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The Stereochemistry of Cross-coupling Adducts of Norbornenes with Butadiene Catalyzed by Ni Complex

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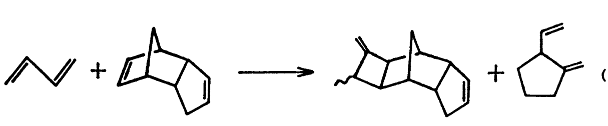
Synopsis. The stereochemistry of cross-coupling adducts of norbornenes with butadiene catalyzed by Ni complex generated in situ by $NiBr_2(Ph_3P)_2$ and $NaBH_4$ in ethanol was investigated. The configuration of four-member cross-coupling products could be confirmed by means of independent synthesis.

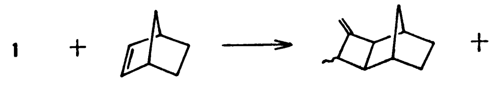
The Ni catalyzed cross-coupling reaction of butadiene (**1**) with strained olefins, such as *endo*-tricyclo[5.2.1.0^{2,6}]-deca-3,8-diene (**2**), gives the four-member cross-coupling product (**3**) together with a small amount of 1-methylene-2-vinylcyclopentane (**4**) (Eq. 1).[1,2]


(1)

1 **2** **3** **4**

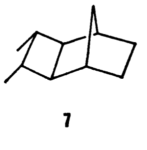
Unfortunately, the stereochemistry on coupling reactions has not been established because of the difficulty in determining the configuration of the coupling products. However, this unusual coupling reaction is of interest from the synthetic and mechanistic aspects. Thus, the coupling reactions of **1** with some strained olefins having a bicyclo[2.2.1]heptene skeleton catalyzed by $NiBr_2(Ph_3P)_2$ and $NaBH_4$ were studied to confirm the stereochemistry of cross-coupling products; the stereochemical course of coupling reactions is briefly discussed here.

In order to obtain the most simple cross-coupling product, **1** was allowed to react with bicyclo[2.2.1]-heptene (**5**), in the presence of $NiBr_2(Ph_3P)_2$ and $NaBH_4$ in ethanol (Eq. 2).


1 + ⟶ + **4** (2)

5 **6**

The four-member coupling product (**6**) was obtained in 60% yields together with **4** (12%). The exo-configuration of adduct **6** was readily assigned from the characteristic ^{13}C NMR chemical shift of the bridge carbon (C-9).[3] The hydrogenation of **6** on Pd/C suggested the formation of **7** or **8**, but not **9**, because the ^{13}C NMR spectrum of the hydrogenation product consisted of six carbon signals. The determination of configuration, either **7** or **8**, could be achieved by the independent synthesis of **8**.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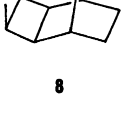
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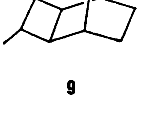
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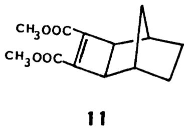
Under the influence of $RuH_2(Ph_3P)_4$ catalyst, **5** reacts with dimethyl acetylenedicarboxylate (**10**) to give [2+2] cross-adduct (**11**) which on subsequent hydrogenation on Pd/C is converted into a saturated compound (**12**), whereupon both methoxycarbonyl groups are oriented in the syn-direction.[4]



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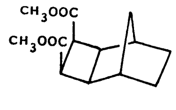

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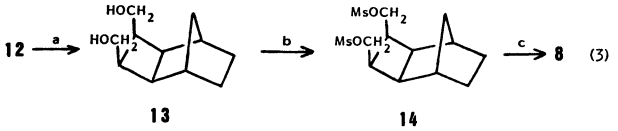


(3)

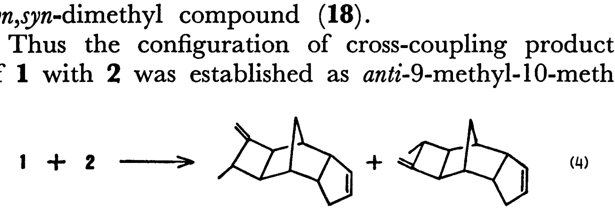
13 **14**

a : $LiAlH_4$, Et_2O b : MsCl, Et_3N c : $LiAlH_4$, THF

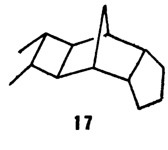
Since the subsequent interconversion of **12** to **8** proceeds with complete retention of the stereochemistry, **12** was converted into *syn,syn*-3,4-dimethyl-*exo*-tricyclo[4.2.1.0^{2,5}]nonane (**8**) (Eq. 3). From the comparison of spectral data of **8** with those of the compound obtained by the hydrogenation of **6** derived from Ni catalyzed reaction, it was identified as *anti,anti*-3,4-dimethyl-*exo*-tricyclo[4.2.1.0^{2,5}]nonane (**7**). Thus the configuration of **6** could be assigned to *anti*-3-methyl-4-methylene-*exo*-tricyclo[4.2.1.0^{2,5}]nonane.

On the other hand, the reaction of **1** with **2** catalyzed by Ni-complex gave cross-coupling products which consisted of two components[5] with approximately 1:1 ratio, whose NMR spectral patterns were very similar. The hydrogenation of coupling products led to the same saturated compound, which was identified to *anti,anti*-9,10-dimethyl-2-*endo*-8-*exo*-tetracyclo[5.4.2.1.0^{2,6}.0^{8,11}]dodecane (**17**), since the Ru-catalyzed reaction of **2** with **10** followed by the interconversion of functional groups afforded the corresponding *syn,syn*-dimethyl compound (**18**).

Thus the configuration of cross-coupling products of **1** with **2** was established as *anti*-9-methyl-10-meth-


1 + **2** ⟶ + (4)

15 **16**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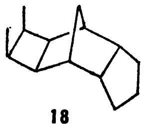
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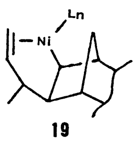

19

ylene-2-*endo*-8-*exo*-tetracyclo[5.4.1.$0^{2,6}$.$0^{8,11}$]dodec-3-ene (**15**) and its regioisomer (**16**).

Kiji[2] suggested that the active species of coupling reaction of **1** with **2** catalyzed by $NiCl_2(n\text{-}Bu_3P)_2$ and $NaBH_4$ is a nickel hydride such as $HNiBr(n\text{-}Bu_3P)_2$,[6] and that the reaction proceeds through a π-crotyl nickel intermediate. Consequently, π-crotyl nickel thus generated couples with a strained olefin coordinated to nickel to form an intermediate such as **19** which subsequently undergoes β-elimination after coupling to give the four-member cross-coupling adduct. This reaction path explains satisfactorily the formation of regioisomers of **15** and **16** for the coupling reaction of **1** with **2**.

Experimental

The ^{1}H NMR and ^{13}C NMR spectra were recorded with a JEOL PMX-60 and a JNM-PS-100 FT-NMR spectrometer, respectively. The IR spectra were taken with a JASCO-A202 spectrometer. The GLC analyses were carried out on a Yanagimoto G1800 apparatus. The melting and boiling points are uncorrected.

Materials. Unless otherwise noted, the materials were obtained from commercial suppliers and used without further purification, except for solvents. *endo*-Tricyclo[5.2.1.$0^{2,6}$]-deca-3,8-diene (**2**) was prepared from the dimerization of cyclopentadiene obtained by the destructive distillation of commercially available **2**. Solvents were purified by the conventional methods.

*Coupling Reactions of **1** with **2** and **5** Catalyzed by $NiBr_2(Ph_3P)_2$–$NaBH_4$.* A solution of $NiBr_2(Ph_3P)_2$[7] (4 mmol) and $NaBH_4$ (4 mmol) in ethanol (30 cm^3) was placed in an autoclave and then **1** (72 mmol) and **5** (60 mmol) was added to this solution at −78 °C under nitrogen stream. The mixture was allowed to react under stirring at 80 °C for 24 h, and the reaction mixture was extracted with hexane (50 cm^3×4). After evaporation of solvents, the residue was distilled under reduced pressure to give (**6**) (60%), bp 118—120 °C/3300 Pa; IR(neat) 3050, 2940, 1680, 1450, 880 cm^{-1}; ^{13}C NMR($CDCl_3$) δ=158.2(s), 105.2(t), 49.1(d), 46.6(d), 40.8(d), 39.4(d), 39.3(d), 32.9(t), 28.4(t), 27.4(t), 20.1(q). Found: C, 89.10; H, 10.85%. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88%.

The hydrogenation of **6** (1 mmol) in hexane (10 cm^3) on 5% Pd/C (30 mg) under 50 kg/cm^2 H_2 gave a saturated compound **7** (95%), bp 119—123 °C/3300 Pa; IR(neat) 2930, 2850, 1450, 1210, 750 cm^{-1}; ^{13}C NMR($CDCl_3$) δ=48.1(d), 38.5(d), 33.2(t), 33.0(d), 27.8(t), 15.6(q).

The coupling reaction of **1** with **2** was carried out in a similar manner to that above to give a regioisomeric mixture of **15** and **16** in 70% yields; this was hydrogenated to give **17** (95%), bp 124—126 °C/2660 Pa; IR(neat) 2940, 1470, 1450, 1060, 890 cm^{-1}; ^{13}C NMR($CDCl_3$) δ=44.7(d), 43.7(d), 41.7(d), 37.7(t), 32.9(d), 29.2(t), 15.8(q). Found: C, 88.38; H, 11.60%. Calcd for $C_{14}H_{22}$: C, 88.35; H, 11.65%.

*Preparation of **8** and **18**.* To a solution of $LiAlH_4$ (18 mmol) in ether (70 cm^3) was added dropwise an etheral solution of **12** (15 mmol) prepared according to the literature procedure,[4] and then the mixture was refluxed for 5 h. After decomposition of unreacted $LiAlH_4$ with ethyl acetate, followed by H_2O, the reaction mixture was extracted with ether. Removal of solvents yielded **13** (85%); the immediate mesylation of **13** according to the method of Jung[8] gave dimesylate (**14**) (42%). The treatment of **14** (4.5 mmol) with $LiAlH_4$ (10.8 mmol) in THF (20 cm^3) by the method of Mitsudo[9] afforded hydrocarbon **8** (44%), which was separated by MPLC on silica gel (elution with 10% ether in hexane); IR(neat) 2920, 2850, 1450, 1090, 660 cm^{-1}; ^{13}C NMR($CDCl_3$) δ=44.7(d), 36.7(t), 35.5(d), 31.9(d), 29.3(t), 9.2(q). Found: C, 87.85; H, 12.10%. Calcd for $C_{11}H_{18}$: C, 87.93; H, 12.07%.

Compound **18** was prepared by the same method as above; IR (neat) 2940, 1470, 1440, 1050, 760 cm^{-1}; ^{13}C NMR($CDCl_3$) δ=46.2(d), 41.1(t), 40.4(d), 37.8(d), 31.5(d), 29.1(t), 26.9(t), 9.1(q). Found: C, 88.30; H, 11.70%. Calcd for $C_{14}H_{22}$: C, 88.35, H, 11.65%.

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