Anal. Calcd for $C_{13}H_{20}$: C, 88.58; H, 11.42. Found: C, 88.85; H, 11.70.

The two isomers were separated by vpc using an 8-m 10% diisodecyl phthalate on 60–80 mesh silanized diatomaceous earth column (Diatoport S). Data on tetraallylmethane are as follows: ir 3068, 3000, 2980, 2840, 1638, 1440, 1410, 989, 905, and 850 cm^{-1}; nmr (neat) δ 5.8 (m, 4, =CH–), 5.13 (sharp singlet, 4, one-half $H_2C=$, see Discussion), 4.87 (q, 4, J = 2 and 17 Hz, one half $H_2C=$), and 1.98 (d, 8, J = 7 Hz, $-CH_2-$). Data on the isomeric compound (believed to be 4-allyl-4-vinyl-1,7-octadiene) are as follows: ir 3068, 3000, 2980, 2920, 2845, 1638, 1450–1430, 1410, 989, and 905 cm^{-1}. The nmr spectrum was similar to that of tetraallylmethane except for the following: the singlet at δ 5.13 and the quartet at 4.87 merged to give an eight-proton multiplet from 5.2 to 4.8; the sharp doublet at 1.98 now accounted for only six protons including a one proton shoulder from 2.0 to 1.7; and there was a two-proton multiplet from 1.7 to 1.2.

Registry No.—Tetraallylmethane, 19255-02-8; triallylmethyl chloride, 19255-03-9; **4**, 19255-04-0.

Negatively Substituted Acetylenes. II.[1] Cycloaddition Reactions with Styrenes

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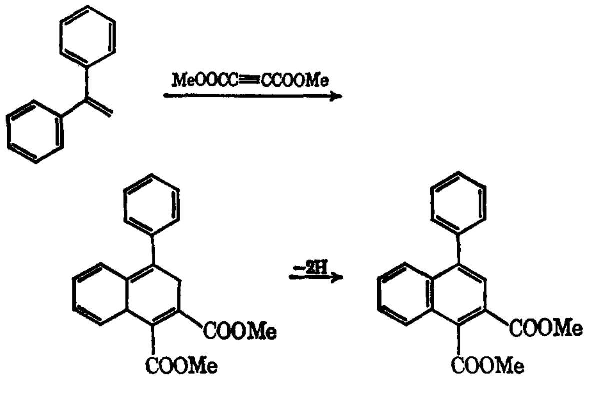
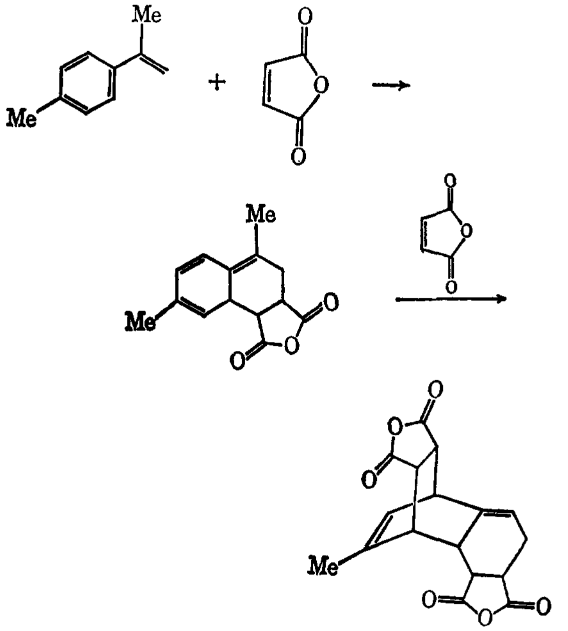
Activated acetylenes, such as dicyanoacetylene, acetylenedicarboxylic ester, and benzyne, react with styrenes to give 1:2 adducts of type **2** by a sequence of Diels–Alder addition and ene reaction. Unlike in previously reported additions of this nature, the styrene, and not the acetylene, acts as the enophile in the second step. From the reactions of dicyanoacetylene and benzyne with styrene, mixtures of *threo* and *erythro* adducts have been isolated, resulting from exoid and endoid attack by the styrene in the ene reaction. The fact that no β-phenylethyldihydronaphthalenes (*e.g.*, **22**) could be detected among the products indicates that in the transition state of the second-step ene reaction, hydrogen transfer has proceeded to a larger extent than carbon–carbon bond formation. The scope of these reactions is discussed.

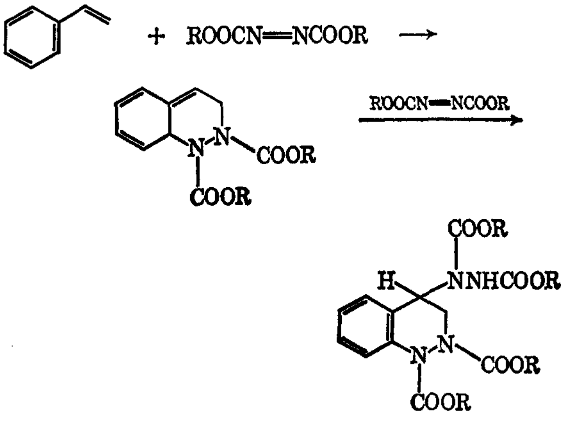
The vinyl group and one of the aromatic double bonds of styrene form a diene system that is potentially capable of undergoing the Diels–Alder reaction. Although this possibility was foreseen at an early stage, examples of such additions are not so numerous as might be expected because of the tendency of styrenes to polymerize and copolymerize under the reaction conditions required. As a rule, only very reactive dienophiles will give nonpolymeric products in acceptable yields. The initial 1:1 adducts usually cannot be isolated; they either aromatize to give derivatives of dihydro- or tetrahydronaphthalene as exemplified in eq 1,[2,3] or add a second molecule of the dienophile. This second addition can either be another Diels–Alder reaction (*e.g.*, eq 2[4,5]), an ene reaction[6] as shown in



(1)



(2)



(3)

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[1] E. Ciganek and C. G. Krespan, *J. Org. Chem.*, **33**, 541 (1968) is considered to be paper I in this series.

[2] K. Alder, F. Pascher, and H. Vagt, *Ber.*, **75**, 1501 (1942).

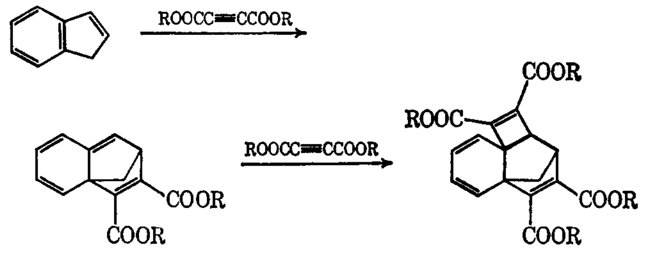
[3] For reviews of the Diels–Alder addition, see A. S. Onishchenko, "Diene Synthesis," English translation, D. Davey, New York, N. Y., 1964; J. Sauer, *Angew. Chem.*, **78**, 233 (1966).

[4] This type of addition was first observed by T. Wagner-Jauregg, *Ber.*, **63**, 3213 (1930); *Ann. Chem.*, **491**, 1 (1931). The example of eq 2 is from ref 5.

[5] J. Hukki, *Acta. Chem. Scand.*, **5**, 31 (1951).

[6] For a brief review of the ene reaction see W. R. Roth, *Chimia (Aarau)*, **20**, 229 (1966).

eq 3,[7] or a 2 + 2 cycloaddition (*e.g.*, eq 4[2,8]). Only in special cases, such as the reaction of 2-vinylnaphthalene with tetracyanoethylene, can a simple 1:1 Diels–Alder adduct be obtained.[9]



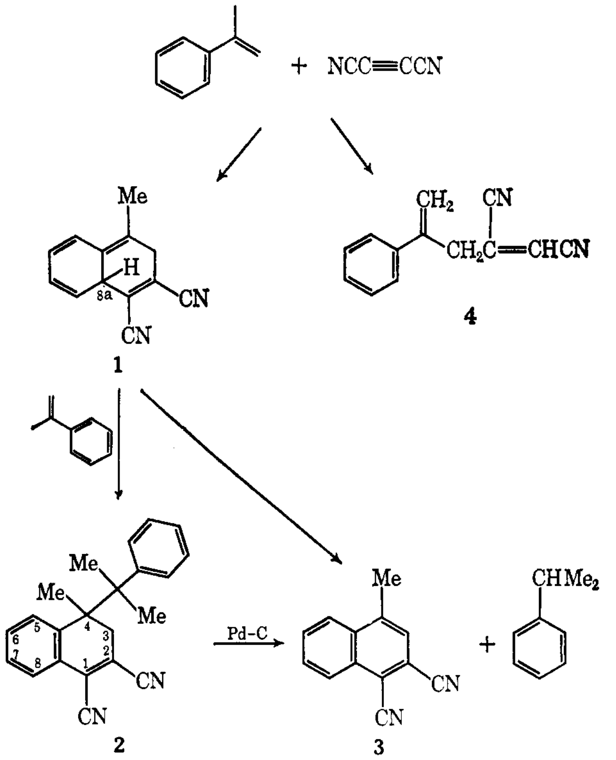
(4)

The extremely high reactivity of dicyanoacetylene in the Diels–Alder reaction[10] led us to investigate its reaction with styrenes. It was hoped that the addition would occur at sufficiently low temperatures so that secondary reactions could be avoided, the initial 1:1 adduct could be isolated, and its properties could be studied.

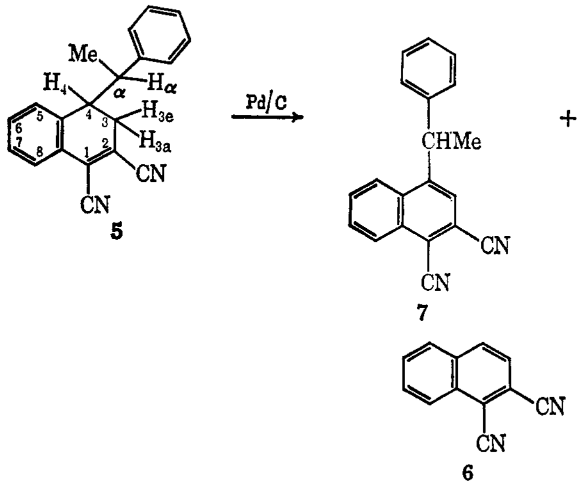
Results

The reaction of dicyanoacetylene with excess α-methylstyrene proceeded quite rapidly at room temperature (pseudo-first-order half-life *ca.* 5 hr), but, as in previous cases, the 1:1 adduct was not obtained. The main product, formed in 63% yield, was an adduct of two molecules of α-methylstyrene to one of dicyanoacetylene to which structure **2** was assigned. Its nmr spectrum showed nine aromatic protons at τ 2.5–3.2, the two protons on C-3 as an AB quartet (J = 18 cps) at 7.0 and 7.6, and a singlet at 8.8 (methyl on C-4). The two geminal α-methyl groups gave rise to a barely split signal at τ 8.5, which at 220 Mc was resolved into two singlets of equal intensity separated by 3.5 cps. The two α-methyl groups are magnetically nonequivalent as a consequence of their proximity to an asymmetric center (C-4).[11] Further structure proof was obtained by the catalytic or photochemical aromatization of **2** to give 1,2-dicyano-4-methylnaphthalene (**3**) and isopropylbenzene. In addition to the diadduct **2**, the reaction of dicyanoacetylene with α-methylstyrene gave, in 4% yield, a compound believed to be 1,2-dicyano-4-phenyl-1,4-pentadiene (**4**) on the basis of its nmr spectrum (see Experimental Section) as well as 1,2-dicyano-4-methylnaphthalene (**3**, 1% yield) (Scheme I). Attempts to trap the intermediate 1:1 adduct (**1**) with excess isobutene or acetone were unsuccessful.

SCHEME I



The reaction of dicyanoacetylene with excess styrene also proceeded at room temperature, but at a somewhat diminished rate (pseudo-first-order half-life *ca.* 40 hr). The products, isolated in 70% yield, proved to be a mixture of the *threo* and *erythro* isomers of 1,2-dicyano-3,4-dihydro-4-(α-methylbenzyl)naphthalene (**5**). The structure proof again rests on the nmr spectra and the fact that both isomers could be aromatized to give a mixture of 1,2-dicyanonaphthalene (**6**) and 1,2-dicyano-4-(α-methylbenzyl)naphthalene (**7**) (eq 5).



(5)

The two isomers were formed in a ratio of 70:30. The nmr spectrum of the major isomer showed the aromatic protons as well-separated multiplets at τ 2.4–2.9 (6 H) and 3.0–3.3 (3 H), the protons on C-3 and C-4 and the α proton as an unresolved multiplet at 6.9–7.2 (4 H), and the methyl group as a doublet (J = 7 cps) centered at 8.68. The spectrum of the minor isomer displayed the nine aromatic protons as a single group of signals at τ 2.4–3.0, the protons on C-3 and C-4 and the α proton

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[7] O. Diels and K. Alder, *Ann. Chem.*, **450**, 237 (1926); K. Alder and H. Niklas, *Ann. Chem.*, **585**, 97 (1954); C. K. Ingold and S. D. Weaver, *J. Chem. Soc.*, **127**, 378 (1925).

[8] K. W. Muir, G. A. Sim, P. Stracham, and C. F. Huebner, *Chem. Ind.* (London), 1581 (1964); C. F. Huebner, P. L. Strachan, E. M. Donogue, N. Cahoon, L. Dorfman, R. Margerison, and E. Wenkert, *J. Org. Chem.*, **32**, 1126 (1967); K. W. Muir and G. A. Sim, *J. Chem. Soc., B*, 667 (1968).

[9] W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Krespan, *J. Amer. Chem. Soc.*, **80**, 2783 (1958).

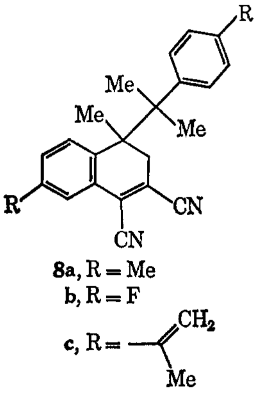
[10] C. D. Weis, *J. Org. Chem.*, **28**, 74 (1963); R. C. Cookson and J. Dance, *Tetrahedron Lett.*, 879 (1962); R. C. Cookson, J. Dance, and M. Godfrey, *Tetrahedron*, **24**, 1529 (1968); E. Ciganek, *Tetrahedron Lett.*, 3321 (1967).

[11] M. van Gorkom and G. E. Hall, *Quart. Rev.* (London), **22**, 14 (1968).

at 7.0–7.5, and the methyl group as a doublet ($J = 7$ cps) centered at 8.85. Unlike the major isomer, the τ 7.0–7.5 region of the minor isomer was well resolved at 220 Mc and the signals due to H-3 and H-α became amenable to first-order analysis. In both isomers, H-4 is believed to be equatorial, and the α-methylbenzyl group axial, since models show serious interactions between H-3, H-5 and the phenyl- and α-methyl groups in the reverse situation precluding free rotation around C-4–C-α. With this assumption, the following assignments were made in the 220-Mc nmr spectrum of the minor isomer: H-3 (equatorial), doublet, ($J_{3e,3a} = 18$ cps) split into doublets ($J_{3e,4e} = 1.5$ cps); H-3 (axial), doublet ($J_{3e,3a} = 18$ cps) split into doublets ($J_{3a,4e} = 6.5$ cps); H-α, doublet ($J_{4e,\alpha} = 9$ cps) split into quartets ($J_{\alpha,\mathrm{Me}} = 7$ cps). H-4e was an unresolved multiplet. The coupling constants provide further evidence for H-4 being equatorial; if it were axial, it would be *trans* and almost coplanar to one of the protons on C-3, and a coupling constant larger than 6.5 cps would result. The dihedral angle between H-3a and H-4e from models is about 50° (and decreases as the 1,3-cyclohexadiene portion of the molecule becomes flatter); on the basis of the Karplus equation, $J_{3a,4e}$ should be *ca.* 4 cps (or larger in a flatter molecule); similarly, $J_{3e,4e}$ should be 2 cps (or smaller) for a dihedral angle of 65° (or more in a flatter molecule).

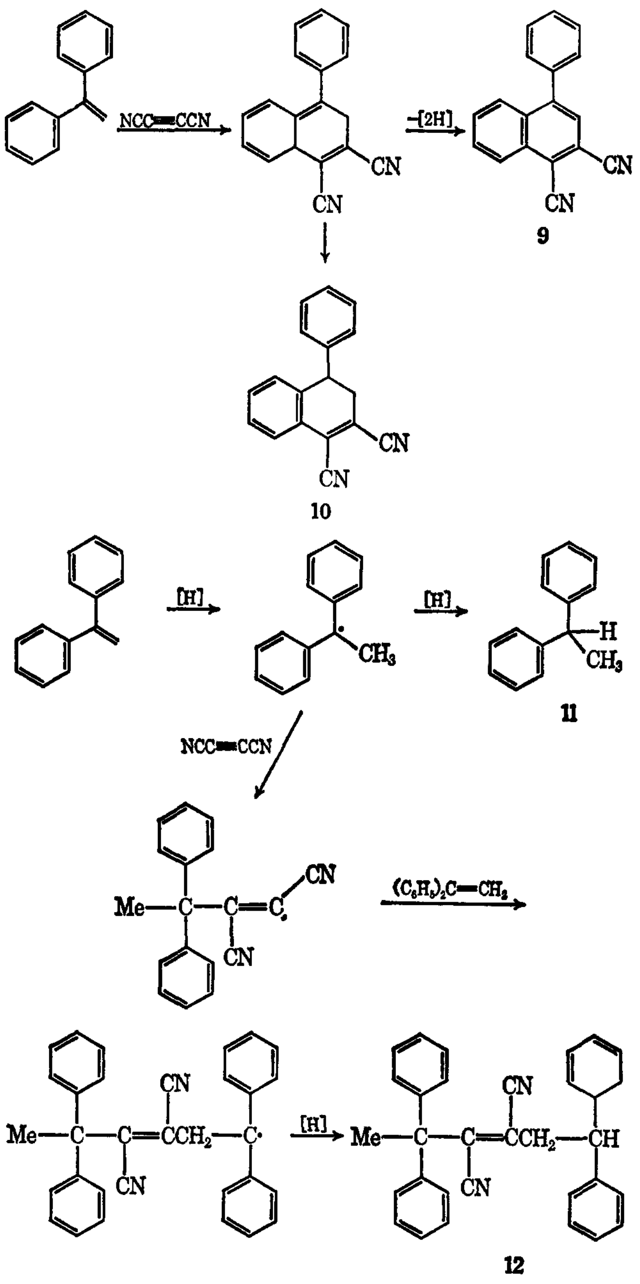
Knowledge of the coupling constant between H-4e and H-α forms the basis of the stereochemical assignments to the two isomers. $J_{4e,\alpha}$ in the minor isomer is 9 cps, indicating that in the most populated rotamer the substituents on C-4 and C-α are either eclipsed (H-4e and H-α *cis* and coplanar) or staggered (H-4e and H-α *trans* and coplanar). Models show that the latter situation is much more likely and that, in this case, the phenyl group on C-α points away from the molecule in the *erythro* isomer. In the *threo* isomer the C-α phenyl group resides over the C-5 to C-6 portion of the molecule, which should result in an upfield shift of some of the aromatic protons as a result of the diamagnetic shielding. Whereas all aromatic protons are in the normal region ($\tau < 3$) in the minor isomer, three are shifted upfield in the major isomer. On the basis of this argument, the major isomer would thus have the *threo*, and the minor the *erythro* configuration.

A number of α-methylstyrenes substituted in the *para* position gave analogous 2:1 adducts with dicyanoacetylene. Thus, α,p-dimethylstyrene, *p*-fluoro-α-methylstyrene, and *p*-diisopropenylbenzene gave adducts **8a**, **8b**, and **8c**, respectively. Dicyanoacetylene reacted readily also with 1,1-diphenylethylene, but the main product, isolated in 52% yield, was 1,2-dicyano-4-phenylnaphthalene (**9**) (Scheme II). The reaction thus followed the same path as that reported for dimethyl acetylenedicarboxylate (eq 1).[2] The recovered 1,1-diphenylethylene contained 1,1-diphenylethane (**11**) identified by nmr spectroscopy and by comparison of its retention time on gas chromatography with that of an authentic sample. There were also isolated, in 0.3 and 7% yield, two compounds assigned structures **10** and **12**, respectively. The nmr spectrum of **10**[12,13] showed an unsymmetrical doublet (separation



8a, R = Me
b, R = F
c, R = $-C(=CH_2)Me$

SCHEME II



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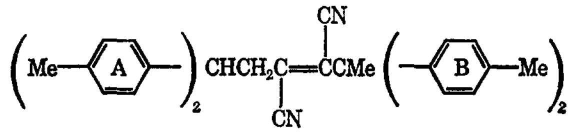
(12) A very similar spectrum has been reported[13] for the related 9-phenyl-9,10-dihydrophenanthrene (**19**).

(13) W. L. Dilling, *Tetrahedron Lett.*, 939 (1966).

8.5 cps) at τ 7.0 (2 H) and an unsymmetrical triplet (separation 8.5 cps) at 5.7 (1 H). The aromatic absorption (τ 2.1–3.1) corresponded to 11.5, rather than 9.0 protons, indicating that the sample may have been contaminated by a small amount of 1,2-dicyano-4-phenylnaphthalene (**9**). Dehydrogenation of compound **10** gave 1,2-dicyano-4-phenylnaphthalene (**9**).

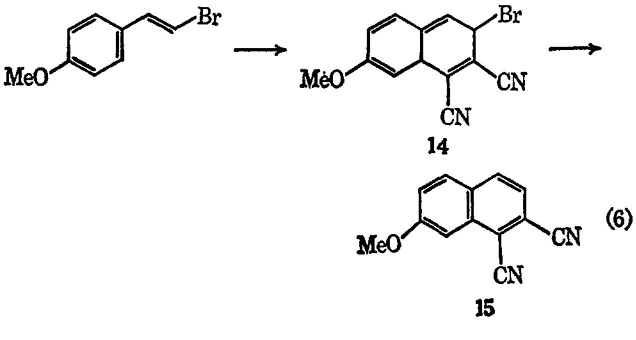
The nmr spectrum of compound **12** displayed 20 aromatic protons at τ 2.5–3.3, a triplet (J = 8.5 cps) at 5.5 (1 H), a doublet (J = 8.5 cps) at 6.5 (2 H), and a singlet at 8.0 (3 H). The analogous product **13** was prepared from dicyanoacetylene and 1,1-di-p-tolylethylene; although the amount isolated was too small to be characterized by micro analysis, its nmr spectrum (at 100 Mc) strongly indicated structure **13**.



13

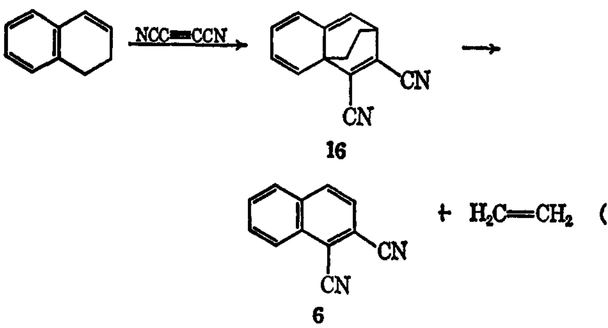
The spectrum showed the aromatic protons in ring A as a weakly split single band at τ 2.8, the aromatic protons in ring B as an AB quartet (J = 8.5 cps) at 2.9 and 3.2, a triplet (J = 8 cps) at 5.6 (1 H), a doublet (J = 8 cps) at 6.5 (2 H), two singlets (6 H each) at 7.6 (separation 3 cps at 100 Mc and 1.6 cps at 60 Mc), and a singlet at 8.0 (3 H). The observation of only two signals due to methyl groups attached to aromatic rings indicates the presence of two pairs of equivalent phenyl rings in **13** and, consequently, also in **12**. A possible mechanism for the formation of compound **12** is shown in Scheme II.

Reaction of dicyanoacetylene with p-methoxystyrene caused polymerization of the latter; with p-methoxy-β-bromostyrene, 1,2-dicyano-7-methoxynaphthalene (**15**) was formed in 42% yield, presumably by 1,4-dehydrobromination of the initial adduct **14** (eq 6).



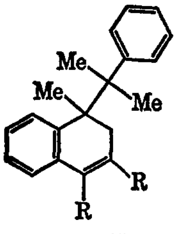
(6)

Indene and dicyanoacetylene reacted readily below room temperature; the only product isolated (in 10% yield) had the composition of an adduct of two molecules of dicyanoacetylene and one of indene. The structure was not determined, but it is probably analogous to that of the product[8] from the reaction of dimethyl acetylenedicarboxylate with indene (eq 4). Reaction of dicyanoacetylene with 1,2-dihydronaphthalene required heating to 120°. The product, isolated in 36% yield, was identified as 1,2-dicyanonaphthalene (**6**) (eq 7); it was probably formed by retrodiene fission of the initial adduct **16**. The analogous reaction course was reported for the interaction of 1,2-dihydronaphthalene with dimethyl acetylenedicarboxylate.[14] No reaction occurred between dicyanoacetylene and methyl cinnamate, coumarin, or acetophenone at elevated temperatures. Reaction between dicyanoacetylene and vinylmesitylene required heating to 100°, but no pure adducts could be isolated.

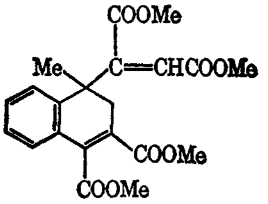


(7)

The formation of 2:1 adducts of type **2** was also observed with other activated acetylenes, but elevated temperatures were required. Thus, reaction of hexafluoro-2-butyne with excess α-methylstyrene at 100° gave the adduct **17a** in 58% yield. Dimethylacetylenedicarboxylate reacted with excess α-methylstyrene at 100° to give the 1:2 adduct **17b** (23% yield) as well as a second product (10% yield) believed to be the 2:1 adduct **18** on the basis of its nmr spectrum (see Experimental Section). Alder and co-workers[2] reported the formation of dimethyl 4-methylnaphthalene-1,2-dicarboxylate (in unspecified yield) in the reaction of equimolar amounts of α-methylstyrene and dimethyl acetylenedicarboxylate at 120°. From the reaction of styrene with dimethyl acetylenedicarboxylate, they obtained a 1:2 adduct of unspecified structure; this may have been an adduct of type **18**.



17a, R = CF$_3$
b, R = COOMe



18

The reaction of benzyne with styrene[13] and with α-methylstyrene[15] has been reported. With styrene (fivefold excess), 9-phenyl-9,10-dihydrophenanthrene (**19**) was isolated in 87% yield; this product corresponds to an adduct of two molecules of benzyne to one of styrene and the reaction thus is analogous to that of azodicarboxylic ester with styrene (eq 3).[7,16,17] The reaction between α-methylstyrene and benzyne[15] gives mainly the product of an ene reaction involving the isopropenyl group of α-methylstyrene; a small

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(14) F. Pascher, Ph.D. Thesis, University of Cologne, 1944.

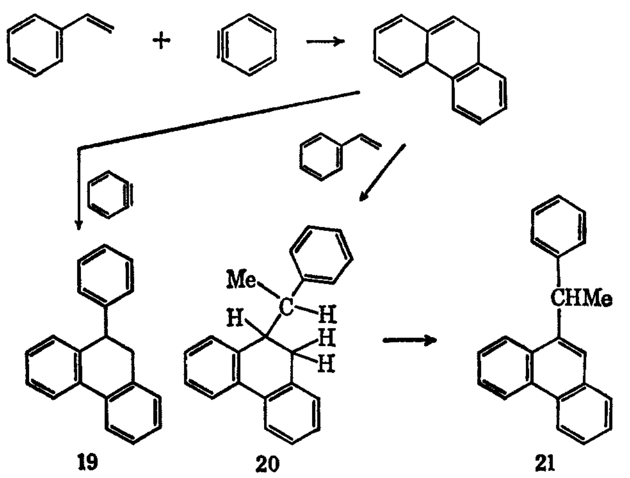
(15) E. Wolthuis and W. Cady, *Angew. Chem.*, **79**, 575 (1967).

(16) Dilling[13] suggests a three-step ionic mechanism for the addition of the second molecule of benzyne to the initial Diels–Alder adduct. A more likely mechanism would be a concerted, one-step ene reaction, since benzyne is known[15,17] to undergo this type of addition very readily.

(17) R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Verlag Chemie Gmbh, Weinheim, 1967, pp 197–199.

amount of 9-methylphenanthrene, the aromatization product of an initial Diels-Alder adduct, was also isolated. We repeated the reaction of benzyne with styrene using a large (fiftyfold) excess of the latter. In this case, the 1:2 adducts **20** (*threo* and *erythro* isomers) were obtained instead of the 2:1 adduct isolated[13] when a small excess of styrene was used. The ratio of the two isomers was about 1:1. The structures follow from the nmr spectra and the fact that catalytic aromatization of **20** gave 9-(α-methylbenzyl)-phenanthrene (**21**) (Scheme III), an authentic sample of which was prepared by standard methods.

SCHEME III

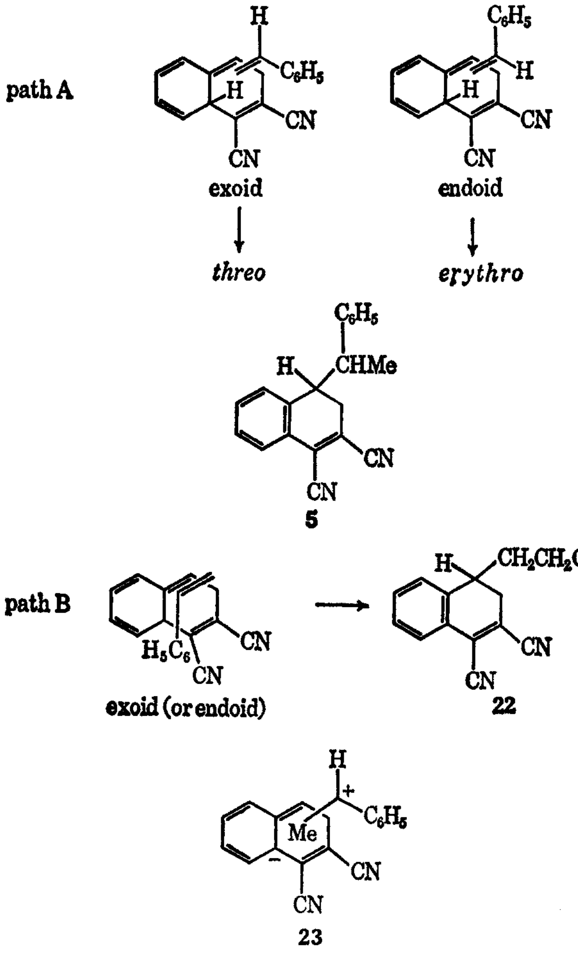


Discussion

The formation of 2:1 adducts such as compound **2** (Scheme I) from styrenes and activated acetylenes is most easily explained as proceeding by a sequence of a Diels-Alder addition and an ene reaction. The unusual features of these reactions are that both proceed under such mild conditions and that the styrene, rather than the acetylene, acts as the enophile in the second step. The driving force for the ene reaction is provided by the rearomatization of ring A. Even so, the low activation energy of this reaction is surprising in view of the stringent entropy requirements and the fact that in the case illustrated in Scheme I, carbon-carbon bond formation produces a crowded hexasubstituted ethane derivative. It is noteworthy in this connection that 1,2-dicyano-1,4-cyclohexadiene, which is analogous to **1** except for the lack of ring A, does not react with α-methylstyrene at 150°.

The two centers of the allylic system involved in the ene reaction, namely the π orbitals of the exocyclic double bond, and the C-8a-H bond in **1** (Scheme I), are almost coplanar and thus well oriented for a concerted reaction. In principle, the enophile can approach the allylic system in four different ways as illustrated in Scheme IV. There may be *exo-* or *endo*-like transition states, and the allylic hydrogen may be transferred either to the methylene carbon of styrene, or to the one carrying the phenyl group. The latter course is not followed to any significant extent since the product of such a reaction, 1,2-dicyano-2,3-dihydro-4(β-phenylethyl)naphthalene (**22**), could not be detected. Models indicate that there is little difference in nonbonded interactions between the transition states of paths A and B. It is thus likely that the ene reaction, at least in this case, is not completely synchronous. In the transition state, carbon-hydrogen bond formation has proceeded to a larger extent than carbon-carbon bond formation, resulting in a partial carbonium, carbanion, or radical character of the carbon carrying the phenyl group. A two-step process, involving complete transfer of the hydrogen followed by carbon-carbon bond formation, is considered unlikely since the allylic anion, cation, or radical (*e.g.*, **23**) should be prone to side reactions such as aromatization or hydrogen abstraction, unless recombination of the two fragments is favored by occurring in a cage. Furthermore, the observed transfer of optical activity in two examples of an ene reaction[18,19] precludes intermediates of type **23** in these reactions.[20a]

SCHEME IV



As far as orientation of the styrene in path A is concerned, it appears that exoid attack is slightly favored in the case of the dicyanoacetylene adduct, if one accepts the rather tentative stereochemical assignments of the isomers of **5**. There is no stereochemical preference in the formation of adducts **20** from benzyne and styrene. In the case of the ene reaction of maleic anhydride with *cis-* and *trans*-2-butenes,[19] slight

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[18] R. K. Hill and M. Rabinowitz, *J. Amer. Chem. Soc.*, **86**, 965 (1964).

[19] J. A. Berson, R. G. Wall, and H. D. Perlmutter, *ibid.*, **88**, 187 (1966).

[20] (a) See footnote 7 in ref 19; (b) see footnote 10 in ref 19.

preference for endoid attack was observed. Orbital symmetry considerations predict that endoid attack should be favored in the ene reaction, but that the preference should be smaller than in the Diels–Alder reaction.[20b]

Experimental Section

Reaction of Dicyanoacetylene with Styrene.—A mixture of 3.75 g of dicyanoacetylene[1] and 60 ml of styrene (Eastman White Label, undistilled) was allowed to stand at room temperature for 190 hr. Gas chromatographic analysis (silicone grease column, 95°) showed the half-life of dicyanoacetylene to be *ca.* 40 hr. Most of the excess styrene was removed at 40° bath temperature (0.5 mm), the residue was passed through 100 g of Florisil, and the material eluted with 1.75 l. of methylene chloride was kept at 100° under 0.1-μ pressure for 1 hr to give 9.81 g (70% yield) of a viscous oil. Its nmr spectrum showed the ratio of the two isomeric 2:1 adducts (see below) to be *ca.* 70:30. The mixture could be short-path distilled at 115° bath temperature (0.1-μ pressure) without change in composition. The two isomers could be separated by chromatography on Florisil and elution successively with hexane-benzene (1:1), benzene, and methylene chloride–tetrahydrofuran (THF) (99:1). The minor isomer was eluted first. However, isolation of larger amounts by this method was tedious. The crude mixture (5.86 g) was dissolved in 30 ml of hot ethanol; the mixture was cooled, filtered, and seeded with a crystal of the major isomer obtained by chromatography. There was obtained 1.82 g of the major isomer in the form of colorless crystals; a second crop of 0.81 g was obtained by crystallization of the concentrated mother liquor from 15 ml of ethanol. Removal of the solvent from the mother liquors of the second crystallization gave 3.04 g of an oil, which was dissolved in 9 ml of ethanol. Seeding with a crystal of the minor isomer gave 1.10 g of that product in the form of colorless crystals. Analytical samples of the two isomers of 1,2-dicyano-3,4-dihydro-4-(α-methylbenzyl)naphthalene were prepared by recrystallizations from ethanol.

The major isomer had mp 100–101°; λ_{max}^{MeCN} 311 mμ (ε 9800) and 243 (11,800); ν_{max}^{KBr} 3080, 3040, 2980, 2920, 2235 (sh), 2220, 1610, and 1575 cm^{-1}, among others.

Anal. Calcd for $C_{20}H_{16}N_2$: C, 84.48; H, 5.67; N, 9.85. Found: C, 84.58; H, 5.81; N, 9.68.

The minor isomer had mp 121–122°; λ_{max}^{MeCN} 308 mμ (ε 10,900) and 242 (12,200); ν_{max}^{KBr} 3080, 3030, 2980, 2220 (sh), 2210, 1605 and 1565 cm^{-1}, among others.

Anal. Calcd for $C_{20}H_{16}N_2$: C, 84.48; H, 5.67; N, 9.85; mol wt, 284. Found: C, 84.52; H, 5.79; N, 9.76; mol wt, 299 (cryoscopically in benzene).

The nmr spectra of the two isomers are presented in the Discussion.

Aromatization of 1,2-Dicyano-3,4-dihydro-4-(α-methylbenzyl) naphthalene.—The crude mixture of the two adducts (1.060 g) was stirred and heated under reflux in 25 ml of xylene with 400 mg of palladium on charcoal (10%) for 2 hr. Removal of the solvent from the filtered solution gave 1.059 g of a dark semisolid. Chromatography over Florisil gave first 576 mg of a product (eluted with benzene followed by methylene chloride) consisting mostly of 1,2-dicyano-4-(α-methylbenzyl)naphthalene; methylene chloride–THF (7:3) eluted 226 mg of a mixture of the above product and 1,2-dicyanonaphthalene. An analytical sample of 1,2-dicyano-4-(α-methylbenzyl)naphthalene, prepared by crystallization from isopropyl alcohol, had mp 145–146°; uv λ_{max}^{MeCN} 348 mμ (ε 5600), 330 (4700), 315 (7800), 305 (sh, 6600), 242 (63,000), and 219 (32,000); ir ν_{max}^{KBr} 3080, 3030, 2980, 2230, 1585, 760, 750, 710, and 675 cm^{-1}, among others; nmr (in $CDCl_3$) multiplets at τ 1.7–1.9 (2 H) and 2.2–2.4 (3 H), a fairly sharp singlet at 2.8 (5 H), a quartet (*J* = 7 cps) centered at 5.0 (1 H), and a doublet (*J* = 7 cps) centered at 8.2 (3 H).

Anal. Calcd for $C_{20}H_{14}N_2$: C, 85.08; H, 5.00; N, 9.92. Found: C, 85.02; H, 4.84; N, 10.29.

The 1,2-dicyanonaphthalene had mp 194–195° after crystallization from isopropyl alcohol (lit.[21] mp 190°); uv λ_{max}^{MeCN} 345 mμ (ε 3700), 330 (3300), 311 (5300), 300 (sh, 4900), 247 (68,000), and 214 (36,000); nmr only aromatic protons.

Anal. Calcd for $C_{12}H_6N_2$: C, 80.89; H, 3.40; N, 15.72. Found: C, 81.43; H, 3.42; N, 15.86.

Reaction of Dicyanoacetylene with α-Methylstyrene.—A mixture of 3.098 g of dicyanoacetylene[1] and 55 ml of freshly distilled α-methylstyrene was allowed to stand at room temperature for 24 hr. The half-life of dicyanoacetylene, determined gas chromatographically, was *ca.* 5 hr. Removal of excess α-methylstyrene at 40° (0.3 mm) gave 11.39 g of a dark solid which was purified by chromatography on 100 g of Florisil. Elution with 1 l. of methylene chloride gave 9.27 g of the crude adduct. Crystallizations from benzene and acetonitrile gave a total of 8.04 g (63%) of 1,2-dicyano-3,4-dihydro-4-methyl-4-(α,α-dimethylbenzyl)naphthalene (**2**). An analytical sample (acetonitrile) had mp 193–194°; uv λ_{max}^{MeCN} 313 mμ (ε 8100), 245 (12,700), and 240 (sh, 11,100); ir ν_{max}^{KBr} 3050, 3010, 2970, 2870, 2220, 1620, 1600, 770, 755, and 700 cm^{-1}, among others; for nmr, see Discussion.

Anal. Calcd for $C_{22}H_{20}N_2$: C, 84.58; H, 6.45; N, 8.97; mol wt, 312. Found: C, 84.90; H, 6.45; N, 8.63; mol wt, 320 (ebullioscopically in benzene).

The nmr spectrum of the combined mother liquors showed the presence of 1,2-dicyano-4-phenyl-1,4-pentadiene (**4**, *ca.* 5% yield) and 1,2-dicyano-4-methylnaphthalene (**3**, *ca.* 1% yield) in addition to 1,2-dicyano-3,4-dihydro-4-methyl-4-(α,α-dimethylbenzyl)-naphthalene. Chromatography over Florisil and elution with benzene first gave fractions enriched in **2**, followed by fractions enriched in **4**. The nmr spectrum of 1,2-dicyano-4-phenyl-1,4-pentadiene (**4**) showed a triplet (*J* = 1.5 cps) at τ 4.1 (1 H), a singlet at 4.3 (1 H), a broadened singlet (width at half-height 2 cps) at 4.7 (1 H), and a narrow multiplet at 6.4 (2 H) in addition to aromatic absorption. No further purification and characterization were attempted. Elution with methylene chloride–THF (95:5) and crystallization from isopropyl alcohol gave 1,2-dicyano-4-methylnaphthalene (**3**), identified by comparison of its ir spectrum with that of the sample obtained by aromatization of 1,2-dicyano-3,4-dihydro-4-methyl-4-(α,α-dimethylbenzyl)-naphthalene (see below).

Aromatization of 1,2-Dicyano-3,4-dihydro-4-methyl-4-(α,α-dimethylbenzyl)naphthalene.—A mixture of 400 mg of 1,2-dicyano-3,4-dihydro-4-methyl-4-(α,α-dimethylbenzyl)naphthalene, 200 mg of palladium on charcoal (10%), and 10 ml of toluene was stirred under reflux for 4 hr. Removal of the solvent from the filtered solution and crystallization of the residue from acetonitrile gave 1,2-dicyano-4-methylnaphthalene: mp 206.5–207.5°; uv λ_{max}^{MeCN} 348 mμ (ε 5000), 332 (4100), 318 (6900), 307 (6000), 246 (69,000), and 219 (29,000); ir ν_{max}^{KBr} 3080 3050, 2990, 2960, 2230, 1595, 890, 765, 695, and 675 cm^{-1}, among others; nmr (in $CDCl_3$) multiplets at τ 1.7–2.1 (2 H) and 2.1–2.4 (2 H) and singlets at 2.6 (1 H) and 7.2 (3 H).

Anal. Calcd for $C_{13}H_8N_2$: C, 81.23; H, 4.20; N, 14.58; mol wt, 192.21. Found: C, 81.12; H, 4.32; N, 14.70; mol wt, 222 (ebullioscopically in benzene).

Reaction of Dicyanoacetylene with 4,α-Dimethylstyrene.—A mixture of 1.55 g of dicyanoacetylene[1] and 40 ml of 4,α-dimethylstyrene (Shell Chemical Co.) was allowed to stand at room temperature for 15 hr. Removal of excess styrene under 0.1-mm vacuum at 40° and crystallization of the residue from 30 ml of acetonitrile gave 3.75 g of 1,2-dicyano-3,4-dihydro-4-(4′,α,α-trimethylbenzyl)-4,7-dimethylnaphthalene (**8a**), mp 191.5–193°, unchanged on recrystallization from acetonitrile. A second crop of 0.45 g of product was obtained from the mother liquors. The combined yield was 4.20 g (61%); uv λ_{max}^{MeCN} 345 mμ (sh) (ε 3800), 307 (8000), and 250 (15,000); ir ν_{max}^{KBr} 2220, 1615, 1565, 840, and 820 cm^{-1}, among others; nmr (in $CDCl_3$) multiplet at τ 2.6–2.8 (3 H), AB quartet at 2.9 and 3.2 (*J* = 8 cps, 4 H), AB quartet at 7.0 and 7.6 (*J* = 18 cps, 2 H), and singlets at 7.5 (3 H), 7.6 (3 H), 8.5 (6 H), and 8.7 (3 H).

Anal. Calcd for $C_{24}H_{24}N_2$: C, 84.67; H, 7.11; N, 8.21. Found: C, 84.51; H, 7.17; N, 8.25.

Reaction of Dicyanoacetylene with *p*-Diisopropenylbenzene.—To a refluxing solution of 18.20 g of *p*-diisopropenylbenzene (Shell Development Co.) in 100 ml of benzene was added, under nitrogen, during 35 min, a solution of 1.79 g of dicyanoacetylene in 20 ml of benzene. The mixture was heated under reflux for 2.5 hr and then allowed to stand at room temperature for 4 days. The solvent was removed and most of the unreacted diisopropenyl benzene was sublimed at 110° (0.1 mm). The residue, on chromatography over 180 g of Florisil and elution with methylene chloride, gave a slowly solidifying solid which on crystallization from isopropyl alcohol gave 2.08 g (23% yield) of 1,2-dicyano-3,4-

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(21) P. T. Cleve, *Ber.*, **25**, 2475 (1892).

dihydro-4-methyl-4-(α,α-dimethyl-4-isopropenylbenzyl)-7-isopropenylnaphthalene (**8c**): mp 163–165°; uv $\lambda_{\max}^{\mathrm{MeCN}}$ 360 mμ (sh, ϵ 200), 310 (8300), 260 (35,000), and 206 (35,000); nmr (in $CDCl_3$) multiplets at τ 2.3–2.8 (5 H), 3.0–3.3 (2 H), and 4.5–5.0 (4 H), AB quartet (J = 18 cps) at 7.0 and 7.6 (2 H), singlet, split further, at 7.8 (6 H), and singlets at 8.5 (6 H) and 8.7 (3 H).

Anal. Calcd for $C_{28}H_{28}N_2$: C, 85.68; H, 7.19; N, 7.14. Found: C, 85.65; H, 7.23; N, 7.25.

Reaction of Dicyanoacetylene with *p*-Fluoro-α-methylstyrene.—A mixture of 23 g of *p*-fluoro-α-methylstyrene (Aldrich Chemical Co, Inc.) and 1.302 g of dicyanoacetylene was allowed to stand at room temperature for 5 days. Most of the excess styrene was removed at 30° (0.1 μ). The residue was heated with 20 ml of ethanol. The mixture was cooled and the tan crystals were collected by filtration and washed with cold ethanol to give 4.430 g (74%) of 1,2-dicyano-3,4-dihydro-4-methyl-4-(α,α-dimethyl-4-fluorobenzyl)-7-fluoronaphthalene. An analytical sample (ethyl acetate) had mp 230–231°; uv $\lambda_{\max}^{\mathrm{MeCN}}$ 335 mμ (ϵ 3800), 295 (7700), and 244 (13,500); ir $\nu_{\max}^{\mathrm{KBr}}$ 3080, 2990, 2900, 2225 and 1610 cm^{-1}, among others.

Anal. Calcd for $C_{22}H_{18}F_2N_2$: C, 75.85; H, 5.21; F, 10.91; N, 8.04. Found: C, 75.79; H, 4.91; F, 10.92; N, 8.49.

Reaction of Dicyanoacetylene with 1,1-Diphenylethylene.—A mixture of 4.91 g of dicyanoacetylene and 100 ml of 1,1-diphenylethylene, contained in a large molecular still, was allowed to stand at room temperature for 137 hr. Excess diphenylethylene was distilled at 95° bath temperature (0.1 μ). The nmr spectrum of the recovered 1,1-diphenylethylene indicated the presence of 1,1-diphenylethane (quartet at τ 6.6 and doublet at 9.0). This was confirmed by gas chromatography [1-m 20% *m*-bis(phenoxy)-phenoxybenzene column] which showed a peak (5% of the total area) having the same retention time as that of authentic 1,1-diphenylethane. This peak was not present in the 1,1-diphenylethylene used.

The residue from the distillation was heated with 30 ml of acetonitrile and the crystals obtained on cooling were collected by filtration to give 8.65 g (52% yield) of 1,2-dicyano-4-phenylnaphthalene: mp 196–197°; uv $\lambda_{\max}^{\mathrm{MeCN}}$ 353 mμ (ϵ 8400), 322 (9100), 250 (63,000), and 215 (31,000); nmr only aromatic protons at τ 1.5–3.1.

Anal. Calcd for $C_{18}H_{10}N_2$: C, 85.02; H, 3.97; N, 11.02; mol wt, 254. Found: C, 84.82; H, 3.96; N, 11.14; mol wt, 259.

The mother liquor was concentrated and the residue (7.19 g of a brown oil) was chromatographed over 200 g of Florisil. Elution with benzene–hexane (1:1) gave additional 1,1-diphenylethylene; with methylene chloride there was first eluted 2.30 g of a slowly solidifying oil which on crystallization from ethanol gave 1.95 g (7% yield) of 1,2-dicyano-1-(2,2-diphenylethyl)-2-methyldiphenylmethylethylene (**12**): mp 130–131°; uv (in MeCN) only end absorption with a long trail (ϵ_{300} 600, ϵ_{250} 7500, and ϵ_{220} 25,000); ir $\nu_{\max}^{\mathrm{KBr}}$ 3070, 3030, 2990, 2910, 2220, and 1600 cm^{-1}, among others; for nmr, see Discussion.

Anal. Calcd for $C_{32}H_{26}N_2$: C, 87.63; H, 5.98; N, 6.39. Found: C, 87.55; H, 5.79; N, 6.77.

Further elution with methylene chloride gave a mixture of 1,2-dicyano-4-phenylnaphthalene (**9**) and 1,2-dicyano-3,4-dihydro-4-phenylnaphthalene (**10**). Crystallization from isopropyl alcohol first gave pure **9**; concentration of the mother liquors and two crystallizations of the residue from isopropyl alcohol gave *ca.* 50 mg (0.3% yield) of 1,2-dicyano-3,4-dihydro-4-phenylnaphthalene (**10**): mp 127–128°; ir $\nu_{\max}^{\mathrm{KBr}}$ 3080 (s), 3030 (s), 2930 (w), 2850 (s), 2200 (m), 1600 (m), and 1560 cm^{-1} (m), among others; uv $\lambda_{\max}^{\mathrm{cyclohexane}}$ 347 mμ (shoulder, ϵ 1500), 305 (12,300), 249 (14,600), 242 (18,800), and 235 (sh, 13,700);[22] for nmr, see Discussion.

Anal. Calcd for $C_{18}H_{12}N_2$: C, 84.35; H, 4.73; N, 10.93. Found: C, 84.13; H, 4.74; N, 10.84.

A solution of 15 mg of 1,2-dicyano-3,4-dihydro-4-phenylnaphthalene in 15 ml of xylene was heated under reflux with 124 mg of 10% palladium on charcoal for 1 hr. Concentration of the filtered solution left 12 mg of a solid, the ir spectrum of which was that of 1,2-dicyano-4-phenylnaphthalene (**9**). Recrystallization from ethanol gave a sample, mp and mmp 196–197°.

Reaction of Hexafluoro-2-butyne with α-Methylstyrene.—A mixture of 124 g of freshly distilled α-methylstyrene and 10 g of hexafluoro-2-butyne, contained in a 400-ml stainless steel cylinder, was heated to 100° for 12 hr. Removal of the excess α-methylstyrene and short-path distillation of the residue [120–140° bath temperature (0.2 μ)] gave 14.23 g (58%) of 1,2-bis-(trifluoromethyl)-3,4-dihydro-4-methyl-4-(α,α-dimethylbenzyl)-naphthalene (**17a**) as an oil which crystallized slowly on scratching. An analytical sample (acetonitrile) had mp 84.5–85.5°; uv $\lambda_{\max}^{\mathrm{MeCN}}$ 276 mμ (ϵ 6700) and 223 (sh, 17,300); ^1H nmr (in $CDCl_3$) multiplet at τ 2.6–3.0 (9 H), AB quartet at 7.05 and 7.82 (J = 20 cps, all components are split further, 2 H), and singlets at 8.68 (6 H) and 8.73 (3 H); ^{19}F nmr (in $CDCl_3$, shifts in cycles per second from external Freon 11) two quartets of equal intensities (J = 13.5 cps) at +3206 and +3475, both of which are split further.

Anal. Calcd for $C_{22}H_{20}F_6$: C, 66.33; H, 5.07; F, 28.61. Found: C, 66.40; H, 5.00; F, 28.56.

Reaction of Dimethyl Acetylenedicarboxylate with α-Methyl styrene.—A mixture of 1.018 g of dimethyl acetylenedicarboxylate and 25 ml of α-methylstyrene was allowed to stand at room temperature for 23 hr. Removal of excess ester and styrene from a 10-ml aliquot gave only 46 mg of an oil. The remaining mixture was transferred to a Carius tube, which was sealed under vacuum and heated to 100° for 4 hr. The unreacted starting materials were removed at 40° (0.5 μ), leaving 986 mg of a colorless semisolid. Chromatography on Florisil (30 g), elution with methylene chloride, and crystallization from ethanol gave 387 mg (23%) of dimethyl 3,4-dihydro-4-methyl-4-(α,α-dimethylbenzyl)-naphthalene-1,2-dicarboxylate (**17b**). An analytical sample (acetonitrile) had mp 135–137°; uv $\lambda_{\max}^{\mathrm{MeCN}}$ 299 mμ (ϵ 10,400) and 232 (16,600); ir $\nu_{\max}^{\mathrm{KBr}}$ 1740, 1715, and 1635 cm^{-1}, among others; nmr ($CDCl_3$) multiplet at τ 2.6–3.1 (9 H), singlets at 6.1 (3 H) and 6.2 (3 H), AB quartet at 6.8 and 7.7 (J = 18 cps, 2 H), and singlet at 8.7 (9 H).

Anal. Calcd for $C_{24}H_{26}O_4$: C, 76.16; H, 6.93. Found: C, 75.89; H, 6.92.

Further elution with methylene chloride–THF (9:1) gave 140 mg (10% crude yield) of an oil, which, according to its nmr spectrum in $CDCl_3$, appeared to be mostly dimethyl 3,4-dihydro-4-(1,2-dicarbomethoxyvinyl)-4-methylnaphthalene-1,2-dicarboxylate: singlet at τ 8.3 (3 H), AB quartet (J = 17 cps) at 6.8 and 7.5 (2 H), four singlets of equal intensities at 6.1–6.4 (3 H each), singlet at 4.7 (1 H), and aromatic protons at 2.5–2.8.

Reaction of Dicyanoacetylene with 1,2-Dihydronaphthalene.—A mixture of 10 ml of 1,2-dihydronaphthalene and 447 mg of dicyanoacetylene was heated in a sealed Carius tube to 120° for 10 hr. Removal of the excess dihydronaphthalene gave 931 mg of a dark residue which on chromatography over Florisil gave 382 mg (36% yield) of 1,2-dicyanonaphthalene, eluted with methylene chloride and identified by comparison of its ir spectrum with that of the minor aromatization product of the styrene–dicyanoacetylene adducts (see above).

Reaction of Dicyanoacetylene with Indene.—To a solution of 10 ml of freshly distilled indene in 50 ml of toluene was added, at −50°, under nitrogen, a solution of 1.05 g of dicyanoacetylene in 10 ml of toluene. The mixture was stirred at −70° for 3 hr and at room temperature for 60 hr. The solvent and excess indene were removed under vacuum, leaving 1.614 g of a dark oil. Chromatography on Florisil first gave 300 mg of indene. Elution with methylene chloride gave 400 mg of a mixture of an oil and crystals. Trituration with methylene chloride gave 185 mg (10% yield) of the crystalline adduct. A sample crystallized from acetonitrile melted with decomposition at 250°: uv $\lambda_{\max}^{\mathrm{MeCN}}$ 242 mμ (ϵ 14,700) and 235 (14,300).

Anal. Calcd for $C_{17}H_8N_4$: C, 76.10; H, 3.01; N, 20.89. Found: C, 76.41; H, 3.04; N, 20.97.

Reaction of Dicyanoacetylene with *p*-Methoxy-β-bromostyrene.—A mixture of 900 mg of *p*-methoxy-β-bromostyrene,[23] 738 mg of dicyanoacetylene, and 7 ml of benzene was heated in a Carius tube to 160° for 6 hr. Removal of the solvent left 1.357 g of a tan solid, which on chromatography on Florisil first gave 334 mg of a yellow semisolid, eluted with benzene. Elution with methylene chloride and crystallization from acetonitrile gave 371 mg (42% yield) of 1,2-dicyano-7-methoxynaphthalene in the form of pink fluffy needles: mp 187–188°; uv $\lambda_{\max}^{\mathrm{MeCN}}$ 373 mμ (ϵ 4600), 306 (3500), 295 (4400), 286 (sh, 3600), 257 (54,000), and 222 (39,000); ir $\nu_{\max}^{\mathrm{KBr}}$ 2235 and 1630 cm^{-1}, among

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(22) Part of these absorptions may be due to a small amount of 1,2-dicyano-4-phenylnaphthalene (**9**) present in this sample; see Discussion.

(23) W. Manchot, *Ann.*, **387**, 257 (1912).

others; nmr (in hexadeuteriodimethyl sulfoxide) multiplet at τ 1.6–2.9 (5 H) and singlet at 6.1 (3 H).

Anal. Calcd for $C_{13}H_8N_2O$: C, 74.98; H, 3.88; N, 13.46. Found: C, 74.81; H, 4.06; N, 13.45.

Reaction of Benzyne with Styrene.—To a refluxing mixture of 250 g (2.32 mol) of styrene and 200 ml of methylene chloride were added, simultaneously from two addition funnels, solutions of 6.60 g (48.2 mmol) of anthranilic acid in 30 ml of THF and of 6.15 g (57.2 mmol) of isopentyl nitrite in 35 ml of methylene chloride. The addition took 4 hr. After heating under reflux for an additional 2 hr, the solvents and excess styrene were removed and the residue was short path distilled, giving 4.11 g of viscous oil boiling at 150–170° bath temperature (0.3 μ). The nmr spectrum showed the ratio of *threo-* and *erythro*-9,10-dihydro-9-(α-methylbenzyl)phenanthrenes to be 1:1 as judged from the ratio of the two methyl doublets. Chromatography of 1.10 g of this material over 55 g of silicic acid (elution with hexane) gave a total of 951 mg (26% yield) of the two isomers. The nmr spectrum of the isomer being eluted first showed multiplets at τ 2.1–3.2 (13 H) and 6.8–7.9 (4 H) and a doublet (J = 6.3 cps) at 9.0 (3 H). The spectrum of the other isomer showed multiplets at τ 2.1–3.7 (13 H) and 6.8–7.5 (4 H) and a doublet (J = 6.4 cps) at 8.8 (3 H). Complete separation of the two isomers could not be achieved. The fractions were combined and short path distilled at 150° bath temperature (0.5 μ) to give an analytical sample of a *ca.* 1:1 mixture of the two isomers: uv $\lambda_{\max}^{\text{cyclohexane}}$ 299 mμ (ϵ 3900), 266 (15,000), and 210 (48,000).

Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.08; mol wt, 284. Found: C, 93.10; H, 7.08; mol wt, 284 (mass spectroscopically).

Dehydrogenation of 9,10-Dihydro-9-(α-methylbenzyl)phenanthrene.—A mixture of *threo* and *erythro* isomers (ratio 1:1, 400 mg), 10% palladium on charcoal (350 mg), and toluene (3 ml), contained in a sealed Carius tube, was heated to 220° for 6 hr. Removal of the solvent from the filtered solution gave 353 mg of a colorless oil consisting mostly of 9-(α-methylbenzyl)-phenanthrene as judged from its nmr spectrum. Chromatography over silicic acid gave first a small amount of unknown hydrocarbons (eluted with hexane), followed by 198 mg (50% yield) of 9-(α-methylbenzyl)phenanthrene (eluted with benzene). A sample crystallized from cyclohexane had mp 118.5–119.5°, undepressed by admixture of an authentic sample of 9-(α-methylbenzyl)phenanthrene (see below). The ir spectra of the two samples were also identical.

9-(α-Styryl)phenanthrene.—To a stirred solution of 20.0 g (91 mmol) of 9-acetylphenanthrene (Columbia Organic Chemicals Co., Inc.) in 400 ml of anhydrous ether was added, over a period of 30 min, 35 ml of a 3 *M* solution of phenylmagnesium bromide (105 mmol) in THF. The mixture was then heated under reflux for 1 hr, cooled, and treated with 100 ml of 5% hydrochloric acid. The layers were separated, the aqueous phase was extracted twice with 100-ml portions of ether, and the combined ether extracts were washed with water, 5% sodium bicarbonate solution, and concentrated sodium chloride solution, and dried. Removal of the solvent gave 27.0 g of a viscous oil. It was dissolved in 100 ml of glacial acetic acid and 8.0 g of *p*-toluenesulfonic acid hydrate was added with stirring. A pale yellow crystalline precipitate formed after *ca.* 20 min; it was collected by filtration after 12 hr, washed with glacial acetic acid, and dried. The yield of crude 9-(α-styryl)phenanthrene, mp 133–135°, was 4.22 g (17%). An analytical sample (glacial acetic acid) had mp 136–137°; nmr (in $CDCl_3$) multiplets at τ 1.3–1.6 (2 H) and 2.1–3.0 (12 H) and doublets (J = 1.5 cps) at 4.1 and 4.6 (1 H each); uv $\lambda_{\max}^{\text{cyclohexane}}$ 348 mμ (ϵ 270), 340 (300), 332 (360), 324 (370), 298 (12,600), 286 (10,600), 272 (sh, 15,500), and 255 (65,000).

Anal. Calcd for $C_{22}H_{16}$: C, 94.25; H, 5.75. Found: C, 94.11; H, 5.92.

9-(α-Methylbenzyl)phenanthrene.—Catalytic hydrogenation of 571 mg of 9-(α-styryl)phenanthrene in 10 ml of ethyl acetate with 450 mg of 10% palladium on charcoal at room temperature resulted in the uptake of 1 mol equiv of hydrogen. The filtered solution was concentrated to dryness and the residue was sublimed at 150° bath temperature (0.1 μ) to give 454 mg (80% yield) of 9-(α-methylbenzyl)phenanthrene: mp 118.5–119.5°, unchanged on crystallization from cyclohexane; nmr (in $CDCl_3$) multiplets at τ 1.3–1.7 (2 H) and 1.9–3.0 (12 H), quartet (J = 7 cps) at 5.2 (1 H), and doublet (J = 7 cps) at 8.3 (3 H); uv $\lambda_{\max}^{\text{cyclohexane}}$ 347 mμ (ϵ 230), 339 (240), 331 (280), 324 (240), 317 (230), 297 (12,000), 285 (10,700), 277 (14,100), 270 (20,800), 254 (63,000), and 248 (sh, 49,000).

Anal. Calcd for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.88; H, 6.50.

Registry No.—**2,** 19291-71-5; **3,** 19291-72-6; **4,** 19291-73-7; **5** (*threo*), 19291-74-8; **5** (*erythro*), 19291-75-9; **6,** 19291-76-0; **7,** 19291-77-1; **8a,** 19291-78-2; **8b,** 19291-79-3; **8c,** 19291-80-6; **9,** 19291-81-7; **10,** 19291-82-8; **12,** 19291-83-9; **17a,** 19291-84-0; **17b,** 19291-85-1; **18,** 19291-86-2; **20** (*threo*) 19291-87-3; **20** (*erythro*), 19291-88-4; **21,** 19291-89-5; 1,2-dicyano-7-methoxynaphthalene, 19291-90-8; 9-(α-styryl)phenanthrene, 19291-91-9.