427. *Reactive Acetylenic Intermediates: the Synthesis of 1-Bromoacetylenes and Mercury Acetylides.*

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Methods for the preparation of 1-bromoacetylenes and of mercury acetylides are described.

BROMOACETYLENES, $R{\cdot}C{\equiv}CBr$, are required for the important Cadiot–Chodkiewicz coupling procedure[1] which is commonly utilised for the synthesis of unsymmetrically substituted conjugated diacetylenic compounds:

$$R{\cdot}C{\equiv}CH + Br{\cdot}C{\equiv}CR' \xrightarrow{Cu^{+},\ R''{\cdot}NH_2} R{\cdot}[C{\equiv}C]_2{\cdot}R' + HBr$$

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[1] *Inter al.*, Chodkiewicz, *Ann. Chim.* (*France*), 1957, **11**, 821; Chodkiewicz and Cadiot, *Compt. rend.*, 1959, **248**, 116.

Cadiot and Chodkiewicz adopted the preparative method of Straus, Kollek, and Heyn[2] which involves the interaction of the ethynyl compound and sodium hypobromite:

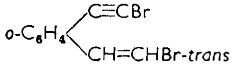
$$\mathrm{R{\cdot}C{\equiv}CH + NaOBr \longrightarrow R{\cdot}C{\equiv}CBr + NaOH}$$

This procedure generally gives good yields but may require prolonged reaction times, especially for alkylacetylenes. Other disadvantages are the strongly basic medium and the necessity for purification of the products which are invariably contaminated with the unchanged ethynyl compound.

The present work describes a re-evaluation of several known, but little used, procedures for the preparation of 1-bromoacetylenes. Bromination of the mercury derivative is shown to be a useful alternative to the method of Straus and his co-workers.[2]

The direct bromination of sodium or lithium acetylides,[3] suspended in inert solvents, was briefly reinvestigated, as was similar treatment of acetylenic Grignard reagents.[3] The results were discouraging and further attempts were abandoned. However, bromination of the corresponding mercury derivatives, first reported in 1933 by Jacobsen and Carothers,[4] was more promising: a solution of bromine in carbon tetrachloride, when added to a mercury acetylide dissolved in the same solvent, rapidly deposited mercuric bromide. A little mercuric bromide remained in solution but could be removed by precipitation with chilled light petroleum and passage of the filtrate through a column of charcoal containing one part in ten of 10% palladium-charcoal.[5] Other brominating agents, such as pyridinium bromide perbromide[6] and the complex of bromine with dioxan,[7] also effected this reaction but offered little advantage. The reaction takes place preferentially at the mercury atom and other reactive centres, *e.g.*, double bonds, are not attacked when only the requisite quantity of bromine is employed. Thus, it was possible by this route to prepare the intermediate (I) which is otherwise[8] difficult to obtain.

$$\mathrm{R{\cdot}C{\equiv}C{\cdot}Hg{\cdot}C{\equiv}CR + 2Br_2 \longrightarrow 2R{\cdot}C{\equiv}CBr + HgBr_2\downarrow}$$

(I) 

$$o\text{-}\mathrm{C_6H_4}\begin{cases}\mathrm{C{\equiv}CBr}\\ \mathrm{CH{=}CHBr}\text{-}trans\end{cases}$$

In consequence we also examined several routes to the mercury acetylides themselves. Only the method of Johnson and McEwan,[9] *i.e.*, reaction of the ethynyl material with a solution of mercuric chloride and potassium iodide in concentrated aqueous alkali, has been in general use up to the present (cf. recent work[10]). Another reaction, that between a 1-iodoacetylene and a mercuric salt,[11] seems of little value. Two new procedures are now described. In the first, the use of an acetylenic Grignard reagent eliminates the necessity for a base: acetylenic Grignard reagents in tetrahydrofuran react with mercuric chloride to give the corresponding mercury acetylide. This provides a ready, if somewhat indirect, means of preparing mercury acetylides under neutral conditions:

$$\mathrm{R{\cdot}C{\equiv}CH + C_2H_5{\cdot}MgBr \longrightarrow R{\cdot}C{\equiv}C{\cdot}MgBr + C_2H_6\uparrow}$$
$$\mathrm{2R{\cdot}C{\equiv}C{\cdot}MgBr + HgCl_2 \longrightarrow (R{\cdot}C{\equiv}C)_2Hg + 2MgClBr}$$

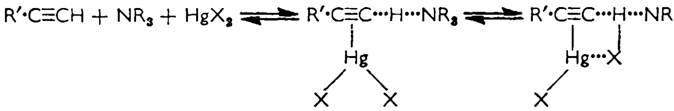
In the second method, the ethynyl compound is used as such and the necessary alkaline conditions are ensured by employing an organic base in which all the reactants are soluble.

[2] Straus, Kollek, and Heyn, *Ber.*, 1930, **63**, 1868.
[3] McCusker and Vogt, *J. Amer. Chem. Soc.*, 1937, **59**, 1307.
[4] Jacobsen and Carothers, *J. Amer. Chem. Soc.*, 1933, **55**, 4667.
[5] Dobson, Eglinton, Krishnamurti, Raphael, and Willis, *Tetrahedron*, 1961, **16**, 16.
[6] McElvain and Morris, *J. Amer. Chem. Soc.*, 1951, **73**, 206.
[7] Kosolapoff, *J. Amer. Chem. Soc.*, 1953, **75**, 3596.
[8] Behr, Ph.D. Thesis, Glasgow, 1960.
[9] Johnson and McEwan, *J. Amer. Chem. Soc.*, 1926, **48**, 469; Elsner and Paul, *J.*, 1951, 893.
[10] Iwai and Yura, *Chem. Abs.*, 1961, **55**, 4400 (*Takamine Kenkyusho Nempo*, 1958, **10**, 30); 1962, **56**, 4794 (Jap. P. 11,124/1961).
[11] Vaughn, *J. Amer. Chem. Soc.*, 1933, **55**, 3453.

A solution of mercuric acetate in n-butylamine reacts immediately with the ethynyl compound; the resultant mercury acetylide is isolated by dilution of the reaction mixture with water and extraction of the residue with a suitable organic solvent:

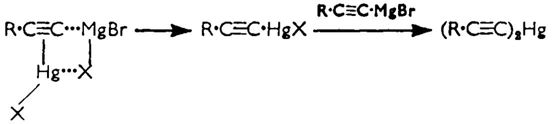
$$2R\cdot C{\equiv}CH + Hg(OAc)_2 \longrightarrow (R\cdot C{\equiv}C)_2Hg + 2AcOH$$

A similar system has been investigated recently by Dessy, Budde, and Woodruff[12] who made a detailed kinetic study of the reaction between a monosubstituted acetylene, a mercuric salt, and a tertiary amine, all dissolved in dioxan–water. They suggest that formation of the mercury acetylide proceeds through an initial π-complex and a subsequent four-centre transition state:



$$R'\cdot C{\equiv}CH + NR_3 + HgX_2 \rightleftharpoons R'\cdot C{\equiv}C\cdots H\cdots NR_3\ (\underset{X\quad X}{Hg}) \rightleftharpoons R'\cdot C{\equiv}C\cdots H\cdots NR_3\ (\underset{X}{Hg}\cdots X)$$

The product, R′·C≡C·HgX, can then initiate a similar sequence with a second molecule of the acetylene, to form the mercury acetylide. In the present work, an analogous transition state could be invoked for the formation of a mercury acetylide from the Grignard reagent:



$$R\cdot C{\equiv}C\cdots MgBr\ (\underset{X}{Hg}\cdots X) \longrightarrow R\cdot C{\equiv}C\cdot HgX \xrightarrow{R\cdot C\equiv C\cdot MgBr} (R\cdot C{\equiv}C)_2Hg$$

We have attempted the synthesis of a cyclic mercury acetylide by using a high-dilution modification of one of the above procedures, but only limited success has been achieved. In the most promising experiment, the addition of a tetrahydrofuran solution of mercuric chloride and tetradeca-1,13-diyne to a suspension of potassium t-butoxide in the same solvent resulted in the precipitation of an amorphous solid, the infrared spectrum and analysis of which were in accordance with the expected formulation, namely, $\llcorner[(CH_2)_{10}\cdot C{\equiv}C\cdot Hg\cdot C{\equiv}C]_n\lrcorner$. Unfortunately this material was extremely insoluble and it was not possible to evaluate it properly.

The mercury derivatives of α-hydroxy-acetylenes could not be prepared by any of the above methods. The proximity of the hydroxyl grouping seems to initiate the formation of ketonic material, presumably by internal hydration of the triple bond. However, in one case protection of the hydroxyl function as the tetrahydropyranyl ether was effective when the mercuric acetate procedure was employed.

EXPERIMENTAL

Syntheses of 1-*Bromoacetylenes.*—(*a*) *Sodium hypobromite procedure.*[2] The hypobromite solution was prepared immediately before use by mixing crushed ice (100 g.), 10N-sodium hydroxide (50 c.c.), and bromine (11 c.c.). In a typical experiment, a solution of phenylacetylene (20·4 g.) in tetrahydrofuran (10 c.c.) was added to the above hypobromite solution, and the mixture was then agitated (" Vibromischer ") for 5 hr. After the addition of sufficient ammonium chloride solution to decompose the excess of hypobromite, the mixture was extracted several times with ether. The ethereal layer was washed well with water, dried, and evaporated, to yield 1-bromophenylacetylene as a pale yellow oil (32·4 g., 89%), n_D^{25} 1·6080, with $\nu_{max.}$ (film) 2200 cm.$^{-1}$ but no absorption at 3300 cm.$^{-1}$ (C≡CH) (Found: C, 52·7; H, 2·7; Br, 44·0. Calc. for C_8H_5Br: C, 53·0; H, 2·8; Br, 44·2%).

In a similar experiment, octa-1,7-diyne was still only partly converted after 24 hours' agitation. The ethynyl-containing material was removed by treating a solution of the oily

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[12] Dessy, Budde, and Woodruff, *J. Amer. Chem. Soc.*, 1962, **84**, 1172.

product in ethanol with excess of an aqueous, ammoniacal silver nitrate solution. The ethereal extracts furnished colourless 1,8-dibromo-octa-1,7-diyne,[1] m. p. 19—20°, in 56% yield (Found: C, 36·5; H, 3·3; Br, 60·4%. Calc. for $C_8H_8Br_2$: C, 36·4; H, 3·1; Br, 60·5%).

(*b*) *Bromination of lithium and sodium acetylides.*[3] Phenylacetylene (5·0 g.), in dioxan (50 c.c.), was added to a stirred suspension of lithamide (from 0·35 g. of lithium) in liquid ammonia (250 c.c.). After 30 min. the ammonia was evaporated in a stream of nitrogen and replaced by dry dioxan (200 c.c.). The solution was heated under reflux for 45 min., then cooled to room temperature, and bromine (0·8 g.) in dioxan (50 c.c.) added during 1 hr. After isolation in the usual way the crude 1-bromophenylacetylene had appreciable absorption at 3300 cm.$^{-1}$ (C≡CH) and near 1710 cm.$^{-1}$ (C=O). Similar unsatisfactory results were obtained when the lithium acetylide had been prepared by the interaction of phenylacetylene with n-butyl-lithium or phenyl-lithium. The sodium derivative of phenylacetylene, obtained as a purple solution in 2,2′-dimethoxydiethyl ether also gave an impure product.

(*c*) *Bromination of the mercury acetylides.*[4] To a stirred solution of the mercury derivative [3·4 g.; following experiment (*c*)] of 1-*trans*-2′-bromovinyl-2-ethynylbenzene in benzene (150 c.c.) was added dropwise a solution of bromine (1·81 g.) in benzene (20 c.c.). A red colour persisted after ~80% of the bromine had been added. When addition was complete the mixture was stirred for a further 10 min. and the solvent then removed under a vacuum at 60°. The residue was extracted several times with chilled light petroleum, and the extract freed from dissolved mercuric bromide by passage through a short column of charcoal (5 g.) containing one part in ten of 10% palladium–charcoal. Evaporation of the eluate gave 1-trans-2′-*bromovinyl*-2-2′-*bromoethynylbenzene* as a pale-yellow oil (2·45 g., 79%), m. p. *ca.* −10°, b. p. (bath) 60°/10^{-4} mm., which was gas-chromatographically pure, and had $\nu_{max.}$ (film) 2220 (C≡CBr) and $\nu_{max.}$ (in CCl_4) 3060, 1605, 952, and 939 cm.$^{-1}$ (*trans*-CH=CHBr) (Found: C, 42·1; H, 2·2. $C_{10}H_6Br_2$ requires C, 42·0; H, 2·1%).

1-Bromo-oct-1-yne and 1-bromophenylacetylene were similarly obtained in 75% and 87% yield, respectively, carbon tetrachloride being used as solvent instead of benzene.

Preparation of Mercury Acetylides.—(*a*) *Mercuric chloride–potassium iodide procedure.*[9] Mercuric chloride (16·5 g.) and potassium iodide (40·5 g.) were warmed with water (40 c.c.) until they dissolved, and 10% sodium hydroxide solution (35 c.c.) was then added. In a typical experiment phenylacetylene (5·1 g.) in ethanol (250 c.c.) was added dropwise to the above stirred solution during 45 min. The crystalline deposit of mercury derivative recrystallised from ethanol as colourless plates (10 g., 92%), m. p. 124—125°, $\nu_{max.}$ (in Nujol) 2140 cm.$^{-1}$ [a peak in this region was found to be characteristic of all the mercury derivatives and was ascribed to ν(C≡C)]. The yield was 54% when dilute aqueous ammonia was used in place of sodium hydroxide (Johnson and McEwan [9] record m. p. 124·5—125°).

(*b*) Via *the acetylenic Grignard reagent.* A solution of mercuric chloride (6·0 g.) in tetrahydrofuran (25 c.c.) was added during 5 min. to a solution of phenylethynylmagnesium bromide (from 5·1 g. of phenylacetylene) in tetrahydrofuran (100 c.c.) which was being heated under reflux. After 1 hr. the mixture was treated with aqueous ammonium chloride, most of the solvent removed under reduced pressure, and the residue extracted with ether. The ethereal extract gave the mercury derivative (6·38 g., 84%) as colourless plates, m. p. 123—124° (from ethanol). In a similar experiment the mercury derivative of oct-1-yne was obtained, in 69% yield, as colourless flakes, m. p. 82—83° (from light petroleum) (Found: C, 45·8; H, 6·4; Hg, 45·3. Calc. for $C_{16}H_{26}Hg$: C, 45·8; H, 6·2; Hg, 48·0%). Johnson and McEwan [9] record m. p. 83—84°.

(*c*) *Mercuric acetate*–n-*butylamine procedure.* In a typical experiment, a solution of 1-*trans*-2′-bromovinyl-2-ethynylbenzene [8] (3·96 g.) in n-butylamine (10 c.c.) was added to a solution of mercuric acetate (3·8 g.) in the same solvent (15 c.c.). After 2 min., when the evolution of heat had ceased, the mixture was poured into ice-cold 0·5N-sulphuric acid (50 c.c.), and the neutral fraction was isolated with ethyl acetate. The mercury derivative (4·5 g., 78%) crystallised from benzene in colourless plates, m. p. 187—188°, $\nu_{max.}$ (in Nujol) 2130 cm.$^{-1}$.

The mercury derivatives of phenylacetylene, oct-1-yne, and 3-tetrahydropyranyloxyprop-1-yne were obtained in a similar fashion in 98%, 78%, and 86% yield, respectively. The last compound separated from benzene as needles, m. p. 104—105°.

Cyclic (?) *Mercury Derivative of Tetradeca-*1,13-*diyne.*—Tetradeca-1,13-diyne (3·8 g.) and mercuric chloride (5·42 g.) were separately dissolved in tetrahydrofuran (30 c.c.) and the solutions were mixed. This mixture was entrained during 10 hr. in the stream of condensate returning to a boiling suspension of potassium t-butoxide (from potassium, 3 g.) in tetrahydrofuran (250 c.c.) contained in a high-dilution apparatus.[13] The solid precipitate was collected, washed successively with water and methanol, and dried. The *mercury derivative* (5·77 g., 74%) so obtained was an off-white, amorphous solid, softening at 160° with no definite m. p. below 360°, and with no absorption near 3300 cm.$^{-1}$ (C≡CH) [Found: C, 43·5; H, 5·7; Hg, 50·6. $(C_{14}H_{20}Hg)_n$ requires C, 43·3; H, 5·1; Hg, 51·5%]. This material was insoluble in all the common organic solvents.

Tetradeca-1,13-diyne (m. p. and mixed m. p. 32—33°) was obtained when a sample of this mercury derivative was decomposed under reflux for 6 hr. with an excess of aqueous potassium cyanide.

We thank Professor R. A. Raphael, F.R.S., for his critical interest. We are also indebted to Mr. J. M. L. Cameron, B.Sc., and his staff for the microanalyses and to D.S.I.R. for a Research Studentship (to W. McC.).

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[*Received, November* 29*th*, 1962.]

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[13] Eglinton and Galbraith, *J.*, 1959, 889.