identical with a sample obtained from a reliable manufacturer.

2-Methyl-3-butanol from Bromoacetone.—The same procedure was used except that one mole of bromoacetone[12] was added to two moles of the Grignard reagent.

Methylmagnesium bromide with chloroacetyl chloride gave a 51% yield of 2-methyl-3-butanol; with ethyl chloroacetate, 40%; with bromoacetyl bromide, 21%; with ethyl bromoacetate, 32%; with bromoacetone, 18%.

Methylmagnesium iodide with chloroacetyl chloride gave a 48% yield; with bromoacetyl bromide, 16%; with bromoacetone, 12%.

Summary

2-Methyl-3-butanol has been prepared from the reactions of methylmagnesium bromide and methylmagnesium iodide with chloroacetyl chloride, ethyl chloroacetate, bromoacetyl bromide, ethyl bromoacetate and bromoacetone.

EAST LANSING, MICHIGAN RECEIVED DECEMBER 26, 1940

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[12] Levene, "Organic Syntheses," Vol. X, p. 12.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Polymerization of Olefins. IV.[1] The Nonenes from the Dehydration and Copolymerization of *t*-Butyl and *t*-Amyl Alcohols[2]

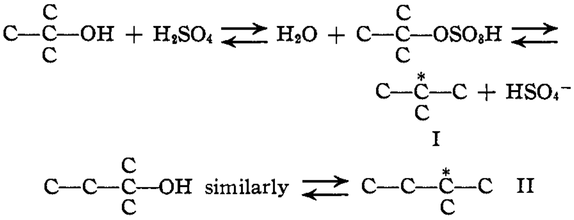
BY FRANK C. WHITMORE AND L. W. MIXON[3]

The present study was undertaken to throw additional light on the mechanism of the polymerization of olefins. Two tertiary alcohols were chosen because the related olefins polymerize with extraordinary ease in the presence of acid catalysts.

The dehydration of an equimolar mixture of *t*-butyl alcohol and *t*-amyl alcohol with 65% sulfuric acid at 80° gave the following percentage yields: isobutylene, 0.5; isoamylenes, 30; diisobutylenes, 22; nonenes, 17; diamylenes, 6; triisobutylenes, 6; higher polymers, 1.5. Satisfactory separation of the isomeric nonenes could not be effected by repeated fractionation through a column equivalent to 23 theoretical plates. The identification of the nonene mixture was effected by ozonolysis of the mixture and subsequent separation and identification of the products of ozonolysis, namely, formaldehyde, acetaldehyde, acetone, trimethylacetaldehyde, dimethylethylacetaldehyde, pinacolone, methyl neopentyl ketone and 3,4,4-trimethyl-2-pentanone.

From the nature and amounts of the ozonolysis products, the nonenes were concluded to be the following with the indicated percentages of the total nonenes: 2,3,4,4-tetramethyl-1-pentene (V, 50%), and its -2-isomer (VI, 10%), 3,5,5-trimethyl-2-hexene (VII, 23%), and its -3-isomer (VIII, 5%), and 2,4,4-trimethyl-2-hexene (IX, 10%).

The course of nonene formation may be pictured as follows, the asterisk indicating a carbon with only six electrons[4]:



$$\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}OH} + \mathrm{H_2SO_4} \rightleftarrows \mathrm{H_2O} + \mathrm{C{-}\overset{C}{\underset{C}{C}}{-}OSO_3H} \rightleftarrows \underset{\mathrm{I}}{\mathrm{C{-}\overset{*}{\underset{C}{C}}{-}C}} + \mathrm{HSO_4^-}$$

$$\mathrm{C{-}C{-}\overset{C}{\underset{C}{C}}{-}OH}\ \text{similarly} \rightleftarrows \mathrm{C{-}C{-}\overset{*}{\underset{C}{C}}{-}C} \quad \mathrm{II}$$

The electronically deficient fragments are not to be considered as ions capable of continued existence. Their half life is more probably of the order of 10^{-13} second. Essentially as rapidly as they are formed they undergo changes to more stable arrangements.

The yields indicate that 88% of the nonenes are formed by addition of a *t*-butyl fragment to an amylene or its equivalent as compared with 12% formed by the addition of a *t*-amyl fragment to isobutylene. This is related to the fact that only 0.5% isobutylene was found as compared with 30% isoamylenes.

The ratio of V to VI indicates that the loss of a proton from two methyl groups takes place about five times as easily as the loss of the tertiary proton which is part of a neopentyl system. This recalls the ratio in which the two isomeric diisobutylenes occur.[5] It is interesting that the reactivity of a tertiary hydrogen under these conditions appears to be somewhat less than that of two sec-

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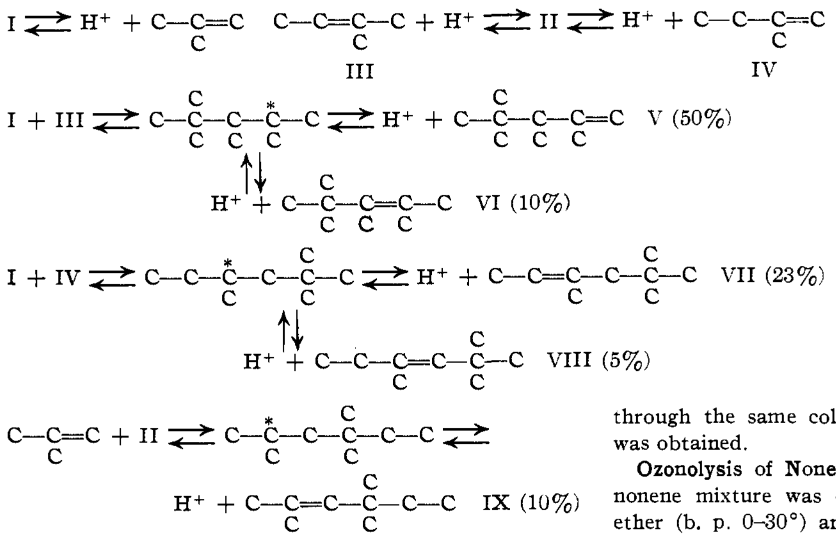
[1] For Paper III of this series see THIS JOURNAL, **63**, 1120 (1941). Original manuscript received February 15, 1940.

[2] Presented at the San Francisco meeting, August, 1936.

[3] Present address, Standard Oil Company of Indiana, Whiting, Indiana.

[4] Whitmore, THIS JOURNAL, **54**, 3274 (1932); *Ind. Eng. Chem.*, **26**, 94 (1934).

[5] Whitmore and Church, *ibid.*, **54**, 3711 (1932).



ondary hydrogens in a neopentyl system. The ratio of VII to VIII indicates that a single ethyl group liberates a proton about five times as readily as a neopentyl group. In this case, a single methyl group failed to yield a proton to an extent detectable by the methods used.

The failure to find any of the 1-isomer of IX is little less than startling and is being further studied.

Experimental

Purification of Alcohols.—Commercial Sharples *t*-amyl alcohol was distilled through an 85 × 1.7 cm. helix-packed column of about 12 theoretical plates; fractions of b. p. 101.5° at 735 mm. $n^{20}\mathrm{D}$ 1.4050 were used in the polymerization. The same column was used to give the constant boiling mixture of *t*-butyl alcohol and water b. p. 79° at 730 mm., $n^{20}\mathrm{D}$ 1.3858 containing 8.6% water by weight.

Dehydration and Copolymerization.—A solution of 2930 g. of concd. sulfuric acid in 1523 g. of water was warmed on the steam-bath to about 80° with 880 g. (10 moles) of *t*-amyl alcohol and 810 g. (10 moles) of the constant boiling mixture of water and *t*-butyl alcohol. Allowing for the water in the alcohol, the acid was 65% by weight sulfuric acid. The reaction flask was equipped with an efficient reflux condenser connected to a dry ice–acetone trap to catch isobutylene. The volume of oil layer became constant after eight hours and the product was cooled, separated, washed with dilute sodium carbonate solution, and dried over calcium chloride. Four similar batches were run. The five runs gave a total of 5600 g. of product (89% yield of olefins). The percentage distribution of the olefins was as follows: isobutylene (in dry-ice trap), 27 g., 0.5%; isoamylenes,[6] b. p. 35–38°, $n^{20}\mathrm{D}$ 1.384–1.387, 1658 g., 30%; diisobutylenes, 99–103.5°, 1.408–1.413, 1251 g., 22%; nonenes, 119–134°, 1.419–1.426, 948 g., 17%; diamylenes, 141–169°, 1.430–1.435, 343 g., 6%; triisobutylenes, 170–185°, 1.430–1.438, 353 g., 6%; higher polymers 1.5%, thus accounting for 83% of the olefins in these limits. The main portion of the nonenes had b. p. 125–130° at 730 mm. and $n^{20}\mathrm{D}$ 1.4233–1.4260. This was fractionated through column N,[7] a partial condensation column equivalent to 23 theoretical plates. The 99 fractions were combined in five batches according to refractive indices and these were twice fractionated by parts[6] through the same column. No evidence of separation was obtained.

Ozonolysis of Nonenes.—A total of 2.5 moles of the nonene mixture was ozonized in low-boiling petroleum ether (b. p. 0–30°) and decomposed by the zinc–water–catalyst method.[8] The oil obtained was dried over sodium sulfate and fractionated through the 12-plate column.[6] The products were identified as follows: Fraction 1, 6.4 g. impure trimethylacetaldehyde, b. p. 60–81°, 2,4-dinitrophenylhydrazone m. p. and mixed m. p. 208–209°; fraction 2, 27 g., 90–107°, a mixture of pinacolone and dimethylethylacetaldehyde. On refractionation, the lower boiling fractions gave the 2,4-dinitrophenylhydrazone of pinacolone m. p. and mixed m. p. 130–131° and semicarbazone, m. p. and mixed m. p. 154–155°. The higher boiling fractions gave the semicarbazone of dimethylethylacetaldehyde m. p. 154–155° mixed m. p. 153–155.5°. Fraction 3, 33.5 g. b. p. 117–124°, yielded the 2,4-dinitrophenylhydrazone of methyl neopentyl ketone, m. p. and mixed m. p. 99–100°, and semicarbazone, m. p. and mixed m. p. 174–176°. Fraction 4, 83.6 g. b. p. 138–143°, gave the 2,4-dinitrophenylhydrazone of 3,4,4-trimethyl-2-pentanone, m. p. and mixed m. p. 110°, semicarbazone m. p. and mixed m. p. 145–147°.[9] The known derivatives of the last substance were kindly supplied by Dr. N. L. Drake of the University of Maryland.

The water layer from the ozonolyses contained formaldehyde, identified by its reaction with resorcinol and concd. sulfuric acid, and acetone, identified by the preparation of dibenzalacetone. Acetaldehyde was identified in the ether trap of the ozonide decomposition apparatus by formation of aldehyde ammonia. Methyl ethyl ketone was not identified.

Summary

1. The dehydration of an equimolar mixture of *t*-amyl and *t*-butyl alcohols with 65% sulfuric acid yields 17% nonenes. The mixture could not be separated by repeated fractionation.

2. Ozonolysis of the nonene mixture and identification of the ozonolysis products indicates the percentage composition of the nonene mixture

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[6] The details of the analytical distillations can be found in L. W. Mixon's Dissertation, "Studies on the Products of the Mixed Dehydration and Polymerization of *t*-Amyl Alcohol and *t*-Butyl Alcohol." % Willard P. Lewis, Librarian, State College, Pa.

[7] Laughlin, Nash and Whitmore, THIS JOURNAL, **56**, 1396 (1934).

[8] Church, Whitmore and McGrew, *ibid.*, **56**, 176 (1934).

[9] Drake, Kline and Rose, *ibid.*, **56**, 2076 (1934).

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

BY EDMUND L. NIEDZIELSKI AND F. F. NORD

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

$$\mathrm{ArH + ClCH{=}N{-}CH{=}NH \xrightarrow{-HCl} ArCH{=}N{-}CH{=}NH \xrightarrow{H_2O} ArCH{=}NH + NH_3 + HCOOH \xrightarrow{H_2O} ArCHO + NH_3}$$

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).