[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA, LOS ANGELES]

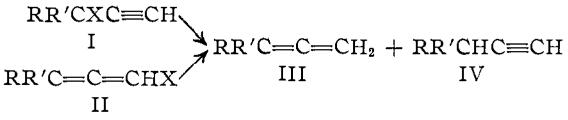
The Dehalogenation of Allenic Halides[1]

BY THOMAS L. JACOBS, EUGENE G. TEACH[2] AND DANIEL WEISS

RECEIVED JUNE 10, 1955

The allenic halides 1-chloro-1,2-hexadiene, 1-chloro-3-methyl-1,2-butadiene and bromopropadiene reacted with a zinc-copper couple to give the same mixtures of allenic and acetylenic hydrocarbons as the corresponding propargyl halides 3-chloro-1-hexyne, 3-chloro-3-methyl-1-butyne and 3-bromopropyne. Rearrangement of the propargyl halides to the allenic halides did not occur under these conditions. These same compounds were dehalogenated with lithium aluminum hydride. The propargyl halides gave results qualitatively like those obtained with zinc-copper, but the ratio of allenic hydrocarbon to acetylenic hydrocarbon was different except with 3-chloro-3-methyl-1-butyne which gave only 3-methyl-1,2-butadiene with either reagent. Bromopropadiene gave results but little different from 3-bromopropyne, but the two chloroallenes gave mainly saturated hydrocarbons and olefins, along with minor amounts of the corresponding acetylenic hydrocarbons.

The dehalogenation of propargyl halides I (R = alkyl, R′ = alkyl or H) to yield allenic hydrocarbons III mixed in most instances with some of the corresponding acetylenic hydrocarbons IV has been effected in several ways; the process has practical value as a method for the synthesis of allenes III when the dehalogenating agent is lithium aluminum hydride[3,4] or a zinc–copper combination.[5–7]



$$\begin{array}{lcl} \underset{\text{I}}{RR'CXC{\equiv}CH} \searrow & & \\ & & \underset{\text{III}}{RR'C{=}C{=}CH_2} + \underset{\text{IV}}{RR'CHC{\equiv}CH} \\ \underset{\text{II}}{RR'C{=}C{=}CHX} \nearrow & & \end{array}$$

It was of interest to compare allenic halides II with the propargyl halides from which they are obtained by rearrangement to discover whether the former are intermediates in the dehalogenation of the latter and to investigate the course of the reaction in which halogen is replaced by hydrogen in both types of compound.

The reduction of 1-chloro-3-methyl-1,2-butadiene (II, R = R′ = CH_3; X = Cl) by zinc and copper powder in ethanol or butanol was reported to give pure 3-methyl-1,2-butadiene in excellent yield and free from 3-methyl-1-butyne.[5] 3-Chloro-3-methyl-1-butyne (I, R = R′ = CH_3; X = Cl), gave the same product in slightly lower yield (63% compared with 85%).[5] The dehalogenation of 1-chloro-3-ethyl-1,2-pentadiene (II, R = R′ = C_2H_5; X = Cl), required a higher temperature and was carried out in boiling 2-ethoxyethanol.[8] No other reports of dehalogenations of allenic halides were encountered.

The allenic halides used in the present investigation were 1-chloro-1,2-hexadiene, 1-chloro-3-methyl-1,2-butadiene and bromopropadiene. These and the corresponding propargyl compounds were dehalogenated both with lithium aluminum hydride and with a zinc–copper couple in ethanol. The results are summarized in Table I.

TABLE I

DEHALOGENATION OF PROPARGYLIC AND ALLENIC HALIDES

Halogen compound	Solvent[a]	Yield of hydrocarbon, %	Ratio of allene to acetylene
	Zn–Cu		
$BrCH_2C{\equiv}CH$	EtOH	82	2
$BrCH{=}C{=}CH_2$	EtOH	88	2
n-$C_3H_7CHClC{\equiv}CH$	EtOH	63	36
n-$C_3H_7CH{=}C{=}CHCl$	EtOH	55	36
$(CH_3)_2CClC{\equiv}CH$	EtOH	51	[b]
	$LiAlH_4$		
$BrCH_2C{\equiv}CH$	DEC	85	<0.02
$BrCH{=}C{=}CH_2$	DEC	90	[c]
n-$C_3H_7CHClC{\equiv}CH$	Et_2O	56	7
n-$C_3H_7CH{=}C{=}CHCl$	DEC	54	[d]
$(CH_3)_2CClC{\equiv}CH$	THF	54	[b]
$(CH_3)_2C{=}C{=}CHCl$	THF	61+	[d]
	DEC	74	[d]

[a] Solvents: EtOH = anhyd. ethanol, DEC = Diethylcarbitol $(C_2H_5OCH_2CH_2)_2O$, Et_2O = diethyl ether, THF = tetrahydrofuran. [b] No 3-methyl-1-butyne could be detected with ammoniacal silver nitrate solution. [c] No allene could be detected by infrared. The product appeared to be pure propyne. [d] A small amount of acetylenic material could be removed by distillation before hydrolysis. This was shown to be 1-alkyne by reaction with ammoniacal silver nitrate. Hydrolysis of the reaction mixture was an exothermic reaction which gave a mixture of hexane and hexenes from 1-chloro-1,2-hexadiene; isopentane and 3-methyl-1-butene from 1-chloro-3-methyl-1,2-butadiene in tetrahydrofuran; and mainly isopentane in Diethylcarbitol.

When zinc–copper dehalogenation was employed, the allenic halides were found to give the same results as the propargyl compounds. 1-Chloro-1,2-hexadiene and 3-chloro-1-hexyne were found to react at about the same rate under the conditions described by Hennion and Sheehan[6] and the same product was obtained from both as judged by refractive indexes. An experiment starting from 3-chloro-1-hexyne was interrupted after about half the chloride had reacted and the unused chloride was recovered; this recovered material was unchanged 3-chloro-1-hexyne and no 1-chloro-1,2-hexadiene could be detected. It was found that 1-hexyne was unchanged by refluxing in ethanol with a zinc–copper couple or with the zinc–copper residue which had been used to dehalogenate 3-chloro-1-hexyne.

---

[1] This work was carried out largely under a contract with the Office of Naval Research, but a few of the experiments were done under a contract with the Office of Ordnance Research. Reproduction in whole or in part is permitted for any purpose of the United States Government. Part of the material is taken from the Ph.D. thesis of Daniel Weiss. A preliminary report of this work was given at the New York meeting of the American Chemical Society, September, 1954 (see Abstracts of Papers Presented, page 24-O).

[2] Western Regional Laboratory, U. S. Department of Agriculture, Albany, California.

[3] W. J. Bailey and C. R. Pfeifer, *J. Org. Chem.*, **20**, 95 (1955).

[4] J. H. Wotiz, THIS JOURNAL, **73**, 693 (1951).

[5] Ya. I. Ginzburg, *Zhur. Obshchei Khim.*, **10**, 513 (1940); *C. A.*, **34**, 7843 (1940).

[6] G. F. Hennion and J. J. Sheehan, THIS JOURNAL, **71**, 1964 (1949).

[7] T. L. Jacobs, R. Akawie and R. G. Cooper, *ibid.*, **73**, 1273 (1951).

[8] Ya. I. Ginzburg, *Zhur. Obshchei Khim.*, **15**, 442 (1945); *C. A.*, **40**, 4655 (1946).

Dehalogenation of 1-chloro-3-methyl-1,2-butadiene by zinc and copper[5] was not repeated, but the zinc–copper couple method was used with 3-chloro-3-methyl-1-butyne. The reaction of propargyl bromide was slightly exothermic, but no heat seemed to be produced with bromoallene.

The heterogeneous nature of the zinc–copper couple reaction made it difficult to obtain more exact information about it, but the results indicate that a common intermediate is involved for any pair of allenic and propargylic halides. The results are consistent with either the formation of the same organozinc compound from both members of a given pair or a dehalogenation on the surface of the zinc to an intermediate complex or ion of common structure which then takes up hydrogen to give final products. Rearrangement of one halogen compound to the other during the reaction appears to be excluded.

Dehalogenation of propargyl halides by lithium aluminum hydride is qualitatively like the reaction with zinc–copper, and mixtures of the corresponding acetylenic and allenic hydrocarbons are obtained. Bromoallene gave results very like those observed with propargyl bromide although with the former no allene at all could be detected by the infrared spectral method in the propyne formed, while the gas generated from the latter definitely contained some allene; the maximum amount which could be present was no more than 2.5%. The reaction with bromoallene was slightly less vigorous than with propargyl bromide.

The chloroallenes investigated behaved differently from the corresponding propargyl chlorides. 1-Chloro-3-methyl-1,2-butadiene gave an exothermic reaction with excess lithium aluminum hydride in bis-(β-ethoxyethyl) ether (Diethylcarbitol), but very little volatile material was driven off even above 100°. The volatile product gave a precipitate with ammoniacal silver nitrate and the infrared spectrum expected for 3-methyl-1-butyne; however, an impurity may have been present because the silver derivative rapidly turned pink and then black. Addition of water to the lithium aluminum hydride reaction mixture gave mainly isopentane. No 3-methyl-1,2-butadiene could be found. When the molar ratio of lithium aluminum hydride to chloride was reduced to one-half, the volatile material collected before hydrolysis was about the same, but the main product was 3-methyl-1-butene, and the yield of 2-methylbutane was low. An experiment in which solid lithium aluminum hydride was added to the chloride gave approximately the same amount of 3-methyl-1-butyne, but very little hydrocarbon was obtained on hydrolysis. The reaction of 1-chloro-1,2-hexadiene with excess lithium aluminum hydride in Diethylcarbitol resembled that of 1-chloro-3-methyl-1,2-butadiene.

These reactions, which appear to involve the formation of an addition product between chloroallenes and lithium aluminum hydride, are analogous to the reaction of α-olefins with the same reagent.[9] It was reported that with $RCH{=}CH_2$ at temperatures around 100° adducts of the type $Li(RCH_2CH_2)_4Al$ were produced, presumably by addition of the reagent as $\overset{\ominus}{\mathrm{H}}\text{ --- }\overset{\oplus}{\mathrm{Al}}<$, and that these gave saturated hydrocarbons when treated with water. The sequence of events leading from 1-chloro-3-methyl-1,2-butadiene to an adduct which could be hydrolyzed to 3-methyl-1-butene by water or converted by excess reagent to another adduct hydrolyzable to a saturated hydrocarbon is not clear. One would expect that the inert chlorine of a chloroallene would be replaced relatively slowly by hydrogen from the reagent and that the chlorine would activate the allenic system for attack by hydride ion or a hydrogen in $(AlH_4)^-$. Bailey and Pfeifer[3] reported that neither 3-methyl-1,2-butadiene nor 3-methyl-1,2-pentadiene was reduced by lithium aluminum hydride and we have found that 1,2-hexadiene is unattacked by the reagent in Diethylcarbitol on the steam-bath. Although none of these experiments was carried out under precisely the conditions used in the dehalogenation, it seems probable that addition of the lithium aluminum hydride to one of the double bonds in the chloroallene system precedes removal of the chlorine atom. This would account for the difference between propargyl halides and chloroallenes in this reaction; the former possess an active halogen which is replaced by the reagent more rapidly than addition occurs. One would expect a bromine atom to be more reactive than a chlorine, and this may explain the fact that bromoallene behaves like the propargylic compounds. No other bromoallenes have been reported so the general behavior of allenic bromides remains uncertain, but we now have some of these compounds and expect to study their behavior with lithium aluminum hydride; chloroallene will also be examined. It is interesting that lithium aluminum hydride reduces the allenic system in 2,3-butadienoic acid or its ester before the acid group is reduced.[10] The carboxyl or carbethoxyl group would be expected to decrease the electron density of the allenic bonds and promote attack by nucleophilic reagents.

The report[3] that 3-chloro-3-methyl-1-pentyne was converted to 3-methyl-2-pentene by lithium aluminum hydride is of interest because it indicates that the reagent will also attack the triple bond in propargylic chlorides. It is noteworthy that a β-olefin is obtained in this instance while 1-chloro-3-methyl-1,2-butadiene gives an α-olefin. The physical constants reported[3] for the forerun from the products of the reaction suggest that 3-methyl-1-pentene also may have been present.

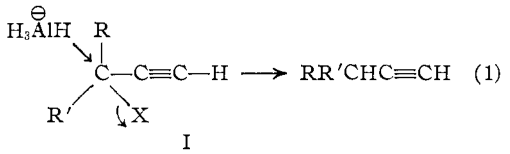
The mechanism of the reaction of lithium aluminum hydride with propargyl halides remains uncertain. Wotiz[4] suggested nucleophilic attack by hydride ion on the carbon carrying the halogen, which could yield a mixture of allenic and acetylenic hydrocarbons if both the propargylic compound and the isomeric allenic halide were present (perhaps in dynamic equilibrium). This possibility is disproved for 3-methyl-3-chloro-1-butyne and 3-chloro-1-hexyne, first because the corresponding chloroallenes give different products, and second because an experiment in which dehalogenation of 3-chloro-1-hexyne was interrupted before

---

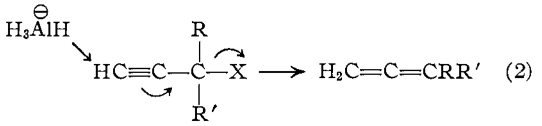
(9) K. Ziegler, *Angew. Chem.*, **64**, 323 (1952).

(10) G. Eglinton, E. R. H. Jones, G. H. Mansfield and M. C. Whiting, *J. Chem. Soc.*, 3197 (1954).

completion showed that the recovered chloride had not rearranged. The results can be explained by a combination of SN2 and SN2′ attack by hydride ion or $(AlH_4)^-$ as pictured in equations 1 and 2, also suggested by Wotiz.[4]

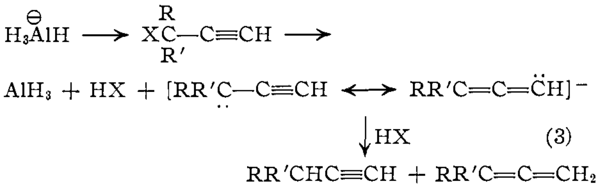


I



According to this mechanism the tertiary halides I (R and R′ = alkyl) should give very little acetylene because a second-order displacement on a tertiary carbon is slow and the SN2′ process (eq. 2) would be expected to be the principal reaction path; secondary halides I (R = H, R′ = alkyl), might give mixtures with the SN2 process (eq. 1) still relatively slow; with propargyl bromide SN2 should be rapid and propyne the main product. Table I shows that the facts are in accord with this picture. The observation[3,11] that propargyl bromides of the type $RC{\equiv}CCH_2Br$ give mainly or exclusively acetylenic hydrocarbons is also in accord with this mechanism.

An alternative mechanism which is not excluded by any of the known facts involves nucleophilic displacement on the halogen (eq. 3).



$$\overset{\ominus}{H_3AlH} \longrightarrow X\overset{R}{\underset{R'}{C}}{-}C{\equiv}CH \longrightarrow$$

$$AlH_3 + HX + [RR'\underset{\cdot\cdot}{C}{-}C{\equiv}CH \longleftrightarrow RR'C{=}C{=}\ddot{C}H]^- \xrightarrow{HX} RR'CHC{\equiv}CH + RR'C{=}C{=}CH_2 \quad (3)$$

Such a nucleophilic displacement was suggested[12] to account for the dehalogenation of 1,2-dibromides to yield olefins. It appears unlikely that an SN1 mechanism involving ionization of the halogen is important because even a tertiary chloride like 3-chloro-3-methyl-1-butyne solvolyzes at a very low rate.[13] There is of course no evidence that all of the propargyl halides react by the same mechanism.

The investigation of the behavior of both allenic halides and propargylic halides with lithium aluminum hydride is being continued.

Experimental Part

The distilling columns used in this work were a 1.4 × 45-cm. glass helix packed, total condensation, partial take-off, Whitmore–Fenske column and a Trubore concentric-tube type, 9.5 mm. i.d., 85 cm. in length.

Propargyl alcohol was obtained from the General Aniline and Film Corp. and distilled through the helix column in the presence of about 1% of succinic acid[14] before use.

***n*-Propylethynylcarbinol** was prepared by the addition of *n*-butyraldehyde to sodium acetylide in liquid ammonia in 50–55% yield.[6] The product was distilled through the helix column, b.p. 73–74° at 50 mm., $n^{25}D$ 1.4340.

Dimethylethynylcarbinol was obtained as a gift from the Air Reduction Chemical Co. and had a boiling point of 104° when distilled through the helix column before use.

3-Bromopropyne and bromopropadiene were prepared as described earlier.[15]

3-Chloro-1-hexyne and 1-Chloro-1,2-hexadiene.—*n*-Propylethynylcarbinol was treated with thionyl chloride following the directions of Hennion and Sheehan[6] but the reaction mixture was fractionally distilled through the helix-packed column at 50 mm. directly without treatment with water. Both 3-chloro-1-hexyne and 1-chloro-1,2-hexadiene were obtained in total yield of 79–84%. The propargyl chloride obtained in the first fractionation, b.p. 47–51° (50 mm.), $n^{25}D$ 1.4400, yield 66–74%, contained a little of the chloroallene; redistillation through the Trubore column gave material, b.p. 63.8–64.1° (100 mm.), $n^{20}D$ 1.4389; another sample, b.p. 47–48° (50 mm.), $n^{25}D$ 1.4373. Hennion and Sheehan[6] reported b.p. 63–64° (100 mm.), $n^{25}D$ 1.4375.

1-Chloro-1,2-hexadiene, b.p. 56–58° (50 mm.), $n^{25}D$ 1.4655, was obtained in only 6% yield, but appreciable losses occurred during the fractionation. If one assumes a linear relationship between refractive index and composition, the material obtained in the first fractionation (total of all fractions) contained about 20% of the allene and 80% of the acetylene.

3-Chloro-1-hexyne (116.5 g., 1 mole) was rearranged by shaking at room temp. for 14 days with a mixture of 20 g. of cuprous chloride, 16 g. of ammonium chloride, 10 ml. of concd. hydrochloric acid, 50 ml. of water and 0.6 g. of copper bronze. After separation and drying over potassium carbonate, 75% of crude chlorides remained, $n^{22}D$ 1.4621. Fractionation through the helix column gave 61 g. of nearly pure 1-chloro-1,2-hexadiene, b.p. 54–57° (50 mm.), $n^{25}D$ 1.4567–1.4680, 52% yield. About 8% of the starting chloride was recovered and a small amount of a higher boiling fraction, perhaps an impure dichloride, was obtained by reducing the pressure as far as possible; the residue was polymeric. When the rearrangement was carried out by shaking for shorter periods, less 1-chloro-1,2-hexadiene was formed.

1-Chloro-1,2-hexadiene was obtained in over-all yield of 44% directly from 1-hexyn-3-ol by reaction with thionyl chloride in a mixture of diethyl ether and diisopropyl ether; the product was slightly easier to purify. This procedure will be described in detail in a later paper.

Carefully refractionated 1-chloro-1,2-hexadiene had b.p. 58° (50 mm.), $n^{25}D$ 1.4673, $d^{25}{}_4$ 0.9279; *MR*D obsd. 34.91, *MR*D calcd. 34.28.[16]

Slightly impure 1-chloro-1,2-hexadiene was purified by treatment with 80% aqueous diethylamine (24 hr. standing) much as described for bromopropadiene.[15] Recovery was fairly good, and the product was the best obtained by any procedure as judged by analysis. The analytical sample had b.p. 45° (25 mm.), $n^{25}D$ 1.4676.

Anal. Calcd. for C_6H_9Cl: C, 61.81; H, 7.78; Cl, 30.41. Found: C, 61.98, 62.00, 62.25; H, 8.12, 8.15, 7.99; Cl, 29.90, 29.98. Unless great care was taken with the purification and handling of the analytical sample, carbon values were high by over 1% and chlorine low by about the same amount.

Infrared spectra were obtained with a Beckman IR2-1/2 spectrophotometer using a sodium chloride prism and cell, liquid sample and a cell thickness of about 0.03 mm. 3-Chloro-1-hexyne gave a strong band at 3330 cm.$^{-1}$ (acetylenic hydrogen stretching) and a weak band at 2150 cm.$^{-1}$ (—C≡C— stretching); there was no band near 1965 cm.$^{-1}$ the region characteristic for allene stretching. Other bands were observed at 3000, 1467, 1387, 1330, a broad band from 1300 to 1250, 1215, 1120, 1060, 1025, 955, 940, 885, 840, 781, 767, 754 and 735 cm.$^{-1}$. 1-Chloro-1,2-hexadiene had a medium strength band at 1980 cm.$^{-1}$ and no bands at 3330 or 2150 cm.$^{-1}$. Other bands were observed at 2970, an unresolved broad band from 1480 to 1370, 1250, 1145, 1125, 1105, 1075, 1050, 1015, 965, 890, 880, 845, 830, 780, a broad, very strong band from 760 to 730 and 710 cm.$^{-1}$.

---

(11) O. R. Sammul, C. A. Hollingsworth and J. H. Wotiz, This Journal, **75**, 4856 (1953).

(12) L. W. Trevoy and W. G. Brown, *ibid.*, **71**, 1675 (1949).

(13) G. F. Hennion and D. E. Maloney, *ibid.*, **73**, 4735 (1951).

(14) J. W. Copenhaver and M. H. Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publishing Corp., New York, N. Y., 1949, p. 106.

(15) T. L. Jacobs and W. F. Brill, This Journal, **75**, 1314 (1953).

(16) Calculated using values of atomic refractions from Landolt–Börnstein, "Physikalisch-Chemische Tabellen," 5th ed., Vol. II, p. 985. The value for the allene bond was taken as 3.9 instead of 3.466, the value for two isolated double bonds. See ref. 15, note 23.

3-Chloro-3-methyl-1-butyne was prepared by the reaction of 2-methyl-3-butyn-2-ol with concd. hydrochloric acid and calcium chloride.[17] Distillation through the helix column gave material, b.p. 35–36° (175 mm.), n^{25}D 1.4155, in 50–55% yield; reported[3] b.p. 75°, n^{26}D 1.4142–1.4149.

1-Chloro-3-methyl-1,2-butadiene was prepared by the rearrangement of 3-chloro-3-methyl-1-butyne by shaking for 4 hr. with the cuprous chloride rearrangement mixture.[17] Distillation through the helix column gave 45–51% yields of material, b.p. 61–62° (175 mm.), n^{25}D 1.4739.

Dehalogenations with Zinc–Copper Couple.—The procedure for preparation of the couple and dehalogenation of 3-chloro-1-hexyne was that of Hennion and Sheehan.[6] No exothermic reaction was observed during addition of the chloride to the couple, but gentle heating after addition was complete initiated such a reaction which maintained the flask contents at reflux for 20 minutes. The yield of 1,2-hexadiene distilled through the Trubore column, b.p. 75.0–75.5, n^{20}D 1.4283, was 59%; reported[18] b.p. 76° (760 mm.), n^{20}D 1.4282, n^{25}D 1.4252; reported for 1-hexyne,[17] b.p. 71.33° (760 mm.), n^{20}D 1.3989, n^{25}D 1.3960. 1-Chloro-1,2-hexadiene appeared to behave in just the same way; the yield of 1,2-hexadiene was 50%. A small amount of 1-hexyne was obtained as a forerun (mixed with some 1,2-hexadiene) in each case. Assuming a linear relationship of the refractive indexes of mixtures of these hydrocarbons, the ratio of allene to acetylene from 1-chloro-1,2-hexadiene was 36/1; from 3-chloro-1-hexyne a somewhat larger ratio was obtained, but since the once distilled hydrocarbon mixture had precisely the same refractive index as the corresponding mixture from 1-chloro-1,2-hexadiene at the same stage, the difference in ratios based on the products of final distillation was believed to result from experimental error.

3-Chloro-3-methyl-1-butyne was dehalogenated similarly; dimethylallene, b.p. 39.5–40.5°, n^{25}D 1.4159–1.4165, was obtained in 51% yield (reported b.p. 40.0–40.2°, n^{25}D 1.4148,[3] n^{25}D 1.407[18]). Neither the early part of the distillate nor forerun gave a test with ammoniacal silver nitrate.

3-Bromopropyne and bromopropadiene were dehalogenated by dropping 0.05 mole of the halide in an equal volume of anhyd. ethanol into the zinc–copper couple from 6.5 g. (0.1 g.-atoms) of commercial zinc dust under 30 ml. of anhyd. ethanol. An all-glass apparatus with magnetic stirring was used and the evolved gases were passed through a coil reflux condenser cooled by ice-water to return ethanol to the reaction flask. After addition of the halide was completed the reaction mixture was refluxed for 3 hr. During the addition of 3-bromopropyne the flask warmed slightly; there was no apparent heat effect with bromopropadiene. The product was collected in a receiver cooled in Dry Ice and, after redistillation to remove traces of alcohol, analyzed for propyne and allene in the infrared spectrophotometer.

Dehalogenations of Propargyl Halides with Lithium Aluminum Hydride.—To 22 g. (0.58 mole) of lithium aluminum hydride in 500 ml. of ether was added 58.5 g. (0.5 mole) of 3-chloro-1-hexyne dropwise with stirring during 45 minutes. No evolution of heat was detected. The reaction mixture was refluxed for 3 hours, allowed to stand overnight, and hydrolyzed with water. The ether layer was separated and dried over anhyd. potassium carbonate. After removal of the ether in the helix column the residue was distilled through the Trubore column. Early fractions, b.p. 70–75°, n^{25}D 1.4130–1.4205, contained 2.73 g. of 1,2-hexadiene and 2.87 g. of 1-hexyne, assuming a linear relationship for the refractive indexes of the mixtures. These fractions gave positive tests with ammoniacal silver nitrate solutions. The main fractions, 17.4 g. (42%), b.p. 75–76°, n^{25}D 1.4260 (rising at the end to 1.4267), gave no test with ammonical silver nitrate. The dark residue from the distillation was flash-distilled at reduced pressure and gave 10 g. of starting chloride, n^{25}D 1.4384.

3-Chloro-3-methyl-1-butyne (51.5 g., 0.5 mole) was added dropwise with stirring during 45 minutes to a slurry of 22 g. (0.58 mole) of lithium aluminum hydride in 200 ml. of tetrahydrofuran. The reaction was exothermic. When addition was completed, the mixture was refluxed for 2 hours and then distilled directly through a simple distilling head, b.p. 49–55°. The distillate was washed 5 times with 75-ml. portions of water, dried over anhyd. potassium carbonate and distilled through the Trubore column, b.p. 40.5–41.0°, n^{25}D 1.4165, yield 18.5 g. (54% of theory). This product gave no test with ammoniacal silver nitrate. Both the boiling point and refractive index are slightly higher than values reported earlier[3,18] or from dimethylallene which we prepared by zinc–copper dehalogenation, but 3-methyl-1-butyne and all more saturated hydrocarbons with the same carbon skeleton have lower boiling points and refractive indexes, and isoprene which has n^{25}D 1.4185 boils at 34°. The residual reaction mixture was hydrolyzed with water and gave a small amount of hydrocarbon with which the ammoniacal silver nitrate test was negative.

Propargyl bromide was dehalogenated by adding 5.95 g. (0.05 mole) in an equal volume of Diethylcarbitol during 20–35 min. to 1.9 g. (0,05 mole) of lithium aluminum hydride in 20 ml. of the same solvent with magnetic stirring. A pressure-equalizing dropping funnel was used and the evolved gases were collected in a receiver cooled in Dry Ice. The reaction mixture was cooled in ice during addition of the bromide; a steady evolution of gas was observed throughout the addition. The reaction mixture was then allowed to warm to room temperature and finally heated on a water-bath until no more gas was evolved (about 30 minutes). The reaction mixture was cooled again, hydrolyzed with distilled water (dropwise addition) and heated as before, collecting the gas in a separate receiver. The yield of propyne–allene mixture before hydrolysis was 1.40 g. (70%) and after hydrolysis 0.30 g. (15%). Infrared analysis of the mixture showed that a maximum of 2.5% of allene was present; there appeared to be very slightly more allene in the gas obtained before hydrolysis.

Dehalogenation of Allenic Halides with Lithium Aluminum Hydride.—A slurry was prepared from 22 g. (0.58 mole) of powdered lithium aluminum hydride in 200 ml. of Diethylcarbitol and 51.5 g. (0.5 mole) of 1-chloro-3-methyl-1,2-butadiene was added dropwise with stirring during 1 hour. The reaction was quite exothermic and the flask was cooled occasionally in an ice-bath. When addition was complete the flask was heated for 1.5 to 2 hours. A gas-tight apparatus was used and volatile products were collected in a receiver cooled in Dry Ice. Approximately 1.5 g. (4% yield) of a low-boiling hydrocarbon which gave a positive test with ammoniacal silver nitrate and characteristic acetylenic infrared bands at 3335 and 2135 cm.$^{-1}$ was obtained. The reaction mixture was hydrolyzed by the dropwise addition of water and heated with a Glas-col mantle until no more volatile material came over. The product was collected in a receiver cooled in Dry Ice; after drying over anhyd. potassium carbonate it weighed 29 g., n^{20}D 1.3562. Distillation through the Trubore column gave 9.1 g., b.p. 23–25°, n^{20}D 1.3575 (slight test with ammoniacal silver nitrate); 11.7 g., b.p. 25–26° and 4.3 g., b.p. 26–30°, n^{20}D 1.3550, for both of these fractions; reported[18] for 2-methylbutane, b.p. 27.852°, n^{20}D 1.35373; 3-methyl-1-butyne, b.p. 26.35°, n^{20}D 1.3723; 2-methyl-2-butene, b.p. 38.568°, n^{20}D 1.3874; 3-methyl-1-butene, b.p. 20.061°, n^{20}D 1.3643. Neither of the final two fractions gave a positive test with ammoniacal silver nitrate nor did they decolorize bromine in carbon tetrachloride. The fraction b.p. 25–26° showed the infrared spectrum characteristic of isopentane, and no bands typical for 3-methyl-1-butyne.

A similar experiment was carried out using 10 g. (0.264 mole) of lithium aluminum hydride. The yield of 3-methyl-1-butyne, n^{20}D 1.3725, obtained before hydrolysis was 1.7 g. (5%). Fractionation (Trubore column) of the product obtained after hydrolysis gave 14.6 g., b.p. 20–20.6°, n^{17}D 1.3660; 7.3 g., b.p. 20.6–21.3°, n^{17}D 1.3657 (n^{17}D for 3-methyl-1-butene, 1.3661); 3.4 g., b.p. 21.3–25.1°, n^{17}D 1.3605; and 3.7 g., b.p. 25.1–26.5°, n^{17}D 1.3598. The total yield of hydrocarbons in this experiment was 88% and of essentially pure 3-methyl-1-butene, 63%. The fraction b.p. 20–20.6° gave positive tests with bromine in carbon tetrachloride and 2% potassium permanganate solution; its infrared spectrum was in good agreement with that reported for 3-methyl-1-butene.

One experiment was also carried out with 21 g. of lithium aluminum hydride suspended in 150 ml. of tetrahydrofuran. Some loss occurred because it was necessary to remove small

---

(17) G. F. Hennion, J. J. Sheehan and D. E. Maloney, THIS JOURNAL, **72**, 3542 (1950).

(18) "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," by F. D. Rossini, *et al.*, American Petroleum Institute Research Project 44, Carnegie Press (1953).

amounts of solvent from the once-distilled product by washing with water. The product which came over before hydrolysis gave 5.8 g. of crude 3-methyl-1-butyne (positive ammoniacal silver nitrate test), and the product after hydrolysis gave 12.7 g., b.p. 20.5–24.0°, $n^{17}\mathrm{D}$ 1.3659–1.3657, and 8.5 g., b.p. 26.0–28.4°, $n^{17}\mathrm{D}$ 1.3575–1.3550 (Trubore column).

A single run was made with 15 g. (0.39 mole) of lithium aluminum hydride and 44 g. (0.38 mole) of 1-chloro-1,2-hexadiene in 200 ml. of Diethylcarbitol following the directions given above. The product that came over before hydrolysis, 1.5 g., $n^{25}\mathrm{D}$ 1.4065, gave a positive test with ammoniacal silver nitrate. The material obtained after hydrolysis was fractionally distilled through the Trubore column to yield 22.8 g. (50% yield) of hydrocarbons distributed as follows: 2.1 g., b.p. 50–65°, $n^{25}\mathrm{D}$ 1.3748; 3.2 g., b.p. 65–66.1°, $n^{25}\mathrm{D}$ 1.3798; 4.1 g., b.p. 66.1–66.7°, $n^{25}\mathrm{D}$ 1.3798; 5.9 g., b.p. 66.7–68°, $n^{25}\mathrm{D}$ 1.3789; 3.1 g., b.p. 68–68.5°, $n^{25}\mathrm{D}$ 1.3765, and 2.9 g., b.p. 68.5–69.0°, $n^{25}\mathrm{D}$ 1.3755; reported[18] for 1-hexene, b.p. 63.485°, $n^{25}\mathrm{D}$ 1.38502; *cis*-2-hexene, b.p. 68.84°, $n^{25}\mathrm{D}$ 1.3948; *trans*-2-hexene, b.p. 67.87°, $n^{25}\mathrm{D}$ 1.3907; hexane, b.p. 68.740°, $n^{25}\mathrm{D}$ 1.37226. Thus the final fraction appears to be relatively pure hexane, and earlier fractions are mixtures probably containing more than one hexene.

Bromopropadiene was dehalogenated exactly as described for propargyl bromide. The evolution of gas during the addition was somewhat slower; this gas was pure propyne within the limits of accuracy of the infrared spectrophotometer. A yield of 1.37 g. (68.5%) was obtained before hydrolysis and 0.42 g. (21.0%) after hydrolysis.

LOS ANGELES 24, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTH CAROLINA]

Benzoin Condensations with Pivalaldehyde[1]

BY T. GLENN ROBERTS AND PEYTON C. TEAGUE

RECEIVED APRIL 25, 1955

The aliphatic aldehyde, pivalaldehyde, fails to form pivaloin by the benzoin condensation. Crossed condensation with benzaldehyde gives a mixture of isomeric acyloins, phenylpivalylcarbinol and benzoyl-*t*-butylcarbinol.

The benzoin condensation is a common reaction of aromatic aldehydes such as benzaldehyde, 4-phenylbenzaldehyde, 3,4-methylenedioxybenzaldehyde, 2- and 4-methoxybenzaldehyde, furfural and the pyridine and quinoline aldehydes. Certain substituted benzaldehydes fail to undergo the reaction. These include 4-dimethylaminobenzaldehyde, 4-hydroxy-3-methoxybenzaldehyde and 4-nitrobenzaldehyde.[2] Even though 4-dimethylaminobenzaldehyde will not undergo self-condensation, it will condense with benzaldehyde to produce an unsymmetrical benzoin.[3] The carbonyl group of the product is adjacent to the ring having the electron-releasing substituent.[4] In practically all crossed condensations this result has been reported.[5]

The only benzoin condensations of aldehydes in which the carbonyl group is not attached directly to an aromatic ring have been achieved in the glyoxal series. Benzoylformoin ($C_6H_5COCOCH$-$OHCOC_6H_5$) was prepared from phenylglyoxal[6] and acetylformoin from methylglyoxal.[7]

An aliphatic aldehyde which has an α-hydrogen atom undergoes aldol condensation in alkaline solution. Thus the major product of the treatment of isobutyraldehyde with sodium cyanide was found to be the cyanohydrin of isobutyraldol.[8]

Pivalaldehyde is the simplest aliphatic aldehyde, other than formaldehyde, with no α-hydrogen atom. The only report of an attempt to cause the benzoin condensation of pivalaldehyde is that of Franke and Hinterberger.[9] They isolated a small amount of an acidic substance. This material was apparently not extensively investigated, but solely on the basis of its equivalent weight it was assumed to be the aliphatic analog of benzilic acid, di-*t*-butylglycolic acid [$(t\text{-Bu})_2COHCOOH$]. The authors explained its formation by supposing that pivaloin was formed initially and was oxidized by air to pivalil which in turn underwent the benzilic acid rearrangement. We have made numerous attempts to obtain a benzoin condensation with pivalaldehyde and to duplicate the results of Franke and Hinterberger. Pivalaldehyde was heated with various proportions of sodium or potassium cyanide for periods ranging from forty-five minutes to one week. The majority of the reactions were carried out in an atmosphere of nitrogen. With the exception of small amounts of pivalic acid, probably produced after the reaction mixtures were exposed to the air, the only product which could be detected was pivalaldehyde cyanohydrin. In an attempt to obtain the acidic substance described by Franke and Hinterberger, the reaction was run while a slow stream of air was passed through the reaction mixture. Pivalaldehyde cyanohydrin was again produced along with a considerable amount of pivalic acid. The infrared absorption spectrum of the acid matched that of pure pivalic acid so closely that it did not seem possible that another acid could be present.

Pivaloin was prepared from ethyl pivalate by the acyloin condensation and was oxidized to pivalil. The pivalil was very resistant to the action of hot sodium hydroxide solution and no evidence of a benzilic acid rearrangement was found.

The failure of pivalaldehyde to undergo the benzoin condensation may be due to the inductive effect of the *t*-butyl group which would reduce to some

---

[1] This work was supported by the Office of Ordnance Research, Contract No. DA-36-034-ORD-1518RD.

[2] For a general review and bibliography of the reaction see W. S. Ide and J. S. Buck, "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 272–286.

[3] H. Staudinger, *Ber.*, **46**, 3530, 3535 (1913); S. S. Jenkins, J. S. Buck and L. A. Bigelow, THIS JOURNAL, **52**, 4495 (1930).

[4] S. S. Jenkins, L. A. Bigelow and J. S. Buck, *ibid.*, **52**, 5198 (1930).

[5] For an extensive bibliography of these reactions see ref. 2.

[6] H. G. Soderbaum and P. W. Abenius, *Ber.*, **24**, 3034 (1891).

[7] R. Nozu and S. Kunitika, *Bull. Chem. Soc. Japan*, **15**, 211 (1940), from *C. A.*, **34**, 6931 (1940).

[8] L. Claisen, *Ann.*, **306**, 322 (1899).

[9] A. Franke and H. Hinterberger, *Monatsh.*, **43**, 655 (1923).