magnitude is a function of the "electron-sharing ability" of the radical linked to the amine group.

## Summary

It is pointed out that the electron-sharing ability of the aliphatic carbon radicals varies over a range extending from values more positive than hydrogen to values more negative than chlorine. The available physical data have been assembled to show the position of glucose (and other polyalcohols) among the more familiar aliphatic and aromatic radicals. These data agree in showing the intermediate position of this group of compounds as summarized in the following figures.

| Nature of radical | Dissoc. const. of amine | Dissoc. of hydroxide | Heat replacement of H by Na |
|---|---|---|---|
| Methyl- | $5 \times 10^{-4}$ | $10^{-15}$ | 32 |
| 2-Glucosyl- | $6 \times 10^{-7}$ | $10^{-13}$ | 37 |
| Phenyl- | $4 \times 10^{-10}$ | $10^{-11}$ | 39 |

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# STUDIES ON THE PREPARATION OF THE HIGHER ACETYLENES. I. (PRELIMINARY PAPER.) DEHALOGENATION OF 1,1-DICHLOROHEPTANE IN THE VAPOR PHASE

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Acetylenes, more particularly those of the normal, or alpha type, $RC{\equiv}CH$, are peculiarly reactive and in consequence may be used for the preparation of many interesting and important types of organic compounds. Unfortunately, however, their applicability in synthetic work is rather restricted because of the difficulty of preparing many of the $\alpha$-acetylenes in quantity and in a state of purity. The usual methods of preparation involve dehalogenation of dihalides, or olefinic monohalides, with solid, aqueous or alcoholic alkalies, alcoholic sodium ethylate, metallic sodium, sodium amide and, in a few cases, soda lime,[1] magnesium,[2] zinc dust and alcohol[3a] and the Grignard Reagent.[3b]

Failure to obtain satisfactory yields, apart from incomplete removal of halogen, is usually due to one, at least, of the following causes, namely, (*a*) molecular rearrangement by aqueous or alcoholic alkaline reagents to diolefins and *iso*-acetylenes ($RC{\equiv}CR$); (*b*) ether formation, when alcoholic alkalies are employed; (*c*) polymerization. The use of sodium

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[1] Peratoner, *Chem. Zentr.*, **1892**, II, 737.

[2] Porcher, *Bull. soc. chim.*, [4] **31**, 334 (1922).

[3] (a) Lespieau, *Compt. rend.*, **170**, 1584 (1920); (b) **171**, 111 (1920).

amide[4] in dehalogenation practice constitutes an important advance in the preparation of $\alpha$-acetylenes. Thus, like sodium, it is stated to effect the isomerization of an *iso*- to an $\alpha$-acetylene; as a function of this property, a minimum of *iso*-acetylene is apparently produced when sodium amide is used to dehalogenate a given halide.

Vapor phase dehalogenation of dihalides has apparently received but little attention, except in connection with the preparation of certain 1,3-diolefins used in the preparation of synthetic rubber. The present investigation (the first of the series) has involved a study of the dehalogenation of 1,1-dichloroheptane[5] (I), $CH_3(CH_2)_5CHCl_2$, in the vapor phase. Halides of this type, in consideration of their constitution, should theoretically undergo dehalogenation with the formation of a larger amount of the $\alpha$-acetylene and a smaller amount of diolefinic and *iso*-acetylenic isomers than 1,2-dihalides. Moreover, in view of the fact that dry alkalies are stated not to have the rearranging effect[6] of aqueous or alcoholic alkalies, dehalogenation of dichloroheptane in the vapor phase over soda lime should give a reaction product containing a preponderance of the normal acetylene, 1-heptine (II), ($CH_3(CH_2)_4C{\equiv}CH$).

The writers have passed dichloroheptane over soda lime in an electrically heated iron tube (see Fig. 1). Temperatures below 360° were found to be unsatisfactory because dehalogenation was incomplete, whereas above 430° extensive decomposition took place. The yield of normal heptine was never above 30% of the unsaturated compounds constituting the reaction product. The isomerization of $\alpha$-heptine was apparently affected but slightly by temperature changes between 360 and 420°. At 420° the normal acetylene content of the reaction product was 28% (10% calculated from dichloroheptane), while at 360° the yield was 25% (6% calculated from dichloroheptane). Losses through decomposition and polymerization were also large. The fact that the $\alpha$-acetylene constituted so small a portion of the unsaturated distillate indicated extensive molecular rearrangement, unless 1-heptine is far more susceptible to polymerization or decomposition than its isomers. Certainly the $\beta$-acetylene, and other unsaturated compounds derived from the initially formed $\alpha$-acetylene, were decidedly in predominance in the reaction product.

Variations in the composition of the soda lime did not appreciably affect isomerization. This was decidedly advantageous in view of the fact that soda lime containing 25% of sodium hydroxide was less efficient as a dehalogenating agent than that containing 50% of the alkali. So

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[4] Among others, see Bourguel, *Ann. chim.*, **10**, 191, 325 (1925).

[5] Dichloroheptane, rather than a lower homolog, was chosen for this preliminary investigation by reason of the accessibility of the corresponding aldehyde and the fact that the derived acetylenes, being oils, were easily handled.

[6] Faworsky, *J. prakt. Chem.*, **37**, 382, 417, 531 (1888).

far, then, as rearrangement phenomena are concerned, the vapor phase procedure does not appear to give results very different from those obtained by the employment of alkaline solutions.

A pyrogenetic dehalogenation of the dichloride at 470° over aluminum silicate effected almost complete decomposition and the yield of α-acetylene was very small—less than 2%.

## Experimental Part

**1,1-Dichloroheptane.**—Although dichloroheptane has found fairly extensive use, there is insufficient detailed information regarding its preparation from heptaldehyde[7] and phosphorus pentachloride. In order that large quantities of the dichloride might be employed, and suitable technique developed for the preparation of other similarly constituted dihalides, a number of experiments were carried out to determine conditions most favorable for its preparation.

The chief loss in the preparation of dichloroheptane is due to polymerization of the aldehyde by the acidic reaction mixture. To obviate this effect to some degree, the writers found it necessary to use a solvent and stir rapidly in order to effect immediate dispersion of the aldehyde. The most favorable temperature was 20°; above this temperature the residual material, after distillation, increased very appreciably, and at 65° polymerization had increased to such an extent that the yield was approximately one quarter that obtained at 20°. Amounts of phosphorus pentachloride above or below $1-1^1/_4$ molecular equivalents were not as effective as the latter figures. Some loss is also incurred by the formation of chloroheptene.[8] A serious factor also to be reckoned with is the purity of the phosphorus pentachloride. Erratic and unsatisfactory results, characterized by excessive polymerization, were often obtained when other than fresh samples of phosphorus pentachloride were used. Although the best yield under optimum conditions was 70%, this was not as readily achieved when large quantities of the aldehyde were used.

**Apparatus.**—A wide-mouthed flask equipped with dropping funnel, the stem of which reaches below the surface of the liquid; a thermometer with bulb in the reaction mixture, and a mercury-sealed stirrer capable of rapid rotation.

**Procedure.**—25 g. of heptaldehyde was added, during forty-five minutes, to a suspension of 45 g. of phosphorus pentachloride in 15 g. of benzene. The temperature was not allowed to rise above 20°. After addition of the aldehyde, the mixture stood at 25° for several hours (it may be allowed to stand overnight). Throughout the experiment the liquid remained light yellow in color. The phosphorus oxychloride was removed by adding ice to the reaction mixture and the dichloride extracted with benzene, washed with sodium carbonate, and dried over sodium sulfate. Distillation at 40 mm.

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[7] The writers are greatly indebted to Dr. Herbert Guest of the J. B. Williams Company, Glastonbury, Conn., who kindly furnished the heptaldehyde used in this investigation.

[8] Cf. Bourguel, *Compt. rend.*, **177**, 823 (1923).

gave 28 g. of crude dichloroheptane boiling at 75–100° (b. p. 82–84° at 30 mm.). The residue was 11.2 g.

As stated in the introduction, the yields with larger quantities are liable to be lower. The following is a typical run in which 100 g. of heptaldehyde was used, Fraction 3 being practically pure dichloroheptane.

Fraction 1 50–70° (30 mm.) = 5 g.
Fraction 2 70–80° (30 mm.) = 5 g.
Fraction 3 80–100° (30 mm.) = 73 g.
Fraction 4 100–115° (30 mm.) = 5 g.
Fraction 5 115–140° (30 mm.) = 11 g.

**1-Heptine.**—The soda lime used in these experiments was prepared by adding the desired amount of pulverized quicklime to molten sodium hydroxide at 900–1100°. The fused mass, after cooling, was crushed to 6 to 12 mesh.

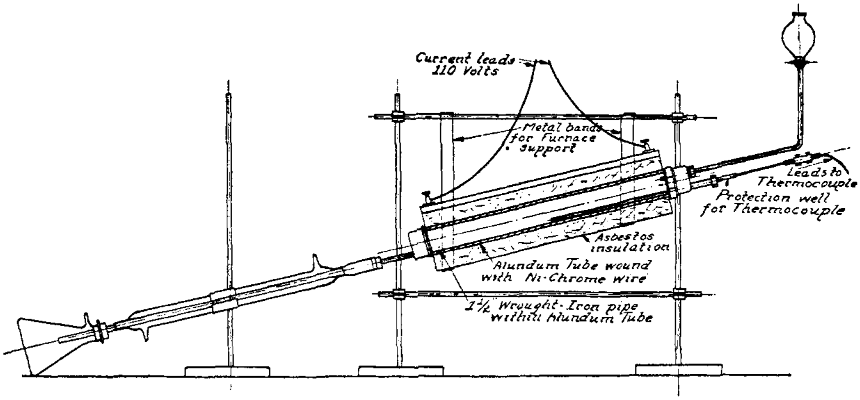

Fig. 1.—Electric furnace for dehalogenation experiments with soda lime.

The reactions were carried out in an electrically heated iron tube which is illustrated above (Fig. 1).

The accompanying chart gives a résumé of some typical experiments with this apparatus. Fresh soda lime was used in each experiment. This precaution appeared necessary for after each run, in which 100 g. or more of dichloroheptane was used, there was an appreciable deposit of carbon.

TABLE I

THE ACTION OF SODA LIME ON DICHLOROHEPTANE

| Expt. no. | Dichloroheptane, g. | Soda lime, g. | Temp., °C. | Fraction to 116°, g. | 1-Heptine in 116° fraction, % | Yield of 1-heptine calcd. from dichloroheptane, % |
|---|---|---|---|---|---|---|
| 1 | 100 | 350 (50% NaOH) | 360 | 11.3 | 30 | 6 |
| 2 | 150 | 300 (50% NaOH) | 400 | 31.6 | 14 | 5 |
| 3 | 100 | 300 (50% NaOH) | 420 | 21.0 | 28 | 10 |
| 4 | 30 | 250 (50% NaOH) | 430 | 14.0 | 7 | 6 |
| 5 | 100 | 350 (25% NaOH) | 410 | 13.4 | 25 | 6 |
| 6 | 100 | 300 (Aluminum silicate) | 470 | 8.7 | 14 | 2 |

The conditions represented by Expt. 3 were found in general to be the most favorable. The distillation figures in experiments of this type were usually of the following order:

| | | | | | |
|---|---|---|---|---|---|
| Fraction 1 | 80–90° | 0.7 g. | Fraction 4 | 116–150° | 4.7 g. |
| Fraction 2 | 90–100° | 2.3 g. | Fraction 5 | 150–180° | 16.2 g. |
| Fraction 3 | 100–116° | 18.0 g. | Residue | ........ | 3.5 g. |

The isomeric heptines, alpha, or 1-heptine, and beta, or 2-heptine, boil at 99–100° and 111–113°, respectively. In consequence, the distillates up to 116° contained the isomeric acetylenes; these were analyzed for 1-heptine as described below. The acetylene distillates were halogen free, or at most contained but a trace of chlorine.

In Expt. 6 the furnace was charged with aluminum silicate in the form of porous cylindrical sticks, $^1/_2''$ long by $^1/_4''$ in diameter. Throughout this run copious fumes of hydrogen chloride issued from the furnace and decomposition was very pronounced. All fractions contained chlorine, hence the analyses were not wholly accurate. The data obtained, however, indicated very small amounts of 1-heptine. A typical distillation is given below:

| | | |
|---|---|---|
| Fraction 1 | Up to 116° | 8.7 g. |
| Fraction 2 | 116–150° | 12.0 g. |
| Fraction 3 | 150–200° | 9.4 g. |

The experiment demonstrated the impracticability of pyrogenetic dehalogenation without the use of some acceptor for the hydrogen chloride resulting from the thermal dissociation.

**Procedure for the Determination of 1-Heptine.**—In order to determine the $\alpha$-acetylene formed in each experiment, two methods of analysis were employed, namely, (*a*) precipitation with ammoniacal cuprous chloride and (*b*) precipitation with an alcoholic silver nitrate solution. The former was carried out by agitating the heptine-containing oil with ammoniacal cuprous chloride for six hours. The yellow copper salt was filtered, washed with ether, and dried and weighed as $CuC{\equiv}C(CH_2)_4CH_3$. The rate of precipitation was slow and greatly affected by the concentration of ammonia. With strong solutions it was decidedly incomplete. The slowness of precipitation of the copper salt and the consequent inaccuracies led the writers to place greater reliance on the silver nitrate method.

**Silver Nitrate Procedure.**—This method, first introduced by Behal,[9] is based on the insolubility of the salts of the formula $RC{\equiv}CAg.AgNO_3$, formed in accordance with the following equation

$$CH_3(CH_2)_4C{\equiv}CH + 2AgNO_3 = CH_3(CH_2)_4C{\equiv}CAg.AgNO_3 + HNO_3$$

A 5% solution of silver nitrate in 95% alcohol was used by the writers. A few preliminary experiments showed that a moderate excess of silver nitrate did not affect the analytical results.

[9] Behal, *Ann. chim. phys.*, [6] 15, 424 (1888).

To carry out an analysis, 0.5 g. of the heptine-containing oil was placed in an excess of the silver nitrate solution. Precipitation of the fine, white crystalline salt took place immediately, but the mixture was usually allowed to stand for six hours before filtration. At this point two procedures were followed. One method was to filter the precipitate upon a weighed Gooch crucible. It was then washed thoroughly with alcohol and dried at 60°. The other procedure consisted in titrating the nitric acid liberated by the formation of the silver salt. In this case the precipitate was first filtered and washed. The united filtrates were then diluted with water to about 300 cc. and the excess silver precipitated by the addition of pure sodium chloride. The nitric acid was then titrated with sodium hydroxide, phenolphthalein being used as an indicator. The titration procedure was utilized in this investigation, since the gravimetric method gave results 2–3% higher than the former method, probably because of adsorption of silver and the retention of moisture. The salt decomposed slowly above 100°, so that thorough drying at atmospheric pressures was impracticable.

## Summary

1. Dichloroheptane has been passed over soda lime at various temperatures in an electrically heated tube and the 1-heptine content of the reaction products determined by the silver nitrate method.
2. The yield of 1-heptine was small on account of molecular rearrangement, polymerization reactions and decomposition resulting from the employment of high temperatures necessary to effect dehalogenation.
3. The extent of molecular rearrangement by this method, contrary to previous views on the effect of dry alkalies, is apparently quite comparable to that resulting from the use of alkali solutions.
4. A procedure for the preparation of 1,1-dichloroheptane is described.

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