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# Reaction of Norbornene with Butadiene Catalyzed by Low-valent Cobalt, Giving *trans*-1-(*exo*-Norbornyl)-1,3-butadiene

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Transition metal-catalyzed reactions between olefins and butadiene generally occur through hydrogen transfer from the olefins to butadiene to give substituted 1,4-hexadienes[1] according to

$$CH_2{=}CHR + CH_2{=}CH\text{-}CH{=}CH_2 \longrightarrow \left\{\begin{array}{l} CH_2{=}CR\text{-}CH_2\text{-}CH{=}CH\text{-}CH_3 \\ RCH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}CH_3 \end{array}\right. \quad (1)$$

$$(R{=}H,\ \text{alkyl},\ COOEt)$$

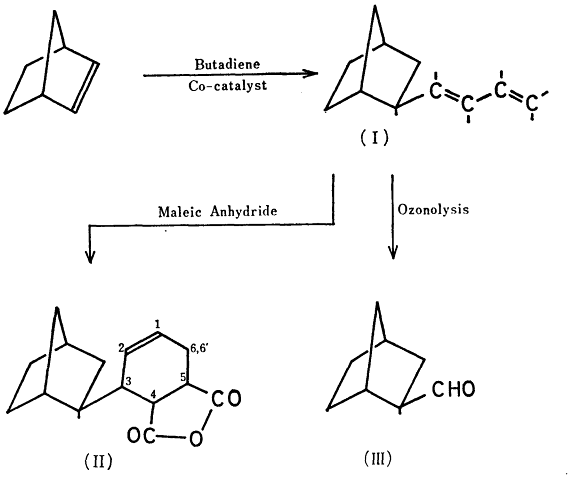
We recently reported,[2] however, that norbornadiene reacts with butadiene in the presence of cobalt catalysts of low valency, involving hydrogen transfer converse to that above, to give 5-butadienylnorborn-2-ene. This seems to be the first example of butadienylation of an internal carbon-carbon double bond. A similar butadienylation of terminal double bonds has been documented but is incomplete[3] and somewhat dubious,[4] except when the olefin is ethylene.[5]

We wish to report here another example of butadienylation, the reaction of norbornene with butadiene by low valent cobalt catalyst giving *trans*-1-(*exo*-norbornyl)-butadiene (I) with high stereochemical selectivity.

## Results

Norbornene and butadiene were heated in a stainless steel reactor at 20—40°C for several hours under nitrogen in the presence of the catalysts prepared from $Co(acac)_3$ and $Et_3Al$. The reaction gave 30—40% yield of a mixture of 1: 1 adducts (codimers), which was found by glpc analysis to consist of a main component (80—95%) and four minor ones. Practically no homodimers or oligomers were formed as by-products. The main product was separated by preparative glpc and its structure was determined as (I) from the following observations (Chart 1).

It has MW 148 (mass spectrum). The UV spectrum shows a typical s-*trans* 1,3-diene absorption, $\lambda_{max}$ 230 nm, $\varepsilon_{max}$ 28100, in cyclohexane, and the IR spectrum (liquid film) shows the $\nu_{C=C}$ at 1603 and 1650 $cm^{-1}$, $\delta_{C-H}$ of vinyl group at 892 and 1000 $cm^{-1}$, and $\delta_{C-H}$ of internal *trans* hydrogens at 949 $cm^{-1}$. That the butadiene moiety is *trans* substituted at its 1-position is proved by the facile reaction with maleic anhydride to give a Diels-Alder adduct whose NMR and IR spectra are consistent with the assigned structure of 3-norbornylcyclohexene-4,5-dicarboxylic anhydride (II). The butadienyl group is specifically located at the *exo* position of norbornane because *exo*-2-formylnorbornane (III) free from the *endo* isomer is obtained on ozonolysis of the main product. Consequently we conclude that it is *trans*-1-(*exo*-norbornyl)-1,3-butadiene (I).



Chart

Temperature around 40°C was found optimum for preparation of (I): at higher temperatures the selectivity for (I) tends to decrease presumably owing to the concomitant Diels-Alder reactions and the conversion decreases sharply. The molar ratio of $Et_3Al$:

TABLE 1. REACTIONS OF NORBORNENE WITH BUTADIENE USING SEVERAL COBALT CATALYST SYSTEMS[a)]

| Catalyst components (mmol) | | Conversion[b)] (%) | Selectivity[c)] (%) |
|---|---|---|---|
| $Co(acac)_3$ (0.5) | $Et_3Al$ (1.5) | 36 | 84.5 |
| $Co(acac)_3$ (0.5) | $Et_3Al$[d)] (1.5) | 36 | 90 |
| $Co(acac)_3$ (0.5) | $Et_3Al$[e)] (1.5) | 34 | 80 |
| $CoCl_2$ (0.5) | $Et_3Al$ (1.5) | 20 | 80 |
| $Co(acac)_3$ (0.5) | *i*-$Bu_3Al$(2.0) | 32 | 82 |
| $Co(acac)_3$ (0.5) | $Et_2(OEt)Al$ (2.0) | 32 | 82 |

a) Reaction at 40°C, 4 hr; norbornene 43 mmol, butadiene 50 mmol, and *ca.* 2 m*l* of benzene.
b) Conversion of norbornene as determined from unreacted norbornene (glpc).
c) Percentage of (I) in the codimer fraction.
d) Plus ethylenediamine (1 mmol).
e) Plus ethanolamine (1 mmol).

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[1] *Cf.* C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Academic Press, London (1967), Chapter 2.

[2] A. Takahashi and T. Inukai, *Chem. Commun.*, **1970**, 1473. See also A. Carbonaro, F. Cambisi, and G. Dall'Asta, *J. Org. Chem.*, **36**, 1443 (1971).

[3] D. Wittenberg, *Angew. Chem.*, **75**, 1124 (1963); H. Müller, D. Wittenberg, H. Seibt, and E. Scharf, *ibid.*, **77**, 318 (1965). Butadienylation of several terminal olefins and acrylates was claimed without evidence to prove the structures of the reaction products.

[4] Different structures have been given: A. Misono, Y. Uchida, T. Sato, and K. Uchida, This Bulletin, **40**, 1889 (1967); H. Singer, W. Umbach, and M. Dohr, *Synthesis*, **1971**, 265.

[5] T. Saito, Y. Uchida, and A. Misono, This Bulletin, **38**, 1397 (1965).

Co(acac)$_3$ can be varied from 1 to 6 without remarkable effect on selectivity and conversion. The molar ratio of norbornene to butadiene showed only minor effect on yield of (I) within the range 0.5—1.5. Excessive imbalance of the reactant ratio proved undesirable. The results with various catalyst combinations are summarized in Table 1.

Other internal double bond compounds such as cyclopentene, cyclohexene, cyclooctene, *endo*-dicyclopentadiene and *cis*-butene gave little if any codimers with butadiene under similar reaction conditions. Thus butadienylation at an internal double bond seems to be specifically limited to norbornene and norbornadiene.[2]

The reaction provides a convenient route to *exo* norbornane derivatives which are difficult to prepare in stereochemically pure state. As an example, *exo*-2-formylnorbornane prepared by the method given by Alder and Stein[6] was found to be contaminated with the *endo* isomer which could not be completely removed. Pure *exo* (I) and (III) are evidently versatile starting materials for various *exo* substituted norbornanes.

## Experimental[7]

*Materials.* Norbornene (Aldrich Co.) solution in benzene was dehydrated and deaerated by distillation under nitrogen. Butadiene was dried by passing through a CaCl$_2$ column and deaerated by distillation in vacuum. Desiccated Co(acac)$_3$ (EP grade) was used. Alkylaluminums were purified by vacuum distillation of commercial products.

trans-*1-(*exo-*Norbornyl)-butadiene (I).* In a typical example, butadiene (0.2 mol), norbornene (0.2 mol), Co(acac)$_3$ (2 mmol), Et$_3$Al (6 mmol), and 2 m*l* of benzene were put into a 100 m*l* stainless steel autoclave under nitrogen and heated to 40°C for 4 hr. The catalysts were killed with acetone (2 m*l*) and the mixture was subjected to steam-distillation with a trace of hydroquinone. The oily product was dried with anhydrous sodium sulfate and distilled to give 10.3 g of a codimer fraction, bp 72.5°C at 9 mmHg. The product was 96% pure (I) by glpc (Silicone DC-550). It was purified by glpc using a Silicone DC-550 preparative column.

Found: C, 89.0; H, 11.1%. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88%.

*Diels-Alder Adduct (II).* A solution of 3.01 g of (I) and 1.96 g of maleic anhydride in 25 m*l* of benzene was warmed to 45°C for 5 hr and was let to stand overnight at room temperature. The solvent was removed under reduced pressure, and the residue with mp 95—120°C, was recrystallized repeatedly from benzene-hexane solvent (1 : 2 by volume) to attain mp 148—149°C.

Found: C, 73.3; H, 7.5%. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.33%.

NMR (in CDCl$_3$): $\tau$ 4.02 (2H; $H_{(1)}$ and $H_{(2)}$, apparent doublet, *J ca.* 4 Hz); $\tau$ 6.60 (2H; $H_{(4)}$ and $H_{(5)}$, multiplet); $\tau$ 7.28 (1H; $H_{(3)}$, a pair of triplets); $\tau$ 7.6—9.2 (13H; $H_{(6)}$, $H_{(6')}$, and norbornyl protons, overlapped multiplets).

*2-*exo-*Formylnorbornane (III).* Ozonized oxygen was bubbled through a solution of 0.034 mol of (I) in methanol (100 m*l*) at −70°C, excess ozone was purged with stream of nitrogen, and triphenylphosphine (0.12 mol) in ether (100 m*l*) was added dropwise to the ozonide solution during a period of 40 min. The dry ice-acetone bath was removed to let the reaction mixture stand overnight at room temperature. (III) was codistilled with the solvent under reduced pressure into a cold trap (−70°C) and redistilled, bp 66—68°C at 12 mmHg; yield 2.5 g (59% of theory). By comparison of its glpc peak (Golay column R-45, polypropylene glycol, Hitachi) with those of the *exo*- and *endo*-2-formylnorbornane mixture obtained by the method of Alder and Stein starting from cyclopentadiene and acrolein,[6] it was found that the product was pure *exo* III free from *endo*.

Semicarbazone, mp 173—174°C (lit,[6] mp 178°C), showed IR and NMR spectra which are superposable with those of the authentic *exo* semicarbazone.

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[6] K. Alder and G. Stein, *Ann. Chem.*, **525**, 247 (1936).

[7] All melting points are uncorrected. IR and UV spectra were determined with Nihon Bunko Model 402G and Hitachi Model EPS-III spectrophotometers, respectively. NMR spectra were taken with a Varian A-60A spectrometer.