15. Reaction of Tribenzylaluminium with Acetylene

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Summary. Acetylene reacts smoothly with tribenzylaluminium both by 'normal' addition to the Al—C bond and by aromatic substitution in *ortho* position; further addition reactions can take place.

In connection with our work on the preparation and behaviour of unsaturated organoaluminium compounds, we wish to report the following results for the reaction between tribenzylaluminium (I) and acetylene.

Acetylene reacts rapidly with I in benzene under mild conditions, *i.e.* room temperature and atmospheric pressure, as is to be expected for monomeric organoaluminium compounds [1]. The rate of further uptake of acetylene decreases considerably after one equivalent has been absorbed. The reaction was quenched with water after absorption of three equivalents of acetylene and the hydrolysis products were examined. A full picture of the composition of the resulting hydrocarbon mixture is shown in the Table.

All the products were isolated by means of preparative VPC. and separately characterized: the NMR., IR., and mass spectra of III and IV were identical with those of authentic samples.

The structures of V and VI were elucidated from their NMR. and mass spectra:

V: mass spectrum, *m/e*: 129 (100%), 128 (70), 144 (M^+, 69.5), 115 (40), 127 (20), 143 (18), 130 (12), 117 (10), 141 (9.5), 39 (9.5). – NMR. spectrum (CCl_4, 220 MHz): $\tau_A = 7.68$, *s*, 3H; $\tau_B = 4.71$, *q*, 2H; $\tau_C = 4.47$, *q*, 2H; $\tau_D = 3.06$, *q*, 2H; $\tau_E = 2.95$, *t*, 1H; $\tau_F = 2.74$, *d*, 2H; $J_{B-C} = 2$ Hz $J_{B-D(cis)} = 11$ Hz; $J_{C-D(trans)} = 17$ Hz; $J_{E-F} = 8$ Hz.

VI: mass spectrum, *m/e*: 129 (100%), 221 (67), 236 (M^+, 41), 105 (30.5), 91 (23), 104 (16), 128 (15), 115 (14), 144 (14), 130 (13). – NMR. spectrum (CCl_4, 60 MHz): $\tau_A = 8.67$, *d*, 3H; $\tau_B = 8.02$, *s*, 3H; $\tau_C = 7.80$, *s*, 3H; $\tau_D = 6.12$, *m*, 1H; $\tau_E = 4.12$, *q*, 1H; $\tau_F = 3.57$, *d*, 1H; $\tau_G = 2.60–3.20$, *m*, 8H; $J_{A-D} = 7$ Hz; $J_{D-E} = 9$ Hz; $J_{E-F} = 11$ Hz.

Unexpectedly the product of 'normal' addition of the benzylaluminium to the triple bond, *i.e.* allylbenzene, accounts for only a minor fraction of the hydrocarbon mixture; the *ortho* substitution in the aromatic ring yielding toluene derivatives appears to be the predominant mode of reaction[1].

The formation of disubstituted product V is remarkable. This seems to exclude a migration of the aluminium atom during the reaction as was suggested in the mechanisms proposed in other cases in which *ortho* substitution in benzyl-metal compounds occurred [2] [3]. In addition, we feel that the formation of VI, formally a dimer of IV, can not be reasonably explained by a coupling reaction. Although no evidence is

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[1] In the reaction between I and diphenylacetylene 'normal' addition occurs exclusively [2]; on the other hand, *ortho* substitution in the benzyl group was observed in the high temperature reaction between tribenzylboron and ethoxyacetylene [3], and in the reaction between I and carbon dioxide [2].

Hydrolysis products obtained from addition of acetylene to I

Compound	Yield %[a]	D atom content after deuterolysis
Toluene (II)	26	1
Allylbenzene (III)	9	1
o-Vinyltoluene (IV)	40	1–2[b]
2,6-Divinyltoluene (V)	10	1–2[c]
1,3-Ditolyl-1-butene (VI)	13	2

[a] Based on the starting benzyl groups (VPC. evaluation).

[b] Mono- and di-deuterated species present in an approximately 2:1 ratio.

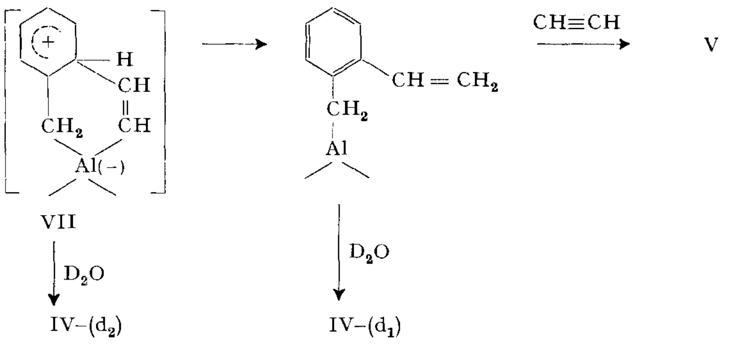
[c] Mono- and di-deuterated species present in an approximately 1:1 ratio.

available for the relative position of the aromatic substituents in VI, analogy with the other products strongly indicates bis-*ortho* substitution.

In order to throw some light on the mechanism of this reaction, we decomposed the initial addition products with deuterium oxide.

The deuterium content in each component of the resulting hydrocarbon mixture is given in the Table. The position of the deuterium atoms in V and VI was determined from their NMR. spectra: V has one D on the methyl group (the signal at $\tau = 7.68$ is split into three equivalent peaks, $J_{D-H} = 2$ Hz), and a second D, when present, on a methylenic group (as shown by the attenuation of the signal in the $=CH_2$ region); VI has one deuterium atom on each aromatic methyl group (the signals at $\tau = 8.02$ and $\tau = 7.80$ are split into three equivalent peaks, $J_{D-H} = 2$ Hz).

Although no definite mechanism can be postulated from these results, we nevertheless think that an intermediate such as VII (see Scheme) could explain both the formation of mono- and dideuterated IV and V upon deuterolysis and the double substitution in the aromatic nucleus, *i.e.* the formation of V.



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