

Asymmetric Catalysis. 61¹. Optically Active Nortricyclenes by Enantioselective Catalysis

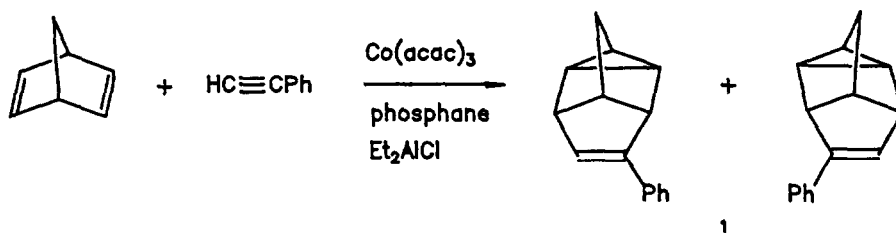
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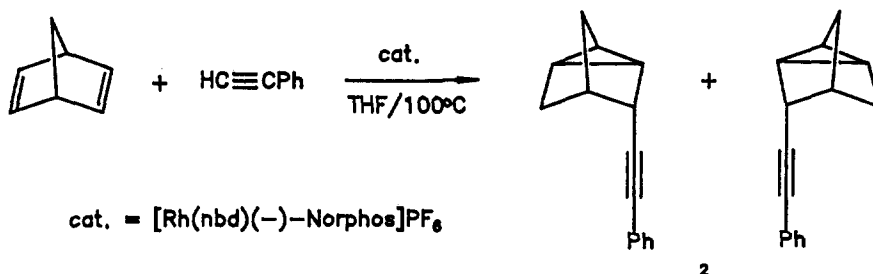
Abstract: Phenylacetylene reacts with norbornadiene at 100 °C in THF to give 3-phenylethynylnortricyclene in 45 % chemical yield and 60 % optical yield, [Rh(nbd)(-)-Norphos]PF₆ (1 mol%) being used as a catalyst. Replacement of (-)-Norphos by other diphosphanes leads to other products or product mixtures.

Recently we reported, that the phenyl-substituted deltacyclene **1** is formed in the reaction of phenylacetylene with norbornadiene in quantitative yield with 98,4 % ee, using a Co(acac)₃/Norphos/Et₂AlCl-catalyst in THF at 35 °C (Scheme 1).^{2,3}



Scheme 1

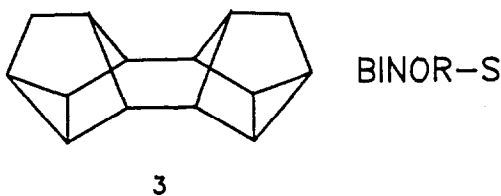
Homologous Rh-based in-situ catalysts [Rh(cod)Cl]₂/diphosphane failed to react under similar conditions. More vigorous conditions (autoclave, THF, 100 °C), with 1 mol% [Rh(nbd)(-)-Norphos]PF₆ as catalyst, gave a crude product, which was distilled in high vacuum. A colourless oil was obtained in 45 % yield, boiling at 90 °C/0,05 Torr, which turned out to be 3-phenylethynylnortricyclene (3-phenylethynyltricyclo[2.2.1.0^{2,6}]heptane)^{2,4,5}



Scheme 2

Formation of nortricyclene derivatives has been described as a side reaction in the homo Diels-Alder reaction of acetylenes with norbornadiene.⁶ However, there are also examples of rhodium complexes, derived from $[\text{Rh}(\text{nbd})\text{Cl}]_2$ and acetylenes, which have been isolated as possible intermediates in [2+2+2]-cycloadditions similar to Scheme 1.^{7,8}

Nortricyclene derivatives of type 2 are interesting, because of their symmetry properties. The nortricyclene skeleton has a C_3 -axis, passing through the bridgehead carbon atom and the midpoint of the cyclopropane ring, which makes the three 3-positions equivalent. Therefore, nortricyclene derivatives monosubstituted in the 3-position form a pair of enantiomers. The reaction of Scheme 2 proceeds only in a limited temperature range. Below 90 °C formation of 2 was no longer observed. On high vacuum distillation of the reaction mixture a product could be isolated, which was identified by comparison of melting point and ¹H-NMR spectrum as the norbornadiene dimer (Binor S) 3 (Scheme 3).⁹

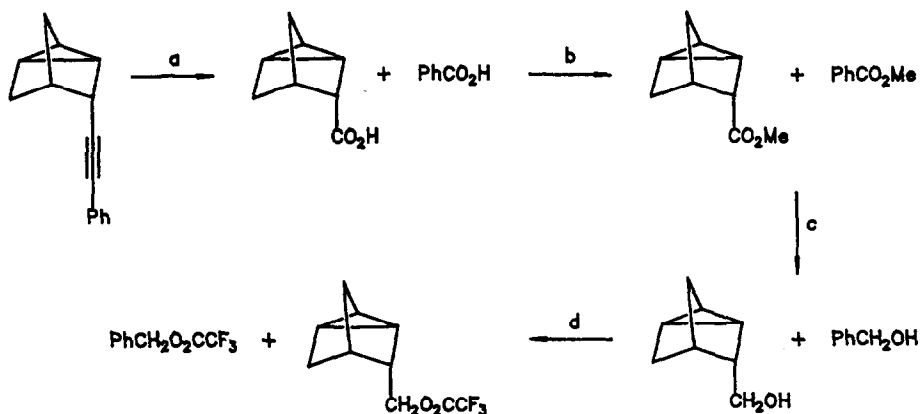


Scheme 3

With a catalyst, containing (-)-Diop¹⁰ instead of (-)-Norphos^{11,12}, only 3 was obtained up to a reaction temperature of 150 °C. Analogous runs with Diphos (bis(diphenylphosphino)ethane) yielded a mixture of 2 and 3 in a 1:1 ratio.

The determination of the enantiomeric purity of 2 was a problem. Finally we succeeded in carrying out the reaction sequence of Scheme 4. In step a) the triple bond of 2 was oxidized by ⁿBu₄NMnO₄¹³ to give nortricyclanic acid and benzoic acid. After successive treatment with NaHSO₃ and 20% HCl as well as extraction with diethylether, the acids were esterified

with methanol und and a few drops of conc. H_2SO_4 in step b). Ester formation was confirmed by the $^1\text{H-NMR}$ signals (CDCl_3/TMS) of the methyl groups at 3,65 ppm and at 3,90 ppm for the methyl esters of nortricyclanic acid and benzoic acid. Reduction of the crude reaction mixture in step c) with 0,75 mol% LiAlH_4 afforded the corresponding alcohols as a yellow oil, which was bulb-to-bulb distilled at $105\text{ }^\circ\text{C}/0,1\text{ Torr}$. In step d) the alcohols were derivatised with trifluoroacetic anhydride to give the corresponding esters.



a: $^n\text{Bu}_4\text{NMnO}_4$, CH_2Cl_2 ; b: MeOH , H_2SO_4 ; c: LiAlH_4 , Et_2O ; d: trifluoroacetic anhydride.

Scheme 4

The enantiomeric trifluoroacetates of 3-hydroxymethylnortricyclene could be separated on a 40 m perpentylated cyclodextrin column.¹² The retention times were 28,3 min for the trifluoroacetate of benzyl alcohol, 46,6 min and 47,4 min for the (–)- and (+)-trifluoroacetate of 3-hydroxymethyltricyclo[2.2.1.0^{2,6}]heptane (conditions: column temperature $50\text{ }^\circ\text{C}$, pressure 1,0 bar H_2 , flow 2-3 ml/min, injector temperature $200\text{ }^\circ\text{C}$). Integration gave an enantiomer ratio (+)-2:(–)-2 = 79,9:20,1.

Thus, it is possible to influence the enantioselective product formation in the codimerisation of phenylacetylene with norbornadiene just by varying the metal centre in the catalytically active species. While the deltacyclene 1 is formed with Co-catalysts, the nortricyclene 2 can be obtained with Rh-containing complexes.

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References and Notes

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- (4) Numbering according to E. Dinjus, D. Walther, H. Schütz, *Z. Chem.*, **23**, 408 (1983).
- (5) In a nitrogen flushed autoclave, 80 mg (0,1 mmol) $[Rh(nbd)(-)-Norphos]PF_6$ are dissolved in 1 ml THF. 1,2 mL phenylacetylene (10,0 mmol) and 1,0 mL norbornadiene (10,0 mmol) are added. The mixture is heated 48 h at 100 °C. After removing the low boiling compounds, the product is distilled at 90 °C/0,05 Torr. Chemical yield 45 %; optical purity 60 %.
 Analytical data for 3-phenylethynyltricyclo[2.2.1.0^{2,6}]heptane:
¹H-NMR (250 MHz, CDCl₃/TMS): 7,20 ppm (m, 5H, Ph); 2,92 ppm (s, 1H, C¹H); 2,40 ppm (s, 1H, C³H); 2,20 ppm (s, 1H, C²H); 1,72 ppm (s, 1H, C⁶H); 1,40-1,00 ppm (m, 5H, C⁴H, C⁵H₂, C⁷H₂).
 Optical rotation: $[\alpha]_D^{25} = +50,4$ (c=1, CHCl₃, 25 °C).
 IR (film): 3060 cm⁻¹, olefinic CH; 2940, 2870 cm⁻¹, aliphatic CH; 2220 cm⁻¹, CC-triple bond; 1600, 1575, 1500 cm⁻¹, olefinic CC; 810, 760 cm⁻¹ cyclopropane.
 MS: m/e 194.
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