

CCLII.—*A New Synthesis of Aldehydes.*

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THE basis of this new method is the conversion of a nitrile through the imino-chloride (which need not be isolated) into an aldehyde with the same number of carbon atoms. The most suitable reducing agent is anhydrous stannous chloride \* dissolved in ether saturated with hydrogen chloride. Finely powdered, anhydrous stannous chloride ( $1\frac{1}{2}$  mols.) is suspended in dry ether, which is then saturated with dry hydrogen chloride until the mixture separates into two layers, the lower viscous layer consisting of stannous chloride dissolved in ethereal hydrogen chloride. The nitrile (1 mol.) is now added with vigorous shaking and, after a few minutes, separation begins of a white, crystalline aldimine stannichloride,



The course of the formation and reduction of the imino-chloride is therefore as follows :  $\text{R}\cdot\text{CN} + \text{HCl} \rightarrow \text{R}\cdot\text{CCl}\cdot\text{NH}$  ;  $\text{R}\cdot\text{CCl}\cdot\text{NH} + \text{SnCl}_2 + 2\text{HCl} \rightarrow \text{R}\cdot\text{CH}\cdot\text{NH},\text{HCl} + \text{SnCl}_4$ . After removal of this

\* The anhydrous stannous chloride for these reactions was prepared by heating the crystalline variety until the temperature reached  $180^\circ$ . The product contained some stannous oxide, but this appears to be insoluble in ether saturated with hydrogen chloride. A convenient and rapid method for preparing pure anhydrous stannous chloride is to dissolve the fused mass obtained as above in pyridine. Solution takes place with evolution of heat and the insoluble stannous oxide is then filtered off. The filtrate deposits fine, white needles of a *double* compound,  $\text{SnCl}_2, 2\text{C}_5\text{H}_5\text{N}$  (Found :  $\text{SnCl}_2$ , 53.2 ;  $\text{C}_5\text{H}_5\text{N}$ , 46.4.  $\text{SnCl}_2, 2\text{C}_5\text{H}_5\text{N}$  requires  $\text{SnCl}_2$ , 53.2 ;  $\text{C}_5\text{H}_5\text{N}$ , 46.8%). When the double compound is heated under diminished pressure the pyridine is removed ; the residue is anhydrous stannous chloride.

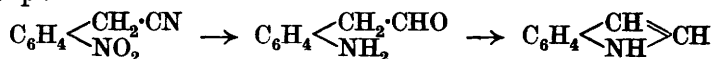
salt the ether may be again employed for another preparation. The salt is readily hydrolysed by warm water, and the aldehyde formed may be removed by distillation with steam or extraction with a solvent.

The method is applicable to aliphatic and aromatic nitriles, and the yields are usually almost quantitative. As the rate of deposition of the stannichloride varies in different cases, it is advantageous to allow at least two hours for completion of the reaction.

3 : 4 : 5-Trimethoxybenzotrile and other nitriles which are only sparingly soluble in cold ether may be dissolved in chloroform and the solution added to the reducing agent.

*o*-Toluonitrile and  $\alpha$ -naphthonitrile give only small yields of the respective aldehydes. This is no doubt due to steric hindrance, of which the two nitriles form well-known examples; both, for instance, fail to give imino-ethers (Pinner, "Die Imidoäther und ihre Derivate," 1892, pp. 4, 81), for the formation of which an imino-chloride is essential.

A special application of the method is the formation of indole by reduction of *o*-nitrophenylacetoneitrile; sufficient reducing agent is employed to reduce both the imino-chloride and the nitro-group :



(compare Pschorr, *Ber.*, 1910, 43, 2543).

#### EXPERIMENTAL.

*n*-Octaldehyde.—Octonitrile was prepared by warming a solution of octoamide in thionyl chloride on the water-bath for 30 minutes and removing the excess of thionyl chloride under diminished pressure. The residue of nitrile (b. p. 87°/10 mm.) was almost pure and the yield quantitative. The method has been applied to the amides of myristic, palmitic, and stearic acids with equally good results.

Octonitrile (25 g.) was brought into reaction with stannous chloride (57 g.) in dry ether (200 c.c.), saturated with hydrogen chloride as described above. The aldehyde produced by hydrolysis of the stannichloride was isolated by distillation with steam and extraction with ether. It was obtained as a colourless oil, b. p. 65°/11 mm., having a strong lemon-like odour. Prepared by the usual methods and crystallised from methyl alcohol, the oxime was obtained in fine, silky needles, m. p. 60°, the semicarbazone in needles, m. p. 98°, and the *p*-nitrophenylhydrazone in bright yellow needles, m. p. 80° (Found: N, 15.8.  $\text{C}_{14}\text{H}_{21}\text{O}_2\text{N}_3$  requires N, 15.9%).

*Myristaldehyde* was prepared from the corresponding nitrile, but being only slightly volatile in steam it was extracted with warm ether after hydrolysis of the stannichloride. It was obtained as thin, colourless laminæ, m. p. 23°, b. p. 155°/10 mm., and rapidly polymerised to a white solid, m. p. 65°. The oxime and semicarbazone crystallised from methyl alcohol in needles, m. p. 82·5° and 106·5°, respectively (compare Le Sueur, J., 1905, **87**, 1900). The *p*-nitrophenylhydrazone is a bright yellow, crystalline powder, m. p. 95° (Found: N, 12·4.  $C_{20}H_{33}O_2N_3$  requires N, 12·1%).

*Palmitaldehyde* formed thin plates with nacreous lustre (from ether), m. p. 34°; the polymeride had m. p. 73—74°. The oxime and semicarbazone crystallised from methyl alcohol in needles, m. p. 88° and 107°, respectively (Le Sueur, *loc. cit.*). The *p*-nitrophenylhydrazone formed yellow needles, m. p. 96·5°, from alcohol (Found: N, 11·3.  $C_{22}H_{37}O_2N_3$  requires N, 11·2%).

*Stearaldehyde* has m. p. 38°, not 63·5° as stated by Krafft (*Ber.*, 1880, **13**, 1417). It rapidly polymerises to a white solid, m. p. 80°. The oxime and semicarbazone crystallise in needles, m. p. 89° and 108—109°, respectively. The *p*-nitrophenylhydrazone forms yellow needles, m. p. 101°, from methyl alcohol (Found: N, 10·6.  $C_{24}H_{41}O_2N_3$  requires N, 10·4%).

*Benzaldehyde*.—Benzonitrile is rapidly and almost quantitatively converted into benzaldehyde by the new method. The *stannichloride* was obtained in white needles from alcohol (Found: Sn, 21·2.  $C_{14}H_{16}N_2Cl_6Sn$  requires Sn, 21·8%). The salt, if dry, may be preserved indefinitely. It dissolves in water, but is rapidly hydrolysed when the solution is warmed.

*3 : 4 : 5-Trimethoxybenzaldehyde*.—The corresponding nitrile is readily obtained by the action of thionyl chloride on the amide (yield 90%), and without further purification melts at 93° as stated by Harding (J., 1911, **99**, 1594). A solution of the nitrile (9 g.) in 20 c.c. of chloroform is added to anhydrous stannous chloride (9 g.) in ether (150 c.c.) saturated with hydrogen chloride. After an hour the yellow stannichloride is filtered off, hydrolysed by boiling water, and the solution filtered. *3 : 4 : 5-Trimethoxybenzaldehyde* crystallises from the filtrate in shimmering leaves, m. p. 74—75°. The oxime has m. p. 88°; the semicarbazone, m. p. 218°; and the *p*-nitrophenylhydrazone, m. p. 201° (compare Mauthner, *Ber.*, 1908, **41**, 923).

*Indole*.—*o*-Nitrophenylacetoneitrile (3 g.) is added to a solution of anhydrous stannous chloride (16 g.) in ether (100 c.c.) saturated with hydrogen chloride. After remaining 2 hours, the stannichloride is filtered off, dissolved in water, the solution made alkaline with sodium hydroxide, and the indole removed in a current of

steam. The product, m. p.  $52^\circ$  (yield 1.2 g.), shows all the characteristic properties of indole.

The following aldehydes have been prepared by the new method, and except in the cases marked \* the yields were almost quantitative. *o*-Tolualdehyde,\* b. p.  $94^\circ/10$  mm.; *p*-nitrophenylhydrazone, red needles, m. p.  $222^\circ$ , from alcohol (Found: N, 16.2.  $C_{14}H_{13}O_2N_3$  requires N, 16.4%). *p*-Tolualdehyde, b. p.  $106^\circ/10$  mm.; *p*-nitrophenylhydrazone, similar to the above, m. p.  $200.5^\circ$  (Found: N, 16.5%). *o*- and *p*-Chlorobenzaldehydes, phenyl-, *p*-chlorophenyl-, and *p*-tolyl-acetaldehydes (*p*-nitrophenylhydrazone of the last, yellow needles from alcohol, m. p.  $144.5^\circ$ . Found: N, 15.3.  $C_{15}H_{15}O_2N_3$  requires N, 15.6%), cinnamaldehyde and  $\beta$ -phenylpropaldehyde,  $\alpha$ -naphthaldehyde\* (m. p.  $33-34^\circ$ ; oxime, m. p.  $39^\circ$ ; semicarbazone, m. p.  $222^\circ$ ; *p*-nitrophenylhydrazone, orange needles, m. p.  $234^\circ$ . Found: N, 14.4.  $C_{17}H_{13}O_2N_3$  requires N, 14.4%). The investigation is being continued.

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