Reaction of Lithium Naphthalene Dianion with THF.—To 200 ml of dry THF was added 1.28 g (0.10 mol) of naphthalene and 2.1 g (0.30 mol) of lithium. The mixture was degassed and covered with argon, and then stirred. The solution rapidly turned green and became reddish brown after 1 hr at 25°. The solution was then refluxed for 4 hr and the effluent gases were collected for 2 hr in cooled CCl_4 and then for 2 hr in a solution of bromine in CCl_4. The solution was then cooled and quenched with water. Analysis by gc revealed 1-ethyldihydronaphthalenes, 9%, 1-ethylnaphthalene, 19%, and 72% of naphthalene and dihydronaphthalenes. Analysis by nmr of the CCl_4 solution of effluent gases showed only a sharp singlet at δ 5.3 which moved to 3.70 on addition of bromine. Authentic 1,2-dibromoethane showed an identical nmr spectrum and had a gc retention time on several columns identical with that of this material and with the material obtained by collecting the effluent gases in bromine–CCl_4.

Reaction of lithium naphthalene dianion with 2-methyltetrahydrofuran was carried out in identical fashion except that 2.8 g (0.40 mol) of lithium was used. The nmr spectrum of the material collected in bromine–CCl_4 was identical with that of 1,2-dibromopropane plus a small peak at the position of 1,2-dibromoethane. Analysis of the mixture of dibromides by gc indicated the ratio of dibromoethane to dibromopropane to be *ca.* 1:15. Quenching of the lithium naphthalene solution with water and gc analysis indicated only a very small amount of ethylation products and some even smaller peaks at longer retention time.

Effects of Solvent and Metal on Yield of Ethylated Material.—Ampoules containing 0.320 g (2.5 mmol) of naphthalene in 5.0 ml of different dry solvents and 2.5–7.5 mmol of different alkali metals plus, in some cases, 0.75 g (7.5 mmol) of butyl vinyl ether, were prepared and sealed under nitrogen. After stirring at 25° until deep colors had formed, they were heated at 65° for 13 hr. They were then cooled, opened, quenched with a small amount of water, dried with magnesium sulfate, and analyzed for 1-ethyldihydro- and 1-ethylnaphthalene by gc. The results are shown in Table I.

Reaction of lithium naphthalene dianion with butyl vinyl ether in THF was carried out according to the procedure of Suga, *et al.*[7] A mixture of 3.2 g (25 mmol) of naphthalene, 0.70 g (0.10 mol) of lithium, and 10 g (100 mmol) of butyl vinyl ether in 50 ml of THF under nitrogen was stirred for 1 hr at 25°, then heated at reflux for 3 hr. It was then cooled and quenched with methanol. Usual work-up and analysis by gc indicated ethyldihydronaphthalenes, 6%, and 1-ethylnaphthalene, 3%, relative to the original amount of naphthalene. A reaction carried out in identical fashion except for the absence of butyl vinyl ether afforded a 16% yield of ethyldihydronaphthalenes and a 14% yield of 1-ethylnaphthalene.

Reaction of Lithium and Naphthalene with Ethylene in Tetrahydropyran.—A mixture of 6.25 g (0.049 mol) of naphthalene and 1.05 g (0.15 mol) of lithium in 50 ml of dry tetrahydropyran was stirred at 25° under nitrogen for 3 hr and then ethylene was bubbled through the solution for 1 hr by means of a glass-frit inlet tube. Quenching the solution with water, drying with magnesium sulfate, and analysis by gc revealed a 45% yield of ethyldihydronaphthalenes and 7% of 1-ethylnaphthalene. A control experiment, carried out in identical fashion except for addition of ethylene, yielded no detectable amount (less than 0.1%) of ethylated product.

Reaction of Lithium, Naphthalene, and Butyl Vinyl Ether in Tetrahydropyran.—In a glass ampoule equipped with glass-covered stirring bar were sealed 0.32 g (2.5 mmol) of naphthalene, 0.080 g (11.4 mmol) of lithium, and 0.300 g (3.0 mmol) of butyl vinyl ether in 5.0 ml of dry tetrahydropyran under vacuum. The mixture was stirred for 48 hr at 25°. Analysis by gc of the gas in the ampoule indicated a modest amount of ethylene. Analysis of the water-quenched solution indicated 2.17 mmol (72%) of *n*-butyl alcohol and a 12% (relative to naphthalene) combined yield of ethyldihydro- and ethylnaphthalene.

Registry No.—THF, 109-99-9; ethylene, 74-85-1; 1-ethylnaphthalene, 1127-76-0; 1-ethyl-1,2-dihydronaphthalene, 34599-49-0; 1-ethyl-1,4-dihydronaphthalene, 36789-17-0; lithium naphthalene dianion, 34488-61-4; 2-methyltetrahydrofuran, 96-47-9; butyl vinyl ether, 111-34-2.

Synthesis of 5-Vinylcyclohexa-1,3-diene by a Nickel-Catalyzed Cooligomerization of Acetylene and Butadiene

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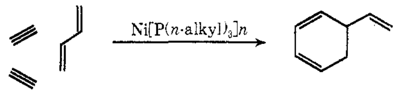
5-Vinylcyclohexa-1,3-diene is the major product formed (*ca.* 60% yield based on acetylene) when acetylene and butadiene are cooligomerized by nickel(0)–tri-*n*-alkylphosphine complexes. By-products are benzene (*ca.* 20% yield based on acetylene) and small amounts of 1,3,6-cyclooctatriene, styrene, 4-vinylcyclohexene, 1,5-cyclooctadiene, and several unidentified compounds. Isolation of 5-vinylcyclohexa-1,3-diene may be achieved by fractional distillation, under diminished pressure, of the volatile portion of the reaction mixture or by preparative glpc. This compound was previously obtained in moderate yield by pyrolysis of 1,3,5-cyclooctatriene.[1,2] As a preparative method, the synthesis described here appears more attractive.



Substituted derivatives of 5-vinylcyclohexa-1,3-diene have previously been prepared by nickel(0)-*tert*-phosphine catalyzed mixed oligomerizations of substituted acetylenes with butadiene.[3,4] However, the identities of reaction products from acetylene and butadiene were not reported, apparently because the course of the reaction was rather ill defined.[5] In yet earlier studies with $(R_3P)_2Ni(CO)_2$ complexes (R = OPh, OMe) as catalysts, acetylene and butadiene yielded small amounts of cyclooctatriene (presumably the 1,3,6 isomer) and a compound believed to be 4,5-divinylcyclohexene.[6] The principle process occurring in this study was a dimerization of butadiene.[6]

The relative simplicity of the product mixtures obtained here results largely from the choice of the *tert*-phosphine. As shown in Table I, the highest selectivity to 5-vinylcyclohexa-1,3-diene occurs with tri-*n*-alkylphosphines at R_3P:Ni mole ratios between 1:1 and 4:1. At low butadiene to acetylene mole ratios, reaction times are shortened and reaction temperatures below 25° may be used, but the selectivity to 5-vinylcyclohexa-1,3-diene suffers and the benzene yield increases.

The nickel catalyst is conveniently prepared *in situ* by treating $Ni(acac)_2$ with $AlEt_3$ at −78° in the presence of the *tert*-phosphine and the monomers, although

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TABLE I

ACETYLENE–BUTADIENE COOLIGOMERIZATIONS CATALYZED BY NICKEL COMPLEXES[a]

	Reaction conditions			Products						
	Mole ratio, C_4H_6: C_2H_2	Temp, °C	Time, hr	% Yield based on acetylene				% Yield based on butadiene		Yield, g, of others[c]
Catalytic system				VCHD[b]	COT[b]	PhH	Sty[b]	VCH[b]	COD[b]	
$Ni(acac)_2$, $3AlEt_3$	4	25	42	4	1	5	<1	<1	*d*	<0.01
$Ni(acac)_2$, $2PEt_3$, $3AlEt_3$	4	25	6	59	<1	16	5	<1	*d*	0.11
$Ni(acac)_2$, $2PPh_3$, $3AlEt_3$	4	25	69	46	2	26	1	1	1	0.09
$Ni(acac)_2$, $2P(OPh)_3$, $3AlEt_3$	4	25	17	<1	<1	2	1	<1	<1	<0.01
$Ni(acac)_2$, $P(n\text{-}Bu)_3$, $3AlEt_3$	4	25	16	61	<1	22	1	<1	*d*	0.06
$Ni(acac)_2$, $4P(n\text{-}Bu)_3$, $3AlEt_3$	4	25	6	66	<1	15	1	<1	*d*	0.06
$Ni(acac)_2$, $8P(n\text{-}Bu)_3$, $3AlEt_3$	4	25	22	41	<1	12	1	<1	*d*	0.02
$Ni(acac)_2$, $2P(n\text{-}Bu)_3$, $3AlEt_3$	1	25	3	56	1	22	1	<1	*d*	0.32
$Ni(1,5\text{-}COD)_2$, $2P(n\text{-}Bu)_3$	4	25	4	52	<1	18	ND[e]	<1	ND	ND
$(Et_3P)_2Ni(o\text{-}tolyl)Br$, MeOH	5	50	18	27	<1	17	2	<1	<1	0.12
$Ni(acac)_2$, $2P(n\text{-}Bu)_3$, MeOH	4	70	16	50	<1	32	4	ND	ND	ND
$Ni(acac)_2$, $2P(n\text{-}Bu)_3$	4	80	6	45	<1	10	1	1	<1	ND
$(Et_3P)_2NiCl_2$, MeOH	4	90	44	15	<1	12	ND	ND	<1	ND
PBu_3	4	80	5	*d*	*d*	0.5	*d*	0.5	*d*	*d*

[a] Reaction mixtures normally contained 200 mmol of butadiene and *ca.* 0.4 mmol of nickel complex. [b] Abbreviations are as follows: VCHD = 5-vinylcyclohexa-1,3-diene; COT = 1,3,6-cyclooctatriene; Sty = styrene; VCH = 4-vinylcyclohexene; COD = 1,5-cyclooctadiene. [c] Others are unidentified compounds which were detected by glpc. [d] The product was not detected by glpc. [e] ND denotes that the product yield was not determined.

the preformed nickel(0) complex $Ni(1,5\text{-}COD)_2$ plus the *tert*-phosphine gave comparable results. The true nature of the catalytically active species in solution has not been established. At −20°, a red-brown crystalline solid formed in reaction mixtures containing triphenylphosphine, but the solid decomposed while being filtered in a drybox. Treating a product mixture, containing triethylphosphine as the *tert*-phosphine ligand, with tetrachloroethylene resulted in the formation of a 23% yield of *trans*-$(Et_3P)_2Ni(CCl{=}CCl_2)Cl$. This organonickel compound can arise by an oxidative addition of tetrachloroethylene to a $(Et_3P)_n$-Ni(0) complex.[7]

Alternatively, the catalyst may be formed *in situ* from nickel(II) complexes at higher temperatures without the aid of organometallic or metal hydride reducing agents (Table I). The actual reducing agent in this case must be either acetylene, the *tert*-phosphine, or methanol, when present. In earlier reported attempts to catalyze a reaction of acetylene with butadiene using $(n\text{-}Pr_3P)_2NiX_2$ complexes, no distillable products were obtained, but $Ni(acac)_2$ afforded cyclooctatetraene by acetylene cyclotetramerization.[6] At higher temperatures, thermal Diels–Alder reactions of butadiene with itself to yield 4-vinylcyclohexene and between acetylene and butadiene to form 1,4-cyclohexadiene may also occur.

On standing, 5-vinylcyclohexa-1,3-diene undergoes spontaneous dehydrogenation to styrene and slowly polymerizes. During glpc analyses of reaction mixtures with an injection port temperature of 250°, the thermal isomerizations of 5-vinylcyclohexa-1,3-diene to tricyclo[2.2.2.0^{2,6}]oct-7-ene and of 1,3,6-cyclooctatriene to 1,3,5-cyclooctatriene were observed.[1,2] These isomerizations are avoided at an injection port temperature of *ca.* 90°. Treatment of 5-vinylcyclohexa-1,3-diene with maleic anhydride in benzene affords the Diels–Alder adduct 7-vinylbicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic anhydride.

Experimental Section[8]

All reactions were carried out under a nitrogen atmosphere with anhydrous reagents and in dry deoxygenated solvents. Triethylaluminum was used as a 25 weight % solution in cyclohexane and was purchased from Texas Alkyls. The complexes $Ni(1,5\text{-}COD)_2$,[9] *trans*-$(Et_3P)_2Ni(o\text{-}tolyl)Br$,[10] and *trans*-$(Et_3P)_2NiCl_2$[11] were prepared by published procedures. Phillips pure grade butadiene was used, and acetylene was passed through two −78° traps to remove acetone.

Acetylene–butadiene reactions were conducted in aerosol compatibility bottles, *i.e.*, thick-walled glass vessels of 3-oz capacity fitted with a stainless steel cap and sealed by a neoprene rubber O-ring. The cap was fitted with a pressure gauge, a gas inlet–outlet port, and a vertical tubular serum-stoppered port encompassing a "ball" type stopcock through which a 12-in syringe needle could be passed.

Cooligomerization of Acetylene with Butadiene to 5-Vinylcyclohexa-1,3-diene. A. By $Ni(acac)_2$, $AlEt_3$, and a *tert*-Phosphine.— To a previously dried pressure bottle was added 0.10 g (0.39 mmol) of $Ni(acac)_2$, 10.0 ml of cyclohexane, and the desired quantity of a *tert*-phosphine. The bottle was capped, flushed with nitrogen, partially evacuated, and cooled to −78°. Then 10.8 g (200 mmol) of butadiene and 1.3 g (50 mmol) of acetylene were introduced followed by 0.80 ml of 25% $AlEt_3$ in cyclohexane by syringe through the vertical port. The ball valve was closed, and the mixture was warmed to 25° and magnetically stirred until the pressure dropped from *ca.* 70 to <15 psig. The unreacted gases were vented, and the crude mixture, spiked with ethylbenzene as a standard, was analyzed by glpc isothermally at 95 and at 140°. Results are reported in Table I. Typical retention times at 95° follow: cyclohexane (1.4 min), 1,4-cyclohexadiene (3.5), 4-vinylcyclohexene (4.2), benzene (4.7), 5-vinylcyclohexa-1,3-diene (5.7), tricyclo[2.2.2.0^{2,6}]oct-7-ene (7.1), 1,3,6-cyclooctatriene (9.2), 1,5-cyclooctadiene (10.5), 1,3,5-cyclooctatriene (14.1), styrene (20.6), and several un-

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[8] Boiling and melting points are uncorrected. Infrared and nuclear magnetic resonance spectra were recorded on a Perkin-Elmer Model 257 spectrophotometer and a Varian T-60 spectrometer, respectively. Mass spectra of pure compounds were obtained on a CEC 21-110 high-resolution instrument. Mass spectra of components in mixtures were obtained with a CEC 21-130 spectrometer coupled to a Perkin-Elmer F-11 gas chromatograph *via* a Phillips-Becker molecular separator. Gas chromatographic analyses were performed on a Hewlett-Packard Model 5750 instrument, and yields were obtained using ethylbenzene as an internal standard with appropriate corrections being made for relative response factors. A 20 ft × 0.125 in. column packed with 20% 1,2,3-tris(2-cyanoethoxy)propane on 60/80 Chromosorb P was used in both chromatographs.

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known compounds (>25). 1,4-Cyclohexadiene, 4-vinylcyclohexene, benzene, 1,5-cyclooctadiene, and styrene were identified by comparison of glpc retention times with those of authentic samples and by combination glpc–mass spectral analysis. Tricyclo[2.2.2.0^{2,6}]oct-7-ene was identified by combination glpc–mass spectral analysis and by its known[1,2] formation from 5-vinylcyclohexa-1,3-diene at elevated temperatures. 5-Vinylcyclohexa-1,3-diene, 1,3,6-cyclooctatriene, and 1,3,5-cyclooctatriene were isolated by preparative glpc and were identified from their mass and nmr spectra. 5-Vinylcyclohexa-1,3-diene could also be isolated by distillation: bp 63–66° (90 mm) [lit.[2] bp 43–46° (42 mm)]; ir identical with that reported in the literature;[2] nmr (neat) τ 4.40 (m, 5, $CH{=}CH_2$ and $CH{=}CHCH{=}CH$), 5.15 (m, 2, $CH{=}CH_2$), 7.25 (m, 1, $CHCH_2$), and 8.00 ppm (m, 2, $CHCH_2$); mass spectrum (70 eV) *m/e* (rel intensity) 106 (49), 105 (31), 91 (100), 79 (51), 78 (80), 77 (41), 51 (26), 39 (25), and 29 (25). Identification of 1,3,6-cyclooctatriene is based upon the following: nmr (CCl_4) τ 3.8 (d, 2, J = 9 Hz, $CH{=}CHCH{=}CH$), 4.27 (m, 4, $CH{=}CHCH{=}CH$ and $CH_2CH{=}CHCH_2$), and 3.15 ppm (dd, 4, J = 7, 3.5 Hz, $CH_2CH{=}CHCH_2$); mass spectrum (70 eV) *m/e* (rel intensity) 106 (27), 91 (49), and 78 (100). Identification of 1,3,5-cyclooctatriene is based upon the following: nmr (CCl_4) τ 4.23 (broad d, 6, $CH{=}CHCH{=}CHCH{=}CH$) and 7.50 ppm (broad s, 4, CH_2CH_2); mass spectrum (70 eV) *m/e* (rel intensity) 106 (24), 91 (52), and 78 (100).

B. By $Ni(1,5\text{-}COD)_2$ and $P(n\text{-}Bu)_3$.—A predried pressure bottle was charged with 0.10 g (0.36 mmol) of $Ni(1,5\text{-}COD)_2$ and capped in a drybox. After the bottle was partially evacuated and cooled to −78°, 0.80 mmol of $P(n\text{-}Bu)_3$ in 6 ml of cyclohexane was syringed into the bottle, and the ball stopcock was closed. Then 12.7 g (235 mmol) of butadiene and 1.5 g (58 mmol) of acetylene were added, the bottle was warmed to 25°, and the reaction was carried out and analyzed as in A. The yield of 5-vinylcyclohexa-1,3-diene was 52%.

C. By Nickel(II) Complexes at Elevated Temperatures.—A predried pressure bottle was charged with cyclohexane, the nickel(II) compound (if any), a *tert*-phosphine (if any), 1–2 ml of methanol (if any), butadiene, and acetylene as in A. As the mixture was stirred, its temperature was increased (the bottle was immersed in a heated oil bath) until the system pressure began to decrease. After no further reaction was apparent, the reaction solution was cooled and then analyzed as in A. Results are reported in Table I.

Treatment of a Cooligomerization Product Mixture with Tetrachloroethylene.—A cooligomerization reaction was carried out as in A except with 0.30 g (1.2 mmol) of $Ni(acac)_2$, 0.27 g (2.3 mmol) of PEt_3, and 2.4 ml of 25% $AlEt_3$ in cyclohexane. After 1 hr at 25°, the cooligomerization was complete, and a product distribution comparable to those shown in Table I for tri-*n*-alkylphosphines was obtained (by glpc analysis). This crude reaction mixture was treated with 3.2 g (19 mmol) of tetrachloroethylene, and the resulting solution was stirred overnight at 25° while unreacted gases were allowed to vent. Concentration of the solution under vacuum left a brown sludge which was chromatographed on acid-washed alumina. A viscous yellow oil was eluted with 50% ether in pentane and was rechromatographed. Elution with benzene afforded 0.12 g (23%) of *trans*-$(Et_3P)_2Ni(CCl{=}CCl_2)Cl$ which, after recrystallization from MeOH, was found to be identical in all respects with an authentic sample.[7]

7-Vinylbicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic Anhydride.—A solution of 1.49 g (14.1 mmol) of 5-vinylcyclohexa-1,3-diene and 1.50 g (15.3 mmol) of maleic anhydride in 2 ml of benzene was stirred at 25° for 48 hr. Pentane (10 ml) was added, and a mushy solid was collected by filtration. The solid was washed with ice water until the filtrate no longer gave a positive test with Congo red paper. Recrystallization of the solid from hot cyclohexane afforded 1.68 g (58%) of the product: mp 81–83°; ir (Nujol) 1840 (m) and 1765 (vs) ($C{=}O$), 1628 (m) ($C{=}C$), 1375 (m), 1350 (w), 1300 (w), 1258 (m), 1245 (m), 1225 (s), 1210 (w), 1175 (w), 1086 (s), 1063 (w), 1042 (w), 1018 (w), 990 (w), 958 (s), 938 (s), 924 (s), 908 (s), 902 (s), 866 (w), 833 (m), 823 (m), 778 (w), 754 (s), 697 (m), and 687 cm^{-1} (m); nmr ($CDCl_3$) τ 3.75 (m, 2, $CH{=}CH$), 4.60 (m, 1, $CH{=}CH_2$), 5.10 (m, 2, $CH{=}CH_2$), 6.85 (broad s, 4, bridgehead CH), 7.6, 8.05, and 8.8 ppm (broad multiplets, 3, CH_2CH); mass spectrum (70 eV) *m/e* (rel intensity) 204 (0.2), 96 (12), 78 (100), and 54 (70).

Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.58; H, 5.92. Found: C, 70.7; H, 6.0.

Registry No.—5-Vinylcyclohexa-1,3-diene, 3725-32-4; acetylene, 74-86-2; butadiene, 106-99-0; $Ni(1,5\text{-}COD)_2$, 1295-35-8; $P(Bu)_3$, 998-40-3; *trans*-$(Et_3P)_2Ni(o\text{-}tolyl)Br$, 26521-33-5; *trans*-$(Et_3P)_2NiCl_2$, 15638-51-4; 7-vinylbicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic anhydride, 36749-22-1; nickel, 7440-02-0.

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Ozonolysis of the 7-Phenylnorcaranes

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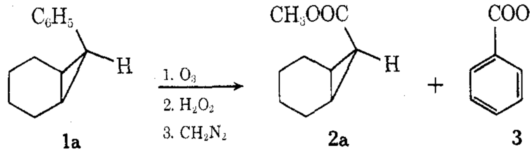
Conflicting reports of Hodgkins,[1] Closs,[2] Jensen,[3] and Ledlie[4] concerning the stereochemical assignments of the 7-phenylnorcaranes **1a** and **1b** have prompted us to reinvestigate the stereochemistry of these compounds. The structural assignments found in the literature have been based primarily on nmr data. In this paper we present the first conclusive chemical evidence supporting Closs', Jensen's, and Ledlie's assignments.

Reduction of a mixture of the 7-phenyl-7-chloronorcaranes[1] employing triphenyltin hydride yields 80% **1a**, ~1% **1b**, and 19% olefin. The olefin was removed with ozone.[1] Then work-up and distillation resulted in a sample of **1a** which was 99% pure. Subjecting **1a** to ozonization[5] furnishes a mixture of two acids which are converted to their corresponding methyl esters **2a** and **3** to facilitate their separation and identification. Preparative gas chromatography employing a 30% SE-30 column allowed separation of these materials. Compound **3** was produced in 20% yield and was identified as methyl benzoate by comparison of its ir spectrum with that of authentic material. **2a** was formed in 14% yield and was identified as *endo*-7-carbomethoxynorcarane, thereby identfying **1a** as the endo isomer of 7-phenylnorcarane. **2a** analyzed correctly for $C_9H_{14}O_2$ and exhibited an absorption band in its ir spectrum at 1734 cm^{-1} due to the $C{=}O$ stretch of the ester function. Further evidence supporting the structure of compound **2a** was obtained



1a **2a** **3**

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