119. An Alkyl-Aluminium Promoted Stereospecific Addition to Vinyl Olefins

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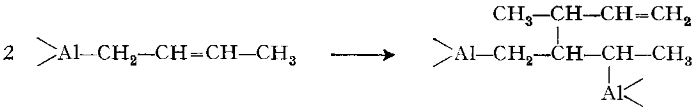
(23. II. 73)

Summary. The reaction of tris-crotyl-boron with vinylic olefins in the presence of triethyl-aluminium, results in the addition of an α-methylallyl group and an aluminium atom to the double bond, as indicated by the hydrolysis products. The stereochemical aspect of the reaction is discussed and a mechanism is proposed to explain the preferential formation of one diastereoisomer.

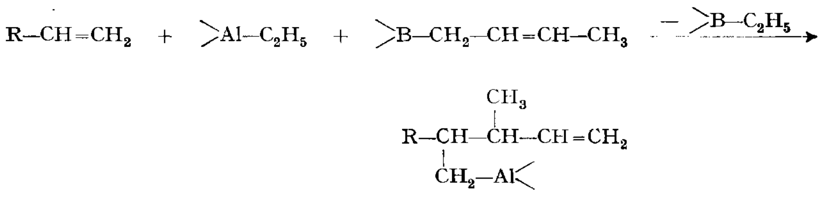
In a recent discussion on allyl-aluminium compounds [1] the particular reactivity of crotyl groups bound to aluminium was pointed out. The investigation of the hydrocarbons obtained from the hydrolysis of the redistribution product between triethyl-aluminium and tris-crotyl-boron at room temperature, showed that the first step of the sequence of reactions leading to polymerization of the organo-aluminium product, is an auto-addition according to equation (1):



$$2\ {>}\mathrm{Al{-}CH_2{-}CH{=}CH{-}CH_3} \longrightarrow {>}\mathrm{Al{-}CH_2{-}CH(CH_3{-}CH{-}CH{=}CH_2){-}CH(Al}{<}\mathrm{){-}CH_3} \qquad (1)$$

In fact the only C_8-component, isolated from the mixture, was identified as 3,4-dimethyl-1-hexene (**1**). This could have been predicted, on the basis of what is known about allyl- [2] and methallyl- [3] aluminium compounds, except for the complete allylic rearrangement of the crotyl group in the addition across the double bond. The subsequent reactions however are much more complicated than expected, for amongst the C_{12}-hydrocarbons, which constitute the major part of the mixture, at least ten different olefins were detected by combined VPC.-MS. investigation.

In order to test the reactivity of the crotyl-aluminium system in addition reactions other than the auto-addition, the redistribution between triethyl-aluminium and tris-crotyl-boron was carried out in the presence of a vinyl olefin in large excess. A smooth, slightly exothermic reaction took place and went to completion soon after mixing the reagents. Hydrolysis of the product, after removal of all the volatile components of the mixture at room temperature, revealed that an addition of the unsaturated organo-aluminium system to the olefinic double bond had occurred predominantly, according to equation (2):



$$\mathrm{R{-}CH{=}CH_2} + {>}\mathrm{Al{-}C_2H_5} + {>}\mathrm{B{-}CH_2{-}CH{=}CH{-}CH_3} \xrightarrow{-\,{>}\mathrm{B{-}C_2H_5}} \mathrm{R{-}CH(CH_2{-}Al}{<}\mathrm{){-}CH(CH_3){-}CH{=}CH_2} \qquad (2)$$

The reaction (2) was carried out in different solvents, such as pentane, cyclohexane, toluene, or the reacting olefin itself, and at different temperatures between −10 °C and +25 °C, without appreciably affecting the qualitative and quantitative results. The final products obtained from different substrates are reported in Table 1.

Table 1. *Main products obtained from the reaction (2) after hydrolysis*

Starting olefin	Product	Yield %[a]
1-Butene	3,4-Dimethyl-1-hexene (**1**)	50
3-Methyl-1-butene	3,4,5-Trimethyl-1-hexene (**2**) **1**[b]	28 24
1-Hexene	3,4-Dimethyl-1-octene (**3**)	55
Styrene	3-Methyl-4-phenyl-1-pentene (**4**) 3-Methyl-5-phenyl-1-pentene (**5**)	48 5

[a] Based on the starting crotyl groups.
[b] Originated from reaction (1).

All the olefins produced were isolated and their identity determined by comparison of their VPC.-retention times, mass spectra and NMR.-spectra with those of standard samples prepared by conventional methods.

In absence of alkyl-aluminium, tris-crotyl-boron had no effect on 1-hexene under normal conditions; an attempt to promote the addition with catalytic quantities of triethyl-aluminium was not encouraging.

When tris-crotyl-boron was replaced with tris-allyl-boron or tris-methallyl-boron, the usual auto-addition reactions [2] [3] prevailed and no addition to the olefin was observed.

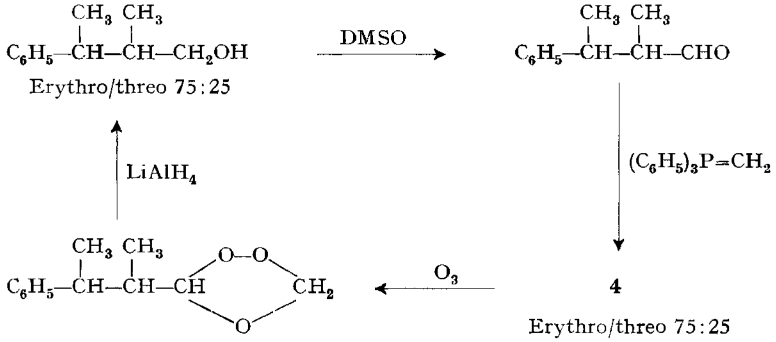
From preliminary experiments, only mono-substituted ethylenes seem capable of addition according to (2); in fact, internal and vinylidene olefins ($CH_2 = CR_1R_2$) gave no addition products under analogous conditions.

Work up of the reaction mixture with (O-d_1)-methanol gave monodeuterated olefins. Only **1**, when obtained as a minor product in the reaction with 3-methyl-1-butene, contained two deuterium atoms, indicating the reaction (1) as the probable origin of this byproduct. The location of the deuterium atom, established by NMR. analysis, was on the methyl group in 5 position, in the major product obtained from styrene, namely 3-methyl-4-phenyl-1-pentene-(5-d_1), as expected from the equation (2).

In the reaction (2) two adjacent asymmetric carbon atoms are formed when $R \neq H$ or CH_3, and therefore the product is a mixture of the two possible diastereoisomers. As the steric course of the reaction could give important information about its mechanism, particular attention was paid to determine the *erythro*:*threo* ratio in the products.

Direct VPC. separation of the two diastereoisomers was possible only in the case of **4**. The assignment of the configuration was made by comparison with a standard prepared from a sample of 2-methyl-3-phenyl-1-butanol of known diastereomeric composition [4], by the following reaction sequence:

Scheme 1



Ozonization of **4** followed by reduction with $LiAlH_4$, proved that no change of configuration occurred through the whole sequence.

1 was converted to 2,3-dimethylpentanoic acid by a known procedure [5], and the two diastereoisomers of its methyl ester were qualitatively identified by NMR. analysis [6] and quantitatively determined by VPC.

By analogous procedure **3** was converted into 2,3-dimethyl-heptanoic acid; the two diastereoisomers of its methyl ester could be separated and evaluated by VPC. The assignment of the configurations was made on the basis of the NMR. spectrum, by virtue of the analogy in the methyl region with that of methyl 2,3-dimethylpentanoate.

On hydrogenation **2** afforded 2,3,4-trimethylhexane, the diastereoisomers of which are separable by VPC. [7] and their relative retention times are known [8].

As it is reasonable to assume that no significant change occurred in the diastereomeric compositions, during the aforementioned transformations, the proportions of the VPC. separable derivatives, reflect those of the relative starting olefins. The results are reported in Table 2.

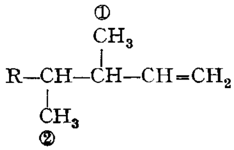
In Table 3 are reported the NMR. parameters relative to the methyl region of the single diastereoisomers, obtained for each compound, from the comparison between spectra of different samples having different diastereomeric composition.

Table 2. *Diastereomeric compositions of the olefins obtained from reaction (2)*

Olefin	Erythro : Threo
1	75 : 25
2	93 : 7
3	67 : 33
4	63 : 37
1[a]	43 : 57

[a] Obtained from reaction (1).

Table 3. *Chemical shifts in the methyl region of the NMR.-spectra of 3,4-dimethyl-substituted vinylic olefins* (CCl_4, 100 MHz)



$$R{-}CH(\underset{②}{CH_3}){-}CH(\overset{①}{CH_3}){-}CH{=}CH_2$$

Olefin	Chemical shift (τ)[a]		
	CH_3 (1)	CH_3 (2)	CH_3 (R)
Erythro-**1**	9.01 (*d*)	9.16 (*d*)	9.04 (*t*)
Threo-**1**	9.05 (*d*)	9.09 (*d*)	9.09 (*t*)
Erythro-**2**	9.00 (*d*)	9.24 (*d*)	9.06 (*d*); 9.18 (*d*)
Threo-**2**	9.06 (*d*)	9.21 (*d*)	9.09 (*d*); 9.24 (*d*)
Erythro-**3**	8.97 (*d*)	9.12 (*d*)	9.03 (*t*)
Threo-**3**	9.00 (*d*)	9.05 (*d*)	9.09 (*t*)
Erythro-**4**	9.17 (*d*)	8.79 (*d*)	–
Threo-**4**	9.03 (*d*)	8.75 (*d*)	–
Erythro-(5-d_1)-**4**	9.17 (*d*)	8.81 (*sext.*)	–
Threo-(5-d_1)-**4**	9.03 (*d*)	8.77 (*sext.*)	–

[a] In each case $J_{H-H} = 7$ Hz, $J_{H-D} = 2$ Hz.

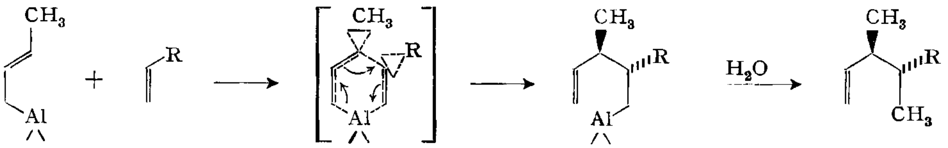
From the above results, the following points are noteworthy:

A. The extraordinary ease of the addition of an α-methyl-allyl group to a simple olefinic double bond, promoted by the system triethyl-aluminium/tris-crotyl-boron, is apparent from the extremely mild conditions and the rapidity of the reaction. For this reason no byproducts due to auto-addition (1) or collateral reactions were found, except in the case of 3-methyl-1-butene, in which reaction (1) seems to compete effectively with the addition (2). This fact, indicating a high sensitivity of the reaction (2) to steric factors, may be due to a lowering of the reaction rate caused by the steric hindrance of branching close to the double bond.

B. The remarkable specificity of the addition, in the case of aliphatic olefins, makes the reaction (2) valuable, for particular cases, as a preparative method. The presence of **5** among the products obtained from styrene reveals that the addition to this olefin can occur in both directions: analogous behaviour was observed in the hydroalumination reaction of styrene [9].

C. From Table 2 the stereospecificity of the reaction (2) is evident, the *erythro*-form being favoured even to the extent of being practically the only diastereoisomer in one case. This fact can be reasonably explained by a mechanism involving a cyclic transition state (Scheme 2), in which the substituents on the two carbon atoms that

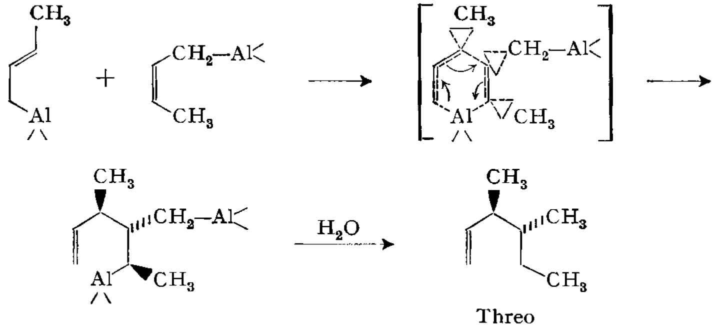
Scheme 2



Erythro

are becoming asymmetric, tend to assume a *trans*-configuration in order to reduce steric interactions. It is not surprising therefore that the highest stereospecificity was observed in the case of the maximum steric encumbrance, namely when R = isopropyl. The predominance of the opposite configuration in **1** obtained from the auto-addition of crotyl groups seems to confirm this hypothesis (*cf.* Scheme 3).

Scheme 3



Experimental

Organometallic materials were handled in a dry nitrogen atmosphere. Commercial triethylaluminium (Fluka) was distilled before use; tris-crotyl-boron was prepared according to [1].

Addition reactions. – Tris-crotyl-boron (1.8 g, 10.2 mmol) was added dropwise to a solution of triethylaluminium (1.2 g, 10.5 mmol) in 1-hexene (10 ml) and cyclohexane (10 ml) under vigorous stirring. After 30 m all the volatile components of the mixture were removed under vacuum at room temperature. The residue was cooled in an ice bath, and methanol (30 ml) added cautiously, and the mixture was distilled. Addition of water to the distillate, caused separation of an organic layer consisting of practically pure **3** (2.35 g, 55% yield); distillation was discontinued when no such layer was formed.

The other addition reactions were performed by analogous procedures. The addition to 1-butene, carried out in pentane at –10°, afforded **1** in 50% yield. The reaction with 3-methyl-1-butene, in absence of other solvents at 0°, gave a mixture of **1** and **2** (30:70 by weight), from which pure samples of the two compounds were obtained, for analytical purposes, by preparative VPC. The product obtained from the reaction with styrene, carried out in toluene at room temperature, was extracted with boiling pentane from the hydrolysed reaction mixture, and both components **4** and **5** (90:10) were collected in one fraction by distillation; their separation was accomplished by preparative VPC.

Preparation of standard olefins. – *3,4-Dimethyl-1-hexene* (**1**). The *Wittig* reaction between methylene-triphenyl-phosphorane and 2,3-dimethylpentanal, prepared according to [10] afforded **1** in 66% yield, b.p. 109–110° (lit. [5] b.p. 109–110°). MS.: 56 (100), 41 (58), 57 (55), 29 (40), 55 (40), 84 (26.5), 27 (15), 39 (12), 83 (9.5), 70 (9); 112 (M^+, 0.5).

3,4,5-Trimethyl-1-hexene (**2**). α-Isopropylacrolein, available in our laboratory from previous work [11], reacted with ethoxymethyl-magnesium chloride to give, according to the general procedure [12], 1-ethoxy-3-isopropyl-3-buten-2-ol, b.p. 80–82°/14 Torr, which was hydrogenated at atmospheric pressure, over Pt/C, to the corresponding saturated ethoxyalcohol. 1-Ethoxy-3,4-dimethyl-2-pentanol was oxydized to the corrresponding ketone using a method adapted from that used in the preparation of methoxyacetone [13]. 1-Ethoxy-3,4-dimethyl-2-pentanone afforded by reaction with methyl-magnesium iodide, 1-ethoxy-2,3,4-trimethyl-2-pentanol, which was converted, by the general procedure [12], to 2,3,4-trimethylpentanal, semicarbazone m.p. 119–120° (lit. [14] m.p. 120–121°). The crude products obtained in the intermediate steps, controlled by VPC., were pure enough to be used without further purification; the mass spectrum of each compound was consistent with the formula assigned. The overall yield for the five steps was 36%. 2,3,4-Trimethylpentanal, obtained 99% pure through its bisulphite derivative, was finally converted, by reaction with methylene-triphenyl-phosphorane, to **2** in 80% yield; b.p. 132–133°. MS.: 43 (100), 71 (70), 55 (33), 70 (29), 41 (21), 29 (10.5), 56 (9), 27 (8.5), 69 (8), 98 (8); 126 (M^+, 0.3).

3,4-Dimethyl-1-octene (**3**). 2,3-Dimethylheptanal, b.p. 176–177°, mass spectrum: M^+ 142 ($<$0.5%), was prepared in 25% yield from 2-bromohexane and methoxyacetone, by a procedure analogous to that followed for 2,3-dimethylpentanal. The aldehyde reacted with methylene-triphenyl-phosphorane to afford **3** in 64% yield; b.p. 154–155°. MS.: 43 (100), 84 (32), 56 (30), 55 (27), 41 (25), 85 (21), 57 (18), 29 (15), 69 (12), 27 (11); 140 (M^+, 0.3).

3-Methyl-4-phenyl-1-pentene (**4**). The preparation of 2-methyl-3-phenyl-1-butanol according to [4] from a diastereomeric mixture of its precursor, gave the *erythro*- and *threo*-forms in the ratio of 75:25 respectively, based on the NMR. spectrum [4] and confirmed by VPC. after a separation performed on a 16 m *Scot* column coated with carbowax 20 M, in which the *erythro*-form has a higher retention time. The oxydation with dimethylsulfoxide [cf. Scheme 1] was effected at room temperature, in the presence of dicyclohexylcarbodiimide and phosphoric acid, according to [15]. 2-Methyl-3-phenyl-butanal, MS.: M^+ 162 (21%), obtained in 63% yield, reacted with methylene-triphenyl-phosphorane to afford *erythro*- and *threo*-**4**, b.p. 42–44°/0.02 Torr, in 35% yield. MS. (identical for both diastereoisomers): 105 (100), 106 (25), 77 (19), 79 (18), 103 (17), 104 (16), 160 (M^+, 7), 51 (6.5), 91 (6), 27 (6).

A sample of **4** was ozonized in pentane at – 70° and the ozonide was reduced with $LiAlH_4$ to give back 2-methyl-3-phenyl-1-butanol, which had the same diastereomeric composition as that used for the synthesis.

3-Methyl-5-phenyl-1-pentene (**5**). 1-Methoxy-2-methyl-4-phenyl-2-butanol, b.p. 108–109°/0.05 Torr, obtained in 70% yield by reaction of 2-phenylethyl-magnesium bromide with methoxyacetone, was converted, by the general procedure [12], to 2-methyl-4-phenyl-butanal, b.p. 93–94°/1 Torr (lit. [16] b.p. 134–136°/2.4 Torr), MS.: M^+ 162 (8%); the yield was 70%. The aldehyde, by reaction with methylene-triphenyl-phosphorane, afforded **5** in 71% yield; b.p. 115–116°/30 Torr (lit. [17] b.p. 90–92°/13 Torr). MS.: 104 (100), 91 (85), 92 (62.5), 105 (50), 41 (25), 69 (20), 65 (16), 160 (M^+, 16), 77 (12.5), 39 (12).

Determination of diastereomeric compositions (cf. Table 2). – Erythro- *and* threo-**1**. A standard sample of methyl 2,3-dimethylpentanoate, in which the ratio *erythro:threo*, evaluated by NMR. analysis [6], was 45:55, was analysed by VPC. on a 33 m *Scot* column coated with apiezon L and gave two peaks having relative areas 45:55 in the order of elution. The olefin **1** of unknown diastereomeric composition was converted to 2,3-dimethylpentanoic acid, through its ozonide and 2,3-dimethyl-1-pentanol, according to [5]. Its methyl ester, obtained by reaction with diazomethane, was analysed by VPC. under the above specified conditions and the *erythro*-form was assigned to the component having lower retention time.

Erythro- *and* threo-**2**, was hydrogenated at atmospheric pressure in the presence of palladium on charcoal. The two diastereoisomers of the paraffin obtained were separated and quantitatively determined by VPC., as satisfactory conditions for their separation [7] and the order of elution [8] have been established.

Erythro- *and* threo-**3**, was converted to methyl 2,3-dimethylheptanoate by a procedure analogous to that followed for the conversion of **1** to methyl 2,3-dimethylpentanoate. Both homologous esters give in the methyl region of their NMR. spectra, separate signals for the two diastereomeric forms (*cf.* [6]), and they show identical patterns and identical chemical shift differences. On this basis the assignments of the frequencies relative to the *erythro*- and *threo*-forms were made by analogy and their ratio approximatively estimated at 2:1 respectively. More accurate quantitative determination was made by VPC. using a 50 m × 0.25 mm column coated with apiezon L, on which the *erythro* form has a lower retention time.

Erythro- *and* threo-**4** were directly separated by VPC. on a 33 m *Scot* column coated with apiezon L; *erythro*- and *threo*-forms were eluted in that order, as determined by comparison with a standard sample.

I wish to thank Mr. *D. Tatone* for help given in the experimental work.

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120. Substoichiometric Extraction of Mercury by Diethyldithiocarbamic Acid

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(31. X. 72)

Summary. The substoichiometric extraction of Hg^{2+} using diethyldithiocarbamic acid and ^{203}Hg tracer was studied. Chloroform was employed to remove the complexes from the aqueous media which were 0.5 M H_2SO_4 or 1 M $HClO_4$ and 0 to 5 M NaCl. – Systems containing Cl^- allowed extraction of Hg^{2+} for all DDC/Hg molar ratios, the extracted complexes being HgCl(DDC) and $Hg(DDC)_2$. Their exchange constant was determined. – In the absence of Cl^-, no extraction could be effected in either system if the DDC/Hg molar ratio was < 1; the H_2SO_4 system remained clear, whereas a precipitate of $HgClO_4(DDC)$ formed in the $HClO_4$ system. For molar ratios > 1, the extraction of Hg^{2+} increased linearly with the addition of DDC, the extracted complex being $Hg(DDC)_2$.

1. Introduction. – The principle of substoichiometric extraction[1]) was introduced into analytical chemistry by *Ruzicka & Stary* [1] and has been recently surveyed [2] [3]. Interest in this method is mainly due to its rapidity, simplicity and high selectivity. Furthermore, it eliminates the need to determine the yield of a radiochemical separation, a distinct advantage in activation analysis.

Application of high-resolution γ-ray spectroscopy to activation analysis diminishes the demand for very high decontamination factors in most radiochemical separations, often making rapid, one-step separations possible. Substoichiometric

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[1]) Substoichiometric extraction involves the use of a chelating agent, the quantity of which is chosen so as to extract only a part of the metal present.