

Tableau 1. *Distillation fractionnée, sous 15 Torr, de 602 g de produit de la réaction de l'ainoéthanol avec 3 équiv. d'acide aminoéthylsulfurique et 6 équiv. de NaOH*

Fraction	p.éb./15 Torr °C	Quantité		Analyses centésimales				Composition du mélange HOCH ₂ CH ₂ NH(CH ₂ CH ₂ NH) _n H
		g	%	C	H	N	O ^{a)}	
I	35–65	38	6,3	22,3	11,5	10,7	55,5%	H ₂ O, HOCH ₂ CH ₂ NH ₂ + très peu de produits à n = 1 et 2
II	65–91	87	14,4	38,5	11,6	22,9	27,0%	HOCH ₂ CH ₂ NH ₂ + davantage de produits à n = 1 et 2, peu d'eau
III	91–148	116	19,2	46,5	11,7	26,5	15,3%	Beaucoup de produit à n = 1 et peu à n = 2
IV	148–208	144	23,9	48,8	11,8	28,0	11,4%	Peu de produit à n = 1, beaucoup à n = 2, peu à n = 3 et 4
V	208–230	106	17,6	51,3	11,7	29,9	7,1%	Beaucoup de produit à n = 3 et 4, peu à n = 5 et 6
VI	230–295	96	15,9	55,3	11,1	31,4	2,2%	Produits à n jusqu'à 9 et davantage, accompagnés très probablement de dérivés pipéraziniques
Résidu (solide)	–	15	2,4					

^{a)} La teneur en oxygène a été calculée par différence.

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113. Allyl-Aluminium Compounds

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Summary. The preparation of aluminium derivatives containing allyl or methallyl groups is reported. Their reactivity and physical properties are discussed.

Allyl-aluminium compounds have been investigated in solution¹⁾ and although the etherates of allyl-, methallyl-, and crotyl-aluminium seem to be stable at room temperature [2], no pure allyl-aluminium has been isolated as yet.

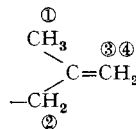
During an investigation on the preparation of 1,3-dialuminium alkanes [3], we carried out redistribution reactions of trimethyl-aluminium with *tris*-allyl-boron,

¹⁾ For a comprehensive review see [1a].

tris-methallyl-boron, and *tris*-crotyl-boron, using $\text{AlR}_3:\text{BR}_3$ molar ratios of 3:1. After removal of trimethyl-boron at low temperature, a crystalline compound was obtained in the case of the allyl and methallyl product mixture, but not in the case of the crotyl derivative.

Methallyl-dimethyl-aluminium (**1**) recrystallized from toluene/pentane is thermally stable, and melts at 72–73°; according to cryoscopic measurements in benzene it is dimeric. By methanolysis, methane and isobutene in the molar ratio of 2:1 are evolved quantitatively.

Chemical shifts in NMR. spectra of methallyl-boron and -aluminium (toluene- d_6 , 60 MHz)



Compound	Temperature	Chemical shift (τ)			
		H(1)	H(2)	H(3)	H(4)
<i>Tris</i> -methallyl-boron	–70°	8.40	7.87	5.14	4.89
	0°	8.34	7.79 (broad)	5.15 (broad)	
	+30°	8.37	High background noise (5–8 ppm)		
	+80°	8.30	6.50		
Methallyl-dimethyl-aluminium (1)	+30°	7.92	6.79		
	–70°	broad unresolved signals			

Allyl-dimethyl-aluminium (**2**) undergoes slow decomposition at room temperature, but can be kept unchanged for days at temperatures below –10°. Because of its instability, attempts at purification by recrystallization failed, and all spectral and physical determinations showed clearly the presence of decomposition products. **2**, washed with pentane, melts between 52° and 57° (dec.). Gas analysis of the methanolysis products was in agreement with the structure **2**.

The crotyl derivative similarly obtained was definitely more reactive. The gas evolved upon methanolysis was a mixture of methane and 1-butene in a 2:1 ratio, as expected for crotyl-dimethyl-aluminium, but only when the crotyl derivative had been kept at temperatures below –10°.

Analogous redistribution reactions carried out between triethyl-aluminium and the allyl derivatives of boron gave in all cases thermally unstable products; if kept at temperatures below –10°, however, the composition of the gases evolved upon methanolysis was consistent with the formulas of allyl-diethyl-aluminium, methallyl-diethyl-aluminium, and crotyl-diethyl-aluminium, respectively.

Investigation of the NMR. spectrum of **1** at +30° and –70°, and comparison with that of *tris*-methallyl-boron at various temperatures give some interesting information on the structure of methallyl-aluminium derivatives.

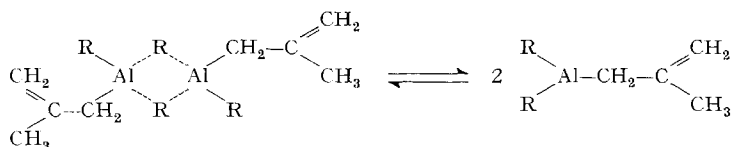
Tris-methallyl-boron at –70° shows a spectrum of the type ABX_2Y_3 (see table); at 0° two broad bands exist, for the methylene group bound to the boron atom and for the terminal methylene group respectively, which disappear at room temperature giving a high background noise, and coalesce to a single signal at higher temperatures.

At $+80^\circ$, a spectrum of the type A_4X_3 exists. This behaviour is completely analogous to that of *tris*-allyl-boron [4], which was interpreted by assuming the existence of a normal allylic structure at low temperature and a dynamic structure involving rapid exchange with allylic rearrangement at higher temperatures.

In the case of **1** only one signal exists for the four methylenic protons at $+30^\circ$, which degenerates into a series of broad bands at -70° . It seems, therefore, that the dynamic structure is present in the aluminium compounds at much lower temperatures than in those of boron. The persistence of the dynamic structure at lower temperatures might be connected with the electron deficient structure of the aluminium compounds; in fact, the less electron deficient etherates of allyl- and methallyl-aluminium maintain the normal allylic structure at least up to room temperature [2].

A sharp signal from the methyl groups bound to the aluminium atom appears at 10.35 ppm at $+30^\circ$, which degenerates to a broad band at -70° .

The aforementioned results show that **1** is a rather stable compound, whereas the analogous allyl- and crotyl-derivatives are more reactive. It is interesting that the stability of **1** is considerably higher than that of the corresponding diethyl derivative, which very easily yields di- and tri-merization products, as will be discussed in a following paper. The difference in their stability might be connected with the equilibrium between monomeric and dimeric forms



which is well-known to be more displaced toward the dimer when methyl groups are involved in the bridging bonds [1 b].

Experimental. – All operations were carried out in a dry nitrogen atmosphere. Solvents were distilled over sodium. Commercial trimethyl-aluminium (*K & K Laboratories*) and triethyl-aluminium (*Ftuka*) were distilled before use.

Tris-methallyl-boron. Boron trifluoride etherate (0.95 moles) in ether (150 ml) was added dropwise to a solution of methallyl-magnesium chloride (1 mole) in ether (1 l). The reaction mixture was refluxed for 1 h, the solvent distilled off at atmospheric pressure and the product twice distilled in vacuo. *Tris*-methallyl-boron, b.p. $77-78^\circ/10$ Torr, was obtained in 71% yield.

Tris-allyl-boron, b.p. $48-50^\circ/10$ Torr (lit. [5] $44-46^\circ/10$ Torr), and *tris-crotyl-boron*, b.p. $90-92^\circ/8$ Torr (lit. [6] $94^\circ/12$ Torr), were prepared by analogous procedures.

Methallyl-dimethyl-aluminium (1). A solution of *tris*-methallyl-boron (8.8 g, 0.05 moles) in toluene (50 ml) was added to a solution of trimethyl-aluminium (10.8 g, 0.15 moles) in toluene (100 ml) cooled at -70° . After one night at room temperature, the solvent and all volatile products were removed from the mixture by prolonged evacuation with stirring at room temperature. The solid residue was dissolved without heating in toluene (20 ml), an equal volume of pentane was added, and the product recrystallized by cooling at -70° . Rapid filtration through a sintered glass filter applied to a lateral neck of the reaction vessel, washing with pentane, and drying under vacuum, were carried out without transferring the product from the original flask. **1**, m.p. $72-73^\circ$, was obtained in 75% yield. The gas-volumetric analysis gave the following result: 0.211 g of **1** on hydrolysis yielded 125 ml (at normal conditions) of gas (calc. 126 ml), 67% methane and 33% isobutene evaluated by VPC.

The other redistribution reactions were carried out by analogous procedures.

Allyl-dimethyl-aluminium (**2**), m.p. 52–57° (dec.), was isolated in 61% yield. The gas-volumetric analysis gave the following result: 0.165 g of **2** on hydrolysis yielded 107 ml (at normal conditions) of gas (calc. 113 ml), 68% methane and 32% propylene evaluated by VPC.

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114. Die Dienol-Benzol-Umlagerung von Propargylcyclohexadienolen: aromatische [1,2]-, [3,3]- und [3,4]-sigmatropische Umlagerungen

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Summary. The acid catalysed dienol-benzene rearrangement of methyl substituted *o*- and *p*-propargylcyclohexadienols (**18–22**, **34** and **35**) was investigated. In the first step water is eliminated to yield the corresponding methyl propargyl benzonium ions (cf. scheme 6, **a**), which undergo [1*s*, 2*s*] sigmatropic rearrangements to give propargylbenzenes (**28**, **29**, **30**, **38**) and [3*s*, 4*s*] sigmatropic rearrangements to give allenylbenzenes (**24–27**, **40**) (cf. schemes 2, 3, 5, 6). [3*s*, 3*s*] sigmatropic rearrangements occur only to a small extent. In the rearrangement of 2-propargyl-2,4,6-trimethylcyclohexa-3,5-dien-1-ol (**18**) a [1*s*, 2*s*] sigmatropic methyl shift is observed (4%).

1. Einleitung. – Vor einiger Zeit berichteten wir ausführlich über die Dienol-Benzol-Umlagerung von Allylcyclohexadienolen [2], in deren Verlauf [1*s*, 2*s*]-, [3*s*, 3*s*]- und [3*s*, 4*s*]-sigmatropische Umlagerungen auftreten. So wird z. B. sowohl das *o*-Allyldienol **1** als auch das *p*-Allyldienol **2** bei der Behandlung mit *p*-Toluolsulfonsäure in Äther über das Benzoniumion **a** in 2-, 3- und 4-Allyltoluol (**3**, **4** bzw. **5**) im Verhältnis von etwa 5:1:3 umgelagert. Wir untersuchten nun die Dienol-Benzol-Umlagerung einer Reihe von *o*- und *p*-Propargylcyclohexadienolen, bei denen [1*s*, 2*s*]-sigmatropische Umlagerungen zu Propargylbenzolen, [3*s*, 3*s*]- und [3*s*, 4*s*]-sigmatropische Umlagerungen hingegen zu Allenylbenzolen¹⁾ führen müssten. Die benötigten Propargyldienole wurden durch Propargylierung entsprechender Phenole und anschließende Reduktion der Propargyldienone mit Lithiumaluminiumhydrid erhalten.

¹⁾ Eine solche [3*s*, 4*s*]-Umwandlung wurde von uns schon bei der Umlagerung eines Propargyldibenzo-cyclohexadienols in Eisessig beobachtet [3]. Hierüber wird noch ausführlich berichtet.