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

The Formation of Cyclopropanes from Monohalides. III.[1] Action of Sodium Alkyls on Aliphatic Chlorides. Relation to the Wurtz Reaction

BY FRANK C. WHITMORE AND HARRY D. ZOOK[2]

The formation of benzene and ethylene in addition to ethylbenzene from the reaction of sodium phenyl and ethyl bromide has been explained by Schlubach and Goes[3] on the basis of a disproportionation between two free radicals. Since the postulation of sodium alkyls as intermediates in the Wurtz reaction,[4] Morton has studied the reaction of sodium amyl, prepared from amyl chloride and sodium, with various alkyl halides.[5] Low yields of the coupling products were obtained. Little attention has been given, however, to the "disproportionation products" from such reactions.

It appeared to us that, since sodium alkyls are strong hydrocarbo bases, the so-called disproportionation products may not arise by a free radical mechanism, but may be formed by the action of the hydrocarbo base on the halide.[6] Such a mechanism would give the saturated hydrocarbon corresponding to the sodium alkyl and the olefin corresponding to the halide in each case, rather than two saturated and two unsaturated hydrocarbons.

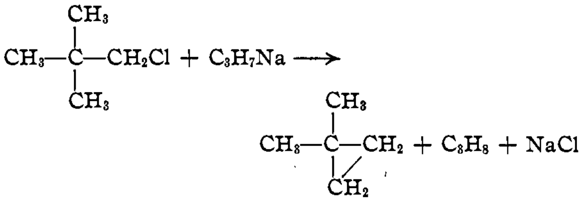
We have prepared sodium ethyl and sodium propyl from the corresponding mercury compounds and have treated these sodium alkyls with alkyl halides.

The reaction of sodium with excess mercury diethyl in *n*-pentane solution at 25° gave an 80% yield of sodium ethyl, the other product being a 5.8% sodium amalgam. This reaction mixture, when treated with *n*-hexyl chloride at $-10°$ to 0°, gave a 40% yield of *n*-octane, a 46% yield of 1-hexene, and a 52% yield of ethane along with a small amount (2%) of ethylene.

$$\begin{aligned} C_2H_5Na + C_6H_{13}Cl &\longrightarrow C_4H_9CH{=}CH_2 + C_2H_6 + NaCl \\ &\searrow n\text{-}C_8H_{18} + NaCl \end{aligned}$$

To see what would happen when a halide having no alpha hydrogen atoms was treated with an alkylsodium compound, we have investigated the reaction of sodium *n*-propyl and neopentyl chloride. This sodium alkyl was prepared in 88% yield from sodium and excess mercury di-*n*-propyl in *n*-octane solution. No appreciable reaction took place between the sodium propyl and neopentyl chloride at temperatures below 50°, in contrast to the action of sodium ethyl and *n*-hexyl chloride. However, reaction proceeded smoothly at 50–60° to give a 75% yield of **1,1-dimethylcyclopropane** and a 4% yield of the coupled product, 2,2-dimethylhexane. The other products were **propane** (70%) and propene (5%), the latter compound probably coming from the decomposition of part of the propyl sodium at the temperature used. No neopentane was formed. It was found that neopentyl chloride would not react with a 6% sodium amalgam such as was present in this case from the preparation of the sodium propyl.

The hydrocarbo base has caused cyclization by the removal of a beta hydrogen atom as hydrogen halide.



$$CH_3\text{—}\underset{CH_3}{\overset{CH_3}{C}}\text{—}CH_2Cl + C_3H_7Na \longrightarrow CH_3\text{—}\underset{CH_2}{\overset{CH_3}{C}}\text{—}CH_2 + C_3H_8 + NaCl$$

Although 3-ring closure has been accomplished many times by the removal of hydrogen halide with an aquo or alcoholo base, the hydrogen removed has usually been activated by an adjacent carboxyl or other strongly negative group.[7] The first step in our reaction may be the removal of one of the nine beta hydrogens by the sodium propyl to give propane.[8] Some indication of the base strength of the sodium alkyl may be seen from the fact that neopentyl chloride is inert to alcoholic potassium hydroxide in a sealed tube for twenty hours at 100°.[9] The reaction of sodium alkyls as well as other bases on halides of this type is being investigated further.

Yields of sodium alkyls from the mercury compounds were obtained indirectly in three ways: from the mercury recovered from the hydrolysis

---

[1] Whitmore and Carney, THIS JOURNAL, **63**, 2633 (1941).

[2] Allied Chemical and Dye Corporation Fellow, 1941–1942.

[3] Schlubach and Goes, *Ber.*, **55B**, 2889 (1922).

[4] *Cf.* Wooster, *Chem. Rev.*, **11**, 1 (1932).

[5] Morton and Fallwell, THIS JOURNAL, **59**, 2387 (1937).

[6] *Cf.* Whitmore and Thurman, *ibid.*, **51**, 1491 (1929).

[7] See, for example, Fuson in Gilman "Organic Chemistry," John Wiley and Sons, New York, N. Y., 1938, p. 21.

[8] *Cf.* Hauser, THIS JOURNAL, **62**, 933 (1940).

[9] Whitmore and Fleming, *ibid.*, **55**, 4161 (1933).

of the amalgam, from the sodium hydroxide thus obtained, and from the sodium chloride formed in the main reaction. The yields of sodium ethyl calculated by these three methods were 80 ± 1%. Quantitative sodium and chlorine material balances were obtained in each case. Solvents were recovered in better than 90% yields, showing that metalation of the normal paraffin hydrocarbons is not appreciable under the conditions used.

Mechanism of the Wurtz Reaction

Sodium alkyls[4] and free radicals[10] have been postulated by many workers as intermediates in the Wurtz reaction.

It has been shown that the Wurtz reaction may be carried out in such a manner that sodium alkyls play a major part in the mechanism.[11] Morton and Richardson found that by increasing the sodium surface per mole of amyl chloride the yields of acids formed by carbonation of the intermediate sodium compounds may go as high as 95% as the decane formed approaches zero.[11]

Part of the evidence for the free radical theory is based on the formation of disproportionation products such as ethane and ethylene in equimolar amounts from the reaction of ethyl iodide and sodium.[10b] Our work indicates that in cases where sodium alkyls play a major part in the reaction, the by-product saturated and unsaturated hydrocarbons obtained do not arise from the disproportionation of free radicals but from the action of the sodium alkyl as a hydrocarbo base with the alkyl halide.

Thus *n*-hexyl chloride and sodium ethyl give 40% *n*-octane by coupling and about 50% each of 1-hexene and ethane. The coupling product may be formed by a Walden inversion type of reaction. This is similar to the action of *n*-hexyl chloride with alcoholic bases to give mainly *n*-hexyl ethyl ether and a little 1-hexene.[12] The failure of neopentyl chloride and sodium propyl to give more than a few per cent. of coupling product is probably connected with the sluggishness of this halide in metathetical reactions of the Walden type.[13] In this case the by-product hydrocarbons become the main product and the "unsaturated" one appears as 1,1-dimethylcyclopropane. It would thus seem that the earlier work from this Laboratory on the action of sodium with neopentyl chloride[10a] and neohexyl chloride[1] may go through sodium alkyls formed from free radicals. These would react with the halides as does sodium propyl in the present study.

Experimental

The Reaction of Sodium Ethyl and *n*-Hexyl Chloride.—The apparatus consisted of a three-necked flask equipped with a reflux condenser, thermometer, dropping funnel, and mercury sealed stirrer. Gases were led from the reflux condenser through two dry-ice–acetone traps and collected over saturated sodium chloride solution. The air from the entire apparatus was swept out by a stream of nitrogen.

Exactly 23.1 g. of freshly cut sodium was weighed out in a glass-stoppered bottle under pentane. The sodium was then cut into very thin slices under pentane, the pentane decanted, and the sodium dried with a stream of nitrogen. The dry sodium was transferred in an atmosphere of nitrogen to the reaction flask and covered with 122.5 g. of olefin-free *n*-pentane; b. p. 36° (737 mm.), n^{20}D 1.3580. The addition of 200 g. of mercury diethyl, b. p. 67.5° (30 mm.), required thirty minutes during which time the flask was held at 25° by adding small pieces of dry-ice to an acetone-bath in which it was immersed. Reaction was rapid giving a fine suspension of sodium ethyl and sodium amalgam. No gas was formed. The mixture was allowed to stir for an hour, after which the flask was cooled to −10°.

The addition of 121.5 g. of *n*-hexyl chloride, b. p. 134° (738 mm.) and n^{20}D 1.4200, took place over a period of two and one-half hours. Gas was evolved at the rate of a liter an hour for twelve hours at temperatures between −10° and 0°. The reaction mixture was charged directly to a 13-plate column and 118 g. (96%) of the pentane solvent was removed; b. p. 35.5–37° (734 mm.); n^{20}D 1.3580–1.3592.

The clear liquid portion of the residue was decanted. The solid amalgam and sodium chloride were washed with small portions of pentane and filtered. The amalgam was decomposed with 500 cc. of water and 250 cc. of 0.927 *N* sulfuric acid. Back-titration with 23.7 cc. of standard sodium hydroxide (1 cc. base = 1.08 cc. of acid) indicated the presence of 4.76 g. of sodium in the amalgam. The mercury, after washing well with water, acetone, and dry ether, weighed 78.5 g. Analysis of the neutralized aqueous solution showed the presence of 47.1 g. of sodium chloride.

The yields of sodium ethyl in the first step of the reaction calculated from the mercury formed, from the sodium present in the amalgam, and from the sodium chloride formed by the reaction are 40.8, 41.4 and 41.8 g., respectively.

The liquid organic products from the reaction were fractionated at 733 mm. through a 13-plate column. Fractions: 3–9, 10.9 g., b. p. 44–62°, n^{20}D 1.3605–1.3872; 10–18, 23.7 g., 62–65°, 1.3880–1.3881; 19–21, 6.3 g., 75–123°, 1.3898–1.4000; 22–27, 29.9 g., 123°, 1.4020–1.4032; 28–31, 19.1 g., 124° (733 mm.) to 60° (40 mm.). The yields of 1-hexene and *n*-octane, taken from boiling point and refractive index curves, were 30.7 g. and 36.1 g., respectively.

---

(10) (a) *Cf.* ref. 1, and Whitmore and co-workers, THIS JOURNAL, **63**, 124 (1941); (b) Richards, *Trans. Faraday Soc.*, **36**, 956 (1940); (c) Bachmann and Clarke, THIS JOURNAL, **49**, 2089 (1927).

(11) Morton and Richardson, *ibid.*, **62**, 123 (1940).

(12) Unpublished results by A. H. Popkin of this Laboratory.

(13) Ref. 9; also *cf.* Bartlett and Rosen, THIS JOURNAL, **64**, 543 (1942).

The gas from the reaction was analyzed in a modified Orsat apparatus using a solution saturated with bromine and sodium chloride to remove the ethylene.[14] The gas evolved consisted of 0.50 g. of ethylene and 12.6 g. of ethane.

Identification of 1-Hexene.—Fractions 9–18 (24 g.) from the products of the reaction of sodium ethyl and *n*-hexyl chloride were diluted with 200 cc. of olefin-free pentane, and a stream of oxygen containing 3% ozone passed through at an average rate of 25 l. per hour for seven hours. The ozonide was decomposed according to the method of Whitmore and Church.[15] Formaldehyde was found in the water layer from the decomposition, and was identified by its dimethylcyclohexanedione derivative; m. p. 190.5–191.5°. Fractionation of the oil layer gave 8.2 g. of valeraldehyde; b. p. 95–99° (715 mm.); identified by its 2,4-dinitrophenylhydrazone, m. p. 107–108° and mixed m. p. with an authentic sample 107.5–108.5°.

Reaction of Sodium *n*-Propyl and Neopentyl Chloride.—The same apparatus and technique were used as for the reaction of sodium ethyl and *n*-hexyl chloride. The two cold traps were held at −40° in order to retain 1,1-dimethylcyclopropane but not propane. *n*-Octane, 232 g., b. p. 124.5° (729 mm.) and $n^{20}\text{D}$ 1.3982, was used as the dispersing medium. The propyl sodium was prepared from 23.0 g. of sodium and 202.5 g. of mercury di-*n*-propyl; b. p. 86.5° (25 mm.). No gas was evolved while stirring for an hour at room temperature. The reaction mixture was cooled to 0° for the addition of 89.5 g. of neopentyl chloride; b. p. 82–84° (740 mm.) and $n^{20}\text{D}$ 1.4048. After about a third of the chloride was added the mixture was slowly warmed to 50° at which temperature a slow evolution of gas began. The remainder of the chloride was added over a period of three hours. Gas was evolved at the rate of 500 cc. per hour for a period of about eight hours. At this point the stirrer was replaced by a 10-plate column to which was attached a series of traps held at −15, −80 and −80°, respectively. Ice water was circulated through the head and jacket of the column as the flask was gradually heated to 107° over a period of fifteen hours in order to complete the reaction and drive off all low boiling products. The residue was decomposed with water and standard acid as previously described. There was obtained 87.7 g. of mercury representing an 88% yield of sodium propyl. The amount of sodium in the amalgam (4.56 g.) and the sodium chloride from the reaction (46.1 g.) correspond to a 79% yield of sodium propyl. (Some sodium propyl decomposed, however, to give propylene.)

Material collected in the traps held at −80° was distilled through a low temperature micro column to give 22.0 g. boiling below −38° and a residue which, together with material collected in the traps held at −40°, was fractionated at 730 mm. through a 40-plate low temperature column. Obtained were fractions: 1–4, 2.3 g., b. p. −15 to 17°; 5–6, 7.7 g., 18–19.8°; 7–11, 31.0 g., 20.2–20.8°, $n^{20}\text{D}$ 1.3660–1.3675. The material from fractions 7–11 would not react with bromine in carbon tetrachloride. The residue from this distillation was combined with the other liquid organic products from the reaction and fractionated through a 40-plate column. From a complete distillation curve of both fractionations there was calculated to be 41.3 g. (75%) of 1,1-dimethylcyclopropane; 3.0 g. of recovered neopentyl chloride; 4.0 g. (4%) of impure 2,2-dimethylhexane, b. p. 104–111° (722 mm.), $n^{20}\text{D}$ 1.3998–1.4001; 214 g. (92.5%) of recovered octane solvent, b. p. 120° (722 mm.) to 70° (40 mm.), $n^{20}\text{D}$ 1.3982–1.3986; and 74 g. of recovered mercury dipropyl, b. p. 95–97° (40 mm.).

The material collected below −38° was vaporized, and the gas collected over saturated sodium chloride solution. Analysis of all the gaseous products indicated that there was present 1.85 g. (5%) of propene and 27.5 g. (71%) of propane. Again, a solution saturated with sodium chloride and bromine was used to absorb the olefin.

Attempted Reaction of Neopentyl Chloride with Sodium Amalgam.—Into a 500-cc. flask was placed 59 g. of neopentyl chloride, b. p. 82–84° (740 mm.), $n^{20}\text{D}$ 1.4048 and 209 g. of freshly prepared 6% sodium amalgam. The flask was attached to a 20-plate column and the neopentyl chloride refluxed for six hours. Fractionation then gave 6 fractions, 56.3 g., b. p. 83° (745 mm.), $n^{20}\text{D}$ 1.4048 along with 1.8 g.; $n^{20}\text{D}$ 1.4060 driven from the column when the jacket was heated to 160°. No low boiling products were collected in a dry-ice trap connected to the column. The recovery of neopentyl chloride was 98%.

Summary

1. Sodium ethyl and sodium propyl were prepared from sodium and the corresponding mercury compounds in yields of 80 and 88%, respectively. No appreciable reaction took place between the alkylsodium compounds and *n*-paraffin hydrocarbon solvents.

2. Sodium ethyl reacts with *n*-hexyl chloride to give octane (40%), ethane (52%), 1-hexene (46%), and a trace of ethylene.

3. The products of the reaction of sodium propyl and neopentyl chloride were 1,1-dimethylcyclopropane (75%), propane (70%), propene (5%), and the coupled product, 2,2-dimethylhexane (4%).

4. The major reaction is one of a hydrocarbo base splitting out hydrogen chloride from an alkyl chloride.

5. The possible relationship of these results to the mechanism of the Wurtz reaction is discussed.

STATE COLLEGE, PENNSYLVANIA

RECEIVED APRIL 27, 1942

---

[14] Lang, *Ind. Eng. Chem., Anal. Ed.*, **7**, 150 (1935).

[15] Whitmore and Church, THIS JOURNAL, **54**, 3710 (1932).