CHEMISTRY

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1957

SovietRxiv

Abstract

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CHEMISTRY

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PREPARATION OF ALDEHYDES BY REDUCTION OF NITRILES WITH DIISOBUTYLALUMINUM HYDRIDE

(Presented by Academician A. N. Nesmeyanov, May 8, 1957)

K. Ziegler, K. Schneider, and I. Schneider found for the first time that diethylaluminum hydride $(C_2H_5)_2AlH$ and diisobutylaluminum hydride $(u\text{-}C_4H_9)_2AlH$ can be used for the reduction of the carbonyl group in aldehydes and ketones to the corresponding alcohols (^{1}). The same authors pointed out that, owing to the availability and lower cost of diisobutylaluminum hydride, it may find application in organic synthesis as a reducing agent cheaper than $LiAlH_4$. In the present work we have shown that diisobutylaluminum hydride can be successfully used for the preparation of aldehydes by reduction of nitriles. The reaction proceeds according to the scheme:

$$RCN + (u\text{-}C_4H_9)_2AlH \to RCH = NAl(C_4H_9\text{-}u)_2 \xrightarrow{H_2O} RCHO.$$

We studied the reduction of butyronitrile, capronitrile, benzonitrile, the nitriles of phenylacetic, anisic, α-naphthoic, pyromucic, and terephthalic acids, as well as 1,1-dichloro-5-cyanopentene-1. The results obtained are summarized in Table 1. The yields of aldehydes in most of the cases studied—

Table 1

Nitrile	Molar ratios of reagents, nitrile : $HAl(C_4H_9)_2$	Solvents	Reaction temperature, °C	Aldehyde yield, %	M.p. of derivatives, °C, found (from alcohol)	M.p. of derivatives, °C, lit.
C_3H_7CN	1 : 1.17	Ether, Heptane	15–20	85	122 (a)	122 (^{2})

Nitrile	Molar ratios of reagents, nitrile : $HAl(C_4H_9)_2$	Solvents	Reaction temperature, °C	Aldehyde yield, %	M.p. of derivatives, °C, found (from alcohol)	M.p. of derivatives, °C, lit.
$C_5H_{11}CN$	1 : 1.12	Ether, Heptane	18–20	87	104 (a)	104 (^{2})
C_6H_5CN	1 : 1.18	Ether, Heptane	40–45	86	154–155 (b)	155.5 (^{3})
n-$CH_3OC_6H_4CN$	1 : 1.20	Benzene	40–45	88	254 (a)	254 (^{4})
α-$C_{10}H_7CN$	1 : 1.17	Benzene	25–30	87	98 (c)	98 (^{5})
n-$C_6H_4(CN)_2$	1 : 2.10	Benzene	30	90	200 (d)*	198 (^{6})
$CCl_2{=}CH(CH_2)_3CN$	1 : 1.07	Ether	0–2	48 (e)	117 (a, f)	–
furan ring–CN	1 : 1.05	Ether	15–20	80	212 (a)	202–213 (^{7})
$C_6H_5CH_2CN$	1 : 1.10	Ether	0–2	50	110 (a)	111 (^{8})

Note. a –2,4-dinitrophenylhydrazone, b –phenylhydrazone, c –oxime, d –dioxime; e –1,1-dichlorohexen-1-al-6, b.p. 82°/4 mm, n_D^{20} 1.4808, d_4^{20} 1.2100; found %: C 43.27; 43.11; H 4.44; 4.55; Cl 43.04; 42.90; calculated %: C 43.22; H 4.24; Cl 42.74: f –analysis of 2,4-dinitrophenylhydrazone –found %: C 41.78; 41.71; H 3.43; 3.98; Cl 21.10; 20.15; calculated %: C 41.51; H 3.48; Cl 20.04.

* From aqueous alcohol.

in some cases, especially in the reduction of aromatic nitriles, are good and amount to 80-90% of theory. The reaction of diisobutylaluminum hydride with nitriles can be carried out in various solvents (ether, benzene, heptane, etc.) or without solvent, which has a number of advantages over $LiAlH_4$. Depending on the nature of the nitrile, the reduction reaction was carried out at a temperature of 0-40°. When diisobutylaluminum hydride was used in nearly equimolecular ratios to the nitriles, we did not observe reduction of the latter to amines. Decomposition of the addition product of diisobutylaluminum hydride to the nitrile must be carried out with great care, especially when obtaining such readily changing aldehydes as, for example, phenylacetaldehyde. We isolated, in 93% of theory yield, the addition product of diisobutylaluminum hydride to butyronitrile, $C_3H_7CH = NAl(C_4H_9\text{-u})_2$, which distills in vacuum without decomposition and, on treatment in the cold with 10% sulfuric acid, gives butyraldehyde in 88% yield. The addition product of $(u\text{-}C_4H_9)_2AlH$ to capronitrile cannot be distilled without decomposition in a 1 mm vacuum. The lower yields of phenylacetaldehyde and 1,1-dichlorohexen-1-al-6 are explained by the fact that, in the process of decomposition of the addition product of $(u\text{-}C_4H_9)_2AlH$ to the corresponding nitrile, these aldehydes partially condense. However, if the decomposition is carried out in the presence of 2,4-dinitrophenylhydrazine, the yields of the corresponding 2,4-dinitrophenylhydrazones are 80 and 72%, respectively.

Experimental Part

The reduction of nitriles with diisobutylaluminum hydride is carried out in a stream of dry and pure nitrogen. To a solution of the nitrile in the solvent, with stirring, a solution of the hydride is added dropwise in such a way that the temperature does not exceed that specified. After all the hydride has been added, stirring is continued for another 0.5 hour at room temperature. Then the reaction mixture is poured, with stirring, into a mixture of 100-150 g of ice with 50-80 ml of 10% sulfuric acid or, in the case of readily changing aldehydes, 10% acetic acid. In order for complete decomposition of the intermediate aldimines to take place, the temperature of the mixture is brought to room temperature and then heated at 30° for 0.5 hour. The organic layer is separated, and the aqueous layer is extracted; the extracts are combined, washed with a sodium bicarbonate solution, and dried. The residue after removal of the solvent is distilled.

Interaction of diisobutylaluminum hydride with butyric acid nitrile. To a solution of 9.6 g (0.12 mole) of butyronitrile in 25 ml of abs. ether is added a solution of 20.5 g (0.14 mole) of diisobutylaluminum hydride in 25 ml of ether. The reaction temperature is 15-20°. After completion of the addition of the hydride, the mixture is stirred for 0.5 hour. After removal of the solvent, the pale-yellow residue is distilled in vacuum and 27 g (93%) of a substance is obtained with b.p. 160.5-161°/1 mm, n_D^{20}1.4605, d_4^{20}0.8550.

Found, %: Al 12.58; 12.49
$C_{12}H_{26}NAl$. Calculated, %: Al 12.73

A solution of 15 g (0.07 mole) of the addition product in 30 ml of abs. ether is poured, with stirring, into a mixture of 100 g of ice and 50 ml of 10% sulfuric acid; the decomposition temperature is -5, -2°. After dissolution of the aluminum hydroxide, the temperature of the mixture is brought to room temperature, then heated at 30° for 30-40 min. The ether layer is separated, and the aqueous layer is extracted with ether. The combined extracts are washed with a sodium bicarbonate solution, then with water, and dried with $MgSO_4$. After removal of the solvent, the residue is distilled and 4.5 g of butyraldehyde is obtained.

Reduction of terephthalic acid dinitrile. To a solution of 1.7 g (0.0130 mole) of terephthalic acid dinitrile in 100 ml of abs. benzene, a solution of

3.8 g (0.027 mole) of diisobutylaluminum hydride in 15 ml of benzene is added dropwise in such a way that the reaction temperature is kept within 30–35°. After the entire amount of diisobutylaluminum hydride has been added, the slightly cloudy reaction mixture is heated at the same temperature for another 0.5 hr; then, at 0–2°, it is decomposed with 10% acetic acid and worked up as indicated above. After removal of the solvent under reduced pressure, 1.6 g of solid terephthalaldehyde is obtained, m.p. 116° (from alcohol).

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Received
7 V 1957

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