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A METHYLNICKEL ENOLATE AND A DIMETHYLALUMINIUM ENOLATE FROM DIPHENYLKETENE

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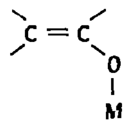
Summary

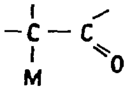
$Me_2Ni(PMe_2Ph)_3$ and Me_3Al add to diphenylketene giving $MeNi(OCMe{=}CPh_2)(PMe_2Ph)_2$ and $Me_2AlOCMe{=}CPh_2$, respectively. Trimethylaluminium converts the nickel enolate to the aluminium enolate. IR spectra suggest a pseudo-π-allyl bonding between nickel and the oxapropenyl group in the nickel enolate, whereas the aluminium enolate has a vinyloxy structure.

Introduction

Few Main Group metal enolates have been isolated. However, such compounds are of importance in organic synthesis because they can be prepared in situ and condensed with aldehydes and ketones (the aldol condensation). Three types of structures are possible for the enolates: covalent (I), keto (II) and ionic (III). Compounds with structures I and II have been isolated [1, 2] but the fully ionic structure III has not been reported.



I



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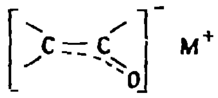
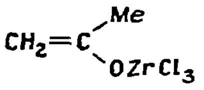


III

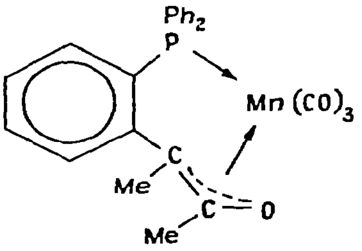
By contrast, transition metal enolates are rare and their reactions unknown. Structures like those of the Main Group metals are possible (e.g. IV, a zirconium enolate [3]), but so too is pseudo-π-allyl bonding, as in V [4]. A π-allyl structure could drastically alter the reactions undergone by the enolate.

Recently, we have isolated and characterised several dimethylaluminium enolates [5, 6]. To prepare one of these enolates we used a nickel acetylacetonate-



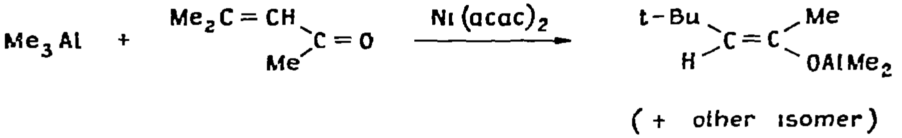
$CH_2{=}C(Me)OZrCl_3$

IV



V

catalysed conjugate addition of trimethylaluminium to mesityl oxide (eqn. 1) [5].



$$Me_3Al + Me_2C{=}CH(Me)C{=}O \xrightarrow{Ni(acac)_2} t\text{-}Bu(H)C{=}C(Me)OAlMe_2 \quad (+\ \text{other isomer})$$

(1)

For this reaction we prefer a mechanistic scheme in which Me_3Al oxidatively adds to Ni^0 to form $MeNiAlMe_2$, which then attacks the carbonyl oxygen of the ketone via its aluminium centre and adds MeNi to the 4-position of the ketone. However, a nickel enolate could possibly be involved*.

The preparation of a nickel enolate therefore appeared desirable not only because of the possible occurrence of a π-allyl structure but also because of its relevance to the mechanism of the nickel-catalysed conjugate addition.

Experimental

General

Experimental methods have been described previously [5, 6]. Diphenylketene, prepared according to the method of Taylor et al. [8], was distilled under vacuum, handled under nitrogen, and stored in sealed ampoules at −18°. Tris(dimethylphenylphosphine)dimethylnickel(II) was obtained as described previously [9].

Dimethylaluminium-1,1-diphenylprop-1-en-2-olate (VI)

Diphenylketene (1.13 g, 5.8 mmol) in benzene (5 ml) was added dropwise to a stirred solution of trimethylaluminium (0.47 g, 6.5 mmol) in benzene (10 ml). After 15 h the benzene was removed in vacuo and the solid product (1.55 g, 100%), m.p. > 200° (dec.), was recrystallised from toluene/hexane.

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* Tang and Riviere have postulated [7] copper enolates as intermediates in conjugative addition to α,β-unsaturated ketones using organocopper reagents, but most authors view organocopper additions as proceeding without formation of copper enolates.

(Found: Al, 10.3. $C_{17}H_{19}AlO$ calcd.: Al, 10.1%). PMR (C_6D_6): δ (ppm) 7.20-7.02 (m, 10H, Ph), 1.92 (s, 3H, CH_3), −0.68 (s, 6H, CH_3Al). IR (cyclohexane): 1642 (C=C) cm^{-1}. Molecular weight by ebulliometry in benzene 513 (calcd. for dimer 532). The product sublimed under high vacuum at 180-200° bath temperature, with slight decomposition.

Hydrolysis of the enolate with dilute HCl and extraction of the organic products with ether gave a near-stoichiometric yield of 1,1-diphenylacetone, identical by PMR and IR spectra with an authentic sample. PMR (C_6D_6): δ (ppm) 7.20-7.00 (m, 10H, Ph), 4.77 (s, 1H, CH), 1.82 (s, 3H, CH_3). IR (nujol): 1710 (C=O) cm^{-1}.

Bis(dimethylphenylphosphine)methylnickel(II)-1,1-diphenylprop-1-en-2-olate (VII)

Diphenylketene (0.29g, 1.49 mmol) in benzene (5 ml) was added dropwise to tris(dimethylphenylphosphine)dimethylnickel(II) (0.75g, 1.49 mmol) in benzene (20 ml); very little colour change occurred. After ca. 1 h the benzene was removed in vacuo and the product was recrystallized from toluene/hexane (rigorous exclusion of all oxygen was particularly important otherwise Me_2PhPO was formed). The yellow-brown crystals were separated, washed several times with hexane, then pumped dry (0.53g, 50%), m.p. 95° (dec.) (Found: Ni, 10.5. $C_{32}H_{38}NiOP_2$ calcd.: Ni, 10.5%). PMR (C_6D_6): δ (ppm) 7.67-6.83 (m, 20H, Ph), 2.31 (s, 3H, CH_3), 1.18 (br. s, 12H, PMe), −1.10 (s, 3H, CH_3Ni). IR (C_6D_6): 1595, 1530, 1490, 1435 cm^{-1}.

Hydrolysis of a small sample (40 mg) using hydrochloric acid, ether extraction and separation of the organic products by column chromatography (silica gel column, CH_2Cl_2/hexane eluant) gave 1,1-diphenylacetone (ca. 10mg, 60%), identified by comparison of its PMR spectra with an authentic sample; other products were not identified.

When excess trimethylaluminium (0.06g, 0.8 mmol) in benzene (0.4 ml) was added dropwise to VII (0.10g, 0.18 mmol) in benzene (0.4 ml) in a PMR tube, the red-brown solution turned black and the PMR spectrum showed that all the nickel enolate had reacted giving VI in ca. 60% unisolated yield (determined by integration of peaks). Hydrolysis by addition of one drop of HCl resulted in formation of 1,1-diphenylacetone (as indicated by the PMR spectrum).

Results and discussion

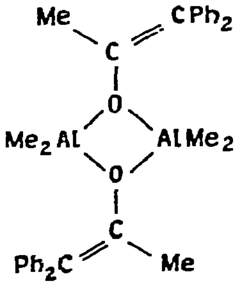
Addition of organometal compounds to ketenes is a well established preparation for metal enolates [1]. We have now added Me_3Al and $Me_2Ni(PMe_2Ph)_3$ to the carbonyl group of diphenylketene (reactions 2 and 3) to obtain the corresponding aluminium and nickel enolates:

$$Ph_2C{=}C{=}O + Me_3Al \rightarrow Me_2AlOCMe{=}CPh_2 \qquad (2)$$

$$Ph_2C{=}C{=}O + Me_2Ni(PMe_2Ph)_3 \rightarrow MeNi(OCMe{=}CPh_2)(PMe_2Ph)_2 + PMe_2Ph \qquad (3)$$

Addition 2 was stoichiometric and the product, $Me_2AlOCMe{=}CPh_2$, was dimeric in benzene, whereas addition 3 gave unisolated side-products and the product, $MeNi(OCMe{=}CPh_2)(PMe_2Ph)_2$, was probably monomeric*.

The IR olefin stretch at 1642 cm^{-1} for the aluminium enolate indicated a covalent enolate structure similar to that of type I found for other dimethylaluminium enolates [5, 6] and is consistent with structure VI. By contrast, the nickel enolate had no IR stretching frequencies in the C=O or C=C regions, suggesting that keto structure II is very unlikely and that structure I is either not present or, less likely, that it is present but the olefin stretching frequency is too weak to observe. We tentatively propose that the nickel enolate has structure VII in which the oxapropenyl group is π-bonded to the nickel centre.



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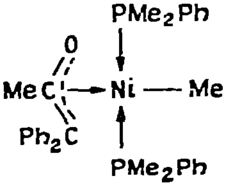

VII

Addition of excess trimethylaluminium to VII gave a moderate unisolated yield of VI together with ethane, nickel metal and other products. This qualitative result implies that a nickel enolate, if formed during the nickel-catalysed 1,4-addition of trimethylaluminium to α,β-unsaturated ketone, would readily generate dimethylaluminium enolate by redistribution with trimethylaluminium.

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* Low solubility of the product in cold benzene prevented an accurate molecular weight determination.