

## Experimental Section

**Phenylallene** was prepared through the reaction of 2,2-dibromo-1-phenylcyclopropane<sup>10</sup> with methyllithium in ether at  $-50^{\circ}$ ; it had bp  $64-65^{\circ}$  (10 mm),  $n_D^{20}$  1.5819 [lit.<sup>11</sup> bp  $64-65^{\circ}$  (11 mm),  $n_D^{20}$  1.5809], and the expected spectral properties.

**2,3-Dimethyl-1-phenyl-naphthalene 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  $175^{\circ}$  for 1 hr. Concentration of the reaction mixture and short-path distillation give a yellow liquid, bp  $100-130^{\circ}$  (0.15 mm). A portion of this distillate soluble in carbon tetrachloride gave, upon concentration, 100 mg of colorless rosettes, mp  $67-75^{\circ}$ . Sublimation gave material of close to analytical purity: mp  $78-80^{\circ}$ ;  $\lambda_{\text{max}}^{\text{CCl}_4}$  230 nm ( $\log \epsilon \sim 5$ ), 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  $84-85^{\circ}$  (lit.<sup>6</sup> mp  $85-86^{\circ}$  for 2,3-dimethyl-1-phenyl-naphthalene). A solution of the hydrocarbon in 95% ethanol saturated with picric acid gave the picrate derivative, mp  $110-111^{\circ}$  (lit.<sup>6</sup> mp  $112^{\circ}$ ).

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

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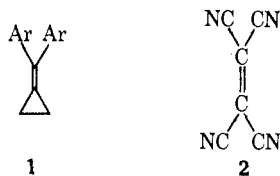
Diarylmethylene-Tetracyanoethylene  
Cycloadditions<sup>1</sup>

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Received September 3, 1970

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

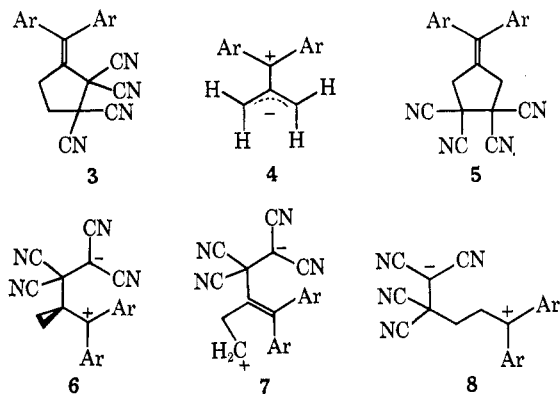


a, Ar = C<sub>6</sub>H<sub>5</sub>; b, Ar = *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>

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<sub>1</sub>-C<sub>2</sub> bond to give 3 in what could be formally described as a thermally allowed [ $\pi_s^2 + \pi_s^2 + \sigma_s^2$ ] cycloaddition.<sup>4</sup> By analogy with the behavior of appropriately substituted aziridines,<sup>5-8</sup> and with one perception of the cycloaddi-

tion behavior of cyclopropanones,<sup>9,10</sup> 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<sub>1</sub> 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.<sup>11</sup>



Cycloadducts from diphenylmethylenecyclopropane (1a) and bis(*p*-methoxyphenyl)methylenecyclopropane (1b) were obtained when these homoallenes were heated to  $120^{\circ}$  with TCNE in toluene. The adducts, mp  $215$  and  $191^{\circ}$ , 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<sub>2</sub>CH<sub>2</sub> 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 ( $J = 8, \sim 2$  Hz), and the signals for the methylene protons were appropriate to an A<sub>2</sub>M<sub>2</sub> 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,  $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$  253 (log  $\epsilon$  4.67), 305 (3.56), 318 (3.61), 341 (3.45), and 356 (3.56); for adduct b,  $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$  265 (4.77), 298 (3.64), 313 (3.63), 372 sh (3.67), and 385 (3.72).<sup>12</sup> The substantial bathochromic shift for both the <sup>1</sup>B<sub>a</sub> and <sup>1</sup>L<sub>a</sub> bands (253 → 265 nm, 356 → 385 nm) on going from adduct a to the methoxy-substituted system b suggested a con-

(1) Supported initially by Public Health Service Research Grant GM 16570 and subsequently by National Science Foundation Grant GP 9259 and the Research Corporation.

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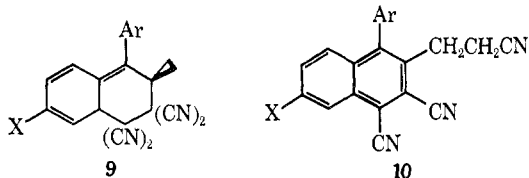
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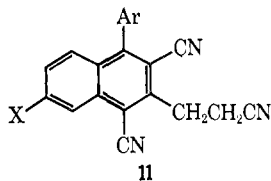
jugative interaction between MeO- and NC- groups separated by four carbon atoms.

These data and mechanistic considerations led to formulation of the adducts as 1-phenyl-2-(2-cyanoethyl)-3,4-dicyanonaphthalenes, derived from an initial Diels-Alder addition between **1** and TCNE giving the relatively unstable triene system **9**, which through loss of HCN and a cyclopropylcarbinyl to allylcarbinyl rearrangement may give the isolated products **10**.



The  $A_2M_2$  nmr pattern for methylene protons is in accord with the conformationally mobile cyanoethyl group, and the low field aromatic proton in **10a** may be ascribed to H-C<sub>5</sub>, strongly deshielded by the peri-positioned NC-C<sub>4</sub> function, and in **10b**, counter shielded by the adjacent CH<sub>3</sub>O group.<sup>13</sup>

The experimental data seem compatible with both formulation **10** and with structure **11** for the adducts; only a substantial discrepancy in mechanistic plausibility favors the former alternative.



This cycloaddition behavior parallels one mode of reaction available to arylallenes: Diels-Alder dimerization followed by rearrangement, as in the conversion of phenylallene to 2,3-dimethyl-1-phenylnaphthalene<sup>14</sup> or of 1,3-diphenylallene to 2,3-dibenzyl-1-phenylnaphthalene.<sup>15</sup>

Further efforts to achieve additions across the C<sub>1</sub>-C<sub>2</sub> or the C<sub>2</sub>-C<sub>3</sub> bond of methylenecyclopropanes **1** will be made with other olefins and with other systems lacking vinyl or phenyl substitution at the exocyclic methylene carbon.

### Experimental Section

Melting points were obtained on a Kofler Micro Hot Stage apparatus and are uncorrected. Infrared spectra were run in chloroform solution on a Beckman Model IR-5 spectrophotometer, and ultraviolet spectra were recorded on a Cary 15 spectrophotometer. Proton magnetic resonance spectra (in CDCl<sub>3</sub>) were determined on Varian Models A-60, A-60A, A-56/60A, HA-100 spectrometers. Mass spectra were run on a CEC 21-110B spectrometer by Mrs. Mary Mitchell. Elemental analyses were determined by Chemalytics Inc., Tempe, Ariz. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride and stored over sodium wire.

**$\alpha$ -Triphenylphosphoniumbutyrolactone Bromide.**<sup>16</sup>—A solution of 9.86 g (0.03 mol) of triphenylphosphine and 4.96 g (0.03 mol) of  $\alpha$ -bromo- $\gamma$ -butyrolactone in 15 ml of THF was heated at reflux for 4 hr. The mixture was cooled, filtered, and washed

with THF. The crude material was dissolved in 50 ml of hot methanol, 150 ml of ethyl acetate was added, and the cloudy solution was cooled. Filtration and drying gave 6.90 g (53.8%) of product, mp 188° (lit.<sup>16</sup> mp 196–197°).

Further purification was accomplished by grinding the crystalline material to a fine powder with a mortar and pestle and washing the solid several times with ether. Thorough drying in a vacuum oven at 60° (20 mm) gave salt sufficiently pure for synthetic utilization: ir 3500, 3250, 2900, 1710, 1600, 1485, 1110, 1025, and 956 cm<sup>-1</sup>; nmr  $\tau$  2.10 (m, 15), 5.30 (m, 3), and 6.70 (m, 2).

**Cyclopropyltriphenylphosphonium bromide**<sup>17,18</sup> was prepared from  $\alpha$ -triphenylphosphoniumbutyrolactone bromide in 98% yield, crushed to a fine powder with a mortar and pestle, washed thoroughly with ether, and dried in a vacuum oven at 60° (20 mm) to give material of melting point 190° (lit.<sup>18</sup> mp 189–190°): ir 3300, 2870, 1590, 1480, 1340, 1220, 1115, 1000, and 900 cm<sup>-1</sup>; nmr  $\tau$  2.17 (m, 15), 6.60 (m, 1), 8.21 (m, 2), and 9.37 (m, 2).

*Anal.* Calcd for C<sub>21</sub>H<sub>20</sub>BrP: C, 65.79; H, 5.22; Br, 20.88. Found: C, 64.13; H, 5.35; Br, 20.66.

**Diphenylmethylenecyclopropane.**<sup>19</sup>—Under a dry nitrogen atmosphere and with stirring, a mixture of 3.54 g (7.8 mmol) of cyclopropyltriphenylphosphonium bromide in 45 ml of THF was treated with 4.5 ml of 1.6 M *n*-butyllithium in hexane (Foote Chemicals). The reaction mixture was stirred and heated gently for 2 hr, and then 1.42 g (7.8 mmol) of benzophenone in THF was slowly added. The mixture was gently heated at reflux for 21 hr. Tetrahydrofuran was distilled from the mixture, the residue was extracted with chloroform, and the extracts were washed with water and dried (Na<sub>2</sub>SO<sub>4</sub>). Evaporation of the chloroform and chromatography of the remaining material with hexane on 21 g of silica gel afforded 657 mg (41%) of product.

A pure sample was obtained by recrystallization from petroleum ether (bp 30–60°) to give material of mp 61–64° (lit.<sup>19</sup> mp 65°): ir 3080, 2950, 1960, 1890, 1820, 1595, 1490, 1075, and 895 cm<sup>-1</sup>; nmr  $\tau$  2.81 (m, 10) and 8.65 (s, 4).

**Bis(*p*-methoxyphenyl)methylenecyclopropane.**—To a stirred slurry of 4.31 g (11.2 mmol) of cyclopropyltriphenylphosphonium bromide in 35 ml of THF was added 7.5 ml (12.9 mmol) of *n*-butyllithium. The solution was warmed gently and stirred for about 1 hr, and 2.7 g (11.2 mmol) of 4,4'-dimethoxybenzophenone in 10 ml of THF was slowly added. The reaction mixture was heated to reflux for 18 hr and then cooled; solvent was removed by distillation, and the residue was dissolved in chloroform. The chloroform solution was washed with water, dried (Na<sub>2</sub>SO<sub>4</sub>), filtered, and concentrated. The remaining oil was chromatographed with hexane on 30 g of silica gel. The desired product, 830 mg (28%), eluted with the first 100 ml of hexane. Recrystallization from hexane gave pure material: mp 106–107°; ir 2950, 2840, 1605, 1560, 1490, 1105, 1030, 895, and 828 cm<sup>-1</sup>; nmr  $\tau$  2.76 (m, 8), 6.12 (s, 6), and 8.61 (s, 4).

*Anal.* Calcd for C<sub>18</sub>H<sub>18</sub>O<sub>2</sub>: C, 81.17; H, 6.81. Found: C, 80.91; H, 6.74.

**Diphenylmethylenecyclopropane-TCNE Addition.**—A solution of 114 mg (0.55 mmol) of **1a** and 78 mg (0.61 mmol) of TCNE in 10 ml of toluene was heated gently to reflux under nitrogen for 17 hr. The toluene was removed by distillation, and the dark residue was chromatographed on 6 g of silica gel with chloroform. The first 20-ml fraction contained 62 mg of material shown by nmr to be a mixture of 75% adduct and 25% **1a**. From the second fraction eluted, 39 mg (total yield 85 mg, 46%) of adduct was obtained.

A pure sample of adduct, mp 215°, was obtained by recrystallization from methanol: mass spectrum (10 eV) *m/e* 307 (M<sup>+</sup>); ir 2250, 1560, 1450, 1420, and 1380 cm<sup>-1</sup>; for nmr and ultraviolet data, see text above.

*Anal.* Calcd for C<sub>21</sub>H<sub>13</sub>N<sub>3</sub>: C, 82.07; H, 4.26. Found: C, 81.74; H, 4.23.

**Bis(2-methoxyphenyl)methylenecyclopropane-TCNE Addition.**—A solution of 122 mg (0.46 mmol) of **1b** and 60 mg (0.47 mmol) of TCNE was heated to reflux in 10 ml of toluene under nitrogen for 13 hr. Concentration and chromatography led to

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53 mg (29%) of yellow adduct: mp 190–191° from methanol; mass spectrum (9 eV)  $m/e$  367 ( $M^+$ ); ir 2245, 1625, 1465, 1430, 1225, 1033, and 837  $\text{cm}^{-1}$ ; the nmr and ultraviolet data are given above.

Anal. Calcd for  $\text{C}_{23}\text{H}_{17}\text{N}_3\text{O}_2$ : C, 75.19; H, 4.66. Found: C, 75.02; H, 4.53.

Registry No.—1a, 7632-57-7; 1b, 28228-81-1; 2, 670-54-2;  $\alpha$ -triphenylphosphoniumbutyrolactone bromide, 28228-78-6; cyclopropyltriphenylphosphonium bromide, 14114-05-7.

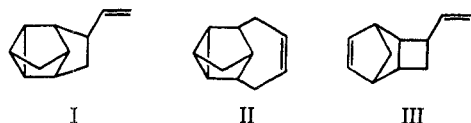
### Catalytic Behavior of Some Ziegler-Natta Catalysts in the Norbornadiene-Butadiene Codimerization

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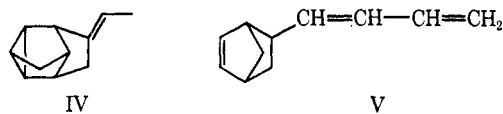
Received October 1, 1970

In a previous paper<sup>1</sup> we described the reaction between norbornadiene (NBD) and 1,3-butadiene (BD) catalyzed by organometallic iron compounds. The reaction products are 1:1 adducts, two of them (I and II) with the nortricyclic and one (III) with the norbornenic structure.



In an attempt to set up selective syntheses of the above compounds and to discover new NBD-BD adducts, we investigated the behavior of catalysts containing transition metals different from iron. We employed two- as well as three-component systems, the third component always being a phosphorus-containing ligand. The most significant new results are summarized in Table I.

A new isomer was obtained employing the catalyst system  $\text{NiCl}_2\text{-Et}_2\text{AlCl-2PPh}_3$ . On the basis of chemical and physicochemical data, formula IV was attributed to it. The same product, but with lower con-



version, was obtained using a phosphine-free catalyst, prepared from a soluble nickel compound such as the diacetylacetonate.

Adduct IV is always accompanied by smaller amounts of adduct I. Since I and IV only differ in the position of the double bond of the side chain, we tried to isomerize I to IV by contact with the above nickel catalysts (under the same conditions in which IV is synthesized) but were unsuccessful. Also, other catalysts known for their activity in the isomerization of vinyl derivatives of cycloolefins to ethylidene compounds,

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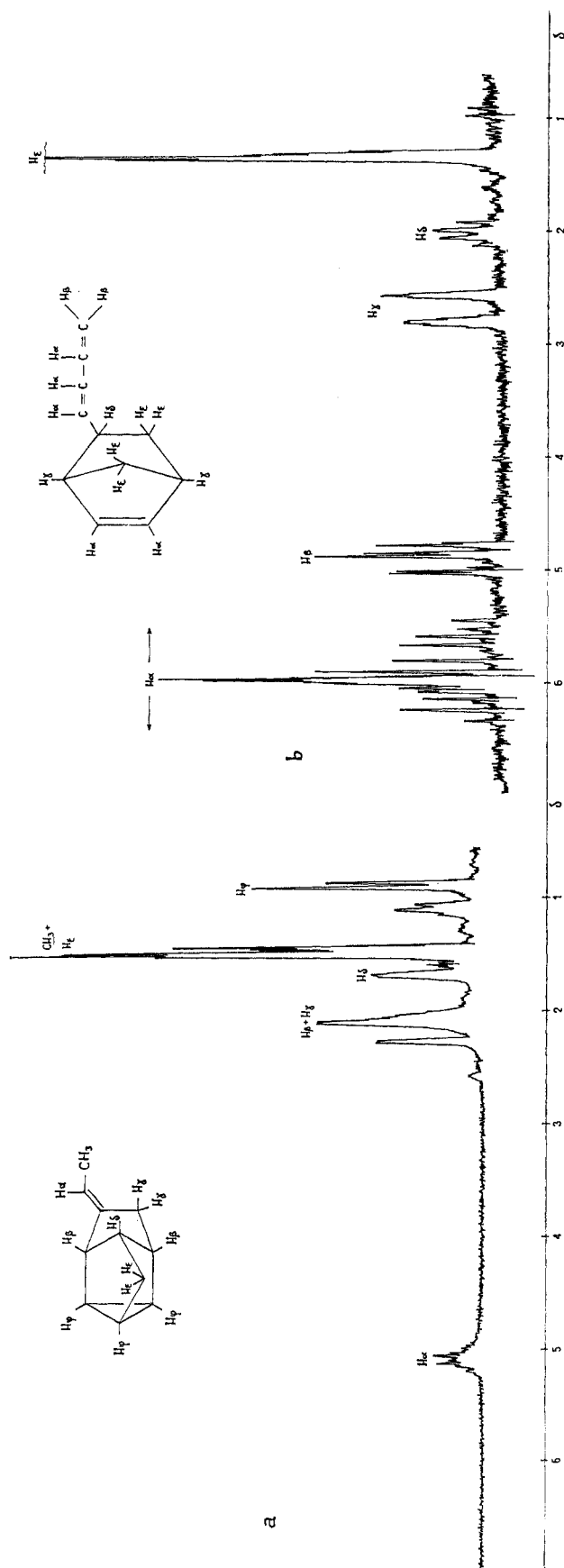


Figure 1.— $^1\text{H}$  nmr spectra of compounds IV (a) and V (b) (Varian HA-100,  $\text{CCl}_4$ , room temperature, TMS).