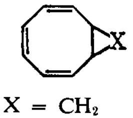
Reaction of Cyanonitrene with Cyclooctatetraene. 1,4 and 1,2 Addition[1]

A. G. Anastassiou[2]

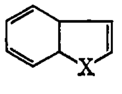
Contribution No. 1267 from the Central Research Department,
Experimental Station, E. I. du Pont de Nemours and Company,
Wilmington, Delaware 19898. *Received September 1, 1967*

Abstract: Cyanonitrene, generated thermally from cyanogen azide, reacts with cyclooctatetraene to yield two primary products, a stable 1,4 adduct **6** and a labile 1,2 adduct **1d**. At room temperature, cyanogen azide reacts with cyclooctatetraene to afford the alkylidene cyanamide **5** exclusively. Mechanisms are discussed.

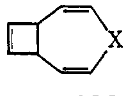
There exists a large body of compelling experimental evidence in the literature that additions of carbenes to dienes and polyenes occur strictly in a 1,2 fashion.[3] In many cases, this is not apparent from a simple examination of the reaction products since quite frequently the initially formed three-membered compounds are thermally unstable and readily isomerize. This frequent instability of the primary adducts introduces complications in determining the sources of the various products. The complications are especially serious in cases where (1) the primary adduct(s) are completely consumed at the termination of the reaction, and (2) the primary adducts are not completely consumed, but the structure(s) of the isomer(s) produced are such that they could be readily mistaken for primary products. A particularly relevant example in connection with case 2 is the reaction of methylene with butadiene to yield vinylcyclopropane and cyclopentene. Both isomers were originally thought to be primary products,[4] the three-membered ring arising from 1,2 addition and the cyclopentene from 1,4 addition. Upon more careful examination, however, it was revealed that cyclopentene was produced not by a 1,4 addition of methylene to the diene but *via* thermal reorganization of vinylcyclopropane.[5] Isomerization of the primary adducts does not always pose problems as it may require conditions more drastic than those involved in the reaction. This situation is well exemplified by the reaction of carbenes with cyclooctatetraene.[6] Here the originally formed 1,2 adducts **1a** and **1b** are usually thermally stable at room temperature but at *ca.* 90–150°, they rapidly reorganize to the corresponding dihydroindenes **2a** and **2b**.



1a, X = CH_2
b, X = CHR, CR_2
c, X = $NCOOC_2H_5$
d, X = NCN
e, X = O



2a, X = CH_2
b, X = CHR, CR_2
c, X = $NCOOC_2H_5$
d, X = NCN

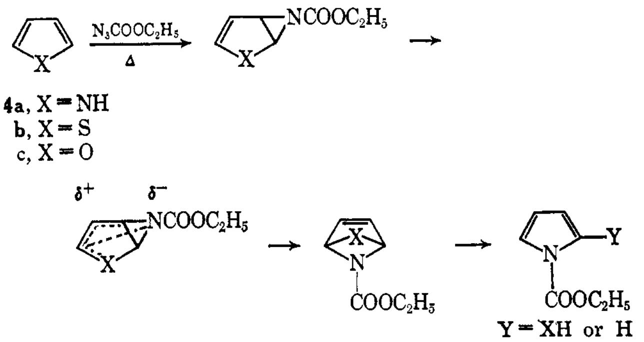


3a, X = $NCOOC_2H_5$
b, X = NCN

Nitrenes appear to react with conjugated dienes and polyenes in much the same way as carbenes, and here too some of the results are ambiguous. For example, carbethoxynitrene, generated photolytically from ethyl azidoformate, reacts with butadiene exclusively in a 1,2 manner to afford N-carbethoxy-2-vinylaziridine.[7] Similarly, the same nitrene generated by α elimination adds to cyclooctatetraene strictly in a 1,2 manner to yield aziridine **1c**.[8] On the other hand, addition of carbethoxynitrene, generated thermally (*ca.* 130°) from ethyl azidoformate, to furan, pyrrole, and thiophene produces in each case an N-carbethoxypyrrole[9] skeleton with no indication of any 1,2 adduct. Furthermore with 2,5-dimethylthiophene, the nitrene yields not N-carbethoxy-2,3-dimethylpyrrole, but N-carbethoxy-2,5-dimethylpyrrole instead.

At first glance, these results seem to indicate that the pyrrole is formed in each case by addition of the nitrene across the 2,5 positions of the heteroaromatics followed by extrusion of the heteroatom. Upon closer examination, however, it is seen that although the available evidence eliminates a process involving 1,2 addition followed by *concerted* conversion to products, it does not in any way exclude a process involving initial 1,2 addition followed by isomerization to the 1,4 adduct which could in turn collapse to the observed product. This alternate possibility[9] is shown in Scheme I. Hence until it is shown that the 1,2 adducts do not afford N-carbethoxypyrrole at the reaction temperature, this

Scheme I



4a, X = NH
b, X = S
c, X = O

Y = XH or H

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(1) Communicated in part in *J. Am. Chem. Soc.*, **87**, 5512 (1965).

(2) Address correspondence to the Department of Chemistry, Syracuse University, Syracuse, N. Y. 13210.

(3) See, for example, W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964.

(4) V. Franzen, *Ber.*, **95**, 571 (1962).

(5) H. M. Frey, *Trans. Faraday Soc.*, **58**, 516 (1962). However, it has also been suggested that cyclopentene may partly be the product of direct 1,4 addition: B. Grzybowska, J. H. Knox, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 3826 (1962).

(6) See, for example, G. Schroder, "Cyclooctatetraen," Verlag Chemie, Weinheim, Germany, 1965, p 32.

(7) K. Hafner, W. Kaiser, and R. Puttner, *Tetrahedron Letters*, 3953 (1964).

(8) S. Masamune and N. T. Castellucci, *Angew. Chem.*, **76**, 569 (1964).

(9) K. Hafner and W. Kaiser, *Tetrahedron Letters*, 2185 (1964).

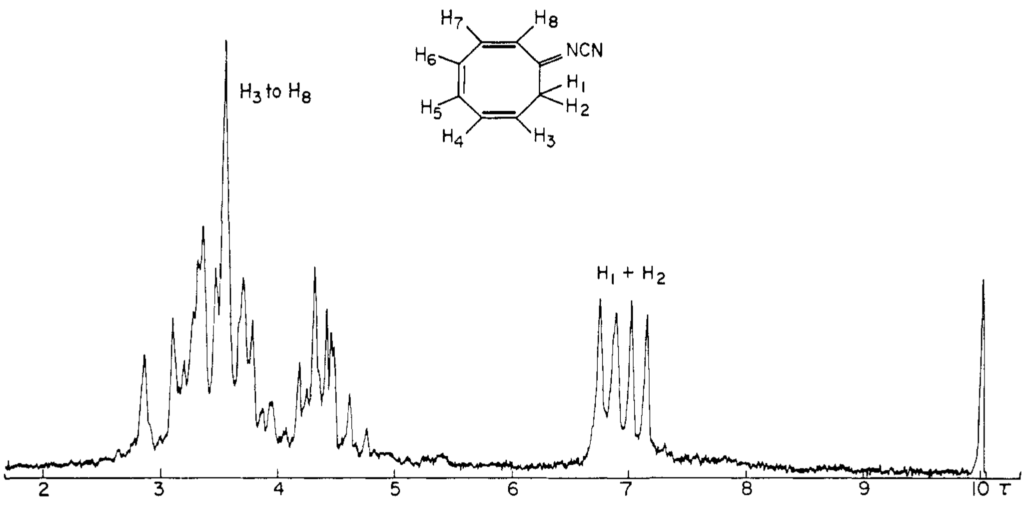

Figure 1. Nmr spectrum of N-cyano-1-iminocycloocta-2,4,6-triene (5).

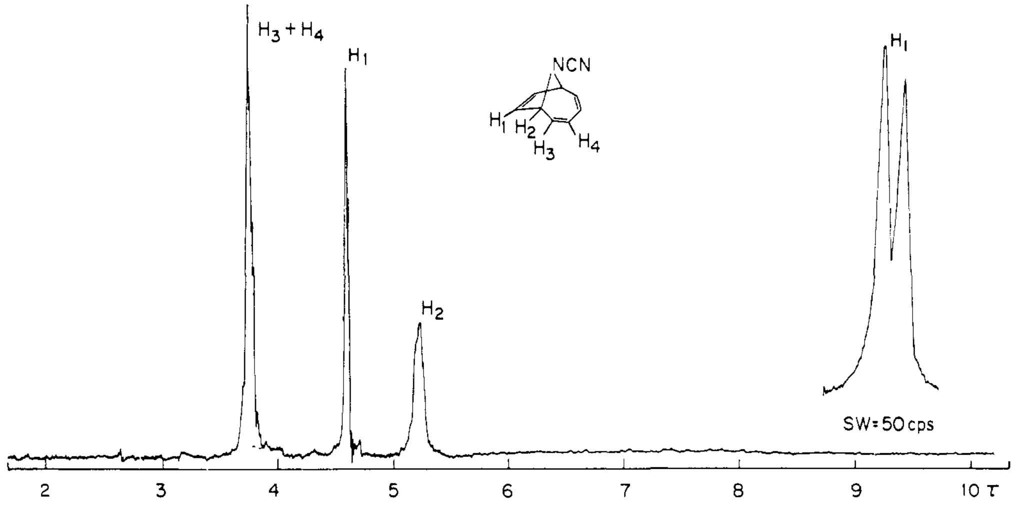

Figure 2. Nmr spectrum of N-cyano-9-azabicyclo[4.2.1]nona-2,4,7-triene (6).

case of 1,4 addition ought to be viewed as equivocal. Equally ambiguous results were obtained from the reaction of nitrene (NH), generated from hydroxylamine-O-sulfonic acid by α elimination, with butadiene to yield 2,5-dihydropyrrole.[10] Here again we may be witnessing a situation akin to that involved in the reaction of methylene with butadiene in which initial 1,2 addition is followed by rearrangement to the 1,4 adduct. Finally it should be pointed out that neither in the thermal reaction of ethyl azidoformate with heteroaromatics nor in the base-catalyzed addition of hydroxylamine-O-sulfonic acid to butadiene has the intermediacy of a nitrene been demonstrated.

Results and Discussion

Reaction and Structural Elucidation of Products. Treatment of a dilute solution of cyclooctatetraene (COT) in ethyl acetate (*ca.* 12%) with cyanogen azide (N_3CN) at the boiling temperature (78°) leads to rapid nitrogen evolution and the formation of two stable $C_9H_8N_2$ products in 30% yield. The major component (68% of the mixture) is a viscous dark orange liquid displaying ultraviolet (uv) absorption at 243 (ϵ 16,000) and 331 mμ (6900) and strong infrared absorption at 2180 (C$\equiv$N) and 1540 cm^{-1} (C=NCN). In the nmr (Figure 1), it exhibits two well-separated multiplets at τ 3.1–3.8 (5 H) and τ 4.2–4.6 (1 H) and two sets of equally spaced doublets centered at τ 6.7 (1 H; J = 4 cps) and τ 7.1 (1 H; J = 4 cps). The spectral properties of this substance coupled with its elemental composition strongly suggest the alkylidenecyanamide structure **5**. Chemical evidence for the presence of an alkylidene cyanamide function in this material was obtained from its conversion to the known[11] cyclooctatrienone **7** upon treatment with moist alumina.[12] The less abundant $C_9H_8N_2$ isomer (32% of the mixture) is a white, highly crystalline solid which displays uv absorption at 255 mμ (ϵ 4500) and strong infrared absorption at 2220 cm^{-1} (C$\equiv$N). In the nmr (Figure 2), it exhibits narrow multiplets at τ 3.7 (4 H) and 4.6 (2 H) and a broader peak at τ 5.3 (2 H; width at half-height = 5 cps). The relatively simple nmr spectrum of this material requires a symmetrical arrangement while the presence of six olefinic protons suggests a bicyclic structure. Hence of the many possible $C_9H_8N_2$

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(10) R. Appel and O. Buchner, *Angew. Chem.*, **74**, 430 (1962).

(11) A. C. Cope and B. D. Tiffany, *J. Am. Chem. Soc.*, **73**, 4158 (1951).

(12) Moist alumina readily converts C=NCN groups to C=O functions: F. D. Marsh and M. E. Hermes, *ibid.*, **86**, 4506 (1964); A. G. Anastassiou, *J. Org. Chem.*, **31**, 1131 (1966).

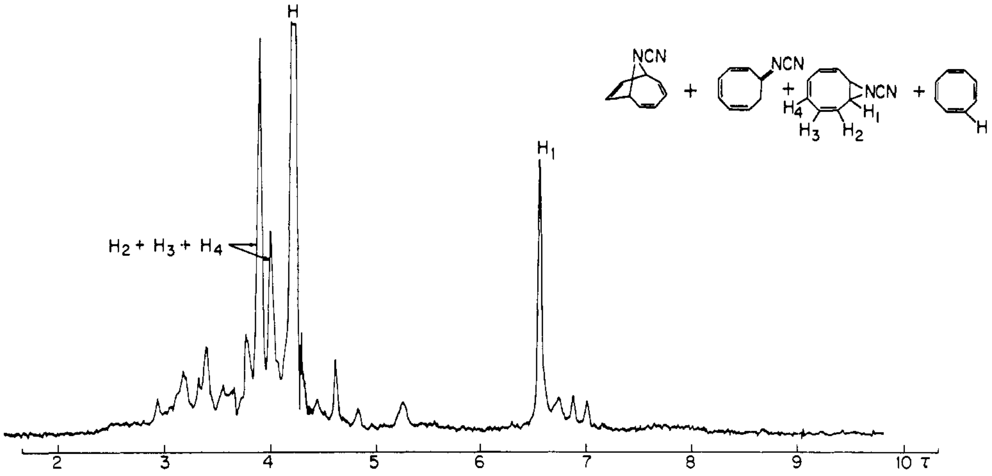


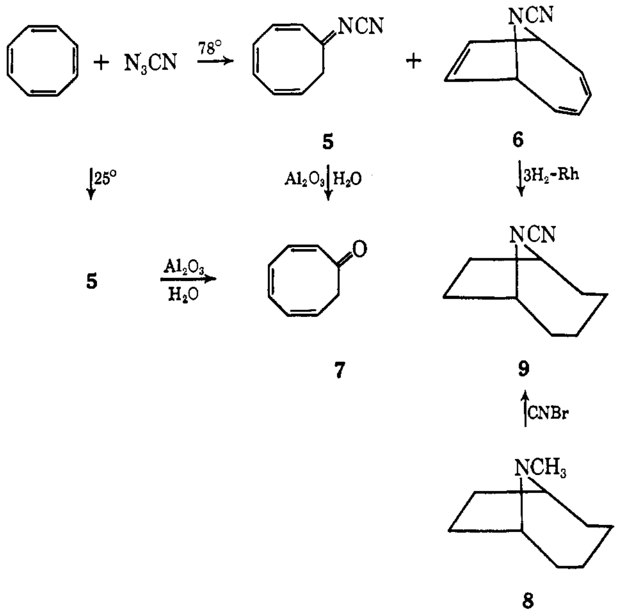
Figure 3. Nmr spectrum of a mixture of N-cyano-1-iminocycloocta-2,4,6-triene (**5**), N-cyano-9-azabicyclo[4.2.1]nona-2,4,7-triene (**6**), N-cyano-9-azabicyclo[6.1.0]nona-2,4,6-triene (**1d**), and cyclooctatetraene; reaction 3 in Table I.

structures, only **1d**, **3b**, and **6** need be considered. Compounds **1a**,[6] **1c**,[8] and a great number where X is a substituted carbon[6] are known and, unlike the less abundant $C_9H_8N_2$ isomer, they all exhibit only one fairly narrow olefinic multiplet and an allylic signal which appears invariably as a sharp singlet (width at half-height ~1.4 cps) in all compounds in which X does not contain an α-hydrogen. The nmr spectrum of our minor product is equally incompatible with structure **3b** since such an assignment would require the unlikely coincidence of two pairs of nonequivalent protons. In fact in the structurally related compound **3a**, the olefinic protons give rise to three distinct multiplets.[8] Hence on the basis of nmr evidence alone, the minor product of the reaction is best depicted as **6**. The various nmr assignments are given in Figure 2, and the dihedral angles estimated from "Dreiding" molecular models are: H_1–H_2 ~42°, H_2–H_3 ~18°, and H_3–H_4 ~0°. Definitive chemical evidence for structure **6** was obtained as follows. Treatment of homotropane[13] (**8**) with cyanogen bromide afforded a $C_9H_{14}N_2$ cyanamide formulated as **9**. In the infrared, this material displays strong C≡N absorption (2200 cm^{-1}) and no N–H band, and in the nmr it shows multiplets centered at τ 5.9 (2 H) and τ 7.5–8.4 (12 H). On catalytic hydrogenation, over rhodium at atmospheric pressure and room temperature, **6** consumed 3 equiv of hydrogen to afford **9**, identical (nmr, infrared) with synthetic material (Scheme II).

At room temperature, a mixture of cyanogen azide and COT slowly evolves 1 equiv of nitrogen and affords exclusively **5** in 73% yield. This material does not isomerize to **6** at 78°.

Source of the 1,4 Adduct. The exclusive formation of alkylidenecyanamide **5** when the reaction was conducted at room temperature, coupled with the temperature (*ca.* 40°) at which cyanogen azide is known[14] to fragment to cyanonitrene (NCN) and molecular nitrogen, requires that the 1,4 adduct be a product not of cyanogen azide but of NCN. Furthermore since aziridine **1c** is known[8] to isomerize at 80° to **3a** and not to a 1,4 adduct, it appears reasonable to assume by analogy that **6** does not arise from thermal isomerization of an initially formed 1,2 product **1d**. Nevertheless to firmly exclude isomerization of the alleged 1,2 adduct **1d** as a source of **6**, it was necessary to demonstrate the nonoccurrence of such a process under the reaction conditions. We therefore sought conditions which would allow the isolation of **1d** and found that this could be accomplished simply by interrupting the high-temperature reaction (78°) at some early stage. The nmr spectrum of a partially reacted mixture displays, besides the usual absorptions of **5** and **6**, signals highly characteristic of a structure such as **1d**: fairly narrow multiplet centered at τ 3.9 (6 H) and a sharp singlet at τ 6.6 (2 H; width at half-weight = 1.4 cps). The spectrum of the mixture is shown in Figures 3 and 4. This new material was found to be very unstable thermally, and all attempts to separate it from its isomers **5** and **6** invariably led to conversion to a highly insoluble, probably polymeric, solid. Hence its characterization rests on its nmr spectrum which is virtually identical with those of the structurally related com-

Scheme II



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(13) A. C. Cope, H. R. Nace, and L. L. Estes, Jr., *J. Am. Chem. Soc.*, **72**, 1123 (1950).

(14) A. G. Anastassiou, H. E. Simmons, and F. D. Marsh, *ibid.*, **87**, 2296 (1965).

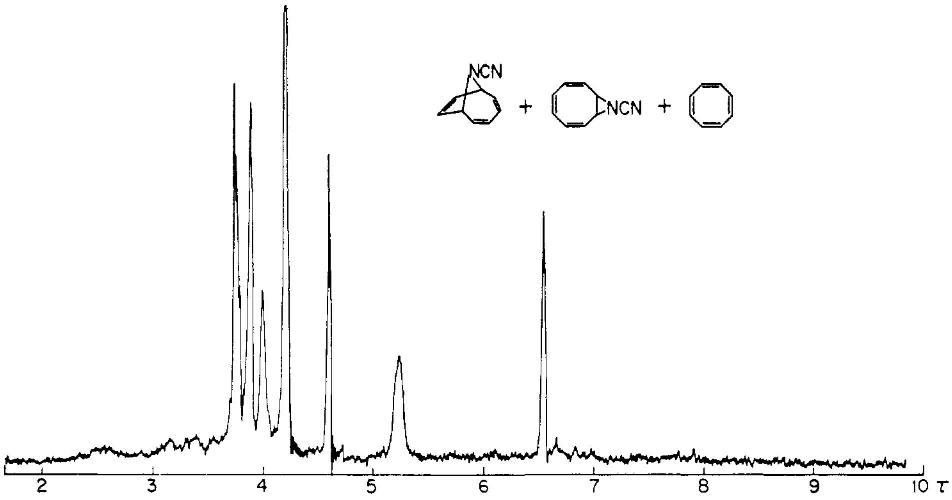

Figure 4. Same as in Figure 3; reaction 6 in Table III.

pounds **1c**[8,15] and **1e**.[11] Furthermore the insoluble solid to which **1d** is transformed upon standing has the required amount of nitrogen for $(C_9H_8N_2)_x$.

With the 1,2 adduct at hand, it became possible to unambiguously establish its relation to the other two products **5** and **6**. We have accomplished this by determining the relative amounts of the three products **1d**, **5**, and **6** at various stages of the reaction since if an isomerization occurs, one should be able to observe a gradual buildup of the stable isomer as the reaction progresses. It is amply clear from the data shown in Table I (reactions 1–4) that this is not the case since from as early as 10% (4 min) reaction to as late as 75% (40 min) reaction, the composition of the mixture is essentially constant. This constancy clearly indicates the occurrence of three independent competing rates. The drastic decrease of the amount of **1d** and corresponding increase of the proportions of **5** and **6** at longer reaction times (reaction 5) are undoubtedly due simply to decomposition of **1d**. Definitive evidence for the nonoccurrence of a **1d** to **6** isomerization under the conditions of the reaction was provided by a set of control experiments. In these, known mixtures of **1d**, **5**, **6**, and dimethyl phthalate (an nmr reference) in ethyl acetate were heated at the reaction temperature (78°) for various lengths of time and the composition of the mixture determined in each case by nmr. The results are compiled in Table II. From these data it can be easily estimated that upon heating for 0.5 hr, **1d** and **5** decreased by 24 and 10%, respectively, whereas **6** remained unaltered. This, taken in conjunction with the fact that as much as 14% of **6** is present in the first 4 min of the reaction, establishes beyond doubt that *the 1,4 adduct* **6** *does not arise to any appreciable extent from rearrangement of either* **1d** *or* **5**. It should be noted that on heating the control mixtures for longer periods (Table II, runs 2 and 3) of time, the amount of **6** does gradually change, increasing by a maximum of *ca.* 18% in 210 min. This may be due to slow isomerization of either **1d** or **5** to **6** but could also be the result of gradual decomposition of the nmr standard. In any event, this possible source of **6** should be of no consequence in the buildup of this material during reaction.[16]

Table I. Relative Amounts of **5**, **1d**, and **6** at Different Stages of Reaction of N_8CN with COT in Ethyl Acetate at 78°

Reaction	Reaction time, min	Nitrogen evolved, %	Product comp, %[a]			[6]/[1d]
			1d	**6**	**5**	
1	4	12	43	14	43	0.3
2	11	25	50	14	36	0.3
3	28	50	50	14	36	0.3
4	40	75	47	17	36	0.4
5	130	91	11	33	56	3.0

[a] Determined from the nmr spectra of the crude mixtures.

Table II. Absolute Change of Amounts of **1d**, **5**, and **6** in Ethyl Acetate at 78 and 25°

Run	Temp, °C	Time	Composition[a]		
			1d	**6**	**5**
			1.7[b]	0.9[b]	2.0[b]
1	78	30 min	1.3	0.9	1.8
2	78	60 min	1.2	1.0	1.5
3	78	210 min	0.6	1.1	1.4
4	25	1 week	1.3	0.9	1.7

[a] Determined from the nmr spectra of the mixtures. [b] Initial composition.

Electronic Multiplicity of NCN in Additions to COT. We will now examine the mechanism of the addition more closely with special emphasis on the electronic multiplicity of reacting NCN.

In principle, addition of NCN to COT could occur either across a double bond (1,2 process) or across a single bond (1,8 process) or across no bond (1,4 and 1,6 process). The first two processes will generate **1d** while the last two will produce **6**. In turn, each of the four different modes of addition could occur either

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(15) For purposes of direct comparison, we have prepared **1c** by the procedure described by Masamune and Castellucci[8] and found that except for the ethyl absorption, its nmr spectrum is indistinguishable from that described here for **1d**.

(16) In contrast to the failure of the 9-azabicyclo[6.1.0]nonatrienes **1c**[8] and **1b** to thermally rearrange to the corresponding 9-azabicyclo[4.2.1]nonatrienes, the phosphorus analog **1** ($X = PC_6H_5$) was recently reported to undergo this type of thermal reorganization: T. J. Katz, C. R. Nicholson, and C. A. Reilly, *J. Am. Chem. Soc.*, **88**, 3832 (1966).

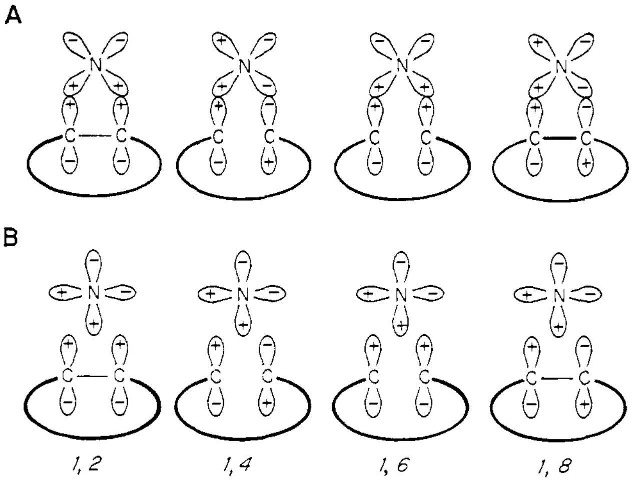

Figure 5. Symmetry requirements in 1,2, 1,4, 1,6, and 1,8 additions of cyanonitrene to cyclooctatetraene.

in a concerted fashion or in two steps. This of course would depend on the electronic multiplicity of the attacking nitrene since conservation of spin considerations require that only singlets be capable of concerted addition. Even among singlets, however, concerted addition would in all probability occur only if the *acceptor* molecular orbital (lowest unoccupied MO) of the electron-deficient fragment has the necessary symmetry for a bonding interaction with the highest occupied MO of the donor. In previous reports[17,18] we discussed the various known spectroscopic states of cyanonitrene[19] at some length in connection with addition and insertion reactions. For purposes of clarity, we will now briefly repeat some salient features of these discussions. Cyanonitrene has ten bonding electrons. In the linear molecule, eight of these are employed to fill one σ_g, one σ_u, and two orthogonal π_u MO's while the remaining two have to be accommodated among two π_g MO's. This arrangement gives rise to three electronic states: a . . . $\pi_g{}^1(x)\pi_g{}^1(y)$ triplet (T), a . . . $\pi_g{}^1(x)\pi_g{}^1(y)$ singlet (S_1), and a . . . $\pi_g{}^2(x)$ or $\pi_g{}^2(y)$ singlet (S_2), each of which should be chemically distinct.[20] Of these, the triplet (${}^3\Sigma_g{}^-$) was shown both spectroscopically[19] and chemically[18] to represent the ground state. The S_1 and S_2 states are undoubtedly very close energetically so that both ought to be considered in chemical reactions. These two low-lying singlets are similar in connection with the symmetry properties of the *acceptor* MO (π_g) but differ in the way this MO is partially occupied, the electrons being more evenly distributed in the S_1 state. The more even electronic distribution of S_1 would in all probability make it the more prone of the two singlets to undergo concerted addition. The possible ways in which the two low-lying singlets could undergo 1,2, 1,4, 1,6, and 1,8 additions are shown diagrammatically in Figure 5. The symmetry characteristics of the nucleophiles are of course those of the end carbons of the highest occupied MO's of ethylene, butadiene, hexatriene, and octatetraene for 1,2, 1,4, 1,6, and 1,8 additions, respectively. In the case of the S_2 state (Figure 5B), the overlapping MO is in all cases a vacant π_g. A number of interesting points emerge. In the first place, it is seen that equally effective bonding interactions can arise in all four cases; *i.e.*, on the basis of symmetry considerations alone, NCN should be able to undergo all four modes of addition with equal ease. Secondly, within the frame of the model we chose here to represent additions of the S_2 state (Figure 5B), concerted 1,4 and 1,8 additions by this species ought to be particularly unfavorable because of the π_g symmetry[21] of the end atoms of the diene systems. This would force the vacant MO of the acceptor to overlap with only one end p orbital of the olefin, giving rise to an arrangement more favorable to heterolytic cleavage than to concerted addition. An interesting point in connection with the orbital symmetries of COT, and of fully unsaturated polyenes in general, is that they are such that the nature of the product formed ought to be independent of the symmetry requirements of the adding electrophile. This is because invariably segments of the polyene with opposite orbital symmetries can lead to the same product.

Thus far, we have examined the requirements for concerted additions of NCN strictly from a symmetry standpoint and have altogether neglected any possible spatial factors. Obviously the primary spatial requirement for concerted addition is that the distance between the two reacting atoms of the olefin should be short enough so that effective three-center overlap with the atom of the acceptor could occur. Also the end atoms of the olefin should be arranged in such a way as to allow their p orbitals to lie in a plane described by their axes. Clearly the first requirement is best satisfied by either the 1,2 or the 1,8 process since here the atoms of the donor are constrained by a bond to a considerably shorter distance than that involved in cases where no bond is present. In COT, the nonbonded C_1–C_4 and C_1–C_6 separations are the same, and in the puckered molecule one can estimate from "Dreiding" models a distance of *ca.* 2.8 Å. In connection with the second requirement, *i.e.*, relative disposition of the p orbitals of the end atoms, COT presents an interesting case in that in the puckered molecule the p orbitals of the nonbonded atoms are tilted toward each other while still in a plane. This type of arrangement could be quite favorable in concerted processes since its net effect would obviously be to reduce the effective distance between nonbonded atoms. It is doubtful, however, whether this effect would be of any significance at the distances involved in the present case. It is evident, therefore, from the point of view of spatial factors, that unless the butadiene and hexatriene segments of COT

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[17] A. G. Anastassiou and H. E. Simmons, *J. Am. Chem. Soc.*, **89**, 3177 (1966).

[18] A. G. Anastassiou, *ibid.*, **89**, 3184 (1966).

[19] (a) G. Herzberg and D. N. Travis, *Can. J. Phys.*, 42, 1658 (1964); (b) G. J. Pontrelli and A. G. Anastassiou, *J. Chem. Phys.*, 42, 3735 (1965); (c) E. Wasserman, L. Barash, and W. A. Yager, *J. Am. Chem. Soc.*, 87, 2075 (1965); (d) D. E. Milligan, M. E. Jacox, and A. M. Bass, *J. Chem. Phys.*, **43**, 3149 (1965).

[20] It should be noted that due to the open-shell arrangement of NCN, the actual configurational wave functions are appropriate linear combinations of the electronic arrangements denoted here as T, S_1, and S_2. In terms of diagonals of Slater determinants, the proper antisymmetrized functions are

$$|\ldots\pi_g(x)(9)\pi_g(y)(\overline{10})| + |\ldots\pi_g(x)(\bar{9})\pi_g(y)(10)| \qquad {}^3\Sigma_g{}^-$$

$$|\ldots\pi_g(x)(9)\pi_g(y)(\overline{10})| - |\ldots\pi_g(x)(\bar{9})\pi_g(y)(10)| \qquad {}^1\Delta_g$$

$$|\ldots\pi_g(x)(9)\pi_g(x)(\overline{10})| - |\ldots\pi_g(y)(9)\pi_g(y)(\overline{10})| \qquad {}^1\Delta_g$$

$$|\ldots\pi_g(x)(9)\pi_g(x)(\overline{10})| + |\ldots\pi_g(y)(9)\pi_g(y)(\overline{10})| \qquad {}^1\Sigma_g{}^+$$

[21] This is the π symmetry of an imaginary bond joining the two end p orbitals.

Table III. Reaction of Cyanogen Azide with Cyclooctatetraene at 75–80° in Various Solvents

		Concn, %[a]			Product compn, %[b]			
Reaction	Solvent	A	B	Nitrogen evolution	6	1d	5	[6]/[1d]
3	$CH_3COOC_2H_5$	13	8	50	14	50	36	0.3
6	$CH_3COOC_2H_5$	1.3	1.2	50	49	37	13	1.3
7	CH_2Br_2	13	8	50	22	13	65	1.7
8	CH_2Br_2	3.7	3.1	50	39	18	43	2.2
9	CH_2Br_2	1.3	1.2	50	49	15	36	3.3
10	CH_3CN	13	8	50	14	30	56	0.5
11	CH_3CN	1.3	1.2	50	14	58	26	0.2
12	C_6H_{12}	33	17	90	7	46	45	0.2

[a] Per cent of COT in solvent (v/v), A = initial concentration, B = final concentration. [b] Determined from the nmr spectra of the mixtures.

undergo major distortions, concerted addition would occur across a bond by either a 1,2 or a 1,8 process.

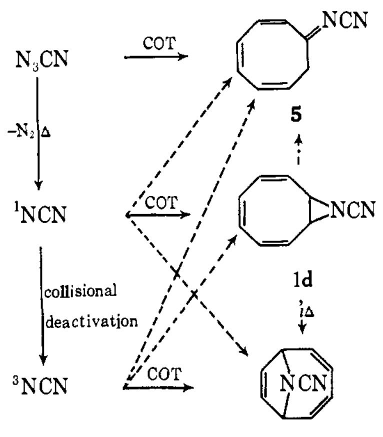
In view of the stringent space demands of concerted additions discussed here, we originally suggested that adduct **6** is a product not of concerted addition but of a two-step process. Furthermore since stepwise processes in the area of neutral electron-deficient intermediates are commonly identified with triplet species, we proposed[1] that triplet NCN is primarily responsible for the formation of this product. In contrast, the 1,2 adduct **1d** was depicted to arise from singlet NCN. We have now examined the question of the origins of both **6** and **1d** employing our recent findings[18] that the multiplicity of reacting NCN can be effectively controlled by the proper choice of solvents. Thus from a study of the stereochemical course of insertion into paraffinic C–H bonds, it was found that NCN reacts exclusively as a triplet in methylene bromide, predominantly as a triplet in ethyl acetate, and exclusively as a singlet in acetonitrile and in the absence of a solvent. In the light of this information, it is evident that if the cyanonitrene producing **6** and **1d** differs in its electronic multiplicity, the ratio of these two products ought to vary with the solvent employed in a qualitatively predictable fashion, whereas if nitrene of the same multiplicity is involved in both cases, the product composition does not have to change with solvent. With this in mind, we studied the course of the reaction employing methylene bromide, ethyl acetate, acetonitrile, and cyclohexane as solvents. The ratio of products was also determined as a function of concentration since here too the composition of the mixture should vary in a predictable manner, if **6** and **1d** have different NCN precursors, the more dilute solutions allowing for more efficient collisional deactivation of the originally generated NCN and thus a better opportunity for the reacting species to be in its triplet ground state. The results are compiled in Table III. It is abundantly clear from the data that the predicted trend exists. For example, the ratio of **6** to **1d** is highest in CH_2Br_2 and reaches a maximum value in the most dilute solution studied. In ethyl acetate, a similar dilution effect is observed albeit the **6** to **1d** ratio is consistently smaller than that observed in CH_2Br_2, in keeping with the lower efficacy of the ester in deactivating NCN.[18] In CH_3CN and C_6H_{12}, markedly lower **6** to **1d** ratios were obtained as expected. Hence both the solvent and dilution effects observed here are strongly indicative of the mechanism we originally proposed.[1] However it should be noted that the results presented here are not as well defined as those obtained from the study of the stereochemistry of the insertion reaction, *i.e.*, the present system appears to be less effective in controlling the electronic multiplicity of NCN. In most of the cases described here, this difference is undoubtedly due to a greater affinity of both electronic variants of NCN toward addition to the double bonds of COT than insertion into the tertiary C–H bonds of 1,2-dimethylcyclohexane, the reference compound employed in the stereochemical experiments.[18] We verified the greater reactivity of double bonds toward singlet NCN through a competition experiment between COT and cyclohexane in a small amount of acetonitrile. In this manner, we found the reactivity of a double bond to be *ca.* 40 times that of a C–H bond of cyclohexane and by an indirect[18] estimate *ca.* 12 times that of a tertiary C–H bond of *trans*-1,2-dimethylcyclohexane. Undoubtedly triplet NCN, being a lower energy species, would discriminate even more between addition and insertion than its singlet counterpart.

The net effect of the greater reactivity of the olefinic functions will obviously be to lower the effectiveness of the solvents in controlling the multiplicity of the nitrene. For example, in CH_2Br_2 and $CH_3COOC_2H_5$, some singlet NCN could be trapped by COT prior to collisional deactivation to the triplet ground state, thus giving rise to some 1,2 adduct, and in CH_3CN, COT could probably compete effectively with solvent in scavenging triplet NCN, thus producing some 1,4 adduct. The occurrence of this latter process in acetonitrile is strongly indicated from the results obtained at the two different concentrations (reactions 10 and 11). Here it is seen that the ratio of **6** to **1d** changes with dilution in a manner opposite to that observed in either CH_2Br_2 or $CH_3COOC_2H_5$, *i.e.*, the proportion of 1,4 adduct decreases with dilution! Of course it could be reasoned that the larger **6** to **1d** ratio in reaction 10 could be merely a consequence of a greater tendency of **1d** to decompose in the more concentrated solution. This is not likely to be the case, however, as the two adducts are produced in comparable over-all yields at the two concentrations (see Experimental Section). The occurrence of a reaction between NCN and acetonitrile is also strongly indicated by the appearance of additional absorption (τ 7.5–8) in the nmr spectra of the product mixtures obtained from reactions 10 and 11. As expected, this absorption is much more prominent in the mixture obtained from the more dilute solution.

One result which cannot be rationalized on the basis of the great affinity of NCN for double bonds is the appearance of both **6** and **1d** when the reaction was conducted in cyclohexane. In this solvent, reacting NCN should be exclusively in a singlet state since, as has been reasoned earlier,[18] reaction of initially produced singlet NCN with the C–H bonds ought to occur more rapidly than deactivation to the lower energy triplet. The additional presence here of COT clearly does not alter this prediction since this material, being more reactive than cyclohexane toward NCN, is undoubtedly even less effective than the cycloalkane in promoting a singlet to triplet change. Hence unless in cyclohexane **1d** isomerizes rapidly to **6**, we are forced to conclude that singlet NCN gives rise mostly to **1d** and to a lesser extent to **6**. Concerning the mode of addition of triplet NCN, it is not clear from the data collected in this work whether this species gives rise to both adducts or to **6** only since some **1d** still appears even under the most favorable conditions employed here for generating triplet NCN (reaction 9). In any event even if both adducts are formed by way of singlet as well as triplet NCN, it is amply clear from *all* the results collected in Table III that *triplet NCN displays a distinct preference for 1,4 (or 1,6) addition and singlet NCN exhibits an equally pronounced discrimination in favor of 1,2 (or 1,8) addition.* Another interesting feature of the results collected in Table III concerns the source of the alkylidenecyanamide **5**. Invariably the proportion of this material in the mixture decreases with increasing dilution. This concentration dependence clearly indicates that even at 78°, **5** is predominantly, if not solely, produced from N_3CN (bimolecular process) rather than NCN (unimolecular decomposition).

The results reported here suggest Scheme III for the reaction of NCN with COT. In this, full arrows represent predominant processes, while dashed arrows depict uncertain or minor paths.

Scheme III



6

The Nature of the Thermal Rearrangement in Azabicyclo[6.1.0]nona-2,4,6-trienes.

From what was mentioned in previous sections, it is obvious that the structurally related aziridines **1c** and **1d** behave differently on thermolysis. Both are heat sensitive but, unlike **1c**, the 1,2 adduct reported here does not yield any tractable products upon heating or upon standing at ambient temperatures (run 4 in Table II). Obviously unless the anticipated rearrangement products, *e.g.*, **2d** and/or **3b**, are unstable to the reaction conditions, which is unlikely,[22] the source of the discrepancy between **1c** and **1d** is undoubtedly to be found in the properties of the intermediate(s) to which these two materials are converted prior to rearrangement or decomposition. For theoretical reasons to be discussed in the accompanying section, this intermediate has in all probability the azacyclononatetraene skeleton **10a**. 1-Azacyclonona-2,4,6,8-tetraene (**10a**) possesses ten π electrons ($4n + 2$; $n = 2$) and should on this basis display qualities characteristic of aromatic compounds. Thus, Hückel (HMO) theory predicts stability for this system by virtue of a *closed* molecular shell configuration, a well-distributed electron distribution, and a relatively large energy separation between highest occupied (ψ_5) and lowest vacant (ψ_6) MO's. Furthermore from what is known concerning its carbocyclic ten π-electron counterpart cyclononatetraenide,[23] **10a**, ought to be able to assume a planar all-*cis* arrangement. Some pertinent MO constants of **10a** are shown in Figure 6A. In Figure 6B are presented the corresponding MO values for the N-cyano derivative **10b**, the monocyclic isomer of **1d**. Comparison of the two sets of constants reveals a pronounced resemblance in both the distribution of the energy levels and the electron densities at the various sites of the ring. Only the ring nitrogen is somewhat depleted of its electron density in going from **10a** to **10b**. This resistance of the ring to undergo change would undoubtedly have a diverse effect on the over-all stability of **10b** since its net result will be to introduce a substantial positive charge on the nitrile carbon and thus make this site of **10b** quite susceptible to attack by nucleophiles. To ensure that the substantial charge predicted to reside on the nitrile carbon of **10b** is a result of the inherent aromaticity of the system rather than the specific parameters chosen for the computation, we carried out similar calculations on azepine and N-cyanoazepine,[24] the eight π-electron analogs of **10a** and **10b**, and found that indeed in the azepine system, the electron density of the ring nitrogen is predicted to reduce by as much as 10% upon cyanation as compared to the *ca.* 5% reduction predicted for the **10a** to **10b** change (Figure 6). Furthermore as a result of this difference, the nitrile carbon in N-cyanoazepine is predicted to have a higher electron density (0.58) and thus be less susceptible to nucleophilic attack than **10b**. Exchange of carbethoxyl for cyano (compound **10c**) should partly suppress the reactivity of the system since the $COOC_2H_5$ function should be able to better accommodate a positive charge.

We will now consider the various ways in which azabicyclo[6.1.0]nona-2,4,6-triene can rearrange thermally. It was pointed out recently[6] that the **1c** to **3a** change is similar to the thermal isomerization of bicyclo[6.1.0]nona-2,6-diene (the carbocyclic analog of **1c** minus the remote double bond) to bicyclo[5.2.0]nona-2,5-diene (the carbocyclic analog of **3a** minus the olefinic function in the four ring) which occurs readily at 20°. At first glance, the comparison appears reasonable. However, it does not survive closer examination for two reasons. (1) There is no reason as to why the remote double bond in **1c** should be a nonparticipant in the change as is required by a direct **1c** to **3a** process, and (2) even if the rearrangement does occur exclusively

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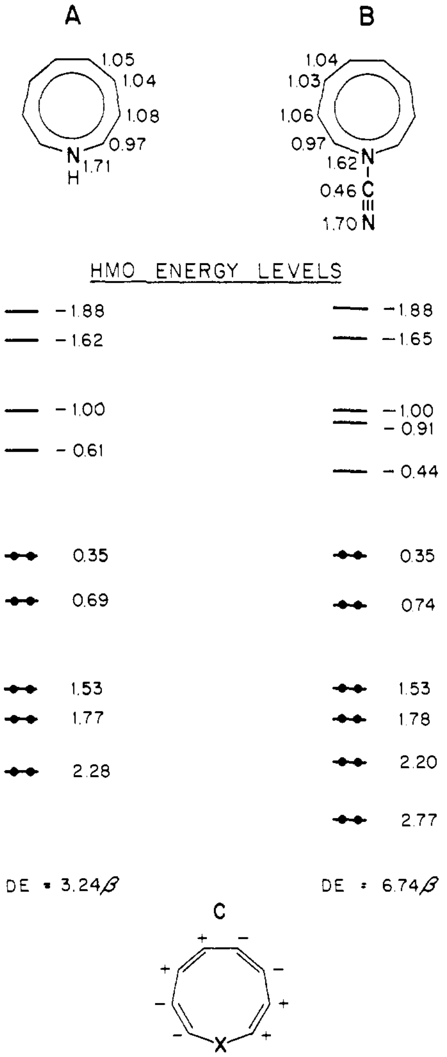
[22] By analogyw ith previous work,[12b] the N-cyanoenamine (C=CNCN) functionality present in these systems ought to be reasonably stable thermally.

[23] (a) T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc.*, **86**, 5194 (1964); (b) E. A. LaLancette and R. E. Benson, *ibid.*, **87**, 1941 (1965).

[24] N-Cyanoazepine has been prepared recently: F. D. Marsh and H. E. Simmons, *ibid.*, **87**, 3529 (1965).



10a, X = NH
b, X = NCN
c, X = $NCOOC_2H_5$
d, X = CH_2

Figure 6. (A) HMO charge densities, energy levels, and delocalization energy (DE) of 1-azacyclonona-2,4,6,8-tetraene. (B) Same molecular constants of N-cyano-1-azacyclonona-2,4,6,8-tetraene. (C) Symmetry characteristics of highest occupied MO. The following parameters were employed in the calculation: $\alpha(\text{-N-}) = \alpha_0 + 1.5\beta_0$, $\beta(\text{C-N-C}) = 0.8\beta_0$; $\alpha(\equiv\text{N}) = \alpha_0 + 2\beta_0$, $\alpha(\text{—C}\equiv) = \alpha_0$; $\beta(>\text{N-C}) = 0.8\beta_0$, $\beta(\text{C}\equiv\text{N}) = 1.2\beta_0$.

via the *cis*-1,2-divinylaziridine portion of **1c**, considerations of orbital symmetry, which no doubt would dictate the mode of ring opening and subsequent cyclization, suggest that the product should possess not the *cis*-fused, all-*cis* frame shown in **3a** but the prohibitively strained *trans*-fused, *trans,cis,cis* skeleton shown in **11**! The assumption in case 2 is of course that the aziridine in **1c** would rupture in a manner analogous to that of the isoelectronic cyclopropyl anion. It can be easily shown, employing symmetry arguments analogous to those first introduced by Woodward and Hoffmann,[25] that 1,2-divinylcyclopropyl anion ought to rupture to cycloheptatrienyl anion containing one *trans* bond and that subsequent thermal ring closure should occur in a conrotatory fashion, leading to *trans* fusion. It can also be readily seen that even in the event that the originally produced **11** rapidly isomerizes to the all-*cis* frame, a process which may be facilitated by the presence of the nitrogen lone pair, the two rings in the final product would still be fused in a *trans* fashion. Finally it is doubtful, in view of the low temperatures involved, that ring rupture and subsequent closure would occur in a fashion contrary to that dictated by orbital symmetry. Hence we conclude that **1c** cannot afford **3a** by a simple *cis*-1,2-divinylcyclopropane reorganization. In addition, we can readily exclude the occurrence of any ring closures involving solely the unsaturated segment **1c** and neglecting the three-membered ring since such cyclizations are either unlikely from considerations of skeletal strain, *e.g.*, closure at the 3,6 positions of the hexatriene system, or lead to tricyclic arrangements which cannot be converted to bicyclic structures without extensive rearrangement, *e.g.*, the symmetry-allowed closure at the 1,6 carbons of the hexatriene segment.[26] Hence the only remaining alternative for the **1c** to **3a** conversion involves initial rupture of the aziridine C–C link of **1c**. The mode of thermal ring cleavage will be determined by the relative symmetry of the originally bonded atoms in the highest occupied MO of the product. With this in mind and assuming that **1c** has an all-*cis*, *cis*-fused arrangement, one can easily show that the symmetry of the highest occupied MO (Figure 6C) requires the initially formed azacyclononatetraene to possess the arrangement depicted in **12a**. Ring closure of **12a** can produce three new bicyclic systems, **2c**, **3a**, and **14a**. Of these, **2c** and **3a** will possess prohibitively strained arrangements containing either *trans* bonds or *trans* ring fusions or both, while **14a** can form in a stable all-*cis* configuration with a *cis* fusion between the rings. All-*cis*, *cis*-fused **2c** and **3a** can form only from isomers **10c** and **13a**, respectively. From "Dreiding" molecular models, it can be seen that of the three azacyclononatetraene isomers considered here **12a** contains the greatest skeletal strain while the all-*cis* isomer **10c** is the least strained. Furthermore, the all-*cis* compound **10c** is in all probability the only one of the three that can assume a planar arrangement and thus derive full advantage of its potential aromaticity. For these reasons and since the conversion of **12a** to **10c** can in principle occur by a simple isomerization of a strained double bond, it is quite conceivable that initially formed **12a** will isomerize to **10c** prior to collapse to bicyclic product. On the other hand, isomerization of originally formed **12a** to **13a**, the sole monocycle which can generate the observed product **3a**, is not likely to occur as it requires a more complex process. In addition, generation of **13a** does not provide any conceivable driving force. Hence, it appears likely that, if correctly formulated, **3a** is not a primary product but arises from isomerization of either **14a** (formed from **12a**) or the dihydroindole **2c** (formed from **10c**). Of course, **3a** could arise from electronically excited **10c** since the lowest vacant orbital of the latter has the correct symmetry for such a ring closure. The occurrence of such a process, however, under the condi-

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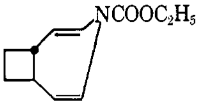
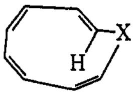
[25] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

[26] This process is probably operative in the **1b** to **2b** change when R_1 and R_2 are halogen atoms, since in the product these invariably end up in vicinal rather than geminal positions: E. Vogel, *Angew. Chem. Intern. Ed. Engl.*, 2, 1 (1963).

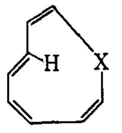
tions employed[8] for the conversion of **1c** to **3a**, would require that the first electronically excited state of **10c** be thermally accessible at 80°. This is not very likely. Finally it should be noted that the arguments employed in the present section concerning the isomerization of **1c** are equally applicable to the rearrangements of its carbocyclic analogs **1a** and **1b** since, as can be seen from Figure 6C, the symmetry properties of the highest occupied MO of **10c** are the same as those of the corresponding MO of the octatetraene system present in **10d**.



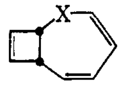
11



12a, X = $NCOOC_2H_5$
b, X = CH_2



13a, X = $NCOOC_2H_5$
b, X = CH_2



14a, X = $NCOOC_2H_5$
b, X = CH_2

Product Analysis

In all quantitative runs, the reaction was carried to the required extent and then immediately quenched by cooling in an ice bath. Work-up was conducted at room temperature in as short a period as possible, the time lapse between interruption of the reaction and determination of the nmr spectrum being 3–4 hr. From the results shown in Table II (run 4), it can be seen that no significant decomposition of **1d** should occur under the work-up conditions.

The NCN–COT reaction was also carried out in the absence of a solvent as this should present the most favorable environment for singlet NCN. However this reaction did not provide any information concerning the mechanism of addition of the nitrene, as the N_3CN–COT product **5** was produced to the virtual exclusion of **1d** and **6**. Considerable "2 + 2" dimer of COT was also produced under these conditions. The dimer was isolated and characterized by its infrared and nmr spectra,[27] the latter being as expected very similar to that of **1c** and **1d**. The dimer is also formed to a small extent in many of the reactions conducted in the presence of a solvent, but its presence does not interfere in the determination of the amount of **1d** in the mixtures. The two can be readily distinguished from the different chemical shifts of their allylic protons. Thus, the sharp allylic singlet arising from **1d** always coincides with the lowest field signal of the quartet due to **5** while the corresponding singlet of the COT dimer has a chemical shift identical with that of the next higher signal of the quartet of **5**.

Experimental Section[28]

Materials. The cyclooctatetraene employed was >99.5%. Of the solvents, ethyl acetate was "Fisher Reagent Grade," acetonitrile was Eastman (White Label), and cyclohexane was Eastman Spectrograde and were used without further purification. Methylene bromide was purified by careful distillation immediately before use (>99.5% pure).

Reaction of Cyanogen Azide with Cyclooctatetraene at Room Temperature. To a rapidly stirring solution of cyclooctatetraene (80 ml) in ethyl acetate (50 ml) was added a solution of cyanogen azide (*ca.* 8 g) in ethyl acetate (80 ml) over 1 hr and at room temperature. Stirring at the same temperature for *ca.* 60 hr resulted in the evolution of the theoretical amount (3200 ml) of nitrogen. The resulting dark suspension was filtered to give a highly insoluble tan powder (3.8 g, mp >300°) and a red filtrate which was concentrated at room temperature, first at water-aspirator pressure and then at *ca.* 0.5 mm to a red viscous oil (15.3 g). Distillation of this material at high vacuum (*ca.* 0.03 μ) and a bath temperature of 100–120° gave, after a slight yellow forerun, 6.4 g (35%) of **5** as a viscous dark orange liquid; ν_{max}^{neat} 1540 and 2180 cm^{-1}; $\lambda_{max}^{CH_3CN}$ 331 mμ (ϵ 6900) and 243 mμ (ϵ 16,000); nmr ($CDCl_3$), multiplets centered at τ 3.50 (5 H) and 4.50 (1 H) and a quartet at τ 7.15 (2 H); parent ion at *m/e* 144.

Anal. Calcd for $C_9H_8N_2$: C, 74.97; H, 5.59; N, 19.43. Found: C, 74.66; H, 5.73; N, 19.85.

The same reaction was carried to partial completion. After a reaction time of *ca.* 3 hr, the crude product was obtained as described above. The nmr spectrum of this material was essentially identical with that of pure **5** with no traces of either **1d** or **6**.

A solution of pure **5** (3 g) in ethyl acetate (100 ml) was maintained at a reflux under nitrogen for 15 hr. Removal of the solvent under reduced pressure gave unaltered (nmr) **5**.

A 2.1-g sample of pure **5** was dissolved in benzene (200 ml), the solution mixed with 100 g of activity IV Woelm neutral alumina, and the resulting slurry stirred overnight. The yellow benzene solution was filtered free from alumina and concentrated at water-aspirator pressure and *ca.* 50° to yield a residual yellow liquid (1.3 g). Distillation of this material gave 1.1 g (63%) of **7** as a bright yellow mobile liquid; bp 54° (0.8 mm); ν_{max}^{neat} 1670 cm^{-1}; nmr (neat) multiplets centered at τ 3.90 (5 H) and 4.70 (1 H) and a doublet at τ 7.50 (2 H); parent ion at *m/e* 120.

Anal. Calcd for C_8H_8O: C, 79.97; H, 6.71; O, 13.32. Found: C, 80.02; H, 6.89; O, 13.26.

Reaction of Cyanogen Azide with Cyclooctatetraene at 78°. To a rapidly stirring solution of cyclooctatetraene (50 ml) in ethyl acetate (400 ml), maintained at the reflux temperature (*ca.* 80°), was added a solution of cyanogen azide (*ca.* 10 g) in ethyl acetate (125 ml) over a period of 1.5 hr. Nitrogen evolution was complete after stirring at the same temperature for an additional 3 hr. The resulting dark suspension was filtered (5.0 g of a tan powder; mp >300°) and the red filtrate concentrated at *ca.* 45° (5 mm) to a red viscous oil (15.4 g). This was suspended in benzene (200 ml) and filtered, the clear benzene solution mixed with 100 g of activity IV Woelm neutral alumina, and the resulting slurry stirred overnight. Filtration gave a light orange solution which was stirred with an additional 100 g of alumina for *ca.* 10 hr and the yellow filtrate concentrated at *ca.* 45° (5 mm) to a yellow mobile oil (3.1 g). The nmr spectrum ($CDCl_3$) of this material was identical with that of ketone **7** and had additional signals at τ 3.7, 4.6, and 5.3, the ratio of the τ 5.3 signal to that due to the methylene function in **7** being *ca.* 0.6. The yellow oil was dissolved in the minimum amount of benzene (*ca.* 20 ml) and the resulting solution was added dropwise to *ca.* 30 ml of petroleum ether (bp 30–60°). The slightly yellow crystalline precipitate (0.82 g) that formed was collected, washed with petroleum ether, and sublimed at *ca.* 90° (0.05 mm). The pale yellow sublimate was again washed with petroleum ether to yield **6** (0.72 g, 3.4%) as white crystals, mp 102–103°; ν_{max}^{KBr} 2220 cm^{-1}; $\lambda_{max}^{CH_3CN}$ 255 mμ (ϵ 4500); nmr ($CDCl_3$) narrow signals at τ 3.7 (4 H) and 4.6 (2 H) and a broader signal at τ 5.3 (2 H; width at half-height = 5 cps); parent ion at *m/e* 144.

Anal. Calcd for $C_9H_8N_2$: C, 74.97; H, 5.59; N, 19.43. Found: C, 75.22; H, 5.68; N, 19.36.

Concentration of the benzene-soluble crude product at *ca.* 0.01 mm prior to treatment with alumina afforded 5.7 g (30%) of a red viscous oil. The nmr spectrum of this material indicated the presence of only **5** and its isomer **6**. The ratio of the τ 5.3 signal of **6** to that of the methylene signal of **5** was *ca.* 0.5.

Preparation of N-Cyano-9-azabicyclo[4.2.1]nonane (9). Homotropane **8** was prepared by a known procedure.[13] A solution of this material (0.62 g) in benzene (5 ml) was added to a stirring solution of cyanogen bromide (0.6 g) in benzene (8 ml) over a period of 10 min, while the temperature was maintained at *ca.* 52°. After stirring at the same temperature for 50 min and then at room tem-

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[27] (a) G. Schröder, *Ber.*, **97**, 3131 (1964); (b) G. Schröder, J. F. M. Oth, and R. Merenyi, *Angew. Chem. Intern. Ed. Engl.*, **4**, 752 (1965).

[28] All melting points and boiling points are uncorrected. Infrared spectra were obtained with a Perkin-Elmer 21 spectrometer, nmr spectra were determined with a Varian A-60 spectrometer, and ultraviolet spectra were measured with a Cary 14 spectrometer of the Applied Physics Corp.

Table IV. Reaction of Cyanogen Azide with Cyclooctatetraene at 78–80° in Various Solvents

Reaction	N_3CN, g	Solvent	Concn[a]		Reaction time, min	Nitrogen evolution, %	Products			Product mixture, g[d]	Overall yield, %[e]
			A[b]	B[c]			**6**	**1d**	**5**		
3	6.8	$CH_3COOC_2H_5$	25:200	25:265	20	50	14	50	36	8.0	60
6	3.1	$CH_3COOC_2H_5$	9:670	9:735	19	50	49	37	13	2.4	62
7	1.6	CH_2Br_2	25:200	25:265	9	50	22	13	65	1.4	70
8	1.7	CH_2Br_2	13:350	13:415	8	50	39	18	43	1.5	56
9	2.2	CH_2Br_2	12:900	12:965	8	50	49	15	36	1.4	53
10	7.1	CH_3CN	25:200	25:265	16	50	14	30	56	6.3	65
11	2.1	CH_3CN	9:670	9:735	18	50	14	58	26	2.0	49[f]
12	1.4	C_6H_{12}	30:100	30:200	13	90	7	46	45		

[a] The concentration is given in terms of cyclooctatetraene in solvent (v/v). [b] Initial concentration. [c] Final concentration. [d] Contains some COT. [e] Calculated on the basis of 50% reaction; cyclooctatetraene free. [f] Adjusted for the amount of NCN–CH_3CN product.

perature overnight, the reaction mixture was filtered and the residue washed thoroughly with benzene. Concentration of the yellow benzene filtrate afforded a yellow semisolid which upon recrystallization from hexane afforded **9** as a finely divided white solid (mp 114–116°); $\nu_{\max}^{\text{KBr}}$ 2200 cm^{-1}; nmr ($CDCl_3$), two broad multiplets, τ 5.9 (2 H) and τ 7.5–8.5 (12 H).

Anal. Calcd for $C_9H_{14}N_2$: C, 71.95; H, 9.39; N, 18.65. Found: C, 71.69; H, 9.28; N, 18.45.

Preparation of 9 by Catalytic Hydrogenation of 6. A solution of **6** (0.75 g) in tetrahydrofuran (25 ml) and 5% rhodium-on-charcoal catalyst (0.75 g) was treated with hydrogen at room temperature and atmospheric pressure. Uptake was complete after *ca.* 36 hr and amounted to a total of 382 ml (102% of theory). The mixture was filtered free of catalyst and the filtrate evaporated to 0.6 g of a cream-colored solid (80%) with spectral characteristics (infrared, nmr) identical with those of synthetic **9**.

Observation of the 1,2 Adduct 1d. A solution of cyanogen azide (*ca.* 7.8 g) in ethyl acetate (65 ml) was added over *ca.* 20 min to a boiling solution (78°) of cyclooctatetraene (25 ml) in ethyl acetate (200 ml). After a total reaction time, from beginning of addition, of 28 min, 1400 ml of nitrogen had evolved; 50% of theory. The reaction was immediately quenched by immersing the flask in an ice bath and the red reaction mixture filtered to afford a highly insoluble tan powder (0.44 g) and a red filtrate. The filtrate was concentrated at room temperature, first at the water aspirator and then at the oil pump (*ca.* 0.5 mm). (*Caution! Since the ethyl acetate still contains ca. 50% of the originally present N_3CN, the cold trap into which the volatiles are collected should be well shielded and maintained at a temperature not lower than the freezing point of the solvent employed.*) The dark red residual oil amounted to 6.75 g; 81% yield (based on 50% reaction). The nmr spectrum of this material displayed, besides the signals of **5** and **6**, absorption expected of **1d**; unsymmetrical doublet centered at τ 3.9 (6 H) and a sharp singlet at τ 6.6 (2 H; width at half-height = 1.5 cps).

The reaction was interrupted at various stages, and the reaction mixtures were worked up as described above. The results are compiled in Table I. Invariably some "2 + 2" dimer of COT was produced in these reactions. The nmr spectrum of this material is virtually identical with that of **1c**. The two, however, can be readily distinguished from the chemical shifts of the singlets arising from the allylic protons. In **6**, this singlet coincides with the lowest field signal of the quartet of **5**, whereas that arising from the cyclooctatetraene dimer invariably coincides with the second lowest field signal of the quartet.

A 2.5-g sample of the mixture obtained when the reaction was allowed to proceed to 25% completion was dissolved in benzene (150 ml) and maintained at a boil under nitrogen for 3 hr. The resulting suspension was filtered to give a brown powder and a red filtrate which upon evaporation afforded a red oil (1.3 g) which contained (nmr) very little **1d**. The residual solid was analyzed.

Anal. Calcd for $(C_9H_8N_2)_n$: C, 74.97; H, 5.59; N, 19.43. Found: C, 70.70; H, 5.46; N, 19.36.

Control Experiments. A mixture of **5**, **6**, and **1d** (3.5 g) was treated with benzene (50 ml) and filtered. To the filtrate was added 0.6 g of dimethyl phthalate and the solvent removed under reduced pressure to afford a red oil (3.8 g). This was dissolved in ethyl acetate (200 ml), and the resulting solution was divided into four portions. Three of these were stirred at the boiling temperatures for 30, 60, and 210 min, respectively, while the fourth portion was allowed to stir at room temperature over a period of a week. The mixtures were subsequently filtered free of any precipitate that might have formed and the filtrates evaporated at room temperature, first at the water aspirator and subsequently at the oil pump (*ca.* 0.5 mm) to red viscous materials. In each case, the relative amounts of the three adducts were determined by nmr employing the allylic protons of the adducts and the methyl, as well as aromatic hydrogens of the standard. The results are compiled in Table II.

General Procedure for Reaction of NCN with COT at 78° in Different Solvents. For the reactions conducted in methylene bromide and cyclohexane, cyanogen azide was prepared from *ca.* 2 g of sodium azide and cyanogen chloride (50 ml), the latter being employed as both reactant and solvent.[18] For the runs in acetonitrile and ethyl acetate, stock solutions of N_3CN in these solvents were employed. In every case, the cyanogen azide solution was analyzed quantitatively immediately before use by means of an azotometer. The solution (65 ml) was then added to a stirring mixture of cyclooctatetraene in the solvent, present in the amounts shown in column 4 of Table IV, and maintained at 75 to 80°. In each case, addition required from 5 to 8 min. After the necessary amount of nitrogen was evolved, the reaction vessel was immediately cooled in an ice bath. The reaction mixture was then filtered free of any precipitate and the filtrate concentrated at room temperature, first at the water-aspirator pressure and then at the oil pump (*ca.* 0.5 mm). The mixtures were analyzed by means of their nmr spectra which displayed absorptions characteristic of **5**, **6**, and **1d**, as well as a singlet due to unreacted COT. The results are compiled in Table IV.

Competition Experiments between Cyclooctatetraene and Cyclohexane for Singlet NCN. A solution of cyanogen azide (*ca.* 1.6 g) in acetonitrile (12 ml) was added over a period of 6 min to a stirring solution of cyclooctatetraene (*ca.* 10 ml) in cyclohexane (*ca.* 100 ml) present in the exact molar ratio (nmr) of 1:12, respectively. The temperature of the mixture was maintained at *ca.* 61° throughout the addition and subsequent reaction. After a reaction time of 20 min, there was evolved 330 ml (57% of theory) of nitrogen. The mixture was then cooled in ice and filtered free of traces of precipitate and the filtrate concentrated under vacuum (0.5 mm). The residual red oil was then shaken thoroughly with benzene (*ca.* 100 ml) and the benzene solution filtered free of any precipitate that might have formed. The filtrate was concentrated at room temperature (*ca.* 0.5 mm) to a red oil with an nmr spectrum consisting of absorptions characteristic of **5**, **6**, **1d**, and cyclohexyl cyanamide.[17] The ratio of **6** + **1d** to cyclohexyl cyanamide was 0.9.

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