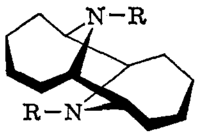
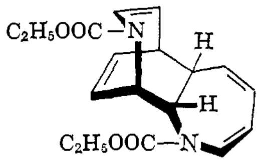
hydrolysis of IIIa with anhydrous hydrogen bromide in glacial acetic acid.



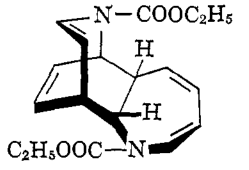
IIIa, R = $COOC_2H_5$
b, R = CH_3
c, R = H

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] $\lambda_{\max}^{\mathrm{EtOH}}$ 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.

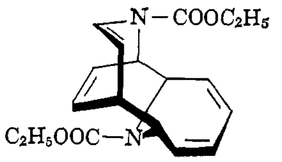
Application of the Hoffmann-Woodward analysis[8,11] to I suggested the allowed concerted formation of two (4 + 2) *endo* adducts (IV and V) and a (4 + 6) *exo* adduct (VI). Structures IV and V were quickly removed from consideration because of the observation that hydrogenation of the low-melting dimer 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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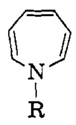
13,14-Diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene and Its Derivatives

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, $\nu_{\max}^{\mathrm{KBr}}$ 3040 (CH=CH), 2210 (CN), and 1660 cm^{-1} (C=C), $\lambda_{\max}^{\mathrm{CH_3CN}}$ 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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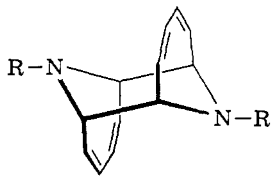

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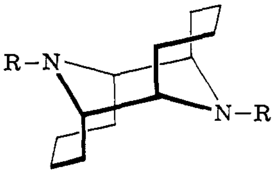

3

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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, $\lambda_{\max}^{\mathrm{CH_3CN}}$ 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).

to an azepine[5] has since been disproved.[6–8] It is therefore most reasonable that **2** arises solely from a rearrangement of the dimer of N-cyanoazepine.

Hydrolysis of the cyano compound **2** (R = CN) with 50% sulfuric acid at 100° for 2–6 hr produces in 80% yield the biscarbamoyl derivative **2** (R = CONH$_2$), mp >300° dec, ν_{max}^{KBr} 3420, 3300, 3160, 1650, and 1585 cm^{-1} (NCONH$_2$), $\lambda_{max}^{50\%\ H_2SO_4}$ 234 mμ (ϵ 9450), nmr (CF$_2$ClCOCF$_2$Cl-D$_2$O, external TMS) τ 3.96 (broad singlet, eight vinyl protons), 5.32 (broad singlet, four tertiary + four exchange protons), mol wt, 272. Further hydrolysis of **2** (R = CN or CONH$_2$) with 50% sulfuric acid at 120° for 24 hr produces in 40–50% yield the parent diamine **2** (R = H), sublimes at 110° (0.1 mm), mp 147–148° dec, ν_{max}^{KBr} 3030 (CH=CH) and 1655 cm^{-1} (C=C), $\lambda_{max}^{CH_3CN}$ 240 (ϵ 15,800) and 234 mμ (ϵ 16,400), nmr (CDCl$_3$, internal TMS) τ 3.99 (singlet, eight vinyl protons), 6.43 (broad singlet, four tertiary protons), and 8.33 (singlet, two exchangeable protons), mol wt, 186.

The following difunctional derivatives of **2** (R = H) were prepared by conventional means, and their infrared, ultraviolet, nmr, and mass spectral data indicate clearly their relationship to the parent diamine: R = H$_2^+$Cl$^-$, mp >300° dec; R = C$_6$H$_5$CO, mp 314–315° dec; R = *p*-BrC$_6$H$_4$CO, mp 322–323° dec, R = C$_6$H$_5$NHCS, mp 211–212°; R = C$_6$H$_5$NHCO, mp >350° dec; R = CH$_3$, mp 165–166°, sublimes at 115° (0.1 mm); R = COCH$_3$, mp 317–319° dec; R = NO, mp >250° dec.

Zinc dust distillation of **2** (R = CN) at 350° produced a low yield of aniline, identified by comparison of its infrared spectrum and vpc retention time with an authentic sample.

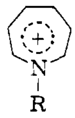
Diamine **2** (R = H) readily absorbs 4 molar equiv of hydrogen in dilute hydrochloric acid over platinum oxide at 25° (760 mm) to yield the completely saturated diamine **3** (R = H), mp 61–62°, sublimes at 70° (0.1 mm), ν_{max}^{KBr} 2900 and 1450 cm^{-1}, no $\lambda_{max}^{H_2O}$ >200 mμ, nmr (CCl$_4$, internal TMS) τ 7.29 (multiplet, four tertiary protons), 8.29 (multiplet, 16 methylene protons), and 8.50 (singlet, two exchangeable protons), mol wt, 194. The following derivatives of this new 13,14-diazatricyclo[6.4.1.1^{2,7}]tetradecane system exhibit the expected analytical and spectral properties: R = H$_2^+$Cl$^-$, mp >320° dec; R = H$_2^+$Br$^-$, mp >320° dec; R = CH$_3$, mp 95–96°, sublimes at 90° (0.1 mm);[8a] R = C$_6$H$_5$CO, mp 319.5–320.5° dec; R = C$_6$H$_5$NHCO, mp 374–375° dec; R = C$_6$H$_5$NHCS, mp 289.0–289.5° dec; R = NO, mp 180–182.5° dec.

In summary, the evidence for structures **2** and **3** rests upon these observations. (1) Compounds **2** show only weak double bond absorption in the 1600 cm^{-1} region of the infrared spectrum. However, compounds **2** (R = H and CH$_3$) possess an intense Raman band at 1615 cm^{-1} characteristic of conjugated dienes. Polarization studies on this band indicate that it is produced by a symmetrical diene vibration.[9] This fact and the weak infrared absorption can be accounted for by the proposed centrosymmetric C$_{2h}$ structure.

(2) The intense ultraviolet absorption in the 230–240 mμ region (ϵ 9000–16,000) of compounds **2** is consistent with the presence of two independent cisoid diene chromophores.

(3) The extremely simple nmr spectra of these compounds enable the protons to be assigned readily. The eight-proton vinyl signal of compounds **2** appears as a broad singlet in the τ 3.5–4.0 region, while the four tertiary bridgehead protons adjacent to nitrogen produce signals in the τ 5.2–5.8 region. In compounds **3**, the vinyl proton signals of **2** are replaced by a broad 16-proton multiplet near τ 8.3, and the four bridgehead protons are now shifted upfield by 1.0–1.5 ppm.

(4) The mass spectra of the unsaturated compounds **2** confirm the expected molecular weights and consistently exhibit a half-parent ion as the base peak. The lower mass values fall into a pattern characteristic of the azepine. Clearly, structure **2** undergoes ready fragmentation into azepinium ions C$_6$H$_6$NR$^+$ (**4**).[10] The mass spectra of compounds **3** also confirm their molecular weights and usually exhibit base peaks corresponding to protonated half-parent ions C$_6$H$_{11}$NR$^+$ (**5**).



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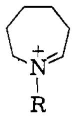

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(5) Examination of Dreiding models of **2** and **3** indicates that they are extremely rigid structures. The *trans* arrangement of the two four-carbon bridges is almost certainly favored over a *cis* arrangement from the viewpoint of nonbonded interactions and the unusual thermal stability of the compounds in the two series. The low dipole moment (0.57 D. in carbon tetrachloride) of **2** (R = CH$_3$) lends support to this structural assignment.

(6) A final piece of evidence concerning structure **2** was obtained by treating the diamine **2** (R = H) with 2 molar equiv of ethyl chloroformate and 2 equiv of sodium carbonate in ether. The bis(ethylurethan) **2** (R = CO$_2$C$_2$H$_5$), mp 195.5–196.5°, was obtained in 83% yield and was shown to be identical by mixture melting point and infrared, ultraviolet, and nmr spectra with the compound obtained by thermal treatment of N-carbethoxyazepine (**1**, R = CO$_2$C$_2$H$_5$).[11] Photochemical reversal of the dimerization of **1** (R = CO$_2$C$_2$H$_5$) was observed by irradiating **2** (R = CO$_2$C$_2$H$_5$) in 1% acetonitrile solution at 12° with a low-pressure mercury lamp in a water-cooled quartz apparatus. The monomer **1** (R = CO$_2$C$_2$H$_5$) was isolated in 12% yield by distillation.

Quaternization of **2** and **3** (R = CH$_3$) proceeds under moderately vigorous conditions (CH$_3$I in CH$_3$CN at 100°; 24 hr) to produce the crystalline monomethiodides **6**, mp >300°, and **7**, mp 246–248° dec. The

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(5) K. Hafner, *Angew. Chem. Intern. Ed. Engl.*, 3, 165 (1964).

(6) J. H. van den Hende and A. S. Kende, *Chem. Commun.*, 384 (1965).

(7) J. E. Baldwin and R. A. Smith, *J. Am. Chem. Soc.*, 87, 4819 (1965).

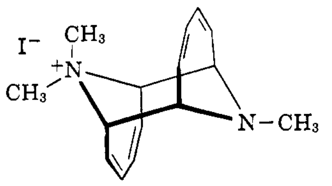
(8) A. S. Kende, P. T. Izzo, and J. E. Lancaster, *ibid.*, 87, 5044 (1965).

(8a) NOTE ADDED IN PROOF. The identity of samples of **3** (R = CH$_3$) prepared by different routes has now been established by direct comparison of analytical and spectral data. After repeated sublimation, our sample melted at 125–130°. Professor Paquette's sample, after sublimation, melted at 128–145°, and after recrystallization from Skellysolve B, it showed the sharper melting point, 148–150°.

(9) We wish to thank Dr. A. J. Dahl, Plastics Department, E. I. du Pont de Nemours and Co., for carrying out this measurement.

(10) Compare F. W. McLafferty, "Mass Spectrometry of Organic Ions," Academic Press Inc., New York, N. Y., 1963, p 506.

(11) We are grateful to Professor L. A. Paquette, Ohio State University, for kindly communicating his results to us privately prior to publication, and for furnishing us with a sample of his compound for direct comparison.



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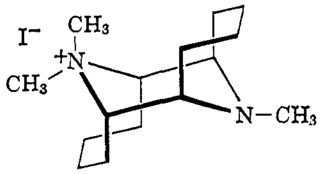

7

formation of only monoquaternary derivatives has been observed in other bridged piperazines.[12]

A full account of the chemistry of these compounds is in preparation.

[12] M. V. Rubtsov and E. S. Nikitskaya, *Usp. Khim. USSR,* **34,** 1040 (1965).

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Received April 14, 1966

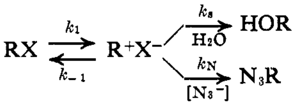
Identification of an Ion-Pair Intermediate in an SN2 Reaction[1]

Sir:

On the basis of rather indirect evidence we recently suggested[2] that a bimolecular displacement reaction, having all of the defining characteristics of an SN2 reaction, actually had as its mechanism the reversible formation of an ion pair whose subsequent attack by nucleophile was rate determining. Direct confirmatory evidence that this is the case is now available and constitutes the subject matter of this report.

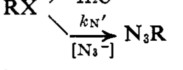
The earlier suggestion[2] was predicated upon the following observations: (1) reaction of optically active 2-octyl brosylate in 75 vol. % aqueous dioxane (25% water) containing sodium azide gave rise to inverted 2-octyl azide[3] at a rate dependent on the concentration of azide ion. Clearly the reaction exhibits the defining characteristics of an SN2 reaction, bimolecular kinetics and inversion of configuration. (2) On the other hand when optically active 2-octyl mesylate was solvolyzed in the more aqueous system, 25 vol. % aqueous dioxane (75% water), in the presence of sodium azide, 2-octyl azide was again obtained[3] at a rate *nearly independent* of the concentration of sodium azide. Significantly, the 2-octyl azide formed in this system proved to be highly inverted. Clearly, in this more aqueous system, an intermediate must be formed in the rate-determining step whose transition state does not include azide ion (kinetic fact) but which must be asymmetric since subsequent attack by azide ion gives rise to optically inverted 2-octyl azide. It was suggested[2] that this intermediate is an ion pair.

The above evidence seemed consistent with, if not conclusive for, a common mechanism for the reactions of 2-octyl sulfonates in the two solvent systems, a mechanism which includes in both an ion-pair intermediate whose formation is rate determining in the more aqueous solvent ($((k_s + k_N[N_3^-]) > k_{-1})$ and whose destruction (by water and azide ion) is rate determining in the poorer ionizing solvent ($(k_{-1} > (k_s + k_N[N_3^-]))$.



$$RX \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} R^+X^- \begin{cases} \xrightarrow[H_2O]{k_s} HOR \\ \xrightarrow[[N_3^-]]{k_N} N_3R \end{cases} \qquad (1)$$

If this were the case it seemed to us that there should exist some solvent composition intermediate between the above extremes, in which the rate of formation of ion pair was comparable in magnitude with its rate of destruction. In such a solvent system a clean experimental distinction can be made between the suggested ion-pair scheme (1) and a true SN2 mechanism (2) in which attack by nucleophiles takes place directly on covalent starting material. In essence this distinction arises since in a true SN2 process rates and products



$$RX \begin{cases} \xrightarrow[H_2O]{k_s'} HOR \\ \xrightarrow[[N_3^-]]{k_N'} N_3R \end{cases} \qquad (2)$$

are determined in the same steps of reaction, whereas in the ion-pair mechanism products are determined in the steps labeled k_s and k_N while the rate is a composite function of all four rate constants. The following equations provide a quantitative basis for this distinction.

A steady-state treatment of the ion-pair mechanism (1) establishes the following relationship[4]

$$k_{\text{exptl}}/k_{NA} = (x + 1)(1 + k_N[N_3^-]/k_s)/(x + 1 + k_N[N_3^-]/k_s) \qquad (3)$$

where k_{exptl} is the experimental rate constant, k_{NA} the rate constant in the absence of azide ion, x is defined as k_{-1}/k_s, and the ratio k_N/k_s is given experimentally as the slope of a plot of $[RN_3]/[ROH]$ *vs.* $[N_3^-]$. Simple algebra establishes the following relationship (4) for a true SN2 reaction (2) where k_N'/k_s' is given experimentally as the slope of a plot of $[RN_3]/[ROH]$ *vs.* $[N_3^-]$.

$$k_{\text{exptl}}/k_{NA} = 1 + k_N'[N_3^-]/k_s' \qquad (4)$$

Kinetic data for solvolyses of 2-octyl mesylate in both 25 and 30 vol. % aqueous dioxane were obtained titrimetrically. Since alkyl azide formation is not accompanied by the liberation of acid, the difference between the experimental and theoretical infinity titers was used to determine the relative amounts of 2-octanol and of 2-octyl azide. Since rate constants (treated as pseudo first order) were calculated using the experimental infinity titers they are measures of the sum of the rate constants for all processes which result in the destruction of starting material. Corrections (relatively small) for the normal salt effects produced on rates by sodium azide were made by assuming them to be equal in magnitude to those produced by lithium perchlorate[5] and by assuming them to be linear in $[N_3^-]$. The data are summarized in Tables I and II and the data of Table II are represented graphically in Figure 1. Scrutiny will make it immediately apparent that the

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[1] Supported in part by the National Science Foundation.

[2] H. Weiner and R. A. Sneen, *J. Am. Chem. Soc.,* **87,** 292 (1965).

[3] Accompanied by inverted 2-octanol.

[4] Note that, in the limit, as x becomes very large, eq 3 reduces to eq 4. As x becomes very small eq 3 reduces to $k_{\text{exptl}}/k_{NA} = 1$; *i.e.*, to SN1 behavior.

[5] In separate control experiments it has been established that sodium nitrate, lithium bromide, sodium acetate, and lithium perchlorate all have nearly identical salt effects in these solvent systems.