Conversion of αβ-Unsaturated Nitriles into Saturated Aldehydes by use of Dicobalt Octacarbonyl

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αβ-UNSATURATED aliphatic nitriles were converted into saturated aldehydes with the original carbon skeletons by the use of dicobalt octacarbonyl in acidic methanol. The reaction takes place under nitrogen at room temperature. $Co_2(CO)_8$, excess of acrylonitrile and concentrated hydrochloric acid were added to methanol, after 7 hr. at 20°, the resulting solution contained Co^{2+} ($\sim$90%), NH_3 ($\sim$85%) and propionaldehyde ($\sim$85%). No cobalt carbonyls were detected. From its stoicheiometry, the reaction can be formulated as:

$$CH_2{=}CHCN + Co_2(CO)_8 + 5HCl + H_2O \rightarrow CH_3{\cdot}CH_2{\cdot}CHO + 2CoCl_2 + NH_4Cl + 8CO$$

None of the αβ-unsaturated nitriles examined failed to give saturated aldehydes, whereas saturated aliphatic nitriles and aromatic nitriles gave no aldehydes.

Though no effort was made to improve yields of individual aldehydes, they seem to be dependent on the structure of the nitriles used.

TABLE

Nitriles	Aldehydes	Yields (%)†	Reaction time‡ (hr.)
Acrylonitrile	propionaldehyde	61	4
Crotononitrile	n-butyraldehyde	14	14
Methacrylonitrile	isobutyraldehyde	21	7
Cinnamonitrile	hydrocinnamaldehyde	50	5
Fumaronitrile	β-cyanopropionaldehyde	32	3
Maleonitrile		15	1
α-Methyleneglutaronitrile	γ-cyano-α-methylbutyraldehyde	18	3

Reaction temperature, 50°.

† Based on $Co_2(CO)_8$ charged. ‡ Time required for disappearance of $Co(CO)_4^-$ in the reaction mixture.

The chemical species which hydrogenate unsaturated nitriles may be formed *in situ* by the valence disproportionation of dicobalt octacarbonyl in acidic methanol. When n-hexane solution of cobalt carbonyl hydride is brought into contact with excess of acrylonitrile, the hydride disappears in a short time to give propionitrile.[1] No aldehyde can be detected from the reaction mixture. The reaction in acidic methanol gave practically no propionitrile.

In the reaction to give propionaldehyde from acrylonitrile, dicobalt octacarbonyl can be replaced by cobalt carbonyl hydride or its salt, hydrochloric acid by sulphuric acid, methanol by tetrahydrofuran. Sodium cobalt carbonylate in methanol did not react with acrylonitrile, and iron carbonyl hydride gave no aldehyde in acidic methanol.

The infrared spectrum of the solution during the conversion suggested the existence of a positively charged cobalt carbonyl derivative as an intermediate. Such a species may be formed by the protonation of cyanoethylcobalt carbonyl, similar to the cyanoethyliron complexes.[2]

The preparative method, which makes use of the valence disproportionation of dicobalt octacarbonyl in the presence of strong acid, has wide scope of application in the stoicheiometric hydroformylation, hydrogenation, carbonylation, and related reactions of unsaturated compounds.

(*Received, September 19th,* 1967; *Com.* 1003.)

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[2] J. K. P. Ariyaratne and M. L. H. Green, *J. Chem. Soc.*, 1963, 2976.