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 cm^{-1}; the nmr and ultraviolet data are given above.

Anal. Calcd for $C_{23}H_{17}N_3O_2$: 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; α-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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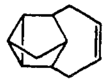
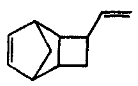
Received October 1, 1970

In a previous paper[1] 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 nortricyclenic and one (III) with the norbornenic structure.

I



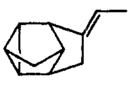
II



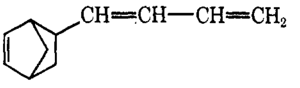
III

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 $NiCl_2$–Et_2AlCl–$2PPh_3$. On the basis of chemical and physicochemical data, formula IV was attributed to it. The same product, but with lower conversion, was obtained using a phosphine-free catalyst, prepared from a soluble nickel compound such as the diacetylacetonate.



IV



V

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,

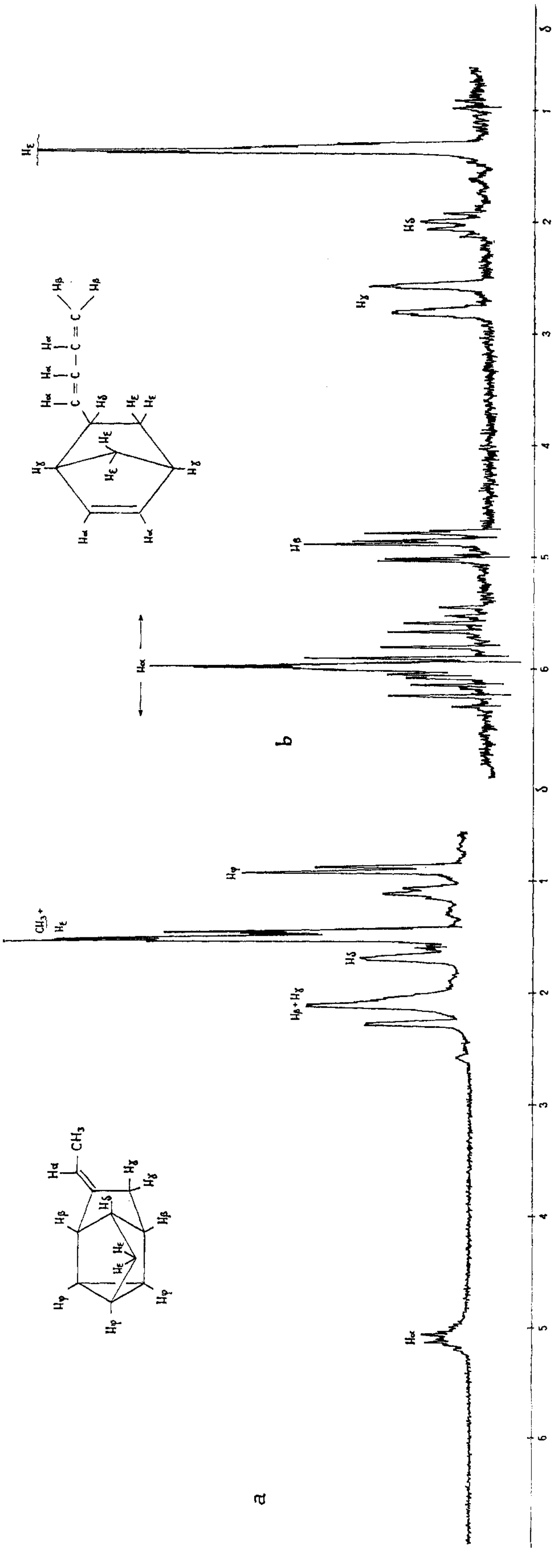


Figure 1.—^1H nmr spectra of compounds IV (a) and V (b) (Varian HA-100, CCl_4, room temperature, TMS).

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[1] A. Greco, A. Carbonaro, and G. Dall'Asta, *J. Org. Chem.*, **35**, 271 (1970).

Table I[a]

Norbornadiene–1,3-butadiene Codimerization Induced by Different Organometallic Catalyst Systems

Catalyst system				Main products[b]	
Transition metal compd, mmol	Organometallic compd, mmol	Ligand, mmol	Solvent,[c] ml	Structure	% yield[d]
$NiCl_2$,[e] 0.04	$(C_2H_5)_2AlCl$, 0.5	$P(C_6H_5)_3$,[e] 0.08	TOL, 30	IV I	8 2.5
$CoCl_2$, 0.36	$(i\text{-}C_3H_7)MgCl$, 3.6		DEE, 30	V	12
CoA_3,[f] 0.09	$(C_2H_5)_3Al$, 0.9		TOL, 25	V	43
$CoCl_2$,[e] 0.03	$(C_2H_5)_3Al$, 0.4	$[(C_6H_5)_2PCH_2]_2$,[e] 0.06	TOL, 20	II	44
$CoCl_2$,[e] 0.07	$(C_2H_5)_2AlCl$, 0.7	$[(C_6H_5)_2PCH_2]_2$,[e] 0.14	TOL, 35	II	68
MnA_2,[f] 0.12	$(i\text{-}C_3H_7)MgCl$, 1.2		DEE, 15	V III	4.5 3
MnA_2,[f] 0.19	$(C_2H_5)_3Al$, 1.9		HEX, 25	V III	5 3
MnA_2,[f] 0.13	$(i\text{-}C_3H_7)MgCl$, 1.3	$(C_6H_5)_2P(OC_4H_9)$, 0.6	DEE, 15	V III	13 8

[a] NBD = 19.7 mmol; BD = 24 mmol; temperature, 75°; time, 5 hr. [b] By-products mainly consist of NBD dimers. [c] TOL = toluene, DEE = diethyl ether, HEX = *n*-hexane. [d] Moles of the main product/moles of NBD introduced. [e] Transition metal compound/ligand complex preformed. [f] A = acetylacetonate.

such as $Fe(CO)_5$ or cobalt diacetylacetonate–Et_3Al,[2] were found to be almost uneffective at 150°.[3]

Isomerization of I to IV (to more than 90%: Experimental Section) could be achieved in the presence of the $Ti(OBu)_4$–Et_3Al catalytic system at 150° for 1 hr. No other catalysts, among those investigated, yield appreciable amounts of oligomer IV. We should therefore deduce that IV is a primary product of the NBD–BD codimerization induced by organometallic nickel catalysts.

The behavior of the soluble cobalt catalysts is strongly influenced by the presence or absence of the bidentate 1,2-bis(diphenylphosphino)ethane ligand. The complex of $CoCl_2$ with the said phosphine, when combined with both Et_3Al and Et_2AlCl (Table I), yields adduct II in a very selective way. By contrast, the system obtained from an acetylacetonate of Co and Et_3Al or from $CoCl_2$ and $(i\text{-}C_3H_7)MgCl$ in diethyl ether yields, in an equally specific way, a new adduct to which structure V was assigned.[3a]

Other catalysts examined are those prepared from a manganese compound and Et_3Al or from a chloroisopropyl Grignard reagent. NBD and BD are induced to codimerize to a mixture of III and V, the latter being the main compound.[4] The presence of mono- and bidentate phosphorus ligands does not influence, in the case of manganese catalysts, the nature of the final products, but only the conversion.

Among the NBD–BD codimers, compound V is the only one formed through a hydrogen shift from one to the other reacting olefin. This type of addition of a butadiene to one cycloolefinic double bond was never observed before, as far as we know. It may be formally compared with one of the ethylene–butadiene codimers, *i.e.*, 1,3-hexadiene, formed by hydrogen shift from these two monomers by the action of analogous $CoCl_2$–Et_3Al catalysts.[5]

Assignment of Structures IV and V. Adduct IV.—The mass spectrum parent peak is at *m/e* 146. The ^1H nmr spectrum (Figure 1a) shows multiplets centered at δ 5.1 (1 H), 2.27 (1 H), 2.1 (3 H), 1.69 (1 H), 1.48 (5 H), 1.1 (1 H), and 0.9 ppm (2 H). The signal at δ 5.1 may be attributed to the only hydrogen attached to an unsaturated carbon atom. The methyl protons, together with two others, originate the signal at δ 1.48; this position is justified by the presence of the double bond in α. All other signals are derived from the nortricyclenic protons.

The ir spectrum shows absorptions at 790 (vs) and 821 cm^{-1}, attributed to the nortricyclenic system,[6] whereas a band at 3040 cm^{-1} is due to the C—H stretching of the C=C double bond. The spectrum is rich in bands especially in the region between 500 and 1350 cm^{-1}.[7]

Adduct V.—The mass spectrum parent peak is at *m/e* 146. The ^1H nmr spectrum (Figure 1b) shows a peak system between δ 6.35 and 5.45 (5 H), as well as multiplets centered at about δ 4.9 (2 H), 2.8 (1 H), 2.56 (1 H), 2.02 (1 H), and 1.35 ppm (4 H). The two protons of the cycloolefin double bond and the three CH groups of the butadienyl residue should originate the system of bands at δ 6.35–5.45,[8] whereas the vinyl protons of the butadienyl residue should be attributed to the signal at about δ 4.9 (system of three bands). The two nonequivalent protons at δ 2.8 and 2.56 should be those α to the cycloolefinic unsaturation,[8] whereas at about δ 2 there should be the proton at the ring carbon atom bearing the side group. The remaining four saturated methylene hydrogens likely originate the signal at δ 1.35.[8]

The ir spectrum of V shows characteristic absorptions of the norbornenic system[5] at 3060, 1568, 1332, and 712 cm^{-1}; of the vinyl group at 1415, 1000, and 900 cm^{-1}; and of the internal trans double bonds at 951 cm^{-1}.[9] The uv maximum at 230 nm (log ϵ 4.59) is due to the trans double bond.

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[2] M. W. Schneider (to B. F. Goodrich), French Patents 1,555,199 and 1,556,198 (priority 1967).

[3] According to our results, compound III isomerizes to the corresponding ethylidene derivative in the presence of said Fe or Co catalysts.

[3a] Note Added in Proof.—Compound V has recently been described also by A. Takahashi and T. Inukai, *Chem. Commun.*, 1473 (1970).

[4] Our unpublished results show that manganese-based catalysis selectively trimerizes butadiene to *trans,trans,trans*-1,5,9-cyclododecatriene.

[5] D. Wittenberg, *Angew. Chem.*, **75**, 1124 (1963); A. Carbonaro, G. Dall'Asta, and A. Greco, *Chim. Ind.* (*Milan*), **52**, 49 (1970).

[6] J. J. Mrowca and T. J. Katz, *J. Amer. Chem. Soc.*, **88**, 4012 (1966), and references quoted therein.

[7] The main ir bands of IV are at 2920 (vs), 2845, 1683, 1447 (s), 1428 (s), 1371, 1309 (s), 1290 (s), 1250 (s), 1167, 1122, 1049, 980 (s), 960, 950, 883, 841 (s), 700, 589, and 511 cm^{-1} (s).

[8] P. Laszlo and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964).

[9] Other significant ir bands of V are at 3087, 3038, 2965 (vs), 2870, 1648 (s), 1601, 1460, 1446 (s), 1415, 1282 (s), 1250 (s), 1135, 1098, 1082, 869 (s), 835, and 650 cm^{-1}.

Experimental Section

Reagents.—Toluene, *n*-hexane, and diethyl ether were dried by distillation over $LiAlH_4$ and stored under nitrogen. Norbornadiene (Fluka, practical grade) and butadiene (Phillips, special purity) were used as supplied. Triphenylphosphine (BDH) and other phosphines (Strem) were commercial products. Cobalt and nickel chlorides were dried by treatment with $SOCl_2$. $(i\text{-}C_3H_7)MgCl$ Grignard reagent was prepared from 2-chloropropane (Fluka, practical grade) and Mg turnings. Et_3Al and Et_2AlCl (Fluka, practical grade) were used as supplied.

Oligomerizations.—The reactions were run in glass vials under nitrogen. The reagents were introduced into the reactor in the following order: transition metal compound, ligand (when used), solvent, BD, NBD, and organometallic compound. A small amount of *n*-decane was added as internal standard for quantitative estimations in the glc analysis. The mixture was normally prepared at −78° and kept in a thermostatic bath. At the end of the reaction small amounts of methanol and phenyl-β-naphthylamine were added.

Characterization of the Compounds.—The quantitative composition of the reaction products was determined by glc (C. Erba, Fractovap C, methylsilicone SE 30, P 30–60 mesh, 2 m, 80°, He) on the crude mixture. Isolation of pure C_{11} compounds was accomplished by preparative glc (C. Erba, Fractovap P 100, Apiezon L, Chromosorb W 50–60, 8 m, 220°, He) on fractions enriched by distillation. Spectroscopic characterizations were performed on a Perkin-Elmer 125 ir spectrophotometer (NaCl optics), Varian HA 100-MHz nmr spectrometer (CCl_4, room temperature, TMS reference), and Hitachi RMU 6 E (70 eV, 250°) mass spectrometer.

Anal. Calcd for $C_{11}H_{14}$: C, 90.42; H, 9.58. Found for IV: C, 90.19; H, 9.22. Found for V: C, 90.78; H, 9.61. Physical properties of IV and V: IV, bp 187–189°, n^{24}_{D} 1.4955; V, bp 190–192°, n^{24}_{D} 1.5188.

Registry No.—IV, 28229-18-7; V, 28229-10-9.

Facile Olefin Hydrogenation with Soluble Lithium-Based Coordination Catalysts

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There has been considerable interest in soluble hydrogenation catalysts in recent years. Numerous Ziegler-type catalysts have been developed to effect facile hydrogenation of olefins using alkylaluminum compounds as reducing agents.[1-5] Although Sloan, *et al.*,[1] mention the use of alkyllithiums as reducing agents combined with transition metal salts of groups IV–VIII metals, they prefer alkylaluminums, claiming shorter reduction times. Several patents have also briefly mentioned alkyllithiums as cocatalysts in olefin reductions, but the use of alkylaluminums was preferred.[2-5] We have now found that previous investigators severely underestimated the reactivity of reduction catalysts prepared from alkyllithiums. In our studies Ziegler-type hydrogenation catalysts made from organolithium compounds and transition metal salts of 2-ethylhexanoic acid were fully as active as alkylaluminum-based catalyst systems at convenient concentration levels of catalyst. They are preferable because of the ease of handling of organolithiums compared with alkylaluminums. While these catalysts are generally referred to as soluble, they might exist in a finely divided suspended form. They do not deteriorate when aged for several months.

Active lithium-based hydrogenation catalysts may be prepared by slowly adding a solution of transition metal 2-ethylhexanoate in cyclohexane to a solution of an alkyl- or aryllithium dissolved in cyclohexane or benzene under a nitrogen atmosphere. This catalyst, in the presence of hydrogen, will reduce a variety of cyclic and acyclic olefins, as shown in Table I, utilizing mild conditions of temperature, 50°, and pressure, 50 psi of hydrogen. Cyclic, mono-, and disubstituted acyclic olefins are easily reduced quantitatively in 30 min or less. Trisubstituted olefins such as 1-methylcyclohexene and 2-methylpentene-2 are more resistant to hydrogenation, and the tetrasubstituted olefin 2,3-dimethylbutene-2 is the most resistant. Unsaturation adjacent to an aromatic nucleus is easily hydrogenated, as evidenced by the quantitative reduction of the vinyl group in styrene in 20 min.

TABLE I

HYDROGENATION OF OLEFINS WITH SOLUBLE HYDROGENATION CATALYSTS[a]

Olefin	Catalyst level, mol %	Li/Co	Time, min	% conversion[b]
Cyclooctene	0.6	4.0	30	100
Cyclohexene	0.5	4.0	20	100
Cycloheptene	0.5	3.0	30	100
1-Methylcyclohexene	0.2	6.0	90	44
cis-Pentene-2	0.4	4.0	20	100
Hexene-1	0.5	4.0	20	100
2-Methylpentene-2	0.5	4.0	60	92
trans-Pentene-2	0.4	4.0	30	100
Styrene[c]	0.6	4.0	20	100
2,3-Dimethylbutene-2	0.5	4.0	90	37

[a] Hydrogen pressure, 50 psi; 50°; *n*-butyllithium–cobalt 2-ethylhexanoate cocatalysts. [b] Determined by gas chromatography. [c] Reduction of the vinyl moiety.

The catalytic activity of lithium–cobalt hydrogenation catalysts compares favorably with an aluminum–cobalt catalyst having an aluminum to cobalt ratio (3.3:1) shown by Sloan, *et al.*,[1] to give facile hydrogenations.[6]

The activity of hydrogenation catalysts prepared from alkyl- or aryllithium and transition metal salts of 2-ethylhexanoic acid is a function of the molar ratio of lithium to cobalt (Table II, entries 1–5). At low lithium/transition metal ratios, Li/Co = 1.7, active hydrogenation catalysts are not formed, while at a higher lithium/cobalt ratio, 9.9, hydrogenation activity is greatly diminished. Intermediate ratios give quite active hydrogenation catalysts.

The rate of hydrogenation increases with an increase in catalyst concentration (Table II, entries 6–8). At 0.3 mol % catalyst cyclooctene is rapidly hydrogenated, while at 0.1 mol % catalyst the reaction is slightly slower. At 0.05 mol % catalyst, reduction ceases. The failure to observe hydrogenation of cyclooctene

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(1) M. F. Sloan, A. S. Matlack, and D. S. Breslow, *J. Amer. Chem. Soc.*, **85**, 4014 (1963); U. S. Patent 3,113,986 (Dec 10, 1963).

(2) W. R. Kroll, U. S. Patent 3,412,174 (Nov 19, 1968).

(3) French Patent 1,575,046 (June 9, 1969).

(4) Belgian Patent 718,668 (Sept 30, 1968).

(5) S. J. Lapporte, U. S. Patent 3,205,278 (Sept 7, 1965); *J. Org. Chem.*, **28**, 1947 (1963).

(6) A triethylaluminum–cobalt 2-ethylhexanoate catalyst having an Al/Co of 3.3 and at a concentration of 0.3 mol % quantitatively hydrogenated cyclooctene in cyclohexane in 20 min at 50° and 50 psi of hydrogen.