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Preliminary communication

NICKEL COMPLEX INDUCED C–C-LINKAGE OF CARBON DIOXIDE WITH TRIENES

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Summary

Reaction of (bipyridine)(1,5-cyclooctadiene)nickel with carbon dioxide and 1,3,7-octatriene yields products which indicate that the CO_2 attacks only at the diene part of octatriene. In the same reaction 1,3,5-hexatriene couples with CO_2 to yield 1/1, 1/2 and 2/2 adducts.

Monoolefins are known to react stoichiometrically with nickel(0) compounds and carbon dioxide to yield nickelaoxacyclopentanes. One of the first olefins studied was norbornene [1], but less activated, acyclic monoolefins such as ethene or hexenes [2,3] also couple with carbon dioxide. Non-conjugated diolefins such as norbornadiene [4,5] or dicyclopentadiene [4,6] can also react in the same manner, yielding carboxylate complexes which can be decomposed into a number of valuable carboxylic acids.

Conjugated dienes are also possible reaction partners for nickel(0) compounds and CO_2. 2,3-Dimethylbutadiene yields an allylic nickel carboxylate complex which after acidic treatment gives 3,4-dimethyl-3-pentenoic acid [7–11]. When piperylene is used sorbic acid is formed [12,13]. With butadiene several products are obtained, depending on the ligand of the nickel complex and on the reaction and work-up conditions. Reaction with a molar proportion of carbon dioxide gives 2,4-pentadienoic acid [13] or 3-pentenoic acid [14]. Further addition of carbon dioxide results in insertion of a second CO_2 molecule to give *cis*-dimethyl-3-hexenedioate [15].

The reactions with monoolefins and conjugated dienes presumably proceed via different mechanistic pathways. The question thus arises of which of the pathways is preferred when an unsaturated molecule such as 1,3,7-octatriene contains both a monoene and a diene unit. For comparison, 1,3,5-hexatriene, a fully conjugated triene, has also been studied in the reaction.

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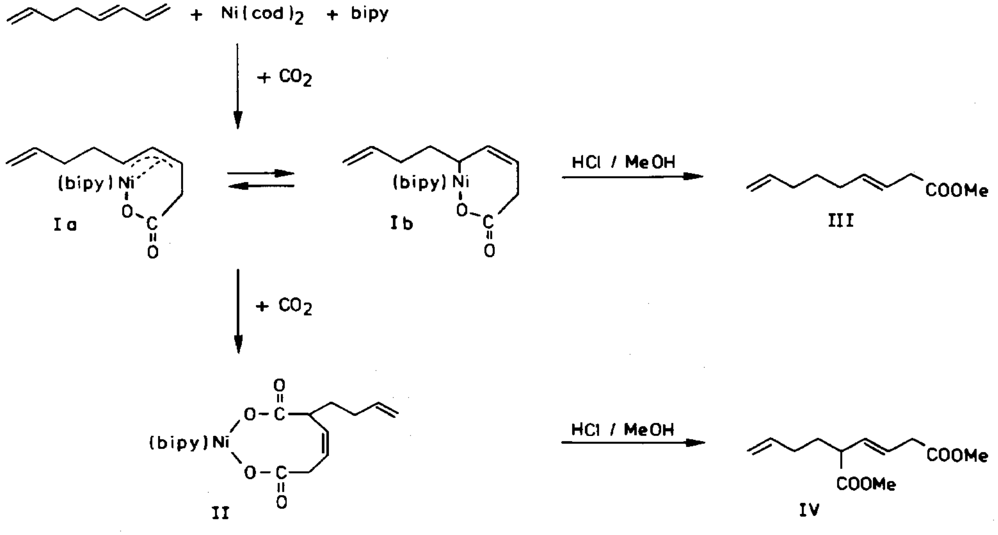
Results and discussion

A *trans/cis*-mixture of 1,3,7-octatriene reacts with (bipyridine)(1,5-cyclooctadiene)nickel and an excess of carbon dioxide to give a mixture of the nickel carboxylates I and II. The infrared spectrum shows a strong absorption at 1605 cm^{-1} consistent with the presence of metal carboxylates [4]. The mass spectrum of the mixture of nickel complexes shows all the characteristic fragments of I and II. A signal at 185.7 ppm in the ^{13}C NMR spectrum confirms the insertion of carbon dioxide. Acidic decomposition of the complexes and concomitant esterification with methanol gave the monocarboxylic esters *cis/trans*-methyl-3,8-nonadienoate (III) and the dicarboxylic esters *cis/trans*-dimethyl-5-carboxylato-3,8-nonadienoate (IV) (Scheme 1).

The products obtained confirm that the coordination of 1,3,7-octatriene and the subsequent reaction of carbon dioxide take place at the diene part of the molecule. Oxidative coupling of CO_2 with the nickel carboxylate gives complex Ia, in which the hydrocarbon chain is attacked in η^3-allyl fashion to the metal. This complex is in equilibrium with its isomer Ib containing a nickel–carbon σ-bond. Upon hydrolysis with HCl/MeOH, esterification of the carboxylate and hydrogen transfer to the σ-bound carbon atom take place to yield ester III. In addition, insertion of a second carbon dioxide into the nickel–carbon bond takes place to form the dicarboxylate II, which can be decomposed to diester IV. The esters III and IV are present in a 1/2 ratio, demonstrating the preference of nickel for formation of the dicarboxylate II. This is the first example of double C–C bond formation with carbon dioxide in a one-pot reaction.

No products could be isolated which resulted from an attack of carbon dioxide at the single bond of 1,3,7-octatriene. It can be assumed that the fact that coordination of the diene part is much faster than that of the monoene part is because the former process leads to a stable η^3-allyl complex. When earlier results [4] are taken into account it can be concluded that the reactivity of hydrocarbons with nickel(0)



SCHEME 1

complexes and carbon dioxide decreases in the order: dienes > monoenes > strained cycloalkanes.

Oxidative coupling of 1,3,5-hexatriene and carbon dioxide at a nickel(0) center gave a mixture of various nickel carboxylates. Their IR spectra showed strong absorptions at 1603 cm^{-1}, characteristic of a metal carboxylate structure. Decomposition of the carboxylates with HCl/MeOH yielded a mixture of esters. GC/MS analysis suggested that the 1,3,5-hexatriene and carbon dioxide reacted to give 1/1 ($m/e = 140$), 1/2 ($m/e = 198$) and 2/2 adducts ($m/e = 278$). The 1/1 and 1/2 adducts can be accounted for by analogy to Scheme 1 for 1,3,7-octatriene. However, the GC/MS analysis indicates also the formation of a 2/2 adduct, the C_{14}-dicarboxylic dimethyl ester. This 2/2 adduct of 1,3,5-hexatriene and carbon dioxide is the first example of dimerisation of an organic substrate accompanied by double C–C bond formation with carbon dioxide.

Experimental

A glass autoclave was charged under a stream of argon with a mixture of 1.39 g (5.05 mmol) $\mathrm{Ni(cod)_2}$ and 1.3 g (8.3 mmol) of 2,2′-bipyridine in 80 ml of tetrahydrofuran. The solution was cooled to $-50\,^{\circ}\mathrm{C}$ and saturated with carbon dioxide. After addition of 1.05 g (9.71 mmol) of 1,3,7-octatriene the solution was stirred and allowed to warm up. A solid separated, and was filtered off and washed with tetrahydrofuran and n-pentane. After drying in vacuo 1.64 g (95%) of a mixture of I and II was obtained, and this was treated with a 1/1 mixture of methanol and concentrated hydrochloric acid to yield the esters III and IV. The products were identified by use of the GC/MS system Varian 3700/MAT 112 S. Pure samples were isolated by preparative GC (Hupe APG 402) and characterized by ^{1}H NMR (Varian EM 390), ^{13}C NMR (Bruker CXP 200), and IR (Perkin–Elmer 577) spectroscopy. The reaction with 1,3,5-hexatriene was carried out similarly.

Spectral data for cis/trans-methyl-3,8-nonadienoate(III). ^{1}H NMR (90 MHz, $\mathrm{CDCl_3}$): δ 1.50 (m, 2H, $\mathrm{CH_2C}H_2\mathrm{CH_2}$); 2.08 (m, 4H, $\mathrm{C}H_2\mathrm{CH{=}}$); 3.08 (m, 2H, $\mathrm{{=}CC}H_2\mathrm{COOCH_3}$); 3.71 (s, 3H, $\mathrm{COOC}H_3$); 4.96 (m, 2H, $\mathrm{C}H_2\mathrm{{=}}$); 5.75 (m, 3H, $\mathrm{C}H\mathrm{{=}}$) ppm. ^{13}C NMR (50.3 MHz, $\mathrm{CDCl_3}$): δ 25.7 ($\mathrm{CH_2}C\mathrm{H_2CH_2}$); 27.4 ($C\mathrm{H_2CH{=}CH}$); 32.1 ($\mathrm{CH_2{=}CH}C\mathrm{H_2}$); 36.9 ($\mathrm{CH{=}CH}C\mathrm{H_2}$); 50.7 ($\mathrm{O}C\mathrm{H_3}$); 113.5 ($C\mathrm{H_2{=}CH}$); 120.0/120.7 ($C\mathrm{H{=}CHCH_2}$); 132.0/133.4 ($\mathrm{CH{=}}C\mathrm{HCH_2}$); 137.5 ($\mathrm{CH_2{=}}C\mathrm{H}$); 171.3 ($\mathrm{CH_2}C\mathrm{O_2CH_3}$) ppm. IR: 1750 ($\nu$(C=O)), 1647 ($\nu$(C=C)), 998 ($\delta(\mathrm{CH{=}CH_2})$), 972 ($\delta\ (\mathrm{RCH{=}CHR})_{trans}$), 701 ($\delta(\mathrm{RCH{=}CHR})_{cis}$) cm^{-1}.

Spectral data for cis/trans-dimethyl-5-carboxylato-3,8-nonadienoate(IV). ^{1}H NMR (90 MHz, $\mathrm{CDCl_3}$): δ 1.60 (m, 2H, $\mathrm{CH_2C}H_2\mathrm{CH}$); 2.00 (m, 2H, $\mathrm{{=}CHC}H_2\mathrm{CH_2}$); 3.05 (m, 3H, $\mathrm{C}H\mathrm{CH{=}CHC}H_2$); 3.64 (s, 6H, $\mathrm{COOC}H_3$); 4.96 (m, 2H, $\mathrm{C}H_2\mathrm{{=}}$); 5.69 (m, 3H, -$\mathrm{C}H\mathrm{{=}CH}$-) ppm. ^{13}C NMR (50.3 MHz, $\mathrm{CDCl_3}$); δ 31.0 ($\mathrm{CH_2}C\mathrm{H_2CH}$); 31.3 ($\mathrm{CH_2{=}CH}C\mathrm{H_2}$); 37.6 ($\mathrm{CH{=}CH}C\mathrm{H_2}$); 48.2 ($\mathrm{CH}C\mathrm{HCH_2}$); 51.8 ($\mathrm{O}C\mathrm{H_3}$); 115.4 ($C\mathrm{H_2{=}CH}$); 124.9 $\mathrm{CH{=}}C\mathrm{HCH_2}$); 131.4 ($\mathrm{CH}C\mathrm{H{=}CH}$); 137.4 ($\mathrm{CH_2{=}}C\mathrm{H}$); 171.8 ($\mathrm{CH_2}C\mathrm{O_2CH_3}$); 174.3 ($\mathrm{CH}C\mathrm{O_2CH_3}$) ppm. IR: ν 1745 (ν(C=O)), 1647 (ν(C=C)), 998 ($\delta(\mathrm{CH{=}CH_2})$), 975 ($\delta(\mathrm{RCH{=}CHR})_{trans}$) cm^{-1}.

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