

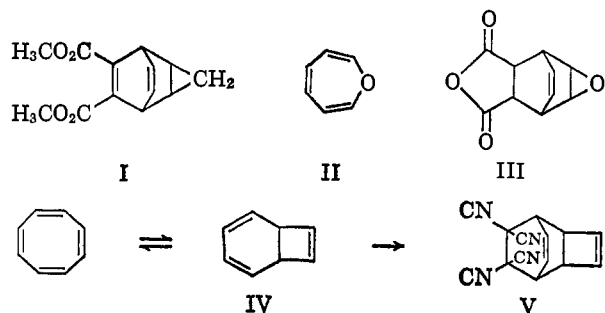
Conformational Studies in the 2-Azabicyclo[3.2.2]nonene Series by Spin Decoupling. Structure of the N-Carbethoxyazepine-Tetracyanoethylene Adduct

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The crystalline 1:1 adduct between *N*-carbethoxyazepine (VI) and tetracyanoethylene, originally formulated as the 2,7-adduct VII by Hafner, has been shown to be the 2-azabicyclo[3.2.2]nona-3,6-diene XII by a detailed spin-decoupling analysis of its n.m.r. spectrum in d_6 -dimethyl sulfoxide. The adduct reacts with 1 equiv. of bromine in methanol to give two isomeric methoxybromides, m.p. 191 and 148°, in about 3:1 ratio; these two methoxybromides are formed in similar proportion by treatment of the adduct with 1 equiv. of bromine in chloroform followed by methanolysis. Ultraviolet spectra and spin-decoupling studies lead to the conclusion that the 191° methoxybromide has a *trans* stereochemistry and the conformation depicted in structure XVI, whereas the 148° methoxybromide has a *cis* stereochemistry and the conformation depicted in structure XXI. The unexpected conformation XVI, which has been independently confirmed by X-ray crystallographic analysis, is believed to predominate largely because it lacks dipole-dipole repulsions between C-Br and C-OMe which would be present in the alternative conformation. The moderate stereoselectivity of the methoxy bromination is attributed to the intermediacy of the bridged bromonium ion XXIV in both the direct and two-step process. It is suggested on quantum chemical grounds that cycloaddition of dienophiles to cycloheptatrienes should normally give Diels-Alder adducts analogous to I except where the cyclic triene is much more stable than its bicyclic valence tautomer, as may be the case with *N*-carbethoxyazepine.

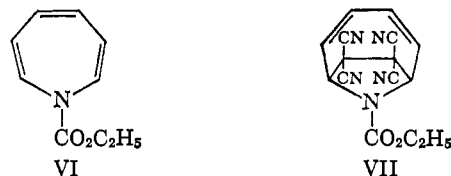
The additions of dienophiles to medium-ring polyenes frequently lead to abnormal products. Thus cycloheptatriene and dimethyl acetylenedicarboxylate react to give the tricyclic adduct I formally derived from norcaradiene,¹ and similarly oxepine (II) is reported to give the epoxide III with maleic anhydride.² Recent



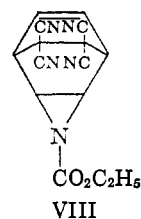
- (1) K. Alder and G. Jacobs, *Chem. Ber.*, **86**, 1528 (1953).
 (2) E. Vogel, W. A. Böll, and H. Günther, *Tetrahedron Letters*, **10**, 609 (1965).

kinetic studies by Huisgen³ indicate that the formation of the tricyclic adduct V from cyclooctatetraene and tetracyanoethylene in dilute solution involves a rapid pre-equilibrium between the tetraene and its valence tautomer bicyclo[4.2.0]octatriene (IV), with the latter reacting to form the adduct in a rate-determining step.

In the light of these observations, the recent report⁴ that *N*-carbethoxyazepine (VI)⁵ reacts readily with dienophiles and specifically with tetracyanoethylene to give what appears to be the unusual 2,7-adduct VII seemed to deserve reinvestigation.



In our hands the azepine VI proved surprisingly inert to dienophiles such as maleic anhydride or dimethyl acetylenedicarboxylate even at temperatures above 100° without solvent. The azepine did, however, react readily with tetracyanoethylene in benzene at room temperature to give a sparingly soluble crystalline 1:1 adduct in good yield. The ultraviolet spectrum of this adduct, $\lambda_{\max}^{\text{CH}_3\text{OH}}$ 244 m μ (ϵ 7600) was compatible with structure VII since 1,3-cycloheptadiene absorbs at λ_{\max} 248 m μ (ϵ 7500).⁶ However, the proton magnetic resonance spectrum of the adduct in d_6 -dimethyl sulfoxide (Figure 1) was far too complex to be rationalized in terms of the symmetrical structure VII. One alternative, the tricyclic structure VIII, was likewise incompatible on symmetry grounds as well as on the basis of the observed ultraviolet spectrum.



Structure of the Adduct. Extensive application of proton decoupling⁷ has allowed an analysis of the prin-

- (3) R. Huisgen and F. Mietzsch, *Angew. Chem.*, **76**, 36 (1964).
 (4) K. Hafner, *ibid.*, **75**, 1041 (1963).
 (5) K. Hafner and C. König, *ibid.*, **75**, 89 (1963); W. Lwowski, T. J. Maricich, and T. W. Mattingly, Jr., *J. Am. Chem. Soc.*, **85**, 1200 (1963); R. J. Cotter and W. F. Beach, *J. Org. Chem.*, **29**, 751 (1964).
 (6) E. Pesch and S. L. Friess, *J. Am. Chem. Soc.*, **72**, 5756 (1950).
 (7) Decoupling was carried out on the DP-60 spectrometer using L. Johnson's field sweep method employing a modified Varian integrator (Varian Bulletin, Volume III, No. 3, Varian Associates, Inc., Palo Alto, Calif., 1965); frequencies were read with a frequency counter.

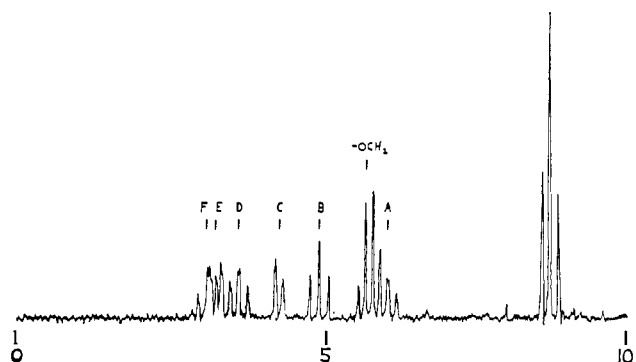


Figure 1. Proton magnetic resonance spectrum of the N-carbethoxyazepine-tetracyanoethylene adduct, taken in d_6 -DMSO and measured at 56.4 Mc.; solvent peaks are not shown.

cipal spin-coupling interactions in the spectrum of Figure 1 and has permitted an *a priori* deduction of structure for the adduct. For example, the region between τ 3 and 4 (Figure 2a) contains, in addition to the triplet for proton D centered at τ 3.54, a complex multiplet centered at about 3.1 corresponding to two protons, E and F. Decoupling 60 c.p.s. upfield of sweep (Figure 2b) removes long-range secondary couplings of E and F and clearly reveals that E is a sharp doublet centered at τ 3.18 and F is a pair of doublets centered at 3.13. If instead proton B is irradiated, one obtains the collapse of doublet E to a broad singlet, showing that E and B are strongly coupled with $|J_{BE}| = 9.1$ c.p.s. Finally, irradiation of proton A leaves E unchanged but causes the collapse of F to a simple doublet, revealing the strong coupling $|J_{AF}| = 7.2$ c.p.s.

In other regions of the spectrum similar demonstrations of spin coupling can be carried out; thus irradiation of proton A (τ 6.05) causes collapse of the B signal to a doublet; the same effect upon B is obtained when proton E is irradiated. The signal of proton D is likewise converted to a doublet by decoupling of proton C. This leaves only the protons D and F with strong unassigned couplings; hence these must be coupled with each other. Table I summarizes the observed major couplings, which are of the expected magnitudes for 1,2 rather than long-range couplings and thus indicate the bond topology of the core of the molecule.

Table I

Proton label	Chemical shift, τ	Principal couplings, c.p.s. ^a
A	6.05	$ J_{AB} = 8.9$, $ J_{AF} = 7.2$
B	4.88	$ J_{AB} = 8.9$, $ J_{BE} = 9.1$
C	4.20	$J_{CD} = 7.4$
D	3.54	$J_{CD} = 7.4$, $ J_{DF} = 8.8$
E	3.18	$J_{BE} = 9.1$
F	3.03	$ J_{AF} = 7.2$, $ J_{DF} = 8.8$

^a Values of the coupling constants are accurate to ± 0.5 c.p.s.

The data of Table I define the following sequence of CH groups but leave the units $\text{NCO}_2\text{C}_2\text{H}_5$ and $\text{C}(\text{CN})_2$ still unplaced.

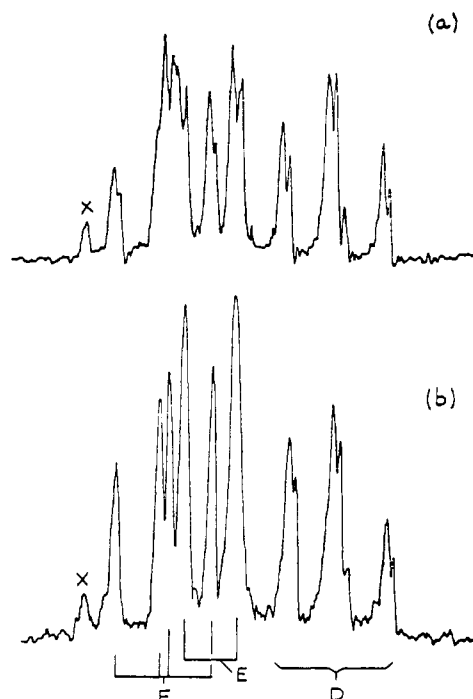
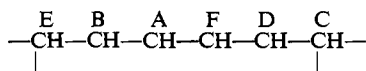
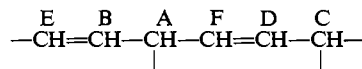
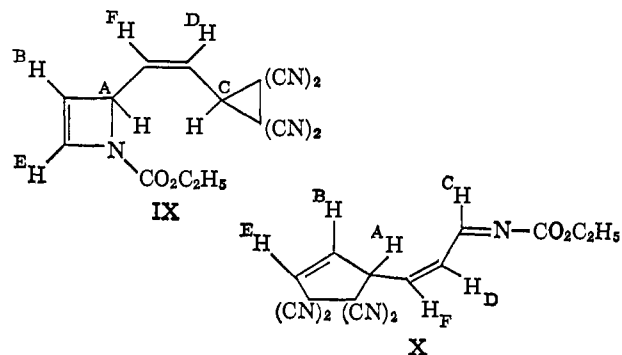


Figure 2. (a) Region between τ 3 and 4 of Figure 1, before decoupling. (b) Region between τ 3 and 4 of Figure 1 upon decoupling 60 c.p.s. upfield of sweep, which removes long-range coupling of protons E and F to proton C.

If now one makes the reasonable assumptions that protons E and F are olefinic protons while proton A is not an olefinic proton, two double bonds are required and can be uniquely placed as follows.



Placement of the unassigned functional units as bridges across the remaining four open valences of the methine chain defines four possible structural permutations, IX through XII. Each of the first three situates an olefinic bond within a four- or five-membered ring, a situation entirely incompatible with the large (8.8–9.1 c.p.s.) values observed for $|J_{BE}|$ and $|J_{DF}|$.⁸ This objection does not hold for structure XII, which fits the ultraviolet spectrum, since the chromophore $\text{C}=\text{NHCOC}_2\text{H}_5$ is reported to absorb at λ_{max} 240 m μ (ϵ 6600),⁹ and, in fact, represents the *normal Diels-Alder adduct* of the diene portion of VI.



(8) O. L. Chapman, *J. Am. Chem. Soc.*, **85**, 2014 (1963); G. V. Smith and H. Kriloff, *ibid.*, **85**, 2016 (1963); P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2018 (1963).

(9) G. Rosencranz, O. Mancera, F. Sondheimer, and C. Djerassi, *J. Org. Chem.*, **21**, 520 (1956).

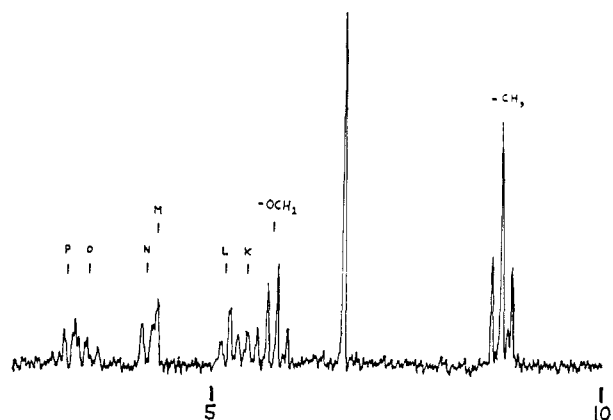
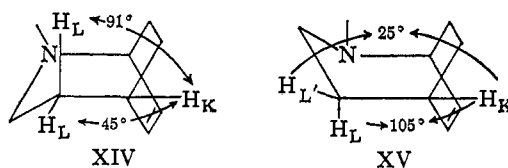
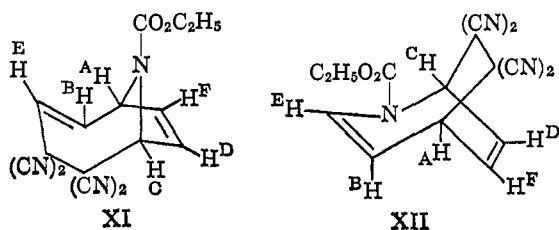
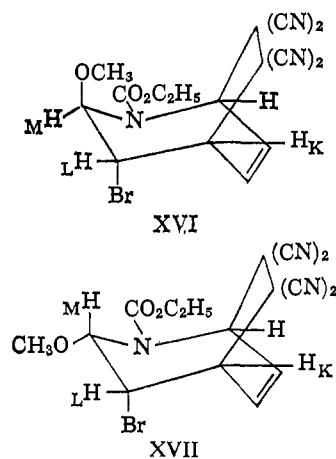
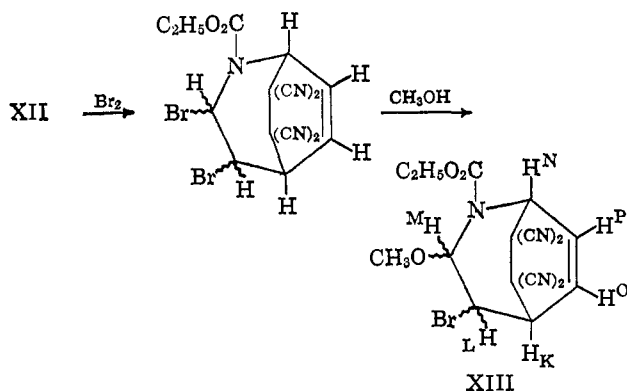


Figure 3. Proton magnetic resonance spectrum of 191° methoxybromide, taken in *d*₆-DMSO and measured at 56.4 Mc.; solvent peaks are not shown.



the dihedral angles $\theta_{KL} = 45^\circ$, $\theta_{KL'} = 91^\circ$ of conformation XIV, and the dihedral angle $\theta_{KL'} = 105^\circ$ of conformation XV are incompatible with $|J_{KL}| = 6.5$ c.p.s. On the other hand, the remaining dihedral angle $\theta_{KL'} = 26^\circ$ of conformation XV leads to a predicted coupling constant of 6–7 c.p.s., as found. This allows us to write the stereoformulas XVI or XVII, in each of which the bromine ends up *anti* to the tetracyanoethane bridge, as one would expect from the greater hindrance by that bridge to oncoming bromine in the initial halogenation.

Methoxybromination. Independent chemical support for the structure XII deduced from the magnetic resonance data was sought from the reaction of the adduct with bromine. With 1 equiv. of bromine in methylene chloride at room temperature, the adduct was converted to an amorphous dibromide, which persistently resisted all attempts at crystallization from inert solvents. However, on trituration with methanol, this material gave two crystalline methoxybromides, m.p. 191 and 148°, in over-all yields of 45 and 13%, respectively. These methoxybromides lacked ultraviolet absorption above 220 $m\mu$, and both lacked the strong 6.05- μ enamine band found in the infrared spectrum of the initial adduct. This evidence suggests that the enamine double bond has selectively undergone bromine addition followed by methanolysis of the bromine on the carbon next to nitrogen, as in the sequence shown.



Unfortunately, the observed $|J_{LM}|$ of *ca.* 0 c.p.s. does not allow a choice between the *cis*- and *trans*-methoxybromide, XVI or XVII, since both have a dihedral angle θ_{LM} near 60°. On the other hand, the very fact that the compound exists in conformation XV rather than in the less crowded form XIV requires a special explanation. No such explanation is apparent

The rapid solvolysis of halogen on carbon bearing nitrogen has good analogy,¹⁰ but the stereochemistry of the halogen addition as well as of the methanolysis in the present case remain to be defined. This point

(10) H. Böhme, E. Mundlos, and O.-E. Herboth, *Chem. Ber.*, **90**, 2003 (1957); H. Böhme, L. Koch, and E. Köhler, *ibid.*, **91**, 340 (1958).

(11) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); *J. Am. Chem. Soc.*, **85**, 2870 (1963). "Calculated" *J* values in our paper are obtained from the 1959 Karplus equations; angles were measured from Dreiding models.

(12) For apparent deviations from the Karplus equation in bicyclo-[2.2.2]octenes, see D. B. Roll, B. J. Nist, and A. C. Huitric, *Tetrahedron*, **20**, 2851 (1964).

Table II

Proton label	Chemical shift, τ	Principal couplings, c.p.s. ^a
K	5.45	$ J_{KL} \approx 6.5$, $ J_{KO} \approx 7.0$
L	5.12	$ J_{KL} \approx 6.5$, $ J_{LM} \approx 0.0$
M	4.30	$ J_{LM} \approx 0.0$
N	4.18	$ J_{NP} \approx 7.5$
O	3.42	$ J_{KO} \approx 7.0$, $ J_{OP} \approx 9.0$
P	3.12	$ J_{NP} \approx 7.5$, $ J_{OP} \approx 9.0$

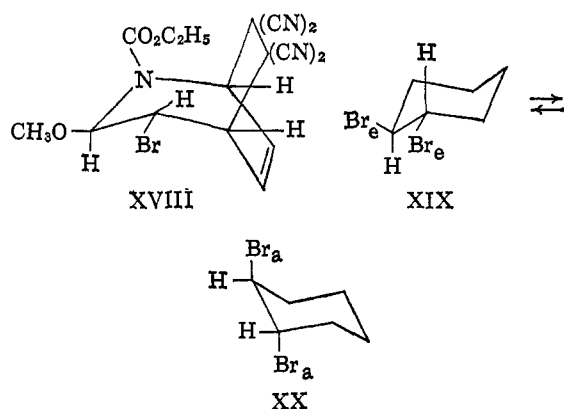
^a The values of $|J|$ are accurate to ± 1.0 c.p.s.

Table III

Proton label	Chemical shift, τ	Principal couplings, c.p.s. ^a
R	5.51	$ J_{RS} \approx 0$, $ J_{RW} \approx 7.0$
S	5.10	$ J_{RS} \approx 0$, $ J_{ST} \approx 5.0$
T	4.41	$ J_{ST} \approx 5.0$
U	4.19	$ J_{UV} \approx 6.8$
V	3.31	$ J_{UV} \approx 6.8$, $ J_{VW} \approx 8$
W	3.06	$ J_{RW} \approx 7.0$, $ J_{VW} \approx 8$

^a The values of $|J|$ are accurate to ± 1.0 c.p.s.

for the *cis*-methoxybromide, whereas for the *trans* isomer the alternative conformation XIV would place the $>\text{CHOCH}_3$ and $>\text{CHBr}$ dipoles into the electrostatically unfavorable *gauche* (diequatorial) relationship (cf. XVIII), and would also generate steric repulsions between the adjacent substituents Br, OCH_3 , and COOC_2H_5 . The conformational equilibrium would therefore be expected to resemble that of *trans*-1,2-dibromocyclohexane, for which the diaxial conformer XX is known to predominate over the diequatorial conformer XIX.¹³ Therefore, we might conclude that the conformation XV is only to be expected if the 191° compound were the *trans* isomer, which leads to the choice of stereoformula XVI for this substance. A molecular structure corresponding to a slightly distorted version of formula XVI has been independently substantiated by a single crystal X-ray analysis recently completed by Dr. J. H. Van den Hende of these laboratories.¹⁴



Turning now to the minor methoxybromide, m.p. 148°, the nuclear magnetic resonance spectrum (Figure 4), analyzed by decoupling, allows the chemical

(13) P. Bender, D. L. Flowers, and H. L. Goering, *J. Am. Chem. Soc.*, **77**, 3463 (1955).

(14) A preliminary report of these X-ray studies has been given at the American Crystallographic Association Meeting, Gatlinburg, Tenn., June 30, 1965.

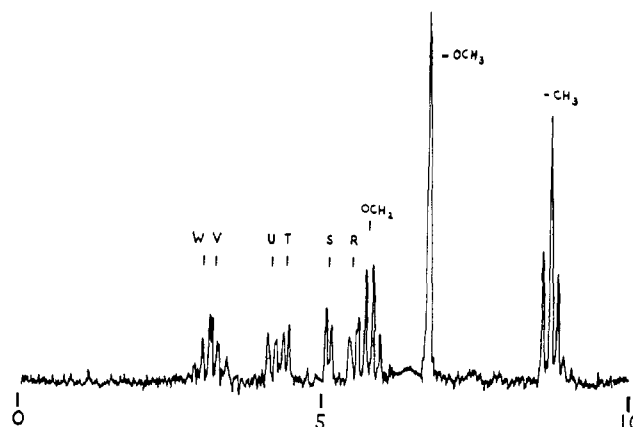
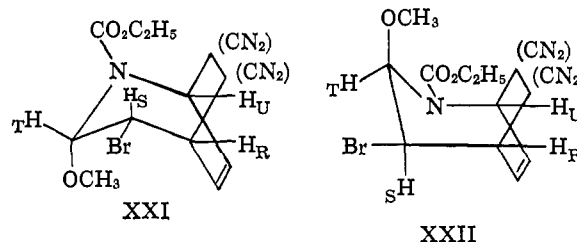


Figure 4. Proton magnetic resonance spectrum of 148° methoxybromide, taken in *d*₆-DMSO and measured at 56.4 Mc.; solvent peaks are not shown.

shifts and coupling constants of Table III to be assigned as indicated in formula XXI.

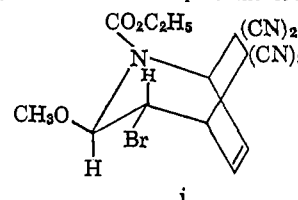
The near-zero bridgehead to CHBr coupling $|J_{RS}|$ is compatible here with either the 91° dihedral angle $\theta_{KL'}$ of conformation XIV or the 105° dihedral angle $\theta_{KL'}$ of conformation XV. However, when taken with the observed $|J_{ST}|$ of 5 c.p.s., only the two structures XXI and XXII are even remotely possible.¹⁵ Of these structure XXI, with dihedral angle $\theta_{ST} = 46^\circ$ cor-



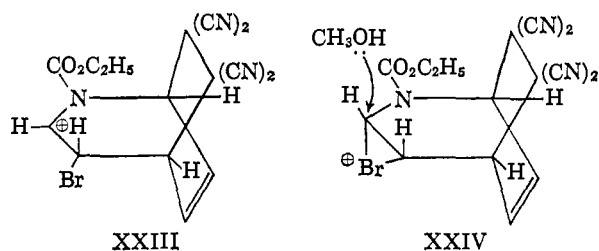
responding to a calculated 4-c.p.s. coupling, is clearly preferable to XXII with dihedral angle $\theta_{ST} = 65^\circ$ corresponding to a 1.2-c.p.s. coupling. It is seen therefore that the *cis*-methoxybromide XXI, unlike the *trans* isomer XVI, exists in the sterically "normal" conformation of the parent azabicyclo[3.2.2]nonene system, since in the *cis* case there is nothing to be gained in electrostatic or steric stabilization by adopting the "abnormal" conformation.

Predominant formation of the *trans*-methoxybromide XVI in the direct methoxybromination of the adduct XII probably does not involve methanolysis of an sp^2 -hybridized carbonium ion (XXIII), since that would not explain approach of the methoxyl from the more hindered side. The result is accommodated by a mechanism in which a cyclic bromonium ion (XXIV) *anti* to the tetracyanoethane bridge is initially formed

(15) These coupling constants would also accommodate a *trans*-methoxybromide in conformation (i); this formulation is unreasonable since a low-energy conformational flip to the 191° methoxybromide

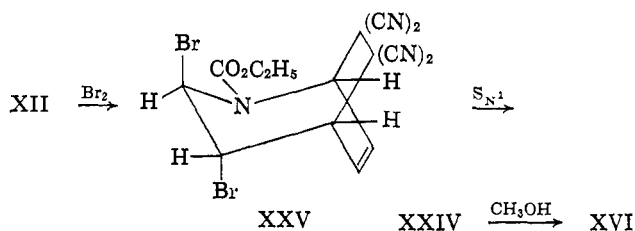


conformer XVI should render i incapable of independent existence.

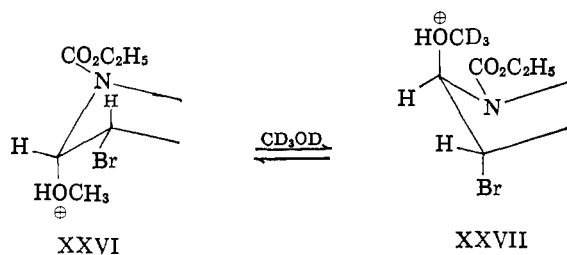


and subsequently undergoes irreversible diaxial methanolysis adjacent to nitrogen.

Predominant formation of the identical *trans*-methoxybromide from the two-step reaction can be rationalized in a similar manner. In this case an initially-formed *trans* diaxial dibromide (XXV) could undergo ionization to the same cyclic bromonium ion (XXIV) as above, followed by methanolysis. There is ample analogy for such bromine participation in ionic processes of this type.¹⁶ An alternative explanation for the predominance of XVI, that it is the ultimate product of the equilibrium methanolysis of a *cis*-methoxy-



bromide (for example, XXVI \rightleftharpoons XXVII), is rendered untenable by the observation that *trans*-methoxybro-



mid is recovered undeuterated after vigorous treatment with acidic *d*₄-methanol. Finally, the 148° *cis*-methoxybromide, which is formed in roughly the same relative proportion by the one-step as by the two-step reaction, probably originates from kinetically controlled methanolysis of the open carbonium ion XXIII which is assumed to be in equilibrium with the cyclic bromonium form.

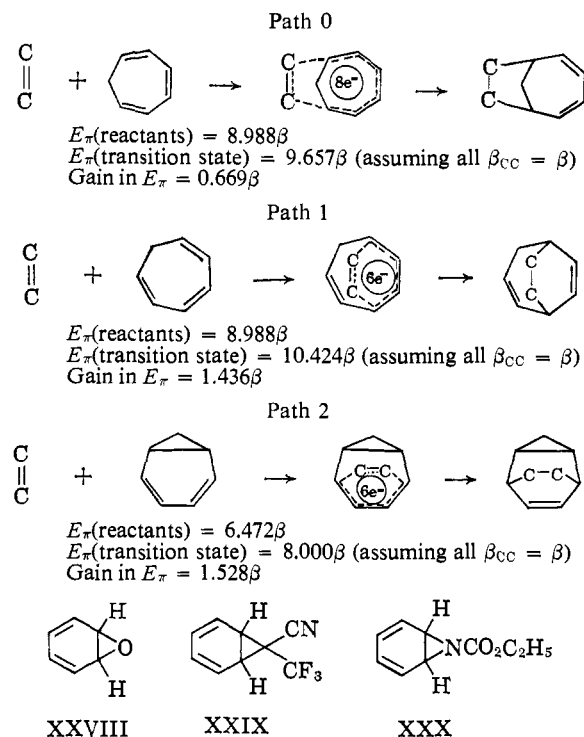
Course of Dienophile Additions to Cycloheptatrienes. Hoffmann and Woodward have recently emphasized that thermal 1,6-cycloaddition of a dienophile to a cyclic triene should be electronically unfavorable because there is a change in the symmetry of bonding orbitals on going from reactants to product.¹⁷ There are two additional paths for dienophile addition to cyclic trienes: (1) direct 1,4-Diels-Alder addition to two of the three double bonds of the triene, as is observed with N-carbomethoxyazepine, or (2) pre-equilibrium valence tautomerization of the triene to a bicyclic diene followed by Diels-Alder addition, as is the case,

(16) D. H. R. Barton and E. Miller, *J. Am. Chem. Soc.*, **72**, 1066 (1950); G. M. Alt and D. H. R. Barton, *J. Chem. Soc.*, 4284 (1954).

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

for example, with oxepine. A simple Hückel molecular orbital calculation comparing transition state models 0, 1, and 2 (Scheme I) for these three processes

Scheme I. H.M.O. Comparison of Transition-State Models for Addition of Ethylene to Cycloheptatriene or Norcaradiene



illustrates the Hoffmann-Woodward rule and suggests further that the π -electronic contribution to the activation energy should slightly stabilize transition state 2 over transition state 1.¹⁸ This would suggest that at least in the cycloheptatrienes, where the barrier to valence tautomerism appears to be low, path 2 addition should normally predominate except when the triene is much more stable than its bicyclic valence tautomer. This hypothesis is in qualitative agreement with the fact that at room temperature the oxepine II in isooctane exists in equilibrium with about 30% of the benzene oxide tautomer XXVIII.² The free-energy difference between cycloheptatriene and norcaradiene is certainly somewhat greater, but the recent demonstration that some 20% of the substituted norcaradiene XXIX is present at equilibrium with the corresponding cycloheptatriene¹⁹ suggests that in general the cycloheptatriene-norcaradiene energy difference is not very large.²⁰ Recent n.m.r. studies of N-carbomethoxyazepine down to -110°, carried out by Dr. H. Günther (Köln), show no evidence for the presence of the bicyclic tautomer XXX.²¹ Thus the relative stability of XXX is much lower than that of the corresponding equilibrium components XXVIII and XXIX, so that the formation of the path 1 Diels-

(18) In this connection it is of interest that *trans*-1-phenylbutadiene reacts one-fifth as fast with maleic anhydride as *trans*-1-methylbutadiene: J. Sauer, D. Lang, and A. Mielert, *Angew. Chem.*, **74**, 352 (1962).

(19) E. Ciganek, *J. Am. Chem. Soc.*, **87**, 1149 (1965).

(20) For cycloheptatriene itself the energy difference between tautomers is apparently large enough that at least some of the path 1 product can be formed: see E. M. Mil'vitskaya and A. F. Plate, *Zh. Obshch. Khim.*, **32**, 2566 (1962); *Chem. Abstr.*, **58**, 8927 (1963).

(21) We are indebted to Dr. H. Günther for communicating these results to us prior to publication.

Alder adduct XII, while not necessarily predictable, is certainly consistent with this trend.^{21a}

Experimental Section²²

8,8,9,9-Tetracyano-2-azabicyclo[3.2.2]nona-3,6-diene-2-carboxylic Acid Ethyl Ester (XII). To a solution of 2.00 g. of N-carbethoxyazepine in 5 ml. of benzene was added a solution of 1.44 g. of freshly sublimed tetracyanoethylene in 25 ml. of benzene. The resulting deeply colored solution was allowed to stand at room temperature overnight. Removal of benzene under vacuum and crystallization of the resulting syrup from hexane-ethyl acetate gave 1.7 g. of light brown crystals, m.p. 154–157°. A second crystallization from the same solvent gave 1.60 g. of tan crystals, m.p. 156–157°. The adduct showed principal infrared maxima (KBr disk) at 5.89, 6.05, 7.50, 7.91, 8.70, 9.82, 10.39, 11.05, 12.98, 13.4, and 13.5 μ .

Anal. Calcd. for $C_{15}H_{11}N_5O_2$: C, 61.43; H, 3.78; N, 23.88. Found: C, 61.46; H, 3.96; N, 23.70.

Direct Methoxybromination of Adduct XII. To a stirred suspension of 250 mg. of adduct XII in 11 ml. of anhydrous methanol at room temperature was added dropwise over a 15-min. period 1.20 ml. of a carbon tetrachloride solution which was 0.75 *M* in bromine. A heavy precipitate began to crystallize during the addition. When addition was complete, the suspension was cooled to 0° and filtered by suction; the filter cake was washed with cold methanol and the washings were combined with the mother liquors.

The dried filter cake weighed 241 mg. (70% yield) and was nearly pure *trans*-methoxybromide, m.p. 181–183° dec. Recrystallization from ethyl acetate gave analytically pure product, m.p. 191–192° dec. This *trans* isomer had characteristic infrared maxima at 5.85, 7.61, 7.95, 9.31, 9.74, 10.40, 11.37, 12.3, 13.0, and 13.6 μ .

Anal. Calcd. for $C_{16}H_{14}BrN_5O_3$: C, 47.54; H, 3.49; Br, 19.77. Found: C, 48.08; H, 3.81; Br, 20.01.

(21a) NOTE ADDED IN PROOF. N.m.r. spectroscopic studies leading to the 2-azabicyclo[3.2.2]nona-3,6-diene structure XII for the N-carbethoxyazepine-tetracyanoethylene adduct have been carried out independently by J. E. Baldwin and R. A. Smith, *J. Am. Chem. Soc.*, in press. We are grateful to Professor Baldwin for sending us his data prior to publication.

(22) We are indebted to W. Fulmor and his associates for the infrared and ultraviolet spectra and to L. Brancone and his group for the microanalyses reported in this investigation.

Concentration of the mother liquors gave 96 mg. (27%) of the nearly pure *cis* isomer, m.p. 144–147°. A single recrystallization from methanol gave the analytical sample, m.p. 146–148° dec.; the melting point varied slightly with rate of heating. This *cis* isomer had characteristic infrared maxima at 5.84, 7.70, 7.78, 7.88, 9.40, 9.89, 10.67, 10.80, 11.20, 12.98, 13.4, and 14.0 μ .

Anal. Calcd. for $C_{16}H_{14}BrN_5O_3$: C, 47.54; H, 3.49. Found: C, 47.76; H, 3.83.

Two-Step Methoxybromination of Adduct XII. To a solution of 200 mg. of adduct XII in 6 ml. of methylene chloride was slowly added, dropwise and with stirring, 0.80 ml. of a carbon tetrachloride solution containing 140 mg. of bromine per milliliter. The resulting pale yellow solution was evaporated at room temperature under vacuum, and the residue was dissolved in 5 ml. of dry benzene. A second evaporation gave a non-crystalline, white powder which was warmed briefly to 45° with methanol. The powder went largely into solution which subsequently deposited a voluminous crystalline precipitate. This methanolic suspension was allowed to stand at room temperature and was filtered to give 126 mg. (45%) of the *trans*-methoxybromide XVI, m.p. 187–188° dec. The infrared spectrum of this material was superimposable on that of the analytical sample from the direct methoxybromination. The analytical sample was recrystallized once from chloroform, m.p. 192–193° dec., and dried at 60° under vacuum.

Anal. Calcd. for $C_{16}H_{14}BrN_5O_3$: C, 47.54; H, 3.49; N, 17.33. Found: C, 47.58; H, 3.43; N, 17.45.

Concentration of the filtrate from removal of the *trans* isomer and crystallization from methanol gave 28 mg. (13%) of the *cis*-methoxybromide, m.p. 146–147° dec. A second crystallization from methanol gave colorless crystals, m.p. 148–149° dec.; the melting point varied slightly as a function of rate of heating. An infrared spectrum and mixture melting point comparison of this product with the 146–148° product from the one-step methoxybromination established their identity.

Anal. Calcd. for $C_{16}H_{14}BrN_5O_3$: C, 47.54; H, 3.49; Br, 19.77. Found: C, 48.16; H, 3.87; Br, 19.62.