

METHYLALUMINIUM ENOLATES AND KETOLATES FROM STERICALLY HINDERED KETONES

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Summary

Both 1,1,1-triphenylacetone and *t*-butyl methyl ketone are enolised by trimethylaluminium, but the types of products and their subsequent reactions are quite different.

1,1,1-Triphenylacetone gives dimeric $\text{CH}_2=\text{C}(\text{CPh}_3)\text{OAlMe}_2$, II, which condenses with acetone to yield the dimeric ketolate III.

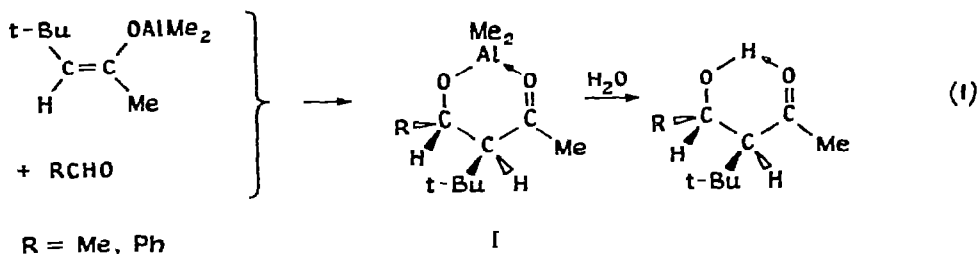
By contrast, addition of *t*-butyl methyl ketone to two equivalents of trimethylaluminium gives initially the hemialkoxide, IV, which with further ketone at room temperature forms a mixed-bridge alkoxide-ketolate, V. Heating V with more trimethylaluminium (or IV) gives a mixed-bridge μ -alkoxide- μ -enolate, VI, which does not condense with ketones.

Introduction

Enolisation and condensation are the principal steps of the aldol condensation. They also occur as important side-reactions when ketones or aldehydes are alkylated by organometallic compounds such as Grignard reagents [1]. A knowledge of the metalorganic intermediates is essential if enolisation, condensation and alkylation of ketones and aldehydes are to be understood and controlled.

We have previously studied [2] the aldol condensation (eqn. 1) of dimethylaluminium (*Z*)-4,4-dimethylpent-2-en-2-olate with aldehydes. The key intermediate I was isolated, found to be dimeric (the monomers linked through the Al—O bonds) and to contain the rare 5-coordinate aluminium. Chelate stabilisation of I probably accounts for the stereospecificity and high overall yield for the reaction.

We now describe products from condensation of ketones with dimethylaluminium enolates. Ketones do not condense with the enolates so readily as aldehydes; in order to obtain isolable ketolates we had to use enolates with no terminal substituents, $\text{CH}_2=\text{C}(\text{R})\text{OAlMe}_2$, prepared by deprotonation of methyl ketones with trimethylaluminium.

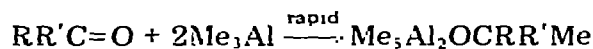
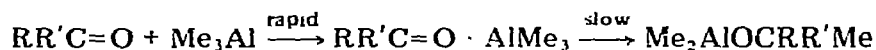


1,1,1-Triphenylacetone was slowly deprotonated to the expected enolate (II), which readily condensed with acetone to form a crystalline ketolate (III). By contrast, *t*-butyl methyl ketone (pinacolone) gave unexpected and more interesting products (see IV, V and VI, below).

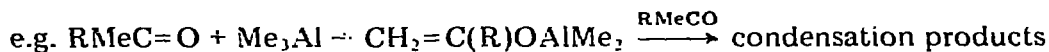
Discussion

Saturated ketones undergo two main reactions [3] with trimethylaluminium at ambient temperature*:

(a). Methylation:



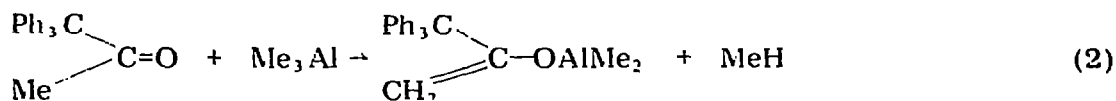
(b). Enolisation followed by condensation:



Little is known about aluminium enolate formation, but where the ketone is sterically hindered towards methylation, enolisation might be expected to dominate.

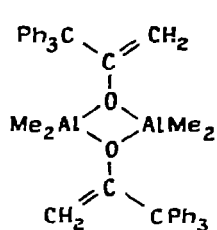
Enolisation and condensation of 1,1,1-triphenylacetone

The enolisation (eqn. 2) of 1,1,1-triphenylacetone has been postulated to occur during the reaction of triphenylacetic acid with excess trimethylaluminium at elevated temperature [5].

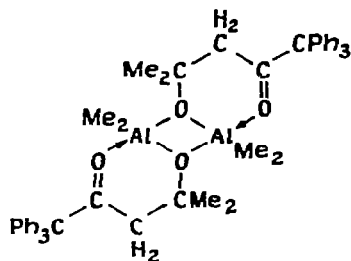


Accordingly, 1,1,1-triphenylacetone was heated with an equivalent of trimethylaluminium in toluene (enolisation was slow). The expected enolate was isolated and found to be dimeric in benzene. Both the PMR vinyl resonances and the IR C=C stretching frequency supported structure II.

* Elevated temperatures may lead to *gem*-dimethylation [4]. Use of higher trialkylaluminums can give reduction [3].



II

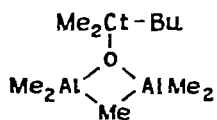


III

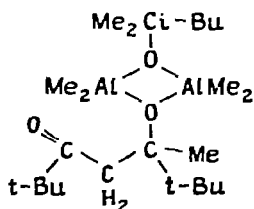
II did not condense with excess 1,1,1-triphenylacetone but condensed readily with the less hindered ketone, acetone, to give a high yield of a crystalline ketolate (dimeric in benzene). The low carbonyl stretching frequency at 1688 cm^{-1} implied that both carbonyl groups were coordinated and suggested structure III. The ketolate hydrolysed readily to the corresponding β -hydroxyketone.

*Methylation, enolisation and condensation reactions of *t*-butyl methyl ketone (pinacolone)*

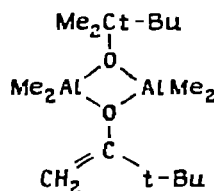
(a). *Formation of hemialkoxide IV.* Pinacolone is somewhat less sterically hindered than 1,1,1-triphenylacetone not only towards methylation of the carbonyl group, but also towards self-condensation under the influence of trimethylaluminium. Addition of pinacolone to two equivalents of trimethylaluminium in benzene gave the hemialkoxide IV. This is the most stable hemialkoxide known; it could be sublimed and the stability of the bridge structure was reflected in its PMR spectrum at 35° which showed sharp bridge and terminal methylaluminium resonances [6].



IV



V



VI

(b). *Formation of ketolate V.* Slow addition of two equivalents of pinacolone to one equivalent of IV (or $4/3$ equivalents of trimethylaluminium) leads to condensation product V; surprisingly no μ -enolato- μ -alkoxide VI was observed at any stage during the addition. V could also be prepared by addition of trimethylaluminium to $3/2$ equivalents of pinacolone in benzene at ambient temperature.

The PMR of V showed two (not four) equally intense methylaluminium resonances, indicating either that the carbonyl group was not coordinated or that it was coordinated but rapidly fluctuating between both aluminium centres [2]. The IR $\text{C}=\text{O}$ stretching frequency at 1715 cm^{-1} indicated a non-coordinated carbonyl group.

(Found: Al, 7.8. $C_{23}H_{23}AlO$ calcd.: Al, 7.9%.) PMR (C_6D_6): δ (ppm) 7.60-7.00 (m, 15H, PhC), 5.22 and 4.89 [AB quartet, $J(AB)$ 2.4 Hz, 2H, $CH_2=C$], -0.84 (s, 6H, CH_3Al). IR (C_6H_6): 1626 (C=C) cm^{-1} . Molecular weight by ebulliometry in benzene 631 (calcd. for dimer 685).

Tetramethylbis[μ -(2-methyl-4-oxo-5,5,5-triphenylpentan-2-olato- O^2 , O^1)]dialuminium (III)

A solution of dry acetone (0.123 g, 2.12 mmol) in toluene (2 ml) was added dropwise to a stirred suspension of II (0.67 g, 0.99 mmol of dimer) in toluene (8 ml) at 5°. II dissolved on gentle warming; later colourless crystals of product appeared. After 20 min at 50°, then 15 h at 3°, the crystals of III were washed with cold toluene and pumped dry (0.65 g, 82%), m.p. 156-157° (dec.). (Found: Al, 6.5. $C_{26}H_{29}AlO_2$ calcd.: Al, 6.7%.) PMR (C_6D_6): δ (ppm) 7.6-7.0 (m, 15H, C_6H_5), 3.05 (s, 2H, CH_2), 1.21 (s, 6H, CH_3C), -0.52 (s, 6H, CH_3Al). IR (KBr): 1713 w*, 1688 s (C=O) cm^{-1} . Molecular weight by cryometry in benzene 817 (calcd. for dimer 801).

III (0.39 g, 0.49 mmol of dimer) was hydrolysed with ice-cold saturated ammonium chloride solution (pH 9) and extracted with ether. The crude organic product was chromatographed on alumina; toluene-ether eluted 4-hydroxy-4-methyl-1,1,1-triphenylpentan-2-one (0.26 g, 0.74 mmol, 80% yield), m.p. 111.5-112.5°. (Found: C, 83.9; H, 7.1. $C_{24}H_{24}O_2$ calcd.: C, 83.7; H, 7.0%.) PMR (CCl_4): δ (ppm) 7.30 (br. s, 15 H, C_6H_5), 3.50 (m, 1H, OH), 2.59 (s, 2H, CH_2), 0.91 (s, 6H, Me_2C). IR (KBr): 3528 (OH), 1687 (C=O) cm^{-1} ; (CCl_4): 3543 (OH), 1699 (C=O) cm^{-1} . Mass spectrum (m/e , I): 344, 1, M^+ ; 329, 1; 244, 26; 243, 100; 239, 12; 166, 18; 165, 98; 105, 12; 91, 11; 83, 20; 70, 15; 59, 23; 58, 23; 57, 22; 55, 20; 43, 75; 41, 19.

μ -Methyltetramethyl[μ -(2,3,3-trimethylbutan-2-olato)]dialuminium (IV)

Pinacolone (2.04 g, 20.4 mmol) in benzene (8 ml) was added dropwise to a stirred solution of trimethylaluminium (2.95 g, 40.7 mmol) in benzene (15 ml) at 5°. The solution was warmed briefly to 60°, the solvent was removed in vacuo and the residue sublimed (70°/0.3 mm) to give IV, m.p. 70-75°. (Found: Al, 21.9. $C_{12}H_{30}Al_2O$ calcd.: Al, 22.1%.) PMR (C_6H_6): δ (ppm) 1.21 (s, 6H, Me_2C), 0.84 (s, 9H, t-Bu), 0.22 (s, 3H, bridge MeAl), -0.47 (s, 12H, terminal MeAl). Molecular weight by ebulliometry in benzene 219 (calcd. 244).

Tetramethyl[μ -(2,2,3,6,6-pentamethyl-5-oxoheptan-3-olato- O^3)] [μ -(2,3,3-trimethylbutan-2-olato)]dialuminium (V)

Pinacolone (1.45 g, 14.4 mmol) in benzene (12 ml) was added dropwise to a vigorously stirred solution of IV (8.15 mmol) in benzene (15 ml) at ambient temperature. Methane was evolved (156 ml at STP) over 4 h. The white crystals of V which separated at 5° were dried under high vacuum (1.36 g,

* The product was particularly sensitive to hydrolysis; this weak band is attributed to free ketone from hydrolysis.

44%), m.p. 71-74° (dec.). (Found: Al, 12.5. $C_{23}H_{50}Al_2O_3$ calcd.: Al, 12.6%.) PMR (C_6D_6): δ (ppm) 3.21 and 2.80 [AB quartet, $J(AB)$ 17.6 Hz, 2H, CH_2], 1.71 (s, 3H, CH_3), 1.36 (br. s, 6H, Me_2C), 0.99 (s, 18H, 2 t-Bu), 0.96 (s, 9H, t-Bu), -0.19 (s, 6H, CH_3Al), -0.30 (s, 6H, CH_3Al). IR (C_6H_6): 1715 (C=O) cm^{-1} . Molecular weight by cryometry in benzene 423 (calcd. 428).

V (6.92 g; 15 mmol) was hydrolysed by ice-cold saturated ammonium chloride and extracted with ether. The ethereal layer was dried and distilled to give 5-hydroxy-2,2,5,6,6-pentamethylheptan-3-one (2.46 g, 53%), n_D^{25} 1.4378, b.p. 64-65°/0.9 mm (lit. b.p. 89-90°/5 mm, n_D^{25} 1.4383 [8]). PMR (CCl_4): 2.78 and 2.41 (br.) (AB quartet, J 16.9 Hz, 2H, CH_2), 1.26 (m, 3H, CH_3), 1.13 (s, 9H, t-Bu), 0.93 (s, 9H, t-Bu). IR (CCl_4 , 0.005 M): 3505 (OH), 1693 (C=O) cm^{-1} .

[μ -(3,3-Dimethylbut-1-en-2-olato)]tetramethyl[μ -(2,3,3-trimethylbutan-2-olato)]-dialuminium (VI)

t-Butyl methyl ketone (0.40 g, 4.0 mmol) was added dropwise at room temperature to trimethylaluminium (0.36 g, 5.0 mmol) in toluene (6 ml). The solution was warmed (30-45 min) to 100° (methane was evolved), then allowed to cool. Removal of solvent by freeze-drying in vacuum left a colourless waxy solid (0.70 g), shown by PMR spectroscopy to be mainly alkoxide-enolate VI with a trace of bis- μ -enolate VII. Sublimation under high vacuum gave colourless crystalline VI (0.44 g, 66%), m.p. 105-110°. (Found: Al, 16.2. $C_{17}H_{32}Al_2O_2$ calcd.: Al, 16.4%.) PMR (C_6H_6): δ (ppm) 4.60-4.40 (m, 2H, $CH_2=C$), 1.28 (s, 6H, $(CH_3)_2C$), 1.06 (s, 9H, t-Bu), 0.89 (s, 9H, t-Bu), -0.33 (s, 12H, CH_3Al). IR (C_6H_6): 1641 (C=C) cm^{-1} . Molecular weight by ebulliometry in benzene 349 (calcd. 328).

PMR spectroscopy indicated that V heated with IV at 80° in benzene for 3 h, also gave VI in near quantitative yields.

Tetramethyl[μ -(2,3,3-trimethylbutan-2-olato)][μ -(3,3,3-triphenylprop-1-en-2-olato)]dialuminium (VIII)

A solution of 1,1,1-triphenylacetone (1.72 g, 6.0 mmol) in benzene (25 ml) was added to hemialkoxide IV (6.15 mmol) in benzene (5 ml) at 5°. Methane (112 ml at STP, 84%) was collected on warming to 55° for 3 h. The solvent was removed and the residue partly dissolved in warm hexane. Filtration yielded a residue (0.87g) of enolate II (identified by PMR) and a solution from which VIII was fractionally crystallised as colourless plates (0.52g, 17%). (Found: Al, 10.5. $C_{32}H_{14}Al_2O_2$ calcd.: Al, 10.5%.) PMR (C_6D_6): δ (ppm) 7.60-7.07 (m, 15H, Ph), 5.31 and 4.84 (AB quartet, J 1.8 Hz, 2H, $CH_2=C$), 1.23 (s, 6H, Me_2C), 0.85 (s, 9H, t-Bu), -0.58 (s, 12H, MeAl). Molecular weight by ebulliometry in benzene 523 (calcd. 515).

The mother liquours from crystallisation of VIII yielded a further crop of $(Me_2AlOCMe_2t-Bu)_2$ (0.59g). PMR (C_6H_6): δ (ppm) 1.31 (s, 6H, Me_2C), 0.92 (s, 9H, t-Bu), -0.28 (s, 6H, MeAl).

Acknowledgements

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