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ALKYNYLALUMINIUM COMPOUNDS

V *. COMPLEXES AND REACTION MECHANISM OF DIMETHYLALKYNYLALUMINIUM WITH KETONES

K.B. STAROWIEYSKI, A. BĘCALSKA and A. OKNIŃSKI
Chemistry Department, Technical University (Politechnika), 00-664 Warsaw (Poland)

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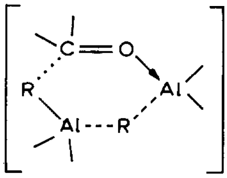
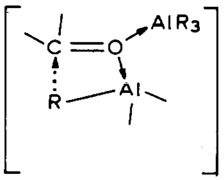
Summary

Dimethyl(alkynyl)aluminium compounds and diethyl ether or acetone have been found to form 2/1 complexes, and structures are suggested for these. The mechanism of formation of the 2/1 complexes was studied. On the basis of the nature of the proposed structure of the 2/1 complex and that of the resulting mixed dimer $Me_2Al(CCMe)(RO)AlMe_2$ a modified six-centre transition state and rearrangement pathway are proposed.

Introduction

In the first step of the reactions of ketones with organoaluminium compounds (OAC) strong donor–acceptor complexes are formed [2]. The nature of the transition state in the addition reactions of OAC to ketones in hydrocarbon solvents depends on the ratio of the substrates; for a 1/1 OAC/ketone molar ratio a σ complex is formed in the first reaction step [3–5]. For an AlR_3/R'_2CO molar ratio of 2/1 the reaction pathway also depends on the nature of the OAC and the structure of the transition state is less clear. For the reaction of $(Me_3Al)_2$ with R_2CO in hydrocarbon solvents, which initially involves formation of the σ complex $R_2CO \cdot AlMe_3$, the transition states **A**, **B** and **C** were suggested for the reaction of that complex with another $AlMe_3$ molecule [4,6–12].


(A)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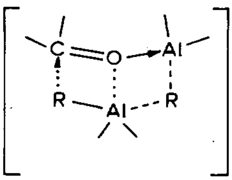
(C)

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* for part IV see ref. 1.

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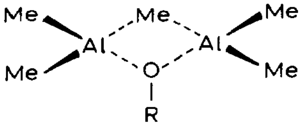
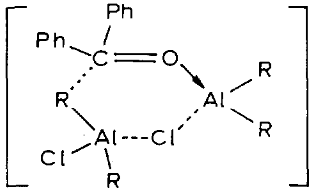
Structure **C** was considered to be the most probable [4], and can be regarded as a hybrid of structures A and B.

The presence of a transition state containing two molecules of R_3Al was confirmed by the formation of μ-alkoxy-μ-methyltetramethyldialuminium (**D**) in the reaction of two moles of trimethylaluminium with acetone [11].



(D)

It was proposed that mixing $(Me_2AlCl)_2$ with Ph_2CO in a hydrocarbon solvent gives a 2/1 complex produced by cleavage of only one Al–Cl bond, the transition state being involved [10,12–14].



(E)

Formation of a 2/1 complex of the type E from $(Me_2AlCl)_2$ and anisole was also thought to occur even when a stoichiometric mixture of the substrates was used [15].

In the present paper the mechanism of the reaction of alkylalkynylaluminium compounds with ketones in a 2/1 molar ratio was investigated. Due to the strong bridging ability of the alkynyl groups in alkynylaluminium dimers [16], the formation of a six-centre transition state could be expected, analogous to that in the reaction of $(R_2AlCl)_2$ with ketones in 2/1 molar ratio (transition state E). It was of interest to find out whether the proposed 2/1 species could be detected and to see how stable they were. The aim of the work described below was to determine the reaction pathway and the structure of the transition state for the reaction of alkylalkynylaluminium compounds with ketones, and to find evidence for the six centre transition state in the reaction of OAC with ketones in the 2/1 molar ratio.

Results and discussion

Interaction of di-μ-propynyltetramethyldialuminium (I) with diethyl ether

Complexes of I with diethyl ether were investigated by ^1H NMR and IR spectroscopy and the relevant data are shown in Table 1. The ^1H NMR spectra at −60 and 20°C of the $Me_2(MeC{\equiv}C)Al \cdot OEt_2$ complex show a sharp singlet from the propynyl group attached to the Al atom upfield with respect to the uncomplexed OAC. The chemical shift of this propynyl group is very similar to that of the non-bridging propynyl group in the $Me_2(MeC{\equiv}C)Al \cdot$ diox complex (diox = dioxane). The $\nu(C{\equiv}C)$ frequency for $Me_2(MeC{\equiv}C)Al \cdot OEt_2$ is similar to that in $Me_2(MeC{\equiv}C)Al \cdot$ diox [17].

In the ^1H NMR spectrum at 20°C of a 2/1 $Me_2(MeC{\equiv}C)Al/Et_2O$ mixture there

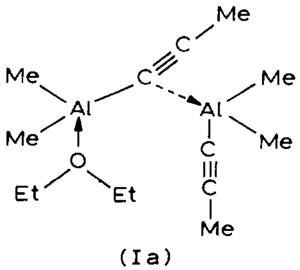
TABLE 1

^{1}H NMR DATA FOR THE MeC≡C PROTONS AND THE POSITIONS OF THE ν(C≡C) BONDS OF DIMETHYLPROPYNYLALUMINIUM-DIETHYL ETHERATES. SOLUTIONS IN CH_2Cl_2.

Run	Compound	Chemical shift (τ) for the propynyl group relative to TMS (ppm)		Temperature (°C)	IR ν(C≡C) (cm^{-1})
1	$(Me_2AlC{\equiv}CMe)_2$	8.02		20	2110
2	$(Me_2AlC{\equiv}CMe)_2 + 2Et_2O$	8.40		20	2143
3	$(Me_2AlC{\equiv}CMe)_2 + 2Et_2O$	8.45		−60	[a]
4	$(Me_2AlC{\equiv}CMe)_2 + Et_2O$	8.25(11)	8.37(1)	20	2143 2107
5	$(Me_2AlC{\equiv}CMe)_2 + Et_2O$	8.27(10)	8.37(1)	−30	[a]
6	$(Me_2AlC{\equiv}CMe)_2 + Et_2O$	8.27(3) (broad)	8.37(1)	−60	[a]
7	$(Me_2AlC{\equiv}CMe)_2 + Et_2O$	8.18(7) (broad)	8.37(9)	−80	[a]

[a] Not investigated.

is a sharp singlet from the propynyl group attached to Al atoms; its chemical shift lies between those of the 1/1 complex and uncomplexed OAC. The ^{1}H NMR spectrum at −80°C for the 2/1 $Me_2AlC{\equiv}CMe/Et_2O$ mixture shows two broad peaks for the propynyl groups attached to Al atoms (8.18 and 8.37 ppm), neither of them have a chemical shift corresponding to the bridging propynyl group of I or the non-bridging propynyl group in the 1/1 $Me_2(MeC{\equiv}C)Al \cdot OEt_2$ complex. At −60°C there is a new peak at 8.27 ppm and the peak at 8.18 ppm has disappeared, while the intensity of that at 8.37 ppm has decreased. No serious changes in the spectrum except for the decrease of the peak intensity at 8.37 ppm were observed at −40, −20, and 20°C. The peak at τ 8.18 ppm (at −80°C) was assigned to the bridging propynyl group and that at τ 8.37 ppm to the non-bridging propynyl group in the 2/1 complex of I with Et_2O. The coalescence of these peaks at temperatures between −80 and −60°C gives the peak with the chemical shift at 8.27 ppm. The very weak peak at τ 8.37 ppm must be assigned to an impurity. The IR spectrum for the 2/1 $Me_2AlC{\equiv}CMe$ to Et_2O ratio showed two bands for ν(C≡C). One of these was identical with the ν(C≡C) band of the 1/1 $Me_2(MeC{\equiv}C)Al \cdot Et_2O$ complex. The position of the second was very similar to that for the bridging propynyl group in the dimer I. The above results are in agreement with the formation of the 2/1 complex with the cleavage of only one bridging bond [16]. The formation of this complex is similar to that of the 2/1 Me_2AlCl/Ph_2CO [10].



(Ia)

Interaction of di-μ-propynyltetramethyldialuminium with ketones

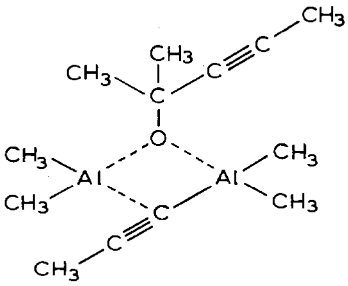
Di-μ-propynyltetramethyldialuminium (I) and acetone were used as model compounds to investigate the nature of the transition state in the reaction of alkylalkynylaluminium compounds with ketones. It was found [1] that the reaction rate of I with acetone and acetophenone at a 2/1 molar ratio was higher than that at a 1/1 ratio.

The ^{1}H NMR spectrum of the 1/1 mixture of I with acetone at −70°C shows a singlet at τ 8.40 ppm for the propynyl group attached to the Al atom, this shift is similar to that for the non-bridging propynyl group in $Me_2(MeC{\equiv}C)Al \cdot$ diox. (τ 8.30 ppm) and $Me_2(MeC{\equiv}C)Al \cdot OEt_2$ (τ 8.40 ppm). The chemical shift of the acetone methyl groups (τ 7.5 ppm) is also consistent with the formation of a complex of I with acetone.

The ^{1}H NMR spectrum at −70°C for the 2/1 $Me_2(MeC{\equiv}C)Al$ to Me_2CO differs from that of the 1/1 complex. Although the chemical shifts of the acetone methyl groups in the two complexes coincide, the peak of the Me–C≡ group is shifted downfield (τ 8.25 ppm) and its shift is similar to that for the 2/1 $Me_2AlC{\equiv}CMe/Et_2O$ complex. These results suggest the formation of the complex from I and acetone in a 2/1 molar ratio involves cleavage of only one bridging bond, the process resembling that of the formation of the proposed 2/1 complex between I and diethyl ether.

Rearrangement in the binary system $(Me_2AlCCMe)_2 + Me_2CO$ and $Me_2Al(MeCC)[Me_2(MeCC)CO]AlMe_2 + Me_2CO$

The rearrangement product formed from the 2/1 complex between I and acetone was examined by means of ^{1}H NMR, ^{13}C NMR and IR spectroscopy, Table 2. The methyl groups attached to Al atoms of the product gave rise to singlets in the ^{1}H and ^{13}C NMR spectra. In the ^{1}H and ^{13}C NMR spectra the chemical shifts for the propynyl group attached to Al atoms are similar to those of the bridging propynyl group of $(Me_2AlC{\equiv}CMe)_2$. They differ from the corresponding chemical shifts for the non-bridging propynyl group of $Me_2(MeC{\equiv}C)Al \cdot$ diox [17] in the ^{1}H NMR and ^{13}C NMR spectra and those for $Me_2(MeC{\equiv}C)Al \cdot OEt_2$ in the ^{1}H NMR spectrum. The position of the band of the stretching vibrations of the C≡C bond in the propynyl group attached to Al atoms of the product corresponds to that for $(Me_2AlC{\equiv}CMe)_2$, and is about 50 cm^{-1} lower than that for the non-bridging propynyl group of $Me_2(MeC{\equiv}C)Al \cdot$ diox [17] or $Me_2(MeC{\equiv}C)Al \cdot OEt_2$. These results are in agreement with formulation of the product as II.

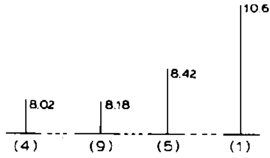
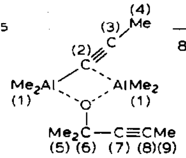
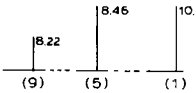
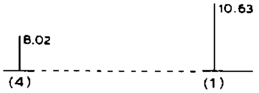
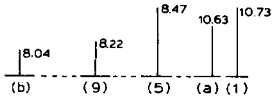
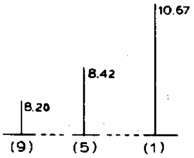
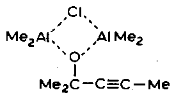


(II)

The number of peaks in the ^{1}H NMR spectrum increased after addition to II of

TABLE 2

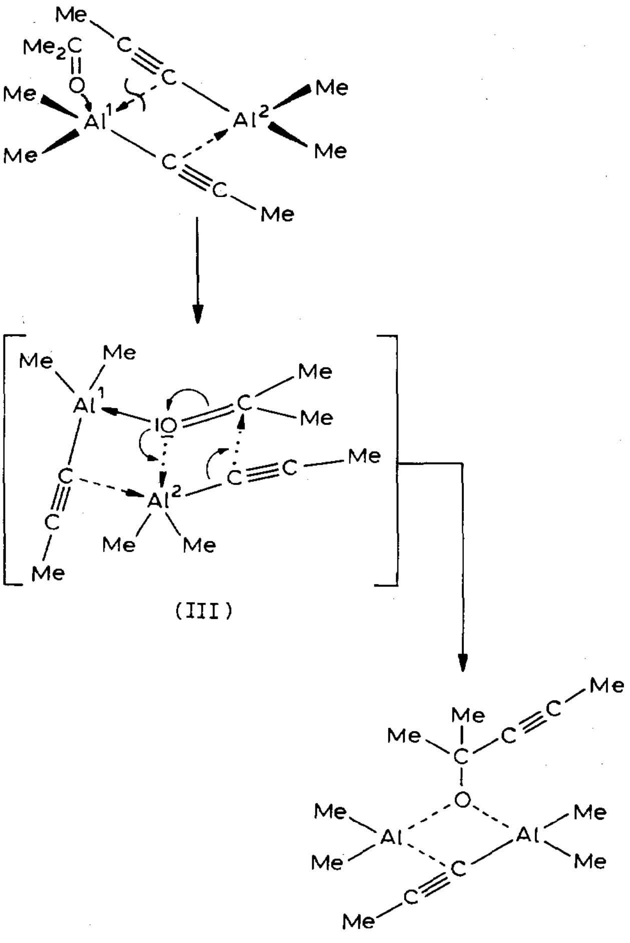
^1H NMR SPECTRA IN CH_2Cl_2, ^{13}C NMR SPECTRA IN CYCLOPENTANE AND BANDS IN THE $\nu(C{\equiv}C)$ REGION OF THE IR SPECTRA IN CYCLOPENTANE AT ROOM TEMPERATURE. ASSIGNEMENT OF C ATOMS AND Me GROUPS ARE GIVEN FOR COMPOUND II, ATOM NUMBERS ARE GIVEN IN PARENTHESES

^1H NMR (τ, ppm from TMS)	Compounds	^{13}C NMR (ppm from TMS)							IR (cm^{-1})
		(1)	(2)	(3)	(4)	(5)	(6)(7)(8)	(9)	
 1 / 1 / 2 / 4 Integration	 (II)	8.24	91.49	130.9	4.71	31.25	69.77 81.44 81.54	2.16	2250 2110
 1 / 2 / 2 Integration	$(Me_2AlOCMe_2C{\equiv}CMe)_2$ (VIII)	8.28	–	–	–	31.64	68.08 80.13 81.95	2.08	2250
 1 / 2 Integration	$(Me_2AlC{\equiv}CMe)_2$ (I)	8.8	90.18	131.03	5.02	–	–	–	2110
 1 / 2 / 2 Integration[a]	VIII + $(Me_2AlC{\equiv}CMe)_2$ (a) (b)	Not investigated							2250 2108
 1 / 2 / 4 Integration	 (VII)	7.68	–	–	–	31.25	71.18 80.65 84.41	2.31	2250

[a] Integration a/b = 2/1

either $(Me_2AlC{\equiv}CMe)_2$ or $(Me_2AlOCMe_2C{\equiv}CMe)_2$ but the position of the new peaks coincided with those of the added compounds, Table 2.

II was distilled under high vacuum (10^{-5} Torr) at room temperature without disproportionation. It was not formed from $(Me_2AlC{\equiv}CMe)$ and $(Me_2AlOCMe_2$-$C{\equiv}CMe)_2$ in cyclopentane or methylene dichloride, the required *syn*-proportionation did not occur. In the ^1H NMR spectrum of such a mixture only peaks of the substrates, but none for II, were observed after 24 h at room temperature. From the



(III)

(II)

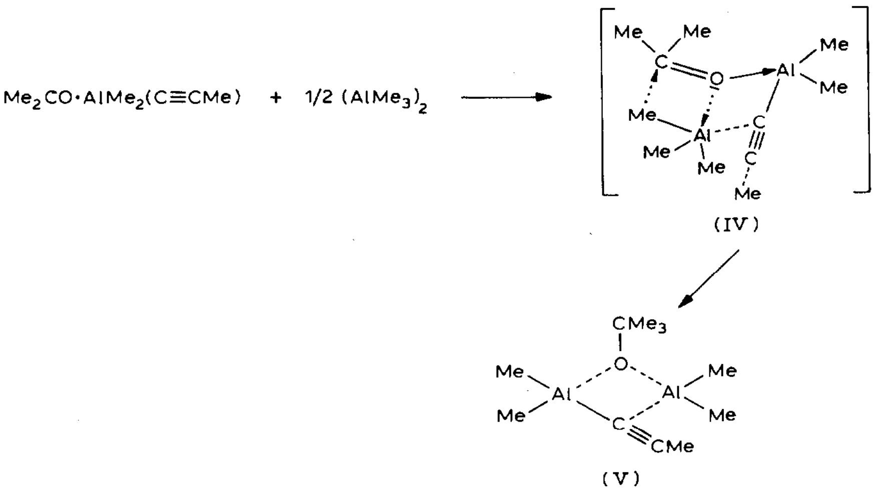
(1)

solution of these two components, the solvent and dimethylpropynylaluminium contaminated with small amounts of $(Me_2AlOCMe_2C{\equiv}CMe)_2$ were distilled off. The residue was almost pure $(Me_2AlOCMe_2C{\equiv}CMe)_2$. No II was found in the distillate or in the residue.

It is unlikely that II was formed from the hypothetical monomeric alkoxy compound (obtained in the reaction of the 1/1 complex) and dimeric $(Me_2AlC{\equiv}CMe)_2$. In such a case symmetrical dimers of both components should be observed as well.

The above results are in agreement with the possible reaction pathway shown in eq. 1.

The attack of the ketone must proceed from the side of the weaker bridge bond [16] and so the 2/1 complex is formed in which the second bridging bond is preserved. The geometry of this complex, the magnitude of the negative charge and the orientation about the triple bond favour the interaction of $C^{\delta+}_{\text{carbonyl}}$ with $C{\equiv}C^{\delta-}$ and the formation of the reactive complex III. The process from the proposed transition state to the product can be regarded as a four centre rearrangement



(2)

involving 6 electrons in which the Al^2 atom is involved. It seems that the only role of the Al^1 atom in III is to polarise the carbonyl bond and to preserve its geometry in the reaction.

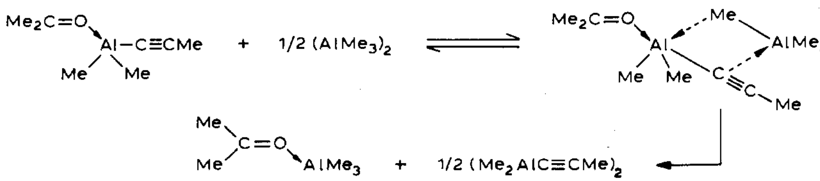
An analogous mechanism can be postulated for the reaction of II with acetone. Due to the greater donor ability of the alkoxy than that of the propynyl group, reaction via the complex similar to III, but with an alkoxy bridge is even more probable. The Al–O(R)–Al system can more effectively stabilize the transition state and the polarization of the Al–C≡ bond is expected to be greater. This reaction was examined and the yield and selectivity were both found to be very high. It is suggested that the complex formed from II and acetone is a little more stable than that from III because the temperature required for the reaction for II was higher.

Rearrangement in the ternary mixture $1/2(Me_2AlCCMe)_2 + 1/2(AlMe_3)_2 + Me_2CO$

It was expected that the reaction in a mixture of the complex $Me_2(MeCC)Al \cdot OCMe_2$ with trimethylaluminium would also proceed via a six centre transition state IV, to form mainly, if not exclusively, the methylated compound V.

However, both methylated and propynylated compounds were found in the products, Table 3, the latter usually being in excess. The presence of alkynylated products can be explained in terms of fast exchange reactions which occur in the mixture of substrates independently of the rearrangement shown eqns. 3, 4, 5.

(1) Radical exchange:



(3)

(2) Lewis acid exchange:

$$\begin{aligned}&Me_2C{=}O \cdot Al(C{\equiv}CMe)Me_2 + 1/2(Me_3Al)_2 \rightleftharpoons \\ &\quad [Me_2C{=}O + Al(C{\equiv}CMe)Me_2 + 1/2(AlMe_3)_2] \rightleftharpoons \\ &\quad Me_2C{=}O \cdot AlMe_3 + 1/2(Me_2AlC{\equiv}CMe)_2\end{aligned} \tag{4}$$

TABLE 3

REACTIONS OF ACETONE WITH $(\mathrm{Me_2AlC{\equiv}CMe})_2$ AND $(\mathrm{Me_3Al})_2$

Reaction number	Acetone or its complex with organoaluminium compound	Organoaluminium compoun(s) added	Solvent	Reaction conditions temperature/ time (°C/h)	Ratio of methylated to propynylated products
1	$\mathrm{Me_2CO\cdot AlMe_2(C{\equiv}CMe)}$	$1/2(\mathrm{Me_3Al})_2$	cyclopentane	20°/4	1/2.9
2	$\mathrm{Me_2CO\cdot AlMe_3}$	$1/2(\mathrm{Me_2AlC{\equiv}CMe})_2$	cyclopentane	20°/4	1/2.8
3	$\mathrm{Me_2CO}$	$1/2(\mathrm{Me_2AlC{\equiv}CMe})_2$ $+(\mathrm{Me_3Al})_2$	cyclopentane	20°/4	1/1.5
4	$\mathrm{Me_2CO\cdot AlMe_2(C{\equiv}CMe)}$	$1/2(\mathrm{Me_3Al})_2$	cyclopentane	−12°/120	1/1.15
5	$\mathrm{Me_2CO\cdot AlMe_3}$	$1/2(\mathrm{Me_2AlC{\equiv}CMe})_2$	cyclopentane	−12°/120	1/1.5
6	$\mathrm{Me_2CO}$	$1/2(\mathrm{Me_2AlC{\equiv}CMe})_2$ $+(\mathrm{Me_3Al})_2$	cyclopentane	−12°/120	1/1.45
7	$\mathrm{Me_2CO}$	$1/2(\mathrm{Me_2AlC{\equiv}CMe})_2$ $+(\mathrm{Me_3Al})_2$	diethyl ether	−12°/120	1/3.6
8	$\mathrm{Me_2CO}$	$1/2(\mathrm{Me_2AlC{\equiv}CMe})_2$ $+(\mathrm{Me_3Al})_2$	diethyl ether	−12°/120	1/17.5
9	$\mathrm{Me_2CO}$	$\mathrm{diox\cdot AlMe_2(C{\equiv}CMe)}$ $+1/2(\mathrm{Me_3Al})_2$	cyclopentane	20°/4	1/6.3

(3) Equilibration of the 1/1 and 2/1 complexes:

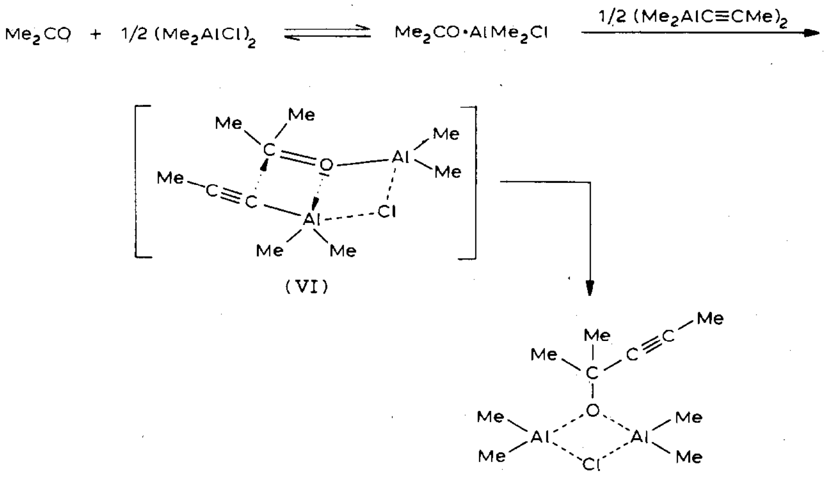
$$\mathrm{2Me_2C{=}O\cdot Al(C{\equiv}CMe)Me_2 \rightleftharpoons Me_2C{=}O + Me_2C{=}O\cdot 2[Al(C{\equiv}CMe)Me_2]}$$
$$\downarrow +(\mathrm{Me_3Al})_2$$
$$\mathrm{Me_2C{=}O\cdot 2(Me_3Al) + Me_2C{=}O\cdot Me_5Al_2C{\equiv}CMe + Me_2C{=}O\cdot Me_4Al_2(C{\equiv}CMe)_2} \qquad (5)$$

There are also other reactions which proceed during or after the rearrangement. These increase the yield of alkynylated products, e.g. in the aforementioned reaction of mixed dimers II or V with free ketones. In order to obtain more information about the formation of the reactive complex, the influence of change in the sequence of the addition of the reactants on the products was investigated. The results (Table 3) show the variation of the products ratio with the change in the addition sequence.

The reaction carried out with an equimolar amount of 1,4-dioxane, reaction 9, resulted in a reasonably selective alkynylation, close to that for the $\mathrm{Me_2CO}$ and $\mathrm{Me_2AlC{\equiv}CMe}$ systems. All the reactions listed in Table 3 were slower in the final step than corresponding reactions of the simple $\mathrm{Me_2CO/Me_2AlC{\equiv}CMe}$ system (1 h at 20°C was required for completion of the reaction). The results indicate that, (i) the presence of the second molecule of the triorganoaluminium compound significantly influences the reaction path, (ii) the second molecule of the OAC forms a moderately strong complex with $\mathrm{Me_2CO\cdot AlR_2R'}$ (since the presence of basic dioxane strongly changes the ratio of the reaction products), (iii) there are different complexes and associate species in the reaction mixture (one of them may be $\mathrm{Me_2CO\cdot 2AlMe_3}$, which could slow down the rate of the final step).

Rearrangement in the system 0.5 $(\mathrm{Me_2AlCCMe})_2 + \mathrm{Me_2CO\cdot Al(Cl)Me_2}$

The $\mathrm{Me_2CO\cdot Al(Cl)Me_2}$ complex, which is more stable towards dissociation, and less reactive, in alkylation should not so easily undergo exchange reactions when I is



(VII)

(6)

added (see reactions 3, 4, 5). It was expected that I would be able to form the complex VI with $Me_2CO \cdot Al(Cl)Me_2$, which in turn would react to give the mixed dimer VII.

The reaction product was distilled off under a vacuum of 10^{-5} Torr at room temperature to leave a large amount of a yellow polymeric residue. No change in the composition of the product was observed during the distillation; the distillate was investigated spectroscopically and the results are presented in Table 2. Analysis by GLC after hydrolysis showed that no propyne was present in the gas phase and the only product in the liquids was 2-methyl-3-pentyn-2-ol. The Al/Cl ratio was 1.98/1. The results either confirm or do not conflict with the suggested structure VII. The carbinol yield was rather low (about 22%) because of the high Lewis acidity of Me_2AlCl, which accelerates the reactions leading to polymeric species. Use of $MeAlCl_2$, a stronger Lewis acid in place of Me_2AlCl in reaction 6 led to the formation of only a brown undistillable polymer.

Compound VII in contrast to the mixed dimers III or V was also formed from dimethylaluminium chloride and I in methylene dichloride. However, the substrates were still present in the mixture even after a long time as indicated by the ^1H NMR spectrum. Disproportionation of VII was not observed even over a long period after distillation.

Conclusions

These results provide further evidence in favour of the presence of a six-centre transition state in the reaction of organoaluminium compounds with ketones in a 2/1 Al/CO molar ratio.

The formation of the complex of di-μ-propynyltetramethyldialuminium with diethyl ether in a 2/1 stoichiometry suggests that only one bridging bond of OAC is split in the first step of the reaction of I with acetone in 2/1 molar ratio. μ-Propynyl-μ-(2-methyl-3-pentyn-2-oxy)tetramethyldialuminium is the main product of the reaction of I with acetone in a 2/1 molar ratio. μ-Chloro-μ-(2-methyl-3-

pentyn-2-oxy)tetramethyldialuminium is the main product of the reaction of the $Me_2ClAl \cdot OCMe_2$ complex with 1/2 $(Me_2AlC{\equiv}CMe)_2$.

All these facts are consistent with the postulated mechanistic scheme.

Experimental

All operations were carried out under dry, oxygen free nitrogen.

Materials

Cyclopentane, diethyl ether and 1,4-dioxane were dried over 4A molecular sieves and distilled from Na/K alloy benzophenone. Methylene dichloride and acetone were dried over 4A molecular sieves and distilled under dry nitrogen. Trimethylaluminium and dimethylaluminium chloride were distilled under dry nitrogen. Dimethylpropynylaluminium was obtained from $MeC{\equiv}CNa$ and Me_2AlCl in cyclopentane [17].

Analytical methods

The product mixtures were hydrolyzed with distilled water. The organic layer and the products extracted from the water layer with diethyl ether were collected and identified by GC/MS. The ratios of methylated to propynylated products were determined by GLC.

The ^1H NMR spectra were recorded on JEOL JNM-100 MHz and Tesla BS 487-C80 MHz spectrometers. ^{13}C NMR spectra were recorded on a Varian CFT-20, 20 MHz spectrometer. IR spectra were recorded on a Perkin–Elmer 577 PE spectrophotometer using polyethylene 'bags' to provide an inert atmosphere. GC/MS spectra were recorded on a 6 CMR LKB 2091 spectrophotometer.

General synthetic procedure

A solution of one of the reagents was placed in a 100 cm^3 round bottom flask in a dry ice/methanol bath. Calculated amount(s) of reagent(s) in solution was (were) added dropwise, and in some experiments a magnetic stirrer was used. The solution after the addition(s) was (were) completed was slowly heated to the required temperature and kept there for the time specified below.

Formation of complex I with Et_2O. The calculated amount of Et_2O was added to the stirred solution of I in CH_2Cl_2. The complex obtained was used for further investigation.

Reaction of I with acetone (Al/CO 2/1) in cyclopentane. A 30% solution of acetone was added to a stirred 30% solution of I, reaction temperature 20°C, time 4 h. After the completion of the reaction cyclopentane was distilled off at 10^{-1} Torr.

Reaction of μ-(2-methyl-3-pentyn-2-oxy)-μ-propynyltetramethyldialuminium (II) with acetone in cyclopentane. A 30% solution of acetone was added to a stirred 30% solution of II; reaction temperature 20°C, time 4 h.

Synthesis of di(2-methyl-3-pentyn-2-oxy)tetramethyldialuminium in cyclopentane. A 30% solution of 2-methyl-3-pentyn-2-ol was added to a stirred 30% solution of trimethylaluminium, reaction temperature 20°C, time 4 h. The cyclopentane was distilled off at 10^{-1} Torr and the product sublimed at 10^{-5} Torr.

Reaction of $Me_2(MeCC)Al$-diox with acetone and trimethylaluminium in cyclopentane (reaction 9 in Table 3). To a stirred 30% solution of I were added successively equimolar amounts of a 30% solution of acetone in 1,4-dioxane, and, after 10 min, a 30% solution of trimethylaluminium, reaction temperature 20°C, time 4 h.

Reaction of acetone with I and trimethylaluminium in cyclopentane or diethyl ether (reactions 1, 2, 4, 5). A 30% solution of an equimolar amount of one of the OAC groups was added to a 30% solution of acetone. After 15 min a 30% solution of an equimolar amount of the second OAC was introduced; reaction temperature 20°C, time 4 h (reactions 1, 2) or −12°C and 5 days (reactions 4, 5).

Reaction of acetone with the mixture of I and trimethylaluminium in cyclopentane. A 30% solution of an equimolar mixture of I with trimethylaluminium was added to a 30% solution of acetone. Reactions 3 and 7 were carried out at 20°C for 4 h, and reactions 6 and 8 at −12°C for 5 days.

Reaction of acetone with dimethylaluminium chloride and I in cyclopentane. A 30% solution of an equimolar amount of acetone was added at −78°C to a stirred solution of Me_2AlCl. The solution was warmed to 0°C, kept there for 20 min, then cooled to −78°C, and a 30% solution of an equimolar amount of I was added. The solution was then heated to 20°C and stirred for 2 h. After completion of the reaction the cyclopentane was distilled off under vacuum (10^{-1} Torr). The product was distilled at 10^{-5} Torr at room temperature.

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