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ON THE REACTIVITY OF ORGANOMETALLIC COMPOUNDS TOWARDS FUNCTIONAL SUBSTRATES

IV*. THE REACTION OF ALIPHATIC 1-ALKYNES WITH TRIISOBUTYLALUMINUM: DEPENDENCE ON THE STRUCTURE OF THE ACETYLENIC SUBSTRATE

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Summary

The reaction between triisobutylaluminum and aliphatic 1-alkynes having alkyl groups of different structure on the 3-carbon atom has been investigated. At room temperature and in the absence of solvents, products which correspond to metallation, reduction and carbalumination processes, are isolated after hydrolysis. The extent of such reactions, and in particular the regiospecificity of the carbalumination is dependent on the experimental conditions adopted and on steric factors associated with the structure of the 1-alkyne used. On the basis of these results and the complete stereospecificity of the reaction when (+)(*S*)-3,4-dimethyl-1-pentyne is used, possible mechanisms are discussed.

Introduction

Although the dynamics and the stereochemistry of the reaction between organoaluminum compounds and disubstituted acetylenes have been widely studied [1], no systematic investigation has been carried out on the reactivity of triisobutylaluminum with terminal alkynes [2,3]. In the course of researches on the reactivity of β-branched organometallic compounds of 2nd and 3rd Group elements towards functional substrates [4,5], and in connection with studies on the transition metal-catalyzed reactions between organoaluminum compounds and unsaturated hydrocarbons [6], we undertook an investigation on the reactivity of triisobutylaluminum with 1-alkynes by using acetylenic substrates of general formula (I).

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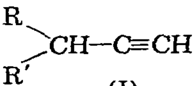
* For Part III see ref. 4d.



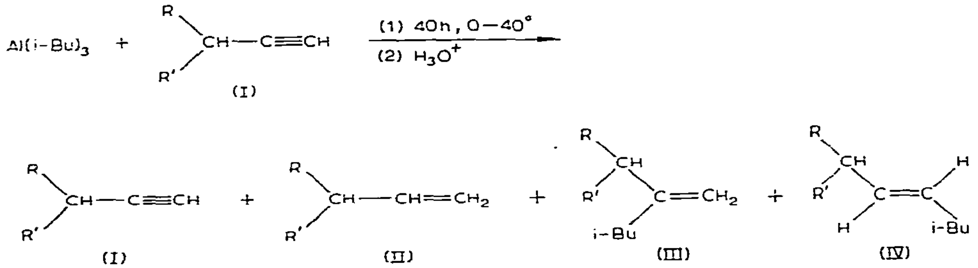
(I)

(a) R = Pr, R′ = H;
(b) R = Et, R′ = Me;
(c) R = i-Pr, R′ = Me;
(d) R = t-Bu, R′ = Me.

Results and discussion

Under the experimental conditions used, the reaction between triisobutylaluminum and 1-alkynes (I) yields a complex mixture of products [2,3,7], which, after hydrolysis, gives (I) (resulting from alkynyldiisobutylaluminum formed), and the corresponding 1-alkenes (II), in addition to minor amounts of (III) and (IV) (Scheme 1). The reaction between Al(i-Bu)$_3$ and 1-hexyne (Ia) also gives a diene (V) in a low yield, but no similar products were detected in the other cases (Table 1).

SCHEME 1



The structures of (IIIa) and (IVa) were assigned on the basis of NMR data on samples recovered by preparative GLC, while (IVb-d) were identified by comparison of their retention times with those of authentical samples [8], prepared from (I) by a published method [9]. The mass spectrum of (IIIb) was consistent with the assumed structure. On the basis of spectral data, (V) seems to be 2,3-di-n-butyl-6-methyl-1,3-heptadiene.

The results obtained (Table 1) show that the course of the reaction depends

TABLE 1

PRODUCTS FROM REACTION BETWEEN 1-ALKYNES AND TRIISOBUTYLALUMINUM

Run	No.	Temp. (°C)	Molar ratio (I)/Al(i-Bu)$_3$	Conversion (%) after 40 h	Yields [a] (%)					Molar ratio	
					(I)	(II)	(III)	(IV)	(V)	(I)/(II)	(IV)/(III)
1	(Ia)	25	1.0	94	39.8	47.0	1.9	9.9	1.4	0.8	5.2
2	(Ib)			97	36.2	48.5	≈0.7	14.6		0.7	≈22.0
3	(Ic)			100	56.9	34.9	Trace	8.3		1.6	
4	(Id)			100	82.6	15.1		2.3		5.5	
5	(Ia)		0.5	98	49.8	37.4	1.9	10.1	≈0.8	1.3	5.3
6			2.0	92 [b]	30.5	48.8	2.9	13.1	4.7	0.6	4.6
7				129 [c]	32.0	50.9	2.0	9.6	2.9	0.6	4.7
8		0	1.0	21	43.3	45.9	1.2	8.7	≈0.8	0.9	7.2
9		40		100	34.4	46.5	3.0	12.5	3.6	0.7	4.2

[a] Evaluated by GLC analysis on the reaction mixture upon hydrolysis. [b] After 20 hr. [c] Based on reacted triisobutylaluminum.

on the reactant molar ratio, on the temperature conditions adopted, and most of all, on the structure of (I).

Increase in the molar ratio of (Ia) to Al(i-Bu)$_3$ (runs 5, 1, 6) favours the formation of (V) and lowers the yield of the metallation product: with an excess of (Ia), the overall reaction rate is increased and other isobutyl groups of Al(i-Bu)$_3$ [2] are available for reaction with (Ia) (runs 6, 7).

Raising the temperature results in generally greater degrees of conversion, and increases the yields of the carbalumination products (runs 8, 1, 9). While the reaction between Al(i-Bu)$_3$ and (Ia) or (Ib) (runs 1, 2) results mainly in the reduction of the triple bond to (II), compounds (Ic) and (Id) react under similar conditions (runs 3, 4) to give the metallation product in higher yields, in addition to smaller amounts of the reduction and carbalumination products. In all the cases investigated, however, the competitive carbalumination of the triple bond [1b, 1f] results in the predominant formation of (IV) (Table 1) which corresponds to an anti-Markownikov *cis*-addition, in agreement with results previously obtained for (Ia) [3].

The reaction of (+)(*S*)-3,4-dimethyl-1-pentyne (Ic) with Al(i-Bu)$_3$ at 25° for 40 h occurs without any racemization; in fact (+)(*S*)-(Ic), optical purity (o.p.) 42.6% [10], reacts with Al(i-Bu)$_3$ to yield, together with unracemized (+)(*S*)-(Ic), (+)(*S*)-3,4-dimethyl-1-pentene (IIc), o.p. 44.5% [10], and (+)(*S*)-2,3,7-trimethyl-*trans*-4-octene (IVc), having the same optical rotation of a sample previously prepared [8] from (+)(*S*)-(Ic), o.p. 42.6%, by an independent route [9].

From the overall experimental results, it seems reasonable to assume that the reactions leading to the formation of (II) and (III) proceed through linked mechanistic pathways. Increase in the steric hindrance on the 3-carbon of (I) substantially lowers the reduction to (II), correspondingly (III) disappears and the alkynyldiisobutylaluminum is formed predominantly (runs 1—4). This might be explained in terms of steric factors, operative in an intermediate π complex (VI) [1b, 1f] (Scheme 2); when the bulk of the alkyl group bound to the 3-carbon of (I) is increased, the migration of the hydride ion to the 2-carbon will be hindered and that of the isobutyl group prevented. Consequently the competitive metallation process will be enhanced*.

The reason for the preferred formation of (IV) over (III) is not completely clear [1f, 3]. Firstly, the terminal carbon atom of (I) should be more able to sustain the electron deficiency of aluminum atom. Secondly, if the intermediate complex (VI) were responsible for both the carbalumination reactions, the diisobutylaluminum group would have to be attached to the terminal carbon rather than to the 2-carbon, adjacent to the bulky alkyl group, and the increase of the steric hindrance on the 3-carbon atom of (I) should give rise to an increase in the yield of (III) with respect to (IV). In our opinion the formation of (IV), which can, in fact, be taken off at reduced pressure before hydrolysis**, must be associated with a more complex mechanistic scheme, which might involve the interaction between the adduct (VI) and another molecule of (I).

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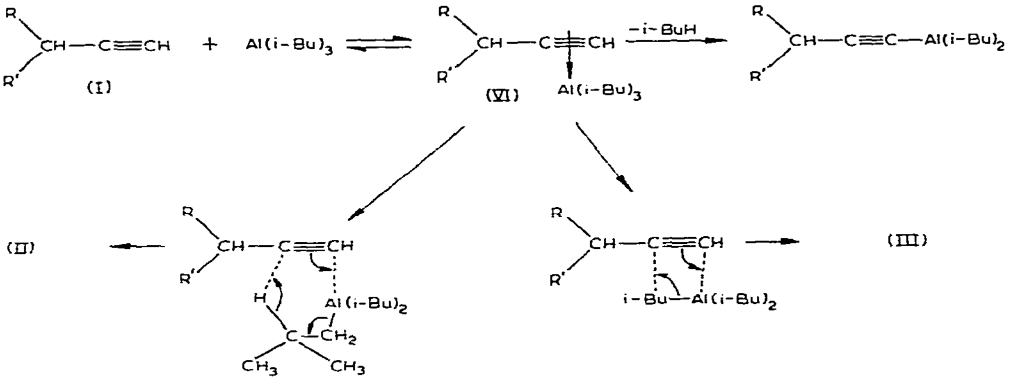
* In our opinion, and in agreement with previous suggestions [1b, 7] the metallation does not seem to be related to the acidity of the acetylenic substrate. It is noteworthy that under similar experimental conditions phenylacetylene reacts with Al(i-Bu)$_3$ to give 41% of the metallation product, 33% of styrene, and 26% of *trans*-β-isobutylstyrene.

** Deuterolysis of reaction mixtures between AlR$_3$ and 1-alkynes at 20° gave non-deuterated *trans*-alkenes [3].

SCHEME 2



Steric factors may also be responsible for the decrease in yields of (IV) and for the lack of reductive dimerization products [1b, 1f] from (Ib—d) (runs 2—4).

On the basis of the information available, all the processes involved in the reaction between trialkylaluminum compounds and 1-alkynes can reasonably be regarded as proceeding by concerted mechanisms, such as those in Scheme 2, rather than through ionic intermediates. In particular, we note that since ionic species should not retain the configuration of the asymmetric carbon atom adjacent to the triple bond, the reaction between Al(i-Bu)$_3$ and optically active 1-alkynes (I) should involve racemization, which is in disagreement with our experimental results.

Experimental

General

Triisobutylaluminum (Texas Alkyl Inc., Houston) and 1-hexyne (Ia) (Fluka A.G. Co., Buchs) were commercial products. Al(i-Bu)$_3$ was carefully redistilled under vacuum and stored in sealed glass vials, in weighed amounts. (*R*)(*S*)-3-Methyl-1-pentyne (Ib), (*R*)(*S*)- and (+)(*S*)-3,4-dimethyl-1-pentyne (Ic), and (*R*)(*S*)-3,4,4-trimethyl-1-pentyne (Id) were prepared through the corresponding α-olefins [10,11] by published methods [10,12]. Samples of 2,6-dimethyl-*trans*-4-octene (IVb), 2,3,7-trimethyl-*trans*-4-octene (IVc), and 2,2,3,7-tetramethyl-*trans*-4-octene (IVd) were obtained from (Ib), (Ic) and (Id) respectively, following established procedures [9]. (+)(*S*)-(IVc), $[\alpha]_D^{25}$ + 16.03 (*c* 17.65, n-heptane) was prepared [8] from (+)(*S*)-(Ic), $[\alpha]_D^{25}$ + 12.90 (neat) [10b].

Distillation and handling of all the reactants were performed under dry, purified nitrogen. The reactions were carried out (each at least in duplicate), in the absence of solvent, in the range of temperature from 0° to 40°.

Infrared spectra were recorded on a Perkin—Elmer spectrophotometer, Model 225. Mass spectra were recorded with a Hitachi Perkin—Elmer RMU-6L instrument at 70 eV. NMR spectra were measured with a Jeol JMN PS-100 instrument at 100 MHz. Optical rotations were taken on a Schmidt—Haensch polarimeter (sensitivity ± 0.005°). GLC analyses were performed on a C. Erba Fractovap Mod. GT instrument, with flame ionization detector, and nitrogen as carrier gas. Preparative GLC were carried out on a Perkin—Elmer F21 instrument.

Reaction between triisobutylaluminum and 1-alkynes (I)

In a typical run a weighed amount of Al(i-Bu)$_3$ (1.98 g, 10 mmole) was placed in a two-necked flask (25 ml), equipped with a magnetic stirrer, a rubber septum fitted on a Teflon stopper, and a glass stopcock. (Ia) (0.821 g, 10 mmole) was added, at 0°, from a calibrated hypodermic syringe and the vessel was then placed in a thermostat bath at 25° ± 0.2°. After 40 h, 0.1 ml of the reaction mixture was withdrawn by a hypodermic syringe, quenched in dilute sulphuric acid (1 ml) and submitted to GLC analysis. After removal of the volatile products [isobutane, isobutene, unreacted (Ia) and partially (IVa)] at 0.1 mm at room temperature, the residual reaction mixture was cautiously hydrolyzed with dilute sulphuric acid, extracted with ether and analyzed by GLC (100 m squalane capillary column, operating at programmed temperature in the range 35—100°, and 200 X 0.30 cm columns packed with 5% SE 30 on 80—100 mesh HMDS-Chromosorb W, in the range 100—150°). Conversions were evaluated on the basis of unreacted (Ia).

3-Methyl-1-pentyne (Ib), 3,4-dimethyl-1-pentyne (Ic) and 3,4,4-trimethyl-1-pentyne (Id) were treated with Al(i-Bu)$_3$ following the above procedure. The reaction mixtures were analyzed by GLC on 200 X 0.30 cm columns packed with 10% squalane on 60—80 mesh Chromosorb W, with programmed temperatures in the range 35—120°.

Identification of the products

All the reaction products, unless otherwise indicated, were identified by comparison of their GLC retention times with those of authentic samples, their relative percentages being determined from the areas of the corresponding chromatographic peaks.

2-n-Butyl-4-methyl-1-pentene (IIIa) and 2-methyl-*trans*-4-nonene (IVa) were recovered by preparative GLC on 450 X 0.8 cm columns packed with 5% Se 52 on 60—80 mesh Chromosorb G, at 110°.

The NMR spectrum (CDCl$_3$) of (IIIa) showed resonance signals at δ 0.89 (m, 9, CH$_3$), 1.33 (m, 4, CH$_2$), 1.60 (m, 1, CH), 1.92 (m, 4, CH$_2$—C=), 4.61 (d, 1, =CH$_2$), 4.65 ppm [d, 1, =CH$_2$; J(HH) 2.3 Hz].

The NMR spectrum of (IVa) (CDCl$_3$) showed signals at δ 0.89 (m, 9, CH$_3$), 1.32 (m, 4, CH$_2$), 1.60 (m, 1, CH), 1.92 (m, 4, CH$_2$—C=), 5.39 ppm [two sextets of lines, 2, CH=CH; J(HH) 14.1 Hz].

The structure of 2-sec-butyl-4-methyl-1-pentene (IIIb) was, because of the small amount present in the reaction products, assigned only on the basis of the mass spectrum: *m/e* (rel. intensity): 140 (13.0, parent), 112 (15.2), 111 (6.5), 98 (6.5), 97 (13.0), 84 (15.2), 83 (37.0), 70 (47.8), 69 (100), 67 (10.9), 57 (17.4), 56 (28.3), 55 (87.0), 43 (41.3), 41 (52.2), 29 (15.2), 27 (15.2).

The diene (V) was recovered from the product mixture by careful distillation. The infrared spectrum showed prominent bands at 3080, 1630, 1050, 895 cm^{-1}. The NMR spectrum consisted of resonances at δ 0.90 (m, 12, CH$_3$), 1.33 (m, 8, CH$_2$), 1.60 (m, 1, CH), 2.02 (m, 6, CH$_2$—C=), of two triplets of lines at 4.62 (1, =CH$_2$; J 2.6, J 0.5 Hz) and at 4.92 (1, =CH$_2$; J 2.6, J 1.5 Hz) and of a triplet of triplets at 5.19 ppm (1, =CH—; J 7.0, J 1.2 Hz). Mass spectrum *m/e* (rel. intensity): 222 (57.1, parent), 207 (10.0), 179 (41.4), 165 (100), 151 (12.9), 137 (25.7), 124 (38.6), 123 (72.8), 109 (85.7), 95 (65.7), 93 (15.7), 91 (14.3), 83 (12.9), 82 (20.0), 81 (68.6), 79 (20.0), 77 (14.3), 69 (31.4), 67 (41.4), 57 (18.6), 55 (41.4), 53 (11.4), 43 (35.7), 41 (42.9), 39 (8.6), 29 (17.1), 27 (11.4).

Reaction between $Al(i\text{-}Bu)_3$ *and (+)(S)-3,4-dimethyl-1-pentyne (Ic)*

In the general procedure described, 10.90 g (55 mmole) of $Al(i\text{-}Bu)_3$ reacted at 25° for 40 h with 5.30 g (55 mmole) of (+)(*S*)-3,4-dimethyl-1-pentyne, n_D^{25} 1.4007, $[\alpha]_D^{25}$ +12.90 (neat) [10b]. The crude products were fractionally distilled. Preparative GLC of the low-boiling fraction on 270 × 0.8 cm 20% Carbowax 20M on Chromosorb A 45-60 mesh plus 200 × 0.8 cm 20% Carbowax 1500 on Chromosorb W 60-80 mesh columns at 70° afforded 1.7 g of (+)(*S*)-(Ic), n_D^{25} 1.4007, $[\alpha]_D^{25}$ +12.94 (neat) and 1.0 g of (+)(*S*)-3,4-dimethyl-1-pentene (IIc), n_D^{25} 1.3963, $[\alpha]_D^{25}$ +19.80 (neat) [10b]. Preparative GLC of the residual fraction on 500 × 0.8 cm 25% 3,3′-oxydipropionitrile on Chromosorb P 60-80 mesh columns gave (+)(*S*)-2,3,7-trimethyl-*trans*-4-octene (IVc), $[\alpha]_D^{25}$ +16.33 (*c* 22.41, n-heptane).

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