[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF YALE UNIVERSITY AND THE OHIO STATE UNIVERSITY]

The Chemistry of the Acetylenes. I. The Preparation of 1-Heptyne by Dehalogenation Methods

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The preparation and dehalogenation of various chloro- and bromo-derivatives of heptane and heptene has been undertaken with a view to determining the relative amounts of 1-heptyne formed. The following types of halogen derivatives were studied

(1) RCH_2CHX_2
(2) RCX_2CH_3
(3) $RCHXCH_2X$
(4) $RCH{=}CHX$
(5) $RCX{=}CH_2$
(6) $RCH{=}CX_2$

For the present work $R = C_5H_{11}$ and X = Cl or Br.

Two series of dehalogenation experiments were run: the one in the vapor phase using soda lime, the other in the liquid phase using potassium hydroxide suspended in mineral oil.[1]

Attempts to improve the yields obtained previously[2] in the vapor phase method were only partially successful, and a series of experiments on the heat stability of heptyne indicated the probable futility of further efforts in this direction. Liquid phase dehalogenation of 1-bromoheptene gave 1-heptyne in 85 to 90% yields (by analysis).

1-Heptyne was found to polymerize rapidly at temperatures of 300° and above. The polymer so formed cracks at 400°. Below the polymerizing temperature dry alkalies were found to have no rearranging effect on 1-heptyne as was first observed for other normal acetylenes by Faworsky,[3] but later questioned by Guest.[1]

Experimental Part

The following materials were prepared or their preparation was attempted as indicated.

1,1-Dichloroheptane.—Heptaldehyde was treated with phosphorus pentachloride in benzene as recommended by Hill and Tyson.[2] The product had the constants: b. p. 82° (20 mm.); d_4^{20} 1.011; n_D^{20} 1.4440.

Anal. Calcd. for $C_7H_{14}Cl_2$: Cl, 42.0. Found: Cl, 41.9.

1,1-Dibromoheptane.—Like Kirrmann[4] we were unable to repeat Bruylant's[5] preparation of this substance. Attempts to prepare it by reduction of 1,1-dibromoheptene-1 and by treatment of 1,1-dichloroheptane with sodium bromide in methanol–acetone solution using potassium iodide and a crystal of iodine as catalyst were likewise unsuccessful.

2,2-Dichloroheptane and 2-Chloroheptene-1.—Fifty grams of methyl *n*-amyl ketone was added during the course of an hour to 125 g. of phosphorus pentachloride in 100 cc. of dry benzene. The temperature was maintained below 10° and the mixture was stirred constantly. Copious fumes of hydrochloric acid were evolved after about half of the ketone was added. The mixture was allowed to stand at 10° for another hour and then at room temperature overnight. Water and ice were added and the mixture stirred vigorously until all of the phosphorus oxychloride was decomposed. The product was washed with water, 2% sodium carbonate solution, and finally again with water. Upon fractionation under diminished pressure two fractions were obtained: (a) b. p. 71° (75 mm.), 23 g.; (b) b. p. 77° (25 mm.), 17 g.

Fraction (a) was found by analysis to consist of 2-chloroheptene-1 (yield 40%): physical constants, d_4^{20} 0.8895; n_D^{20} 1.4349.

Anal. Calcd. for $C_7H_{13}Cl$: Cl, 26.8. Found: Cl, 26.8.

Fraction (b) consisted of 2,2-dichloroheptane (yield 23%): physical constants, d_4^{20} 1.012: n_D^{20} 1.4440.

Anal. Calcd. for $C_7H_{14}Cl_2$: Cl, 42.0. Found: Cl, 41.4.

2,2-Dibromoheptane and 2-Bromoheptene-1.—When methyl *n*-amyl ketone was treated with phosphorus trichlorodibromide in dry benzene the only products which formed in appreciable amounts were a monobromo and a dibromo ketone,[6] methyl α-bromo-*n*-amyl ketone (yield 43%), b. p. 80° (9 mm.), d_4^{20} 1.261, n_D^{20} 1.4613; and methyl α,α-dibromo-*n*-amyl ketone (yield 39%), b. p. 118–120° (9 mm), d_4^{20} 1.618, n_D^{20} 1.5060.

Anal. Calcd. for $C_7H_{13}OBr$: Br, 41.5. Found: Br, 41.9.

Anal. Calcd. for $C_7H_{12}OBr_2$: Br, 58.8. Found: Br, 58.8.

1,2-Dichloroheptane.—1-Heptene was prepared by the method of Brooks and Humphrey from allyl bromide and butylmagnesium bromide. The chlorination was carried out in carbon tetrachloride solution at −5°. There were copious amounts of hydrogen chloride evolved and only a 13% yield of 1,2-dichloroheptane (based on the allyl bromide) was obtained. Much better success (30–40% yields) attended the use of sulfuryl chloride[7] as a chlorinating agent. The product was a colorless fragrant oil of b. p. 68–72° (7 mm.), d_4^{20} 1.064, n_D^{20} 1.4490.

Anal. Calcd. for $C_7H_{14}Cl_2$: Cl, 42.0. Found: Cl, 42.8.

1,2-Dibromoheptane.—The conversion of 1-heptene into dibromoheptane has been described by Kirrmann[8]

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(1) Guest, THIS JOURNAL, **50**, 1744 (1928).

(2) Hill and Tyson, *ibid.*, **50**, 172 (1928).

(3) *Cf.* Faworsky, *J. prakt. Chem.*, **37**, 382 (1888).

(4) Kirrmann, *Bull. soc. chim.*, **41**, 316 (1927).

(5) Bruylant, *Ber.*, **8**, 409 (1875).

(6) *Cf.* Faworsky, *J. prakt. Chem.*, [2] **88**, 641 (1913).

(7) *Cf.* Badische Co., French Patent 433,309; *J. Soc. Chem. Ind.*, **31**, 151 (1912).

(8) Kirrmann, *Bull. soc. chim.*, **39**, 988 (1926).

and by Guest.[1] The compound may be distilled at atmospheric pressures with but slight decomposition, b. p. 227–229° (corr.), the reddish color thereby resulting being removed conveniently by shaking with solid sodium hydrogen carbonate.

1-Chloroheptene-1.—The preparation of this substance by dehalogenation of 1,1-dichloroheptane with alcoholic potassium hydroxide has already been described.[9] The authors found, however, that the yields were low by this method and that the principal product was an unsaturated liquid boiling at about 150° at 75 mm. pressure. When 1,1-dichloroheptane was mixed with five mole equivalents of solid potassium hydroxide and heated in an oil-bath (bath temperature 200°), the desired substance gradually distilled out of the reaction mixture and was obtained finally in 62% yields (pure product). The chloroheptene was difficult to purify but careful fractionation led to a product boiling at 78–82° at 75 mm. pressure.

1-Bromoheptene-1.—In a recent paper[10] the preparation of this substance in a pure state was described. In the dehalogenation experiments a monobromoheptene[11] resulting from the dehalogenation of 1,2-dibromoheptane was also used. This doubtless consisted of a mixture of monobromoheptenes.

1,1-Dibromoheptene-1.—This substance was prepared as described by one of us in a paper hereinbefore cited.[10]

Vapor Phase Dehalogenation

In these experiments the procedure and apparatus described by Hill and Tyson was used with but few modifications. The best results were obtained when 50 g. of dichloroheptane was swept with a stream of nitrogen over 400 g. of granulated soda lime (8-mesh commercial product) at 420° in the course of about an hour. Numerous experiments were tried in which one or more of the above conditions were varied. In no case did the yields equal those for the procedure outlined above.

Results.—The table summarizes the results of the most successful experiments on the several halides used. For the purpose of conserving space the results of the remainder of the vapor phase dehalogenation experiments are not included.

Halide	1-Heptyne in product, %	Yields of 1-heptyne, %
1,1-Dichloroheptane	34	23
1,2-Dichloroheptane	7	3
1,2-Dibromoheptane	4	3

The negligible quantities of 1-heptyne arising from the 1,2-dihalides are quite striking. Even from 1,1-dichloroheptane the yields were not satisfactory although considerably better results were obtained than those recorded in previous work.

Liquid Phase Dehalogenation

For these experiments a specially constructed 3-necked steel pot was used. This was necessary since strong alkalies attack glass readily at elevated temperatures. It was found that a Pyrex flask could not be used for more than four or five runs at most. The iron pot, of about 1.5 liters capacity, was fitted with a steel stirrer, mercury seal, a thermometer and a delivery tube extending into a condenser arranged for downward distillation. The pot was suspended in an oil-bath. The powdered potassium hydroxide and the mineral oil were placed in the vessel and the halide added before heating was started.[12] Stirring was began and the oil-bath was gradually heated until the product began to distil into the receiver. This evolution of product was maintained at a slow steady rate by gradually increasing the temperature of the oil-bath to about 250°. The products were treated in exactly the same manner as the products from the vapor phase experiments, and finally they were analyzed for their content of normal acetylene using 0.5-g. sample with 50 cc. of 5% alcoholic silver nitrate solution. The best results were obtained when 4 to 8 moles of potassium hydroxide were used per mole of halide, depending on the number of molecules of hydrogen halide to be removed. Thus, for example, with 100 g. of 1,1-dichloroheptane there were used 200 g. of powdered potassium hydroxide and 400 cc. of mineral oil. With 1-bromoheptene-1 half as much potassium hydroxide and mineral oil sufficed. A few experiments were carried out in which the mineral oil was eliminated and the halide was dropped into the hot or even molten potassium hydroxide. While this procedure seems to work best for the preparation of phenylacetylene[13] it gave only fair yields of 1-heptyne. The presence of the mineral oil seemed to prevent rapid vaporization of the material being dehalogenated until a temperature considerably above its normal boiling point was reached. This is particularly advantageous in the case of low boiling substances as, for example, 1-chloroheptene-1, which may be distilled practically unchanged from molten potassium hydroxide, whereas it is almost completely dehalogenated in the mineral oil suspension.

Results.—The table shown below indicates the outcome of these experiments. Each result represents the average of several determinations.

Halide	1-Heptyne in product, %	Yield of 1-heptyne, %
1,1-Dichloroheptane	76	40
2,2-Dichloroheptane	Trace	0
1,2-Dichloroheptane	66	33
1,2-Dibromoheptane	78	64
1-Chloroheptene-1	74	37
1-Bromoheptene-1	91	88
2-Chloroheptene-1	Trace	0
1,1-Dibromoheptene-1	80	21
Monobromoheptene (mixt.)	79	65

It is interesting to note that the discrepancy between the yields of 1-heptyne from the 1,1-dihalides and from the 1,2-dihalides is not nearly so marked as was the case in the vapor phase dehalogenations. Obviously, 1-bromoheptene-1 is the most satisfactory substance from which to

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[9] Limpricht, *Ann.*, **103**, 82 (1857); Welt, *Ber.*, **30**, 1495 (1897).

[10] Bachman, THIS JOURNAL, **55**, 4279 (1933).

[11] The authors are indebted to Dr. H. H. Guest of the J. B. Williams Co., Glastonbury, Connecticut, for the monobromoheptene used in these experiments.

[12] This was found to give much better results than dropping the halide into the already hot dehalogenating mixture as recommended by Guest. When this was done dehalogenation was much less complete.

[13] *Cf.* J. C. Hessler, "Organic Syntheses," Vol. II, 1922, p. 67.

prepare 1-heptyne. On the other hand, 1,1-dichloroheptane is the cheapest starting material.

Heat Stability of 1-Heptyne

The low yields from the vapor phase dehalogenation experiments led the authors to seek for an explanation in the effect of high temperatures on 1-heptyne. It was believed at first that dry alkalies such as soda lime would cause the rearrangement of 1-heptyne to 2-heptyne in much the same fashion as this rearrangement is caused by alcoholic potassium hydroxide.[3] Such a postulate is contrary to the early work of Favorsky, but is apparently supported by the work of Guest. To determine which view is correct, heptyne of predetermined 1-heptyne content was heated at various temperatures and for various periods of time with solid soda lime in sealed Pyrex glass tubes. Temperatures below 275° for periods up to five hours had no effect except to increase slightly (from 76 to 81%) the 1-heptyne content of the mixture. At temperatures of 300°, however, the 1-heptyne content of the mixture was reduced to zero even on one hour of heating. In fact, the material was so polymerized that it closely resembled petroleum in appearance and almost none of it distilled below 116°. Evidently then the polymerization of heptyne, while almost negligible at 250°, becomes quite rapid at 300°. Experiments were next carried out at still higher temperatures. The material which was heated to 400° first polymerized and then cracked, so that considerable gas pressure was developed in the sealed tubes, and, although analysis indicated the total absence of normal acetylenes, nevertheless about one-third of the product distilled below 116°.

Results.—These results are shown in tabular form. The column headed "Residue" shows in each case the amount of material from 5 g. of heptyne which, after heating, did not distil below 116°. The last column shows the results of the analysis of the distillate.

Substance	Hours of heating	Temp., °C.	Residue, g.	1-Heptyne before heating, %	1-Heptyne after heating, %
Heptyne	5	100	0.0	76.0	76.5
Heptyne	5	200	.0	76.0	77.7
Heptyne	5	250	.3	76.0	81.5
Heptyne	1	275	1.8	74.5	75.7
Heptyne	1	300	5.0	74.5	0.0
Heptyne	1	400	3.5	71.0	.0
Heptyne	0.6	400	2.5	74.5	20.0
Heptyne + 2 g.	1	200	0.5	74.5	77.7
of soda lime	1	250	1.5	74.5	79.3

One experiment was carried out in which 8 g. of 1-heptyne (63%) was heated with 2.5 g. of potassium hydroxide and 8 g. of alcohol. Rearrangement of the 1-heptyne was complete within five hours at a temperature of 200°.

Summary

A study has been made of the preparation of 1-heptyne by vapor and liquid phase dehalogenation methods. The relative yields of 1-heptyne obtained from the various possible halide types were determined. Dehalogenation of 1-bromoheptene-1 with 4 moles of potassium hydroxide suspended in mineral oil gave 85 to 90% yields of 1-heptyne.

Several new compounds have been prepared and their properties determined. These include 1,2-dichloroheptane, 2,2-dichloroheptane, 2-chloroheptene-1, methyl α-bromo and methyl α,α-dibromo-n-amyl ketones. A more satisfactory preparation of 1-chloroheptene-1 has been developed.

The action of heat on heptyne-1 both in the presence and in the absence of soda lime has been studied. Dry alkalies have been found not to rearrange 1-heptyne to 2-heptyne. 1-Heptyne polymerizes rapidly at 300° and the polymer cracks at 400°, giving products part of which boil in the heptyne range, but which contain no 1-heptyne.

Vapor phase dehalogenation with soda lime has been found to be unsatisfactory for the preparation of acetylenes such as 1-heptyne because of the high temperatures which are necessary to cause dehalogenation to take place. The acetylenes, when formed, are rapidly polymerized at these temperatures and the yields of the desired products are consequently low.

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