Nickel- and Palladium-Catalyzed Additions of Nucleophiles to Cyclic 1,3-Dienes

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Andell, Ove S., Bäckvall, Jan-E. and Moberg, Christina, 1986. Nickel- and Palladium-Catalyzed Additions of Nucleophiles to Cyclic 1,3-Dienes. – Acta Chem. Scand. B 40: 184–189.

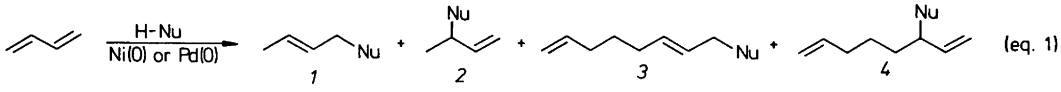
Carbon nucleophiles have been found to add smoothly to 1,3-cyclohexadiene using either a preformed nickel-ligand complex or Ni(0) prepared by *in situ* reduction of Ni(II) in the presence of a ligand to give 1,2- and 1,4-addition products. Analogous adducts were also obtained from 1,3-cyclopentadiene and 1,3-cyclooctadiene, but the yields were considerably lower. Attempts to add benzenesulfinic acid to 1,3-cyclohexadiene using Ni(0) were unsuccessful; this reaction was instead found to be catalyzed by Pd(0)-phosphite complexes.

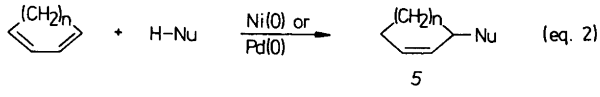
Nickel(0)- and palladium(0)-catalyzed additions of various nucleophiles to acyclic conjugated dienes have been extensively studied [eqn. (1)][1]. Simple 1,2- and 1,4-additions, to give *1* and *2*, are usually accompanied by telomerization yielding 2:1 adducts (*3* and *4*) of the diene and the nucleophile, the product distribution being dependent on the reaction conditions. Analogous nucleophilic additions to cyclic conjugated dienes have received little attention and to our knowledge the only examples reported are the additions of secondary amines to 1,3-cyclohexadiene and 1,3-cyclopentadiene.[2]

In connection with other studies on metal-catalyzed reactions of conjugated dienes[3] we have now investigated the addition of nucleophiles (H–Nu) to cyclic dienes [eqn. (2)]. The reactions, which are formally 1,2- and 1,4-additions, lead to the synthetically useful products *5*.

Results

Active methylene compounds were readily added to cyclic dienes under mild conditions in the presence of nickel(0). Thus, reaction of 1,3-cyclohexadiene with diethyl malonate in ethanol containing 0.5 equivalents of sodium ethoxide gave diethyl 2-(2-cyclohexen-1-yl)malonate (*6*) in 95% yield after 20 h at ambient temperature using a catalyst prepared from nickel(II) acetylacetonate and triethylaluminium. The corresponding reaction of 1,3-cyclohexadiene with ethyl acetoacetate afforded ethyl 2-(2-cyclohexen-1-yl)-3-oxobutanoate (*7*) in 71% yield (Scheme 1).





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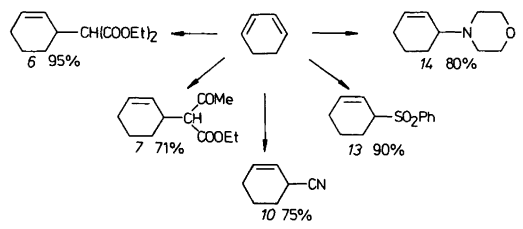
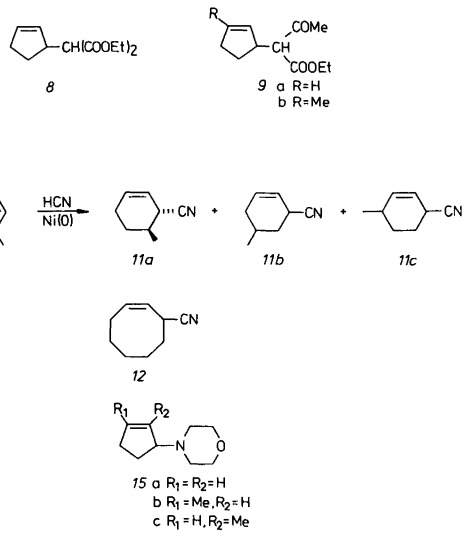
Scheme 1





The analogous reactions of 1,3-cyclopentadiene with active methylene compounds resulted in modest yields of adducts due to competing Diels-Alder dimerization of the diene. Addition of diethyl malonate and ethyl acetoacetate to 1,3-cyclopentadiene gave *8* and *9a*, respectively (35 and 32%). Adducts were also obtained from active methylene compounds and methylcyclopentadiene,* although these reactions are of limited synthetic interest since mixtures of isomers were obtained. For example, starting from ethyl acetoacetate and methylcyclopentadiene, a *ca.* 5:1 mixture (GLC) of two isomers was obtained. The main isomer was identified (^{1}H NMR) as ethyl 2-(3-methyl-2-cyclopenten-1-yl)-3-oxobutanoate (*9b*).

Addition of hydrogen cyanide to 1,3-cyclohexadiene was also readily achieved under slightly different reaction conditions. In the presence of tetrakis(triphenyl phosphite)nickel a 75% isolated yield of 2-cyclohexene-1-carbonitrile (*10*) was obtained within 3.5 h at 60 °C in acetonitrile. From the corresponding reaction with 5-methyl-1,3-cyclohexadiene, the three possible regioisomers, *11a–c*, were isolated in a 1:2:1 ratio in a total yield of 60%. 1,3-Cyclooctadiene was found to be less reactive, the addition of hydrogen cyanide resulting in a low yield (22%) of *12* under the same reaction conditions.

Sulfones are versatile reagents in organic synthesis,[5] and it was therefore of interest to investigate the addition of sulfinates to cyclic dienes. From the attempted reaction of benzenesulfinic acid and sodium benzenesulfinate with 1,3-cyclohexadiene using tetrakis(triphenyl phosphite) nickel(0) as catalyst, no adduct was, however, obtained within 18 h at 60 °C in acetonitrile.

It has previously been reported by Julia *et al.*[6] that benzenesulfinic acid adds to acylic conjugated dienes using a palladium-triphenylphosphine catalyst. Attempts to use the Julia conditions on 1,3-cyclohexadiene led only to a slow reaction which gave 2-cyclohexenyl phenyl sulfone (*13*) in modest yields.* The reaction conditions were therefore modified. Changing the ligand from triphenylphosphine to triphenyl phosphite had a great effect on the rate of the reaction, resulting in a 90 % yield of the allylic sulfone *13*.

Dzhemilev *et al.*[2] have previously shown that secondary amines, e.g. morpholine, can be added to 1,3-cyclohexadiene and 1,3-cyclopentadiene using a catalyst prepared from nickel(II) acetylacetonate, tributylphosphine, triethylaluminum and trifluoroacetic acid. We repeated these reactions and obtained the amines *14* and *15a* in high yields. Furthermore, we obtained the same compounds when tetrakis(triethyl phosphite)nickel(0) was used as the catalyst together with sulfuric acid. Reaction of methylcyclopentadiene with morpholine gave a complex mixture of products from which the main products *15b* and *15c* (ratio *ca.* 4:1) were isolated by

*Methylcyclopentadiene consists of a mixture of approximately equal amounts of the 1- and 2-substituted isomers and <1 % of the 5-substituted isomer.[4]

*To make sure that there was no difference in our experimental technique, we repeated the sulfinic acid addition to isoprene as reported by Julia.[6] This reaction proceeded rapidly as described and produced the allylic sulfone in excellent yield (96 %).

preparative GLC. We were not able to add secondary amines to 1,3-cyclooctadiene under any of these conditions, in accordance with previous findings.[2]

Discussion

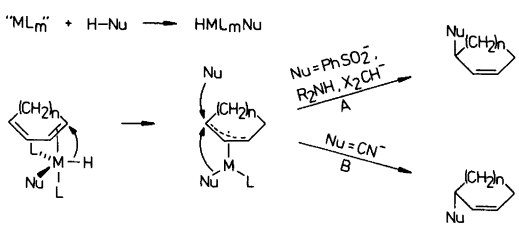
There is strong evidence that nickel- and palladium-catalyzed additions of nucleophiles to 1,3-butadiene proceed *via* π-allylmetal intermediates, the 1:1 adducts resulting from attack on a π-butenyl- and the 2:1 adducts from attack on a bis-π-octadienediylmetal complex.[1,7] The π-butenyl compounds, in turn, are presumed to be formed by protonation of the diene *via* a metal hydride complex. Consequently, 1:1 adducts are favoured when any species capable of protonating M(0) is present.[8]

The mechanism for the nickel- and palladium-catalyzed additions reported here most likely also involves π-allylmetal intermediates (Scheme 2). Protonation of, or oxidative addition to the metal(0) complex would yield a metal hydride complex, which can add to the diene to give the π-allylmetal intermediate. It has been shown that nickel hydride adds *cis* to cyclopentadiene to give a η^3-cyclopentenylnickel complex.[9]

The attack by the nucleophile on the intermediate π-allylmetal complex may now take place in two different ways (Scheme 2), either *via* external *trans* attack (path A) or *via* intramolecular *cis*-migration (path B). For palladium, it is known that stabilized carbon and hetero nucleophiles prefer the external mode of attack (path A), whereas unstabilized alkyl anions add *via* *cis*-migration (path B).[10] In fact, benzenesulfinate, which was used here, has been found to add *trans* to π-allylpalladium intermediates in catalytic reactions.[3f,11,12] Although additions of nucleophiles to π-allylnickel complexes are much less studied, the same trend as for π-allylpalladium complexes is emerging.[13-15] It is of relevance to this study that *trans* attack by amine[13] and *cis*-migration of cyanide[14] have been demonstrated in π-allylnickel systems. In analogy with palladium chemistry it is likely that the stabilized carbon nucleophiles add in a *trans* fashion. For the nickel-catalyzed additions reported here we therefore assume that the amination and addition of active methylene compounds and sulfinic acids take place *via* path A, whereas the hydrocyanation reaction occurs *via* path B (Scheme 2).

From a synthetic point of view, compounds of

Scheme 2



type *5* are of interest. Allylic sulfones have recently received much attention as versatile reagents in organic synthesis.[5,12,16] Primary allylic sulfones can be readily prepared starting from the appropriate allylic halide, whereas secondary allylic sulfones can be obtained from allylic halides or acetates only by palladium-catalyzed nucleophilic displacement.[11,12]

Compound *6* has been used as a key intermediate in various synthetic transformations.[17] Originally, this compound was obtained in rather low yield by bromination of cyclohexene followed by nucleophilic attack of malonate.[18] General methods for the synthesis of compounds *6–9* include treatment of the appropriate allylic halide with malonate or acetoacetate [17b,f,18b,19] and palladium-catalyzed nucleophilic substitutions in allylic derivatives.[20] Another, although not general, route starts from simple olefins activated as dicarbonyl-η^5-cyclopentadienyl(olefin) iron cations.[21] The allylic nitrile *10* has hitherto only been prepared in a low yield starting from 3-bromocyclohexene.[22]

The nickel- and palladium-catalyzed additions to cyclic olefins presented in this paper provide an efficient route to compounds with the general structure *5*. In cases where alternative routes are available, the preferred method will depend upon the availability of the appropriate substrates.

Experimental

All reactions were carried out in a nitrogen atmosphere. Cyclopentadiene and methylcyclopentadiene were obtained from their dimers (BDH). Diethyl malonate and ethyl acetoacetate were distilled and stored over molecular sieves (4Å). A solution of hydrogen cyanide was prepared according to a literature procedure.[23] 1,3-Cyclohexadiene, sodium benzenesulfinate, morpholine

and tributylphosphine were commercially available and used as received. Benzenesulfinic acid was obtained by treatment of sodium benzenesulfinate with acid. Triethylaluminium (Merck) was dissolved in dry toluene (20 % solution) before use and stored under nitrogen. Nickel(II) acetylacetonate was obtained from the monohydrate by azeotropic distillation of toluene from a suspension of the salt in toluene followed by heating at 60 °C for 4 h. Tetrakis(triphenyl phosphite)nickel,[24] titrakis(triethyl phosphite)nickel[25] and bis(η3-allylpalladium chloride)[26] were prepared according to literature procedures. Analytical grade ("pro analysi") toluene and acetonitrile obtained from Merck were degassed and kept over molecular sieves (3 Å) under nitrogen.

NMR spectra were recorded in $CDCl_3$ with TMS as an internal standard on a Bruker WP 200-FT spectrometer at 200 MHz and on a Jeol JNM-PMX instrument at 60 MHz. Analytical GLC was performed on a Pye GCD chromatograph using a 1.2 m×2 mm glass column of 5 % SE 30 on Chromosorb W or 20 % Apiezon L + 10 % KOH on Chromosorb W (for the amines).

Diethyl 2-(2-cyclohexen-1-yl)propanedioate (6).[17,18] 1,3-Cyclohexadiene (0.48 ml, 5 mmol) and PBu_3 (0.4 ml, 1.5 mmol) were added to $Ni(acac)_2$ (128 mg, 0.5 mmol). The mixture was cooled to *ca.* −50 °C and Et_3Al (1 mmol) was added (resulting in a colour change from green to reddish-brown) followed by diethyl malonate (0.8 ml, 5 mmol) and EtONa (2.5 mmol) in EtOH (2.5 ml) (prepared from NaH and EtOH) and the cooling bath was removed. After stirring for 20 h at ambient temperature, an excess of KCN was added, the mixture stirred for an additional 2 h to allow the formation of $K_2Ni(CN)_4$ and the product extracted with ether. The organic phase was washed with water, dried ($MgSO_4$), and the solvent was evaporated. Bulb to bulb distillation afforded *6* (1.15 g, 4.79 mmol, 95 %). ^{1}H NMR: δ 1.21 (t, J = 7 Hz, 2 CH_3), 1.3–1.8 (m, 4 H), 1,93 (m, CH_2–C=), 2.85 (m, CH–C=), 3.18 (d, J = 9.2 Hz, 1 H), 4.15 (q, J = 7 Hz, 4 H), 5.45–5.75 (m, 2 H).

Diethyl 2-(2-cyclopenten-1-yl)propanedioate (8)[19a,21] was prepared using the above method starting from 1,3-cyclopentadiene (0.42 ml, 5 mmol). Yield: 35 %. ^{1}H NMR: δ 1.27 (t, J = 7 Hz, 2 CH_3), 1.61 (ddt, J = 13, 8.5, 6.0 and 6.0 Hz, 1 H), 2.14 (dddd, J = 13, 8.0, 7.5 and 5.5 Hz, 1 H), 2.33 (m, 2 H), 3.23 (d, J = 9.5 Hz, 1 H), 3.35 (m, 1 H), 4.20 (q, J = 7 Hz, 4 H), 5.65 (m, 1 H), 5.80 (m, 1 H).

Ethyl 2-(2-cyclohexen-1-yl)–3–oxobutanoate (7) and ethyl 2-(2-cyclopenten-1-yl)-3-oxobutanoate (9)[19b] were prepared analogously to *6* by reaction of ethyl acetoacetate (0.65 ml, 5 mmol) with 1,3-cyclohexadiene (5 mmol) and 1,3-cyclopentadiene (5 mmol), respectively. *7*: Yield: 71 %. ^{1}H NMR: δ 1.25 (t, J = 7 Hz, 3 H), 1.2–2.0 (m, 6 H), 2.22 (s, 3 H), 2.9 (m, 1 H), 3.35 (d, J = 7 Hz, 1 H), 4.18 (q, J = 7 Hz, 2 H), 5.2–5.9 (m, 2 H). *9a*: Yield: 32%. ^{1}H NMR: δ 1.28 (t, J = 7 Hz, 3 H), 1.3–1.6 (m, 1 H), 2.05–2.23 (m, 1 H), 2.241, 2.238 (two s, one CH_3 in each diastereomer), 2.30–2.39 (m, 2 H), 3.28–3.38 (m, 2 H), 4.20 (q, J = 7 Hz, 2 H), 5.56–5.85 (m, 2 H).

2-Cyclohexene-1-carbonitrile (10).[22] A solution of HCN (270 mg, 10 mmol) in dry acetonitrile (2 ml) was added to a stirred suspension of Ni $[P(OPh)_3]_4$ (650 mg, 0.5 mmol) and 1,3-cyclohexadiene (0.95 ml, 10 mmol) in acetonitrile (1 ml) of 60 °C over a period of 4.5 h. After 2 h of stirring at 60 °C the slurry was filtered, the solvent evaporated and the residue was flash chromatographed (pentane : diethyl ether 95 : 5) to give 0.81 g (76 %) of *10*. ^{1}H NMR: δ 1.67 (m, 1 H), 1.81 (m, 1 H), 1.95 (m, 2 H), 2.07 (m, –CH_2–CH=), 3.22 (m, –CHCN), (m, J = 9.9, 4.0 and 2.0 Hz, =C*H*–CHCN), 5.94 (m, CH_2–C*H*=). IR: (neat) 2235 cm^{-1}. MS: m/z 107 (M^+).

Methyl-2-cyclohexene-1-carbonitriles 11a, 11b and 11c. The same procedure as described for the preparation of *10* using 5-methyl-1,3-cyclohexadiene afforded a mixture of products *11a, 11b* and *11c* in a ratio of 1 : 2 : 1, in a total yield of 18 %.

Trans-6-methyl-2-cyclohexene-1-carbonitrile (11a). ^{1}H NMR: δ 1.16 (d, J = 6.5 Hz, CH_3), 1.27 (m, CH_3–C*H*), 1.76–2.03 (m, 2 H), 2.11 (m, 2 H), 2.87 (dt, J = 9.5, 2.5 and 2.5 Hz, CHCN), 5.59 (ddd, J = 10.0, 4.5 and 2.5 Hz, CHCN-C*H*=), 5.92 (ddd, J = 10.0, 7.0 and 3.5 Hz, CH_2–C*H*=).

5-Methyl-2-cyclohexene-1-carbonitrile (11b). ^{1}H NMR: δ 1.01 (d, J = 9.0 Hz, CH_3), 1.40–1.85 (m,

2 H), 1.85–2.30 (m, 3 H), 3.27 (m, CHCN), 5.62 (m, CHCN–C*H*=), 5.94 (m, J = 9.5 Hz, CH_2–C*H*=).

4-Methyl-2-cyclohexene-1-carbonitrile (11c). ^{1}H NMR: δ 0.99 (d, J = 9.0 Hz, CH_3), 1.40–1.85 (m, 2 H), 1.85–2.30 (m, 3H), 3.20 (m, CHCN), 5.56 (m, CHCN–C*H*=), 5.78 (dt, J = 9.5, 2.5 and 2.5 Hz, CH_2–C*H*=).

2-Cyclooctene-1-carbonitrile (12). The same procedure as described for the preparation of *10* using 1,3-cyclooctadiene afforded *12* in 22 % yield. ^{1}H NMR: δ 1.35 (m, 2 H), 1.65 (m, 5 H), 2.08 (m, 3 H), 3.56 (ddd, J = 12.0, 9.0 and 4.5 Hz, CHCN), 5.55 (dd, J = 10.0 and 9.0 Hz, CHCN–C*H*=), 5.86 (dd, J = 10.0 and 9.0 Hz, CH_2–C*H*=).

Benzenesulfinic acid. Sodium benzenesulfinate (10 g, 60 mmol) was dissolved in 50 ml of water at room temperature. The clear solution was then cooled with ice and 6 M HCl (10 ml, 60 mmol) was added slowly. The slurry was left at 0 °C for 1 h and then filtered. The acid was dried *in vacuo* and then stored in the dark (mp. 79–81 (lit. 85) °C.

3-Phenylsulfonyl-1-cyclohexene (13). A slurry of bis-(η^3-allylpalladium chloride) (37 mg, 0.1 mmol), $P(OPh)_3$ (124 mg, 0.4 mmol), $PhSO_2Na$ (82 mg, 0.5 mmol), $PhSO_2H$ (1.42 g, 10 mmol) and 1,3-cyclohexadiene (0.95 ml, 10 mmol) in acetonitrile (20 ml) was stirred at room temperature for 18 h. The solvent was evaporated and the residue was flash chromatographed (hexane : ethyl acetate, 70 : 30) to give 1.98 g (89 %) of *13*m, identical (IR, NMR) to *13* prepared from 2-cyclohexen-1-yl acetate[27] and sodium benzenesulfinate in the presence of 1.4 % $Pd(PPh_3)_4$.[13] ^{1}H NMR: δ 1.50 (m, 1 H), 1.79 (m, 1 H), 1.96 (m, 4 H), 3.77 (m, $CHSO_2Ph$), 5.79 (m, J = 10.3, 5.0 and 2.0 Hz, =CH–$CHSO_2Ph$), 6.08 (m, J = 10.3, 6.3 and 4.0 Hz, CH_2–C*H*=), 7.59 (m, 3 H), 7.89 (m, J = 8.0 Hz, 2 H). IR: (neat) 1140(s), 1305(s) cm^{-1}. Anal. Calc. for $C_{12}H_{14}O_2S$: C, 64.83%, H, 6.35 %. Found: C, 64.70 %, H, 6.22 %.

(2-Cyclohexen-1-yl)morpholine (14),[2] *(2-cyclopenten-1-yl)morpholine* (15a),[2,13] *(3-methyl-2-cyclopenten-1-yl)morpholine* (15b) *and (2-methyl-2-cyclopenten-1-yl)morpholine* (15c). To $[P(OP)_3]_4Ni$ (725 mg, 0.25 mmol) in toluene (2 ml) was added the appropriate diene (2.5 mmol) and H_2SO_4 (0.25 mmol) at 0 °C. After stirring 0.5 h at ambient temperature, morpholine (200 µl, 2.5 mmol) was added, the mixture was stirred for a further 20 h and the products isolated by extraction. *15b*: ^{1}H NMR δ 1.76 (bs, CH_3), 1.80–2.11 (m, 2 H), 2.15–2.30 (m, CH_2–C=), 2.5 (m, 4 H, CH_2N), 3.62 (m, CHN), 3.72 (m, 4 H, CH_2O), 5.39 (m, 1 H). *15c*: ^{1}H NMR δ 1.72 (bs, CH_3), 1.9–2.02 (m, 2 H), 2.16–2.30 (m, CH_2–C=), 2.4–2.5 (m, 4 H, CH_2N), 3.62–3.77 (m, 5 H), 5.52 (m, 1 H).

Acknowledgements. The authors thank Dr Ulla Jacobsson for recording some of the NMR spectra, and Mr. Thomas Antonsson for preparing compound *13* starting from 2-cyclohexen-1-yl acetate. This work was supported by the Swedish Natural Science Research Council.

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Received June 20, 1985.