to be: 2,3,4,4-tetramethyl-1-pentene, 50; 2,3,4,4-trimethyl-2-pentene, 10; 3,5,5-trimethyl-2-hexene, 23; 3,5,5-trimethyl-3-hexene, 5; and 2,4,4-trimethyl-2-hexene, 10.

3. The significance of these results is considered in terms of the mechanism of olefin polymerization.

STATE COLLEGE, PENNA. RECEIVED MARCH 7, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, FORDHAM UNIVERSITY]

On the Mechanism of the Gattermann Aldehyde Synthesis. I

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Recently it has been shown[1] that the Gattermann synthesis of aldehydes from aromatic hydrocarbons and phenolic ethers occurs primarily through the intermediate formation of the arylmethyleneformamidines, and not through the formimino-chlorides, which on hydrolysis yield the aldehydes. The reaction may be represented as

$$ArH + ClCH{=}N{-}CH{=}NH \xrightarrow{-HCl}$$

$$ArCH{=}N{-}CH{=}NH \xrightarrow{H_2O}$$

$$ArCH{=}NH + NH_3 + HCOOH \xrightarrow{H_2O} ArCHO + NH_3$$

However, with aluminum chloride the mechanism was found to take an indirect course. Aluminum chloride and hydrogen cyanide form a compound, $AlCl_3 \cdot 2HCN$, which reacts with hydrogen chloride to form $AlCl_3 \cdot 2HCN \cdot HCl$, identical with the product obtained by the direct union of aluminum chloride and chloromethyleneformamidine, namely, $AlCl_3 \cdot NH{=}CH{-}N{=}CHCl$. This double compound was found to dissociate under the influence of heat, and in the presence of uncombined aluminum chloride, forming the arylmethyleneformamidine hydrochloride; this on hydrolysis yields the aldehyde.

The Gattermann aldehyde synthesis has been modified[2] by the use of zinc cyanide for phenols and phenolic ethers. The zinc cyanide modification was further adapted[1] to the aromatic hydrocarbons.

In the present investigation the usefulness of sodium cyanide in place of the hydrogen cyanide or zinc cyanide has been established. This method is found to be generally applicable to the aromatic hydrocarbons, excepting benzene. It appears, however, that in the case of the higher alkyl derivatives of benzene, this method is influenced by the mobility of the alkyl groups and may be followed by partial isomerization of the reaction products. The success of this synthesis depends on the presence of free aluminum chloride above that calculated for the formation of the double compound, $AlCl_3 \cdot 2HCN$. The ratio of sodium cyanide to aluminum chloride equivalent to $AlCl_3 \cdot 2HCN$ gives zero yield; with 0.5, 1 and 2 moles of aluminum chloride in excess, the yields based on the reacted hydrocarbon, in the case of *p*-tolualdehyde, are, respectively, 23, 31 and 39%.

A similar observation has been reported[3] employing zinc cyanide, in which the yields are expressed on the basis of the chloromethyleneformamidine formation, *i. e.*, 2 moles of hydrogen cyanide is necessary for 1 mole of the phenolic ether or hydrocarbon. The calculated yields, based on the formation of chloromethylene formamidine, when the same amounts of aluminum chloride were used in excess as indicated above, are 35, 53.3 and 86.6%, respectively.

The use of sodium cyanide and of potassium cyanide was found[2] to have produced negligible results with phenolic ethers. However, we have readily obtained yields amounting to 43 to 50% anisaldehyde from anisole alone or when ethylbenzene was employed as solvent. With *o*-xylene as solvent, the aldehyde of *o*-xylene was produced instead of the expected anisaldehyde. When using carbon disulfide, carbon tetrachloride, nitrobenzene, cyclohexane or chlorobenzene as solvents at room temperature, no anisaldehyde was formed. The formation of the 3,4-dimethylbenzaldehyde in the presence of anisole without applying heat is due to the dissociation of the double compound of aluminum chloride and chloromethyleneformamidine which occurs readily

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[1] L. E. Hinkel, E. E. Ayling and J. H. Beynon, *J. Chem. Soc.*, 184 (1936); 674 (1935).

[2] R. Adams, I. Levine and E. Montgomery, THIS JOURNAL, **45**, 2373 (1923); **46**, 1518 (1924).

[3] L. E. Hinkel, E. E. Ayling and W. H. Morgan, *J. Chem. Soc.*, 2793 (1932).

in ethers. Since the difference of the dipole moments of ethylbenzene (0.46)[4] and anisole (1.2)[5] is similar to that between *o*-xylene (0.5)[5] and anisole, this factor cannot account for the formation of anisaldehyde in one case and 3,4-dimethylbenzaldehyde in the other. However, a consideration of the structure of the solvents[6] points to a possible understanding of the contradictory results.

Another factor which appears to play a significant role in this reaction is the effect of the aluminum chloride on the conversion of sodium cyanide into the reacting hydrogen cyanide. It was observed, namely, that the hydrogen cyanide indispensable for the final formation of the aldehyde was only set free in the presence of aluminum chloride and was suppressed completely by its absence. This fact seems to indicate that the aluminum chloride combines with the hydrocarbon to form a complex[7] of the type $(Ar{\cdot}AlCl_3)H$, which may dissociate into $(Ar{\cdot}AlCl_3)^-$ and H^+, thereby forming an ionic condition necessary for the production of the hydrogen cyanide. As soon as the hydrogen cyanide is available the reaction proceeds through the intermediate, $AlCl_3{\cdot}NH{=}CH{-}N{=}CHCl$, as outlined previously.

The reaction in its present form appears to eliminate the original inconveniences of the Gattermann procedure and also avoids the introduction of the zinc cyanide.

Experimental[8]

Preparation of *p*-Tolualdehyde.—Dry hydrogen chloride is passed at a slow rate into a well-stirred mixture of 25 g. (0.4 mole) of reagent sodium cyanide, 100 g. (0.77 mole) anhydrous aluminum chloride, and 100 cc. (excess) toluene at room temperature for one-fourth of an hour, after which the bath temperature is brought up gradually to 100°, the passage of dry hydrogen chloride being maintained for seven hours. Below 100° the yield of *p*-tolualdehyde is appreciably lower. The reaction mixture is hydrolyzed by pouring it into 300 cc. of ice–concd. hydrochloric acid, and subjected to steam distillation. The distillate is extracted with ether, neutralized and dried. It is submitted to fractionation, whereby 35 g. of unreacted toluene is recovered and 26 g. of *p*-tolualdehyde, b. p. 204–207° (amounting to a yield of 39%) is obtained. It was characterized by means of its semicarbazone, m. p. 234° (cor.) (calcd. for $C_9H_{11}ON_3$: N, 23.73. Found: N, 23.80).

***p*-Ethylbenzaldehyde.**—From 100 cc. (excess) of ethylbenzene, 25 g. of sodium cyanide, and 66 g. of aluminum chloride which were allowed to react in the manner described above, 38 g. of unreacted ethylbenzene and 17 g. of a mixture, b. p. 225–240° (yield 27%), were obtained. *p*-Ethylbenzaldehyde was found present in the fraction by means of its 2,4-dinitrophenylhydrazone, m. p. 216° (cor.) (calcd. for $C_{15}H_{14}O_4N_4$: N, 17.84. Found: N, 17.94).

3,4-Dimethylbenzaldehyde.—From 100 cc. (excess) of *o*-xylene, 25 g. of sodium cyanide, and 66 g. of aluminum chloride were obtained 40 g. of a mixture consisting of unchanged and isomerized hydrocarbon and 25 g. of a fraction, b. p. 225–228° (yield 42%). The aldehyde was identified by means of its dinitrophenylhydrazone, m. p. 225° (cor.) (calcd. for $C_{15}H_{14}O_4N_4$: N, 17.84. Found: N, 17.96).

Diisopropylbenzaldehyde.—From 50 cc. (excess) cumene, 20 g. of sodium cyanide, and 40 g. of aluminum chloride which were allowed to react for six hours, 5 g. of unreacted cumene and diisopropylbenzene, and 8 g. of a fraction, b. p. 127–130° (9 mm.) (yield 18%) which had n^{25}_D 1.5284 and d^{20}_{20} 0.973. It was characterized by its dinitrophenylhydrazone with a melting point of 125° (calcd. for $C_{19}H_{22}O_4N_4$: N, 15.14. Found: N, 14.91).

Anisaldehyde.—Fifty cc. (excess) anisole, 25 g. of sodium cyanide, and 40 g. of aluminum chloride were allowed to react at 0° for three hours and for an additional three hours at 40–45°. The mixture usually solidifies, at first, but introduction of dry hydrogen chloride causes the pasty mass to reliquefy. The excess anisole (28 g.) was recovered and 12 g. of anisaldehyde, b. p. 245–248° (43% yield) was obtained. It was characterized by its semicarbazone m. p. 203° (calcd. for $C_9H_{11}O_2N_3$: N, 21.32. Found: N, 21.71).

Summary

1. Sodium cyanide was found to be a convenient reagent to perform the Gattermann aldehyde synthesis.

2. It was established that the solvents used exert a directing influence upon the course of the reaction.

NEW YORK, N. Y. RECEIVED FEBRUARY 10, 1941

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[4] Landolt–Börnstein, "Tabellen."

[5] Hückel, "Theoretische Grundlagen der organischen Chemie," Vol. 2, 2d ed., Leipzig, 1935.

[6] A. G. Mistretta and F. F. Nord, *Nature*, **145**, 387 (1940).

[7] G. Kraenzlein, "Aluminiumchlorid in der organischen Chemie," 3rd ed., Berlin, 1939, p. 20.

[8] We wish to thank Mr. Joseph F. Alicino for the micro-analyses performed.