, resulting in the observed ratio of IVa to IVb.[6]

Mechanism B



A decision between these two mechanisms is possible on the basis of the nmr ring to vinyl ratio of the isomer mixture resulting from pyrolysis of 4-methylene-1-pyrazoline-3,3,6,6-d_4 (V) prepared by the addition of diazomethane to allene-d_4. Using the above values for mechanisms A and B, the predicted percentages of VIa and VIb were calculated and are shown in Table II. The observed value from pyrolysis at 175° is such as to confirm mechanism A, the observation of trimethylenemethane as an intermediate.



VI

Table II

Predicted	R^a	VIa, %	VIb, %
Mechanism A	2.73	73.2 ± 2.0	26.8 ± 2.0
Mechanism B	1.47	59.3 ± 2.0	40.7 ± 2.0
Observed	2.82^b ± 0.10	73.8 ± 0.8	26.2 ± 0.8

^{a} R = ratio of integrated areas of the ring to vinyl protons. ^{b} Result of four measurements taken at different times and checked with a pure sample of methylenecyclopropane, R = 2.01 ± 0.03.

The value of k_H/k_D for rotation about the symmetry axis of I is such that $\Delta\Delta F^* = 286$ cal mole^{-1} and is larger in magnitude than most secondary isotope effects. An important contribution may arise from the ponderal effect of the deuterium as the CD_2 group will have twice the moment of inertia of the CH_2 group. Further attempts to observe the intermediate spectroscopically are currently under investigation.

Acknowledgement. The authors are grateful to the Petroleum Research Fund of the American Chemical Society (Grant 1770-A4) and to the National Research Council of Canada for support of this work.

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Received April 22, 1966

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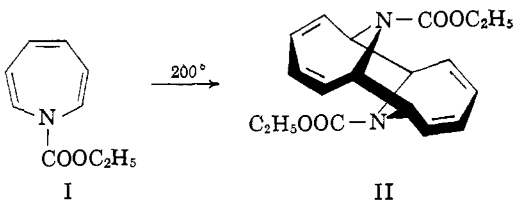
[6] S. Seltzer and F. T. Dunne, *J. Am. Chem. Soc.*, **87**, 2628 (1965).

The Thermal Dimerization of N-Carbethoxyazepine[1]

Sir:

As part of our broad interest in the ground-state[2] and electronically excited-state[3] behavior of medium-sized unsaturated heterocycles, we have investigated the thermal behavior of N-carbethoxyazepine (I) and wish to describe the unusual mode of self-condensation which occurs under these conditions.

When I[4] was heated in a sealed tube for 5–10 min at 200°, there resulted in 75% yield a highly crystalline white solid, mp 196–197°,[5] $\lambda_{\max}^{\mathrm{EtOH}}$ 232 (ϵ 14,100) and 237.5 mμ (ϵ 14,800). The dimeric nature of the latter substance was apparent from its mass spectrum which displayed a molecular ion peak at m/e 330. The nmr spectrum of this dimer (in $CDCl_3$) was suggestive of a highly symmetrical species [two completely superimposable ethoxy groups at δ 4.08 (4 H, quartet, J = 7.5 cps, $-O-CH_2-$) and 1.29 (6 H, triplet, J = 7.5 cps, CH_3-), a pseudo-singlet absorption for the vinyl protons[6] at δ 5.88, and a broad doublet (4 H, J = 8.5 cps) for the bridgehead protons], and was fully compatible with structure II. This formulation (II) was corroborated further by its dipole moment (0.91 D., in dioxane) and by its Raman spectrum which displayed an intense band near 1620 cm^{-1} which was strongly depolarized by a parallel filter, thereby implicating a symmetrical diene vibration. Further, II has been correlated chemically with a dimer of N-cyanoazepine of similar structure.[7]



I II

Catalytic hydrogenation of II (Adams catalyst, 740 mm) proceeded with the uptake of 4 equiv of hydrogen to give IIIa, mp 87–88°,[5] which with lithium aluminum hydride in dioxane afforded IIIb, mp 148–150°.[5] Diamine IIIc, mp 60–61° (sealed tube),[5] resulted from the

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[1] Unsaturated Heterocyclic Systems. XXV. For paper XXIV of this series, refer to L. A. Paquette and J. H. Barrett, *J. Am. Chem. Soc.*, **88**, 1718 (1966).

[2] For a review of certain aspects of this work, see L. A. Paquette, *Proc. N. Y. Acad. Sci. U.S.*, **28**, 387 (1966).

[3] See particularly footnote 9 of ref 1.

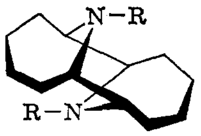
[4] R. J. Cotter and W. F. Beach, *J. Org. Chem.*, **29**, 751 (1964).

[5] Satisfactory analyses were obtained for all new compounds described.

[6] The appearance of a group of vinyl protons, which *a priori* would be expected intuitively to possess differing chemical shifts, as a simple pseudo-singlet nmr absorption is not unique to II, but has been reported for a number of polyunsaturated cyclic systems such as 1,3,5-cyclooctatriene [W. von E. Doering, G. Laber, R. Vonderwahl, N. F. Chamberlain, and R. B. Williams, *J. Am. Chem. Soc.*, **78**, 5448 (1956)] and the cyclooctatetraene dimer mp 53° [G. Schröder and W. Martin, *Angew. Chem. Intern. Ed. Engl.*, **5**, 130 (1966)].

[7] A. L. Johnson and H. E. Simmons, *J. Am. Chem. Soc.*, **88**, 2591 (1966).

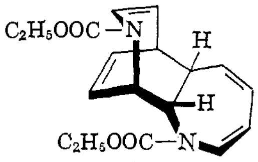
hydrolysis of IIIa with anhydrous hydrogen bromide in glacial acetic acid.



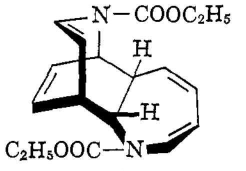
IIIa, R = $COOC_2H_5$
b, R = CH_3
c, R = H

The mechanism by which two molecules of I undergo cycloaddition to give II was deemed of considerable interest. On the basis of theoretical orbital symmetry considerations,[8] this intramolecular conversion, which formally involves a (6 + 6) π thermal cycloaddition, is not allowed to occur in a concerted fashion. Therefore, evidence which would indicate a multistep mechanistic pathway was sought. In a parallel type of reaction, I was heated at 130° and a new dimeric white solid, mp 78°,[5] λ_{max}^{EtOH} 213 (ϵ 13,700) and 241 mμ (ϵ 9350), was obtained in 35% yield.[9] This dimer has also been found to be present in high concentration in samples of I which had been stored for 3 years at ambient laboratory temperatures.[10] This substance likewise manifested a molecular ion peak at m/e 330, but in contrast exhibited a complex nmr spectrum. The strong likelihood that the dimer, mp 78°, is an intermediate in the formation of II was derived from its conversion to II in high yield upon being heated at 200° for a brief period of time.

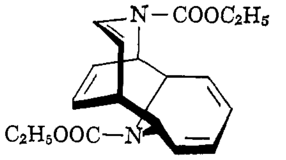
Application of the Hoffmann–Woodward analysis[8,11] to I suggested the allowed concerted formation of two (4 + 2) *endo* adducts (IV and V) and a (4 + 6) *exo* adduct (VI). Structures IV and V were quickly removed from consideration because of the observation that hydrogenation of the low-melting dimer gave an octahydro derivative[5] whose nmr spectrum showed evidence for only five protons on carbon bearing nitrogen (perhydro IV and V require six such protons).



IV



V



VI

Thus, the presently available physical and theoretical evidence suggests VI as the intermediate in the conversion of I to II. Work is continuing to establish this point conclusively by chemical means; also, expansion of the scope of this work to include oxepins and substituted azepines is currently under active investigation.

Acknowledgment. Support of this work by the Petroleum Research Fund, administered by the American Chemical Society, is acknowledged with gratitude. The authors are also especially indebted to Professor D. C. DeJongh for the mass spectra and to Drs. H. Simmons and A. Johnson for the dipole moment and Raman data.

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(8) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965).

(9) Compounds I and II have always accompanied the formation of this dimer under the reaction conditions employed. Careful column chromatography (Al_2O_3) effectively separated the components of the mixture.

(10) The authors are grateful to Dr. Robert J. Cotter, Union Carbide Corp., Bound Brook, N. J., for providing us with these samples. Dr. Cotter has informed us in a private communication that certain of his samples were noted to have increased somewhat in viscosity after 6 months at room temperature.

(11) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 4389 (1965).

(12) Alfred P. Sloan Foundation Research Fellow.

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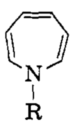
13,14-Diazatricyclo$[6.4.1.1^{2,7}]$tetradeca-3,5,9,11-tetraene and Its Derivatives

Sir:

It was previously reported[1] that N-cyanoazepine (1, R = CN) undergoes spontaneous dimerization at 25° to a white, crystalline product, mp 220–221° dec. We have found that when this dimer, whose structure is under investigation, is heated at 210–215° for 15–30 min in naphthalene as solvent, it is smoothly rearranged in 70% yield to 13,14-dicyano-13,14-diazatricyclo$[6.4.1.1^{2,7}]$-tetradeca-3,5,9,11-tetraene (2, R = CN),[2] $C_{14}H_{12}N_4$, mp >400° dec, ν_{max}^{KBr} 3040 (CH=CH), 2210 (CN), and 1660 cm^{-1} (C=C), $\lambda_{max}^{CH_3CN}$ 237 (ϵ 16,300) and 230 mμ (ϵ 15,150),[3] nmr (in $CF_2ClCOCF_2Cl$–D_2O, external TMS) τ 3.61 (broad singlet, eight vinyl protons), 5.69 (multiplet, four tertiary protons), mol wt, 236. The data described in this communication establish that we have obtained the new diazatricyclotetradecatetraene ring system. The direct formation of a (6 + 6) addition product would not be in accord with the Woodward–Hoffmann rules,[4] and the only other case of 1,6 addition



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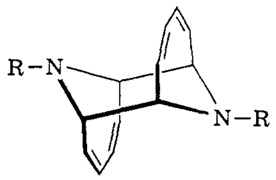

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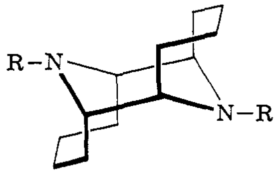

3

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(1) F. D. Marsh and H. E. Simmons, *J. Am. Chem. Soc.*, **87**, 3529 (1965).

(2) Satisfactory elemental and spectral analyses were obtained for all new compounds reported herein.

(3) *Cf.* the 1,4 monoadduct of NCN to cyclooctatetraene, $\lambda_{max}^{CH_3CN}$ 255 mμ (ϵ 4500): A. G. Anastassiou, *J. Am. Chem. Soc.*, **87**, 5512 (1965).

(4) (a) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965); (b) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965); (c) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 4388 (1965); (d) H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045(1965).