with the published spectrum);[7] pmr resonances at δ 1.22 (t, 6 H), 2.95 (q, 4 H), 7.20 (m, 5 H).

*N*,*N*-**Diethyl-4-methoxyphenylethynylamine** was obtained from 4-methoxy-β,β-difluorostyrene: bp 98–100° (0.08 mm); 77% yield; $n^{25}\text{D}$ 1.5106; infrared bands at 2950, 2220, 1600, 1500, 1455, 1405, 1390, 1365, 1320, 1280, 1240, 1180, 1030, 830, and 760 cm$^{-1}$; pmr resonances at δ 1.22 (t, 6 H), 2.93 (q, 4 H), 3.68 (s, 3 H), 6.73 and 7.20 (AB quartet, 4 H).

*Anal.* Calcd for $C_{13}H_{17}NO$: C, 76.80; H, 8.43; N, 6.89. Found: C, 76.6; H, 8.64; N, 7.17.

*N*,*N*-**Diethyl-2-chlorophenylethynylamine** was obtained from 2-chloro-β,β-difluorostyrene: bp 84–86° (0.03 mm); 84% yield; $n^{25}\text{D}$ 1.5785; infrared bands at 2980, 2850, 2220, 1600, 1435, 1415, 1380, 1340, 1250, 1190, 1080, 1050, 1030, and 745 cm$^{-1}$; pmr resonances at δ 1.27 (t, 6 H), 3.00 (q, 4 H), 7.10 (m, 4 H).

*Anal.* Calcd for $C_{12}H_{14}ClN$: C, 69.39; H, 6.79; Cl, 17.07; N, 6.74. Found: C, 69.0; H, 6.96; Cl, 16.8; N, 7.36.

*N*,*N*-**Diethyl-4-chlorophenylethynylamine** was obtained from 4-chloro-β,β-difluorostyrene: bp 87–89° (0.03 mm); 67% yield; $n^{25}\text{D}$ 1.5772; infrared bands at 2950, 2220, 1490, 1185, 1170, 1090, 1060, 1010, and 823 cm$^{-1}$; pmr resonances at δ 1.22 (t, 6 H), 2.95 (q, 4 H), 7.28 (s, 4 H).

*Anal.* Found: C, 69.1; H, 6.96; Cl, 16.9; N, 7.23.

*N*,*N*-**Diethyl-*o*-tolylethynylamine** was obtained from 2-methyl-β,β-difluorostyrene: bp 74–76° (0.03 mm); 80% yield; $n^{25}\text{D}$ 1.5563; infrared bands at 2950, 2220, 1600, 1460, 1370, 1280, 1200, 1070, 1040, 750, and 710 cm$^{-1}$; pmr resonances at δ 1.22 (t, 6 H), 2.93 (q, 4 H), 2.33 (s, 3 H), 7.00 (m, 4 H).

*Anal.* Calcd for $C_{13}H_{17}N$: C, 83.36; H, 9.14; N, 7.48. Found: C, 82.8; H, 9.04; N, 8.34.

*N*,*N*-**Diethylamino-*p*-tolylethynylamine** was obtained from 4-methyl-β,β-difluorostyrene: bp 72–75° (0.03 mm); 73% yield; $n^{25}\text{D}$ 1.5578; infrared bands at 2950, 2900, 2850, 2220, 1600, 1500, 1440, 1365, 1185, 1100, 1065, and 813 cm$^{-1}$; pmr resonances at δ 1.22 (t, 6 H), 2.95 (q, 4 H), 2.26 (s, 3 H), 6.93 and 7.11 (AB quartet, 4 H).

*Anal.* Found: C, 82.3; H, 9.20; N, 7.87.

*N*,*N*-**Diethyl(4-phenyl-but-*trans*-3-ene-1-ynyl)amine** was obtained from 1,1-difluoro-4-phenyl-*trans*-1,3-butadiene: bp 99–104° (0.03 mm); 43% yield; $n^{25}\text{D}$ 1.6288; infrared bands at 3000, 2850, 2200, 1620, 1590, 1490, 1440, 1410, 1370, 1350, 1250, 950, 750, and 690 cm$^{-1}$; pmr resonances at δ 1.20 (t, 6 H), 2.92 (q, 4 H), 6.16 and 6.52, (AB quartet, 2 H, $J$ = 16 Hz (vinyl protons)), 7.18 (m, 5 H).

*Anal.* Calcd for $C_{14}H_{17}N$: C, 84.36; H, 8.60; N, 7.03. Found: C, 83.3; H, 9.00; N, 7.17.

*N*,*N*-**Diethylamino-1-heptyne** was obtained from 1,1-difluoro-1-heptene: bp 59–61° (0.70 mm); 74% yield; $n^{25}\text{D}$ 1.4454; infrared bands at 2950, 2850, 2220, 1460, 1375, 1320, 1250, 1180, 1090, and 1065 cm$^{-1}$; pmr resonances at δ 1.12 (t, 2.78 (q), 0.80–1.7 (m), 2.18 (t, $CH_2C{\equiv}C$).

*Anal.* Calcd for $C_{11}H_{21}N$: C, 78.97; H, 12.66; N, 8.38. Found: C, 78.8; H, 12.4; N, 8.64.

*N*,*N*-**Diethylamino-1-octyne** was obtained from 1,1-difluoro-1-octene: bp 56–58° (0.10 mm); 45% yield; $n^{25}\text{D}$ 1.4490; infrared bands at 2950, 2850, 2220, 1450, 1360, 1290, 1240, 1170, 1080, and 790 cm$^{-1}$; pmr resonances at δ 1.12 (t), 2.78 (q), 0.80–1.7 (m), 2.18 (t, $CH_2C{\equiv}C$).

*Anal.* Calcd for $C_{12}H_{23}N$: C, 79.49; H, 12.79; N, 7.73. Found: C, 78.6; H, 12.8; N, 6.90.

**Registry No.**—*N*,*N*-Diethylphenylethynylamine, 4231-26-9; *N*,*N*-diethyl-4-methoxyphenylethynylamine, 28321-14-4; *N*,*N*-diethyl-2-chlorophenylethynylamine, 28321-15-5; *N*,*N*-diethyl-4-chlorophenylethynylamine, 28321-16-6; *N*,*N*-diethyl-*o*-tolylethynylamine, 28321-17-7; *N*,*N*-diethylamino-*p*-tolylethynylamine, 28321-18-8; *N*,*N*-diethyl(4-phenylbut-*trans*-3-ene-1-ynyl)amine, 28321-19-9; *N*,*N*-diethylamino-1-heptyne, 28321-20-2; *N*,*N*-diethylamino-1-octyne, 4231-37-2.

**Acknowledgment.**—The author is indebted to Dr. F. J. Weigert for helpful discussions about nuclear magnetic resonance and Mrs. Sharon Wheeler for technical assistance.

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## 2,3-Dimethyl-1-phenylnaphthalene from Thermal Dimerization of Phenylallene[1]

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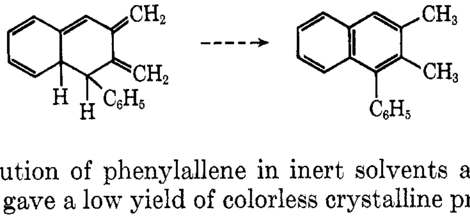
*Received September 3, 1970*

We report that phenylallene may be thermally converted to 2,3-dimethyl-1-phenylnaphthalene and suggest initial Diels–Alder cycloaddition producing a pentaene system, followed by tautomerization, as a mechanistically likely sequence.



A solution of phenylallene in inert solvents at 175° for 1 hr gave a low yield of colorless crystalline product, mp 84–85°, after recrystallization and sublimation. It proved to be a $C_{18}H_{16}$ isomer having ultraviolet absorption bands, $\lambda_{\max}$ 230 nm (log ε ~5), 276 (4.1), 285 (4.15), and 294 (4.0) in $CCl_4$, unlike those expected for a 2-phenylnaphthalene[4] but in close correspondence with those reported for 1-phenylnaphthalene,[4] 2-methyl-1-(*o*-tolyl)naphthalene[4] [227 (4.91), 275 (3.84), 281 (3.87), 284 (3.87), and 292 (3.76) in petroleum ether], and 2,3-dibenzyl-1-phenylnaphthalene[5] [$\lambda_{\max}$ 237.5 nm (4.87) and 286 (3.85) in $CH_2Cl_2$].

The nmr spectrum of the phenylallene dimer had methyl singlets at δ 2.10 and 2.43, and ten aromatic protons at δ 6.9–7.8 ppm.

The physical data and mechanistic possibilities prompted an assignment of 2,3-dimethyl-1-phenylnaphthalene as the probable structure for the $C_{18}H_{16}$ compound. The picrate derivative had mp 110–111°, in good agreement with the literature value, mp 112°, for authentic 2,3-dimethyl-1-phenylnaphthalene.[6] The melting point observed for the phenylallene dimer, 84–85°, was close to that for 2,3-dimethyl-1-phenylnaphthalene cited by Müller and K. Körmendy,[6] 85–86°.

Allene–allene thermal dimerizations giving dimethylenecyclobutanes and derived structures are common.[7–9] The present result, isolation of a 2,3-dimethyl-1-phenylnaphthalene as a thermal dimer from phenylallene, indicates a new mode of dimerization available to arylallenes. Formation of 2,3-dibenzyl-1-phenylnaphthalene through elimination of hydrogen chloride from 2-chloro-1,3-diphenylpropene[5] may well go by way of 1,3-diphenylallene and may then represent another example of this type of arylallene dimerization.

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(3) National Science Foundation Cooperative Graduate Fellow, 1963–1966.

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### Experimental Section

**Phenylallene** was prepared through the reaction of 2,2-dibromo-1-phenylcyclopropane[10] with methyllithium in ether at $-50°$;[11] it had bp 64–65° (10 mm), $n^{20}D$ 1.5819 [lit.[11] bp 64–65° (11 mm), $n^{24}D$ 1.5809], and the expected spectral properties.

**2,3-Dimethyl-1-phenylnaphthalene from Phenylallene.**—A solution containing 5 g of phenylallene and 0.5 g of hydroquinone in 50 ml of 1:1 benzene–vinyl acetate in a glass liner was sealed in a steel reactor and heated to 175° for 1 hr. Concentration of the reaction mixture and short-path distillation give a yellow liquid, bp 100–130° (0.15 mm). A portion of this distillate soluble in carbon tetrachloride gave, upon concentration, 100 mg of colorless rosettes, mp 67–75°. Sublimation gave material of close to analytical purity: mp 78–80°; $\lambda_{max}^{CCl_4}$ 230 nm (log $\epsilon$ ~5), 276 (4.1), 285 (4.15), and 294 (4.0); nmr 2.10 (3 H, s), 2.43 (3 H, s), 6.9–7.8 ppm (10 H, m). Recrystallization from ethanol and vacuum sublimation gave crystals of mp 84–85° (lit.[6] mp 85–86° for 2,3-dimethyl-1-phenylnaphthalene). A solution of the hydrocarbon in 95% ethanol saturated with picric acid gave the picrate derivative, mp 110–111° (lit.[6] mp 112°).

**Registry No.**—2,3-Dimethyl-1-phenylnaphthalene, 27521-96-6; phenylallene, 2327-99-3.

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## Diarylmethylene–Tetracyanoethylene Cycloadditions[1]

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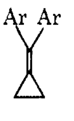
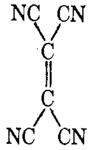
As one potential route to cyclopentane derivatives through (2 + 3) cycloadditions, the reaction between diarylmethylenecyclopropanes (1) and tetracyanoethylene (TCNE, 2) has been examined.



1



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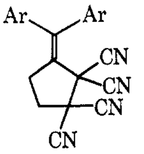
a, Ar = $C_6H_5$; b, Ar = $p$-$CH_3OC_6H_4$

Both concerted and nonconcerted mechanistic possibilities leading to cyclopentane systems seem available. As a homoallene, the methylenecyclopropane unit would be potentially able to add TCNE across its $C_1$–$C_2$ bond to give **3** in what could be formally described as a thermally allowed $[\pi_s^2 + \pi_s^2 + \sigma_s^2]$ cycloreaction.[4] By analogy with the behavior of appropriately substituted aziridines,[5–8] and with one perception of the cycloaddition behavior of cyclopropanones,[9,10] prior isomerization to dipolar intermediate **4**, followed by an allowed $[\pi_s^4 + \pi_s^2]$ cycloaddition, might produce **5**.

Initial formation of one new bond linking methylenecyclopropane **1** at $C_1$ to TCNE, generating a dipolar species **6**, might also yield **3** through a cyclopropylcarbinyl to allylcarbinyl (**6** → **7**) rearrangement before the second bond-making step. A two-step process with a somewhat similar dipolar intermediate **8** has been proposed as one means to account for production of 1,1-diphenyl-2,2,3,3-tetracyanocyclopentane from 1,1-diphenylcyclopropane and TCNE.[11]



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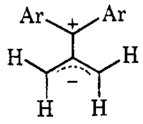

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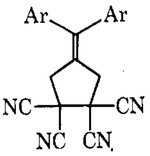

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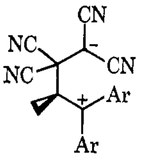

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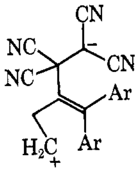

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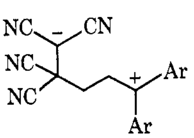

8

Cycloadducts from diphenylmethylenecyclopropane (**1a**) and bis($p$-methoxyphenyl)methylenecyclopropane (**1b**) were obtained when these homoallenes were heated to 120° with TCNE in toluene. The adducts, mp 215 and 191°, respectively, had nmr spectra which immediately ruled out structure **5** as well as spiroheptane (2 + 2) adducts; the methylene protons appeared as two sets of 2 H triplets, centered at $\delta$ 3.22 and 2.63 (adduct **a**) and at $\delta$ 3.19 and 2.59 (adduct **b**), with $J$ = 8 Hz, implicating $CH_2CH_2$ as one moiety in these products. The methoxyl methyl signals in adduct **b** came at $\delta$ 4.00 and 3.93 ppm; both adducts had aromatic protons evident at $\delta$ 7–8 ppm.

Structure **3** seemed consistent with the nmr data, but for two troubling points. In the adduct **a**, one aromatic proton appeared at an unusually low field (8.35 ppm) as a doublet of doublets ($J$ = 8, ~2 Hz), and the signals for the methylene protons were appropriate to an $A_2M_2$ system, rather than to the AA′MM′ pattern expected for **3**.

Elemental analyses and mass spectral determinations of molecular weight firmly excluded structure **3**, since both adducts corresponded to 1:1 adducts. . .less HCN! Their ultraviolet spectra revealed them to be 1-arylnaphthalene derivatives: for adduct **a**, $\lambda_{max}^{CH_2Cl_2}$ 253 (log $\epsilon$ 4.67), 305 (3.56), 318 (3.61), 341 (3.45), and 356 (3.56); for adduct **b**, $\lambda_{max}^{CH_2Cl_2}$ 265 (4.77), 298 (3.64), 313 (3.63), 372 sh (3.67), and 385 (3.72).[12] The substantial bathochromic shift for both the $^1B_a$ and $^1L_a$ bands (253 → 265 nm, 356 → 385 nm) on going from adduct **a** to the methoxy-substituted system **b** suggested a con-

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[1] Supported initially by Public Health Service Research Grant GM 16576 and subsequently by National Science Foundation Grant GP 9259 and the Research Corporation.

[2] Address correspondence to the University of Oregon.

[3] National Defense Education Act Fellow, 1967–1970.

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