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1962

SovietRxiv

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ADDITION OF DIISOBUTYLALUMINUM HYDRIDE AND TRIISOBUTYLALUMINUM TO VINYLACETYLENE

(Presented by Academician B. A. Arbuzov, April 28, 1962)

In a series of works by K. Ziegler and other chemists it was shown that aluminum hydrides and aluminum alkyls are capable of adding to olefins and acetylenes through multiple bonds ([1]-[7]). We became interested in the possibility and direction of addition of these substances to enyne hydrocarbons. This communication describes experiments on the interaction of diisobutylaluminum hydride and triisobutylaluminum with vinylacetylene. As a result of the addition of diisobutylaluminum hydride to vinylacetylene, followed by demetallation with alcohol, the formation of three hydrocarbons could be expected: divinyl (1,2-addition), ethylacetylene (3,4-addition), and methylallene (1,4-addition).

Investigation of the gaseous products obtained showed that the reaction proceeds predominantly in the direction of formation of divinyl and ethylacetylene; 1,4-addition practically does not occur. These conclusions were drawn on the basis of the results of ordinary gas analysis and chromatographic analysis and investigation of the IR spectrum of the mixture obtained. In the latter there were all the principal absorption bands of divinyl (3090, 1820, 1605, 1588, 1012, 996, 926, and 908 cm^{-1}) and ethylacetylene (3323 and 2154 cm^{-1}). The intense bands at 957 and 857 cm^{-1} characteristic of methylallene ([8]) were practically absent (Fig. 1, 1). Divinyl was also demonstrated by bromination to 1,2,3,4-tetrabromobutane and by condensation with maleic anhydride.

Along with the gaseous substances, a small amount of a liquid condensate was also obtained, which, judging from its boiling range (110-130°) and IR spectrum (Fig. 1, 2), was a mixture of the demetallated adducts of diisobutylaluminum hydride with vinylacetylene through the aluminum-carbon bond in all three possible directions (1,3-diene predominates).

Investigation of the IR spectrum of the reaction mixture before treatment with alcohol showed that the aluminum is located predominantly at the double bond (band at 1527 cm^{-1}) and partly at the triple bond (band at 2075 cm^{-1}) ([9],[10]). There is no absorption band of the terminal acetylenic grouping (about 3300 cm^{-1}) in the spectrum (Fig. 1, 3).

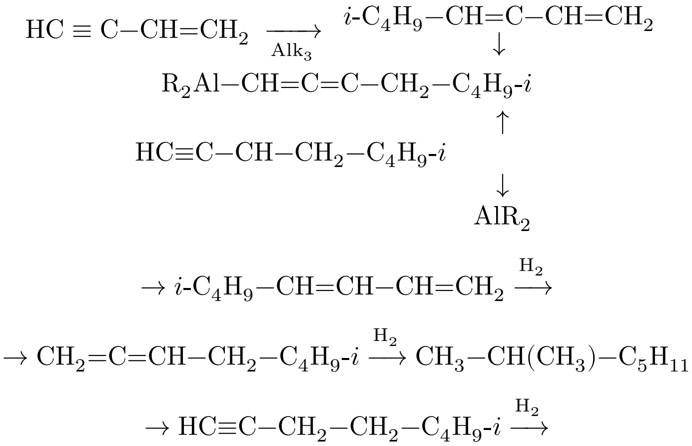
Thus, it was established that the reaction of diisobutylaluminum hydride with vinylacetylene proceeds in the following three directions: 1) addition through the Al—H bond to the double and triple bonds of the enyne (the main direction), 2) addition through the Al—C bond to the double and triple bonds and in the 1,4-position (expressed insignificantly), 3) replacement by aluminum of hydrogen in the acetylene formed*.

As a result of the addition of triisobutylaluminum to vinylacetylene and subsequent demetallation, a mixture of hydrocarbons was obtained which, upon exhaustive catalytic hydrogenation, gave 2-methylheptane. Consequently, the isobutyl radical added only at the ends of the conjugated system. Addition of the radical to the middle atoms should have led to the formation of 2,4-dimethylhexane. Meanwhile

* It is possible that partial addition of diisobutylaluminum hydride to vinylacetylene aluminum takes place in the reaction.

in the region of the bands characteristic of 2,4-dimethylhexane: 996, 970, and 767 cm^{-1}. The IR spectrum of the saturated hydrocarbon obtained by us did not differ from the spectrum of pure 2-methylheptane ([8]).

In the IR spectrum of the initial reaction mixture of hydrocarbons, bands of stretching vibrations of the 1,3-diene (1638, 1595 cm^{-1}), acetylene (2118 cm^{-1}), and allene (1957 cm^{-1}) groupings were found (Fig. 1, 4). Analytical determination revealed 45% acetylene in the mixture. The structure of the 1,4-adduct —the allene hydrocarbon—was unambiguously determined by its IR spectrum. Allenes with a terminal position of the unsaturated grouping have a deformation band near 850 cm^{-1}; allenes with the unsaturated grouping in the middle of the chain, in particular the 4-methylheptadiene-1,2 specially prepared by us (Fig. 1, 7), absorb at 875 cm^{-1}. In the case under study, intense absorption was observed only at 846 cm^{-1}. Consequently, upon formation of the allene, the radical was attached to the ethylene carbon atom, and aluminum to the acetylene carbon atom.



$$HC\equiv C{-}CH{=}CH_2 \xrightarrow[Alk_3]{} i\text{-}C_4H_9{-}CH{=}C{-}CH{=}CH_2$$
$$\downarrow$$
$$R_2Al{-}CH{=}C{=}C{-}CH_2{-}C_4H_9\text{-}i$$
$$\uparrow$$
$$HC\equiv C{-}CH{-}CH_2{-}C_4H_9\text{-}i$$
$$\downarrow$$
$$AlR_2$$
$$\rightarrow i\text{-}C_4H_9{-}CH{=}CH{-}CH{=}CH_2 \xrightarrow{H_2}$$
$$\rightarrow CH_2{=}C{=}CH{-}CH_2{-}C_4H_9\text{-}i \xrightarrow{H_2} CH_3{-}CH(CH_3){-}C_5H_{11}$$
$$\rightarrow HC\equiv C{-}CH_2{-}CH_2{-}C_4H_9\text{-}i \xrightarrow{H_2}$$

The IR spectrum makes it possible to draw a conclusion also about the struc-

Fig. 1. IR transmission spectra

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ture of the 1,2-adduct—the diene hydrocarbon. In this spectrum there were intense bands of stretching and deformation vibrations characteristic of a terminal vinyl group (3088, 997, 901 cm^{-1}), and the usually very intense deformation band of the $CH_2{=}CR_2$ grouping (890 cm^{-1}) was absent. Consequently, addition of triisobutylaluminum at the acetylene bond proceeded in such a way that the radical was attached to the first, and aluminum to the second, carbon atom of the acetylene group. In previously studied cases, addition of aluminum alkyls was observed predominantly according to Markovnikov' s rule (1–7). The IR spectrum also confirms the structure of the adduct at the double bond—the acetylenic hydrocarbon—deduced from exhaustive hydrogenation data. It contains an intense band of the acetylenic CH bond (3320 cm^{-1}). Upon hydration of the reaction mixture with sulfuric acid, methyl isohexyl ketone was obtained, predominantly at the expense of the acetylenic and, possibly, allene hydrocarbons.

The investigation carried out revealed an analogy between the addition to vinylacetylene of alkyl derivatives of aluminum and the addition to its homologs of lithium alkyls (12). In the first case, the principal, and in the second the practically exclusive, direction of addition is associated with entry of the radical into position 4 and with subsequent fixation of the metal in position 1 or 3.

As in the reaction of vinylacetylene with diisobutylaluminum hydride, here also the formation of aluminum-acetylene compounds occurs. In the IR spectrum of the mixture before decomposition there was an intense band of the $Al{-}C{\equiv}C$ bond (2076 cm^{-1}), together with a band of the $Al{-}C{=}C$ bond (1535 cm^{-1}) and $Al{-}C{=}C{=}C$ (1930 cm^{-1}); bands of a free terminal triple bond were absent. In the spectrum of the substance after standing for several days, a gradual disappearance of the bands at 2075 and 1535 cm^{-1} and strengthening of the band···

1930 cm^{-1}, which indicated isomerization of the acetylene and 1,3-diene adducts into an allene adduct (Fig. 1, 6). Indeed, the mixture of hydrocarbons formed upon demetallation after 7 days contains predominantly an allene hydrocarbon.

Fig. 1. IR transmission spectra: 1 —products of addition of diisobutylaluminum hydride via the Al—H bond to vinylacetylene (after demetallation), 2 —the same via the Al—C bond, 3 —addition products before demetallation, 4 —products of addition of triisobutylaluminum to vinylacetylene, fraction 117-119° (after demetallation), 5 —the same, fraction 105-110° (50 mm), 6 —products of addition of triisobutylaluminum to vinylacetylene before demetallation, 7 —6-methylheptadiene-2,3. IKS-14 instrument, except for curve 3, obtained on an IKS-15.

The residue from distillation of the main part of the hydrocarbon mixture, boiling higher, judging from the IR spectrum, is not an adduct of two or more molecules of triisobutylaluminum to vinylacetylene, since it contains only terminal vinyl, allene, and acetylene groupings. Most likely it is formed through secondary addition to vinylacetylene of the primary adduct. Similar reactions have been described in the literature ([9,13]).

Experimental Part

Vinylacetylene (2.1 g-mol), freed from traces of water and oxygen by passage through solid alkali and a 10% solution of triisobutylaluminum in heptane and then through a coil at +6° (to trap heptane vapors), was passed into a flask containing triisobutylaluminum or diisobutylaluminum hydride (0.7 g-mol), equipped with a stirrer, thermometer, and siphon. The rate of introduction of vinylacetylene was regulated depending on the temperature in the reaction mixture. The latter was maintained at 20-25°. The reaction time was 15-16 h.* Excess vinylacetylene was removed in vacuo. The reaction mixture was diluted with a double volume of isopentane and demetallated with alcohol under cooling (about $-5°$), and then treated with 10% sulfuric acid and water.

In experiments with diisobutylaluminum hydride, the evolved gas was condensed in a carbon dioxide-cooled trap. Chromatographic analysis found in it 70% isobutane, 16% divinyl, and 13% ethylacetylene.

By bromination of the gas in a solution of chloroform, followed by distillation of the volatile products, divinyl tetrabromide was obtained, m.p. 116-117° (from alcohol).

In one of the experiments with triisobutylaluminum, distillation of the hydrocarbon layer with a Widmer dephlegmator gave 15 g of material, b.p. 59-62° (100 mm), 2 g of the fraction 50-59° (100 mm), and 4 g of residue.

For the main fraction the following were found: b.p. 117-119°, d_4^{20} 0.7373, n_D^{20} 1.4280.

Found, %: C 87.25; 87.49; H 12.51; 12.73
C_8H_{14}. Calculated, %: C 87.19; H 12.81

Upon exhaustive hydrogenation of 3.7 g of the substance over Pd/$CaCO_3$, 3.4 g of 2-methylheptane was obtained. B.p. 116-117.5°, d_4^{20} 0.6979, n_D^{20} 1.3957, which corresponds to the literature data (14).

Upon hydration of 4.5 g of the main fraction by shaking with 85% sulfuric acid, about 2 g of methyl isohexyl ketone was obtained. B.p. 101-102° (100 mm), d_4^{20} 0.8112, n_D^{20} 1.4140; 2,4-dinitrophenylhydrazone: m.p. 77° (from alcohol), which corresponds to the literature data (15). By distillation of the residue, about 1 g of substance was isolated, b.p. 105-110° (50 mm), the IR spectrum of which is shown in Fig. 1, 5.

By the action of isopropyllithium (12) on penten-1-yne-3 in ether at $-50°$, 6-methylheptadiene-2,3 was obtained in about 80% yield. B.p. 63-64 (100 mm),

d_4^{20} 0.7399, n_D^{20} 1.4380, MR 39.10; calculated 38.21.

Exhaustive hydrogenation of the substance gave 2-methylheptane with constants and IR spectrum not differing from those given in the literature (8, 14).

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Received
23 IV 1962

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* The work was carried out in argon.

Note: Figure translations are in progress. See original paper for figures.