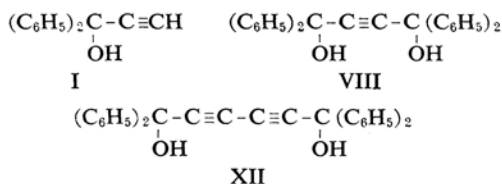


## Reactions of Tertiary Acetylenic Alcohols with Phosphorus Tribromide in Acetic Acid

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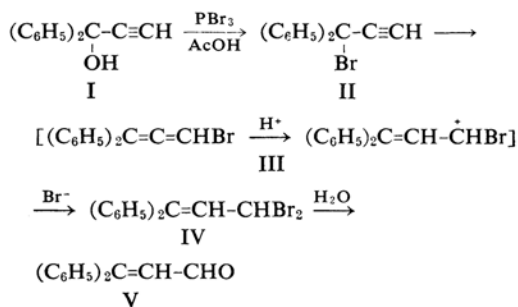
It has been well known that the reaction of acetylenic alcohols with phosphorus tribromide in the presence of pyridine gives corresponding tertiary acetylenic bromides. Some unexpected reactions, however, have been found during the course of studies of the bromination of acetylenic alcohols with phosphorus tribromide in acidic media. The present paper deals with the reaction of some aromatic tertiary acetylenic alcohols, I, VIII, and XII, with phosphorus tribromide in acetic acid.



1,1-Diphenylprop-2-yn-1-ol (I) reacted with phosphorus tribromide in acetic acid to give 1,1-diphenyl-3,3-dibromoprop-1-ene (IV) in a yield of 45%. The structure of the *gem*-bromide IV was determined by the experiments to be described below in addition to elementary analysis and a study of the infrared spectrum.

The ultraviolet spectrum of IV shows the presence of a conjugated system corresponding to 1,1-diphenylethylene, and the NMR spectrum shows the presence of three kinds of hydrogen, i. e., aromatic, vinyl and aliphatic.

The behavior of IV as a representative *gem*-dihalide gave further evidence for the structure.<sup>1)</sup> For example, the heating of II in water afforded 1,1-diphenylprop-1-en-3-al (V) quantitatively; this was also obtained by the treatment of IV with acid, base, or silver nitrate.

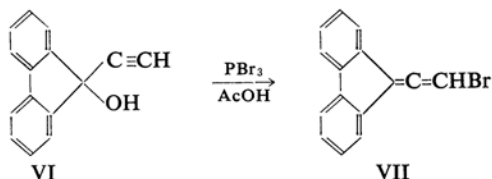


Scheme 1

1) H. Tani and F. Toda, *Chem. & Ind.*, 1963, 1083.

The reaction can be explained by the successive addition of a proton and a bromide anion to the bromoallene intermediate III produced by the Meyer-Schuster rearrangement of the tertiary acetylenic bromide II initially produced, as is shown in Scheme 1. A proof for the initial production of the tertiary acetylenic bromide II in this reaction was given by the experimental evidence that the action of phosphorus tribromide or hydrogen bromide on the bromide II, prepared by the usual method,<sup>23</sup> in acetic acid yielded the *gem*-dibromide IV in a good yield.

The assumption that the above reaction proceeds through a bromoallene intermediate III was indirectly proved by the reaction of 9-ethynylfluorene-9-ol (VI) under the same conditions as those employed for I.



In this case, 9-(bromovinylidene)fluorene (VII) was isolated in a 75% yield as stable yellow leaflets, the structure of which was confirmed by the presence of allenic bands at 1950 and 1915  $\text{cm}^{-1}$  in the infrared region and by comparing its ultraviolet spectrum with that of 9-(chlorovinylidene)fluorene.<sup>33</sup> The stability of the allenic bromide VII is attributable to the resonance stabilization arising from the planarity of the fluorene ring. After this investigation had been completed, Landor and Landor<sup>43</sup> reported that the reaction of 1,1,3-triphenylprop-2-yn-1-ol with thionyl chloride proceeds through a chloroallene intermediate corresponding to III or VII, resulting in 1,1,3-

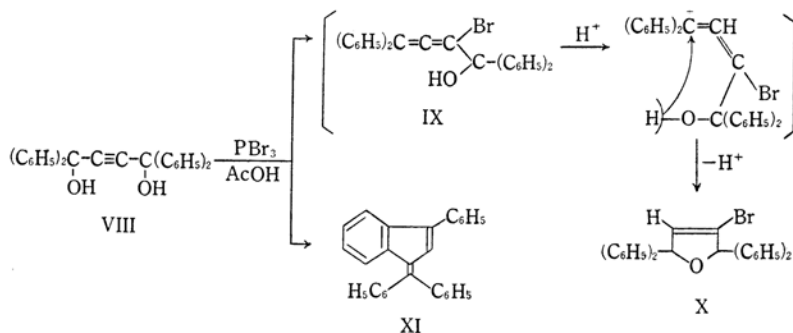
triphenylprop-1-en-3-one and a cyclic dimer.

In contrast with the reaction of terminal acetylenic alcohols, disubstituted acetylenic alcohols reacted with phosphorus tribromide in acetic acid to yield cyclic compounds.

The treatment of 1,1,4,4-tetraphenylprop-2-yn-1,4-diol (VIII) with phosphorus tribromide in acetic acid gave 1,10,10-triphenylbenzofulvene (XI)<sup>53</sup> and 2,2,5,5-tetraphenyl-3-bromodihydrofuran (X) in yields of 30 and 16% respectively.

The structure of the dihydrofuran (X) was confirmed by a study of its ultraviolet spectrum, which showed an absence of conjugation between the benzene ring and the double bond, and by a study of its infrared spectrum, which showed the presence of trisubstituted ethylene, vinyl ether and monosubstituted benzene groups. The formation of X may be explained by the protonation and then the cyclization of the allenic intermediate IX produced by the Meyer-Schuster rearrangement of the monobromide of VIII, as is shown in Scheme 2. On the other hand, the formation of the benzofulvene XI may well be explained by the acid-catalyzed reaction of X through the transitory formation of tetraphenylbutatriene, because it has been reported<sup>53</sup> that the action of hydrogen iodide on an iodo-analog of X gives the benzofulvene XI.

The action of phosphorus tribromide on 1,1,6,6-tetraphenylbuta-2,4-diyne-1,6-diol (XII) resulted in reddish brown needles. The structure of this compound,  $\text{C}_{30}\text{H}_{21}\text{Br}$ , was confirmed to be 2,5,6,6-tetraphenyl-3-bromofulvene (XIV) on the basis of the following data: (i) the NMR spectrum of XIV showed the presence of one vinyl hydrogen and twenty aromatic hydrogens. (ii) The bromine atom of XIV reacted with neither sodium ethoxide nor with sodium amide in liquid ammonia. (iii) XIV



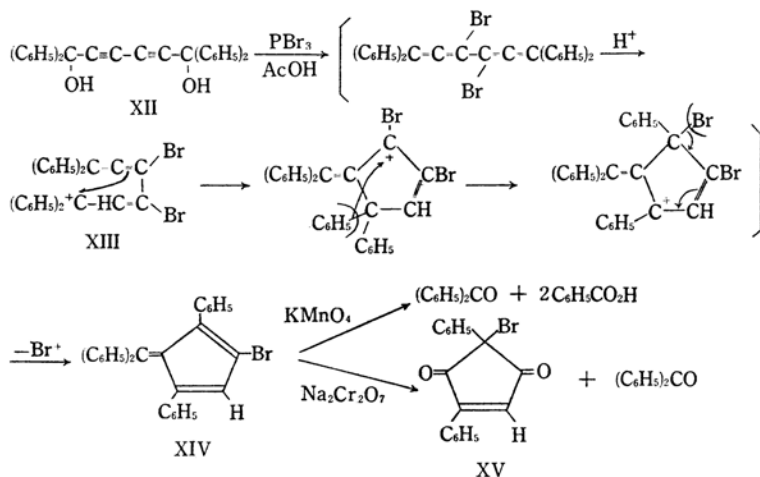
Scheme 2

2) A. Kirmann, *Bull. soc. chim. France*, **39**, 698 (1926).

3) G. F. Hennion and B. Fleck, *J. Am. Chem. Soc.*, **77**, 3253 (1955).

4) P. D. Landor and S. R. Landor, *J. Chem. Soc.*, **1963**, 2707.

5) J. Salkind and A. Kruglow, *Ber.*, **61**, 2306 (1928).



gave a characteristic fulvene absorption spectrum in the visible region. (iv) The oxidation of XIV by potassium permanganate in acetone gave one part of benzophenone and two parts of benzoic acid. (v) The sodium bichromate oxidation of XIV in acetic acid gave 2,5-diphenyl-2-bromocyclopent-4-ene-1,3-dione (XV) and benzophenone, in addition to a small amount of benzoic acid, which was supposed to be produced by the further degradation of the former XV.

The structure of the cyclopentenedione XV was confirmed by elementary analysis and by a study of its infrared, ultraviolet and NMR spectra; the last named indicated the presence of one vinyl hydrogen against ten aromatic hydrogens.

Additional evidence for the structure of the fulvene XIV was given by its infrared spectrum. Two bands of the fulvene XIV appeared at 1310 (weak) and 1265 (strong)  $\text{cm}^{-1}$ , corresponding to those of 6,6-diphenyl-2,3,4,5-tetrabromofulvene which appeared at 1315 (medium) and 1230 (strong)  $\text{cm}^{-1}$ .<sup>6</sup> Moreover, the presence of one nuclear ring hydrogen of the fulvene (XIV) was established by the absorption at 820  $\text{cm}^{-1}$ .

The reaction may be interpreted in terms of the cyclization and the phenyl migration of the dibromo cation intermediate XIII produced by the Meyer-Schuster rearrangement and then the protonation of the dibromide of XII, as is shown in Scheme 3.

#### Experimental\*

**1,1-Diphenyl-3,3-dibromoprop-1-ene (IV).**—Into an ice-chilled solution of 1,1-diphenylprop-2-yn-1-

ol (I, 10.5 g., 0.050 mol.) in acetic acid (25 ml.)-carbon tetrachloride (5 ml.), phosphorus tribromide (7.3 g., 0.027 mol.) was stirred drop by drop over a period of 15 min. under a nitrogen atmosphere; the stirring was then continued for an additional hour. The crude crystals which formed were collected by filtration and washed with cold methanol (20 ml.), resulting in IV in the form of colorless rhombic plates (8.5 g. (45%); m. p. 82°C (decomp.)); this was pure enough without further purification to carry out the following experiments. Two recrystallizations of the crystals from petroleum ether (b. p. 60–70°C) did not raise the melting point. IR: KBr disk, 882 (trisubstituted ethylene) and 768, 700  $\text{cm}^{-1}$  (monosubstituted benzene). UV:  $\lambda_{\text{max}}^{\text{Dioxane}}$ , 242 m $\mu$  ( $\epsilon$ , 10200), 266 (14700), 273 (16500). NMR: in carbon tetrachloride, 2.75  $\tau$  (singlet, aromatic), 3.60  $\tau$  (quartet, vinyl) and 7.90  $\tau$  (siglet, aliphatic).

Found: C, 51.22; H, 3.41; Br, 45.45. Calcd. for  $\text{C}_{15}\text{H}_{12}\text{Br}_2$ : C, 51.14; H, 3.41; Br, 45.65%.

**The Formation of the *gem*-Bromide (IV) from 1,1-Diphenyl-1-bromoprop-1-yne (II).**—When phosphorus tribromide (or gaseous hydrogen bromide) was added to a solution of II in acetic acid under cooling with ice, colorless rhombic plates IV (m. p. 82°C (decomp.)) were formed almost quantitatively; these did not show any depression of the melting point when mixed with the authentic sample described above.

**1,1-Diphenylprop-1-en-3-al (V).**—A solution of 1,1-diphenyl-3,3-dibromoprop-1-ene (IV, 1.0 g., 0.0028 mol.) in alcoholic potassium hydroxide (prepared from 30 ml. of ethanol and 0.5 g. of potassium hydroxide) was refluxed for 1 hr. After cooling, the reaction mixture was poured into water and extracted with ether. The crude crystals obtained by the evaporation of the solvent were

6) J. C. Wood, R. M. Eloffson and D. M. Saunders, *Anal. Chem.*, **30**, 1339 (1958).

\* All melting points are uncorrected. The NMR spectra were obtained in a carbon tetrachloride solution with a Varian model A-60 spectrometer, using tetramethylsilane as an internal standard. The molecular weight was determined in a benzene solution using a Mechrolab vapor pressure osmometer model 301 A.

recrystallized from petroleum ether (b. p. 40–50°C) to give colorless needles (m. p. 43°C, 0.5 g. (90%) (lit.,<sup>7</sup> m. p. 44.5–45.5°C)). For this aldehyde, consistent infrared and ultraviolet spectra were obtained. The 2,4-dinitrophenylhydrazone of the aldehyde melted at 195°C (lit.,<sup>7</sup> m. p. 198°C).

By treating the *gem*-bromide IV with water, aqueous acid or alcoholic silver nitrate in the manner described above, the aldehyde IV was also obtained quantitatively.

**9-(Bromovinylidene)fluorene (VII).**—To a stirred solution of 9-ethynylfluorene-9-ol (VI, 6.2 g., 0.03 mol.) in acetic acid (20 ml.), phosphorus tribromide (4.4 g., 0.017 mol.) was added under cooling with ice over a period of 30 min. The crude crystals which formed were collected by filtration and washed with methanol, water and methanol successively. The dried crystals were recrystallized from ethyl acetate ethanol to give yellow plates (VII) (6.0 g. (75%); m. p. 220°C (decomp.)). IR: in chloroform, 1950 and 1915  $\text{cm}^{-1}$  (allene). UV:  $\lambda_{\text{Dioxane}}^{\text{max}}$ , 266  $\text{m}\mu$  ( $\epsilon$ , 23400), 274 (25700), 380 (16400).

**2, 2, 5, 5-Tetraphenyl-3-bromodehydrofuran (X) and 1, 10, 10-Triphenylbenzofulvene (XI).**—To a stirred solution of 1,1,4,4-tetraphenylbut-2-yne-1,4-diol (VIII, 0.7 g., 0.002 mol.) in a mixture of acetic acid (10 ml.) and carbon tetrachloride (20 ml.), phosphorus tribromide (1.35 g., 0.005 mol.) was added in one portion under cooling with ice; the reaction mixture was then stirred for a further 30 min. After it had been kept standing at room temperature for 1 hr., the reaction mixture was poured into ice-water. The carbon tetrachloride layer was separated, washed with water and dried over sodium sulfate. The evaporation of the solvent yielded a mixture of two kinds of crystals (yellow and colorless), which were then separated mechanically. The recrystallization of the yellow crystals from ethyl acetate resulted in pure bright yellow prisms (XI) (200 mg. (30%); m. p. 204°C (decomp.) (lit.,<sup>5</sup> m. p. 204–205°C)). UV:  $\lambda_{\text{Dioxane}}^{\text{max}}$ , 235  $\text{m}\mu$  ( $\epsilon$ , 34200), 254 (32300), 297 (12500), 350 (15900), 410 (shoulder) (5200). NMR: in carbon tetrachloride, 2.62  $\tau$  (doublet, aromatic) and 3.35  $\tau$  (singlet, fulvene).

Found: C, 93.91; H, 5.69. Calcd. for  $\text{C}_{23}\text{H}_{20}$ : C, 94.34; H, 5.66%.

The recrystallization of the colorless crystals from ethyl acetate resulted in colorless prisms (X) (150 mg. (16%); m. p. 175°C). IR: KBr disk, 1657 (double bond), 1013 (ether), 833, 807 (trisubstituted ethylene) and 753, 700  $\text{cm}^{-1}$  (monosubstituted benzene). UV:  $\lambda_{\text{Dioxane}}^{\text{max}}$ , 233  $\text{m}\mu$  ( $\epsilon$ , 700), 247 (800), 252 (800), 259 (760).

Found: C, 74.21; H, 4.69; Br, 17.82. Calcd. for  $\text{C}_{23}\text{H}_{21}\text{BrO}$ : C, 74.17; H, 4.63; Br, 17.66%.

**2, 5, 6, 6-Tetraphenyl-3-bromofulvene (XIV).**—Phosphorus tribromide (2.2 g., 0.008 mol.) was stirred into an ice-cooled solution of 1, 1, 6, 6-tetraphenylbut-2, 4-diyne-1, 6-diol (XII, 4.2 g., 0.01 mol.) in acetic acid (30 ml.) over a period of 5 min. After stirring had been continued for a further 30 min. the crystals which had formed were filtered

and washed with water and a small amount of methanol successively. Two recrystallizations of the dried crystals from ethyl acetate afforded reddish brown needles (2.1 g. (43%); m. p. 215°C (decomp.)). IR: KBr disk, 1310, 1265 (fulvene), 805 (hydrogen of fulvene ring) and 770, 723, 695  $\text{cm}^{-1}$  (monosubstituted benzene). UV:  $\lambda_{\text{Dioxane}}^{\text{max}}$ , 254  $\text{m}\mu$  ( $\epsilon$ , 21300), 358 (23200), 490 (shoulder) (500). NMR: in carbon tetrachloride, 2.63, 2.90, 3.13 and 3.36  $\tau$  (aromatic, all the areas are almost equal), 3.62  $\tau$  (hydrogen on fulvene ring).

Found: C, 77.81; H, 4.55; Br, 16.95. Mol. wt. 464 (vapor pressure osmometer\*). Calcd. for  $\text{C}_{30}\text{H}_{21}\text{Br}$ : C, 78.10; H, 4.56; Br, 17.34%. Mol. wt. 461.

**The Oxidation of XIV by Potassium Permanganate.**—To a stirred solution of XIV (0.3 g., 0.0065 mol.) in acetone (20 ml.), potassium permanganate (1.0 g., 0.0063 mol.) was added; the mixture was then stirred at 30–40°C for 2 hr. After the mixture had been kept standing overnight at room temperature, the excess potassium permanganate in the reaction mixture was decomposed with a small amount of ethanol. The acetone solution obtained by the removal of the manganese dioxide by filtration was evaporated to dryness. The residue was mixed with water and extracted with ether. The ether extract was washed with aqueous sodium bicarbonate. The alkaline solution was acidified and then saturated with ammonium chloride. The crude crystals thus obtained were recrystallized from petroleum ether (b. p. 60–70°C), resulting in benzoic acid in the form of colorless plates (100 mg. (60%); m. p. 121°C), which did not show any depression of the melting point when mixed with an authentic sample (m. p. 121°C).

The recrystallization of the crude crystals obtained by the removal of the solvent from the dried ether layer from petroleum ether (b. p. 40–50°C) afforded benzophenone (60 mg. (50%); m. p. 47–48°C), which was identified by a mixed melting point determination with an authentic specimen and by a study of its infrared spectrum.

**The Oxidation of XIV by Sodium Bichromate.**—A mixture of XIV (0.5 g., 0.001 mol.), sodium bichromate dihydrate (1.5 g., 0.005 mol.) and acetic acid (30 ml.) was refluxed for 1.5 hr. After it had cooled, the reaction mixture was poured into dilute hydrochloric acid and extracted with ether. The ether layer was washed with aqueous potassium carbonate. From the acidified alkaline solution, a small amount of benzoic acid was isolated in the form of colorless plates. The evaporation of the solvent from the dried ether layer yielded a mixture of yellow needles and an oily material. After the mixture had been washed with methanol (5 ml.), insoluble crystals were recrystallized from ethyl acetate to give XV in the form of pale yellow needles (0.1 g. (30%); m. p. 205–206°C). IR: KBr disk, 1670, 1665 (carbonyl) and 830  $\text{cm}^{-1}$  (trisubstituted ethylene). UV:  $\lambda_{\text{Dioxane}}^{\text{max}}$ , 237  $\text{m}\mu$  ( $\epsilon$ , 19800), 248 (17800), 298 (shoulder) (7300), 332 (3900). NMR: in carbon tetrachloride, 2.10, 2.55, 2.90  $\tau$  (aromatic) and 3.53  $\tau$  (vinyl).

Found: C, 62.78; H, 3.53; Br, 27.41. Calcd. for  $\text{C}_{17}\text{H}_{11}\text{BrO}_2$ : C, 62.38; H, 3.36; Br, 24.46%.

7) H. Lorenz and R. Wizinger, *Helv. Chim. Acta*, **28**, 600 (1945).

The recrystallization from petroleum ether (b. p. 40~50°C) of the crude crystals obtained by the removal of the solvent from the methanol layer yielded benzophenone in the form of colorless needles (90 mg. (50%); m. p. 48°C), the identification of which was made by a mixed melting point determination with an authentic sample and by a study of its infrared spectrum.

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