[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

MONO- AND DI-ALKYLACETYLENES FROM VICINAL DIHALIDES AND SODIUM AMIDE IN LIQUID AMMONIA[1]

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Received May 9, 1954

Pure dialkylacetylenes have not hitherto been prepared by the obvious method of dehydrohalogenating vicinal dibromides, because the dehydrohalogenating agents commonly used cause migration of the triple bond within the formed alkyne and cause the formation of virtually inseparable mixtures. Nieuwland and his coworkers (1), who were the first to prepare monoalkylacetylenes by the action of sodium amide in liquid ammonia on monohalo-olefins, aryl halo-olefins, and olefin dihalides, suggested that this reagent and solvent might be used similarly in the synthesis of dialkylacetylenes, but did not pursue the matter experimentally; neither did they test the method for the preparation of branched *mono* alkylacetylenes.

In the present work, vicinal dibromo-alkanes derived from 9 Type II olefins (2) (*sym*-dialkylethylenes) were treated with sodium amide in liquid ammonia. In some cases the corresponding alkyne was produced, whereas in other cases rearrangement occurred. The preparation of four *branched* chain monoalkylacetylenes by the subject method was also investigated; satisfactory yields and non-rearranged products were obtained in each case (Tables I and II).

Evidence of rearrangement was observed in the dehydrohalogenation reaction products obtained from *d,l*- and *meso*-3,4-dibromohexane and *d,l*-erythro and *d,l*-threo-3,4-dibromoöctane. The dehydrohalogenation product obtained from *meso*-4,5-dibromoöctane was predominately 4-octyne (contaminant not determined) as indicated by the physical properties and distillation data.

Dehydrohalogenation and rearrangement occurred more readily with *d,l*- and *meso*-3,4-dibromohexane than with *d,l*-erythro- and *d,l*- threo-3,4-dibromooctane (see Table II). *Meso*- and *d,l*-3,4-dibromohexane yielded only a small amount of the normal dehydrohalogenation product (3-hexyne) and a considerable amount of rearranged products; *d,l*-erythro- and *d,l*-threo-3,4-dibromooctane gave a relatively large amount of the normal product (3-octyne) and less of the rearranged. The rearranged reaction products appeared to be predominately the corresponding 2-alkynes, as indicated by physical properties. In most cases, no evidence for the formation of allenes was noted in the rectification diagrams, where any appreciable amounts should have been evidenced at least in elevated refractive index. Detection of allenes through infrared spectra was

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[1] This paper was abstracted from a thesis submitted in 1951 by H. N. Miller to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the Degree of Master of Science. It was presented before the Organic Division at the 121st meeting of the American Chemical Society, held in Buffalo, New York, in 1952. The work was sponsored by The American Petroleum Institute (Research Project 45) in cooperation with The Ohio State University Research Foundation.

TABLE I

Physical Properties and Purity of Alkynes

Alkyne (starting olefin)	m.p., °C.	n_D^{20}	d_4^{20}	b.p., °C. (760 mm.)[a]	Estimated[p]-mole-% purity
3-Methyl-1-butyne					
(3-methyl-1-butene)	−90.08	1.3724	—	26.28	*ca.* 98
Literature[i]	−90.0	1.3723	0.666	26.42	—
3,3-Dimethyl-1-butyne					
(3,3-dimethyl-1-butene)	−81.20	1.3741	.6667	37.69	98
Literature[j]	—	1.37493	.6683	37.8	—
[k]	−81.2	1.3748[a]	.6683[o]	37.75	—
4-Methyl-1-pentyne					
(4-methyl-1-pentene)	−104.82	1.3930	.7041	61.17	99
Literature[l]	−105.1	—	.7044[o]	61.1–61.2	—
4,4-Dimethyl-1-pentyne					
(4,4-dimethyl-1-pentene)	−75.68	1.3983	.7142	76.08	97
Literature[m]	—	1.4028	.7154	73–75	—
2-Pentyne					
(*cis*-, *trans*-2-pentene)	−109.32	1.4037	.7104	56.02	99
Literature[d]	−109.31	1.4036	—	—	—
[e]	−109.33	1.4039	.7104	56.07	—
2-Hexyne					
(*cis*-2-hexene)	−90.95	1.4134	.7307	84.19	92–95
(*cis*-3-hexene)	−91.86	1.4134	.7303	84.13	88–91
(*trans*-3-hexene)	—	1.4132	—	83.4	—
[3-hexyne][b, c]	[−93.88]	[1.4134]	[.7297]	[83.50]	[*ca.* 80]
Literature[d]	−89.5	1.4141	—	—	—
[f]	−88.	1.41346	.73172	84.5	—
3-Hexyne					
(*cis*-3-hexene)	—	1.4114	—	81.3	—
(*trans*-3-hexene)	—	1.4117	—	81.2	—
4-Methyl-2-pentyne					
(*cis*-4-methyl-2-pentene)	−110.86	1.4063	.7149	72.75	*ca.* 99
Literature[g]	—	1.4078$^{19^\circ}$	.716$^{19^\circ}$	72.0–72.5	—
4,4-Dimethyl-2-pentyne					
(*trans*-4,4-dimethyl-2-pentene)	−82.37	1.4071	.7180	83.00	97
Literature[h]	—	1.4071	.7176	82.9–83.0	—
2-Octyne					
(Mixture of *cis*-, *trans*-2-octene)	−61.55	1.4278	.7592	137.73	99
(*trans*-3-octene)[c]	−61.87	1.4277	.7591	137.70	96
Literature[e]	−61.6	1.4278	.7596	138.00	—
[f]	−62.	1.42697	.75913	137.9	—
3-Octyne					
(*trans*-3-octene)	−110.22 to −116.66	1.4254 to 1.4262	.7524 to .7535	132.96 to 133.25	75–80
Literature[e]	−103.9	1.4250	.7522	133.14	—
[f]	−105.	1.42501	.75291	133.4	—

TABLE I—*Continued*

Alkyne (starting olefin)	m.p., °C.	n_D^{20}	d_4^{20}	b.p., °C. (760 mm.)[a]	Estimated[p] mole-% purity
4-Octyne					
(*trans*-4-octene)	−107.33 to −107.49	1.4248 to 1.4249	.7501 to 0.7505	131.34 to 131.71	*ca.* 80
Literature[d]	−102.39	1.4251	—	—	—
[e]	−102.55	1.4248	0.7509	131.57	—

[a] Literature values were corrected to 760 mm., where necessary, using appropriate values of dt/dp.

[b] Treated with sodium amide in liquid ammonia.

[c] Probably a prototropic rearrangement product.

[d] M. C. Hoff, Doctoral Dissertation, The Ohio State University, 1948.

[e] Henne and Greenlee, *J. Am. Chem. Soc.*, **67**, 484 (1945).

[f] Campbell and Eby, *J. Am. Chem. Soc.*, **63**, 2683 (1941).

[g] Gredy, *Bull. soc. chim.*, [5], **2**, 1951 (1935).

[h] DeGraef, *Bull. soc. chim. Belg.*, **34**, 427 (1925).

[i] *Selected Values of Properties of Hydrocarbons*, American Petroleum Institute Research Project 44, Table 12a, October 31, 1950.

[j] Pariselle, *Ann. chim.*, [9], **19**, 119 (1923).

[k] Van Risseghem, *Bull. soc. chim. Belg.*, **31**, 62 (1922).

[l] Van Risseghem, *Bull. soc. chim. Belg.*, **42**, 229 (1933).

[m] Ozanne and Marvel, *J. Am. Chem. Soc.*, **52**, 5267 (1930).

[o] Extrapolated value from data reported for other temperatures.

[p] The per cent purities were estimated by cryoscopic methods, wherever possible. When the product did not crystallize well, or at all, the estimates of purity were based on the relative constancy of boiling point and refractive index during distillation, or on the extent of deviation of these properties from known values of pure specimens.

not attempted. In one large (10 l.) distillation of 2-pentyne, about 1% of a compound (b.p. 48–48.5°, n_D^{20} 1.4270) tentatively identified as 2,3-pentadiene was obtained. Also, in the rearrangement experiment on 3-hexyne (described below) presence of an allene (probably 2,3-hexadiene) was suggested by a refractive index maximum. This suggests that an allene was an intermediate in the rearrangement.

In an attempt to determine whether rearrangement took place during the dehydrohalogenation reaction, or thereafter, a sample of 3-hexyne was agitated for 4 hours with sodium amide in liquid ammonia, and was thereby largely converted to 2-hexyne.[2] This indicates prototropic activity on the part of methylene hydrogens *alpha* to acetylenic groups, and higher stability for 2-alkynes than the corresponding 3-alkynes. Hauser and coworkers (3) found that 2-phenyl-1-butene was rearranged to 2-phenyl-2-butene when treated with an excess of potassium amide in liquid ammonia, and called it a prototropic change due to the basic amide. In our work about 35% of excess sodium amide was present in all dehydrohalogenation reactions. Nevertheless, at the low temperature (*ca.* −34°) under which our dehydrohalogenation reactions were carried out,

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[2] Confirming an experiment first done by M. C. Hoff, formerly of this laboratory.

TABLE II

PRODUCTION AND YIELD DATA ON ALKYNES FROM OLEFIN DIBROMIDES

Olefin Brominated	Olefin Purity (mole-%)	Reaction time of De-HX (hrs.)	Over-all Recovery Based on Olefin, %	Major Products of Desaturation	Yield of Alkynes, %
3-Methyl-1-butene	*ca.* 98	4	78.0	3-Methyl-1-butyne	52.0
4-Methyl-1-pentene	*ca.* 97	2.5	84.7	4-Methyl-1-pentyne	74.0
3,3-Dimethyl-1-butene	98.3	24[a]	75.8	3,3-Dimethyl-1-butyne	65.8
4,4-Dimethyl-1-pentene	*ca.* 97	4.5	79.9	4,4-Dimethyl-1-pentyne	53.2
2-Pentene	99 {70 *trans* 30 *cis*	2.25–4	80–88	2-Pentyne	65.2–75.1
cis-2-Hexene	88 *cis*, 12 *trans*	24[a]	86.2	2-Hexyne	64.5
cis-4-Methyl-2-pentene	98.0–98.5	4.5	83.1	4-Methyl-2-pentyne	68.5
trans-4,4-Dimethyl-2-pentene	99.7	4.5	88.2	4,4-Dimethyl-2-pentyne	66.6
2-Octene	*ca.* 65 *trans*, 30 *cis*, 5 *n*-octane	11[b]	68.2	2-Octyne	50.0
cis-3-Hexene	*ca.* 75 *cis*, 20 *trans*, 5 *n*-hexane	3.5	57.0	2-Hexyne[c] 3-Hexyne	43.3 4.2
trans-3-Hexene	*ca.* 98	8.5	70.5	2-Hexyne[c] 3-Hexyne	43.2 5.3
trans-3-Octene	99	24	80.0	2-Octyne[c] 3-Octyne	8.8 52.3
trans-4-Octene	99.5	20	74.4	4-Octyne[d]	56.0
3-Hexyne[e]	99.5	4	73.5	2-Hexyne[c] 3-Hexyne	48.1 6.7

[a] Unnecessarily long reaction time. [b] Insufficient reaction time. [c] Probably a prototropic rearrangement product. [d] Relatively impure. [e] Treated alkyne with $NaNH_2$ in NH_3.

the rearrangement of 2-alkynes (or other dialkylacetylenes) to their monoalkyl isomers appeared to be nil. If formed in appreciable amounts, any 1-alkynes would have been noted as precipitates of their sodium salts, or as flats on the rectification diagrams. This is in contrast to the results of Bourguel (4) who used sodium amide in an inert hydrocarbon solvent at much higher temperatures (*ca.* 160°), and obtained 1-alkynes in every case. Bourguel also found that direct attack of sodium amide on bromine in the dibromides, with consequent formation of olefins, was important. Our results do not altogether exclude this as a side reaction, but the amounts of olefins obtained were very small and probably were present as such in the dibromides, which were not purified before use.

No critical study of the rate of dehydrohalogenation was made, but an inverse relationship of rate to molecular weight was noted. Also, the dibromides from *cis*-alkenes reacted faster than the corresponding dibromides from *trans*-alkenes. For example, *d,l*-3,4-dibromohexane (from *cis*-3-hexene) was completely dehydrohalogenated in 3.5 hours, but the *meso* isomer (from *trans*-3-hexene) required about twice as long.

A mixture of dibromopentanes obtained by bromination of a *cis-trans* mixture of 2-pentene was completely dehydrohalogenated in 2.3 hours, whereas 11 hours was insufficient for a mixture of 2,3-dibromoöctanes (from a *cis-trans* mixture of 2-octene); the 3,4- and 4,5-dibromoöctanes required 24 and 20 hours, respectively. The difference in the required reaction time for *d,l*-3,4-dibromohexane and *meso*-3,4-dibromohexane can be explained stereochemically. The specificity and sterochemistry of the halogenation of a double bond are well accounted for by the stepwise addition mechanism presented by Hammett (5). The addition of bromine to the olefinic double bond is predominately *trans*. Thus, the *meso*-dibromide is obtained from the *trans*-olefin and the *d,l*-dibromide (mixture) is obtained from the *cis*-olefin.

In work with benzene hexachlorides, the *trans* steric requirement for the hydrogen and chlorine atoms in the second order, E_2-type dehydrochlorination has been established (6) conclusively and the mechanism has been pictured as a simultaneous removal of a proton to form a carbanion and expulsion of a chloride ion. The *trans* requirement is also evident in the work of Hoff (7) on the inversion of *cis*- and *trans*-alkene isomers. Thus, the first dehydrohalogenation of a *d,l*-dihalide mixture would yield the monohalo-*trans*-olefin. Since this isomer would satisfy the necessary *trans* requirements for dehydrohalogenation, further elimination would readily occur. From the initial dehydrohalogenation of a *meso*-dihalide, the monohalo-*cis*-olefin would be obtained; this isomer would not satisfy the *trans* requirements and further elimination would be difficult.

The effect of diluting the dehydrohalogenation reaction mixture with an inert hydrocarbon solvent was also evaluated; dilution was varied from zero to a 3 to 1 volume ratio. A mixture of 2,3-dibromopentanes was obtained from a *cis-trans* mixture of 2-pentene by adding to it 95 percent of the theoretical amount of bromine. This mixture, at various ratios of dilution with methylcyclohexane, was added dropwise to a stirred solution of sodium amide in liquid ammonia. After the addition of the dihalide, the reaction mixture was stirred from 2.25 to 4 additional hours for completion of the reaction. No effect of the inert diluent on the yield or rate of formation of 2-pentyne, or on the by-products of the reaction, was noted. It appeared that the only benefit was of aiding in the extraction of the organic reaction products from the reaction mixtures after water-quenching.

In conclusion, it may be said that the present method is of general applicability to the synthesis of 1-alkynes or 2-alkynes, but is of questionable utility in all other cases. This method is preferable to older ones employing sodium amide in an inert solvent at higher temperatures. It is especially recommended for the synthesis of 1-alkynes with branching at the 3 and/or 4 positions, as these cannot be obtained by the reaction of sodium acetylide with alkyl halides.

It is to be preferred in the preparation of almost any 2-alkyne, providing the requisite 2-alkene is available, inasmuch as the alternative methylation of 1-alkynes is relatively inefficient. The 2-alkene need not be especially pure in regard to double bond isomers, as the 2-alkyne produced will have a considerably higher boiling point than any isomeric alkyne or regenerated olefin and can easily be separated by distillation. Also, the 2-alkene may be a mixture of geometric isomers, as either will be converted to the alkyne.

EXPERIMENTAL

Source of olefins. The olefins used in this work were made available from the stock of the American Petroleum Institute Research Project 45. Prior to use, these compounds were checked for hydroperoxide content by iodometric titration in glacial acetic acid. If the hydroperoxide content was less than 30 to 40 meq. per liter, the olefin was percolated once or twice through a Dry Ice-cooled column of silica gel. If more hydroperoxide was present initially, the olefin was shaken with a dilute solution of sodium thiosulfate, then steam-distilled and percolated through silica gel.

Preparation of dibromides. The bromine addition reaction was carried out in a three-neck flask fitted with a dropping-funnel, a gas outlet tube, and a motor-driven glass loop-type stirrer sealed with a rubber sleeve, and immersed in a Dry Ice-acetone bath. The olefin and the solvent, usually 1–3 volumes of methylcyclohexane, were added to the reaction flask and cooled to −70° or lower with Dry Ice and acetone. Liquid bromine, usually equivalent to the olefin in amount, then was added dropwise, while the temperature was held at −60° or below and light was virtually excluded. The reaction mixture was allowed to stir about 12 hours (overnight) at Dry Ice temperature before the next step; no purification was attempted.

Dehydrohalogenation of dibromides. The dehydrohalogenations of the vicinal dihalides with sodium amide in liquid ammonia were carried out in a three-neck flask packed in loose asbestos and fitted with a modified Hershberg stirrer (sealed by a rubber sleeve) and a special reflux condenser consisting of either a ½ inch or ¾ inch (i.d.) tin coil, cooled by a Dry Ice-acetone mixture. The flask was chosen so that the liquid ammonia, sodium amide, and the reaction products occupied somewhat less than one-half the total volume of the flask, in order to leave ample room for subsequent neutralization of the excess sodium amide and hydrolysis.

The ammonia solution used generally contained three to five gram-atoms of sodium amide per liter of liquid ammonia. The ratio of sodium amide to ammonia was not found critical and could be suited to the capacity of the stirrer to keep in suspension the undissolved sodium amide and/or formed sodium bromide. The sodium amide used was freshly prepared, according to the directions of Henne and Greenlee (8).

The crude dihalide in its solvent, Dry Ice-cold, was added at a steady rate to the stirred sodium amide-liquid ammonia solution, usually as fast as the reflux capacity of the condenser would permit. After the addition, stirring was continued for one to 24 hours, depending on the dihalide used, to ensure complete reaction.

When the dehydrohalogenation was considered complete, the excess sodium amide was destroyed in either of two ways: (a) the excess sodium amide was neutralized with an equivalent amount of ammonium chloride, which was added from a side-flask attached to the reactor by Gooch tubing, or (b) the sodium amide was destroyed by direct hydrolysis with a large excess of water. Method (a) was preferred in large runs, or whenever the excess of sodium amide was large, because the sodium hydroxide formed in (b) appears as a viscous gelatinous mass which is difficult to stir. By contrast, the sodium chloride formed in (a) precipitates as a freely stirred slurry of fine crystals, which does not thicken during quenching, *i.e.*, during the addition of water to promote separation of the organic product.

In either case, when enough water had been added to stop the reflux of ammonia, the two liquid phases present were allowed to separate and the lower layer of concentrated aqueous ammonia and dissolved salts was siphoned off. The organic layer remaining then was washed two or three times with equal volumes of water in the original flask, and was steam-distilled to break any emulsion present.

The liquid organic material so obtained was washed once with dilute hydrochloric acid, then three times with cold water, and was dried by percolation through a column packed with anhydrous sodium sulfate. It then was fractionated at 25- to 30-plate efficiency through a 1.5 cm. x 90 cm. column, packed with $\frac{1}{16}$ inch stainless steel helices, to separate solvent and products.

SUMMARY

Vicinal dibromo-alkanes derived from 9 type II olefins (symmetrical dialkylethylenes) were dehydrohalogenated with sodium amide in liquid ammonia; in some cases the corresponding alkynes were produced, but in other cases rearrangement occurred. Similar treatment of 4 branched chain 1,2-dibromoalkanes gave non-rearranged products. The mechanism of the reaction, rates of dehydrohalogenation, and the effect of diluting the reaction mixtures with an inert solvent are discussed. An evaluation of the method is given.

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