Journal of Organometallic Chemistry, 74 (174) 365—371

DIMETHYLALUMINIUM 4,4-DIMETHYLPENT-2-EN-2-OLATE: (*Z*)- AND (*E*)-ISOMERS AND THEIR ASSOCIATION

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(Received February 25th, 1974)

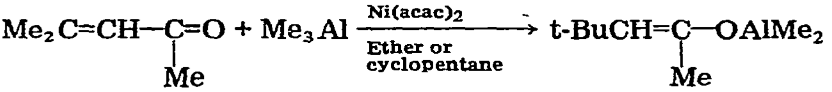
Summary

The (*Z*)- and (*E*)-isomers of dimethylaluminium 4,4-dimethylpent-2-en-2-olate, $Me_2AlOC(Me){=}CH\text{-}t\text{-}Bu$, have been obtained. The (*Z*)-isomer is dimeric; the (*E*)-isomer can be isolated either as a dimer or as a trimer.

The enolates are *O*-acetylated by acetic anhydride to the corresponding enol acetates (no C-acetylation is observed). They form 1/1 complexes with trimethylamine oxide, pyridine, hexamethylphosphoramide and triphenylphosphine oxide.

Introduction

We have recently found [1] that nickel acetylacetonate catalyst diverts the reaction of trimethylaluminium with α,β-unsaturated ketones from the normal course of 1,2-addition to give, instead, 1,4-addition — as for example in eqn. 1. The catalyst opens up a simple route to dimethylaluminium enolates and has led us into a more detailed study of this and other methods by which such enolates can be prepared.



$$\mathrm{Me_2C{=}CH{-}\underset{Me}{C}{=}O + Me_3Al \xrightarrow[\text{Ether or cyclopentane}]{\text{Ni(acac)}_2} t\text{-}BuCH{=}\underset{Me}{C}{-}OAlMe_2} \qquad (1)$$

Our interest was spurred by the rarity of organoaluminium enolates; only diisobutylaluminium ethenolate and prop-1-en-1-olate have been previously reported [2]. Indeed, metal enolates in general (excluding the rather special β-ketoenolates have been extensively studied only for Group IV metals [3]; a few magnesium [4] and boron [5] enolates, and one lithium enolate [6], are also well characterized.

We now describe the isolation of the (*Z*)- and (*E*)-isomers of dimethylaluminium 4,4-dimethylpent-2-en-2-olate from reaction 1. In the following paper we discuss aldol condensations of these enolates.

Experimental

All organometallic reactions and manipulations were carried out under a nitrogen or argon atmosphere. Commercial trimethylaluminium was used without purification. Mesityl oxide (4-methylpent-3-en-2-one), b.p. 73°/121 mm (lit. [7] 68°/121 mm), was separated from isomesityl oxide (4-methylpent-4-en-2-one) by fractional distillation using a spinning-band column. Acetic anhydride was refluxed over magnesium, then distilled under nitrogen. Trimethylamine oxide, m.p. 235° (lit. [8] 210—212°), prepared and purified according to Köster and Morita [8], is extremely hygroscopic and was always handled under nitrogen. Anhydrous nickel acetylacetonate was obtained from recrystallised nickel acetylacetonate hydrate at 100°/0.1 mm. Solvents were dried over metal hydrides and distilled under nitrogen.

PMR spectra were recorded on Varian T60, A60 or HA100 instruments. Chemical shifts are expressed in ppm downfield from tetramethylsilane internal standard (multiplicity, coupling constant, integrated number of protons, and assignment in parentheses; m = multiplet, s = singlet, d = doublet, q = quartet). IR spectra were measured using Perkin—Elmer 521 and 557 grating infra-red spectrometers. Mass spectra were obtained using a Hitachi—Perkin—Elmer RMU-6D model at an electron energy of 70 eV (M^+ refers to the molecular-ion). A Varian Aerograph Series 1800 instrument was used for GLC analyses and separations.

Aluminium was determined complexometrically [9], after acid hydrolysis of the organoaluminium sample. Carbon and hydrogen analyses were preformed by the Australian Microanalytical Service, Melbourne.

1. Preparation and acetylation of the mixed enolates

Trimethylaluminium (0.87 g, 12 mmole) in ether (4 ml) was added dropwise to a rapidly stirred mixture of mesityl oxide (0.98 g, 10 mmole) and nickel acetylacetonate (77 mg, 0.3 mmole) in ether (6 ml) at —50°. The solution turned yellow-brown on warming to —40°; it was recooled to —50° for 15 min, then warmed slowly to —20°, maintained at —20° for 16 h, and finally brought slowly to room temperature (over 5 h).

A small aliquot (6.5% of the solution) was stripped of ether; its PMR spectrum in benzene-d_6 showed that 1,4-addition accounted for ca. 95% of the products (cf. Section 2) and that the (*Z*)- to (*E*)-enolate ratio was 4/1.

The rest of the ethereal solution (93.5%) was acetylated as follows. Acetic anhydride (1.72 g, 16.9 mmole) in ether (4 ml) was added dropwise, and the resulting solution was kept at room temperature for 24 h. The product was hydrolysed by cold saturated aqueous ammonium chloride solution, to which a few ml of 1 *N* hydrochloric acid were later added. The ether layer was dried over sodium sulphate then distilled to give an oil (1.31 g), which was separated by GLC into the following components:

(i). 59% (*Z*)-4,4-dimethylpent-2-en-2-yl acetate, n_D^{25} 1.4215. PMR (CCl_4): δ 4.81 (m, 1H, CH=C), 2.08 (s, 3H, $CH_3C{=}O$), 1.84 (m, 3H, $CH_3C{=}C$), 1.05 (s, 9H, t-Bu) ppm (cf. lit [10]).

(ii). 9% (*E*)-4,4-dimethylpent-2-en-2-yl acetate, b.p. 60°/11 mm, n_D^{30} 1.4212. (Found: C, 69.3; H, 10.3. $C_9H_{16}O_2$ calcd.: C, 69.2; H, 10.3%). PMR (CCl_4):

δ 5.06 (m, 1H, CH=C), 2.01 (s, 3H, CH_3C=O), 1.90 (broad s, 3H, CH_3C=C), 1.15 (s, 9H, t-Bu) ppm. IR (neat): 1754 (C=O), 1688 (C=C) cm^{-1}. Mass spectrum (*m/e*, *I*): 156, M^+, 8; 114, 19; 99, 100; 81, 6; 55, 4; 43, 50.

(iii). 16% 4,4-dimethylpentan-2-one. PMR (CCl_4): δ 2.26 (s, 2H, CH_2), 2.06 (s, 3H, CH_3C=O), 1.02 (s, 9H, t-Bu) ppm.

(iv). 4% mesityl oxide. PMR (C_6H_6): δ 5.83 (m, 1H, CH=C), 2.10 (m, 3H, CH_3C=C), 1.90 (s, 3H, CH_3C=O), 1.53 (m, 3H, CH_3C=C) ppm.

(v). 3% 2,6,6-trimethylhept-2-en-4-one. PMR (CCl_4): δ 5.97 (m, 1H, CH=C), 2.21 (s, 2H, CH_2), 2.11 (m, 3H, CH_3C=C), 1.87 (m, 3H, CH_3C=C), 0.99 (s, 9H, t-Bu). IR (neat): 1642 (C=O), 1612 (C=C) cm^{-1}. Mass spectrum (*m/e*, *I*): 154, M^+, 8; 98, 16; 83, 100; 57, 22; 55, 19; 43, 19.

Similar results (see Table 1) were obtained from reactions at different temperatures or in tetrahydrofuran or cyclopentane. The (*E*)/(*Z*) enolate ratio (determined by integration of the PMR spectrum) is higher than the (*E*)/(*Z*) enol acetate ratio (determined by GLC analysis after acetylation); this may be because side-reactions occur during acetylation.

TABLE 1

(*E*)/(*Z*)-ISOMER RATIOS FOR ENOLATES AND THEIR DERIVED ENOL ACETATES

Solvent (temperature [a]) for enolate preparation	(*E*)/(*Z*) isomer ratio [b] Enolate	Enol acetate
Et_2O (−50°)	0.25	0.18
Et_2O (+20°)	0.42	0.26
Et_2O (−20°) [c]	0.57	0.45
THF (−70°)	2.9	1.3
Cyclopentane (−70°)	1.0	—

[a] Initial reaction temperatures. [b] Enolate ratio by integration of PMR spectra; enol acetate ratio by GLC analysis. [c] Reverse order of mixing; mesityl oxide was added first.

Reaction in the absence of nickel acetylacetonate gave, in ether, 1,2-addition products mixed with unidentified materials, but no products of 1,4-addition; in cyclopentane only 1,2-addition occurred.

2. Isolation of the aluminium enolates

(a). Dimeric dimethylaluminium (Z)-4,4-dimethylpent-2-en-2-olate. Trimethylaluminium (3.79 g, 52.5 mmole), mesityl oxide (4.50 g, 46 mmole) and nickel acetylacetonate (0.35 g, 1.4 mmole) were allowed to react in ether at −50°, as described in section 1 above. After removal of solvent, the product was distilled under high vacuum at 80°. The distillate (6.44 g, 38 mmole) was split into an initial fraction (1.43 g) containing mainly (*Z*)-enolate, a middle fraction (3.43 g, 20 mmole) containing crystalline (*Z*)-enolate, m.p. 61.5—64.5°, and a final fraction (1.58 g) containing a mixture of (*Z*)- and (*E*)-enolates.

The (*Z*)-4,4-dimethylpent-2-en-2-olate from the middle fraction was characterized. (Found: Al, 15.6. $C_9H_{19}OAl$ calcd.: Al, 15.8%.) PMR (C_6D_6): δ 4.52 (q, *J* 0.8 Hz, 1H, CH=C), 1.80 (d, *J* 0.8 Hz, 3H, CH_3C=C), 1.15 (s, 9H, t-Bu), −0.34 (s, 6H, CH_3Al) ppm. Molecular-weight by cryometry in benzene 350 (calcd. for dimer 340). IR (cyclohexane): 1680 (C=C) cm^{-1}. Acetylation with acetic anhydride gave mainly (*Z*)-4,4-dimethylpent-2-en-2-yl acetate [free of (*E*)-enol acetate], isolated by distillation (91% yield). The PMR spectrum and GLC retention time of this (*Z*)-enol acetate were identical with those of the sample described in Section 1, above.

(b). Dimeric dimethylaluminium (E)-4,4-dimethylpent-2-en-2-olate. (*Z*)-Enolate (2.67 g) was heated at 150° for 64 h in a stout-walled sealed glass ampoule inside a steel bomb partly filled with toluene. The bomb was cooled rapidly, and the product was then distilled. The middle-cut distillate (b.p. 110—115°/2.6—3.0 mm) was redistilled into cooled receivers to give crystalline (*E*)-dimer (1.99 g, 75% yield), m.p. 25—28°. (Found: Al, 15.8. $C_9H_{19}OAl$ calcd.: 15.8%.) PMR (C_6D_6): δ 5.23 (q, J 0.8 Hz, 1H, CH=C), 1.83 (d, J 0.8 Hz, 3H, CH_3C=C), 1.00 (s, 9H, t-Bu), —0.34 (s, 6H, CH_3Al) ppm. Molecular-weight by ebulliometry in benzene 315; by cryometry in benzene 385* (calcd. for dimer 340). IR (cyclohexane): 1674 (C=C) cm^{-1}. Acetylation with acetic anhydride gave mainly (*E*)-enol acetate [no (*Z*)-enol acetate], isolated by distillation (60% yield). The PMR spectrum and GLC retention time of this (*E*)-enol acetate were identical with those of the sample described in Section 1, above.

(c). Trimeric dimethylaluminium (E)-4,4-dimethylpent-2-en-2-olate. A 1/1 mixture of (*Z*)- and (*E*)-enolates [5.62 g; (*Z*)-enolate or (*E*)-enolate dimer/trimer worked equally well] was heated at 110° for 64 h in a stout-walled sealed glass ampoule. Distillation of the product at 10^{-6} mm and a bath temperature of 70—90° gave a distillate [mainly (*E*)-dimer and trimer with a little (*Z*)-dimer] and a liquid residue (4.0 g, 69% yield) which was pure (*E*)-trimer. (Found: Al, 16.2. $C_9H_{19}OAl$ calcd.: 15.8%.) PMR (C_6D_6): δ 5.46 (q, J 0.8 Hz, 1H, CH=C), 1.92 (d, J 0.8 Hz, 3H, CH_3C=C), 1.02 (s, 9H, t-Bu), —0.40 (s, 6H, CH_3Al) ppm. Molecular -weight by ebulliometry in benzene 496 (calcd. for trimer 510). IR (cyclohexane): 1673 (C=C) cm^{-1}. Acetylation with acetic anhydride gave mainly (*E*)-4,4-dimethylpent-2-en-2-yl acetate [free of (*Z*)-enol acetate], isolated by distillation (81% yield). The PMR spectrum and GLC retention time of this (*E*)-enol acetate were identical with those of authentic material.

3. *Complexes with Lewis bases*

(a). Trimethylamine oxide. A suspension of trimethylamine oxide (0.35 g, 4.7 mmole) in benzene (10 ml) was added to (*Z*)-enolate (0.82 g, 4.8 mmole). Removal of solvent at low pressure left a clear oil which was induced to crystallise. The crystals were washed with hexane and dried, m.p. 44—46°. (Found: Al, 11.2. $C_{12}H_{28}NO_2Al$ calcd.: 11.0%.) Molecular weight by cryometry in benzene 277 (calcd. for monomer 245). IR (benzene): 1644 (C=C) cm^{-1}. PMR (C_6D_6): δ 4.3 (q, J 0.8 Hz, 1H, CH=C), 2.45 (s, 9H, NMe_3), 1.99 (d, J 0.8 Hz, 3H, CH_3C=C), 1.42 (s, 9H, t-Bu), —0.48 (s, 6H, CH_3Al) ppm. The PMR spectrum of the sublimed product was the same, except that the six methylaluminium protons now appeared as two resonances of roughly equal intensity separated by 2 Hz.

(b). Hexamethylphosphoramide. Addition of a slight excess of hexamethylphosphoramide to (*Z*)-enolate dimer in benzene-d_6 produced a change in the PMR chemical shifts to: 4.27 (s, 1H, CH=C), 2.02 (s, 3H, CH_3C=C), 1.47 (s, 9H, t-Bu), and —0.38 (s, 6H, CH_3Al) ppm. Similar addition to (*E*)-enolate dimer or trimer in benzene-d_6 resulted in chemical shifts of: 4.87 (s, 1H, CH=C), 2.07 (s, 3H, CH_3C=C), 1.27 (s, 9H, t-Bu), and —0.38 (s, 6H, CH_3Al) ppm. The chemical shift of the complexed hexamethylphosphoramide was a doublet (J 9 Hz) centred at 2.47 ppm. Attempts to isolate the complexes failed.

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* The cryometric solution was monitored by PMR, which indicated no change in state of association. Although the dimer is stable for long periods in the crystalline state, it isomerises slowly to a dimer/trimer mixture in solution or when melted. Isomerisation may require traces of air or moisture.

(c). Triphenylphosphine oxide. Addition of a slight excess of triphenylphosphine oxide to (*E*)-enolate dimer or trimer in benzene gave chemical shifts of: 4.93 (s, 1H, CH=C), 2.05 (s, 3H, CH_3C=C), 1.23 (s, 9H, t-Bu) and —0.31 (s, 6H, CH_3Al) ppm.

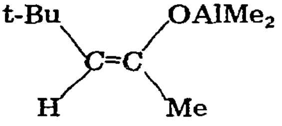
(d). Pyridine. In the presence of ca. 15% excess pyridine the chemical shifts for the (*E*)-enolate in benzene-d_6 were: 4.92 (s, 1H, CH=C), 1.98 (broad s, 3H, CH_3C=C), 1.15 (s, 9H, t-Bu), —0.39 (s, 6H, CH_3Al) ppm, and for the (*Z*)-enolate in benzene-d_6 the shifts were 4.29 (s, 1H, CH=C), 1.85 (broad s, 3H, CH_3C=C), 1.36 (s, 9H, t-Bu), and —0.39 (s, 6H, CH_3Al) ppm.

After the pyridine complex of the (*E*)-enolate (91 mg, 0.53 mmole) was left at room temperature in benzene for two days, distillation gave 2,2,6,8,8-pentamethylnon-5-en-4-one (10 mg, 0.05 mmole), identified by comparison of its PMR and IR spectra with the literature [11]. GLC analysis and PMR integration showed the compound to be a mixture of 20% (*Z*)- and 80% (*E*)-isomers. PMR of (*E*)-isomer (CCl_4): δ 5.90 (m, 1H, CH=C), 2.23 (s, 2H, CH_2), 2.14 (m, 3H, CH_3C=C), 2.02 (s, 2H, CH_2), 1.00 (s, 9H, t-Bu), and 0.96 (s, 9H, t-Bu) ppm; the (*Z*)-isomer had its CH=C multiplet at 6.05 ppm. IR (neat): 1678 (C=O), 1608 (C=C) cm^{-1}. Mass spectrum (*m/e*, *I*): 210, 4, M^+; 195, 2; 154, 9; 139, 39; 98, 48; 83, 71; 57, 100.

Discussion

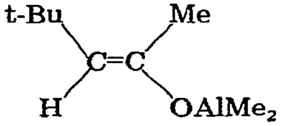
Isolation and structures of the isomeric dimethylaluminium enolates

Low pressure distillation of the crude product from nickel-catalyzed 1,4-addition of trimethylaluminium to mesityl oxide gave dimethylaluminium (*Z*)-4,4-dimethylpent-2-en-2-olate, III, which is dimeric in benzene. At ca. 100—150° III isomerised to dimethylaluminium (*E*)-4,4-dimethylpent-2-en-2-olate, IV, which could be separated by low pressure distillation into a dimeric distillate and a trimeric residue.



III

(*Z*)-enolate dimer, m.p. 63°



IV

(*E*)-enolate: (a) dimer, m.p. 27°
(b) trimer, liquid

The vinyloxy structure of III and IV was apparent from the vinyl proton resonances with allylic couplings in the PMR spectra and from the C=C stretching bands in the IR spectra. The stereochemistry was confirmed by *O*-acetylation to the corresponding (*Z*)- and (*E*)-enol acetates.

The vinyloxy spectroscopic characteristics imply that these dimeric and trimeric enolates are associated through Al—O—Al bridges. They rule out association through Al—O—C—C—Al bridges, which might have been thought possible by analogy to dimeric $Me_2AlOCPh$=NPh [12]. Methyl bridging is not indicated by the PMR spectra and is unlikely since methyl bridges are relatively weak; methyl-bridged organoaluminium trimers are unknown [13]. Such oxygen-bridged association to dimers and trimers is well known for many dialkylaluminium alkoxides [13], and the existence of IV as slowly interconvertible dimer and trimer has a direct precedent in the behaviour of dimethylaluminium phenoxide [14]. As for dimethylaluminium phenoxide, lower temperature favours the trimer of IV as compared with the dimer.

Models indicate that the absence of trimeric III may be due to large steric interactions between t-Bu and Me_2Al groups. Dimers and trimers built from mixtures of monomeric (*Z*)- and (*E*)-enolates probably exist as well. In fact, residues remaining after removal of (*Z*)-enolate dimer from crude reaction mixtures often contained an oligomer which appeared, from its PMR spectrum, to be a trimer formed from one (*Z*)-monomer and two (*E*)-monomers. Unfortunately, this trimer could not be freed of nickel residues for full characterisation.

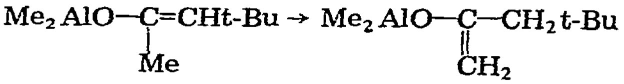
Heating (*Z*)-enolate gives (*E*)-enolate, therefore the latter is the more thermodynamically stable; this is the reverse of the usual finding that the (*Z*)-metal-enolates are thermodynamically favoured [15]. Other than the usually accepted free-radical or protolytic mechanisms for rearrangement of (*Z*)-enolate to (*E*)-enolate, there are at least three further possibilities: firstly that the (*Z*)-enolate rearranges via dimethyl(4,4-dimethyl-2-oxopent-3-yl)aluminium; secondly that (*Z*)-enolate rearranges to dimethylaluminium 4,4-dimethylpent-1-en-2-olate, as in reaction (3) below, and thence to (*E*)-enolate; and thirdly that rearrangement occurs during reversible condensation with ketone generated by trace hydrolysis.

Complexes of the enolates with Lewis bases

The enolates form 1/1 complexes with Lewis bases such as trimethylamine oxide, hexamethylphosphoramide, triphenylphosphine oxide and pyridine. The complex of trimethylamine oxide with (*Z*)-enolate has been isolated and shown to be monomeric (cf. the monomeric complex of trimethylamine oxide with $Me_2AlOCPh{=}NPh$ [12]). Other complexes were indicated by PMR but not isolated. They are likely to be monomeric, since identical PMR spectra were produced by dimeric and trimeric (*E*)-enolate.

With excess pyridine and (*E*)-enolate, a slow condensation (eqn. 2) gave (*Z*)- and (*E*)-2,2,6,8,8-pentamethylnon-5-en-4-one. The overall reaction is formally a condensation of 4,4-dimethylpentan-2-one with enolate from rearrangement (eqn. 3); it may well be initiated by a trace of water.

$$2Me_2AlOC(Me){=}CH\text{-t-Bu} \rightarrow \underset{\text{not isolated}}{[Me_2AlOAlMe_2]} + \underset{20\%\ Z;\ 80\%\ E}{\text{t-BuCH}_2C(Me){=}CHCOCH_2\text{-t-Bu}} \qquad (2)$$



$$Me_2AlO{-}\underset{\displaystyle Me}{\underset{|}{C}}{=}CH\text{t-Bu} \rightarrow Me_2AlO{-}\underset{\displaystyle CH_2}{\underset{\|}{C}}{-}CH_2\text{t-Bu} \qquad (3)$$

Reaction with acetic anhydride

With excess acetic anhydride the (*Z*)- and (*E*)-enolates gave good yields of the corresponding (*Z*)- and (*E*)-enol acetates. Our initial acetylation studies, however, undertaken using the crude reaction mixtures obtained from 1,4-addition, gave unexpected side-products. One, found after hydrolysis, was 2,6,6-trimethylhept-2-en-4-one (up to 15% of product). This product suggests that the enolate from rearrangement (eqn. 3) condenses either with acetone (from the methylation of acetic anhydride by excess trimethylaluminium) or with acetic anhydride (later being methylated). The final product could be formed either by dehydroxyalumination or by dehydration during hydrolysis and work-up.

Although the dimethylaluminium enolates are essentially covalent and associated and were acetylated in non-polar solvents (conditions which all favour *C*-acetylation rather than *O*-acetylation [15]), no *C*-acetylated products were observed. Possibly, the presence of a tert-butyl group on the 3-carbon atom makes *C*-acetylation sterically unfavourable.

Acknowledgements

We thank Mr. G. Heath of this Division, who kindly purified the mesityl oxide, Mr. A.C.K. Triffett, who measured the mass spectra, and our assistant, Mr. L. Bagnell.

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