benzoate and vinyl acetate. The monomers whose polarities are similar to vinylidene cyanide polymerized the slowest. In fact, they were as sluggish as a free radical homopolymerization of vinylidene cyanide. These slow monomers were maleic anhydride, dichloroethylene and acrylic acid.

Experimental

Materials.—The vinylidene cyanide was prepared from di-(acetyl cyanide).[16] It was fractionally crystallized until it had a melting point no lower than 9.0°. The other monomers were commercial materials which were dried and fractionated. Special precaution was taken with the styrene and the vinyl ethers. The styrene was vacuum distilled under nitrogen and used fresh to avoid contamination with peroxides. Both the vinyl isobutyl ether and the vinyl butoxyethyl ether were washed three times with equal volumes of 1% NaOH, dried over CaH, refluxed over sodium for several hours, then fractionally distilled from the sodium. The benzene used was thiophene-free grade, dried over CaH, and then fractionated.

Polymerizations.—The experiments, except system 12, were run in thick-walled, 60-ml. Pyrex glass polymerization tubes with crown-cap closures (aluminum foil liners). The crown capped tubes were not suitable for system 12 due to the low boiling point of vinyl chloride monomer. All of the vinyl chloride polymerizations were run in small-necked glass polymerization tubes. The peroxide was added first; the tube was then evacuated and immersed in a Dry Ice–acetone-bath. The vinyl chloride was introduced into the evacuated tube. The vacuum was then broken and the vinylidene cyanide was added volumetrically. The tube was then sealed off with an oxygen–natural gas flame. The tubes in systems 1, 2, 3, 7, 8, 9, 11 and 15 were gassed with oil-pumped nitrogen; the others were not. They were all kept at constant temperature in water-baths controlled to ±0.1°. The polymers were usually insoluble in the polymerization media. In the instances where the polymer was soluble, it was precipitated easily upon the addition of benzene. The only benzene-soluble polymer found is reported under system 16. It was isolated by low temperature evaporation of the benzene. The other polymers were all thoroughly washed with benzene and then vacuum dried to constant weight. All of the polymer analyses were run in duplicate—the nitrogen estimations by the semi-micro Kjeldahl method, the chlorine determinations by furnace combustion (A. S. T. M. method). The nitrogen values are accurate within 3 to 5 parts per thousand, *i.e.*, 15.13 ± 0.07%. The chlorine values are a little less accurate due to the absence of a good method for the determination of the chlorine content of polymers. The determination of polymer composition by nitrogen analysis was particularly effective since in no instance did both monomers contain nitrogen. However, the analysis of polymers very high in vinylidene cyanide is less accurate because the nitrogen content of these samples changes with time of storage. Linkages of the type $-CH_2-C(CN)_2-CH_2-C(CN)_2-$ are subject to scission by atmospheric moisture at room temperature. Each scission introduces a hydroxyl group on a chain end.[2]

The polymerization time required to achieve the desired low conversions ranged from 12 minutes to over 300 hours.

Acknowledgments.—We are indebted to A. K. Kuder for the chemical analyses of the polymers. We are thankful for the helpful suggestions received from C. B. Budd, R. A. Harrington, H. N. Stevens and C. C. Price.

AVON LAKE, OHIO

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[16] Ardis, *et al.*, THIS JOURNAL, **72**, 1305 (1950).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF NOTRE DAME]

The Preparation of Acetylenic Ketones Using Soluble Silver Acetylides

BY R. B. DAVIS AND D. H. SCHEIBER[1]

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Certain silver acetylides have been found to be soluble in such solvents as carbon tetrachloride, chloroform and benzene. The reaction of these silver acetylides in solution with acid halides yields α,β-acetylenic ketones. By this method some new acetylenic ketones were prepared.

The formation of a precipitate in the presence of alcoholic or ammoniacal silver nitrate has long been used as a diagnostic test and a method of analysis[2] for compounds containing a terminal acetylenic group. The use of this reaction as a synthetic tool has been very limited, although utilized in the preparation of 1-halo derivatives.[3] Silver acetylides also have been employed catalytically in the preparation of acetylenic alcohols[4] and glycols.[5] In 1899, Nef[6] reported that propiolophenone could be produced by dissolving silver phenylacetylide in warm benzoyl chloride and boiling the resultant solution. However, the reaction was said to be quite violent and limited in its use to small quantities. Since that time there appears to be no mention in the literature of the use of silver acetylides to synthesize ketones. One probable reason for the scant attention paid to these compounds is their low solubility in the media in which they are commonly prepared, although some are said to be somewhat soluble in hot alcohol.[7]

We have found that certain silver acetylides (I) dissolve in carbon tetrachloride, chloroform and benzene. The solubility appears to depend on carbon content and also on the presence of other functional groups. Silver butylacetylide is soluble to the extent of at least two moles per liter in carbon tetrachloride.

$$RC\equiv CH + AgNO_3 \xrightarrow[NH_4OH]{CH_3OH} RC\equiv CAg \qquad (I)$$

Although the precipitate of white silver acetylide from ammoniacal silver nitrate and acetylene has been shown[8] to be C_2Ag_2, the composition of other silver acetylides appears to depend somewhat on

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[1] Part of a Dissertation submitted by David H. Scheiber to the University of Notre Dame in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1956.

[2] Thomas L. Jacobs, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 45.

[3] C. Liebermann, *Ann.*, **135**, 270 (1865).

[4] I. G. Farb., U. S. Patent 2,300,969; *C. A.*, **37**, 2014 (1943).

[5] I. G. Farb., German Patent 726,714; *C.A.*, **37**, 6274 (1943).

[6] J. U. Nef, *Ann.*, **308**, 277 (1899).

[7] P. Piganiol, "Acetylene, Homologs and Derivatives," Mapleton House, Brooklyn, N. Y., 1950, p. 276.

[8] *Inter alia*, L. Knorr and H. Mathes, *Ber.*, **32**, 736 (1899); J. Eggert and H. Shimank, *ibid.*, **51**, 454 (1918).

the method of preparation.[9] To ascertain the composition of silver butyl- and hexylacetylide in carbon tetrachloride solution, analyses were carried out for both silver and alkyl acetylene. Silver chloride, formed on treating the carbon tetrachloride solution with hydrochloric acid, was collected and weighed. The liberated alkyl acetylene was determined by the method of Siggia.[10] The mole ratio of silver alkyne was determined as 1:0.85, and is consistent with the simple 1:1 combination, RC≡CAg (I).

Reproducible yields of 95% or better were obtained in the preparation of silver acetylides. These yields were determined from the amount of silver chloride recovered upon refluxing aliquot portions of silver acetylide–carbon tetrachloride solutions with dilute hydrochloric acid.

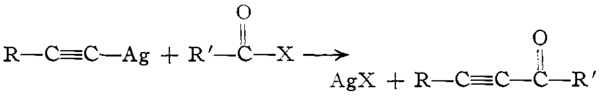
A silver acetylide prepared from ammoniacal silver chloride[11] and butylacetylene was found to be insoluble in carbon tetrachloride.

The infrared spectra of carbon tetrachloride solutions of both silver butyl- and hexylacetylides showed the characteristic terminal triple bond peak shifted from its usual position of 4.7 to 4.9 μ. Dilution of a silver butylacetylide solution until this peak in the infrared was barely discernible produced no change in wave length. Such a shift to longer wave length recently has been shown to correspond to a longer than usual bond.[12]

The carbon tetrachloride solutions of silver butyl- and hexylacetylide deposited solid in 1–2 weeks which darkened upon exposure to light or when removed from the mother liquor.

The principal methods[13,14] of preparing α,β-acetylenic ketones are three: treatment of an alkali metal acetylide with an acid bromide or anhydride in an inert solvent,[15] reaction of an acetylenemagnesium chloride with an acid anhydride at −25°,[16] and the oxidation of an acetylenic secondary alcohol with chromic anhydride.[14]

The acetylenic ketones that we have prepared (Table I) were made by two variations of the same fundamental method; either the silver acetylide in carbon tetrachloride solution was heated at reflux with the appropriate acid halide, or the acid halide was first added to an equimolar amount of aluminum chloride followed by the addition of a solution of the silver acetylide in carbon tetrachloride. In order to prevent side reactions in the preparation of the acetylenic haloketones it is important to use haloacyl halides containing very little or no free acid, to add them to the silver salt solution at room temperature, and then to heat the reaction mixtures. 3,5-Dinitrobenzoyl chloride could not be induced to react under a variety of conditions.



$$\mathrm{R{-}C{\equiv}C{-}Ag} + \mathrm{R'{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}X} \longrightarrow \mathrm{AgX} + \mathrm{R{-}C{\equiv}C{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}R'}$$

TABLE I

Alkyl acetylene	Acid halide	Product	Yield,[17a] %
1-Hexyne	Acetyl chloride	Octyne-3-one-2	42[18]
1-Hexyne	Acetyl bromide	Octyne-3-one-2	60
1-Hexyne	Acetyl chloride	Octyne-3-one-2	44[17b]
1-Hexyne	Propionyl chloride	Nonyne-4-one-3	53
1-Octyne	Acetyl chloride	Decyne-3-one-2	61[19]
1-Hexyne	Benzoyl bromide	Phenyl 1-hexynyl ketone	26
1-Hexyne	Benzoyl bromide	Phenyl 1-hexynyl ketone	67[17b]
1-Hexyne	Benzoyl chloride	Phenyl 1-hexynyl ketone	0
1-Hexyne	Benzoyl chloride	Phenyl 1-hexynyl ketone	72[17b]
1-Hexyne	Chloroacetyl chloride	1-Chloroöctyne-3-one-2	57
1-Octyne	Chloroacetyl chloride	1-Chlorodecyne-3-one-2	41
1-Hexyne	Bromoacetyl bromide	1-Bromoöctyne-3-one-2	36

The structures of the products were verified by using the reaction to synthesize two known ketones, octyne-3-one-2[16] and nonyne-4-one-3,[20] by the formation of 2,4-dinitrophenylhydrazones,[21] and by infrared spectra. The spectra of the acetylenic ketones, run as capillary films, showed exceptionally strong peaks at 4.52 μ for the internal triple bond, and peaks of normal intensity at 6.0 μ for the carbonyl group. With phenyl 1-hexynyl ketone the carbonyl peak appeared at 6.1 μ. With the acetylenic haloketones the peaks for the carbonyl groups appeared as doublets at 5.92 and 6.05 μ. The occurrence of such doublets has been observed in the case of some α-halo esters and is explained as due to the formation of dimers.[22]

That the silver acetylides have a low degree of nucleophilic character was shown by the complete failure of silver butylacetylide to react with acetone. Also, attempted reactions of this salt with *t*-butyl bromide without a catalyst and in the presence of either boron trifluoride etherate or aluminum chloride failed to yield the expected product, 2,2-dimethyloctyne-3, although a small amount of halogen-containing oil which decomposed upon attempted distillation was obtained using aluminum chloride.

In order to compare our method with that of Kroeger and Nieuwland[16] in the specific case of the acetylenic haloketones, we treated chloroacetic anhydride with butynylmagnesium chloride, following meticulously the directions of these authors. A 10% yield of impure product was obtained.

Experimental[23]

Solubility Tests on Silver Acetylides.—The solubilities listed below were obtained in the following manner: in 40

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(9) J. A. Nieuwland and R. R. Vogt, "The Chemistry of Acetylene," Reinhold Publishing Corp., New York, N. Y., 1945, pp. 49–57.

(10) Sidney Siggia, "Quantitative Organic Analysis *via* Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 33.

(11) C. Willgerodt, *Ber.*, **28**, 2107 (1895).

(12) M. Margoshes, F. Fillwalk, V. A. Fassel and R. R. Rundle, *J. Chem. Phys.*, **22**, 381 (1954).

(13) For other methods occasionally used see P. Piganiol, "Acetylene, Homologs and Derivatives," Mapleton House, Brooklyn, N. Y., 1950, p. 301.

(14) K. Bowden, I. M. Heilbron, E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

(15) E. Andre, *Ann. chim.*, **29**, 557 (1913); C. Moureu and M. Brachin, *Bull. soc. chim.*, **31**, 345 (1904); **33**, 134 (1906); **35**, 1176 (1907); D. Nightingale and F. Wadsworth, THIS JOURNAL, **67**, 416 (1945).

(16) J. W. Kroeger and J. A. Nieuwland, *ibid.*, **58**, 1861 (1936).

(17) (a) All yields of ketones reported are based on amount of alkyne starting material. (b) Catalyst was aluminum chloride.

(18) When benzene replaced carbon tetrachloride as solvent, the yield was 26%.

(19) Corrected for recovered octyne.

(20) M. J. Murray and F. F. Cleveland, *J. Chem. Phys.*, **12**, 156 (1944).

(21) This reagent has been shown not to react with the triple bond in the case of α,β-acetylenic ketones; see ref. 14.

(22) E. T. McBee and D. L. Christman, THIS JOURNAL, **77**, 755 (1955), footnote 6; M. L. Bender, *ibid.*, **75**, 5986 (1953).

(23) Carbon, hydrogen and chlorine analyses by Micro-Tech Laboratories, Skokie, Ill.

ml. of distilled water and 25 ml. of methanol was dissolved 10.0 g. of silver nitrate and sufficient concd. ammonium hydroxide added to give a clear solution. To 10 ml. of this solution was added dropwise 2 ml. of the compound to be tested with shaking until precipitation appeared complete. If the acetylene was a solid, 1.5 g. was dissolved in a minimum of methanol and this added to the ammoniacal silver nitrate solution. Then 10 ml. of carbon tetrachloride was added and the mixture shaken to see if the precipitate dissolved. In the test on 1-pentyne, 8.5 g. (0.05 mole) of silver nitrate and 1.7 g. (0.025 mole) of the alkyne were used, followed by 50 ml. of carbon tetrachloride. Treatment of the organic layer, after washing with water, with 1:1 hydrochloric acid gave 1.3 g. (0.0091 mole) of silver chloride.

Soluble	Slightly soluble	Insoluble
1-Hexyne[a,b]	1-Pentyne[a,d]	Acetylene
1-Heptyne[a,b]	3-Methyl-3-ethylhexyne-1-one-4[e]	1-Propyne[f]
1-Octyne[a]		Phenylacetylene[b,g]
2-Ethynyl-2-methylcyclohexanone[c]		1-Ethynylcyclohexene[h]
4-Ethynyl-4-methyloctanone-5[c]		3,3-Dimethylpentyne-1-one-4[e]
		3-Methylpentyne-1-ol-3[i]
		1-Ethynylcyclohexanol[i]
		2,3-Diethynyl-2,3-butanediol[j]

[a] K. N. Campbell and B. K. Campbell, *Org. Syntheses*, **30**, 15 (1950). [b] Same result in chloroform and benzene. [c] Unpublished work. [d] Maximum solubility found to be 0.2 mole per liter in carbon tetrachloride. [e] R. B. Davis and W. F. Erman, THIS JOURNAL, **76**, 3477 (1954). [f] C. D. Hurd, R. N. Meinert and L. U. Spence, *ibid.*, **52**, 1141 (1930). [g] J. C. Hessler, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 438. [h] J. C. Hamlet, H. B. Henbest and E. R. H. Jones, *J. Chem. Soc.*, 2652 (1951). [i] Courtesy Air Reduction Products. [j] R. B. Davis and P. Hurd, THIS JOURNAL, **77**, 3284 (1955).

Preparation of Silver Acetylide Solutions.—To a solution of 180 g. (1.06 moles) of silver nitrate in 350 ml. of distilled water and 200 ml. of methanol was added with stirring sufficient concd. ammonium hydroxide to just give a clear solution. The flask was then cooled to room temperature and the appropriate weight (0.5 mole) of alkyne in 50 ml. of methanol added dropwise over a period of two hours with vigorous stirring. Then 200 ml. of carbon tetrachloride was introduced into the flask by pouring it down the sides with stirring so as to remove the large amount of precipitate which adhered to the walls. The two layers were separated, the dark carbon tetrachloride layer washed with three 100-ml. portions of distilled water, and dried over calcium chloride. The dried solutions were usually diluted with additional solvent before use. The residual aqueous silver nitrate solutions were generally reused. In one reaction, benzene replaced carbon tetrachloride as solvent.

Infrared spectra showed a characteristic peak at 4.9 μ for silver butyl- and hexylacetylides in carbon tetrachloride.

The solid which eventually precipitated from a solution of silver butylacetylide was filtered, washed with dry carbon tetrachloride and then low-boiling (30–60°) petroleum ether, and stored in a vacuum desiccator in the dark. It slowly became pink and then black. It would not detonate when struck sharply or rubbed on a rough surface nor when heated strongly over a flame. When heated slowly, it became somewhat molten and then decomposed vigorously. It dissolved upon warming in carbon tetrachloride, and reprecipitated upon standing several days.

Quantitative Determination of Silver and Alkyl Acetylene in Carbon Tetrachloride Solutions of Silver Butyl- and Hexylacetylides: Silver Butylacetylide.—Bromide–bromate titrations run as described by Siggia[10] on a solution of pure 1-hexyne 0.08 *N* in unsaturation gave an average value of 100% acetylene.

Assuming 100% conversion of alkyl acetylene to acetylide, the amount of silver chloride recovered from the organic layer was within 7% of theory based on I. Including that obtained from the aqueous layer, total silver recovery was 99%.

Using a glass-stoppered erlenmeyer flask, 8.00 g. (0.047 mole) of silver nitrate was dissolved in 40 ml. of distilled water and 25 ml. of methanol. Sufficient concd. ammonium hydroxide was added to give a clear solution, the flask cooled to room temperature and 1.64 g. (0.02 mole) of 1-hexyne in 5 ml. of methanol added three drops at a time with vigorous shaking. The precipitate was then filtered by gravity, washed with a 20% methanol–water solution and treated on the paper with 150 ml. of carbon tetrachloride in 25-ml. portions. The resulting solution was then shaken for one minute with 1:3 hydrochloric acid and filtered rapidly with light suction as previous exploratory work had demonstrated that such solutions would not filter by gravity. The layers were quickly separated, the carbon tetrachloride layer washed with 100 ml. of water and diluted to one liter. Bromide–bromate titrations were then run on aliquots in exactly the same manner that had been used for the pure acetylene. An analysis of 84% acetylenic unsaturation was obtained.

Silver Hexylacetylide.—1-Octyne was first subjected to bromide–bromate titrations and gave an average value of 89% acetylenic unsaturation. The silver salt was analyzed in the same fashion as silver butylacetylide, using 10.00 g. (0.0588 mole) of silver nitrate and 2.75 g. (0.025 mole) of 1-octyne. It analyzed for 85% acetylenic unsaturation after being corrected upward by a factor of 11% based on the analysis for the pure acetylene. Silver recovery was within 4% based on $n\text{-C}_6\text{H}_{11}\text{C}{\equiv}\text{CAg}$ and total recovery was 98%.

Preparation of Ketones: Octyne-3-one-2.—(A) To a stirred solution of 0.28 mole of silver butylacetylide in 250 ml. of carbon tetrachloride was added all at once 22.8 g. (0.29 mole) of acetyl chloride and the resulting light yellow solution heated at reflux for 5.5 hours. The first sign of a precipitate appeared in about an hour. The reaction mixture was then cooled, poured over ice, stirred, 100 ml. of 10% hydrochloric acid added, and the entire mixture filtered by suction.[24] The filtrate was then shaken in a separatory funnel, the layers separated, and the organic layer washed with 100 ml. of 5% potassium carbonate solution, twice with 100-ml. portions of distilled water and dried over calcium chloride. The solvent was removed on a column under reduced pressure at 30°, and the product fractionated to give 14.8 g. (42%) of a water-white oil, b.p. 75.5–76° at 16 mm., $n^{20}_{\rm D}$ 1.4460 (lit.[16] 76.0–76.5° at 15 mm., $n^{25}_{\rm D}$ 1.4446), orange 2,4-dinitrophenylhydrazone, m.p. 88°, semicarbazone, m.p. 109.5–110° (lit.[14] m.p. 87–88° and 109°, respectively). Characteristic infrared absorption bands appeared at 4.52 and 6.0 μ.

(B) Using 0.25 mole of silver butylacetylide in 250 ml. of carbon tetrachloride and 34.4 g. (0.28 mole) of acetyl bromide in 100 ml. of dry carbon tetrachloride, addition being carried out at room temperature over a period of 0.75 hour, it was necessary to add 50 ml. of additional dry solvent to assist stirring. After heating at reflux for 15 minutes and working up the product as before, there was obtained 18 g. (60%) of the ketone, b.p. 75–76° at 16 mm., $n^{20}_{\rm D}$ 1.4462.

(C) In the reaction flask was placed 35.4 g. (0.264 mole) of aluminum chloride in 100 ml. of dry carbon tetrachloride, and 22.6 g. (0.288 mole) of acetyl chloride dissolved in 50 ml. of the same solvent was added slowly with stirring and cooling of the flask in an ice-bath. This was followed by 0.23 mole (240 ml.) of silver butylacetylide solution added in the cold over a period of two hours. When addition was complete, the extremely dark solution was allowed to come to room temperature and then worked up as before. Removal of the solvent and fractionation gave 12.9 g. (44%) of the ketone, b.p. 49–62° at 1.5 to 5.5 mm. Refractionation gave 9.2 g. of product, b.p. 82–82.5° at 17 mm., $n^{20}_{\rm D}$ 1.4492.

(D) Using 0.25 mole of silver butylacetylide in 250 ml. of benzene and heating at reflux for 5.5 hours with 20 g. (0.255 mole) of acetyl chloride, there was obtained 8 g. (26%) of the ketone, b.p. 82–83° at 21 mm., $n^{20}_{\rm D}$ 1.4461, along with 2.3 g. of an unidentified oil, b.p. 107° at 21 mm., $n^{20}_{\rm D}$ 1.4552.

An attempted reaction between the silver salt and acetic anhydride resulted in no reaction after 11 hours of heating at reflux.

Nonyne-4-one-3.—Prepared as in (A) above, using 0.21 mole (228 ml.) of silver butylacetylide in carbon tetrachloride and 24 g. (0.26 mole) of propionyl chloride heated at reflux for 4.5 hours. Fractionation gave 15.3 g. (53%) of nonyne-4-one-3, b.p. 60° at 2.75 mm., $n^{20}_{\rm D}$ 1.4485 (lit.[20]

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(24) The silver chloride recovered from this reaction and the silver halides from subsequent reactions are being sent to Goldsmith Bros. Smelting and Refining Co., 1300 West 59th Street, Chicago 36, Ill., for recovery of the silver.

b.p. 92–94° at 15 mm., n^{23}_{D} 1.4484), orange 2,4-dinitrophenylhydrazone, m.p. 51–52°. Characteristic infrared absorption bands appeared at 4.52 and 6.0 μ.

Decyne-3-one-2.—Prepared as in (A) above, using 0.5 mole of silver hexylacetylide in 250 ml. of carbon tetrachloride and 43.2 g. (0.55 mole) of acetyl chloride heated at reflux for 5 hours. After removal of the solvent, octyne (18 g., 0.164 mole) distilled, followed by decyne-3-one-2 (31.2 g., 61% based on recovered starting material), b.p. 59–62° at 0.5 mm., $n^{20.1}_{\text{D}}$ 1.4495–1.4508, yellow 2,4-dinitrophenylhydrazone, m.p. 52–53°. Material prepared for analysis had b.p. 61–62° at 0.5 mm., $n^{20.1}_{\text{D}}$ 1.4507, $d^{20.1}_{4}$ 0.8563; *MR*D calcd. 46.91, obsd. 47.84.[25] Characteristic infrared absorption bands appeared at 4.52 and 6.0 μ.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.70. Found: C, 78.79; H, 10.44.

Phenyl 1-Hexynyl Ketone.—Refluxing a carbon tetrachloride solution of silver butylacetylide with benzoyl chloride gave no reaction. Using a 66% molar excess of the silver salt and heating at reflux with benzoyl bromide for 21 hours produced after two fractionations a 26% yield of a halogen-contaminated product, b.p. 123° at 1.25 mm., n^{20}_{D} 1.5421. Characteristic infrared absorption peaks appeared at 4.52 and 6.1 μ.

Using 33.4 g. (0.25 mole) of aluminum chloride and 36.5 g. (0.26 mole) of freshly distilled benzoyl chloride as a complex performed at approximately 45° in 275 ml. of carbon tetrachloride and treating this as in (C) above with 0.24 mole (245 ml.) of silver butylacetylide–carbon tetrachloride solution gave upon fractionation 32.5 g. (72.5%) of a clear yellow oil, b.p. 110–114° at 0.7 mm., contaminated with halide. Repeated fractionation of several preparations did not give analytically pure material. *Anal.* Calcd. for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 80.65; H, 7.63. The use of benzoyl bromide did not result in any increase in purity or yield.

An orange 2,4-dinitrophenylhydrazone, made from repeatedly distilled material of b.p. 101–102° at 0.1 mm., n^{20}_{D} 1.5432, and recrystallized from a water, alcohol, ethyl acetate mixture to a constant melting point of 156–156.5°, analyzed correctly. *Anal.* Calcd. for $C_{19}H_{18}N_4O_4$: C, 62.27; H, 4.95. Found: C, 62.50; H, 4.96.

1-Chloroöctyne-3-one-2.—Prepared as in method (A) using 0.25 mole (200 ml.) of silver butylacetylide in carbon tetrachloride and 34 g. (0.3 mole) of chloroacetyl chloride dissolved in 50 ml. of the same solvent. After addition of the acid halide, the solution was heated at reflux for two hours. Rapid distillation of the product gave 22.7 g. (57%) of a faintly yellow oil, b.p. 70–74° at 0.3 mm. Analytical material had b.p. 50.5–52.0° at 0.1 mm., $n^{20.1}_{\text{D}}$ 1.4765, $d^{20.1}_{4}$ 1.0360, yellow 2,4-dinitrophenylhydrazone m.p. 68–69°; *MR*D calcd. 42.45, obsd. 43.23. Characteristic infrared absorption bands appeared at 4.52 μ and as a doublet at 5.95 and 6.05 μ.

Anal. Calcd. for $C_8H_{11}ClO$: C, 60.57; H, 6.99. Found: C, 60.42; H, 6.93.

An attempt to prepare this compound by the method of Kroeger and Nieuwland[16] using 0.25 mole of hexynylmagnesium chloride and 0.5 mole of chloroacetic anhydride[26] gave 5 g. of recovered 1-hexyne, 4.0 g. (10%) of the ketone (b.p. 55–58° at 0.2 mm., n^{20}_{D} 1.4731) and 10 g. of high boiling material which decomposed extensively upon attempted fractionation. The ketone was identified through its 2,4-dinitrophenylhydrazone which had m.p. 67–68° with previous softening, after four recrystallizations from ethanol.

1-Chlorodecyne-3-one-2.—Prepared by method A using 0.19 mole of silver hexylacetylide and 28.2 g. (0.25 mole) of chloroacetyl chloride. Rapid distillation from a Claisen flask gave 14.5 g. (41%) of slightly yellow oil, b.p. 68–69° at 0.1 mm., yellow 2,4-dinitrophenylhydrazone, m.p. 54–55°. Analytical material had b.p. 67° at 0.06 mm., n^{20}_{D} 1.4744, d^{20}_{4} 1.0059; *MR*D calcd. 51.75, obsd. 52.19. Characteristic infrared absorption bands appeared at 4.52 μ and as a doublet at 5.95 and 6.05 μ.

Anal. Calcd. for $C_{10}H_{15}ClO$: Cl, 19.00. Found: Cl, 18.74.

1-Bromoöctyne-3-one-2.—Prepared by method A using 0.22 mole of silver butylacetylide and 46.5 g. (0.23 mole) of bromoacetyl bromide. Additional solvent was necessary to assist stirring and reflux was maintained seven hours. Rapid distillation from a Claisen flask gave 16 g. (36%) of slightly colored oil, b.p. 78–80° at 2 mm., n^{20}_{D} 1.4978, orange 2,4-dinitrophenylhydrazone m.p. 80–82°, plus 9 g. of tarry residue. Analytical material had b.p. 48–49° at 0.05 mm., n^{20}_{D} 1.4973, d^{20}_{4} 1.2879; *MR*D calcd. 45.34, obsd. 46.17. Characteristic infrared absorption bands appeared at 4.52 μ and as a doublet at 5.95 and 6.05 μ.

Anal. Calcd. for $C_8H_{11}BrO$: C, 47.27; H, 5.46. Found: C, 47.30; H, 5.48.

Attempted Reaction of Silver Butylacetylide with *t*-Butyl Bromide.—Refluxing 0.21 mole (220 ml.) of silver butylacetylide with 28.8 g. (0.21 mole) of *t*-butyl bromide for several hours gave no reaction as evidenced by the complete absence of any precipitate. The mixture was then cooled in an ice-bath to 2–4°, 1.5 g. (5 mole %) of boron trifluoride etherate added, stirred in the cold for two hours, and finally at room temperature for three hours. When the reaction mixture was worked up, no ketonic material was obtained.

To 41 g. (0.3 mole) of *t*-butyl bromide dissolved in 100 ml. of dry carbon tetrachloride and maintained at 1° in a salt–ice-bath was added 5 g. (10 mole %) of aluminum chloride. After 15 minutes of stirring this mixture, 0.25 mole (140 ml.) of silver butylacetylide in carbon tetrachloride was added over 2.5 hours, keeping the temperature between 1 and −3°. When addition was complete, stirring was continued in the cold two hours longer and then the mixture poured onto 200 g. of ice. After the reaction mixture was filtered, the organic layer was separated, washed with acid, base, water and dried. The solvent was removed leaving about 10 ml. of a dark, halogen-containing oil which decomposed upon attempted fractionation.

Attempted Reaction between Silver Butylacetylide and Acetone.—In a small round-bottom flask fitted with a condenser was placed 25 ml. (0.042 mole) of a solution of silver butylacetylide in carbon tetrachloride and 6.05 g. (0.104 mole) of acetone. During five hours of heating at reflux the solution darkened but no precipitate appeared. The heat was removed and after standing two days a precipitate had formed. The entire mixture was shaken with 50 ml. of 1:3 hydrochloric acid, all solid was filtered off, the two layers shaken together again and refiltered. The organic layer was then washed with a few ml. of dilute base, water, and dried over calcium chloride. Careful removal of the solvent left only a few drops of oily residue which did not give a positive ceric nitrate test.

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(25) Low calculated values for the molecular refractions are probably due to the fact that no exaltation term, which would be anticipated in view of the conjugated nature of the ketones, was included. No mention could be found in the literature that such a value has been determined for acetylenic ketones.

(26) A. Baroni, G. Marrano and Modigliani, *Gazz. chim. ital.*, **63**, 23 (1933).