The Cycloheptatriene–Norcaradiene System. I. 7,7-Dicyanonorcaradienes. Preparation and Structure Proof[1]

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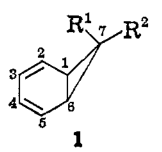
Abstract: Thermolysis of dicyanodiazomethane in benzene and *p*-xylene gave the first simple norcaradiene derivatives. Their structures were proved by physical methods. Dicyanocarbene added mainly to the 1,2 bond of naphthalene to give the expected 7,7-dicyano-2,3-benzonorcaradiene, but isolation of 7,7-dicyano-1,2-benzocycloheptatriene and 7,7-dicyano-3,4-benzocycloheptatriene indicated that addition to the 1,9 and 2,3 bonds had occurred to a significant extent.

In 1885, Buchner and Curtius reported the first thermal decomposition of a diazo compound in an aromatic hydrocarbon.[2] The product obtained from ethyl diazoacetate and benzene was formulated as ethyl 7-norcaradienecarboxylate (**1b**), and a labile pyrazoline derivative was postulated as an intermediate. More recently, the reaction has been recognized to proceed by a carbene mechanism, and a number of other carbenes, generated either thermolytically or photolytically from diazo compounds, have been added to aromatic hydrocarbons.[3] The products have variously been described as norcaradienes (**1**) or cycloheptatrienes (**2**), and a definite proof that all of these products, including Buchner's ester, had the cycloheptatriene structure became available only with the advent of nuclear magnetic resonance spectroscopy.[4] That chemical evidence is of little help in the structure assignment of these products is illustrated by the fact that cycloheptatriene (**2a**), on hydrogenation, gives cycloheptane,[5] whereas addition of dienophiles usually gives products derived from norcaradiene (**1a**).[4b,6] One explanation of this duality of chemical reactions has been the assumption of a rapid equilibrium between **1** and **2**, with an equilibrium concentration of **1** so small as to be undetectable by methods available at this time.[7] Nmr spectroscopy also showed that other supposed norcaradienes, such as the eucarvone enol ethers, were actually cycloheptatriene derivatives.[4a,8] The existence of a simple norcaradiene remained to be demonstrated.[9] The only authentic representatives of this ring system known were compounds stabilized by incorporating one or both double bonds into an aromatic system, or by bridging carbon atoms 1 and 6 with a three-atom bridge. Thus, rearrangement of benzonorcaradiene (**3a**) to its *o*-quinonoid, seven-membered valence tautomer **3b** does not occur to any measurable extent since it would result in the loss of a considerable amount of resonance stabilization.[10] Bridged structures such as **4** or **5** are stable because the corresponding cycloheptatrienes would have two double bonds on bridgeheads.[11] Recently, a third way of forcing a cycloheptatriene into the norcaradiene system became known.[12] The methylenenorcaradiene **6** is stable relative to its seven-membered isomer because there are serious steric interactions in the latter between the 3 and 3′ hydrogens and the methyl groups on C_1 and C_6.



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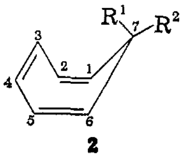

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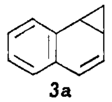
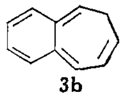
a, $R^1, R^2 = H$
b, $R^1 = H$; $R^2 = COOEt$
c, $R^1, R^2 = CN$
d, $R^1 = H$; $R^2 = CN$



3a



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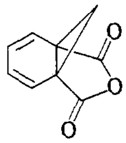

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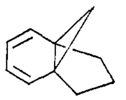

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(1) Parts of this paper were reported in preliminary form: E. Ciganek, *J. Am. Chem. Soc.*, **87**, 652 (1965).

(2) E. Buchner and T. Curtius, *Ber.*, **18**, 2377 (1885), and subsequent papers.

(3) For a review see W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964.

(4) (a) E. J. Corey, H. J. Burke, and W. A. Remers, *J. Am. Chem. Soc.*, 77, 4941 (1955); (b) W. von E. Doering, G. Laber, R. Vonderwahl, N. F. Chamberlain, and R. B. Williams, *ibid.*, **78**, 5448 (1956). For a review of the cycloheptatriene–norcaradiene problem see S. J. Rhoads in "Molecular Rearrangements," P. de Mayo, Ed., Part 1, Interscience Publishers, Inc., New York, N. Y., 1963, pp 700–703.

(5) Under conditions where hydrogenolysis of the cyclopropane ring should be minimized (rhodium catalyst), cycloheptatriene gives less than 0.005% of norcarane: *cf.* footnote 12 in ref 7.

(6) K. Alder and G. Jacobs, *Chem. Ber.*, **86**, 1528 (1953); K. Alder, H. Jungen, and K. Rust, *Ann.*, **602**, 94 (1957); K. Alder, R. Muders, W. Krane, and P. Wirtz, *ibid.*, **627**, 59 (1959); K. Alder, K. Kaiser, and M. Schumacher, *ibid.*, **602**, 80 (1957).

(7) The existence of such an equilibrium in a favorable case has recently been demonstrated: E. Ciganek, *J. Am. Chem. Soc.*, **87**, 1149 (1965).

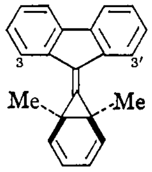
(8) W. von E. Doering and M. R. Willcott, III, *Tetrahedron Letters*, 663 (1962).

(9) A number of stable 3,4-diazanorcaradienes have been described recently: G. Maier, *Chem. Ber.*, **98**, 2446 (1965), and preceding papers. For the system oxepin–benzene oxide see E. Vogel, W. A. Böll, and H. Günther, *Tetrahedron Letters*, 609 (1965).

(10) (a) W. von E. Doering and M. J. Goldstein, *Tetrahedron*, **5**, 53 (1959); (b) R. Huisgen and G. Juppe, *Chem. Ber.*, **94**, 2332 (1961); (c) E. Vogel, D. Wendisch, and W. R. Roth, *Angew. Chem.*, **76**, 432 (1964).

(11) (a) J. Schreiber, W. Leimgruber, M. Pesaro, P. Schudel, T. Threlfall, and A. Eschenmoser, *Helv. Chim. Acta*, **44**, 540 (1961); (b) R. Darms, T. Threlfall, M. Pesaro, and A. Eschenmoser, *ibid.*, **46**, 2893 (1963); (c) E. Vogel, W. Wiedemann, H. Kiefer, and W. F. Harrison, *Tetrahedron Letters*, 673 (1963); *cf.*, however, L. H. Knox, E. Velarde, and A. D. Cross, *J. Am. Chem. Soc.*, **87**, 3727 (1965).

(12) H. Prinzbach, U. Fischer, and R. Cruse, *Angew. Chem.*, **78**, 268 (1966).



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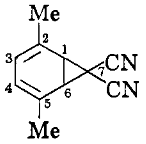
As part of an investigation of the chemistry of dicyanocarbene,[13] its additions to aromatic hydrocarbons were studied. In the light of the above-cited accumulated evidence there was every reason to believe that the products of the reactions should turn out to be 7,7-dicyanocycloheptatrienes.

Preparation and Structure Determination of 7,7-Dicyanonorcaradienes

Thermolysis or photolysis of dicyanodiazomethane[14] in benzene gave, as the sole product, in 82% yield, a crystalline solid which had the composition expected for an adduct of dicyanocarbene to benzene. Its ultraviolet spectrum, which showed a maximum at 271 mμ (ϵ 2800–2900 depending on the solvent), ruled out unconjugated systems such as 7,7-dicyanobicyclo[2.2.1]hepta-2,5-diene and 4,4-dicyanobicyclo[3.2.0]hepta-2,6-diene. The two most likely structures to be considered were 7,7-dicyanocycloheptatriene (**2c**) and 7,7-dicyanonorcaradiene (**1c**). The ultraviolet spectrum pointed to the latter, since it was similar to that of the norcaradienes **4** (λ_{max} 269 mμ)[11b] and **5** (λ_{max} 273 mμ)[11c] and different from that of 7-cyanocycloheptatriene (**2d**, λ_{max} 255 mμ).[15] The nmr spectrum provided even better evidence for the norcaradiene structure. The olefinic protons on C-3 and C-4, C-2 and C-5, and C-1 and C-6 in cycloheptatrienes usually occur in three groups at τ 3–5.[16] Thus, in neat 7-cyanocycloheptatriene (**2d**), these three sets of protons give signal groups centered at τ 3.53, 3.93, and 4.91. The nmr spectrum (in deuteriochloroform) of the dicyanocarbene–benzene adduct, on the other hand, showed four protons as a complex multiplet at τ 3.2–3.9 and two protons as a triplet, split further, centered at τ 6.53. The latter signal, attributed to the protons on C-1 and C-6 in structure **1c**, occurs at rather lower field than is usually observed in cyclopropanes. However, these protons are both allylic, and adjacent to two geminal cyano groups, which have been shown to cause cyclopropyl protons to shift downfield by *ca.* 1–1.5 τ units.[13] Additional evidence was sought by determination of the coupling constant between the protons on C-1 and C-6, which should be large in **1c** and very small or zero in **2c**. Owing to the failure to detect the carbon-13 satellites of the τ 6.53 signal (which had been collapsed into a singlet by double irradiation), a direct determination of this parameter was not achieved. However, a recently published complete analysis of the nmr spectrum of **1c**[17] furnished a $J_{1,6}$ of 8.4 cps, in agreement with the norcaradiene structure. The Raman spectrum of the dicyanocarbene–benzene adduct showed the infrared-inactive, double bond stretching band at 1568 cm^{-1} with a relative intensity of 76 (taking the single cyano band at 2248 as 100). In 7-cyanocycloheptatriene (**2d**) the corresponding band occurs at 1530 cm^{-1} with an intensity of 610 (relative to the cyano band at 2245 cm^{-1}); since the double bond emits (very strongly) at 1535 cm^{-1} in the parent cycloheptatriene,[18] its position appears to be little affected by substitution in the 7 position. The observation of the double-bond frequency at 1568 cm^{-1} and its relatively low intensity lend further support to the assignment of structure **1c** to the benzene–dicyanocarbene adduct. Final proof for the norcaradiene structure came from an X-ray structure determination carried out on 7,7-dicyano-2,5-dimethylnorcaradiene (**7**). Thermolysis of dicyanodiazomethane in *p*-xylene gave two isomeric adducts, assigned structures **7** and **8**, in 41 and 39% yield, respectively. The nmr spectrum of **7** showed three singlets at τ 3.81 (2 H), 6.78 (2 H), and 7.87 (6 H). Compared to 7,7-dicyanonorcaradiene (**1c**), its ultraviolet maximum at 279 mμ was shifted toward longer wavelengths by 8 mμ, as expected for addition of two methyl groups to the chromophore. The nmr spectrum of **8** showed one methyl group as a singlet at τ 8.27, the other as a doublet (J = 1 cps) at 7.97; a doublet (J = 6 cps) at 6.88 was attributed to the cyclopropyl proton. The three olefinic protons in **8** occurred as an AB quartet, superimposed on further bands, centered at τ 3.80. The ultraviolet spectrum of **8** showed a maximum at 276 mμ. The complete X-ray structure determination of **7** has been published elsewhere;[19] the salient features are as follows. The C-1–C-6 bond distance is 1.50 A, the C-1–C-7 and C-6–C-7 distances are 1.56 A. There is evidence that the carbon–carbon bonds in the cyclopropane portion of the molecule are bent by 20 ± 10°. The cyclohexadiene is folded slightly toward C-7 along the C-2–C-5 axis and forms an angle of 72° with the cyclopropane ring.



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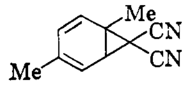

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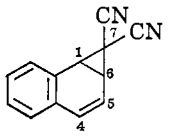
To provide a model for the 7,7-dicyanonorcaradiene system, dicyanocarbene was also added to naphthalene. For reasons discussed in the introduction, there is no ambiguity about the structure of the adduct **9**. 7,7-Dicyano-2,3-benzonorcaradiene (**9**) was obtained in 50% yield and it had the expected nmr spectrum, with the four aromatic protons as a multiplet at τ 2.2–2.7,



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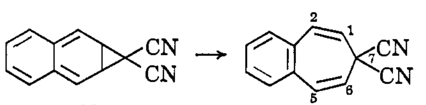
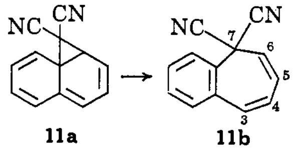


10a **10b**



11a **11b**

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(13) E. Ciganek, *J. Am. Chem. Soc.*, **88**, 1979 (1966).

(14) E. Ciganek, *J. Org. Chem.*, **30**, 4198 (1965).

(15) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **79**, 352 (1957).

(16) (a) K. Conrow, M. E. H. Howden, and D. Davis, *ibid.*, **85**, 1929 (1963); (b) M. R. Willcott, III, Ph.D. Dissertation, Yale University, 1963.

(17) C. Ganter and J. D. Roberts, *J. Am. Chem. Soc.*, **88**, 741 (1966).

(18) M. V. Evans and R. C. Lord, *ibid.*, **82**, 1876 (1960).

(19) C. J. Fritchie, Jr., *Acta Cryst.*, **20**, 27 (1966).

the two olefinic protons as a doublet at 3.03 and a quartet at 3.77 ($J_{4,5}$ = 10 cps), the proton on C-1 as a doublet at 6.20, and H-6 as a quartet at 6.65 ($J_{1,6}$ = 9 cps; $J_{5,6}$ = 5 cps). Some additional allylic splitting was also discernible. The position of the cyclopropane protons in **9** at τ 6.2 and 6.6 provided further evidence for the norcaradiene structure of the benzene–dicyanocarbene adduct **1c**. The ultraviolet spectrum of **9** (in cyclohexane) showed maxima at 272 mμ (ϵ 7900) and 227 mμ (ϵ 25,000) with a shoulder at 233 mμ (ϵ 21,000). This compares with $\lambda_{\max}^{\text{hexane}}$ 306 (ϵ 1000), 274 (ϵ 6600), and 222 mμ (ϵ 15,000) in the parent 2,3-benzonorcaradiene.[10a] The thermolysis of dicyanodiazomethane in naphthalene furnished, in addition to **9**, two further adducts in 12% combined yield. They were assigned structures **10b** and **11b** on the basis of spectral evidence. 7,7-Dicyano-3,4-benzocycloheptatriene (**10b**) showed the four aromatic protons as a barely split singlet at τ 2.39 and the four olefinic hydrogens as an AX quartet at 2.89 and 3.93 ($J_{1,2}$ = 10 cps). Its ultraviolet spectrum [$\lambda_{\max}^{\text{cyclohexane}}$ 228 mμ (ϵ 46,000) and 257 mμ (ϵ 5900)] was almost superimposable on that of the parent 3,4-benzocycloheptatriene [$\lambda_{\max}^{\text{EtOH}}$ 228 mμ (ϵ 44,000) and shoulder at 256 mμ (ϵ 5200)].[20] The nmr spectrum of 7,7-dicyano-1,2-benzocycloheptatriene (**11b**) in deuteriochloroform was taken at 100 Mc to simplify the second-order spectrum obtained at 60 Mc. It showed H-6 as a doublet centered at τ 4.12 ($J_{5,6}$ = 9.5 cps), H-5 as a doublet split into doublets, centered at 3.56 ($J_{5,6}$ = 9.5 cps, $J_{4,5}$ = 5.7 cps), H-4 as a doublet split into doublets, centered at 3.25 ($J_{4,5}$ = 5.7 cps; $J_{3,4}$ = 11.5 cps), and H-3 as a doublet centered at 2.54 ($J_{3,4}$ = 11.5 cps). All bands were split again, indicating some allylic and possibly 3,6 splitting. The aromatic protons occurred as a complex multiplet at τ 2.0–2.5. The assignments of the olefinic protons are based on the assumption that H-3 is less shielded than H-6. The ultraviolet spectrum of **11b** [$\lambda_{\max}^{\text{cyclohexane}}$ 277 mμ (ϵ 8000), $\lambda_{\min}$ 243 mμ (ϵ 2600)] again was superimposable on that of the parent triene, 1,2-benzocycloheptatriene [$\lambda_{\max}$ 275 mμ (ϵ 7400), $\lambda_{\min}$ 243 mμ (ϵ 2900)].[20]

The nmr spectra of **10b** and **11b** show that the protons at C-1 and C-6 in the hypothetical 7,7-dicyanocycloheptatriene (**2c**) would occur at *ca.* τ 4. The remote possibility that the dicyanocarbene–benzene adduct had the cycloheptatriene structure **2c**, but that the protons on C-1 and C-6 had been shifted upfield by the anisotropy of two cyano groups,[21] was thus excluded.

Discussion

While the above data establish the structures of the adducts of dicyanocarbene to benzene and *p*-xylene beyond reasonable doubt, it is much less obvious why they are stable in the norcaradiene form. Any explanation must consider the following facts. (A) The only compounds found so far to exist exclusively or predominantly[22] in the norcaradiene form are 7,7-dicyanonorcaradiene (**1c**), its 1,4- and 2,5-dimethyl derivatives **8** and **7**, and 7-cyano-7-carbamidonorcaradiene.[23] (B) The adduct of cyanotrifluoromethylcarbene to benzene is, at room temperature, a rapidly equilibrating mixture of 7-cyano-7-trifluoromethylcycloheptatriene and its norcaradiene valence tautomer, the latter being the minor component.[7] (C) Recent investigations by low-temperature nmr spectroscopy failed to detect appreciable equilibrium concentrations of norcaradienes in cycloheptatriene,[24,25] 2-*t*-butyl-3,7,7-trimethylcycloheptatriene,[16a] 7,7-bis(trifluoromethyl)-cycloheptatriene,[25] 7-cyanocycloheptatriene,[26] and 7-carbethoxycycloheptatriene.[26] The lower limit of detection by this technique is probably no better than 5%. (D) Two cyano groups apparently stabilize the norcaradiene (or destabilize the cycloheptatriene) form only if they are both in the 7 position; thus, the nmr spectra of 3,7- and 1,4-dicyanocycloheptatriene[23] give no indication for the presence of any appreciable amounts of the corresponding norcaradienes. (E) In view of the low activation energy observed for the interconversion of 7-cyano-7-trifluoromethylcycloheptatriene and its norcaradiene valence tautomer,[7] the stability of the 7,7-dicyanonorcaradienes is most likely thermodynamic in nature and not due to a large energy barrier for valence isomerization. The difference in free energy between 7,7-dicyanonorcaradiene and 7,7-dicyanocycloheptatriene at room temperature is at least 1.7 kcal/mole if one puts an upper limit of 5% on the equilibrium concentration of the triene. The stabilizing effect of two cyano groups must then be at least twice that amount. In view of the rigidity of the norcaradiene system and the flexibility of the cycloheptatriene ring, a positive entropy difference for **1** $\rightleftharpoons$ **2** can be expected; in the case of the system 7-cyano-7-trifluoromethylnorcaradiene $\rightleftharpoons$ 7-cyano-7-trifluoromethylcycloheptatriene, ΔS was found to be *ca.* 5 eu and ΔH close to zero.[27] In terms of enthalpies, the difference between 7,7-dicyanonorcaradiene and its seven-membered valence tautomer will consequently be larger than the difference in free energies.

The effect to be explained thus is fairly substantial. The data available so far require the presence of two electron-withdrawing groups in the 7 position for a simple norcaradiene to be stable. The interrelationship of hybridization and electronegativity of substituents would predict that electron-withdrawing groups in the 7 position would *de*stabilize the norcaradiene system. The bonds directed toward substituents in cyclopropanes are higher in s character than in ordinary sp^3-hybridized systems, and as a rule, "atomic s character concentrates in orbitals directed toward electropositive substituents."[28] If one considers the dipole–dipole interactions between the two cyano groups, however, the correct prediction will be made.

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(20) G. Wittig, H. Eggers, and P. Duffner, *Ann.*, **619**, 10 (1958); the values were taken from the reproduction of the spectrum since positions and intensities of the maxima were not stated in the text.

(21) *Cf.* A. D. Cross and I. T. Harrison, *J. Am. Chem. Soc.*, **85**, 3223 (1963).

(22) Solubility difficulties prevented the determination of the nmr spectrum of 7,7-dicyanonorcaradiene at temperatures lower than −70°. However, an appreciable equilibrium concentration of 7,7-dicyanocycloheptatriene would cause a downfield shift in the signal owing to H-1 and H-6. Since it occurs at a position very similar to the corresponding ones in 7,7-dicyano-2,3-benzonorcaradiene (**9**, which should contain very little of its seven-membered valence tautomer), the presence of anything but minor amounts of 7,7-dicyanocycloheptatriene is excluded.

(23) E. Ciganek, *J. Am. Chem. Soc.*, **89**, 1458 (1967).

(24) F. A. L. Anet, *ibid.*, **86**, 458 (1964); F. R. Jensen and L. A. Smith, *ibid.*, **86**, 956 (1964).

(25) J. B. Lambert, L. J. Durham, B. Lepoutere, and J. D. Roberts, *ibid.*, **87**, 3896 (1965).

(26) E. Ciganek, unpublished results.

(27) The thermodynamic and activation parameters for this system[7] will be published in paper III of this series.

(28) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

Mutual repulsion of the cyano groups will tend to increase the NC–C–CN bond angle and decrease the angle between the two other bonds. This situation is better accommodated by the norcaradiene system with its smaller C-1–C-7–C-6 angle. The X-ray structure determination of 7,7-dicyano-2,5-dimethylnorcaradiene (**7**) furnished values of 115 and 58°, respectively, for the NC–C–CN and C-1–C-7–C-6 bond angles (not considering the bending of the cyclopropane bonds). By comparison, the NC–C–CN and H–C–H bond angles in malononitrile[29] are 114 and 106°, respectively, distorted from the normal tetrahedral angles in the predicted direction.

Alternatively, the stability of 7,7-dicyanonorcaradienes could be due to formation of an internal charge-transfer complex between one cyano group and the planar diene system. The latter should be a better π base than the nonplanar[16a,24,30] cycloheptatriene system. The ultraviolet spectrum of 7,7-dicyanonorcaradiene gives no indication of a charge-transfer band. The position and intensity of the absorption maximum at 271 mμ are essentially independent of solvent polarity and its shape is quite similar to that of the anhydride **4**,[11b] whose geometry precludes any appreciable interaction between the carbonyl groups and the double bonds. However, the dipole moment of 7,7-dicyanonorcaradiene (in dioxane at 25°) was found to be 4.8 D., whereas a value of 3.6 D. has been reported for malononitrile (at 25° in benzene).[31] Since the bond angle between the two cyano groups is essentially the same in both compounds (see above), the larger dipole moment of 7,7-dicyanonorcaradiene may well be an indication of a charge-transfer complex. This rationalization does not account for the instability of 7-*mono*-cyanonorcaradiene (**1d**), unless one postulates that a cyano group is not a sufficiently strong π acid in the absence of another electron-withdrawing group on C-7.

The isolation of 7,7-dicyano-3,4-benzocycloheptatriene (**10b**) and 7,7-dicyano-1,2-benzocycloheptatriene (**11b**) from the products of the thermal decomposition of dicyanodiazomethane in naphthalene deserves some comment. The most probable mechanism involves initial addition of dicyanocarbene to the 2,3 and 1,9 bonds in naphthalene, followed by rearrangement of the resulting nonaromatic norcaradienes **10a** and **11a** to the more stable[10] trienes **10b** and **11b**. This appears to be the first instance of a carbene adding to bonds other than the 1,2 bond in naphthalene.[32,33] The carefully investigated decomposition of diazomethane[10a,35] and ethyl diazoacetate[10b] in naphthalene produces only the 1,2 monoadducts (in addition to diadducts in the latter case). It is of interest to note that both methylene and carbethoxycarbene are less discriminate in carbon–hydrogen bond insertions than dicyanocarbene.[13] All possible adducts of dicyanocarbene to naphthalene were thus isolated, except for the adduct to the 9,10 bond (11,11-dicyanotricyclo[4.4.1.0^{1,6}]-undeca-2,4,7,10-tetraene or its methanocyclopentadecaene valence tautomer). Since the activation energy for the Berson–Willcott rearrangement[36] appears to be low in 7,7-dicyanonorcaradienes,[23,37] it is possible that the adduct was formed but rearranged to 7,7-dicyano-1,2-benzocycloheptatriene (**11b**) under the reaction conditions.

Experimental Section

Thermolysis of Dicyanodiazomethane in Benzene. A solution of dicyanodiazomethane[14] (prepared from 860 mg of carbonyl cyanide hydrazone) in 40 ml of benzene was heated under reflux for 15 min. The solvent was removed, and the residue was chromatographed over Florisil (37 g). Elution with 280 ml of methylene chloride gave 1.071 g of 7,7-dicyanonorcaradiene (82% yield), mp 93–96°.

To avoid isolation of the hazardous[14] dicyanodiazomethane, the following procedure was adopted for larger scale preparation of 7,7-dicyanonorcaradiene. Lead tetraacetate (67.13 g of a commercial sample containing *ca.* 10% acetic acid) was suspended in 900 ml of benzene and a solution of 11.17 g of carbonyl cyanide hydrazone[14] in 50 ml of acetonitrile was added, with mechanical stirring and cooling (ice), within 10 min. The cooling bath was removed, and the mixture was stirred at room temperature for 3 hr. Water (100 ml) was added and stirring was continued for 5 min. The mixture was filtered with the aid of Celite, and the layers of the filtrate were separated. The aqueous layer was extracted once with benzene (100 ml), and the combined organic layers were washed with water and concentrated sodium chloride solution and dried with magnesium sulfate. The filtered yellow solution was then heated under reflux until nitrogen evolution stopped. The solvent was removed and the residue was passed through Florisil (70 g). Elution with 1000 ml of methylene chloride gave 11.37 g of crude product, which on crystallization from 40 ml of methanol gave 8.40 g of 7,7-dicyanonorcaradiene, mp 96.5–98°. A second crop of 0 96 g was obtained from the mother liquor; combined yield: 55%. An analytical sample (cyclohexane) had mp 97–98°. The nmr spectrum (in $CDCl_3$) showed multiplets at τ 6.53 (2 H) and 3.2–3.9 (4 H). The ultraviolet spectrum had $\lambda_{max}^{cyclohexane}$ 271 mμ (ϵ 2920); $\lambda_{max}^{95\%\ EtOH}$ 271 mμ (ϵ 2840); λ_{max}^{MeCN} 271 mμ (ϵ 2830). The infrared spectrum showed ν_{max}^{KBr} 3100 (m–w), 3070 (m), 3030 (m–w), and 2243 cm^{-1} (s), among others. The Raman spectrum (in $CHCl_3$, relative intensities given in parentheses) showed bands at 3067 (64), 2248 (100), 1568 (76), and 1430 cm^{-1} (24), among others.

Anal. Calcd for $C_9H_6N_2$: C, 76.04; H, 4.25; N, 19.71; mol wt, 142.15. Found: C, 75.96; H, 4.21; N, 19.66; mol wt, 138, 142 (ebullioscopically in benzene).

Photolysis of Dicyanodiazomethane in Benzene. Irradiation of a cooled solution of 154 mg of dicyanodiazomethane[14] in 10 ml of benzene, contained in a Pyrex vessel, with a General Electric AH-6 high-pressure mercury lamp for 3.5 hr resulted in the evolution of 0.86 mole equiv of nitrogen. The infrared spectrum of the residue (235 mg) left after removal of the benzene was identical with that of 7,7-dicyanonorcaradiene, with additional weak bands due to unreacted diazo compound.

Spectral Data of 7-Cyanocyclohepta-1,3,5-triene.[15] The nmr spectrum (neat) shows a triplet (J = 6.5 cps) split into triplets (J = 0.5 cps) centered at τ 7.07 (1 H), and multiplets centered at 4.91 (2 H), 3.93 (2 H), and 3.53 (2 H). The positions of these bands at −108° in fluorotrichloromethane were τ 7.07, 4.64, 3.65, and 3.26, respectively. The Raman spectrum (relative intensities in parentheses) showed bands at $\nu_{max}^{CHCl_3}$ 2945 (30), 2860 (41), 2245 (100), 1600 (93), 1530 (610), and 1430 cm^{-1} (36), among others.

Thermolysis of Dicyanodiazomethane in *p*-Xylene. A solution of dicyanodiazomethane[14] (prepared from 1.285 g of carbonyl

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(29) N. Muller and D. E. Pritchard, *J. Am. Chem. Soc.*, **80**, 3483 (1958).

(30) R. E. Davis and A. Tulinski, *Tetrahedron Letters*, 839 (1962); C. LaLau and H. de Ruyter, *Spectrochim. Acta*, **19**, 1559 (1963); M. Traetteberg, *J. Am. Chem. Soc.*, **86**, 4265 (1964).

(31) P. Trunel, *Ann. Chim.* (Paris), [11] 12, 93 (1939).

(32) The 1,2 bond in naphthalene has the highest double-bond character as exemplified by its length of 1.365 A; the other bond lengths are: 1,9: 1.425; 2,3: 1.404, and 9,10: 1.393 A (A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 170).

(33) The copper salt catalyzed decomposition of diazomethane in naphthalene produces small amounts of 1,2-benzocycloheptatriene in addition to 2,3-benzonorcaradiene. Since the ratio of these two products increases with increasing temperature, it is likely that the triene is not a primary product.[34]

(34) E. Müller, H. Fricke, and H. Kessler, *Tetrahedron Letters*, 1525 (1964).

(35) E. Vogel, private communication.

(36) J. A. Berson and M. R. Willcott, III, *J. Am. Chem. Soc.*, **88**, 2494 (1966).

(37) *Cf.* especially footnote **26** in ref 36.

cyanide hydrazone) in 70 ml of *p*-xylene was heated slowly to 80°; after 10 min at that temperature the calculated amount of nitrogen had evolved. Removal of the solvent gave 2.166 g of a dark semisolid. Analysis by nmr spectroscopy, using the methyl bands at 7.87 and at 7.97 and 8.27, respectively (see below), showed the ratio of 7,7-dicyano-2,5-dimethylnorcaradiene (**7**) to 7,7-dicyano-1,4-dimethylnorcaradiene (**8**) to be 52:48. Chromatography on Florisil (35 g, elution with 350 ml of methylene chloride) gave 1.859 g (80% yield) of a mixture of **7**, **8**, and 2,5-xylylmalononitrile, the latter having been formed by rearrangement of **7** and **8** on the chromatography column. To avoid this rearrangement, the crude products from a second run were passed rapidly through a column of alumina (Woelm, acidic, activity 4). The ratio of **7** and **8** in the purified material was virtually unchanged (51:49). Repeated crystallization from cyclohexane gave pure 7,7-dicyano-2,5-dimethylnorcaradiene (**7**), mp 123–124° (the melting point depends on the rate of heating since **7** rearranges to 2,5-xylylmalononitrile at elevated temperatures). The nmr spectrum (in $CDCl_3$) showed three sharp singlets at τ 7.87 (6 H), 6.78 (2 H), and 3.81 (2 H). The ultraviolet spectrum had $\lambda_{\max}^{\text{cyclohexane}}$ 279 mμ (ϵ 4900) and 238 mμ (ϵ 3290). The infrared spectrum had $\nu_{\max}^{\text{KBr}}$ 2250 (m), 2240 (s), and 1655 cm^{-1} (m), among others.

Anal. Calcd for $C_{11}H_{10}N_2$: C, 77.62; H, 5.92; N, 16.46; mol wt, 170.21. Found: C, 77.79; H, 5.62; N, 16.28; mol wt, 167, 165 (cryoscopically in benzene).

Repeated fractional crystallization of the combined mother liquors from cyclohexane gave a sample of 7,7-dicyano-1,4-dimethylnorcaradiene (**8**), mp 91–95°, containing 12% of **7**. The analytical and spectral data were obtained on a sample crystallized once more from cyclohexane. The nmr spectrum (in $CDCl_3$) showed a singlet at τ 8.27 (3 H), a doublet (J = 1 cps) centered at 7.97 (3 H), a doublet centered at 6.88 (1 H), and an AB quartet centered at 3.80 superimposed on further bands on the high-field side (3 H). The ultraviolet spectrum had $\lambda_{\max}^{\text{cyclohexane}}$ 276 mμ (ϵ 2540) and 235 mμ (shoulder, ϵ 1850). The infrared spectrum showed $\nu_{\max}^{\text{KBr}}$ 2245 (s) and 1575 cm^{-1} (m–w), among others.

Anal. Calcd for $C_{11}H_{10}N_2$: C, 77.62; H, 5.92; N, 16.46; mol wt, 170.21. Found: C, 77.51; H, 5.92; N, 16.75; mol wt, 155 (cryoscopically in benzene).

Thermolysis of Dicyanodiazomethane in Naphthalene. A solution of dicyanodiazomethane, prepared from 2.023 g of carbonyl cyanide hydrazone,[14] in 6 ml of acetonitrile was added, over a period of 15 min, to a stirred melt of 50 g of naphthalene (bath temperature 90°). Stirring was continued until gas evolution stopped. The dark semisolid obtained on cooling was kept at 65° bath temperature and 1.5-mm pressure until most of the naphthalene had sublimed; the residual dark semisolid weighed 3.056 g. Chromatography of 2.46 g of this product on Florisil (80 g) gave first 30 mg of naphthalene, eluted with *n*-hexane; elution with *n*-hexane–benzene (1:1) gave 11 50-ml fractions containing a total of 396 mg (12% yield) of products (see below), followed by 1.656 g (50% yield, based on carbonyl cyanide hydrazone) of 7,7-dicyano-2,3-benzonorcaradiene (**9**), contained in 700 ml of effluent. Two crystallizations from isopropyl alcohol gave an analytical sample of **9** (colorless needles), mp 128.5–129.5°. The infrared spectrum had $\nu_{\max}^{\text{KBr}}$ 3080 (w), 2245 (s), 1640 (w), 1610 (w), and 1575 cm^{-1} (w), among others.

Anal. Calcd for $C_{13}H_8N_2$: C, 81.23; H, 4.20; N, 14.58. Found: C, 80.97; H, 4.22; N, 14.27.

Combination of the first four 50-ml fractions eluted with hexane–benzene (see above) gave 209 mg of a yellow oil which partially solidified on keeping under high vacuum (0.1 mm) overnight. Two crystallizations from isopropyl alcohol gave 130 mg of 7,7-dicyano-1,2-benzocycloheptatriene (**11b**), mp 87–88°. The infrared spectrum had $\nu_{\max}^{\text{KBr}}$ 3030 (w), 2230 (w), 1585 (m), 1550 (w), 1480 (m), 800 (s), 775 (m), 755 (s), 692 (w), and 670 cm^{-1} (m), among others.

Anal. Calcd for $C_{13}H_8N_2$: C, 81.23; H, 4.20; N, 14.58. Found: C, 81.01; H, 4.22; N, 14.61.

Combination of fractions 7–11 of the hexane–benzene effluent gave 75 mg of a pale yellow solid, which on crystallization from cyclohexane gave 43 mg of 7,7-dicyano-3,4-benzocycloheptatriene (**10b**), in the form of colorless crystals, mp 85–90°. Owing to lack of material, no further purification could be carried out. The infrared spectrum had $\nu_{\max}^{\text{KBr}}$ 3050 (w), 2240 (m), 1630 (m), 1550 (m), 1485 (m), 825 (s), 770 (s), 735 (m), 707 (s), and 680 cm^{-1} (m), among others.

Anal. Calcd for $C_{13}H_8N_2$: C, 81.23; H, 4.20; N, 14.58. Found: C, 81.65; H, 4.37; N, 14.83.

The nmr and ultraviolet spectra of the three naphthalene–dicyanocarbene adducts are described in the Discussion.

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The Cycloheptatriene–Norcaradiene System. II.[1] Reactions of 7,7-Dicyanonorcaradienes

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Abstract: Thermolysis of 7,7-dicyanonorcaradiene gave a mixture of phenylmalononitrile and 3,7-dicyanocycloheptatriene. Kinetic and other evidence points to the formation of the latter by an intramolecular 1,5-cyano shift in the valence-tautomeric 7,7-dicyanocycloheptatriene. 7,7-Dicyano-2,3-benzonorcaradiene, on heating to 176°, rearranged to 1-naphthylmalononitrile and 3,7-dicyano-1,2-benzocycloheptatriene. Thermolysis of 7,7-dicyano-3,4-benzocycloheptatriene and 7,7-dicyano-1,2-benzocycloheptatriene at lower temperatures gave 7,7-dicyano-2,3-benzonorcaradiene, presumably by a skeletal rearrangement of their respective unstable norcaradiene valence tautomers. In the case of 7,7-dicyano-1,2-benzocycloheptatriene, formation of 3,7-dicyano-1,2-benzocycloheptatriene also occurred. Some photochemical and other reactions of 7,7-dicyanonorcaradiene and its 2,3-benzo derivative are discussed.

In paper I[1] of this series it was shown that the adducts of dicyanocarbene to benzene and *p*-xylene exist in the norcaradiene form. For reasons discussed there, only physical methods were used for their structure proof. Some of the chemical reactions of these compounds are presented in this paper.

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[1] Paper I in this series: E. Ciganek, *J. Am. Chem. Soc.*, **89**, 1454 (1967).