9-Carbomethoxy-*trans*-5,6-trimethylenenorbornane (19).—The saturated acid **18** was esterified in methanol by the same procedure used for the preparation of the ester **17**. The product **19** was obtained in 89% yield as a colorless oil: bp 126–127°; ir (neat) 1750 cm^{-1} (C=O); nmr (CDCl$_3$) δ 3.68 (s, 3, OCH$_3$).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.17; H, 9.35. Found: C, 74.18; H, 9.51.

Registry No.—**5**, 34561-91-6; **6**, 34561-92-7; **7**, 34561-93-8; **8**, 34561-94-9; **12**, 34561-95-0; **13**, 34561-96-1; **14**, 34561-97-2; **15**, 34561-98-3; **16** isomer a, 34599-26-3; **16** isomer b, 34599-27-4; **17** isomer a, 34561-99-4; **17** isomer b, 34562-00-0; **18** isomer a, 34562-01-1; **18** isomer b, 34562-02-2; **19** isomer a, 34562-03-3; **19** isomer b, 34562-04-4.

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Studies on Reactions of Isoprenoids. XVII.[1] The Cycloaddition Reactions of Norbornadiene with Some Unsymmetrically Substituted Dienophiles. Competitive Ionic Additions with Homo-Diels–Alder Reactions

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The reactions of norbornadiene (1) with unsymmetrically substituted acetylenic and heterodienophiles were investigated. Cyanoacetylene and *N-tert*-butylpropiolamide as acetylenic dienophiles gave only homo-Diels–Alder adducts **3a** and **3b**, respectively, while chlorocyanoacetylene afforded 2 + 2 cycloadduct **4** and its skeletal rearrangement product **5** *via* an ionic intermediate **7** together with homo-Diels–Alder adduct **3c**. Phenylacetylene, chloropropiolamide, and dimethylaminocyanoacetylene did not afford any isolable adducts. The reaction of **1** with methylenebisurethane in the presence of boron trifluoride etherate afforded 8-aza-δ-cyclane (**10**) and the 3-aminonortricyclene derivative **11**, while that with benzalbisurethane gave only 3-nortricyclylurethane (**12**). Anhydrochloralurethane did not afford any adduct.

We have previously reported 1,4-cycloaddition reactions of some monoterpenoid diene and triene systems.[1,2] As an extension of these studies, this paper deals with cycloaddition of homoconjugated norbornadiene (**1**) and unsymmetrically substituted acetylenic and heterodienophiles. It is well known that **1** gives δ-cyclane derivatives *via* the homo-Diels–Alder (${}_{\pi}2_s + {}_{\pi}2_s + {}_{\pi}2_s$ cycloaddition) reaction,[3,4] and quadricyclane (**6**) affords tricyclo[4.2.1.0^{2,5}]non-7-ene derivatives *via* the bishomodiene addition (${}_{\pi}2_s + {}_{\sigma}2_a + {}_{\sigma}2_a$ cycloaddition)[5] as the thermally allowed process under the Woodward–Hoffmann orbital symmetry rules.[6] However, only reactions of **1** with symmetrically substituted active acetylenes such as dimethyl acetylenedicarboxylate and dicyanoacetylene seem to have been studied.[4] In order to know the chemical behavior of the homoconjugated diene system of **1** with dienophiles that are strongly perturbed by substituents, we have investigated the reactions of **1** with cyanoacetylene (**2a**), *N-tert*-butylpropiolamide (**2b**), chlorocyanoacetylene (**2c**), phenylacetylene (**2d**), chloropropiolamide (**2e**), and dimethylaminocyanoacetylene (**2f**) as well as those with the heterodienophiles *N*-ethoxycarbonylimines **9a**, **9b**, and **9c**.

Results and Discussion

An equimolar mixture of **1** and **2a** was heated under the conditions shown in Table I. The product **3a** was isolated as a colorless liquid by distillation. The best yield was obtained by heating the reactants without solvent or any addenda at 145–160°, while the presence of aluminum chloride or copper(II) bromide lowered the yields considerably.[7,8]

TABLE I

THE YIELD OF **3a** UNDER VARIOUS CONDITIONS

Solvent	Addenda	Temp, °C	Time, hr	Yield,[a] %
None	None	160	28	31
None	None	145	40	31
Benzene	None	90	69	26
None	$AlCl_3$[b]	80	70	9
Benzene	$CuBr_2$[b]	80	240	Trace

[a] Isolated yield. [b] Trace–0.3 molar equiv amounts were examined but the results were similar.

The structure of **3a** was determined as 8-cyano-δ-cyclene (8-cyanotetracyclo[4.3.0.0.^{2,4}0^{3,7}]non-8-ene)[9] on the basis of analytical and spectral data. The nmr spectrum (CCl$_4$, 60 MHz) revealed a doublet at τ 3.15

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[1] Part XVI: T. Sasaki, S. Eguchi, and H. Yamada, *Tetrahedron*, **27**, 4511 (1971).

[2] (a) T. Sasaki, S. Eguchi, and T. Ishii, *J. Org. Chem.*, **34**, 3749 (1969); (b) T. Sasaki, S. Eguchi, T. Ishii, and H. Yamada, *ibid.*, **35**, 4273 (1970); (c) T. Sasaki, S. Eguchi, and H. Yamada, *ibid.*, **36**, 1584 (1971).

[3] For olefinic and heterodienophiles, see E. F. Ullmann, *Chem. Ind. (London)*, 1173 (1958); R. C. Cookson, J. Dance, and J. Hudec, *J. Chem. Soc.*, 5416 (1964); J. J. Tufariello, T. F. Mich, and P. S. Miller, *Tetrahedron Lett.*, 2293 (1966); see also ref 6.

[4] For symmetrical acetylenic dienophiles, see R. C. Cookson and J. Dance, *ibid.*, 879 (1962); C. F. Huebner, E. Donoghue, L. Dorfman, E. A. Stuber, N. Danieli, and E. Wenkert, *ibid.*, 1185 (1966).

[5] C. D. Smith, *J. Amer. Chem. Soc.*, **88**, 4273 (1966); G. Kaupp and H. Prinzbach, *Chem. Ber.*, **104**, 182 (1971).

[6] R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 827 (1969).

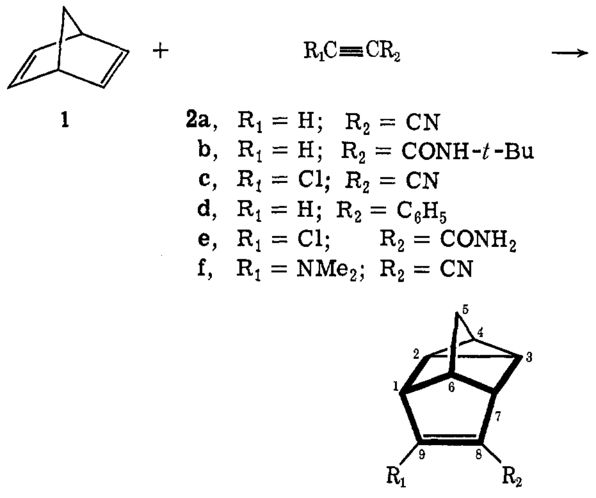
[7] For the catalytic action of aluminum chloride on 1,4 cycloadditions, see P. Yates and P. Eaton, *J. Amer. Chem. Soc.*, **82**, 4436 (1960); T. Inukai and T. Kojima, *J. Org. Chem.*, **31**, 2032 (1966), and references cited therein.

[8] For the formation of norbornadiene di[copper(I) bromide] from **1** and copper(II) bromide, see W. C. Baird, Jr., and J. H. Surridge, *ibid.*, **35**, 2090 (1970).

[9] For the nomenclature, see footnote 3 in P. K. Freeman, D. M. Balls, and J. N. Blazevich, *J. Amer. Chem. Soc.*, **92**, 2051 (1970).

due to the C-9 vinyl proton and two characteristic multiplets at τ 8.18 and 8.53 due to C_4 H and C_2 and C_3 cyclopropyl methine protons supporting the assigned structure (Scheme I).

SCHEME I



2a, $R_1 = H$; $R_2 = CN$
b, $R_1 = H$; $R_2 = CONH\text{-}t\text{-}Bu$
c, $R_1 = Cl$; $R_2 = CN$
d, $R_1 = H$; $R_2 = C_6H_5$
e, $R_1 = Cl$; $R_2 = CONH_2$
f, $R_1 = NMe_2$; $R_2 = CN$

3a, $R_1 = H$; $R_2 = CN$
b, $R_1 = H$; $R_2 = CONH\text{-}t\text{-}Bu$
c, $R_1 = Cl$; $R_2 = CN$

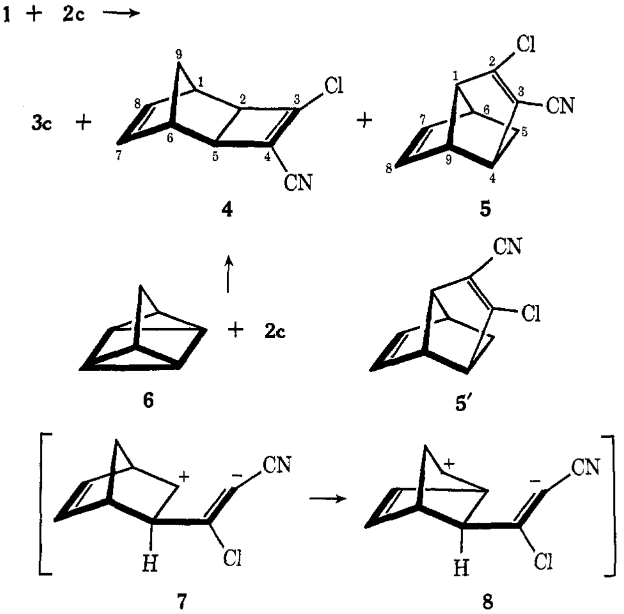
The reaction of **1** with **2b** at 165° for 100 hr afforded also 8-*N*-*tert*-butylcarbamoyl-δ-cyclene (**3b**) in very low yield, but no other isolable products were obtained (Scheme I).

In contrast to the behavior of **2a** and **2b**, chlorocyanoacetylene (**2c**) reacted with **1** under milder conditions (80° for 30 hr). Unexpectedly, at least four products were produced in a 60:10:30:<1 ratio on vpc analysis. The major products **3c**, **4**, and **5** were isolated in 40, 6, and 20% yields, respectively, by preparative vpc. All of these products were 1:1 adducts from analytical and mass spectral data. The mass spectra showed M^+ and $M + 2$ ion peaks at *m/e* 177 and 179 in 3:1 ratio, supporting the molecular formula of $C_{10}H_8NCl$. The presence of a cyano group in **3c**, **4**, and **5** was demonstrated by ir absorptions at 2250, 2260, and 2300 cm^{-1}, respectively. Compound **3c** was shown to be 8-cyano-9-chloro-δ-cyclene, a homo-Diels–Alder adduct by its characteristic nmr signals ($CDCl_3$) at τ 7.08 and 7.20 (broad s, C_1 and C_7 H), 7.65 (broad s, C_6 H), 8.10 (m, C_4 H), 8.35 (m, C_2 and C_3 H), and 8.38 (t, $J = 1$ Hz, C_5 methylene protons).

Compound **4** was determined to be *exo*-3-cyano-4-chlorotricyclo[4.2.1.0^{2,5}]nona-3,7-diene, a 2 + 2 adduct, from its characteristic nmr signals at τ 3.82 (m, C_7 and C_8 vinyl protons), 7.28 (broad s, methine protons at C_1, C_2, C_5, and C_6), and 8.45 (broad s, C_9 methylene protons). The assigned structure **4** was verified by an alternative synthesis *via* the bishomodiene type cycloaddition of quadricyclane **6** to **2c** at 80° in benzene.[10]

Compound **5** exhibited two broad singlet signals at τ 3.85 (2) and 6.92 (2) assignable to the C_7 and C_8 vinyl protons and to the C_6 and C_9 bridgehead protons respectively, a pair of double doublets at τ 6.15 and 7.20, and an unsymmetrically split AB type quartet centered at τ 8.15. The latter signals were assignable to the C_1 and C_4 methine protons, and to the C_5 methylene protons (H_n and H_x), respectively, on the basis of the coupling constants ($J_{1,4} = 8.0$, $J_{1,3} = 2.0$, $J_{4,H_n} = 1.5$, $J_{H_n,H_x} = 10.2$, $J_{H_x,6} = 4.5$, $J_{H_x,7} = 1.5$ Hz). Two structures, 2-chloro-3-cyano- (**5**) and 2-cyano-3-chlorotricyclo[4.3.0.0^{4,9}]nona-2,7-diene (**5′**) were compatible with the nmr data. However, because nucleophilic addition to **2c** occurs always at the β position of the cyano group,[11] the structure was concluded to be **5** (Scheme II).

SCHEME II



The formation of **4** and **5** suggests that an ionic cycloaddition initiated by an exo approach of **2c** to **1** is competing with the homo-Diels–Alder reaction. The ionic character of the cycloaddition to give **4** and **5** was demonstrated by the solvent effect on the product ratio as summarized in Table II. The formation of **5** was favored in polar acetonitrile, while those of **3c** and **4** was favored in nonpolar benzene. This fact could be explained reasonably by assuming the initial formation of a zwitterionic intermediate **7** or more precisely its homoallylic type equivalent which can cyclize to **4** directly and to **5** after a Wagner–Meerwein rearrangement[12] (Scheme II). The facility of the rearrangement in the polar solvent decreases the yields of **4** and **3c**. The possibility that **3c**, **4**, and **5** interconvert was excluded by the fact that all of these

TABLE II

SOLVENT EFFECT ON THE REACTION OF 1 AND 2c[a]

Solvent	Product ratio, %[b]			
	3c	4	5	Other[c]
None	60	10	30	<1
Benzene	50	9	38	3
Acetonitrile	26	2	64	8

[a] An equimolar mixture was heated at 80° for 40 hr. [b] Based on vpc analyses. [c] Unidentified.

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[10] No other products were detected on vpc analysis in this reaction.

[11] T. Sasaki, A. Kojima, and M. Ohta, *J. Chem. Soc. C*, 196 (1971).

[12] For Wagner–Meerwein rearrangments *via* homoallylic intermediates in electrophilic additions to **1**, see J. A. Berson, "Molecular Rearrangements," Part I, Interscience, New York, N. Y., 1963, p 198.

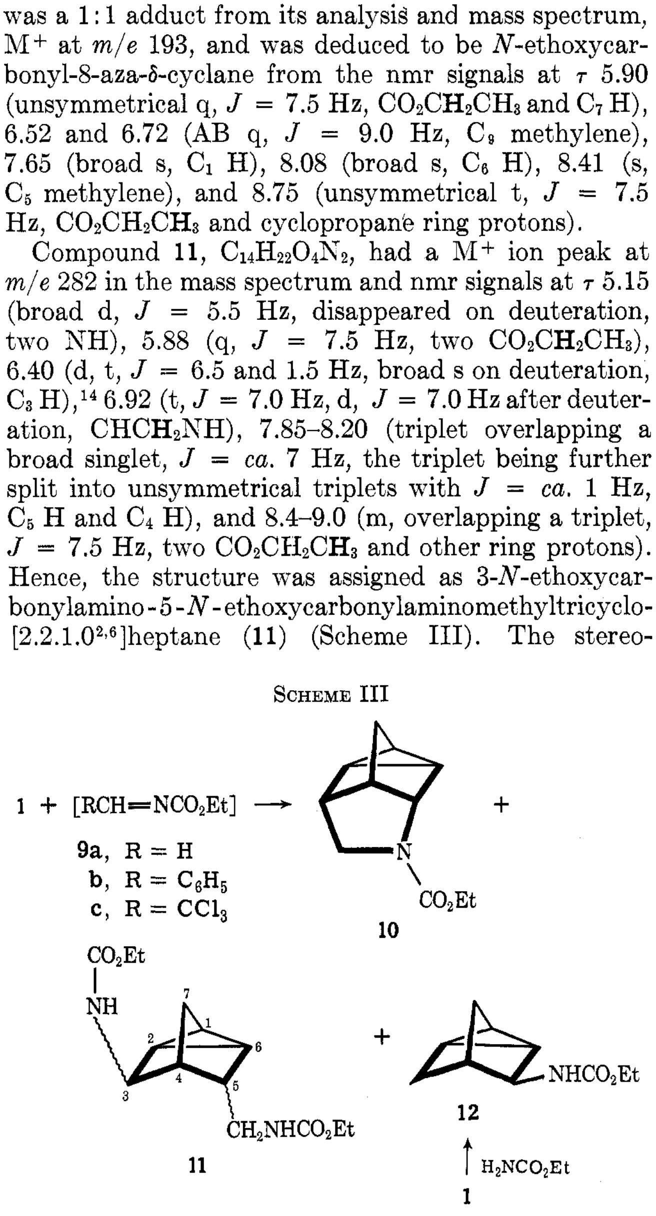
products were stable even on heating at 80° for 40 hr in acetonitrile.

In the reaction of **1** with other unsymmetrical acetylenes such as **2d** (150°, 100 hr), **2e** (90°, 30 hr), and **2f** (80°, 40 hr), no well-defined adducts could be isolated; only intractable side products were produced or unreacted starting materials were recovered.

The reaction of **1** with **9a** was carried out in the usual way by heating a benzene solution of methylenebisurethane in the presence of boron trifluoride etherate.[13] Work-up afforded two major products, **10** and **11**, in 18.5 and 63% yields, respectively. Compound **10** was a 1:1 adduct from its analysis and mass spectrum, M^+ at *m/e* 193, and was deduced to be *N*-ethoxycarbonyl-8-aza-δ-cyclane from the nmr signals at τ 5.90 (unsymmetrical q, J = 7.5 Hz, $CO_2CH_2CH_3$ and C_7 H), 6.52 and 6.72 (AB q, J = 9.0 Hz, C_9 methylene), 7.65 (broad s, C_1 H), 8.08 (broad s, C_6 H), 8.41 (s, C_5 methylene), and 8.75 (unsymmetrical t, J = 7.5 Hz, $CO_2CH_2CH_3$ and cyclopropane ring protons).

Compound **11**, $C_{14}H_{22}O_4N_2$, had a M^+ ion peak at *m/e* 282 in the mass spectrum and nmr signals at τ 5.15 (broad d, J = 5.5 Hz, disappeared on deuteration, two NH), 5.88 (q, J = 7.5 Hz, two $CO_2CH_2CH_3$), 6.40 (d, t, J = 6.5 and 1.5 Hz, broad s on deuteration, C_3 H),[14] 6.92 (t, J = 7.0 Hz, d, J = 7.0 Hz after deuteration, $CHCH_2NH$), 7.85–8.20 (triplet overlapping a broad singlet, J = *ca.* 7 Hz, the triplet being further split into unsymmetrical triplets with J = *ca.* 1 Hz, C_5 H and C_4 H), and 8.4–9.0 (m, overlapping a triplet, J = 7.5 Hz, two $CO_2CH_2CH_3$ and other ring protons). Hence, the structure was assigned as 3-*N*-ethoxycarbonylamino-5-*N*-ethoxycarbonylaminomethyltricyclo[2.2.1.0^{2,6}]heptane (**11**) (Scheme III). The stereochemistry at C_5 and C_3 could not be determined, though an exo orientation of the $CH_2NHCO_2CH_2CH_3$ group is logical considering that **11** should be produced by exo addition of **9a** to **1** followed by addition of urethane. **10** is apparently formed *via* an endo approach of **9a** to **1**.

SCHEME III



The very low yield of **10** in the above reaction was somewhat improved by using addenda (10 wt %) such as copper(II) chloride and bromide to afford 30 and 51%, and 32 and 46%, yields of **10** and **11**, respectively.

The reaction of **1** with benzalbisurethane under identical conditions resulted in the formation of only **12**, an adduct of urethane to **1**,[15] indicating much less reactivity of **9b** than **9a**. A trace amount of **12** was also produced in the reaction with methylenebisurethane.

Anhydrochloralurethane **9c**[16,17] gave no adducts to **1** on heating at 80° for 6 hr in benzene.

Comparison of the above results with those reported for symmetrical dienophiles is of interest in view of the homo-Diels–Alder reactivity of **1**. The fact that even an acetylenic dienophile like **2c** affords considerable amounts of cycloadducts such as **4** and **5** different from the homo-Diels–Alder adduct suggests that the unsymmetrical nature of the dienophiles is one of the important factors in determining the products, since tetracyanoethylene, a very strong symmetrical dienophile, affords quantitatively the corresponding homo-Diels–Alder adduct with **1**, while competitive 1,2 and 1,4 cycloadditions are well known in the reaction of tetracyanoethylene with dienes.[18,19] Furthermore, in the reaction with cyclopentadiene, **2c** affords the normal 1,4 cycloadduct, 2-cyano-3-chloronorbornadiene, in over 73% yield.[20]

Experimental Section[21]

General Procedure for the Reactions of 1 with Dienophiles.—An equimolar mixture of freshly distilled norbornadiene and a dienophile[22] was heated in a sealed tube under an atmosphere of nitrogen (see Tables I and II).

8-Cyano-δ-cyclene (3a).—This was obtained by distillation under reduced pressure of the crude reaction product from **1** and **2a** as a colorless oil: bp 122–124° (27 mm); $n^{19}D$ 1.5342; ir (neat) 3060 (cyclopropane), 2250 (CN), 1575 and 1460 (norbornene), and 795 cm^{-1} (nortricyclene);[9] uv max (EtOH) 224 nm (ε 7100); nmr (CCl_4) τ 3.15 (d, J = 3.3 Hz, 1, C_9 H), 7.20 (m, 2, C_1 and C_1 H_7), 7.84 (broad s, 1, C_6 H), 8.18 (m, 1, C_4 H), 8.35 (t, J = 1 Hz, 2, C_5 H), and 8.53 (m, 2, C_2 and C_3 H); mass spectrum *m/e* (rel intensity) 143 (84, M^+), 142 (73), 116 (100, M − HCN), 115 (83), and 91 (40).

Anal. Calcd for $C_{10}H_9N$: C, 83.88; H, 6.34; N, 9.78. Found: C, 84.04; H, 6.35; N, 9.61.

8-*N*-*tert*-Butylcarbamoyl-δ-cyclene (3b).—A dark brownish, sticky product obtained from **1** and **2b** was purified on a silica gel column eluting with chloroform-methanol to afford **3b** in 9.3% yield as colorless crystals: mp 152–156°; ir (KBr) 3340, 1630, 1580, 814, and 792 cm^{-1}; uv max (EtOH) 240 nm (ε 3400);

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[13] *N*-Ethoxycarbonylimines **9a** and **9b** or their delocalized cations are postulated as the intermediate in the well-known 1,4 cycloadditions of dienes with methylene- and benzalbisurethanes. For a recent review, see H. E. Zaugg, *Synthesis*, 64 (1970).

[14] For nmr data of some nortricyclene derivatives, see B. C. Henshaw, D. W. Rome, and B. L. Johnson, *Tetrahedron*, **27**, 2255 (1971); R. S. Neale and E. B. Whipple, *J. Amer. Chem. Soc.*, **86**, 3130 (1964).

[15] G. Mueller and R. Merten, *Chem. Ber.*, **98**, 1097 (1965).

[16] H. Ulrich, B. Tucker, and A. A. R. Sayigh, *J. Org. Chem.*, **33**, 2887 (1968).

[17] F. Feist, *Ber.*, **45**, 945 (1912).

[18] A. T. Blomoquist and Y. C. Meinwald, *J. Amer. Chem. Soc.*, **81**, 667 (1959).

[19] For a review, see P. D. Bartlett, *Quart. Rev., Chem. Soc.*, **24**, 473 (1970).

[20] Our unpublished data.

[21] Microanalyses were performed with a Perkin-Elmer 240 elemental analyzer. Melting points were determind with a Yanagimoto hot-stage type melting point apparatus and are corrected. Boiling points are uncorrected. Ir spectra were obtained with a JASCO IR-S spectrometer and uv spectra with a JASCO ORD/UV5 spectrometer. Nmr spectra were taken with a JEOL-C-60HL spectrometer at 60 MHz using TMS as internal standard, and mass spectra with a JEOL-01SG spectrometer at 75 eV. Vpc analyses were performed with a NEVA gas chromatograph Model 1400 and preparative vpc with a Varian Aerograph Model 700 (silicone SE-30).

[22] For cyanoacetylene (**2a**), *N*-*tert*-butylpropiolamide (**2b**), chlorocyanoacetylene (**2c**), and chloropropiolamide (**2e**), see footnotes 18–20 in ref 2a, and for dimethylaminocyanoacetylene (**2f**), see T. Sasaki and A. Kojima, *J. Chem. Soc.*, 476 (1970).

nmr ($CDCl_3$) τ 3.46 (d, J = 3.2 Hz, 1, C_9 H), 4.70 (s, 1, NH), 7.14 and 7.32 (m, 2, C_7 and C_1 H), 7.90 (broad s, 1, C_6 H), 8.22 (m, 1, C_4 H), 8.49 (m, 2, C_2 and C_3 H), and 8.60 (s, 11, C_5 H and CH_3).

Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.12; H, 8.83; N, 6.68.

8-Cyano-9-chloro-δ-cyclene (3c), ***exo*-3-Cyano-4-chlorotricyclo[4.2.1.0^{2,5}]nona-3,7-diene (4), and 2-Chloro-3-cyanotricyclo[4.3.0.0^{4,9}]nona-2,7-diene (5).**—The reaction product of **1** with **2c** could not be extensively pruified by a fractional distillation under reduced pressure, and hence preparative vpc separation was performed at 150° on a silicone SE-30 column (20 ft × 0.375 in.). The first peak afforded **4** in 6% yield as a colorless oil which on standing crystallized: mp 36–37°; ir (KBr) 2260 and 1610 cm^{-1}; uv max (EtOH) 228 (infl) and 248 nm (ϵ 1700); mass spectrum m/e (rel intensity) 179 (0.3, M + 2), 177 (1, M^+), 142 (16, M − Cl), 115 (46, M − HCN), 66 (57, cyclopentadiene), and 51 (100, cyanoacetylene).

Anal. Calcd for $C_{10}H_8NCl$: C, 67.62; H, 4.54; N, 7.88. Found: C, 67.52; H, 4.67; N, 7.70.

The second peak afforded **3c** in 40% yield as colorless crystals: mp 40–42°; ir (KBr) 2250 and 1585 cm^{-1}; uv max (EtOH) 240 nm (ϵ 9100); mass spectrum m/e (rel intensity) 179 (20, M + 2), 177 (61, M^+), 142 (99, M − Cl), and 115 (100, M − HCN).

Anal. Calcd for $C_{10}H_8NCl$: C, 67.62; H, 4.54; N, 7.88. Found: C, 67.52; H, 4.67; N, 7.70.

The third peak was very weak and was not resolved well with the fourth peak, and therefore, pure material could not be obtained.

The fourth peak gave **5** in 20% yield as a colorless oil: $n^{16.5}$D 1.5524; ir (neat) 2300 and 737 cm^{-1}; uv max (EtOH) 227 and 238 nm (ϵ 800 and 490); mass spectrum m/e (rel intensity) 179 (0.3, M + 2), 177 (1, M^+), 142 (16, M − Cl), 115 (46, M − HCN), 66 (57, cyclopentadiene), and 51 (100, cyanoacetylene).

Anal. Calcd for $C_{10}H_8NCl$: C, 67.62; H, 4.54; N, 7.88. Found: C, 67.85; H, 4.59; N, 7.60.

Reaction of 1 with Methylenebisurethane.—To a refluxing mixture of methylenebisurethane (9.5 g, 0.05 mol) and 47% boron trifluoride etherate (1.81 g) in dry benzene (50 ml) was added a solution of **1** (4.6 g, 0.05 mol) in dry benzene (20 ml) slowly over a period of 3 hr and the mixture was further refluxed for 3 hr. The cooled mixture was washed with water several times and dried over sodium sulfate. Removal of the solvent gave a dark brownish residue (*ca.* 6 g) which was purified on a silica gel column eluting with chloroform–methanol to give ***N*-ethoxycarbonyl-8-aza-δ-cyclane (10)** as a colorless oil. This was also obtained by distillation of the crude product: bp 88–90° (0.4 mm); n^{20}D 1.5179; ir (neat) 1700, 800, and 770 cm^{-1}.

Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.40; H, 7.82; N, 7.22.

Further elution gave ***N*-ethoxycarbonylamino-5-*N*-ethoxycarbonylaminomethyltricyclo[2.2.1.0^{2,6}]heptane (11)** as colorless crystals: mp 130–131°; ir (KBr) 3260, 1700, 805, and 782 cm^{-1}.

Anal. Calcd for $C_{14}H_{22}N_2O_4$: C, 59.55; H, 7.85; N, 9.92. Found: C, 59.69; H, 7.84; N, 9.76.

Reaction of 1 with Benzalbisurethane.—The reaction was carried out as above. Work-up afforded only **3-nortricyclylurethane (12)** in *ca.* 50% yield as colorless crystals, mp 61–64° (lit.[15] mp 64°); there was no depression of the mixture melting point with an authentic sample.

Reaction of 1 with Anhydrochloralurethane (9c).—An equimolar mixture of **1** and **9c**[16] in dry benzene was heated at 80° for 6 hr. After removal of the solvent, the residue was dissolved in chloroform and was purified on a silica gel column ($CHCl_3$–MeOH). The major product was an adduct of chloralurethane to **9c**, which was isolated in 23% yield as needles: mp 164–166° (lit.[17] mp 163–164°); nmr ($CDCl_3$) τ 3.95–4.70 (broad m, 4, two -NHCH), 5.78 (q, 4, two $CO_2CH_2CH_3$), and 8.70 (t, 6, two $CO_2CH_2CH_3$).

Further elution gave only unidentified oily minor products.

Registry No.—**1**, 121-46-0; **2a**, 1070-71-9; **2b**, 22237-84-9; **2c**, 2003-31-8; **2d**, 536-74-3; **2e**, 33064-30-1; **2f**, 28112-07-4; **3a**, 34627-34-4; **3b**, 34627-35-5; **3c**, 34627-36-6; **4**, 34627-45-7; **5**, 34627-37-7; **9a**, 34627-38-8; **9b**, 27593-62-0; **9c**, 16723-30-1; **10**, 34627-41-3; **11**, 34627-42-4.

Palladium-Catalyzed Vinylic Hydrogen Substitution Reactions with Aryl, Benzyl, and Styryl Halides

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Aryl, benzyl, and styryl halides react with olefinic compounds in the presence of a hindered amine and a catalytic amount of palladium metal to form vinylic derivatives in which the aryl, benzyl, or styryl group has replaced a vinylic hydrogen of the original olefin. The reactions occur readily at 100° and yields are generally good.

Mizoroki[1] and coworkers have recently reported a palladium-catalyzed arylation reaction of olefinic compounds with aryl iodides and potassium acetate in methanol at 120°. We have independently discovered this reaction and find that it can be carried out under much more convenient laboratory conditions than were used by Mizoroki and that the reaction provides an extremely convenient method for preparing a variety of olefinic compounds.

The reaction is undoubtedly closely related to the known olefinic arylations and alkylations achieved at room temperature or below with palladium salts[2,3] using organomercury, -tin, or -lead compounds rather than organic halides. While the known reactions are very useful, they suffer from two major difficulties. There is often a problem of obtaining the necessary organomercury, -lead, or -tin compounds and there is the problem of working with thick slurries of salts, particularly if the reaction is carried out catalytically in palladium. This new method eliminates both difficulties.

Results and Discussion

It is well known that $Pd[P(C_6H_5)_3]_4$ reacts readily with a variety of organic halides to form oxidative addition products of the type $[P(C_6H_5)_3]_2Pd(X)R$.[4,5] In the reaction reported herein, a similar oxidative addition apparently occurs between palladium metal (formed by an *in situ* reduction of the palladium acetate initially

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