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.

Acknowledgments. We are indebted to Professor D. E. Applequist and Professor K. Conrow for helpful discussions.

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

Engelbert Ciganek

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Received November 5, 1966

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).

Table I. Rate Constants for the Thermal Rearrangement of 7,7-Dicyanonorcaradiene to Phenylmalononitrile (k_A) and 3,7-Dicyanocycloheptatriene (k_B)

Solvent	Temp, °C	$k_A + k_B$, sec^{-1}	Ratio of **2**/**3**	k_A, sec^{-1}	k_B, sec^{-1}
$CDCl_3$	99.9	3.66×10^{-6}	1.46	2.17×10^{-6}	1.49×10^{-6}
$CDCl_3$	110.1	1.06×10^{-5}	1.60	6.52×10^{-6}	4.08×10^{-6}
$CDCl_3$	120.6	3.10×10^{-5}	1.83	2.00×10^{-5}	1.10×10^{-5}
$CDCl_3$	140.8	2.13×10^{-4}	2.22	1.47×10^{-4}	6.62×10^{-5}
Tetrahydrofuran	140	2.4×10^{-4}	3	1.8×10^{-4}	6×10^{-5}
C_6D_6	141	1.5×10^{-4}	3	1.1×10^{-4}	4×10^{-5}
Cyclohexane	143	2.3×10^{-4}	5	1.9×10^{-4}	4×10^{-5}
CD_3CN	99.9	2.6×10^{-5} [a]			
MeOH	65[b]	1.0×10^{-5} [a]			

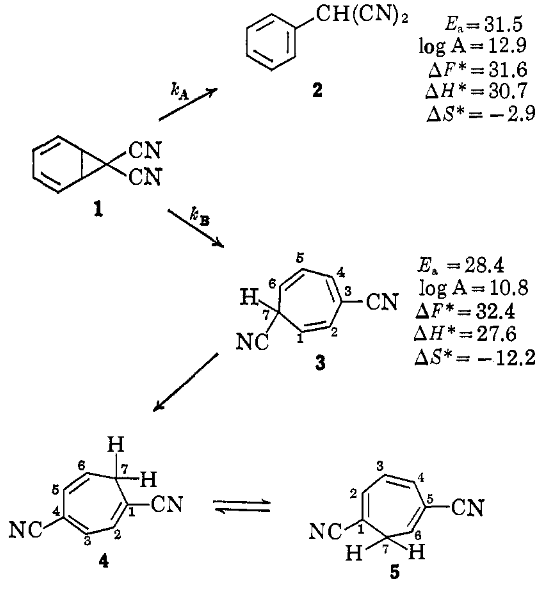
[a] Rate constant for the disappearance of 7,7-dicyanonorcaradiene; **3** is not formed in CD_3CN and MeOH (see text). [b] Reflux temperature of methanol.

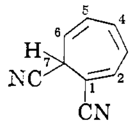
Thermal Rearrangement of 7,7-Dicyanonorcaradienes

Heating solutions of 7,7-dicyanonorcaradiene (**1**) in chloroform, tetrahydrofuran, benzene, or cyclohexane at or above 100° gave phenylmalononitrile (**2**) and 3,7-dicyanocycloheptatriene (**3**) in ratios depending on solvent and temperature (Table I). Further heating of isomer **3** resulted in the formation of 1,4-dicyanocycloheptatriene (**4**), which in turn slowly approached equilibrium ($K_{4/5} \approx 1$ at 178°) with a compound believed to be 1,5-dicyanocycloheptatriene (**5**).

The structure of 3,7-dicyanocycloheptatriene (**3**) was assigned on the basis of its 100-Mc nmr spectrum which showed H-7 as a triplet ($J_{1,7} \approx J_{6,7} \approx 7$ cps), split further ($J < 1$ cps), and centered at τ 6.75; H-1 and H-6 as a multiplet at τ 4.2–4.7; H-2 and H-5 as a multiplet at τ 3.3–3.7; and H-4 as a doublet ($J_{4,5} = 6.5$ cps), split further ($J < 1$ cps), and centered at τ 2.65. The fact that only one proton absorbed at high field ($\tau > 6$) excludes all norcaradiene structures since these would have at least two cyclopropyl protons. Of the 13 possible dicyanocycloheptatrienes only three, the 1,7 (**6**), 2,7 (**7**), and 3,7 (**3**) isomers, should show a single, high-field (H-7) proton. Structure **6** can be excluded since H-7 is flanked by only one proton and should thus be a doublet. Double irradiation of the H-7 signal caused the collapse of the H-1–H-6 multiplet into two doublets; similarly, the H-2–H-5 multiplet gave two doublets on irradiation of the H-4 doublet. The coupling constants $J_{1,2}$ and $J_{5,6}$ both had values of *ca.* 9 cps. These results are clearly consistent with structure **3** and inconsistent with structure **7**. The ultraviolet spectrum of 3,7-dicyanocycloheptatriene (in cyclohexane) showed a maximum at 269 mμ (ϵ 7500).

Scheme I. Thermal Isomerization of 7,7-Dicyanonorcaradiene (Transition-State Parameters in kcal/mole and eu, Respectively, Calculated at 120°)





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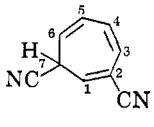

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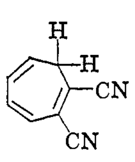
The structure assignment of 1,4-dicyanocycloheptatriene (**4**) also depends largely on its nmr spectrum. It showed the two protons on C-7 as a doublet ($J_{6,7} = 7.2$ cps) centered at τ 7.33; H-6 as a doublet ($J_{5,6} = 9.8$ cps), split into triplets ($J_{6,7} = 7.2$ cps) and centered at τ 4.20; H-5 as a doublet ($J_{5,6} = 9.8$ cps) centered at τ 3.55; and H-2 and H-3 as an AB quartet at τ 3.06 and 2.72 ($J_{2,3} = 6.6$ cps). All bands were split further owing to long-range coupling. The fact that the high-field signal is a two-proton doublet excludes all but the 1,2 (**8**), 1,3 (**9**), 1,4 (**4**), and 1,5 (**5**) isomers of dicyanocycloheptatriene. The splitting pattern, which is that of an ABX_2 system isolated (except for long-range coupling) from another AB system, can be explained only in terms of structure **4**. The two dicyanonorcaradienes whose nmr spectra should show two high-field protons, **10** and **11**, also are excluded by the multiplicities of both the saturated and the olefinic protons. The ultraviolet spectrum of **4** (in cyclohexane) showed maxima at 287 mμ (ϵ 7800) and 213 mμ (ϵ 21,000). The product believed to be 1,5-dicyano-



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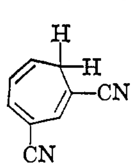

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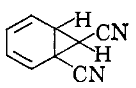

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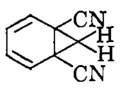

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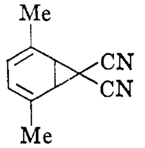
cycloheptatriene (**5**) was not isolated. The tentative structure assignment is based solely on the nmr spectrum of the equilibrium mixture of **4** and **5**; the new bands appearing were a doublet ($J_{6,7}$ = 7.2 cps; 2 H) centered at τ 7.28, a triplet ($J_{6,7} \approx$ 7 cps, 1 H) centered at τ 3.60 and a three-proton multiplet at τ 3.0–3.2.

The over-all rate constants k for the isomerization of 7,7-dicyanonorcaradiene in deuteriochloroform were measured at four temperatures by determining the decrease of the H-1–H-6 multiplet in **1** relative to an internal standard (cyclohexane). First-order plots were obtained in all cases. From these rate constants and the average ratios of **2** to **3**, determined at each kinetic point, the rate constants k_A for the aromatization of 7,7-dicyanonorcaradiene to phenylmalononitrile (**2**) and k_B for its conversion to 3,7-dicyanocycloheptatriene (**3**) were calculated (Table I). This treatment requires that **2** and **3** be the only products formed. Inspection of the nmr spectra showed this to be the case within the limits of detection. Also, since determination of the ratios of **2** to **3** involved integrating small areas (the methine proton in **2** *vs.* the H-7 triplet in **3**), fairly large errors were introduced at this stage. However, there was a definite trend toward larger ratios of **2**/**3** with increasing temperatures, and the Arrhenius plots of both sets of rate constants gave good straight lines. The activation parameters calculated from their slopes are given in Scheme I. Approximate rate constants k_A and k_B at one temperature were also determined in tetrahydrofuran, hexadeuteriobenzene, and cyclohexane. Details are given in the Experimental Section; the rate constants are listed in Table I. When the thermolysis of 7,7-dicyanonorcaradiene was carried out in methanol or deuterioacetonitrile, phenylmalononitrile was formed in approximately the same amount as in the other solvents. However, isomer **3** could not be detected among the products, even though it was shown to be stable in methanol at 100°. In the case of the thermolysis in methanol, at least two new products were formed in addition to **2**; their structures have not been determined.

The thermal rearrangement of a 1:1 mixture of the dicyanodimethylnorcaradienes **12** and **13** occurred rapidly at 130° and very slowly even at room temperature. The only compound detected in the nmr spectrum of the crude product was 2,5-xylylmalononitrile (**14**). Its structure follows from its nmr spectrum (see Experimental Section) and its hydrolysis and decarboxylation to the known 2,5-xylylacetic acid. No efforts were made to isolate any possible minor rearrangement products or to carry out the thermolysis of **12** and **13** in solvents or at different temperatures.



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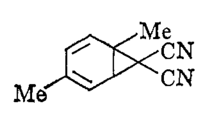

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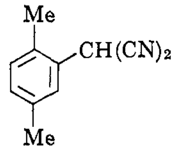

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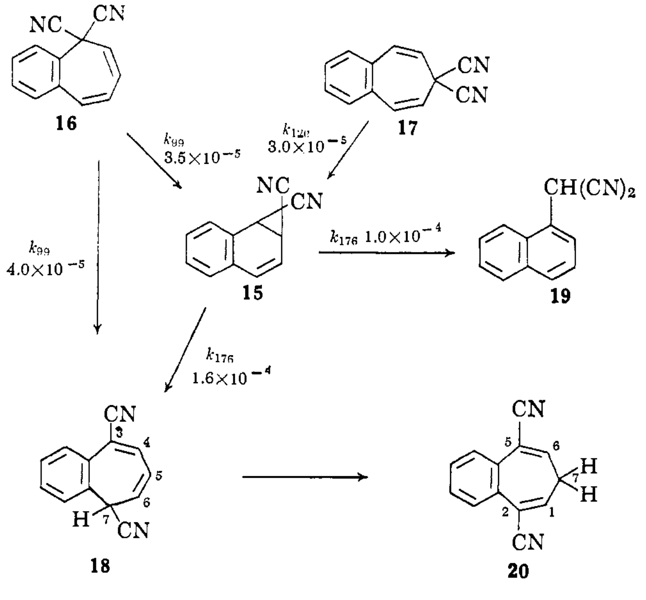
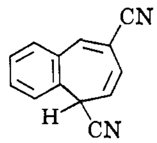
The thermal rearrangement of the dicyanocarbene–naphthalene adducts **15**, **16**, and **17**[1] in deuteriochloroform is summarized in Scheme II. The rate constants listed were determined by nmr spectroscopy essentially as described for the thermolysis of 7,7-dicyanonorcaradiene, except that no internal standard was used.

Scheme II. Thermal Isomerizations of the Naphthalene–Dicyanocarbene Adducts in Deuteriochloroform (Approximate First-OrderRate Constants in Sec^{-1}; Temperatures in Centigrades)



The rearrangement of 7,7-dicyano-1,2-benzocycloheptatriene (**16**) was also carried out in methanol solution; the rate constants at 99° were $k_{16 \rightarrow 18} = 9.7 \times 10^{-5}$ sec^{-1} and $k_{16 \rightarrow 15} = 3.83 \times 10^{-4}$ sec^{-1}. At 99°, only 7,7-dicyano-1,2-benzocycloheptatriene (**16**) rearranged at a reasonable rate to give a mixture of 7,7-dicyano-2,3-benzonorcaradiene (**15**) and 3,7-dicyano-1,2-benzocycloheptatriene (**18**). The rearrangement of 7,7-dicyano-3,4-benzocycloheptatriene (**17**) to give 7,7-dicyano-2,3-benzonorcaradiene (**15**) was very slow at 99°, but appreciable at 120°. No other products were formed within detectability by nmr spectroscopy. Heating a deuteriochloroform solution of 7,7-dicyano-2,3-benzonorcaradiene (**15**) to 99° resulted in a very slow rearrangement to 1-naphthylmalononitrile (**19**), which was present to the extent of *ca.* 16% after 25 hr. There was no evidence for the formation of 2-naphthylmalononitrile. At 176°, aromatization and rearrangement to 3,7-dicyano-1,2-benzocycloheptatriene (**18**) occurred simultaneously, the latter process actually having a somewhat larger rate constant. On prolonged heating at 176°, **18** rearranged to 2,5-dicyano-3,4-benzocycloheptatriene (**20**).

1-Naphthylmalononitrile was identified by comparison of its infrared spectrum with that of an authentic sample, prepared from 1-naphthylacetonitrile by standard methods. The structure assignments of the two isomers **18** and **20** are based mainly on their nmr spectra. That of 3,7-dicyano-1,2-benzocycloheptatriene (**18**) (in deuteriochloroform), taken at 100 Mc, showed H-7 as a doublet ($J_{6,7}$ = 6.1 cps) centered at τ 6.00; H-6 as a doublet ($J_{5,6}$ = 9.9 cps) split into doublets ($J_{6,7}$ = 6.1 cps), centered at τ 3.88; H-5 as a doublet ($J_{5,6}$ = 9.9 cps) split into doublets ($J_{4,5}$ = 5.5 cps), centered at τ 3.67; H-4 as a doublet ($J_{4,5}$ = 5.5 cps) centered at τ 2.69; and the aromatic protons as a complex multiplet at 2.1–2.5. Further splitting of all signals indicated additional long-range coupling (J < 1 cps). Since there was only one proton at high field, tricyclic structures need not be considered. Of the 18 dicyanobenzocycloheptatrienes containing both cyano groups in the seven-membered ring, four should have a single proton as a doublet at high field: the 3,7- (**18**), 4,7- (**21**), and 5,7-dicyano (**22**) derivatives of 1,2-benzocycloheptatriene and 1,7-dicyano-3,4-benzocycloheptatriene (**23**). The multiplicities of the olefinic protons can be explained only in terms of structure **18**. Structures **21** and **23** should show an ABX pattern uncoupled, except for long-range interactions, to the single proton on C-3 and C-2, respectively. An AX system isolated from an AB system is predicted for structure **22**. The ultraviolet spectrum of **18** (in cyclohexane) showed a maximum at 287 mμ (ε 8400).



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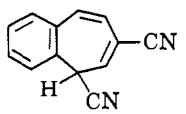

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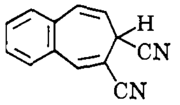

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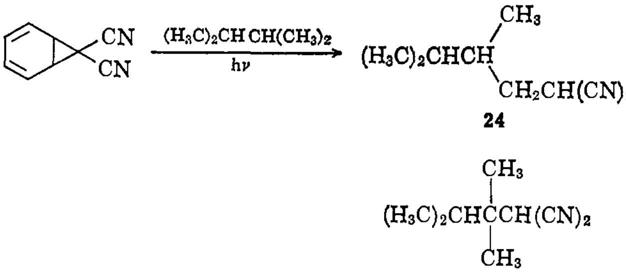
The nmr spectrum of 2,5-dicyano-3,4-benzocycloheptatriene (**20**) showed the two protons on C-7 as a triplet ($J_{1,7} = J_{6,7} = 7.0$ cps) centered at τ 7.32; H-1 and H-6 as a triplet ($J_{1,7} = J_{6,7} = 7.0$ cps) centered at τ 3.19; and the aromatic protons as an A_2B_2 system at τ 2.0–2.6. This spectrum is unique to isomer **20**. Its ultraviolet spectrum (in cyclohexane) had a shoulder at 251 mμ (ε 12,300) and a maximum at 231 mμ (ε 37,000).[2]

Photolytic Reactions of 7,7-Dicyanonorcaradienes

Photolysis of a cyclohexane solution of 7,7-dicyanonorcaradiene in a quartz vessel with a high-pressure mercury lamp gave cyclohexylmalononitrile in 60% yield. Using 2,3-dimethylbutane as the solvent gave, under otherwise identical conditions, a mixture of 2,3-dimethyl-1-butylmalononitrile (**24**) and 2,3-dimethyl-2-butylmalononitrile (**25**), each in 27% yield based on starting material not recovered. Small amounts of other product(s) were also formed. For comparison, the thermolysis of dicyanodiazomethane[5] in 2,3-dimethylbutane was investigated. The insertion products **24** and **25** were formed in 12 and 16% yield, respectively; in addition, the above-mentioned minor products were also observed but not identified. Authentic samples of the alkylmalononitriles **24** and **25** were prepared by standard methods.



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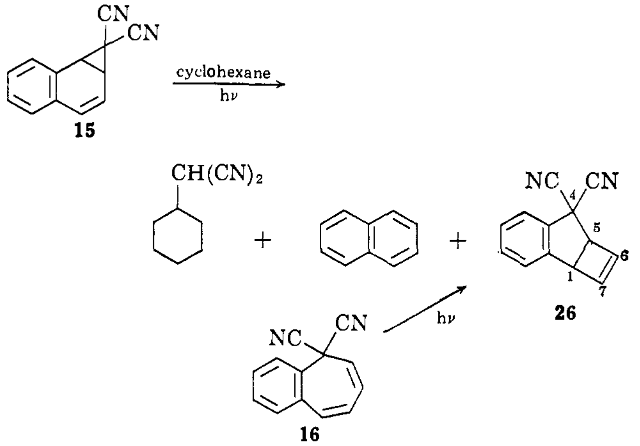
Photolysis of 7,7-dicyano-2,3-benzonorcaradiene (**15**) in cyclohexane proceeded slowly in Pyrex vessels, and more rapidly in quartz, to produce naphthalene (22% yield) and cyclohexylmalononitrile (22%), as well as an isomer of **15** (44%). The same photoisomer was formed rapidly on irradiation of a cyclohexane solution of 7,7-dicyano-1,2-benzocycloheptatriene (**16**) through a Pyrex filter. Neither naphthalene nor cyclohexylmalononitrile was obtained in this reaction. Irradiation of 3,7-dicyano-1,2-benzocycloheptatriene (**18**) under the same conditions did not produce the above-mentioned photoisomer; the structure of the photoproduct(s) of **18** have not yet been determined. The nmr spectrum of the photoisomer (in deuteriochloroform) showed a multiplet at τ 2.2–2.6 (4 H); a doublet (2.6 cps) split into doublets (0.7 cps), split again into doublets (0.3 cps) centered at τ 3.41 (1 H); a doublet (2.6 cps) split into triplets (0.9 cps) centered at τ 3.75 (1 H); a doublet (3.1 cps) split again, but poorly resolved, centered at τ 5.47 (1 H), and a doublet (3.1 cps) split into doublets (0.9 cps), split into doublets (0.3 cps), centered at τ 5.85 (1 H). The two upfield signals are probably due to highly deshielded aliphatic, rather than olefinic, protons. This, together with the fact that catalytic hydrogenation resulted in the uptake of 1 mole of hydrogen, suggests that the photoisomer is tricyclic. The small coupling constant (2.6 cps) between the two olefinic protons excludes a benzonorcaradiene and actually suggests a cyclobutene structure,[6] namely a derivative of 2,3-benzobicyclo[3.2.0]hepta-2,6-diene. Only the 4,4- (**26**) and 1,4-dicyano isomers fit the gross features of the nmr spectrum. Since the 1,4 isomer is a valence tautomer of 3,7-dicyano-1,2-benzocycloheptatriene (**18**), which on irradiation gives different products, 4,4-dicyano-2,3-benzobicyclo[3.2.0]hepta-2,6-diene (**26**) is the most likely structure for the photoisomer. Its ultraviolet spectrum is very similar to that of its dihydro derivative, showing strong end absorption in addition to three low extinction bands at 260–273 mμ. The nmr spectrum of the dihydro derivative



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(2) The only other symmetrical structure that might be considered, namely, 7,7-dicyano-2,3-benzobicyclo[2.2.1]hepta-2,5-diene, is believed to be excluded by the large coupling constant (7 cps) observed between the olefinic and aliphatic protons in **20** and by the chemical shift of the latter (τ 7.32 in deuteriochloroform). In the parent 2,3-benzobicyclo-[2.2.1]hepta-2,5-diene, $J_{1,6}$ has been reported to be 3.0 cps;[3] the chemical shift of the bridgehead protons in deuteriochloroform is τ 6.15. Also, owing to allylic coupling, the multiplicity of these protons in 7,7-dicyano-2,3-benzobicyclo[2.2.1]hepta-2,5-diene should not be that of a clean triplet as observed. The ultraviolet spectrum of **20** speaks against the bicycloheptadiene structure as well. 2,3-Benzobicyclo[2.2.1]hepta-2,5-diene shows only weak benzene absorption (ε <1000) at wavelengths longer than 240 mμ.[4]

(3) K. Tori, R. Muneyuki, and H. Tanida, *Can. J. Chem.*, **41**, 3142 (1963).

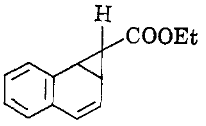
(4) G. Wittig and E. Knauss, *Chem. Ber.*, **91**, 895 (1958).

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

(6) The vicinal coupling constant in cyclic olefins decreases with ring size: (a) O. L. Chapman, *J. Am. Chem. Soc.*, **85**, 2014 (1963); (b) P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2017 (1963); (c) G. V. Smith and H. Kriloff, *ibid.*, **85**, 2016 (1963); (d) S. Borčić and J. D. Roberts, *ibid.*, **87**, 1056 (1965).

(in deuteriochloroform) shows complex multiplets at τ 2.3–2.8 (4 H), 5.8–6.5 (2 H), and 7.2–8.4 (4 H). The photoisomer was stable at 240°.

By comparison, photolysis of 7-ethoxycarbonyl-2,3-benzonorcaradiene (**27**)[7] in cyclohexane gave only a small amount of naphthalene (11% yield) and ethyl



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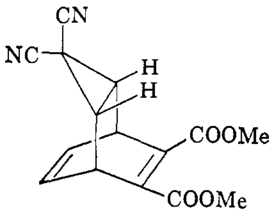
cyclohexylacetate (8%) in addition to intractable, probably polymeric, material.

Miscellaneous Reactions of 7,7-Dicyanonorcaradiene

Catalytic hydrogenation of 7,7-dicyanonorcaradiene over palladium in methanol was complicated by reduction of the cyano groups. The only hydrogenation product isolated which still contained both nitrile groups intact was cyclohexylmalononitrile (12% yield), presumably formed by hydrogenolysis of the cyclopropane ring followed by saturation of the double bonds.

7,7-Dicyanonorcaradiene failed to give a Diels–Alder adduct with tetracyanoethylene at 140°. In neat dimethyl acetylenedicarboxylate at 100°, the adduct **28** was formed in 55% yield. Its structure follows from its nmr spectrum (see Experimental Section).



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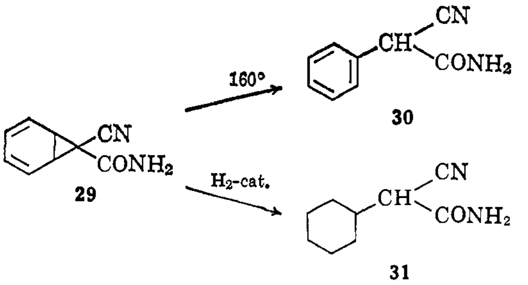
The cyclopropane ring is assumed to be in the *anti* configuration as shown in analogy to the stereochemistry of the adducts of dimethyl acetylenedicarboxylate to cycloheptatriene and some of its derivatives substituted in the 7 position.[8]

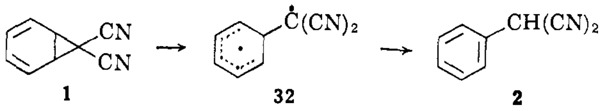
Hydrolysis of 7,7-dicyanonorcaradiene with alkaline hydrogen peroxide produced 7-cyano-7-carbamidonorcaradiene (**29**) in 56% yield. A small amount of benzamide was also isolated, the source of which is unknown. Assignment of the norcaradiene structure to the hydrolysis product follows from the nmr spectrum which shows the two cyclopropane protons as a multiplet at τ 7.3.[9]



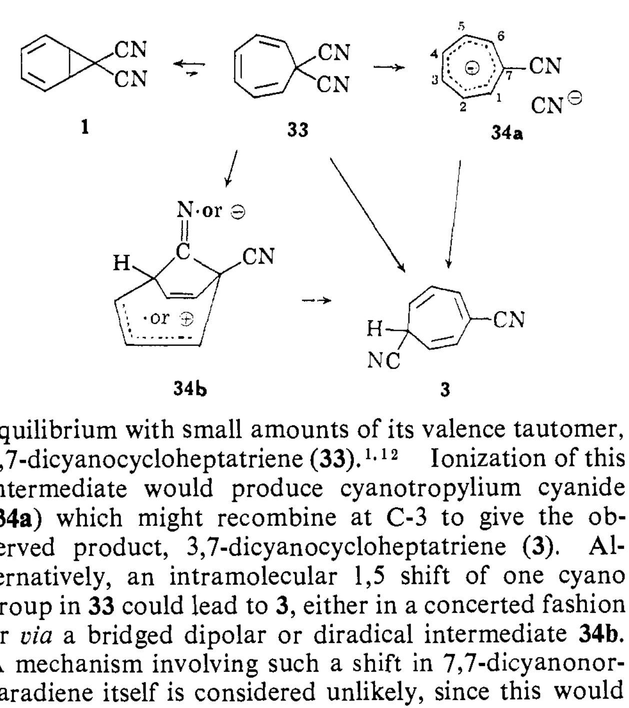
The ultraviolet spectrum (λ_{max}^{MeCN} 269 mμ) also is that expected for the norcaradiene chromophore.[1] Only one of the two possible isomers of **29** (nitrile group *exo* or *endo*) was detected among the products. Thermolysis of **29** gave phenylcyanoacetamide (**30**), catalytic hydrogenation produced cyclohexylcyanoacetamide (**31**).

Discussion

The observed aromatization of 7,7-dicyanonorcaradiene to phenylmalononitrile is unexceptional and requires little comment. The known isomerization of cycloheptatriene to toluene[10] is believed to involve initial valence isomerization to norcaradiene followed by homolytic cleavage of the C-1–C-7 bond and hydrogen shift in the resulting diradical.[10a] An activation energy of 51 kcal/mole has been measured for this process, and the corresponding parameter for the conversion of norcaradiene to toluene has been estimated at 40 ± 5 kcal/mole.[10d] The lower activation energy observed for the aromatization of 7,7-dicyanonorcaradiene is probably a consequence of the stabilization of the diradical **32** by the two cyano groups.[11]



Of the possible mechanisms for the isomerization of 7,7-dicyanonorcaradiene (**1**) to 3,7-dicyanocycloheptatriene (**3**), three deserve more serious consideration. All assume that 7,7-dicyanonorcaradiene is in rapid equilibrium with small amounts of its valence tautomer, 7,7-dicyanocycloheptatriene (**33**).[1,12] Ionization of this intermediate would produce cyanotropylium cyanide (**34a**) which might recombine at C-3 to give the observed product, 3,7-dicyanocycloheptatriene (**3**). Alternatively, an intramolecular 1,5 shift of one cyano group in **33** could lead to **3**, either in a concerted fashion or *via* a bridged dipolar or diradical intermediate **34b**. A mechanism involving such a shift in 7,7-dicyanonorcaradiene itself is considered unlikely, since this would require that 7,7-dicyano-2,3-benzonorcaradiene (**15**)



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[7] E. Buchner and S. Hediger, *Ber.*, **36**, 3502 (1903); R. Huisgen and G. Juppe, *Chem. Ber.*, **94**, 2332 (1961).

[8] M. J. Goldstein and A. H. Gevirtz, *Tetrahedron Letters*, 4417 (1965).

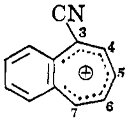
[9] For chemical shifts of cyclopropane protons in norcaradienes see ref 1.

[10] (a) W. G. Woods, *J. Org. Chem.*, **23**, 110 (1958); (b) W. M. Halper, G. W. Gaertner, E. W. Swift, and G. E. Pollard, *Ind. Eng. Chem.*, **50**, 1131 (1958); (c) J. H. Birely and J. P. Chesick, *J. Phys. Chem.*, **66**, 568 (1962); (d) K. N. Klump and J. P. Chesick, *J. Am. Chem. Soc.*, **85**, 130 (1963); (e) W. C. Herndon and L. L. Lowry, *ibid.*, **86**, 1922 (1964).

[11] The benzyl radical is stabilized by introduction of two cyano groups in the α position: H. D. Hartzler, *J. Org. Chem.*, **31**, 2654 (1966).

[12] E. Ciganek, *J. Am. Chem. Soc.*, **87**, 1149 (1965).

rearrange to 4,7-dicyano-1,2-benzocycloheptatriene (**21**), a course of reaction which was not observed. Similar mechanisms can be envisaged for the rearrangement of 7,7-dicyano-1,2-benzocycloheptatriene (**16**) to 3,7-dicyano-1,2-benzocycloheptatriene (**18**, Scheme II). The following pertinent evidence can be cited. (a) The rearrangement of 7,7-dicyanonorcaradiene proceeds at comparable rates in cyclohexane, benzene, chloroform, and tetrahydrofuran (Table I). Since the transition state for ionization is expected to be more like the ion **34**a than the triene **33**, a large solvent effect would be predicted for such a mechanism.[13] The same considerations apply to the rearrangement of 7,7-dicyano-1,2-benzocycloheptatriene (**16**) to 3,7-dicyano-1,2-benzocycloheptatriene (**18**), for which a change of solvent from deuteriochloroform to methanol caused the rate to increase by a factor of only 2.4. The absence of a solvent effect also speaks against a dipolar bridged intermediate **34b**. (b) The rearrangement is highly specific in that only one dicyanocycloheptatriene is formed. Trapping of tropylium ions with nucleophiles usually produces a mixture of isomers.[14] Thus, reaction of phenyltropylium ion with sodium borohydride gave a mixtue of 1-, 2-, and 3-phenylcycloheptatriene in the ratio of 50:25:25.[14d] It can be argued, however, that of the possible products of recombination of **34a**, only the thermodynamically controlled isomer is observed. On the other hand, the geometry of the cycloheptatriene ring is well suited for intramolecular shifts from C-7 to C-3 or C-4. (c) While 7,7-dicyano-1,2-benzocycloheptatriene (**16**) undergoes a cyano shift with an appreciable rate at 100°, the isomeric 7,7-dicyano-3,4-benzocycloheptatriene (**17**) does not, even at 120°. An intramolecular 1,5-cyano shift in the latter would lead to a completely nonaromatic product and thus should require a much higher activation energy than the correspondig process in **16**. To account for the experimental observation in terms of the ionization mechanism, one would have to postulate that the activation energy for the conversion of **16** to its ion, **35**, is considerably lower than that for the formation of the ion **36** from **17**. Although these two activation energies are difficult to estimate, one would not expect a large difference between them.[15] (d) The transition state parameters (Scheme I) for the rearrangement of 7,7-dicyanonorcaradiene to 3,7-dicyanocycloheptatriene are similar to those reported for the well-known, concerted, 1,5-hydrogen shifts in cycloheptatrienes.[16] Thus the activation energies (E_a in kcal/mole) and entropies of activation (in eu) are 31 and −8.2 for 7-deuteriocycloheptatriene,[16b] 27.6 and −11.7 for 7-phenylcycloheptatriene,[16c] 26.4 and −15.0 for 7-methoxycycloheptatriene,[16d] and 30.6 and −3.9 for 1,4-bis(7-cycloheptatrienyl)benzene.[16e] When comparing these values with the ones measured for the conversion of 7,7-dicyanonorcaradiene to 3,7-dicyanocycloheptatriene, it must be kept in mind that the latter still contain the differences in the ground-state enthalpy and entropy between 7,7-dicyanonorcaradiene (**1**) and 7,7-dicyanocycloheptatriene (**33**). Thus, the activation energy for the rearrangement of **33** to **3** will be smaller than 28.4 kcal/mole by the ΔH between **1** and **33**. Since 7,7-dicyanonorcaradiene is a much more rigid molecule than 7,7-dicyanocycloheptatriene, the entropy difference between the two is expected to be positive; the entropy of activation for the isomerization of **33** to **3** will then be more negative than −12.2 eu.



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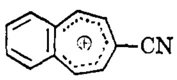

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The one piece of evidence that appears to speak against an intramolecular 1,5-cyano shift is the fact that 3,7-dicyanocycloheptatriene (**3**) is not formed when 7,7-dicyanonorcaradiene is heated in highly polar solvents such as methanol and acetonitrile, even though it was shown that **3** is stable in methanol at 100°. This could be construed as meaning that an ionic intermediate is being intercepted by nucleophilic solvents. However, if 7,7-dicyanocycloheptatriene (**33**) ionizes readily at 64° in methanol, there is no reason why 3,7-dicyanocycloheptatriene (**3**) should not also, at least to some extent, produce the same cyanotropylium cyanide (**34a**) at 100°. Since **3** is stable under these conditions, it either does not ionize, or it does but recombines to give unrearranged starting material. The unidentified products from the thermal rearrangement of 7,7-dicyanonorcaradiene in methanol and acetonitrile thus must arise by a mechanism other than interception of cyanotropylium ion by the solvents. It should be remembered in this context that 7,7-dicyano-1,2-benzocycloheptatriene rearranges to 3,7-dicyano-1,2-benzocycloheptatriene even in methanol solution. The observation that 3,7-dicyanocycloheptatriene is not formed in methanol and acetonitrile therefore speaks neither for nor against the ionization mechanism in the reactions where this product is in fact isolated. The experiment that would distinguish unambiguously between an intramolecular 1,5 shift and the ionization–recombination mechanism, namely the thermolysis of 7,7-dicyanonorcaradiene in the presence of labeled cyanide ion, could not be carried out since the norcaradiene was found to react with tetraethylammonium

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(13) (a) The dipole moment of 7,7-dicyanonorcaradiene is 4.8 D.;[1] that of a tight ion pair **34a** might be estimated at ~18 D. based on complete charge separation and a distance between the counterions of 3.7 A, arrived at by summation of the ionic radii of the cyano group in alkali cyanides (1.92 A[13b]) and the carbon atoms in tropylium iodide and perchlorate (1.77 A[13c]); (b) D. F. C. Morris, *Acta Cryst.*, **14**, 547 (1961); (c) A. I. Kitaigorodskii, Yu. T. Struchkov, T. L. Khotsyanova, M. E. Vol'pin, and D. N. Kursanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 39 (1960).

(14) (a) K. Conrow, *J. Am. Chem. Soc.*, **83**, 2343 (1961); (b) G. A. Gladkowskii, S. S. Skorokhodov, S. G. Slyvina, and A. S. Khachaturov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1273 (1963); (c) J. W. Wilt and D. Piszkiewicz, *Chem. Ind.* (London), 1761 (1963); (d) A. Cairncross, Ph.D. Thesis, Yale, 1963.

(15) (a) In benzotropylium cation, the electron densities at C-3 and C-5 (numbering as in **35**), calculated by simple Hückel theory,[15b] are 0.813 and 0.818, respectively. The destabilizing effect of the cyano group might, thus, if anything, be felt more strongly in **35** than in **36**. If one uses phenylbutadiene and *o*-divinylbenzene, respectively, as ground-state models for **16** and **17**, and the dications of 1,2- and 3,4-benzoheptafulvene, respectively, as models for the two transition states, and if one takes the differences in π energies[15b] as measures for the activation energies, $E_{a,16\rightarrow35}$ should be slightly lower (0.02 β) than $E_{a,17\rightrightarrows36}$. (b) A. Streitwieser, Jr., and J. I. Brauman, "Supplemental Tables of Molecular Orbitals," Vol. I, Pergamon Press, Oxford, 1965.

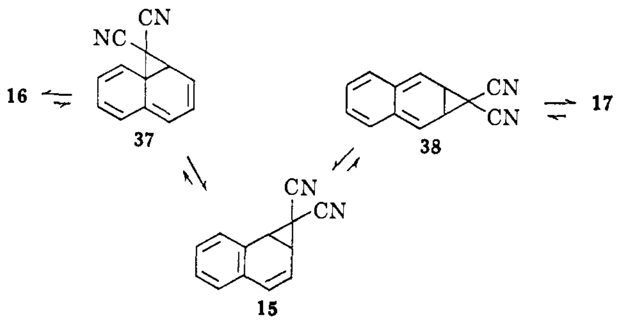
(16) (a) G. Büchi and E. M. Burgess, *J. Am. Chem. Soc.*, **84**, 3104 (1962); (b) A. P. ter Borg, H. Kloosterziel, and N. Van Meurs, *Rec. Trav. Chim.*, **82**, 717 (1963); (c) A. P. ter Borg and H. Kloosterziel, *ibid.*, **82**, 741 (1963); (d) T. Nozoe and K. Takahashi, *Bull. Chem. Soc. Japan*, **38**, 665 (1965); (e) R. W. Murray and M. L. Kaplan, *J. Am. Chem. Soc.*, **88**, 3527 (1966); *cf.* this paper for further pertinent references.

cyanide in methylene chloride at room temperature with the formation of a complex product mixture, from which only benzonitrile was isolated and identified. The presence of phenylmalononitrile in this mixture was inferred by the occurrence of a singlet at τ 4.8 in its nmr spectrum.

The available evidence thus tends to mitigate against an ionization–recombination mechanism as well as a dipolar, bridged intermediate. It does not distinguish between a concerted 1,5 shift and a two-step mechanism involving diradical **34b**. However, since there appears to be no precedent for radical additions to nitrile groups, we consider the latter mechanism less likely. To our knowledge, concerted shifts other than those of hydrogen have not been observed in cycloheptatrienes, but it has been stated[17] that there is no reason why they should not occur in favorable cases. 1,5-Methyl shifts were not observed in the thoroughly investigated thermal rearrangements of 3,7,7-trimethylcycloheptatriene in the gas phase at 300°.[18] This may have been a consequence of a sterically unfavorable transition state. No such effect is expected for cyano shifts in 7,7-dicyanocycloheptatriene, since the cyano group has small steric requirements, and there is no substituent at or near the migration terminus. The observation of 1,5-, to the exclusion of 1,3- and 1,7-hydrogen shifts in thermal rearrangements of cycloheptatrienes has been explained in terms of orbital symmetry relationships.[19] These rules predict the same specific migration for a cyano group, provided that only the σ orbital of the cyano group interacts with the π system of the ring.[20]

The transformation of 3,7-dicyanocycloheptatriene (**3**) to 1,4-dicyanocycloheptatriene (**4**) is another case of the well-documented, 1,5-hydrogen shifts[16] and need not be discussed any further, except to point out that although a 1,5-cyano shift in **3** to give 1,7-dicyanocycloheptatriene is possible, it does not occur to any detectable extent. This is somewhat surprising, since the rate of the 1,5-cyano shift in **33** is larger than that of the 1,5-hydrogen shift in **3**. However, the latter process moves the second cyano group into conjugation with a double bond, whereas another 1,5-cyano shift would not. That such considerations are reasonable is shown by the observation that a cyano group in the 7 position accelerates 1,5-hydrogen shifts in cycloheptatrienes by a factor of 60 relative to the unsubstituted triene, whereas a cyano group in any other position has essentially no influence on the rates.[21]

The facile conversion of 7,7-dicyano-1,2-benzocycloheptatriene (**16**) and 7,7-dicyano-3,4-benzocycloheptatriene (**17**) to 7,7-dicyano-2,3-benzonorcaradiene (**15**) probably involves initial formation of the respective valence-tautomeric norcaradienes **37** and **38** followed by Berson–Willcott rearrangements.[18,22] This rearrangement has been shown to be reversible in at least two cases;[18,22] the formation of 7,7-dicyano-2,3-benzonorcaradiene (**15**) from the two benzocycloheptatrienes **16** and **17** thus reflects the thermodynamic relationship of these compounds and provides another example for the peculiar stabilizing effect that two cyano groups in the 7 position have on the norcaradiene system.[1] The norcaradienes **37** and **38** are believed to be intermediates in the (kinetically controlled) formation of **16** and **17** from dicyanocarbene and naphthalene.[1]



The observed rearrangement of 7,7-dicyano-2,3-benzonorcaradiene (**15**) to 3,7-dicyano-1,2-benzocycloheptatriene (**18**) at 176° might be explained as proceeding through 7,7-dicyano-1,2-benzocycloheptatriene (**16**), if one assumes that the rate of the reverse reaction of **15** to **16** becomes appreciable only at elevated temperatures. The isomerization of 3,7-dicyano-1,2-benzocycloheptatriene (**18**) to 2,5-dicyano-3,4-benzocycloheptatriene (**20**) is formally a 1,3-hydrogen shift. A concerted process should thus be less favored.[19]

The photochemical transformations of 7,7-dicyanonorcaradiene provide another example of the by now well-documented, photolytic carbene transfer reactions of suitably substituted three-membered ring compounds.[23] The product ratios observed in the photolysis of 7,7-dicyanonorcaradiene in 2,3-dimethylbutane, and in the thermolysis of dicyanodiazomethane in the same substrate, show that the species formed from these two sources have essentially the same relative reactivity toward primary and tertiary carbon–hydrogen bonds. The photochemical formation of 4,4-dicyano-2,3-benzobicyclo[3.2.0]hepta-2,6-diene (**26**) from 7,7-dicyano-1,2-benzocycloheptatriene (**16**) has many analogies in cyclic dienes and trienes.[24] In view of the above-mentioned thermal behavior of 7,7-dicyano-2,3-benzonorcaradiene (**15**), its photolytic transformation to **26** probably also proceeds by way of 7,7-dicyano-1,2-benzocycloheptatriene (**16**), the latter being formed from a higher vibrational level of the electronic ground state of **15**.

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(17) D. S. Glass, R.S. Boikess, and S. Winstein, *Tetrahedron Letters*, 999 (1966).

(18) J. A. Berson and M. R. Willcott, III, *J. Am. Chem. Soc.*, **88**, 2494 (1966). In this case, the methyl group can migrate to C-3 and C-4; only the latter process would be observable since the fomer produces starting material.

(19) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 2511 (1965).

(20) In processes where the two degenerate π orbitals of the cyano group become involved in the transition state, 1,3 and 1,7 shifts also become symmetry allowed. However, on the basis of energy considerations, 1,5 shifts would still be favored. We thank Dr. H. E. Simmons for these and other helpful comments.

(21) A. P. ter Borg, E. Razenberg, and H. Kloosterziel, *Rec. Trav. Chim.*, **84**, 1230 (1965).

(22) *Cf.* especially footnote 26 in ref 18.

(23) (a) D. B. Richardson, L. R. Durrett, J. M. Martin, Jr., W. E. Putman, S. C. Slaymaker, and I. Dvoretzky, *J. Am. Chem. Soc.*, **87**, 2763 (1965); (b) P. A. Leermakers and M. E. Ross, *J. Org. Chem.*, **31**, 301 (1966); (c) H. Kristinsson and G. W. Griffin, *Angew. Chem.*, **77**, 859 (1965); (d) H. Kristinsson and G. W. Griffin, *J. Am. Chem. Soc.*, **88**, 1579 (1966); (e) M. Jones, Jr., W. H. Sachs, A. Kulczycki, Jr., and F. J. Waller, *ibid.*, **88**, 3167 (1966); (f) H. Kristinsson, K. N. Mehrotra, G. W. Griffin, R. C. Petterson, and C. S. Irving, *Chem. Ind.* (London), 1562 (1966).

(24) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1962); O. L. Chapman in "Advances in Photochemistry," Vol. 1, W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Ed., Interscience Publishers, Inc., New York, N. Y., 1963.

Experimental Section

Thermal Rearrangement of 7,7-Dicyanonorcaradiene. A. Isolation of Rearrangement Products. A solution of 12.19 g of 7,7-dicyanonorcaradiene[1] in 300 ml of toluene was heated under reflux for 92 hr. Removal of the solvent gave 12.12 g of a dark oil, which on seeding with phenylmalononitrile[25] crystallized partially. The crystals were collected by filtration and washed with a small amount of cold isopropyl alcohol, giving 4.2 g of phenylmalononitrile, identified by comparison of its infrared and nmr spectra with those of an authentic sample.[25] The filtrate and washings were combined, the solvent was removed, and the residue was chromatographed over 200 g of Florisil. Elution with benzene first gave additional phenylmalononitrile; the main fraction of 1,4-dicyanocycloheptatriene was eluted with benzene–methylene chloride (1:1). A mixture of methylene chloride–tetrahydrofuran (9:1) eluted the 3,7-dicyanocycloheptatriene. Combination of the appropriate fractions and two crystallizations from isopropyl alcohol and cyclohexane gave 1,4-dicyanocycloheptatriene, mp 80–81°, in the form of colorless crystals. The infrared spectrum showed $\nu_{\max}^{\mathrm{KBr}}$ 3030 (w), 2920 (w), 2860 (w), and 2210 cm^{-1} (s), among others. There was only weak absorption in the carbon–carbon, double bond stretching region, with bands at 1625, 1600, and 1525 cm^{-1}.

Anal. Calcd for $C_9H_6N_2$: C, 76.04; H, 4.25; N, 19.71. Found: C, 76.05; H, 4.39; N, 19.99.

The fractions containing 3,7-dicyanocycloheptatriene crystallized partially on standing at 0°. The mother liquor was removed and the low-melting crystals were short path distilled at 0.1 μ (90° bath temperature), giving a colorless oil which crystallized on standing at 0°, mp 30–31°. The infrared spectrum showed $\nu_{\max}^{\mathrm{neat}}$ 3070 (w–m), 2970 (w), 2880 (w), 2250 (m), 2220 (s), 1625 (w), and 1525 cm^{-1} (w), among others.

Anal. Calcd for $C_9H_6N_2$: C, 76.04; H, 4.25; N, 19.71. Found: C, 75.96; H, 4.29; N, 19.70.

The ultraviolet and nmr spectra of 3,7- and 1,4-dicyanocycloheptatriene are pesented in the Discussion.

B. Kinetic Runs. Deoxygenated solutions of 55 mg of 7,7-dicyanonorcaradiene[1] in 250 μl of deuteriochloroform or perdeuteriobenzene, containing 5% (weight by volume) of cyclohexane, were sealed under nitrogen in nmr tubes and heated, fully submerged, in an oil bath kept at ±0.1° of the indicated temperatures. The rate of disappearance of the 7,7-dicyanonorcaradiene was determined nmr spectroscopically by measuring the decrease of the integrated area of the H-1–H-6 multiplet at τ 6.5 relative to that of the cyclohexane standard. The reaction was followed to *ca.* one half-life at the lower temperatures and to over two half-lives at the higher temperatures. First-order plots were obtained in all cases. At each kinetic point, the ratio of phenylmalononitrile (**2**) to 3,7-dicyanocycloheptatriene (**3**) was determined from the relative areas of the methine singlet of **2** at τ 4.8 and the H-7 triplet of **3** at τ 6.9. From the average values of these ratios ($K_{2/3}$) and the rate constants (k) for the disappearance of 7,7-dicyanonorcaradiene, the rate constants for the aromatization (k_A) and rearrangement to 3,7-dicyanocycloheptatriene (k_B) were calculated using the relationships $k = k_A + k_B$ and $k_A/k_B = K_{2/3}$. Prolonged heating of the samples caused the appearance of the H-7–H-7 doublet of 1,4-dicyanocycloheptatriene at τ 7.3 at the expense of the triplet due to **3**.

The kinetic run in perdeuterioacetonitrile was carried out in the same manner except that only the rate constant for the disappearance of 7,7-dicyanonorcaradiene was determined since a more complex reaction took place in this case. The nmr spectrum of the product showed, in addition to the bands due to phenylmalononitrile, signals at τ 2.6, 4.2, 6.0, and 6.5. An approximate rate constant for the thermal rearrangement of 7,7-dicyanonorcaradiene in methanol was obtained by heating a 2% solution under reflux, removing samples at intervals, and calculating the amount of remaining starting material from the integrated areas of the H-1–H-6 multiplet at τ 6.5 relative to the total integrated area of the spectrum. The product(s), formed in addition to phenylmalononitrile, showed bands (in $CDCl_3$) at τ 2.4 (singlet) and 3.1–4.6 and 5.9–6.9 (complex multiplets). The kinetic runs in cyclohexane and tetrahydrofuran were carried out by heating solutions of 7,7-dicyanonorcaradiene (1% in the case of cyclohexane, 10% in the case of tetrahydrofuran), contained in sealed Carius tubes, for different periods of time, and determining the rate of disappearance of the norcaradiene as described for the run in methanol. From the ratios of **2**/**3**, determined by nmr spectroscopy, k_A and k_B were then calculated as described for the runs in chloroform.

Thermal Rearrangement of 1,4-Dicyanocycloheptatriene. A deoxygenated solution of 49 mg of 1,4-dicyanocycloheptatriene (**4**) in 300 μl of deuteriochloroform, contained in a sealed nmr tube, was heated to 178°. The formation of a compound believed to be 1,5-dicyanocycloheptatriene (**5**) was observed in the nmr spectra, taken at intervals. The ratio of **4** to **5** was 65:35 after 2.3 hr, 46:54 after 14 hr, and 47:53 after 33 hr. The reaction was accompanied by formation of a dark insoluble solid. The nmr spectrum of **5** is given in the Discussion.

Thermal Rearrangement of 7,7-Dicyano-2,5-dimethylnorcaradiene (12) and 7,7-Dicyano-1,4-dimethylnorcaradiene (13). A 252-mg sample of a 1:1 mixture of 7,7-dicyano-2,5-dimethylnorcaradiene and 7,7-dicyano-1,4-dimethylnorcaradiene[1] was heated in an oil bath. Melting occurred at 80–110° and rearrangement at *ca.* 130°. The nmr spectrum of the product showed essentially only the bands of 2,5-xylylmalononitrile (see below). Chromatography on Florisil (6 g) gave 214 mg (85%) of 2,5-xylylmalononitrile (elution with 60 ml of benzene–*n*-hexane, 1:1). Crystallization from cyclohexane gave an analytical sample, mp 57–58°. The nmr spectrum (in $CDCl_3$) showed singlets at τ 2.68 (1 H), 2.84 (2 H), 4.97 (1 H), and 7.64 (6 H). The ultraviolet spectrum had $\lambda_{\max}^{\mathrm{cyclohexane}}$ 276 mμ (ϵ 800) and 268 mμ (ϵ 750). The infrared spectrum (KBr) showed bands at 3050 (w), 3030 (w), 2980 (m), 2960 (m), 2870 (s), 2255 (m–w), 1620 (m–w), 1510 (s), 1460 (s), and 820 cm^{-1} (vs), among others.

Anal. Calcd for $C_{11}H_{10}N_2$: C, 77.62; H, 5.92; N, 16.46. Found: C, 77.51; H, 5.85; N, 16.55.

Hydrolysis and Decarboxylation of 2,5-Xylylmalononitrile. A mixture of 165 mg of 2,5-xylylmalononitrile and 7 ml of concentrated hydrochloric acid was heated under reflux for 4 hr. On cooling, 120 mg (76%) of crude 2,5-xylylacetic acid, mp 118–123°, was obtained in the form of colorless crystals. Recrystallization from water gave the pure acid, mp 129–130° (lit.[26] mp 128°), the infrared spectrum of which was identical with that published.[27] The nmr spectrum of 2,5-xylylacetic acid (in $CDCl_3$) showed a singlet at τ −0.85 (1 H), two barely separated bands at τ 2.97 (3 H), a singlet at τ 6.40 (2 H), and a singlet at τ 7.72 (6 H).

Thermal Rearrangement of 7,7-Dicyano-2,3-benzonorcaradiene. A deoxygenated solution of 60 mg of 7,7-dicyano-2,3-benzonorcaradiene (**15**)[1] in 300 μl of deuteriochloroform, contained in a sealed nmr tube, was heated to 176°. The disappearance of the starting materials was followed by measuring the areas of the τ 3.1 doublet and 6.6 quartet in **15** as a fraction of the total integrated area of starting material and products. A first-order plot ($k = 2.57 \times 10^{-4}$ sec^{-1}) was obtained. The average ratio of 3,7-dicyano-1,2-benzonorcaradiene (**18**) to 1-naphthylmalononitrile (**19**), measured at each kinetic point by integration of the H-7 doublet in **18** and the methine singlet in **19**, was 1.63. No other product could be detected. From the relationship $K_{18/19} = k_A/k_B$ and $k = k_A + k_B$, the rate constants k_A for the isomerization of **15** to **18** and k_B for the aromatization of **15** to **19** were calculated. They are listed in Scheme II. Further heating of the solution caused the appearance of the peaks owing to 2,5-dicyano-3,4-benzocycloheptatriene (**20**) at the expense of those of 3,7-dicyano-1,2-benzocycloheptatriene. After 30 hr, the ratio of **19**:**18**:**20** was 41:34:25. Heating a solution of 98 mg of 7,7-dicyano-2,3-benzonorcaradiene in 800 μl of cyclohexane to 178° for 16 hr gave the products **19**, **18**, and **20** in the ratio of 25:28:47.

To prepare samples of 3,7-dicyano-1,2-benzocycloheptatriene (**18**) and 1-naphthylmalononitrile (**19**), a degassed solution of 2.66 g of 7,7-dicyano-2,3-benzonorcaradiene[1] in 14 ml of chloroform, contained in a sealed Carius tube, was heated to 177° for 5 hr. Removal of the solvent and chromatography of the residue over Florisil gave 1-naphthylmalononitrile (**19**, eluted with benzene), mp 167–167.5° after two crystallizations from isopropyl alcohol. The infrared spectrum had $\nu_{\max}^{\mathrm{KBr}}$ 3070 (w), 2910 (m), 2250 (w), 1600 (m), 1515 (s), 800 (vs), 770 (vs), 730 (s), and 710 cm^{-1} (m), among others, and it was identical with that of an authentic sample (see below). The ultraviolet spectrum showed $\lambda_{\max}^{\mathrm{MeCN}}$ 317 mμ (ϵ 280), 312 (380), 290 (sh, 4500), 281 (6600), 271 (5600), and 223 (82,000). The nmr spectrum (in perdeuterioacetone) showed a complex multiplet at τ 2.2–3.0 (7 H) and a singlet at τ 4.0 (1 H).

Anal. Calcd for $C_{13}H_8N_2$: C, 81.23; H, 4.20; N, 14.58. Found: C, 81.13; H, 4.24; N, 14.80.

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(25) P. B. Russell and G. H. Hitchings, *J. Am. Chem. Soc.*, 74, 3443 (1952).

(26) E. Buchner and P. Schulze, *Ann.*, **377**, 259 (1910).

(27) Spectrum No. 18242, Sadtler Standard Spectra, The Sadtler Research Laboratories, Inc., Philadelphia, Pa.

Further elution with benzene followed by methylene chloride–THF, 99:1, gave 3,7-dicyano-1,2-benzocycloheptatriene (**18**), mp 164–165° after two crystallizations from ethyl acetate. The ultraviolet spectrum showed $\lambda_{\max}^{\text{cyclohexane}}$ 287 mμ (ϵ 8400). The infrared spectrum had $\nu_{\max}^{\text{KBr}}$ 3070 (w), 3050 (w), 2860 (w), 2250 (w), and 2220 cm^{-1} (m), among others. The nmr spectrum is given in the Discussion.

Anal. Calcd for $C_{13}H_8N_2$: C, 81.23; H, 4.20; N, 14.58. Found: C, 81.16; H, 4.27; N, 14.78.

To prepare a sample of 2,5-dicyano-3,4-benzocycloheptatriene (**20**), a deoxygenated solution of 913 mg of 7,7-dicyano-2,3-benzonorcaradiene[1] in 7 ml of cyclohexane was heated to 180° for 24 hr. Chromatography over Florisil first gave **19** and **18**, eluted with benzene. Elution with methylene chloride gave pale yellow crystals of 2,5-dicyano-3,4-benzocycloheptatriene (**20**), mp 188.5–189.5° after two crystallizations from isopropyl alcohol. The ultraviolet spectrum had $\lambda_{\max}^{\text{cyclohexane}}$ 231 mμ (ϵ 37,000) with a shoulder at 251 mμ (ϵ 12,000). The infrared spectrum (KBr) showed bands, among others, at 3050 (w), 2990 (w), 2220 (s), 1610 (m), and 760 cm^{-1} (doublet, vs).

Anal. Calcd for $C_{13}H_8N_2$: C, 81.23; H, 4.20; N, 14.58. Found: C, 81.38; H, 4.42; N, 14.55.

1-Naphthylmalononitrile. A mixture of 5.00 g of 1-naphthylcyanoacetamide,[28] 16 g of phosphorus pentoxide, and 250 ml of acetonitrile was stirred under reflux for 15 min The cooled mixture was poured into an ice-cold solution of 45 g of sodium carbonate in 400 ml of water. Ether (100 ml) was added, the layers were separated, and the aqueous layer was extracted twice with 50-ml portions of ether. The combined organic phases were washed with water and concentrated sodium chloride solution and dried. Removal of the solvent gave 3.40 g of a yellow solid which on crystallization from 60 ml of isopropyl alcohol gave 2.22 g (49% yield) of 1-naphthylmalononitrile, mp 166–167°. Its infrared spectrum was identical with that of the product obtained from 7,7-dicyano-2,3-benzonorcaradiene.

Thermal Rearrangement of 7,7-Dicyano-1,2-benzocycloheptatriene (16). A degassed solution of 68 mg of 7,7-dicyano-1,2-benzocycloheptatriene[1] in 250 μl of deuteriochloroform, contained in a sealed nmr tube, was heated to 99°. The disappearance of the starting material was followed by measuring the area of the τ 4.1 doublet *in* **16** as a fraction of the total integrated area of the spectrum. The rate constants for the conversion of **16** to 7,7-dicyano-2,3-benzonorcaradiene (**15**) and 3,7-dicyano-1,2-benzocycloheptatriene (**18**) were then calculated from the slope of the first-order plot ($k = 7.5 \times 10^{-5}$ sec^{-1}) and the average ratio of **18** to **15** (1.15) measured at each kinetic point. This ratio remained constant for at least 43 hr. For the runs in methanol, 5% solutions were heated in sealed nmr tubes to 99° for 20, 35, and 85 min, respectively. The solvent was removed, and the nmr spectra of the residues were taken in deuteriochloroform solution. The rate constant for the disappearance of **16**, determined as described above, was 4.8×10^{-4} sec^{-1}. The average ratio of **15**:**18**, measured at each kinetic point, was 3.93. The products were separated by chromatography on Florisil and identified by their infrared spectra.

Thermal Rearrangement of 7,7-Dicyano-3,4-benzocycloheptatriene (17). A degassed solution of 45 mg of 7,7-dicyano-3,4-benzocycloheptatriene[1] in 200 μl of deuteriochloroform was sealed in an nmr tube and heated to 120°. The progress of the reaction was followed by nmr spectroscopy by measuring the area of the τ 4 doublet in **17** as a fraction of the total integrated area of the spectrum. The only product formed initially was 7,7-dicyano-2,3-benzonorcaradiene (**15**); as the reaction progressed, some of its rearrangement product, 1-naphthylmalononitrile, was also observed. Thus, after 11 hr, the mixture consisted of 61% of **15**, 31% of **17**, and 8% of **19**. The 7,7-dicyano-2,3-benzonorcaradiene was identified also by its infrared spectrum.

Photolysis of 7,7-Dicyanonorcaradiene in Cyclohexane. A stirred mixture of 640 mg of 7,7-dicyanonorcaradiene[1] and 500 ml of cyclohexane, contained in an internally water-cooled quartz tube, was irradiated with a Philips HPK 125 high-pressure mercury lamp for 64 hr. Removal of the solvent left 612 mg of a brown oil, which on short-path distillation (0.2 μ, 95° bath temperature) gave 430 mg of a colorless liquid, the infrared spectrum of which was that of cyclohexylmalononitrile[29] with an additional band at 740 cm^{-1}. The nmr spectrum showed the presence of 86% of cyclohexylmalononitrile and 14% of a mixture of 7,7-dicyanonorcaradiene and phenylmalononitrile. Since the nmr spectrum of the crude product showed no evidence for the presence of phenylmalononitrile, it must have been formed by thermal rearrangement of 7,7-dicyanonorcaradiene during the distillation. The yield of cyclohexylmalononitrile was 60% (based on 7,7-dicyanonorcaradiene not recovered).

Photolysis of 7,7-Dicyanonorcaradiene in 2,3-Dimethylbutane. A suspension of 1.046 g of 7,7-dicyanonorcaradiene[1] in 400 ml of 2,3-dimethylbutane (Philips research grade) was irradiated as described above for 63 hr. Removal of the solvent and chromatography of the residue over Florisil (30 g, elution with 900 ml of methylene chloride) gave 789 mg of an oil, the nmr spectrum of which showed the presence of 52% of unreacted 7,7-dicyanonorcaradiene and 48% of 2,3-dimethylbutane insertion products. The latter were shown by gas chromatography (30% Dow Corning FS-1265 silicone oil on 60–80 mesh Chromosorb, 165°) to be a mixture of 47% of 2,3-dimethyl-2-butylmalononitrile, 47% of 2,3-dimethyl-1-butylmalononitrile, and 6% of product(s) having longer retention times. The two major insertion products were isolated by gas chromatography and identified by comparison of their infrared spectra with those of authentic samples (see below). Yields (based on dicyanonorcaradiene not recovered) were 2,3-dimethyl-1-butylmalononitrile, 27%; 2,3-dimethyl-2-butylmalononitrile, 27%.

Thermolysis of Dicyanodiazomethane in 2,3-Dimethylbutane. A stirred suspension of dicyanodiazomethane,[5] prepared from 1.025 g of carbonyl cyanide hydrazone,[5] in 100 ml of 2,3-dimethylbutane was heated under reflux until nitrogen evolution ceased. Removal of the solvent and short-path distillation of the residue gave 540 mg of a pale yellow oil, which was shown by gas chromatography (same conditions as above) to contain 49% of 2,3-dimethyl-2-butylmalononitrile (16% yield) and 36% of 2,3-dimethyl-1-butylmalononitrile (12% yield). These products were isolated by gas chromatography and identified by comparison of their infrared spectra with those of authentic samples (see below).

2,3-Dimethyl-2-butylmalononitrile. A Grignard reagent was prepared from 22.0 g (0.91 g-atom) of magnesium and 98.0 g (0.80 mole) of 2-bromopropane in 400 ml of ether. To this was added, over a period of 1 hr, a solution of 70.0 g (0.66 mole) of isopropylidenemalononitrile[30] in 150 ml of benzene. The mixture refluxed gently during the addition. After heating under reflux for another 30 min, the mixture was poured on ice, and 250 ml of 20% sulfuric acid was added. The layers were separated, the aqueous layer was extracted with two 50-ml portions of benzene, and the combined organic phases were washed with 5% aqueous sodium bicarbonate solution, water, and concentrated sodium chloride solution, and dried. Removal of the solvent and distillation of the residue gave 72.04 g (73%) of 2,3-dimethyl-2-butylmalononitrile, bp 71–72° (1.0 mm), which solidified to a gel. The nmr spectrum ($CDCl_3$) showed a singlet at τ 6.07 (1 H), a multiplet at 7.7 to 8.4 (1 H), a singlet at 8.82 (6 H), and a doublet ($J = 7$ cps) at 9.09 (6 H).

Anal. Calcd for $C_9H_{14}N_2$: C, 71.96; H, 9.40; N, 18.63. Found: C, 72.00; H, 9.38; N, 18.52.

2,3-Dimethyl-1-butylmalononitrile. A mixture of 30.0 g (0.29 mole) of 2,3-dimethyl-1-butanol[31] and 250 ml of pyridine was cooled to −10° and 60 g (0.32 mole) of *p*-toluenesulfonyl chloride was added, with stirring. After standing at 0° overnight, most of the pyridine was removed under reduced pressure. Water (100 ml) was added, and the mixture was extracted with four 80-ml portions of methylene chloride. The combined extracts were washed with ice-cold 10% sulfuric acid, 5% sodium bicarbonate solution, and water, and dried. Removal of the solvent gave 73 g (95%) of crude 2,3-dimethyl-1-butyl tosylate as a yellow oil. The product was added, over a period of 30 min, to a boiling mixture of 30 g (0.34 mole) of sodiomalononitrile and 300 ml of THF. After stirring under reflux for 24 hr the cooled mixture was filtered, and the solids were washed with 400 ml of benzene. The combined filtrates were washed with three 50-ml portions of water and dried. Removal of the solvent and distillation of the residue gave 8.60 g (20% yield) of 2,3-dimethyl-1-butylmalononitrile, bp 80° (1.0 mm), n^{25}D 1.4380.

Anal. Calcd for $C_9H_{14}N_2$: C, 71.96; H, 9.40; N, 18.63. Found: C, 71.96; H, 9.29; N, 18.63.

Photolysis of 7,7-Dicyano-2,3-benzonorcaradiene. A stirred, deoxygenated mixture of 613 mg of 7,7-dicyano-2,3-benzonorcaradiene[1] and 400 ml of cyclohexane was irradiated through a Pyrex filter with a Philips HPK 125 high-pressure mercury lamp for 34 hr.

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(31) S. Sarel and M. S. Newman, *ibid.*, **78**, 5416 (1956).

The nmr spectrum of the product indicated the presence of *ca.* 60% of unreacted starting material in addition to the photoproducts (see below). Irradiation was continued for 43 hr without the Pyrex filter (quartz vessel). Removal of the solvent gave 723 mg of a brown oil which was chromatographed on 20 g of Florisil. Elution with *n*-hexane gave 90 mg (22%) of naphthalene, identified by its infrared spectrum. Further elution with benzene–*n*-hexane, 7:3, benzene, and methylene chloride gave 374 mg of a mixture containing 73% (44% yield) of the photoisomer **26** and 27% (22% yield) of cyclohexylmalononitrile as determined by nmr spectroscopy. The photoisomer was enriched in the earlier fractions. The cyclohexylmalononitrile was isolated by gas chromatography on a 30% silicone grease column at 160° and identified by comparison of its infrared spectrum with that of an authentic sample.[29] The photoisomer (4,4-dicyano-2,3-benzobicyclo[3.2.0]hepta-2,6-diene, **26**), mp 101–102°, was obtained by repeated crystallization from ethanol. Its infrared spectrum had ν_{max}^{KBr} 3050 (w), 2940 (w), 2240 (w), 1480 (m), 1460 (m), 780 (s), 765 (s), 745 (m), and 700 cm^{-1} (m), among others. The ultraviolet spectrum had λ_{max}^{MeCN} 273 mμ (ϵ 570), 266 (550), 260 (370), and 214 (sh, 8000). The nmr spectrum is given in the Discussion.

Anal. Calcd for $C_{13}H_8N_2$: C, 81.23; H, 4.20; N, 14.58. Found: C, 80.89; H, 4.07; N, 14.47.

Photolysis of 7,7-Dicyano-1,2-benzocycloheptatriene. A deoxygenated solution of 114 mg of 7,7-dicyano-1,2-benzocycloheptatriene[1] in 130 ml of cyclohexane, contained in an internally cooled Pyrex vessel, was irradiated with a Philips HPK 125 high-pressure mercury lamp for 90 min. Removal of the solvent gave 112 mg of an off-white solid, the nmr and infrared spectra of which were identical with those of the photoisomer of 7,7-dicyano-2,3-benzonorcaradiene (see above).

Hydrogenation of 4,4-Dicyano-2,3-benzobicyclo[3.2.0]hepta-2,6-diene (26). Hydrogenation of 120 mg of the photoisomer **26** in THF (5 ml) with 104 mg of 5% rhodium-on-carbon catalyst resulted in the uptake of 1.02 molar equiv of hydrogen within 9 min. No further uptake occurred. Removal of the solvent gave 129 mg of crude 4,4-dicyano-2,3-benzobicyclo[3.2.0]hept-2-ene (colorless oil), which was purified by short-path distillation at 80–85° (0.2 μ). The infrared spectrum had $\nu_{max}^{CCl_4}$ 3060 (m), 2980 (s), 2940 (s), 2860 (m), and 2240 cm^{-1} (w), among others. The ultraviolet spectrum had λ_{max}^{MeCN} 272 mμ (ϵ 700), 265 (650), 260 (430), and 212 (sh, 8400). The nmr spectrum is given in the Discussion.

Anal. Calcd for $C_{13}H_{10}N_2$: C, 80.39; H, 5.19; N, 14.42. Found: C, 80.18; H, 5.19; N, 14.37.

Photolysis of 1-Ethoxycarbonyl-2,3-benzonorcaradiene. A solution of 2.760 g of 7-ethoxycarbonyl-2,3-benzonorcaradiene[7] in 400 ml of cyclohexane, contained in an internally water-cooled, quartz vessel, was irradiated with a Philips HPK 125 high-pressure mercury lamp for 87 hr. Removal of the solvent gave 3.298 g of a light brown oil. Chromatography of 1.102 g of this material on 30 g of Florisil gave first 54 mg (11% yield) of naphthalene (eluted with *n*-hexane); elution with methylene chloride gave 698 mg of an oil which on short-path distillation (85° bath temperature, 0.2 mm) gave 49 mg (8% yield) of ethyl cyclohexylacetate, identified by comparison of its infrared spectrum with that of an authentic sample.[32]

Reaction of 7,7-Dicyanonorcaradiene with Dimethyl Acetylenedicarboxylate. A mixture of 300 mg of 7,7-dicyanonorcaradiene[1] and 1.17 g of dimethyl acetylenedicarboxylate was heated to 100° for 2 hr. Most of the ester was removed under 0.1-mm vacuum, leaving 929 mg of a semisolid from which 331 mg (55%) of dimethyl 3,3-dicyanotricyclo[3.2.2.0^{2,4}]nona-6,8-diene-6,7-dicarboxylate, mp 139°, was isolated by crystallization from 3 ml of methanol. An analytical sample, obtained by recrystallization from methanol, had mp 140°. The nmr spectrum (in $CDCl_3$) showed a triplet centered at τ 3.50 (2 H), a septet centered at τ 5.32 (2 H), a singlet at τ 6.20 (6 H), and a triplet centered at τ 7.24 (2 H). The ultraviolet spectrum (in acetonitrile) showed end absorption with shoulders at 260 mμ (ϵ 1400) and 220 mμ (ϵ 4200). In the infrared spectrum (KBr), bands occurred at 3080, 3030, 2990, 2880, 2250, 1725, 1640, and 1605 cm^{-1}, among others.

Anal. Calcd for $C_{15}H_{12}N_2O_4$: C, 63.37; H, 4.26; N, 9.85; mol wt, 284.26. Found: C, 63.57; H, 4.44; N, 9.99; mol wt, 276, 281 (ebullioscopically in benzene).

Hydrogenation of 7,7-Dicyanonorcaradiene. A solution of 324 mg of 7,7-dicyanonorcaradiene[1] in 20 ml of methanol was stirred under hydrogen with 70 mg of palladium on charcoal (10%) until 1.72 molar equiv of hydrogen had been taken up. The sample was still consuming hydrogen at that time. Evaporation of the filtered solution and chromatography of the residue on 10 g of Florisil gave 64 mg of a colorless oil, the infrared spectrum of which was that of cyclohexylmalononitrile with additional bands indicating the presence of phenylmalononitrile. This was further confirmed by the nmr spectrum, which showed singlets at τ 2.4 and 4.7 (ratio 5:1), characteristic of phenylmalononitrile, in addition to a doublet (J = 6 cps) at 6.3 (1 H) and two broad bands at 7.5–9 (11 H) due to cyclohexylmalononitrile. Analysis by gas chromatography (30% Dow Corning FS 1265 silicone oil on 60–80 mesh Chromosorb at 170°), using an authentic sample of cyclohexylmalononitrile[29] as standard, showed the product to contain 65% (42 mg, 12% yield) of this compound.

Phenylmalononitrile was not hydrogenated under the above conditions. Stirring a solution of 97 mg of 7,7-dicyanonorcaradiene in 5 ml of methanol with 32 mg of palladium on charcoal (10%) under nitrogen at room temperature for 20 hr gave an oil which contained *ca.* 45% of unreacted starting material as judged from its nmr spectrum. The remainder was a mixture of phenylmalononitrile and compound(s) showing absorption at τ 2.2–2.5 and 6–7. Stirring a similar solution under nitrogen in the absence of palladium for 64 hr resulted in the complete recovery of the 7,7-dicyanonorcaradiene.

Hydrolysis of 7,7-Dicyanonorcaradiene. To a cooled and stirred mixture of 450 mg of 7,7-dicyanonorcaradiene,[1] 5 ml of acetone, and 2 ml of 30% hydrogen peroxide was added, over a period of 20 min, 2 ml of a 10% sodium carbonate solution, keeping the temperature below 8°. After stirring at ice-bath temperature for 30 min, the acetone was removed, using a rotary evaporator, and the remaining aqueous phase was extracted with three 10-ml portions of methylene chloride. The extracts were washed with water and dried; removal of the solvent gave 357 mg of a colorless solid, mp 140–150°. Crystallization from ethyl acetate gave 152 mg of 7-cyano-7-carbamidonorcaradiene (**29**), mp 153° dec. Evaporation of the solvent from the mother liquor gave 201 mg of a solid. Chromatography of 105 mg of this product on 6 g of Florisil gave an additional 70 mg of **29**, eluted with 170 ml of methylene chloride, and 31 mg (16% yield) of benzamide, eluted with tetrahydrofuran and identified by its infrared spectrum. The total extrapolated yield of 7-cyano-7-carbamidonorcaradiene was 286 mg (56%). An analytical sample, mp 155° dec, was prepared by crystallization from ethyl acetate. The nmr spectrum (in perdeuterioacetone) showed a broad band at τ 3.4 (2 H), a singlet (half-band width 5 cps) at τ 4.2 (4 H), and a multiplet at τ 7.3 (2 H). The ultraviolet spectrum had λ_{max}^{MeCN} 269 mμ (ϵ 3100) and 233 mμ (ϵ 2400). The infrared spectrum showed ν_{max}^{KBr} 3390, 3300, 3180, 3030, 2230, 1705, 1665, and 1600 cm^{-1}, among others.

Anal. Calcd for $C_9H_8N_2O$: C, 67.49; H, 5.04; N, 17.49; mol wt, 160.17. Found: C, 67.50; H, 5.28; N, 17.63; mol wt, 163 (ebullioscopically in benzene).

Thermal Rearrangement of 7-Cyano-7-carbamidonorcaradiene (29). A sample of **29** was heated under nitrogen to 160° for 5 min. The infrared spectrum of the product was identical with that of phenylcyanoacetamide.[33]

Hydrogenation of 7-Cyano-7-carbamidonorcaradiene. A solution of 150 mg of 7-cyano-7-carbamidonorcaradiene in 10 ml of methanol was hydrogenated with 46 mg of palladium on charcoal (10%); the uptake was 2.16 molar equiv. Evaporation of the filtered solution gave 154 mg of a semisolid which was chromatographed on Florisil. Elution with tetrahydrofuran–methylene chloride (5:95) gave 69 mg (42% yield) of cyclohexylcyanoacetamide, identified by comparison of its infrared spectrum with that of an authentic sample (see below). Elution with 60 ml of tetrahydrofuran followed by 60 ml of methanol gave 67 mg of a colorless oil showing no C≡N absorption in the infrared spectrum.

Phenylcyanoacetamide[33] took up no hydrogen under the above conditions and was recovered unchanged.

Cyclohexylcyanoacetamide. A mixture of 28.1 g of ethyl cyclohexylcyanoacetate,[34] 100 ml of 30% aqueous ammonia, and 100 ml of methanol was stirred for 30 min, after which time a clear

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[32] M. G. Darzens, *Compt. Rend.*, **144**, 328 (1907).

[33] J. C. Hessler, *Am. Chem. J.*, **32**, 119 (1904).

[34] W. J. Bailey and J. J. Daly, Jr., *J. Am. Chem. Soc.*, **81**, 5397 (1959).

solution resulted. A crystalline precipitate began to form after 2 hr. It was collected after a total of 48 hr at room temperature, washed with water, and dried, giving 13.24 g (55%) of crude cyclohexylcyanoacetamide. Recrystallization from methanol gave an analytical sample, mp 149–150°.

Anal. Calcd for $C_9H_{14}N_2O$: C, 65.03; H, 8.49; N, 16.86. Found: C, 65.08; H, 8.59; N, 17 12.

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Diels–Alder Reactions of Alkynyltin Compounds with Polychlorocyclopentadienes. Organotin-Substituted Polychloronorbornadienes. Cleavage Reactions and Photochemistry

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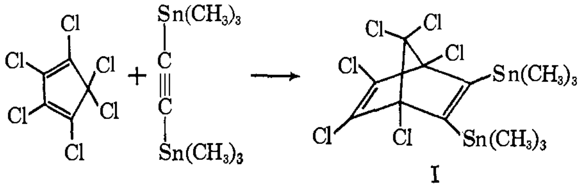
Abstract: The Diels–Alder reaction of hexachlorocyclopentadiene with bis(trimethyltin)acetylene, propynyltrimethyltin, and (phenylethynyl)trimethyltin gave the norbornadienes I, II, and III, respectively. Reaction of 5,5-dimethoxytetrachlorocyclopentadiene with bis(trimethyltin)acetylene resulted in 1,2-bis(trimethyltin)tetrachlorobenzene, but some 1-(trimethyltin)-2,3,4,5-tetrachlorobenzene and 1,2,3,4-tetrachlorobenzene also were formed during work-up. Ultraviolet irradiation of I and II in diethyl ether solution produced the isomeric quadricyclanes XIV and XV, respectively. Proto-, chloro, and bromodestannations of I, II, XIV, and XV were studied, and a number of new norbornadienes (VIII, IX, XI, XII, and XIII) and quadricyclanes (XVI and XVIII) were characterized as products of these cleavage reactions. The thermolysis of II and of 1-(trimethyltin)-2,3,4,5-tetrachlorobenzene was studied. Reaction of the latter with *p*-iodotoluene at 210° gave 2,3,4,5-tetrachloro-4′-methylbiphenyl in 72% yield.

In a previous paper[3] we presented evidence which showed that those Diels–Alder reactions of bis(trimethyltin)acetylene which proceed well represent further examples of Diels–Alder reactions with "inverse electron demand."[4] In agreement with this view, we have found that bis(trimethyltin)acetylene and other organotin-substituted acetylenes react readily with π-electron-deficient hexachlorocyclopentadiene and 5,5-dimethoxytetrachlorocyclopentadiene.

Reaction of equimolar quantities of hexachlorocyclopentadiene and bis(trimethyltin)acetylene in refluxing *n*-butyl ether gave 2,3-bis(trimethyltin)-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene (I) in 50–70% yield.

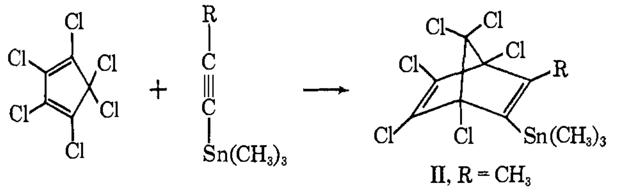


(1)

I

Identification of the adduct, rendered more difficult by the absence of skeletal protons, was made on the basis of elemental analysis, a molecular weight determination, and correlation of the ultraviolet and infrared spectra with those of other norbornadiene systems (see Table I).

Propynyltrimethyltin and (phenylethynyl)trimethyltin also were allowed to react with hexachlorocyclopentadiene. Both gave the expected Diels–Alder adducts. These, II and III, respectively, were identified by the methods mentioned above, but in these cases nmr spectra were useful as well. The spectrum of III is interesting in that the trimethyltin group absorbs at unusually high field, 0.10 ppm (*vs.* 0.35 ppm in I and II), owing to its position above the phenyl substituent which must be skewed to the plane of the 2,3 double bond.



II, $R = CH_3$
III, $R = C_6H_5$

The three Diels–Alder adducts are stable, crystalline solids. On extended standing, however, some decomposition accompanied by formation of methyltin chlorides occurs.[5]

The Diels–Alder reaction of 5,5-dimethoxytetrachlorocyclopentadiene with bis(trimethyltin)acetylene also was investigated. It is known that adducts of this diene with acetylenes aromatize with loss of the bridgehead at moderate temperatures.[6] Loss of the bridgehead

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(1) Alfred P. Sloan Foundation Fellow, 1962–1966.

(2) National Institutes of Health Predoctoral Fellow, 1963–1966.

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