424. *Studies on Hydrogen Cyanide. Part IV. Gattermann's Hydrogen Cyanide Aldehyde Synthesis.*

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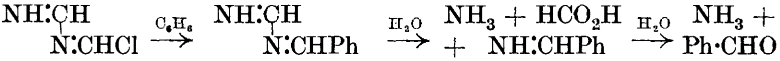
According to Gattermann and his co-workers (*Ber.*, 1899, **31**, 1149, 1766), not only does benzene not react with hydrogen cyanide and hydrogen chloride in the presence of aluminium chloride, but it can be used as a solvent in the synthesis of aromatic aldehydes. However, Baeyer and Co. (D.R.-P. 99568), immediately prior to Gattermann's publications, described the preparation of aldehydes from aromatic hydrocarbons by this method, although no direct reference to benzene was made. If, as is now proposed, chloromethyleneformamidine (Hinkel and Dunn, J., 1930, 1834) be the intermediate chloride in the synthesis, benzene and its homologues should react with hydrogen cyanide : this point is here investigated. The double compound $AlCl_3,2HCN$, formed when hydrogen cyanide is added to a benzene suspension of aluminium chloride (Hinkel and Dunn, J., 1931, 3343), is apparently not decomposed when hydrogen chloride is passed through the mixture, since no benzaldehyde results when Gattermann's procedure is followed to completion. If, however, the mixture be boiled, instead of being kept at 40°, benzaldehyde (14% yield *) is finally obtained. This observation explains why Gattermann could use benzene as an indifferent solvent in the synthesis, since all his reactions were carried out at or below 40°. At the higher temperature the double compound decomposes into its constituents and the liberated hydrogen cyanide can form chloromethyleneformamidine with the hydrogen chloride (the sesquichloride cannot be formed at the higher temperature; Hinkel and Dunn, J., 1930, 1834). The chloromethyleneformamidine then reacts normally with benzene in the presence of the liberated aluminium chloride, as represented by the scheme :



$$\begin{array}{l}\mathrm{NH{:}CH}\\ \quad\mathrm{N{:}CHCl}\end{array} \xrightarrow{C_6H_6} \begin{array}{l}\mathrm{NH{:}CH}\\ \quad\mathrm{N{:}CHPh}\end{array} \xrightarrow{H_2O} \begin{array}{l}\mathrm{NH_3 + HCO_2H}\\ \mathrm{+\ NH{:}CHPh}\end{array} \xrightarrow{H_2O} \begin{array}{l}\mathrm{NH_3 +}\\ \mathrm{Ph{\cdot}CHO}\end{array}$$

(compare *ibid.*; Gattermann and Schnitzspahn, *Ber.*, 1898, **31**, 1770).

With toluene, when the reaction is carried out at 40° under Gattermann's conditions, the yield of *p*-tolualdehyde is 14%, and this is raised to 100% when the reaction temperature is 100°. Similarly, *o*- and *p*-xylenes and mesitylene give yields of 85%, and *m*-xylene 100%, of the respective aldehydes at the higher temperature.

The yield of benzaldehyde can be increased by using larger amounts of aluminium chloride, and it appears to us essential, in the Gattermann synthesis, to have aluminium chloride in the uncombined state. Confirmation of this view is obtained in the

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* All yields, unless otherwise stated, are calculated on the basis that 2 molecules of HCN (necessary for chloromethyleneformamidine formation) are required for each molecule of hydrocarbon or phenolic compound (compare p. 2796).

case of toluene when zinc cyanide is used instead of free hydrogen cyanide (compare Adams and Levine, *J. Amer. Chem. Soc.*, 1923, **45**, 2373; Adams and Montgomery, *ibid.*, 1924, **46**, 1518). When the reaction was carried out with 2 molecules of aluminium chloride to 1 of zinc cyanide (equivalent to $AlCl_3,2HCN + AlCl_3$) a yield of only 65% of aldehyde was obtained at 100°, whereas with 3 molecules of aluminium chloride (equivalent to $AlCl_3,2HCN + 2AlCl_3$) the yield was 100%.

In the preparation of anisaldehyde from anisole, Gattermann (*Annalen*, 1907, **357**, 313) claims to have obtained a 100% conversion into aldehyde by using 4 molecules of hydrogen cyanide to 1·2 molecules of aluminium chloride, corresponding to $AlCl_3,2HCN + 1{\cdot}3HCN$. We, however, repeatedly failed to get more than a 46% conversion, and in experiments in which the proportion of aluminium chloride to hydrogen cyanide was varied, again the yields were best when excess of aluminium chloride was present: *e.g.*, with hydrogen cyanide : aluminium chloride = 2 : 0·85 molecules (equivalent to $AlCl_3,2HCN + 0{\cdot}35\ HCN$) the yield of aldehyde, with excess of anisole, was 45%, and with a proportion equivalent to $AlCl_3,2HCN + AlCl_3$ the yield was 77%.

In comparing these experiments with anisole with the first described above with benzene, it might not be expected, at first sight, that any action should occur at 40°, since with excess of hydrogen cyanide all the aluminium chloride would be fixed as $AlCl_3,2HCN$, which would not be decomposed at the temperature employed. Since, however, this compound readily dissociates in ether (Hinkel and Dunn, J., 1931, 3343), it is to be expected that dissociation will also occur in phenolic ethers, thus giving the necessary conditions for the reaction to take place. Variations of reaction temperature should therefore have little effect on the yield in this case, since increase of temperature in order to cause this dissociation is not essential, and we find that similar yields are obtained at 40° and 100°.

Since it is the hydrogen cyanide which gives rise to the CHO group, the yield of aldehyde is most aptly expressed on the basis of the hydrogen cyanide employed, and not, as Gattermann usually did, on the basis of the phenol taken, when the reaction is carried out with molecular proportions of the reactants, or even with the hydrocarbon or phenolic compound in excess. Consideration of the yield is also influenced by the nature of the intermediate compound, chloromethyleneformamidine necessitating two molecules of hydrogen cyanide, as compared with the one molecule for the supposed imidoformyl chloride (which appears to be incapable of existence; compare Hinkel and Dunn, J., 1930, 1834), in the formation of one molecule of aldehyde. Neither from any hydrocarbon examined nor from anisole is a yield of more than 50% obtained on the hydrogen cyanide basis, which corresponds to 100% based on chloromethyleneformamidine as the intermediate.

Resorcinol is particularly suited for confirming the correctness of our view, since it reacts readily with hydrogen cyanide and hydrogen chloride in ethereal solution, the presence of aluminium chloride being unnecessary. Gattermann and Köbner (*Ber.*, 1899, **32**, 278) employed only 1·4 molecules of hydrogen cyanide to 1 molecule of resorcinol and state that they obtained a quantitative conversion of the resorcinol into aldehyde. This is obviously impossible if chloromethyleneformamidine (requiring 2 molecules of hydrogen cyanide) be the intermediate. Here again, with several repetitions of their experiment, we have not been able to corroborate this result, but find only about 55% conversion of resorcinol into aldehyde, the yield of the latter being equivalent to 78% calculated from the hydrogen cyanide employed, on the chloromethyleneformamidine basis. Moreover, in a series of subsequent experiments, in which resorcinol was present in excess of that required for two molecules of hydrogen cyanide to ensure the maximum reaction of the hydrogen cyanide, the yields all approximated to 78%. Even under the best conditions for maximum conversion of resorcinol into aldehyde, *viz.*, a large excess of hydrogen cyanide, a conversion of more than 69% could not be realised.

EXPERIMENTAL.

Apparatus and Materials.—The vessel was a Pyrex 500 c.c. flask carrying a reflux condenser, a dropping-funnel for addition of HCN, and a tube for delivery of HCl (dried by H_2SO_4). The anhydr. HCN was prepared by the method of Coates, Hinkel, and Angel (J., 1928, 542). C_6H_6 and C_7H_8 were purified by H_2SO_4, dried over $CaCl_2$ and then Na, and distilled. The remaining hydrocarbons and anisole were dried and fractionally distilled. The ether was Na-dried. The solids employed were Merck's chemicals, resorcinol, anhydr. sublimed $AlCl_3$ for synthesis, and $Zn(CN)_2$, which was dried at 120° for 1 hr. and analysed for cyanide content before use.

General Method for the Preparation of Aldehydes from Aromatic Hydrocarbons.—To a mixture of $AlCl_3$ (52 g.; 2 mols.) and the hydrocarbon (50 c.c.; excess), cooled in ice, HCN (15 c.c., equiv. to 2 mols.) is added during 15 min., with shaking. After being kept at room temp. for 5 min., the mixture is heated to about 60°, and a slow current of HCl passed through it. A vigorous reaction occurs and the whole is then maintained at 100° for 5 hr., passage of HCl being discontinued after 2 hr. After standing over-night, the viscous mixture is poured on ice–conc. HCl, and distilled in steam. From the dried ethereal extract of the distillate, the aldehyde is obtained by fractional distillation.

The yields usually obtained (with the exception of C_6H_6) range from 85 to 100%.

Benzene.—(a) $AlCl_3,2HCN$ *at* 0° *and* 40°. HCl was passed for several hr. through a suspension of the double compound in excess of C_6H_6, at 0° and also at 40°, the mixture poured on ice–HCl aq., and the general procedure continued. No benzaldehyde was detected in either case.

(b) *At the boiling point.* HCl was passed into a mixture of $AlCl_3$ (30 g.; 1·15 mols.) and C_6H_6 (15 c.c.) on a steam-bath, and a mixture of HCN (15 c.c.; 2 mols.) and C_6H_6 (9 c.c.) gradually added, the heating being continued for 5 hr. and the passage of HCl discontinued after 1·5 hr. Further treatment as above yielded 2·4 g. (11·6%) of benzaldehyde, b. p. 175—180°.

(c) *General method.* This gave 4·2 g. (20·4%) of aldehyde.

(d) *General method with excess* $AlCl_3$. An expt. similar to (c), only using 78 g. (3 mols.) of $AlCl_3$ (equiv. to $AlCl_3,2HCN + 2AlCl_3$), yielded 8·0 g. (39%) of aldehyde.

Toluene.—(a) *At* 40°. A repetition of the patented method (*loc. cit.*), using toluene (30 g.; 1·7 mols.), $AlCl_3$ (40 g.; 1·5 mols.) and HCN (15 c.c.; 2 mols., equiv. to $AlCl_3,2HCN + 0{\cdot}5AlCl_3$) and a reaction temp. of 35—40° for 4·5 hr., yielded 3·3 g. (14%) of *p*-tolualdehyde, b. p. 200—204°.

(b) $AlCl_3 + 2HCN$ *at* 100°. By the general procedure, but with 26 g. (1 mol., equiv. to $AlCl_3,2HCN$) of $AlCl_3$, a yield of 9·0 g. (38%) was obtained.

(c) *General method.* A quantitative yield (23·3 g.) was obtained.

(d) *General method with excess* $AlCl_3$. With 70 g. (2·6 mols., equiv. to $AlCl_3,2HCN + 1{\cdot}6AlCl_3$) of $AlCl_3$, 22·4 g. (96%) of aldehyde were obtained.

o-Xylene.—By the general method, 22·0 g. (85%) of 3 : 4-dimethylbenzaldehyde, b. p. 225—228°, were obtained.

Treated similarly, *m*-xylene yielded 25·2 g. (97%) of 2 : 4-dimethylbenzaldehyde, b. p. 218—223°, *p*-xylene 22·0 g. (85%) of 2 : 5-dimethylbenzaldehyde, b. p. 219—221°, and mesitylene 24·3 g. (85%) of 2 : 4 : 6-trimethylbenzaldehyde, b. p. 237—240°.

Ethylbenzene yielded a mixture (21·9 g.), b. p. 220—250°. No pure substance was obtained, although *p*-ethylbenzaldehyde (b. p. 221°) was proved to be present in the fraction, b. p. 215—230°, by means of its semicarbazone (compare Fournier, *Compt. rend.*, 1903, **136**, 558).

Experiments with Zinc Cyanide.—*Benzene.* C_6H_6 (50 c.c.; excess), $AlCl_3$ (52 g.; 2 mols.), and $Zn(CN)_2$ (23·4 g.; 1 mol., equivalent to $AlCl_3,2HCN + AlCl_3$) were mixed in the cold and then heated until almost boiling. Passage of HCl was then started, and the general procedure continued. The solids gradually dissolved and the mixture then became pasty with continued heating. Yield of benzaldehyde, 3·2 g. (15·5%).

Toluene. (a) The above expt., repeated with toluene (50 c.c.), yielded 15·2 g. (65%) of *p*-tolualdehyde.

(b) A similar expt., with 78 g. (3 mols., equiv. to $AlCl_3,2HCN + 2AlCl_3$) of $AlCl_3$, gave an almost quantitative yield (23·0 g.) of the aldehyde.

Experiments with Anisole.—(a) *With excess hydrogen cyanide* (Gattermann, *Annalen*, 1907, **357**, 313; compare Gattermann and Frenzel, *Ber.*, 1898, **31**, 1150). HCl was passed through an ice-cooled mixture of anisole (30 g.; 1 mol.) and HCN (30 g.; 4 mols.) for 30 min., $AlCl_3$ (45 g.; 1·2 mols.) then gradually added, the mixture warmed to 40°, with slow passage of HCl, and the reaction continued at 40° for 5 hr. The remainder of the procedure was carried out as previously described, the anisaldehyde being collected at 241—250°; yield 17·2 g., corresponding to 46% conversion of anisole into aldehyde.

(b) *With excess of anisole, and* HCN *in slight excess of that required for* $AlCl_3,2HCN$. With anisole (50 c.c., approx. 5 mols.), HCN (7·5 c.c.; 2 mols.), and $AlCl_3$ (11 g.; 0·85 mol., equiv. to $AlCl_3,2HCN + 0{\cdot}35HCN$), the above procedure yielded 6·0 g. (45%) of anisaldehyde.

(c) *General method at* 40° *and* 100°. By the general method described for hydrocarbons (p. 2796), with anisole (50 c.c.; excess) and a reaction temp. of 40°, 20·5 g. (77%) of anisaldehyde were obtained.

Similar expts. with the normal reaction temp. of 100° yielded 20·4 and 21·3 g. (77 and 81% respectively) of anisaldehyde.

Experiments with Resorcinol.—Repetitions of the exact procedure described by Gattermann and Köbner (*loc. cit.*), in which the proportions are resorcinol, 1 mol. (10 g.); hydrogen cyanide, 1·4 mols. (3·5 g.), yielded only 6·9 and 6·8 g. (78 and 77% respectively) of resorcylaldehyde, calc. on HCN on the chloromethyleneformamidine basis.

Subsequent expts., in which the quantity of HCN was varied, gave yields of aldehyde as follows :

(a) HCN, 3·85 g. (1·54 mols.); yield, 7·9 g., 82%.

(b) HCN, 1·75 g. (0·7 mol.); yield, 3·5 g., 79·5%.

(c) HCN, 6·0 g. (2·4 mols.); yield, 8·6 g., corresponding to 69% conversion of resorcinol into aldehyde.

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