

ALKYNYLALUMINIUM COMPOUNDS

IV *. REACTIONS OF DIMETHYLALKYNYLALUMINIUM COMPOUNDS WITH KETONES

K.B. STAROWIEYSKI and A. BĘCALSKA

Chemistry Department, Technical University (Politechnika), 00-662 Warsaw (Poland)

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Summary

The addition of dimethylpropynyl-, dimethylbutynyl- and dimethylphenylethynyl-aluminium to acetone and acetophenone leads to the products of alkynylation, but the methylated products are also formed. The selectivity of the alkynylaluminium compounds used in alkynylation increases in the order $(\text{Me}_2\text{AlC}\equiv\text{CEt})_2 < (\text{Me}_2\text{AlC}\equiv\text{CMe})_2 < (\text{Me}_2\text{AlC}\equiv\text{CPh})_2$. The selectivity increases when an excess of the organoaluminium compound is used, or when it is applied as a complex with a Lewis base. An increase of reactivity of the investigated compounds toward ketones in the order $(\text{Me}_3\text{Al})_2 < (\text{Me}_2\text{AlC}\equiv\text{CMe})_2 < (\text{Me}_2\text{AlC}\equiv\text{CEt})_2$ is observed.

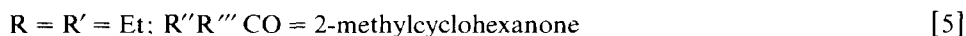
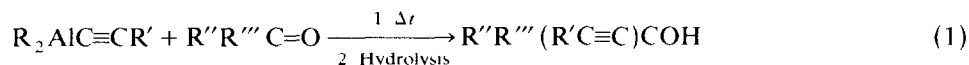
Introduction

In general, organoaluminium compounds react with organic reagents with cleavage of the Al–C bond. The course of the reactions depends on the character of the substrates. In the reactions of alkylphenylaluminium, alkylvinylaluminium and alkylalkynylaluminium compounds with organic reagents cleavage of the Al–phenyl, Al–vinyl and Al–alkynyl bond, respectively, is favoured. For example, alkylalkynylaluminium compounds react with reagents containing an acidic proton, HCl [1], or 2-propanol [2], with elimination of the alkyne. However, in the reaction of alkylalkynylaluminium compounds with phenol [3] or secondary amines [4] both alkyne and alkane are eliminated.

In the present paper the selectivity of the addition of alkylalkynylaluminium compounds to ketones is investigated.

* For part III see ref. 13.

It is claimed in the literature that in the addition reactions of dialkylalkynylaluminiums to carbonyl compounds only alkynylated products are found:



In the reactions of alkylalkynylaluminium compounds with α,β -unsaturated ketones 1,2- or 1,4-addition products were observed and only alkynyl group addition products were formed [7,8]. Similarly, in reactions with epoxy compounds only the reaction of the alkynyl group was observed [9].

Our preliminary experiments with reaction of dimethylpropynylaluminium with acetone did not confirm exclusive alkynylation.

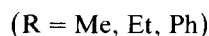
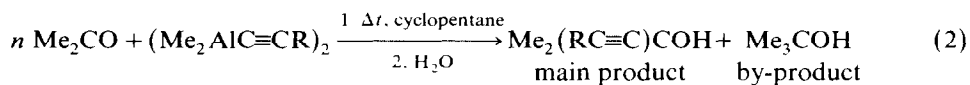
The aim of this work was to investigate the influence of reaction conditions on the selectivity in the alkynylation of ketones with dimethylalkynylaluminium compounds, and the reactivity of alkynyl-substituted organoaluminium compounds toward ketones.

Results and discussion

Selectivity of the alkynylation reactions of ketones with dimethylalkynylaluminium compounds

The first part of this work is concerned with the selectivity in the addition reactions of dimethylalkynylaluminium compounds to ketones. The selectivity in the reactions of acetone and acetophenone with dimethylpropynylaluminium, dimethylbutynylaluminium and dimethylphenylethynylaluminium was investigated and the results are presented in Table 1.

Dimethylalkynylcarbinol was the main product of the reaction (eq. 2) of acetone with dimethylalkynylaluminiums (yield 60–70%) and small amounts of methylation products were also found (reactions 1–3, 6–9 in Table 1):



The mol ratio of ketone to dimethylalkynylaluminium in cyclopentane was 1/1 ($n = 2$) and 1/2 ($n = 1$). The reactions were also carried out in a donor solvent $D = Et_2O$ (reactions 4,5 in Table 1).

It can be seen from Table 1 that the selectivity of the reactions increased (i) when an excess of the organoaluminium compound was used in a non-polar hydrocarbon solvent (reactions 1,2 and 6,7), (ii) in a donor solvent D (in this case the reaction

TABLE 1
REACTIONS OF DIMETHYLALKYNYLALUMINIUM COMPOUNDS WITH KETONES

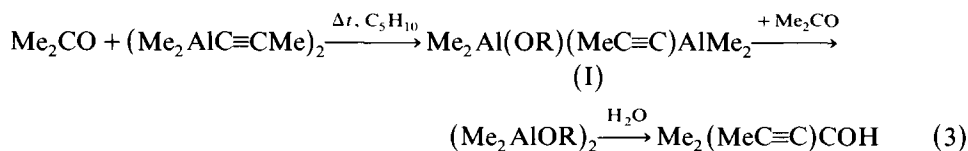
No. Ketone	Organoaluminium compound	Mol ratio CO/Al	Solvent	Reaction condition T/t (°C/h)	Ratio of methylated to alkynylated products	Conversion of acetophenone (%)
1 Me ₂ CO	(Me ₂ AlC≡CMe) ₂	1/1	cyclopentane	20/4 h	1/17.4	
2 Me ₂ CO	(Me ₂ AlC≡CMe) ₂	1/2	cyclopentane	20/4 h	1/32	
3 Me ₂ CO	(Me ₂ AlC≡CMe) ₂	1/2	cyclopentane	~ 30/1 h	traces of t-BuOH	
4 Me ₂ CO	Me ₂ AlC≡CMe·Et ₂ O	1/1	diethyl ether	20/4 h	1/21.6	
5 Me ₂ CO	Me ₂ AlC≡CMe·Et ₂ O	1/1	diethyl ether	34/4 h	1/35.5	
6 Me ₂ CO	(Me ₂ AlC≡CEt) ₂	1/1	cyclopentane	20/4 h	1/9.5	
7 Me ₂ CO	(Me ₂ AlC≡CEt) ₂	1/2	cyclopentane	20/4 h	1/15	
8 Me ₂ CO	(Me ₂ AlC≡CPh) ₂	1/1	cyclopentane	20/1 h	traces of t-BuOH	
9 Me ₂ CO	(Me ₂ AlC≡CPh) ₂	1/2	cyclopentane	20/1 h	traces of t-BuOH	
10 Me ₂ CO	(Me ₂ AlC≡CMe) ₂	1/1	cyclopentane	2-steps	1/40 ^a	
11 PhCOMe	(Me ₂ AlC≡CMe) ₂	1/1	toluene	100/4 h	1/6.3	above 99
12 PhCOMe	(Me ₂ AlC≡CMe) ₂	1/2	n-heptane	90/4 h	1/12.8	95.2
13 PhCOMe	(Me ₂ AlC≡CMe) ₂	1/1	cyclopentane	20/15 min	1/27.5 ^b	63.4
14 PhCOMe	(Me ₂ AlC≡CMe) ₂	1/2	cyclopentane	20/15 min	1/19.6	97.4
15 PhCOMe	(Me ₂ AlC≡CEt) ₂	1/1	cyclopentane	20/15 min	1/10 ^c	92.8
16 PhCOMe	(Me ₂ AlC≡CEt) ₂	1/2	cyclopentane	20/15 min	1/19	above 99
17 PhCOMe	Me ₂ AlC≡CMe·diox	1/1	1,4-dioxane	30/1 h	1/15.5	43.5
18 PhCOMe	Me ₃ Al·diox	1/1	1,4-dioxane	30/1 h		27.0
19 PhCOMe	(MeC≡C) ₃ Al·diox	1/1	1,4-dioxane	30/1 h		63.0

^a The ratio of methylated carbinol to propynylated carbinol in the second reaction step was 1/68; the yield of dimethylpropynylcarbinol in the second step was 94%. ^b After 30 min of the reaction at 20 °C this ratio was 1/11.6 and the conversion of acetophenone was 92.6%. ^c After 30 min of the reaction at 20 °C this ratio was unchanged and the conversion of acetophenone was 94%.

involves a 1/1 complex Me₂(RC≡C)Al·D (reactions 1,4), (iii) with decrease of the reaction temperature (reactions 2,3).

The reaction of acetone with dimethylphenylethynylaluminium was the most selective one, only traces of methylated products were found. Minor amounts of unsaturated products of the type CH₂=C(C≡CR)CH₃ were observed in the reactions of acetone with dimethylbutynyl- and dimethylphenylethynyl-aluminium. It seems that these compounds were formed by the elimination of [Me₂AlOH] after the alkylation reaction and/or of water during hydrolysis.

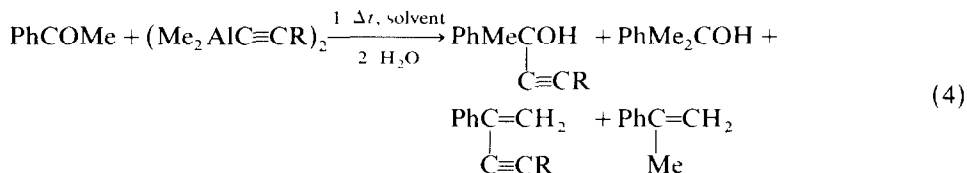
The reaction of acetone with dimethylpropynylaluminium in a 1/1 mol ratio was carried out also in a two-step system (reaction 10 in Table 1):



(R = Me₂(MeC≡C)O)

When the product I* was distilled off and treated stoichiometrically with Me₂CO again, the reaction was much more selective than reaction 1 in Table 1.

In the reactions of acetophenone with dimethylalkynylaluminiums both of the expected carbinols, together with minor amounts of α -substituted styrenes, were obtained after hydrolysis (reactions 11–17 in Table 1):



(R = Me, Et)

Methylphenylalkynylcarbinols were the main products in all the reactions. It can be seen from Table 1 (reactions 11–17) that the selectivity of the reactions of acetophenone with dimethylalkynylaluminium compounds increased (i) with an excess of the organoaluminium compound used in a hydrocarbon solvent, (ii) in a donor solvent, (iii) with decrease of the reaction temperature. The changes in the selectivity of the reactions of acetophenone (reaction 4) were analogous to those of acetone (reaction 2).

Reactivity of dimethylalkynylaluminium compounds toward ketones

In the second part of our investigations the reactivity of triorganoaluminiums towards ketones was studied. Alkynyl-substituted organoaluminium compounds were found to be more reactive toward ketones than trimethylaluminium.

Acetone started to react with dimethylpropynylaluminium in a 1/2 mol ratio at -60°C , and then at about -30°C a rapid reaction was observed. In the case of a 1/1 mol ratio of reactants, the reaction did not start until -30°C and at slightly elevated temperature a rapid reaction was observed. In the case of the 1/1 complex of acetone with trimethylaluminium the reaction did not start until $+20^\circ\text{C}$.

In the reactions of acetophenone with dimethylpropynylaluminium in 1,4-dioxane a similar increase of reactivity, in comparison to trimethylaluminium, was observed (reactions 17–19 in Table 1).

It follows that the reaction rates of organoaluminium compounds with ketones depends on the ratio of the substrates in nonpolar solvents, and increased when an excess of the organoaluminium compound was used. Due to the higher stability of the complexes of organoaluminium compounds with acetophenone than with acetone with respect to subsequent formation of alkyl or alkynyl-carbinol derivatives it was possible to investigate semi-quantitatively the appropriate reaction rates. The conversion of acetophenone after 15 min of the reaction of acetophenone with dimethylpropynylaluminium (reaction 4) at 20°C was used as a measure of the reaction rate. The conversion of acetophenone changed from 63.4% for the 1/1 reactant mixture, to 97.4% for the 1/2 mol ratio of the acetophenone and dimethylpropynylaluminium mixture (reactions 13,14 in Table 1).

Similar results were obtained in the case of the reactions of acetophenone with

* The properties of the product I will be described in a forthcoming paper.

dimethylbutynylaluminium (reactions 15,16 in Table 1). In this case the conversion of acetophenone was higher than in the case of reaction of acetophenone with dimethylpropynylaluminium. In the reaction of acetophenone with dimethylbutynylaluminium at a 1/2 mol ratio, carried out at 20°C, only traces of unreacted acetophenone were found after 15 min.

Conclusions

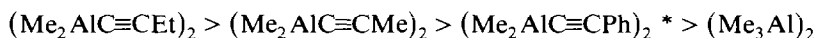
It follows from our results that the selectivity in the reactions of ketones with alkynyl-substituted organoaluminium compounds decreased in the following order:



These results are in agreement with the greater negative charge localized on the phenylethynyl group than on the propynyl or butynyl groups.

The reactivity of organoaluminium compounds toward ketones decreased in the following order

(a) in non-polar hydrocarbon solvents



(b) in a donor solvent (1,4-dioxane)



Furthermore, the rates of the reactions of dimethylpropynylaluminium with ketones in donor solvents were lower, and the selectivity was higher, than in hydrocarbon solvents.

The rate and the selectivity of the reactions at a 1/2 mol ratio of ketone to dialkylalkynylaluminium compound were higher.

Experimental

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

Materials

Cyclopentane, diethyl ether, toluene, 1,4-dioxane and n-heptane were dried over 4A molecular sieves and distilled from Na/K alloy-benzophenone. Methylene dichloride, acetone and acetophenone were dried over 4A molecular sieves and distilled in a dry nitrogen atmosphere. Trimethylaluminium was distilled in a dry nitrogen atmosphere. Dimethylpropynylaluminium was obtained from $\text{MeC}\equiv\text{CNa}$ and Me_2AlCl in cyclopentane [10]. $(\text{MeC}\equiv\text{C})_3\text{Al}\cdot\text{diox}$ was obtained from $\text{MeC}\equiv\text{CNa}$ and AlCl_3 in 1,4-dioxane [11] using a high speed cutting stirrer (4000 rpm). Dimethylbutynylaluminium was obtained from $\text{EtC}\equiv\text{CNa}$ and Me_2AlCl in cyclopentane, as for dimethylpropynylaluminium. Dimethylphenylethynylaluminium was obtained from $\text{PhC}\equiv\text{CH}$ and Me_3Al [12].

Analytical methods

The reaction mixtures were hydrolysed with distilled water. The organic layer,

* Preliminary results.

and the products extracted from the water layer with diethyl ether, were collected together and identified by means of the GLC/MS method and ^1H NMR spectroscopy.

The ratios of methylated products to alkynylated products, and the conversion of acetophenone, were determined by means of the GLC technique. The yields of alkynylated carbinols were determined using the GLC technique; cyclohexanone was used as an internal standard.

The rates of the reactions of acetone with dimethylpropynylaluminium were investigated by means of ^1H NMR spectroscopy; the spectra were recorded at -60 , -40 , -30 , -10 , 0 , 20°C .

The ^1H NMR spectra were recorded on JEOL JNM C-100 MHz and Tesla BS 487-C80 MHz spectrometers. GLC-MS spectra were recorded with a 6CMR LKB 2091 spectrophotometer.

Reactions of ketones with organoaluminium compounds

A 30% solution of the organoaluminium compound (dimethylalkynylaluminium, trimethylaluminium, tripropynylaluminium), in an appropriate solvent (c.f. Table 1), was placed in a round-bottomed flask and a calculated amount of a 30% solution of ketone in the solvent was added dropwise. During this operation the flask was cooled in a dry ice-methanol bath and the solution was stirred vigorously with a magnetic stirrer. After the addition of ketone was completed the solution was slowly heated to the reaction temperature, and the reaction mixture was stirred over a period of time, shown in Table 1.

In the case of reaction of acetone with dimethylpropynylaluminium in a two step system (eq. 3, reaction 10 in Table 1), the first step of the reaction was carried out as described above. The reaction mixture was stirred for 4 h at 20°C , followed by the distillation of cyclopentane under vacuum (10^{-1} Torr). The product I (reaction 3), after distillation under high vacuum (10^{-5} Torr), was placed in a flask, followed by the addition of cyclopentane so that a 30% solution of I in cyclopentane was formed. A 30% solution of acetone in cyclopentane was then added dropwise. During this operation the flask was cooled in a dry ice-methanol bath and stirred with a magnetic stirrer. The reaction mixture was slowly heated to 20°C and stirred for 4 h at that temperature.

Acknowledgement

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References

- 1 L.I. Zakharkin, V.V. Gavrilenko and L.L. Ivanov, Zh. Obshch. Khim., 37 (1967) 992.
- 2 W. Fries, W. Schwartz, H.D. Hansen and J. Weidlein, J. Organomet. Chem., 159 (1978) 373.
- 3 M. Skowrońska-Ptasińska, K.B. Starowieyski, S. Pasykiewicz and M. Carewska, J. Organomet. Chem., 160 (1978) 403.
- 4 K. Haage, K.B. Starowieyski and A. Chwojnowski, J. Organomet. Chem., 174 (1979) 149.
- 5 H. Demarne and P. Cadot, Bull. Soc. Chim. Fr., (1968) 205.
- 6 H. Demarne and P. Cadot, Bull. Soc. Chim. Fr., (1968) 215.
- 7 J. Hooz and R.B. Layton, J. Am. Chem. Soc., 93 (1971) 7320.

- 8 R.T. Hansen, D.B. Carr and J. Schwartz, *J. Am. Chem. Soc.*, 100 (1978) 2244.
- 9 G.A. Crosby and R.A. Stephenson, *J. Chem. Soc., Chem. Commun.*, (1975) 287.
- 10 K.B. Starowieyski, A. Chwojnowski and Z. Kuśmerek, *J. Organomet. Chem.*, 192 (1980) 147.
- 11 P. Chini, A. Baradel, E. Pauluzzi, M. deMalde, *Chim. Ind. (Milan)*, 44 (1962) 1220.
- 12 T. Mole and J.R. Surtees, *Chem. Ind. (London)*, (1963) 1727.
- 13 K.B. Starowieyski and A. Chwojnowski, *J. Organomet. Chem.*, 215 (1981) 151.