Journal of Organometallic Chemistry, 177 (1979) C29—C31

Preliminary communication

NICKEL-CATALYZED ALLYLATION OF NORBORNENE

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(Received June 6th, 1979)

Summary

The products of the nickel-catalyzed allylation of norbornene are mainly those derived from double insertion and ring-opening processes, leading to the most favourable intermediates for reductive elimination.

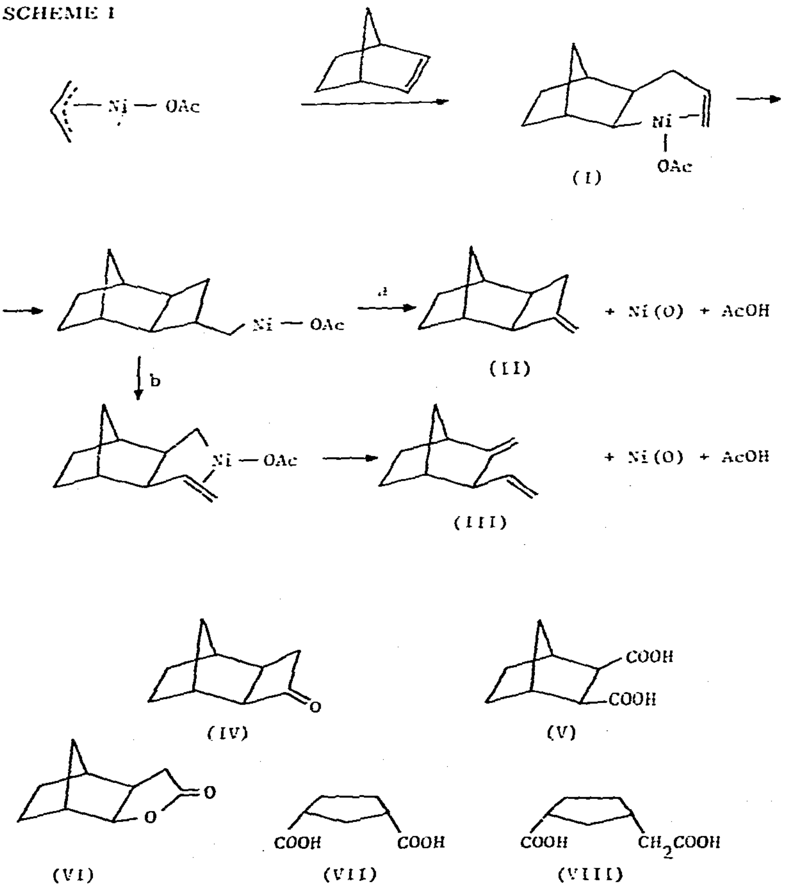
During the past years we described several transition metal-catalyzed processes involving relatively easy reductive elimination steps [1—3]. We now report that the nickel-catalyzed reaction of strained olefins like 2-norbornene with allyl esters like allyl acetate differs remarkably from those previously reported. The expected reductive elimination step is difficult and alternative routes are followed.

Allylation of norbornene takes place in the presence of tetrakis(triisopropyl phosphite)nickel(0) under the mild conditions previously described for the allylation of triple [2] and double [3] bonds. These processes involve hydrogen elimination after insertion of the substrate. With norbornene an intermediate is formed (I) which has been shown to be *cis,exo* [4]. Since an *anti* elimination does not occur easily [5], an alternative route is followed by the complex involving a more favourable reductive elimination process. The result is a second double bond insertion, leading to a four-membered ring, followed in part by hydrogen elimination (path a) to give compound II (*cis,exo*). However, this reductive elimination step, apparently competes with a four-membered ring opening reaction, followed by hydrogen elimination (path b) to give compound III (*exo*), as shown in Scheme 1 (non reactive ligands are omitted). Other minor products are present, which have not been investigated further.

Evidence for structures II and III is based on ^{1}H and ^{13}C NMR spectra and on isolation of the products of $KMnO_4/NaIO_4$ oxidation [6] and of ozonolysis [7] IV—VIII.

The ^{13}C NMR data (taken at 25.2 MHz in $CDCl_3$, ppm from TMS), are in full agreement with the proposed structures. For compound II, in addition to the peaks at 120 ($=CH_2$) and 170 (quaternary unsaturated carbon) the spectrum shows a triplet at 38.5 ppm consistent with the cyclobutane CH_2. The shifts for

SCHEME I



C(3), C(4), C(1) (doublets) of the norbornane ring are 58.7, 42.1 and 45.2 ppm, respectively. The remaining carbons C(5) and C(6) resonate at 30.8 and 32.2 ppm. The *exo* orientation of the cyclobutane ring is deduced from the C(7) (bridging CH_2) shift at 36.3 ppm.

In the spectrum of compound III (2-methylene-3-vinylnorbornane) the peaks at 103 and 113.2 ppm are immediately identified as terminal $=CH_2$ groups on the basis of the chemical shifts, multiplicity, and long range $J(C—CH)$ couplings. The two absorptions at 157 (singlet) and 140 (doublet) are due to the internal carbons of $CH_2=C<$ and $CH_2=CH$, respectively. Positions α and β to these unsaturations are characterized by a downfield shift, thus carbons C(3), C(4), and C(1) are easily assigned by comparison with the corresponding shifts in 2-methylenenorbornane [8]. The remaining carbons C(5), C(6), and C(7) appear as triplets in the off-resonance spectrum at 28.6, 29.5, and 35.9 ppm. The latter (bridging CH_2) moves upfield because of the γ effect of the *exo* orientation of the vinyl group.

^1H NMR spectra were taken at 270 MHz and are in complete accord with the interpretations above.

Compound II was oxidized in acetone to *exo*-IV [9] and in water/K_2CO_3 to *cis,exo*-V [10] by $KMnO_4/NaIO_4$ [6] and to VI [11] by ozonolysis in methanol [7]. Compound III was oxidized to *cis*-VII [12] by $KMnO_4/NaIO_4$ and to VIII [13] by ozonolysis in methanol. The oxidation products were compared with authentical samples and literature data.

The results of our study show that the feasibility of the reductive elimination step can determine the type of products. This may be useful from the synthetic point of view. A reaction can be made to proceed further by rendering more difficult the first reductive elimination and at the same time by providing appropriate groups (such as the allyl double bond, in our case) to induce further reaction.

Experimental

$Ni[P(OPr\text{-}i)_3]_4$ (0.89 g, 1 mmol), allyl acetate (5.0 g, 50 mmol), and 2-norbornene (4.7 g, 50 mmol), in tetrahydrofuran (20 ml) were heated at 80°C (bath temperature) for 2.5 h. Conventional work-up and distillation at 62—64°C/40 mmHg gave II + III (5.36 g, 80% yield) in ca. 3/7 ratio. At 20°C this ratio was ca. 1/1. The two compounds (ca. 90% of the total GLC area) were separated by preparative GLC on a SE 30 (5% silicone) column. Both gave M^+ 134.

We thank the Italian National Research Council for financial support.

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