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ALDOL CONDENSATION OF DIMETHYLALUMINIUM 4,4-DIMETHYLPENT-2-EN-2-OLATE:

SOME NEW DIMETHYLALUMINIUM KETOLATES

E.A. JEFFERY, A. MEISTERS and T. MOLE
Division of Applied Chemistry, C.S.I.R.O., P.O. Box 4331, Melbourne 3001 (Australia)
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Summary

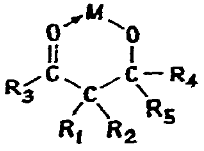
The (*Z*)- and (*E*)- isomers of dimethylaluminium 4,4-dimethylpent-2-en-2-olate, $Me_2AlOC(Me){=}CH\text{-t-}Bu$, have been condensed with acetaldehyde and benzaldehyde. The (*Z*)-enolate with acetaldehyde or benzaldehyde gives dimeric dimethylaluminium chelates, of *threo* configuration, which are crystalline and probably contain five-coordinate aluminium. The *threo*-chelates form 1/1 complexes with trimethylaluminium, in which the alkoxy oxygen, not the carbonyl oxygen, is the coordination site.

The more soluble products from (*E*)-enolate dimer were not isolated, but their immediate hydrolysis gave from acetaldehyde an *erythro*-β-hydroxyketone and from benzaldehyde a *threo*-β-hydroxyketone. The unhydrolyzed *erythro*-intermediate from (*E*)-enolate dimer and acetaldehyde rearranges to the *threo*-form slowly at ambient temperature. Trimeric (*E*)-enolate reacts with acetaldehyde like dimeric (*E*)-enolate, but more slowly.

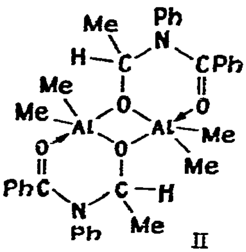
The (*Z*)-enolate condenses with diphenylketene to give, upon hydrolysis, 3-tert-butyl-1,1-diphenylpentane-2,4-dione. With phenyl isocyanate, however, carbon—carbon bond formation does not occur; upon hydrolysis (*Z*)-4,4-dimethylpent-2-en-2-yl *N*-phenylcarbamate results.

Introduction

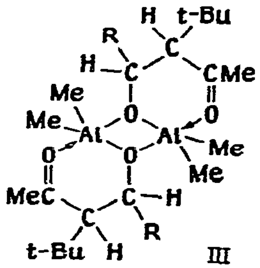
The sparse information available for metal enolates contrasts with the considerable amount known about their *in situ* organic reactions [1], particularly the aldol condensation [2] and related reactions, which provide the organic chemist with important methods of carbon—carbon bond formation. In the aldol condensation an enolate [$R_1R_2C{=}C(R_3)OM$; M is a metal centre] reacts with an aldehyde or ketone ($R_4R_5C{=}O$) to give, after hydrolysis, a β-hydroxyketone. An intermediate metal chelate I is thought [1] to prevent dehydration or second-



I



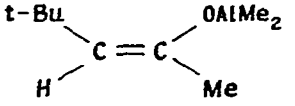
II



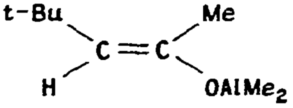
III

ary condensation. In fact, House et al. have successfully eliminated unwanted side-reactions by adding $MgCl_2$, $ZnCl_2$ or $AlCl_3$, so as to promote chelate formation [3].

Products structurally analogous to I have been prepared from dialkylaluminium benzanilides and aldehydes; an X-ray analysis of one such product shows dimeric structure II, with five-coordinate aluminium [4, 5].



(Z)-IV, dimer



(E)-IV {dimer, trimer}

We have recently reported [6] the isolation of the (*Z*)- and (*E*)-isomers of dimethylaluminium 4,4-dimethylpent-2-en-2-olate, IV. We now describe the condensation of these enolates with acetaldehyde or benzaldehyde. The (*Z*)-enolate gives *threo*-chelates of structure III, which are dimeric forms of I and appear to be structurally analogous to II. The isolation and characterisation of compounds of type III provides the first *direct* proof that condensation can proceed by way of chelate compounds such as I, and that such compounds may, under suitable circumstances, be produced almost quantitatively.

III forms a complex with trimethylaluminium like the 1/1 complex formed by the monomer of II [4, 5].

Experimental

1. General

Experimental methods and materials were generally as described in the previous paper [6]. Diphenylketene was prepared by dehydrochlorination of diphenylacetyl chloride [7] and distilled under high vacuum. Phenyl isocyanate was dried over molecular sieve then distilled under nitrogen. Aldehydes were dried over calcium hydride and distilled under nitrogen immediately before use.

2. Reactions of acetaldehyde

(a). With (Z)-enolate dimer. A solution of acetaldehyde (0.43 g, 9.8 mmole)

in toluene (1 ml) was added dropwise to a stirred solution of (*Z*)-enolate dimer (1.67 g, 9.8 mmole) in toluene (10 ml) at —20°. After complete addition, the solution was allowed to warm slowly to room temperature. The resulting white precipitate was filtered and washed with hexane. The combined mother-liquors (and washings) deposited more crystals at 0°; these were filtered, washed, and combined with the initial precipitate of Va, (*threo*-3-tert-butyl-4-oxopentan-2-olato-*O,O'*)dimethylaluminium (total yield 1.75 g; 83%), m.p. 140° (decomp. to red oil). (Found: C, 61.4; H, 10.6; Al, 12.8. $C_{11}H_{23}O_2Al$ calcd.: C, 61.6; H, 10.8; Al, 12.6%.) PMR (C_6D_6): δ 4.60 (m, 1H, C*H*CH$_3$), 1.87 (broad s, 1H, C*H*-t-Bu), 1.69 (s, 3H, CH$_3$C=O), 1.23 (d of d, *J* 1.5 Hz, 8.0 Hz, 3H, C*H*$_3$CH), 1.0 (s, 9H, t-Bu), —0.18, —0.20 and —0.23 (3 singlets, in all 6H, CH$_3$Al) ppm; see Fig. 1. Irradiation at 4.60 ppm collapsed the 1.23 ppm d of d to a broad singlet, at the same time sharpening the singlet at 1.87 ppm. IR (nujol or benzene): 1676 cm^{-1} (C=O). Molecular weight by ebulliometry in benzene 426 (calc. for dimer 428).

The *threo*-ketolate (0.23 g, 1.07 mmole) was hydrolyzed in ether with cold saturated aqueous ammonium chloride solution buffered to pH 8. The ether layer was separated, washed with saturated brine, dried and distilled (3 mm, bath temp. 40°) to give *threo*-3-tert-butyl-4-hydroxypentan-2-one as a colourless oil (0.13 g, 80% yield), n_D^{25} 1.5075. (Found: C, 68.5; H, 11.7. $C_9H_{18}O_2$ calcd.: C, 68.3; H, 11.4%.) PMR (CCl$_4$): δ 4.04 (m, 1H, C*H*CH$_3$), 3.05 (d, *J* 9.0 Hz, 1H, OH, exchanges with D$_2$O), 2.43 (d, *J* 3.0 Hz, 1H, C*H*-t-Bu), 2.23 (s, 3H, CH$_3$C=O), 1.17 (d, *J* 6.8 Hz, 3H, C*H*$_3$CH), 1.04 (s, 9H, t-Bu) ppm; there was no trace of the resonances of the *erythro*-isomer. IR (CCl$_4$, 0.005 *M*): 3633 (sharp) and 3520 (broad) (OH, intensity ratio 1/50, respectively), 1700 (C=O) cm^{-1}. Mass spectrum (*m/e*, *I*): 114, 60; 99, 24; 71, 9; 59, 17; 58, 67, 57, 69; 56, 11; 55, 10; 44, 30; 43, 100; 42, 14; 41, 44; 39, 24. No epimerisation of the *threo*-ketol occurred upon stirring a solution in carbon tetrachloride with aqueous sodium hydroxide (5*N*) or hydrochloric acid (5*N*); the NaOH caused a slow retro-aldol reaction.

(b). With (E)-enolate dimer and trimer. (*i*). A solution of acetaldehyde (0.047 g, 1.06 mmole) in benzene (0.4 ml) was added to a solution of (*E*)-enolate dimer (0.18 g, 1.06 mmole) in benzene (2 ml) at ca. 5°. The PMR of the resulting solution showed resonances at 4.33 (q of d, *J* of q 6.5 Hz, *J* of d 2.7 Hz, 1H, C*H*CH$_3$), 2.85 (broad s, 1H, C*H*-t-Bu), 1.95 (s, 3H, CH$_3$C=O), 1.40 (d, *J* 6.5 Hz, 3H, C*H*$_3$CH)), 0.87 (s, 9H, t-Bu), and —0.40, —0.46, —0.52 (3 singlets, in all 6H, CH$_3$Al) ppm. The PMR slowly changed with time; new resonances appeared, particularly a doublet at 1.56 ppm (*J* 6.5 Hz). Finally large cubic crystals (ca. 0.11 g) separated overnight, and were filtered, washed with hexane and dried. PMR, microanalysis and m.p. showed these air-stable crystals to be identical with the (*threo*-3-tert-butyl-4-oxopentan-2-olato-*O,O'*)dimethylaluminium, Va, described above.

PMR studies indicated that (*E*)-enolate trimer gave similar products with acetaldehyde, although the reaction was slightly slower and gave unidentified side products (ca. 20%).

(ii). A solution of acetaldehyde (0.050 g, 1.13 mmole), in pentane (1 ml) was added dropwise to (*E*)-enolate dimer (0.19 g, 1.13 mmole) in pentane (7 ml) at —20°. The resulting solution was allowed to warm to room temperature, then after 5 min was hydrolysed in the usual way with saturated ammo-

nium chloride solution. The ethereal layer gave upon distillation (0.1 mm, bath temp. 50°) 3-tert-butyl-4-hydroxypentan-2-one as a colourless oil (0.11 g; 93% *erythro*- and 7% *threo*-ketol). (Found: C, 68.3; H, 11.4. $C_9H_{11}O_2$ calcd.: C, 68.3; H, 11.5%.) PMR (CCl_4, of *erythro*-ketol): δ 4.12 (m, 1H, C*H*CH_3), 2.55 (d, *J* 7.5 Hz, 1H, C*H*-t-Bu), 2.32 (broad s, 1*H*, OH, exchanges with D_2O), 2.15 (s, 3H, $CH_3C{=}O$), 1.14 (d, *J* 6.5 Hz, 3H, C*H*$_3$CH), 1.05 (s, 9H, *t*-Bu) ppm; peaks corresponding to the 7% of *threo*-ketol were also observed. Addition of dilute sodium hydroxide sharpened the 4.12 ppm resonance to a doublet of quartets (*J* of d 7.5 Hz; *J* of q 6.0 Hz), but did not epimerise the ketol mixture. Sodium hydroxide (5 *N*) or hydrochloric acid (5 *N*) likewise did not epimerise a solution of the ketols in carbon tetrachloride, although the alkali caused a slow retro-aldol reaction. Separation of the *erythro*- and *threo*-ketols by preparative TLC (silica gel, CH_2Cl_2 eluent) gave pure *erythro*-isomer; IR (CCl_4, 0.005*M*): 3633 (sharp; free OH) 3539 (very weak; associated OH ?), 1711 (C=O) cm^{-1}. Mass spectrum (*m/e*, *I*): 114, 36; 99, 15; 71, 6; 59, 11; 58, 62; 57, 75; 56, 9; 55, 9; 44, 25; 43, 100; 42, 11; 41, 38; 39, 17; 29, 49.

3. *Reactions of benzaldehyde*

(a). With (Z)-enolate dimer. A solution of benzaldehyde (0.36 g, 3.4 mmole) in toluene (1 ml) was added dropwise to a stirred solution of (*Z*)-enolate (0.58 g, 3.4 mmole) in toluene (5 ml) at ca. —20°. A white precipitate of (*threo*-2-tert-butyl-3-oxo-1-phenylbutan-1-olato-*O*,*O'*)dimethylaluminium, Vb, began to separate at +10°. Hexane (10 ml) was added to complete the precipitation, then the product was isolated as in the acetaldehyde reaction 2 (a) above. Yield 0.77 g (82%), m.p. 133° (decomp.). (Found: Al, 9.7. $C_{16}H_{25}O_2Al$ calcd.: 9.8%.) PMR (C_6D_6): δ 7.51—7.06 (m, 5H, Ph), 5.62 and 5.56 (2 s, 2/3 H and 1/3 H respect., C*H*Ph), 2.45 and 2.40 (2 s, 1/3 H and 2/3 H respect., CH-t-Bu), 1.45 and 1.44 (2 s, 2H and 1H respect., $CH_3C{=}O$), 1.09 and 1.03 (2 s, 6H and 3H respect., t-Bu), 0.16 (s, 1H, CH_3Al), —0.33 (s, 4H, CH_3Al), and —0.78 (s, 1H, CH_3Al) ppm; see Fig. 1. IR (nujol): 1667 (C=O) cm^{-1}. Molecular weight by cryometry in benzene 530 (calcd. for dimer 550).

Vb (0.12 g, 0.44 mmole) in ether was hydrolyzed by saturated aqueous ammonium chloride in the usual way; distillation (0.1 mm, bath temp. 60°) gave *threo*-3-tert-butyl-4-hydroxy-4-phenylbutan-2-one as a colourless oil (0.085 g), n_D^{25} 1.5065. (Found: C, 76.4; H, 9.1. $C_{14}H_{20}O_2$ calcd.: C, 76.3; H, 9.2%.) PMR (CCl_4): δ 7.23 (broad s, 5H, Ph), 4.96 (d of d, *J* 8.0 Hz, *J* 3.2 Hz, 1H, C*H*Ph), 3.74 (broad d, *J* 8.0 Hz, 1H, OH, exchanges with D_2O), 2.79 (d, *J* 3.2 Hz, 1H, C*H*-t-Bu), 1.78 (s, 3H, CH_3), 1.06 (s, 9H, t-Bu). IR (CCl_4, 0.005*M*): 3617 (sharp, free OH) and 3487 (broad, associated OH) in intensity ratio 1/10 respect.; 1692 (C=O) cm^{-1}. Mass spectrum (*m/e*, *I*): 160, 23; 146, 9; 145, 59; 117, 11; 114, 27; 107, 9; 106, 100; 105, 98; 99, 11; 91, 9; 78, 16; 77, 80; 58, 40; 57, 52; 51, 36; 50, 20; 43, 86; 41, 25; 39, 18.

(b). With (E)-enolate dimer. A solution of benzaldehyde (0.18 g, 1.7 mmole) in benzene (4 ml) was added dropwise to a stirred solution of (*E*)-enolate dimer (0.29 g, 1.7 mmole) in benzene (5 ml) at ca. 5°. The PMR spectrum of the resulting solution (at ambient temperature) was identical with that of the product from (*Z*)-enolate and benzaldehyde. Hydrolysis led to 3-tert-butyl-4-hydroxy-4-phenylbutan-2-one (0.28 g), as a colourless oil identified by its PMR spectrum.

4. Reaction of Va and Vb with trimethylaluminium

(a). To Va (0.18 g, 0.84 mmole) in benzene (4 ml) was added trimethylaluminium (0.08 g, 1.1 mmole). The solution was stirred for ca. 10 min, then the solvent and excess trimethylaluminium were removed under vacuum to give the chelate—trimethylaluminium complex, VIa, m.p. 70° (decomp.), in quantitative yield (0.24 g). (Found: Al, 18.9. $C_{14}H_{32}O_2Al_2$ calcd.: Al, 18.9%.) PMR (C_6D_6): δ 4.52 (q of d, *J* of q 6.8 Hz, *J* of d 1.2 Hz, 1H, *C*HCH$_3$), 1.96 (broad s, 1H, *CH*t-Bu), 1.56 (d, *J* 0.7 Hz, 3H, $CH_3C{=}O$), 1.06 (d, *J* 6.8 Hz, 3H, *CH*$_3$CH), 0.83 (s, 9H, t-Bu) and —0.25 (broad s, 15H, CH_3Al) ppm. At —20° in cyclopentane the broad methylaluminium resonance split into three peaks, 2.12 (s, 3H), 2.16 (s, 3H), and 2.38 (s, 9H) ppm. to high field of the cyclopentane resonance. IR (cyclopentane): 1640 (C=O) cm^{-1} Molecular weight by cryometry in benzene 310 (expected for monomer 286).

(b). Vb (0.24 g, 0.87 mmole) suspended in benzene (2 ml) was treated with trimethylaluminium (0.09 g, 1.25 mmole) in benzene (0.5 ml) as in the previous example. Addition of a few ml of hexane to the oily product gave a crystalline adduct, m.p. 84°, which was filtered, washed with hexane and dried. (Found: Al, 15.5. $C_{19}H_{34}O_2Al_2$ calcd.: Al, 15.5%.) PMR (C_6D_6): δ 7.31—7.00 (m, 5H, Ph), 5.58 (broad s, 1H, *CH*Ph), 2.66 (d, *J* 0.4 Hz, 1H, *CH*-t-Bu), 1.41 (s, 3H, $CH_3C{=}O$), 0.89 (s, 9H, t-Bu), and —0.27 (s, 15H, CH_3Al) ppm. At —10° in toluene* the broad methylaluminium peak split into 3 peaks, 2.22 (s, 3H), 2.36 (s, 3H) and 2.48 (s, 9H) ppm to high field of the methyl resonance of toluene. IR (toluene): 1641 (C=O) cm^{-1}. Molecular weight by cryometry in benzene 385 (expected for monomer 348).

5. Reaction of (Z)-enolate dimer with diphenylketene

Diphenylketene (0.374 g, 1.97 mmole) in toluene (1 ml) was added to (*Z*)-enolate dimer (0.318 g, 1.87 mmole) in toluene (3 ml) at ca. —76°. The resulting mixture was sealed in an ampoule, kept at 0° for 2 days, and then hydrolysed with saturated aqueous ammonium chloride/ether followed by 0.5 *M* hydrochloric acid/ether. The solid product obtained from the ether layer was crystallised from petrol/diethyl ether to give 3-tert-butyl-1,1-diphenylpentane-2, 4-dione (0.32 g, 57% yield), m.p. 156°. (Found: C, 82.0; H, 7.9. $C_{21}H_{24}O_2$ calcd.: C, 81.8; H, 7.8%.) PMR (CCl_4): δ 7.23 (broad s, 10H), 5.10 (s, 1H, *CH*Ph$_2$), 3.61 (s, 1H, *CH*-t-Bu), 1.80 (s, 3H, $CH_3C{=}O$), 1.02 (s, 9H, t-Bu) ppm. IR (CCl_4): 1730 and 1690 (C=O) cm^{-1}. Mass spectrum (*m/e*, *I*): 308, 15, M^+; 168, 20; 167, 100; 166, 13; 165, 28; 152, 13; 141, 30; 85, 72; 57, 17; 43, 15.

6. Reaction of (Z)-enolate dimer with phenyl isocyanate

Phenyl isocyanate (0.209 g, 1.76 mmole) in cyclopentane (3 ml) was mixed with (*Z*)-enolate dimer (0.300 g, 1.76 mmole) in cyclopentane (3 ml) at ca. —76°. The solution was kept at 0° for 2 days, and was then hydrolysed with aqueous saturated ammonium chloride/ether. The ethereal layer yielded a yellow oil (0.26 g), which was chromatographed from a silica-gel column. Dichloromethane/40—60° petrol eluted a crystalline product (0.11 g), which was distilled at ca. 60° under high vacuum to give white, crystalline (*Z*)-4,4-dimethylpent-2-

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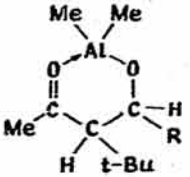
* The complex is sparingly soluble in cyclopentane.

en-2-yl *N*-phenylcarbamate, m.p. 63.5°. (Found: C, 72.4; H, 8.4; N, 5.9. $C_{14}H_{19}NO_2$ calcd.: C, 72.1; H, 8.2; N, 6.0%.) PMR (CCl_4): δ 7.60—6.80 (m, 5H, Ph), 6.66 (broad s, 1H, NH, exchanges with D_2O), 4.82 (q, *J* 1.0 Hz, 1H, CH=C), 1.90 (d, *J* 1.0 Hz, 3H, CH_3C=O), and 1.08 (s, 9H, t-Bu) ppm. IR (CCl_4): 3445 (NH), 1750 (C=O), and 1597 (C=C) cm^{-1}. Mass spectrum (*m/e*, *I*): 233, 3, M^+; 120, 5; 119, 42; 114, 50; 100, 9; 99, 100; 91, 14; 81, 7; 77, 7; 64, 8; 58, 15; 57, 20; 43, 52; 41, 11.

Discussion

Reactions of the enolates with aldehydes

Addition of one mole of acetaldehyde or benzaldehyde to a solution of (*Z*)-enolate gives a crystalline product. Elemental analysis and integration of the PMR spectrum indicates that the product arises from a 1/1 reaction, and the PMR spectrum shows no aldehydic proton. The somewhat low infra-red carbonyl stretching frequency (1676 cm^{-1} for the acetaldehyde product, and 1665 cm^{-1} for the benzaldehyde product) as compared with aliphatic ketones (1705—1725 cm^{-1}) suggests that the carbonyl group is bonded to the aluminium centre. Hydrolysis of the product gives β-hydroxyketone, showing that the aldehyde and enolate have undergone aldol condensation.



Va R=Me

Vb R=Ph

Upon the above basis we propose that the products are (3-tert-butyl-4-oxopentan-2-olato-*O,O'*)dimethylaluminium (Va), from acetaldehyde, and (2-tert-butyl-3-oxo-1-phenylbutan-1-olato-*O,O'*)dimethylaluminium (Vb), from benzaldehyde. Since Va and Vb are dimeric in benzene, they are probably dimerized via coordination through the Al—O covalent linkages, and so contain five-coordinate aluminium atoms*. In this respect they resemble the known structure II, discussed above. Unlike II, however, Va and Vb have little tendency to dissociate to monomer at low concentration.

The PMR spectra of Va and Vb are relatively complex; see Fig. 1. Being dimeric, each compound contains 2 *threo*-ligands (we show in the Appendix that entirely *threo*-ketol is present — no *erythro*-ketol); and each ligand exists in enantiomeric (*R* and *S*) forms. Thus there are two stereoisomeric dimers: one with mirror-image ligands (*RS*), and the other with identical ligands (*RR* or *SS*). Each dimer has two stereochemically different methyl—Al environments: Eqn. 1 below shows the two environments in the *RR/SS* dimer and eqn. 2 shows them in the *RS* dimer. Thus the *RS* dimer ought to display two methylaluminium peaks of equal intensity, and the *RR/SS* dimer ought to show two different methylaluminium peaks, again of equal intensity.

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* Each bridge-oxygen atom is probably coplanar with its neighbours (two Al and one C atom). Va dimer may be fully named *ad,eg*-bis[μ-*threo*-(3-tert-butyl-4-oxopentan-2-olato)-μ-*O,O'*]-*bcfh*-tetramethyldialuminium.

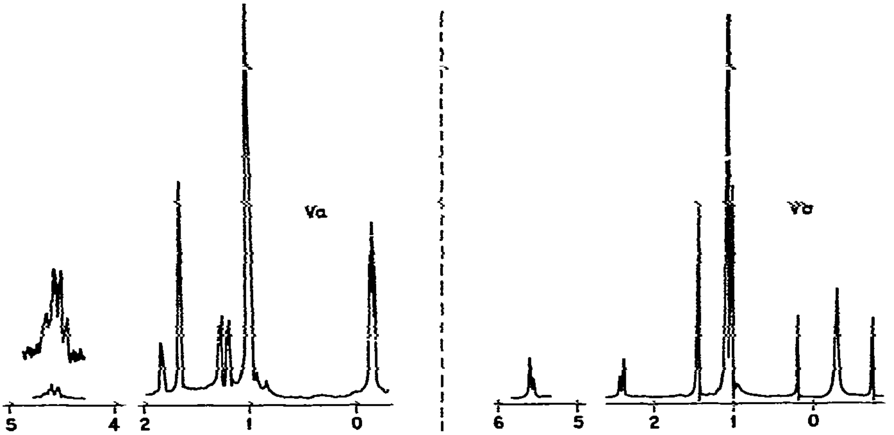

Fig. 1. 100 MHz PMR spectra of Va and Vb in C_6D_6 at 35° (the phenyl proton resonances of Vb are not shown).

The existence of the two stereoisomeric dimers is best seen for Vb, where there are large differences in chemical shift — presumably as a result of the phenyl group's ring current. Vb shows three methylaluminium peaks at room temperature: two sharp, well spaced singlets of equal intensity, which can be assigned to one of the two forms (*RS* or *RR*/*SS*; ca. 33% abundant), between which lies an intense, broad third peak. At low temperature (—40° in toluene) the third peak splits into two well spaced peaks of equal intensity, and so it represents the second, more abundant (ca. 67%) form of the dimer. The coalescence phenomenon of the central methyl-aluminium resonances may be explained by rapid flipping (1) of the coordinated carbonyl groups between the aluminium centres of the *RR* (or *SS*) dimer whilst the Al—O—Al bridges remain intact*.

In eqn. 1 we have depicted the Al_2O_2 bridge and chelate rings in the plane of the paper and have shown those groups above and below the plane with solid and hollow wedges, respectively. It can be seen that interchange (1), of the coordinated carbonyl groups between the two aluminium atoms leads to interchange of the two methylaluminium environments (labelled a and b).

By contrast the corresponding flipping (2) of carbonyl groups in the *RS* dimer leads to no interchange of methylaluminium environments. We therefore predict that the minor form, which does not undergo coalescence, is the *RS* dimer, and that the major coalescing form is the *RR*/*SS* dimer.

Vb also shows a duality in the resonances of the ligand protons. The resonances at 5.56, 2.45, 1.44 and 1.03 ppm are assigned to the *RS* dimer, whilst those at 5.62, 2.40, 1.45 and 1.09 ppm are assigned to the *RR*/*SS* dimer. The relative intensities of these two sets of resonances, like those of the methylaluminium resonances, show that there is twice as much *RR*/*SS* dimer as *RS* dimer. The same kind of dimer stereoisomerism has been found for II, and the same preference has been found for the *RR*/*SS* forms [4].

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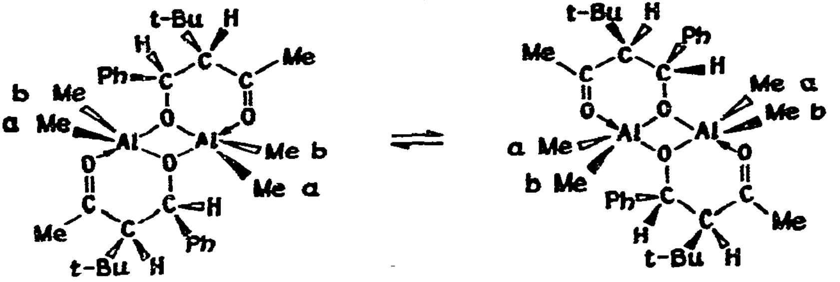
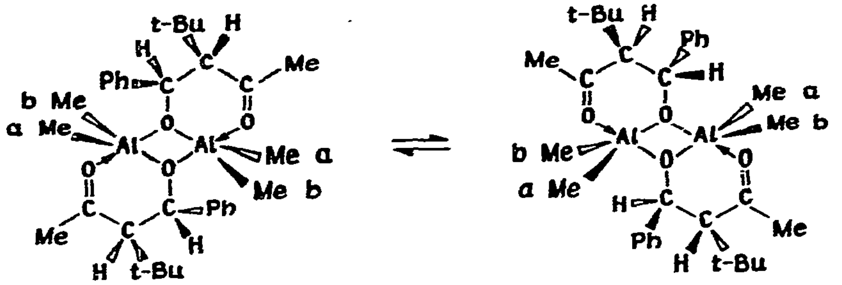
* The transition-state for rearrangements 1 and 2 may involve a dimer in which one aluminium atom is six-coordinate whilst the other is four-coordinate.



(1)



(2)

The difference in chemical shift between the *RR/SS* and *RS* forms of Va is insufficient for such definitive observations as were made for Vb. However, 3 singlets can be observed in the methylaluminium region of the PMR spectrum, indicating the existence of two dimeric forms.

The dimeric character of Va and Vb contrasts with the monomeric nature of dimethylaluminium acetylacetonate [8] and of dimethylaluminium 4-methoxy carbonylbutan-2-olate (chelated via the methoxy group) [9]. The oxygen atoms of the acetylacetonate ligand may be too weakly basic to coordinate; and molecular models suggest that puckering of the seven-membered chelate-ring in the butanolate would lead to serious steric interactions between the *C*-methyl group of one monomer and the Al-methyl groups of the other monomer upon dimerization.

Hydrolysis of Va and Vb under mild conditions gave the corresponding ketols. PMR spectra show these ketols to be stereochemically pure, even though they might exist in *erythro*- and *threo*-forms, and they are identified as the *threo*-ketols in the Appendix. If this identification is correct, then the isomeric ketol obtained by reaction of acetaldehyde with dimeric (*E*)-enolate followed by immediate hydrolysis must be the *erythro*-ketol.

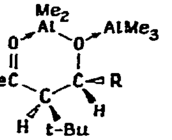
When the organoaluminium product from (*E*)-enolate dimer and acetaldehyde is not immediately hydrolysed, but instead is kept at room temperature, the PMR spectrum slowly changes. Initially the PMR spectrum shows a quartet of doublets centred at 4.33 ppm with doublet HCCH coupling of 2.7 Hz (CH_3—CH coupling 6.5 Hz). This HCCH coupling constant is smaller than one would expect from a conformationally-averaged non-chelate ligand and suggests that the carbonyl group of the *erythro*-ketolate is attached to aluminium so as to afford a chelate structure. With time the PMR spectrum develops new resonances which are not ascribable to *threo*-ketolate dimer; the changes are explicable if the *erythro*-ketolate gives first a mixed *erythro-/threo*-ketolate dimer and eventually *threo*-ketolate dimer*. In the end the solution deposits large air-stable cubic crystals identical to the *threo*-ketolate formed more directly from (*Z*)-enolate and acetaldehyde.

(*E*)-enolate trimer reacts with acetaldehyde more slowly than the dimer, and gives the *erythro*-ketolate as the main product, together with unidentified side-products.

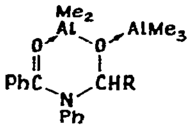
By contrast with the formation of both *threo*- and *erythro*-ketolates from acetaldehyde, reaction of benzaldehyde resulted in rapid formation of *threo*-ketolate, no matter whether (*Z*)-enolate or (*E*)-enolate was used. If *erythro*-ketolate *is* formed from (*E*)-enolate and benzaldehyde, it must rapidly rearrange to the *threo*-isomer.

Complexes of Va and Vb with trimethylaluminium

Va and Vb form 1/1 complexes with trimethylaluminium, which are monomeric in benzene and which show a low (ca. 1640 cm^{-1}) carbonyl stretching frequency in the infra-red spectrum. Structure VI is suggested for these complexes; in this the trimethylaluminium moiety is complexed to the alkoxyl oxygen atom, so preventing dimerization. Since VIa and VIb do not react with excess trimethylaluminium during a day at room temperature, the acetyl group of the ligand is probably deactivated by chelation.



VI a, R=Me
b, R=Ph



VII a, R=Me
b, R=Ph

The proposed structure is analogous to the known structure, VIIa, of the complex derived from II and trimethylaluminium [4, 5]. The PMR spectrum [5] of VIIa shows three methylaluminium singlets in the ratio 1/1/3, corresponding to the two stereochemically different methyls in the Me_2Al group and the three identical methyls in the Me_3Al group. The three singlets do not coalesce over the range —80 to +50°.

By contrast VIa and VIb each show three methylaluminium singlets, in 1/1/3 ratio, only at low temperature (—10° to —20°). At room temperature the singlets coalesce to a broad peak. However, these resonances do not coalesce with added excess trimethylaluminium, indicating that the coalescence of the three singlets is an intramolecular process. We suggest that methyl group exchange involves formation (eqn. 3) of an Al—Me—Al bridge simultaneously with breakage of the oxygen—aluminium coordinate bond. The absence of

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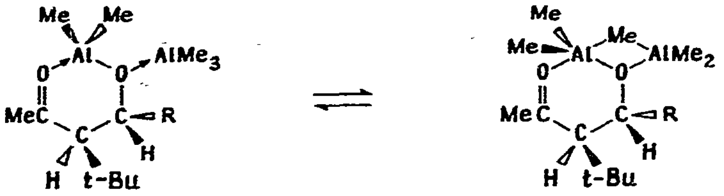
* Slow *erythro* to *threo* rearrangement has been observed for other ketolates [10].

similar methylaluminium exchange in VIIa is presumably due to stronger coordination of its carbonyl oxygen atom*.

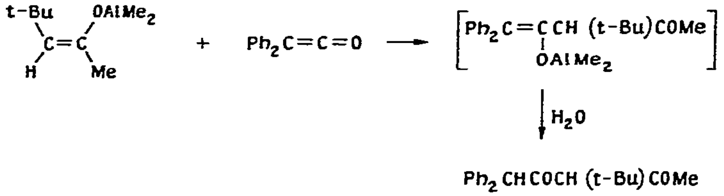


(3)

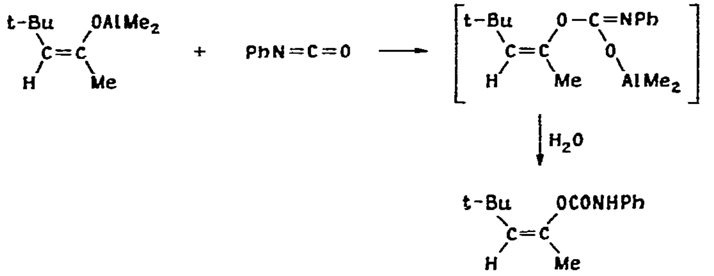
It is worth noting that VIIb (the analogue of VIb) cannot be prepared because of instability [5]. The t-BuCH—CHR bond of VI must be considerably stronger than the PhN—CHR bond of VII. Similarly the PhN—CHMe bond in II is weak compared to the t-BuCH—CHR bond in V; thus hydrolysis of II gives isocyanate and ketone, whereas hydrolysis of V gives a ketol.

Reactions of the (Z)-enolate with heterocumulenes

Carbon dioxide (780 psi) did not react with (*Z*)-enolate dimer in 24 h at room temperature. The more reactive heterocumulenes, diphenylketene and phenyl isocyanate, do react. Diphenylketene gave, after hydrolysis, 3-tert-butyl-



(4)



(5)

1,1-diphenylpentane-2,4-dione (reaction 4). Phenyl isocyanate gave (*Z*)-4,4-dimethylpent-2-en-2-yl *N*-phenylcarbamate. The former reaction (4) resembles the aldol condensation. In the latter reaction (5), the enolate group adds via its oxygen atom to the isocyanate; dialkylaluminium alkoxides are already known [11] to add to isocyanates in this manner.

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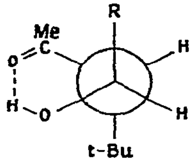
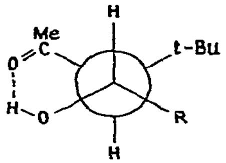
* Coordination in VIIa is favoured by delocalisation of positive charge onto the nitrogen atom.

The hydrogen-bonded cyclic structures of the ketols derived from (*Z*)-enolate and acetaldehyde or benzaldehyde are demonstrated by H—O—C—H coupling in the PMR spectra (*J* 9 or 8 Hz, respectively) and by the broad hydroxyl stretching bands at relatively low wave-number (3520 or 3487 cm^{-1}, respectively) in the IR spectra. By contrast, the major ketol from (*E*)-enolate and acetaldehyde has no H—O—C—H coupling and has a strong sharp IR stretching frequency at 3633 cm^{-1}, typical of a free hydroxyl group.

threo-VIII (a)

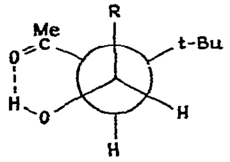


(b)

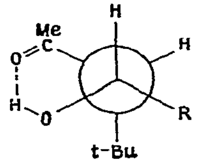


erythro-VIII (a)

(R = Ph or Me)



(b)



Consider the four possible staggered conformers VIII of the hydrogen-bonded ketol. Molecular models show that *threo* conformer VIIIa has the least steric interactions, whilst the other three have appreciable interactions. *Threo*-conformer VIIIb can further be excluded because the small H—C—C—H coupling constant for the hydrogen-bonded ketol (ca. 3 Hz) is consistent with a dihedral angle of 50—70° or 100—120° (depending on the Karplus-type formula)*.

Thus both steric considerations and the observed coupling constants suggest that the hydrogen-bonded ketols are *threo*-isomers. Consideration of the corresponding dimethylaluminium ketolates adds two further arguments for *threo*-assignment VIIIa of the hydrogen-bonded ketol isomer. Firstly, the H—C—C—H coupling in the ketolates is too small to be measured ($<$ 2 Hz) since the relevant resonances are narrow. In the trimethylaluminium adducts of the ketolates the coupling constant can be measured: 1.2 Hz in VIa and 0.4 Hz in VIb. Such small coupling constants are consistent with Va and Vb, having a *threo*-conformation like VIIIa but with the hydrogen atom of the ketol replaced by an AlMe$_2$ group.

Secondly, the direction of attack of an aldehyde molecule upon the (*Z*)-enolate will be such as to minimise interaction between the R and t-Bu groups.

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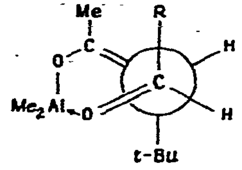
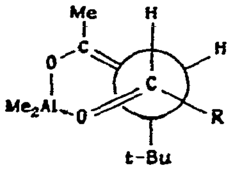
* If we go so far as to consider eclipsed (rather than staggered) conformers then the *erythro*-conformers have zero H—C—C—H dihedral angle, inconsistent with the observed coupling. Eclipsed *threo*-conformers are consistent with the observed coupling.

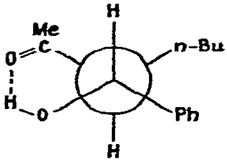
A reasonable transition-state for formation of ketolate from (*Z*)-enolate is IXa*, and this clearly leads to *threo*-ketolate and thence VIIIa. The analogous transition state IXb leading to *erythro*-ketol must be subject to greater steric interaction.





transition states IXa IXb

The steric prefence is not so clear for the condensation of (*E*)-enolate with acetaldehyde; models suggests that either *erythro-* or *threo*-ketolate could result.



X

By contrast with our postulated axial placement in VIIIa, House et al. [3] have postulated equatorial phenyl and n-butyl groups in the *threo*-isomer of the similarly hydrogen-bonded ketol X. Their assignment is consistent with their reported H—C—C—H coupling constant (8.7 Hz, requiring a dihedral angle of ca. 140°). The conformational difference possibly arises because the Ph and n-Bu groups of X can be closer than the R and t-Bu groups of VIII before steric interactions become large.

House et al. [3] make two generalisations for covalent metal enolates: that kinetically controlled reaction of aldehydes with acyclic (*Z*)-enolates favours the *erythro*-isomer [(*E*)-enolates favour the *threo*-isomer], and that the H—C—C—H coupling constant for the *threo*-isomer is generally larger than that for the *erythro*-isomer. Our postulates and findings contradict both these generalisations.

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* The enolate is shown arbitrarily as monomer; however dimer, rather than monomer, may be involved.