Journal of Organometallic Chemistry 70 (1974) 95—99

AN INSERTION AND CYCLOADDITION REACTION OF DIMETHYLKETENE WITH DI-π-CYCLOPENTADIENYLNICKEL

DAVID A. YOUNG

Research Laboratories, Tennessee Eastman Company, Division of Eastman Kodak Company, Kingsport, Tennessee 37662 (U.S.A.)

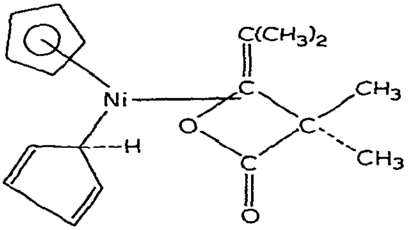
(Received September 25th, 1973)

Summary

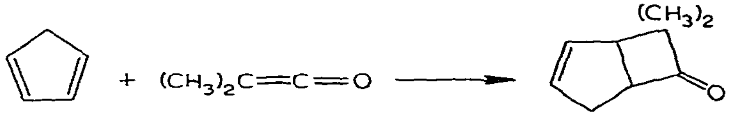
The complex (π-cyclopentadienyl)[σ-α,α-dimethyl-α-{2-3-π-[7,7-dimethyl-6-oxobicyclo[3.2.0]hept-2-en-4-yl]}acetyl]nickel (II) has been identified as the principal product of the reaction of two moles of dimethylketene with di-π-cyclopentadienylnickel. Degradation of II in methanol solution yielded methyl α,α,7,7-tetramethyl-6-oxobicyclo[3.2.0]hept-2-ene-4-acetate (III); and reduction of II gave the 6-hydroxy nickel complex (VI). Complex II is a result of 1,2-cycloaddition of one ketene function to a cyclopentadienyl ring and insertion of a second ketene function into a nickel—carbon bond.

Introduction

Recently, Sato et al. [1] reported the preparation of an orange complex from dimethylketene and di-π-cyclopentadienylnickel. Proton NMR, IR and elemental analysis data led them to postulate a structure bearing a π-complexed, four-memebered ring lactone:



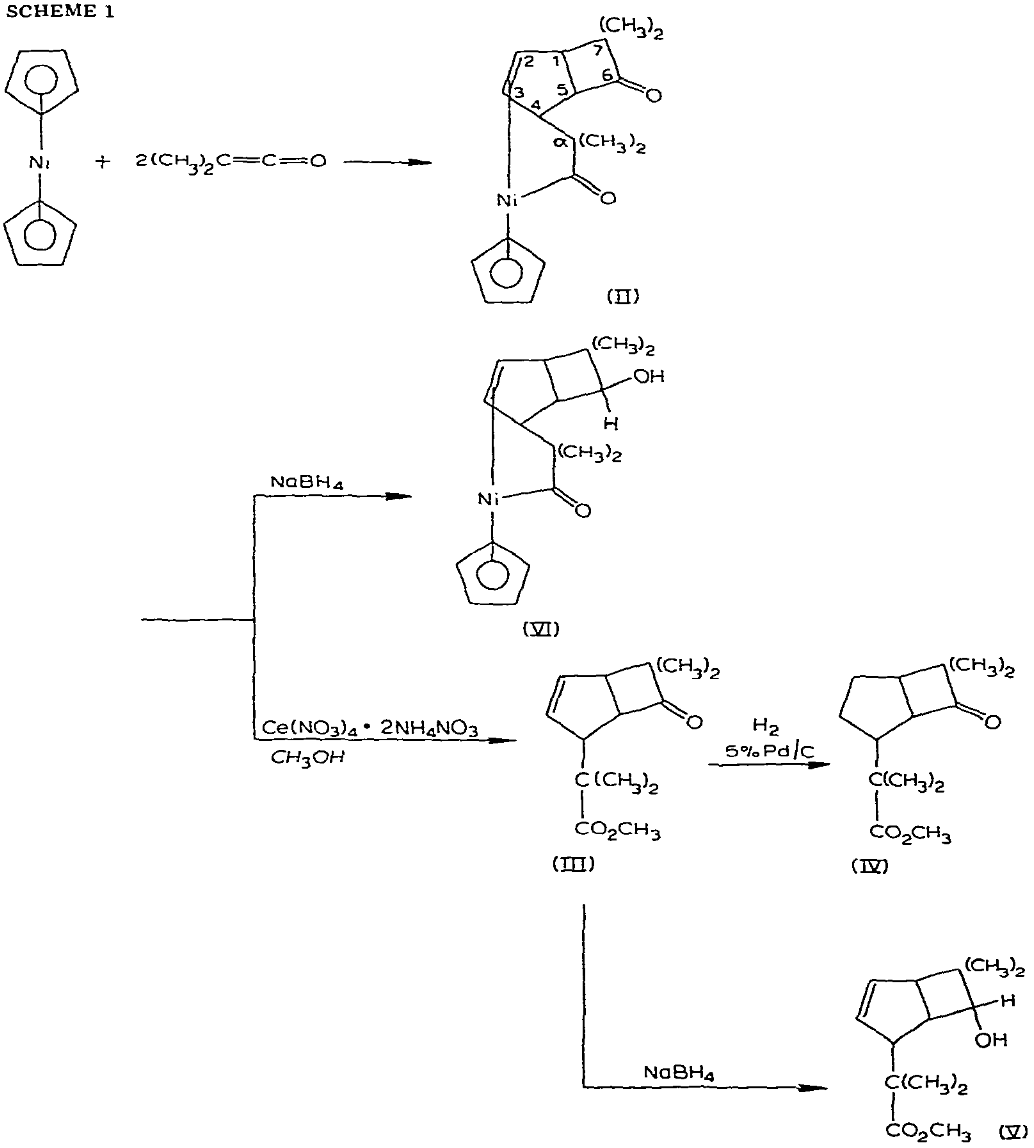
Di-π-cyclopentadienylnickel is known to react as an unsaturated system. For example, hydrogenation [2], 1,2-cycloaddition of tetrafluoroethylene [3], 1,2- and 1,3-cycloadditions of tetrafluorobenzyne [4], and 1,3-cycloaddition of dimethyl acetylenedicarboxylate [5] have been reported. The reaction of cyclopentadiene and dimethylketene is known to produce 7,7-dimethylbicyclo-[3.2.0]hept-2-en-6-one (I) [6].



(I)

In view of these reports, and because of our continuing interest in the organometallic chemistry of ketenes [7], we undertook the degradative analysis of complex II, and now assign a structure quite different from that postulated by Sato et al. [1]. We postulate Scheme 1 for reactions discussed here:

SCHEME 1



Experimental

Synthesis of complex II

The orange crystalline material described by Sato et al. [1] was obtained in 67% yield by reaction of 48.9 g (0.259 mole) of di-π-cyclopentadienylnickel with 70 ml (0.80 mole) of dimethylketene* in 800 ml of dry, oxygen-free benzene under argon. The m.p., elemental analysis, IR and proton NMR spectra of II were in agreement with those reported. Mass spectrum: *m/e* found: 328. $C_{18}H_{22}NiO_2$ calcd.: 328. Peaks were also observed at *m/e*: 300 (—CO), 272 (—2CO), 257 (—2CO, —CH_3), 230[—CO, —$(CH_3)_2C{=}C{=}O$] and 215[—CO, —CH_3, —$(CH_3)_2C{=}C{=}O$].

Degradation of complex II

A solution of 140 g (0.255 mole) of ceric ammonium nitrate in 100 ml water was mixed with 40.0 g (0.121 mole) of II in 1.5 l methanol. The resulting solution was heated at gentle reflux for 2 h, cooled, filtered and concentrated to 300 ml by evaporation of methanol. This solution was diluted with 200 ml of water, extracted three times with methylene chloride, and the combined extracts were washed with water and dried by flitration through anhydrous magnesium sulfate. After evaporation, the resulting red oil was distilled (b.p. 75 to 100°/0.2 mm), and 8.8 g of yellow oil resulted. Analysis by GLC showed this oil to be over 90% one compound. Trituration of the oil in pentane gave a cream-colored solid. Several recrystallizations from methanol saturated with pentane gave 3.4 g of colorless crystals (III) m.p. 32.5 to 33°. (Found: C, 71.04; H, 8.34. $C_{14}H_{20}O_3$ calcd.: C, 71.16; H, 8.53%.) NMR: ($CDCl_3$) δ 0.96 (s, 3, CH_3 on 7 position), 1.08 (s, 6, $2CH_3$'s on α position), 1.27 (s, 3, CH_3 on 7 position), 3.00 (complex, 1, H on 1 or 4 position), 3.07 (complex, 1, H on 1 or 4 position), 3.56 (s, 3, OCH_3), 3.69 (complex, 1, H on 5 position), 5.63 ppm (complex, 2, H on 2 or 3 position). Infrared: (KBr) 1775 (s, four-membered ring ketone), 1730 (s, ester), 1380 and 1360 (w, *gem*-dimethyl), 1135 (s, C—OCH_3), 775 cm^{-1} (m, *cis*-olefin). Mass spectrum (high resolution): *m/e* found: 236.1387. $C_{14}H_{20}O_3$ calcd.: 236.1412. UV: (95% ethanol) λ_{max} = 299 nm, ϵ = 47.

Compound III was also isolated by degradation of II with sodium sulfide in methanol solution.

Reaction of III with hydrogen (40 psi., 40°) over 5% palladium/carbon produced IV. Mass spectrum: *m/e* found: 238. $C_{14}H_{22}O_3$ calcd.: 238. IR: (neat smear) similar to III except that no 775 cm^{-1} (m, *cis*-olefin) band was present. UV: (95% ethanol) λ_{max} = 303 nm, ϵ = 61.

Reaction of III with sodium borohydride in methanol produced the hydroxy derivative (V). Mass spectrum: *m/e* found: 238. $C_{14}H_{22}O_3$ calcd.: 238. IR: (neat smear) 3410 (s, OH), 1730 (s, ester), no 1775 (s, four-membered ring ketone) band was present, 765 cm^{-1} (m, *cis*-olefin).

---

*Attention is drawn to the formation of sensitive, explosive peroxides if dimethylketene is contacted with air. All operations involving monomeric dimethylketene were carried out under an inert atmosphere, see ref. 8.

Reduction of complex II

To a solution of 0.66 g of II in 60 ml of methanol, 0.90 g of sodium borohydride was added (with stirring) over 30 min. The resulting solution was diluted with water, chilled and slowly evaporated under a stream of nitrogen. A crystalline red product (VI) was obtained. Compound VI was dissolved in ether, filtered and the solution was evaporated. Recrystallization from aqueous methanol gave 0.25 g of VI, m.p. 124 to 126°. (Found: C, 64.91; H, 7.26. $C_{18}H_{24}NiO_2$ calcd.: C, 65.30; H, 7.31%.) NMR: ($CDCl_3$) δ 0.87 (s, 3, CH_3), 0.96 (s, 3, CH_3), 1.05 (s, 1, OH), 1.14 (s, 3, CH_3), 1.58 (s, 3, CH_3), 1.65 (complex, 1, H on 5 position), 2.03 (d, *J* 4 Hz, 1, H on 4 position), 2.61 (complex, 1, H on 1 position), 3.78 (complex, 1, H on 6 position), 4.92 (d, *J* 4.8 Hz, 1, H on 2 position), 5.33 (s, 5, C_5H_5) and 6.12 ppm (dd, 1, H on 3 position). IR: (KBr) 3480 (s, OH), 1680 and 1655 (s, metal acyl), 1470 (m), 1355 (m), 1100 (s), 1035 (m) 901 (s), 830 (s) and 795 cm^{-1} (s). Mass spectrum: *m/e* found: 330. $C_{18}H_{24}NiO_2$ calcd.: 330.

Results and conclusions

Reaction of complex II with either ceric ammonium nitrate or sodium sulfide liberated compound III. In this reaction there was no evidence of either 3-hydroxy-2,2,4-trimethyl-3-pentenoic acid β-lactone (the dimethylketene dimer postulated by Sato et al. [1] to be π-coordinated to nickel in II) or methyl 2,2,4-trimethyl-3-oxopentanoate (the expected reaction product of the lactone with methanol). Our structural assignment of III is based upon elemental analysis, spectral data and its hydrogenation to IV and reduction to V. The UV spectrum of III rules out a 6,6-dimethyl-7-oxo structure which would be expected to give an ϵ value between 100 and 160 [9]. The observed ϵ of 47 is similar to the 61 observed for IV. Similarities of the NMR spectra of I and III provide additional support for the bicyclic structure [6].

The structure of III leads us to propose that structure II is the product obtained from the aforementioned reaction. The 1771, 1680, and 1645 cm^{-1} IR bands, previously assigned [1] to a π-complexed, four-membered ring lactone, are actually a result of the four-membered ring ketone and metal acyl. The NMR spectrum of II [1] is partially assigned as follows: δ 0.77, 0.98, 1.19, and 1.43, each (s, 3) to the four methyl groups, 1.86 (d, 1) to H on 4 position, 2.77 (d, 1) and 3.18 (d, 1) to H on 1 position or H on 5 position, 4.63 (d, 1) to H on 2 position, 5.14 (s, 5) to C_5H_5 and 5.76 ppm (m, 1) to H on 3 position.

Our structural assignment of II is also supported by its mass spectrum. While evidence for the loss of dimethylketene was observed, no peak at *m/e* 140, which would represent the loss of a π-coordinated lactone dimer of dimethylketene, was present.

Reduction of II with sodium borohydride produced VI. Such a reduction is characteristic of a ketone functionality.

We thus conclude that two moles of dimethylketene react with di-π-cyclopentadienylnickel, one mole by 1,2-cycloaddition to a π-cyclopentadienyl ring and the other by insertion into a nickel—carbon bond. The former process is similar to reactions cited earlier, and is sterically identical to the reaction between free cyclopentadiene and dimethylketene which gives I [6]. While many examples of the insertion of reactive molecules into metal—carbon bonds are known, we believe this to be the first example of ketene insertion*.

Acknowledgements

I would like to thank Dr. David Pond, Mr. Edward Elam, Dr. John Thweatt, and Dr. Robert Hasek for helpful suggestions.

References

1 M. Sato, K. Ichibori and F. Sato, J. Organometal. Chem., 26 (1971) 267.
2 K. Barnett, F. Mango and C. Reilly, J. Amer. Chem. Soc., 91 (1969) 3387.
3 D. McBride, R. Pruett, E. Pitcher and F. Stone, J. Amer. Chem. Soc., 84 (1962) 497.
4 D. Roe and A. Massey, J. Organometal. Chem., 20 (1969) P1.
5 M. Dubeck, J. Amer. Chem. Soc., 82 (1960) 6193.
6 J. Martin, P. Gott, V. Goodlett and R. Hasek, J. Org. Chem., 30 (1965) 4175.
7 D. Young, Inorg. Chem., 12 (1973) 482.
8 H. Staudinger, Die Ketene, F. Enke, Ed., Stuttgart, Germany, 1912, p. 141.
9 D. Schuster, M. Axelrod and J. Auerbach, Tetrahedron Lett., (1963) 1911.
10 M.R. Churchill, private communication.

---

* Subsequent single crystal X-ray examination has verified the structure of compound II, see ref. 10.