802. *Allenes. Part VII.* The Synthesis of Iodoallenes and Iodoacetylenes*

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Methods for the preparation of iodoallenes are described. The triphenyl phosphite methiodide reagent, both neat and in solution in *NN*-dimethylformamide, gives iodoallenes with prop-2-ynylic alcohols. In solution in methylene chloride it gives iodopropyne and a mixture of 3-iodobutyne and 1-iodobuta-1,2-diene in approximately equal amounts from prop-2-ynol and but-3-yn-2-ol, respectively. A new reagent, trisnonylphenyl phosphite methiodide, is described but its preparation in pure form presents difficulties which make it less attractive than triphenyl phosphite methiodide. The mechanism of these reactions is discussed.

The syntheses of chloroallenes and bromoallenes have already been reported.[1,2] Iodoallenes promised to be even more reactive than bromoallenes and, we reasoned, if they were sufficiently stable they would be most useful synthetic intermediates. Previous attempts to prepare iodoacetylenes and iodoallenes gave mixtures of both as well as substituted iodobuta-1,3-dienes.[3] These authors concluded that iodoacetylenes and iodoallenes are too unstable for isolation. We have now shown that 1-iodoallenes are stable and can be isolated 98% pure, 3-iodoprop-1-yne, although less stable, can be isolated 91% pure, and both can be isolated nearly 100% pure by preparative gas–liquid chromatography (g.l.c.).

Early work in our laboratory showed that the addition of secondary acetylenic alcohols to crystalline triphenyl phosphite methiodide followed by distillation gave allenic iodides of variable yield and purity. Low-boiling iodides such as iodopropadiene and iodobutadiene can be separated readily from phenol which is produced as a by-product,[4] but higher-boiling iodides distil with phenol, extraction of which under basic conditions reduces the yield and introduces impurities.

* Part VI, R. J. Evans and S. R. Landor, *J.*, 1965, 2553.

[1] Y. R. Bhatia, P. D. Landor, and S. R. Landor, *J.*, 1959, 24.
[2] D. K. Black, S. R. Landor, A. N. Patel, and P. F. Whiter, *Tetrahedron Letters*, 1963, 483.
[3] (*a*) T. L. Jacobs and W. F. Brill, *J. Amer. Chem. Soc.*, 1953, **75**, 1314; (*b*) L. F. Hatch and D. J. Mangold, *ibid.*, 1955, **77**, 176; (*c*) T. L. Jacobs and W. L. Petty, *J. Org. Chem.*, 1963, **28**, 1360.
[4] Cf. S. R. Landor and H. N. Rydon, *J.*, 1953, 2224.

Iodoallenes are best prepared by carrying out the reaction in dimethylformamide at a temperature between 50 and 100°, followed by distillation. A mixture of iodoallene and dimethylformamide distils over first which is readily separated by the addition of water; phenol does not distil until all the halide and the bulk of the dimethylformamide have been removed.* Particularly unstable iodides (*e.g.*, conjugated iodoallenenes or allenynes) which cannot be distilled can be extracted from the reaction mixture with light petroleum after addition of water.

Highest yields of iodoacetylenes are obtained at low temperature and in methylene chloride as solvent. Prop-2-ynyl iodide can be prepared in this way 90% pure, but this drops to 43% for 3-iodobutyne. Virtually pure iodoacetylenes can be obtained by preparative g.l.c. However, slight rearrangement to the iodoallene occurs during the determination of the infrared spectrum.

The reaction of pent-4-en-1-yn-3-ol with methiodide gave a mixture of the unstable *cis*- and *trans*-1-iodopent-2-en-4-ynes. Conjugated unsaturated acetylenic and allenic iodides rapidly discoloured at room temperature and had to be stored at 0°. Elemental analyses proved unsatisfactory. However, preliminary work has shown that some of these unstable iodides may be useful intermediates for the synthesis of conjugated allenes.[5]

Trisnonylphenyl phosphite methiodide was investigated as a new and alternative reagent. This reagent has the advantage that nonylphenol, which is produced as a by-product, is high-boiling and does not distil over with the iodide formed in the reaction. The results obtained were similar to those with triphenyl phosphite methiodide. However, pure trisnonylphenyl phosphite methiodide is not as readily prepared as the simpler analogue and there seems little point in using the new reagent where the solution of triphenyl phosphite methiodide in dimethylformamide gives good results.

Neither allenic nor acetylenic iodides could be obtained in reasonable yield by employing triphenyl phosphite di-iodide as a reagent.

Two reaction paths for the formation of these iodides can be visualised: (*a*) a two-step reaction in which the first step is the conversion of acetylenic carbinol into acetylenic iodide which then rearranges to an equilibrium mixture of acetylenic and allenic iodide; (*b*) separate formations of acetylenic and allenic iodides by a different mechanism (*e.g.*, S_N2 or S_N2') affected to a different extent by temperature and solvent.

The following facts have to be taken into consideration. (i) Both iodoacetylenes and iodoallenes are reasonably stable in a pure state at room temperature and the pure compounds or mixtures of both do not change appreciably when stored for several weeks. (ii) At room temperature in dimethylformamide and in the presence of triphenyl phosphite methiodide, 3-iodobutyne rearranges to 1-iodobuta-1,2-diene. (iii) Optically active but-3-yn-2-ol gives only racemic allenic iodide with triphenyl phosphite methiodide in dimethylformamide.† From these, the following tentative conclusions may be drawn. Triphenyl phosphite methiodide is probably largely associated in methylene chloride. The concentration of iodide ion is therefore very small and an S_Ni mechanism is largely responsible for the formation of acetylenic iodide.[7] An S_Ni' mechanism would account for the formation of some allenic iodide.

The concentration of iodide ion in the more polar dimethylformamide is much higher and both S_N2 and S_N2' mechanisms may be operative simultaneously. However, we have shown that acetylenic iodide in dimethylformamide rearranges to the allenic iodide in the presence of triphenyl phosphite methiodide, possibly *via* the allenic carbene.[6]

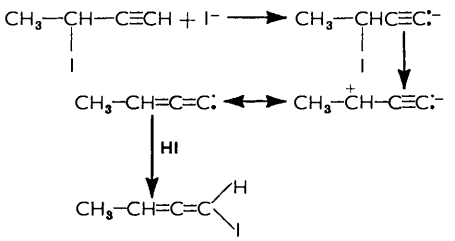
* The system phenol–dimethylformamide forms a maximum boiling point constant-boiling mixture.

† Either S_N2 substitution or elimination to the allenic carbene,[6] followed by addition of hydrogen iodide, would account for racemisation.

[5] C. S. L. Baker, P. D. Landor, and S. R. Landor, *J.*, 1965, in the press.

[6] S. R. Landor and P. F. Whiter, unpublished results; V. J. Shiner and J. W. Wilson, *J. Amer. Chem. Soc.*, 1962, **84**, 2402; H. D. Hartzler, *ibid.*, 1959, **81**, 2024; 1961, **83**, 4990, 4997.

[7] Cf. G. Stork and W. N. White, *J. Amer. Chem. Soc.*, 1956, **78**, 4609.



It is therefore possible that reactions in dimethylformamide proceed by mechanism (*a*), but (*b*) appears more plausible. No definite conclusion can be reached at this stage with the available information.

Experimental

Infrared spectra were determined on liquid films (in a 0·025-mm. cell) with a Perkin-Elmer Infracord spectrometer and ultraviolet spectra on ethanolic solutions with a Unicam S.P. 500 spectrometer. Elemental analyses generally gave high values for carbon and low values for iodine.

1-*Iodopropa*-1,2-*diene*.—*Method* A. Triphenyl phosphite methiodide [4] (78 g., 0·17 mole) was dissolved in *NN*-dimethylformamide (86 ml.) to give a 2M-solution and warmed to 100° on a water-bath. Prop-2-ynol (8·0 g., 0·14 mole) was added quickly and the mixture stirred at 100° for 0·5 hr. After cooling of the reactants to room temperature, distillation gave a mixture (b. p. 45°/18 mm.) of halides and dimethylformamide. The halides were separated by addition of water, washed with water, and dried ($MgSO_4$). The product was 1-iodopropa-1,2-diene containing 3-iodoprop-1-yne (12·84 g., 54%). G.l.c. (dinonyl phthalate, 40°, N_2 2·4 l./hr.) showed two peaks, 1-iodopropa-1,2-diene (80%) (*t*, 50 min.), and 3-iodoprop-1-yne (20%) (*t*, 69 min.). A similar reaction carried out at 0°, the mixture of halides and dimethylformamide being distilled at 25°/3 mm., gave 66% of a mixture of 3-iodoprop-1-yne (75%) and 1-iodopropa-1,2-diene (25%) by g.l.c. At 50°, however, a mixture of allene (60%) and acetylene (40%) was obtained. Preparative g.l.c. (dinonyl phthalate, 40°, N_2 2·3 l./hr.) gave two fractions, collected in traps cooled in acetone–solid carbon dioxide, 1-iodopropa-1,2-diene, $\nu_{max.}$ 1930vs (C=C=C), 855vs (–CH=), 800vs cm.$^{-1}$ (=CHI) and 3-iodoprop-1-yne, $\nu_{max.}$ 3240vs (≡CH), 2110w (C≡CH), 960vs cm.$^{-1}$ (CH_2I).

Method B. Prop-2-ynol (25·4 g., 0·45 mole) was added to solid triphenyl phosphite methiodide (248 g., 0·55 mole) at 0°. When the exothermic reaction had subsided the flask was heated to 80° for 1 hr. Distillation into a cooled trap gave mainly 3-iodoprop-1-yne containing some 1-iodopropa-1,2-diene (60 g.), similar to the product from (A).

A similar experiment at 100° yielded 60% of a mixture of allenic and terminal acetylenic material containing a greater proportion of allenic halide.

Refractionation in the presence of cuprous iodide did not materially alter the proportion of iodoacetylene to iodoallene.

3-*Iodoprop*-1-*yne*.—*Method* C. Triphenyl phosphite methiodide (56 g., 0·12 mole) was dissolved in methylene chloride (62 ml.) to give a 2M-solution, and cooled to 0° in an ice-bath. Prop-2-ynol (5·6 g., 0·1 mole) was added dropwise with stirring, the temperature being kept below 2°. The reaction mixture was stirred at 0° for 3 hr., allowed to warm up to room temperature, the methylene chloride removed under reduced pressure, and the product distilled at 2 mm. into an acetone–solid carbon dioxide cooled trap and then dried ($MgSO_4$) (12 g., 72%). G.l.c. (dinonyl phthalate, 80°, N_2 2 l./hr.) showed two peaks, 1-iodopropa-1,2-diene (10%) (*t*, 15 min.) and 3-iodoprop-1-yne (90%) (*t*, 18 min.).

1-*Iodobuta*-1,2-*diene*.—*Method* A. Triphenyl phosphite methiodide (60 g., 0·13 mole) dissolved in *NN*-dimethylformamide (66 ml.) at 100° with but-3-yn-2-ol (7·7 g., 0·11 mole) gave 1-*iodobuta*-1,2-*diene* (10·6 g., 53%) (Found: C, 27·2; H, 2·7; I, 70·3. C_4H_5I requires C, 26·7; H, 2·8; I, 70·6%), $\nu_{max.}$ 3280w (≡CH), 1940s (C=C=C), 880vs (–CH=), 830vs cm.$^{-1}$ (=CHI). G.l.c. (dinonyl phthalate, 80° N_2 2·1 l./hr.) showed one major peak, 1-iodobuta-1,2-diene (98%) (*t*, 30 min.), and a minor impurity 3-iodobut-1-yne (2%) (*t*, 20 min.).

Similar experiments carried out at 80 and 50° also gave 1-iodobuta-1,2-diene 98% pure in similar yield. At 0° the purity dropped to 88% (owing to the presence of 12% acetylenic

iodide) but the yield increased to 79%. An experiment using a 0·2M-solution of triphenyl phosphite methiodide (47 g., 0·105 mole) in *NN*-dimethylformamide (520 ml.) at 50° gave 1-iodobuta-1,2-diene of 93% purity in 10% yield only.

Method C. Triphenyl phosphite methiodide (45 g., 0·10 mole) dissolved in methylene chloride (50 ml.) at 44° and but-3-yn-2-ol (5·8 g., 0·083 mole) refluxed for 2 hr. gave a mixture of 3-iodobut-1-yne and 1-iodobuta-1,2-diene (5·8 g., 39%), containing a trace of phenol. G.l.c. (dinonyl phthalate, 80°, N_2 2 l./hr.) showed two peaks, 3-iodobut-1-yne (10%) (*t*, 24 min.), and 1-iodobuta-1,2-diene (90%) (*t*, 36 min.).

A similar experiment at 20° gave 62% yield of a mixture containing 1-iodobuta-1,2-diene (70%) and 3-iodobut-1-yne (30%).

Method B. But-3-yn-2-ol (15·5 g., 0·22 mole) and triphenyl phosphite methiodide (120 g., 0·26 mole) were kept at 0° for 3 days, after which time 95% of the methiodide had reacted. After a further 4 weeks at 0° the product showed no signs of further reaction and was distilled at room temperature *in vacuo* into a cooled trap and dried ($MgSO_4$) (19·7 g., 50%). The i.r. spectrum, superimposable upon that of a previous product, was that of 1-iodobuta-1,2-diene containing 7% 3-iodobut-1-yne.

In a similar experiment at 90°, with triphenyl phosphite methiodide (200 g.) and but-3-yn-2-ol (28 g.), the product was distilled off into a cold-trap and purified by chromatography on deactivated * alumina (grade " H," Peter Spence). Elution with pentane gave 1-iodobuta-1,2-diene (37·5 g., 52%) identified by i.r. spectroscopy.

1-Iodobuta-1,2-diene from (−)-But-3-yn-2-ol.—Triphenyl phosphite methiodide (15·5 g., 0·034 mole) was dissolved in *NN*-dimethylformamide (17 ml.) to give a 2M-solution. Optically active but-3-yn-2-ol (2·0 g., 0·028 mole, $[\alpha]_D^{20}$ −4·49°) was added dropwise with stirring at room temperature.

The mixture was stirred for 4 hr. and left overnight. Distillation gave a mixture of halides and dimethylformamide (b. p. 25°/0·4 mm.), which were separated by addition of water, washed, and dried ($MgSO_4$). The i.r. spectrum, superimposable on that of the product from a previous experiment, showed the proportion of 1-iodobuta-1,2-diene to be 90%. The product was optically inactive.

3-Iodobut-1-yne.—*Method* C. Triphenyl phosphite methiodide (61 g., 0·13 mole) dissolved in methylene chloride (68 ml.) with but-3-yn-2-ol (7·0 g., 0·10 mole) at 0° for 3 hr., gave 3-iodobut-1-yne and 1-iodobuta-1,2-diene (12·4 g., 69%). G.l.c. (dinonyl phthalate, 38°, N_2 4·2 l./hr.) showed two peaks, 3-iodobut-1-yne (43%) (*t*, 42 min.), and 1-iodobuta-1,2-diene (57%) (*t*, 68 min.); preparative g.l.c. gave two fractions, 3-iodobut-1-yne, $\nu_{max.}$ 3240vs (≡CH), 2100w (C≡CH), 850vs cm.$^{-1}$ (−CHI−), and 1-iodobuta-1,2-diene, $\nu_{max.}$ 1930s (C=C=C), 880vs, (−CH=), 830s cm.$^{-1}$ (=CHI).

Rearrangement of 3-Iodobut-1-yne to 1-Iodobuta-1,2-diene.—The mixture of 1-iodobuta-1,2-diene (57%) and 3-iodobut-1-yne (43%) (7·0 g., 0·04 mole), prepared by method (C) at 0°, was added dropwise to a 2M-solution of triphenyl phosphite methiodide (27 g., 0·06 mole) in *NN*-dimethylformamide (30 ml.) at 0°, stirred for 3 hr., and set aside overnight at room temperature. Distillation then gave a mixture of allene and dimethylformamide (b. p. 34°/4 mm.) and the allene was separated in the usual way.

The product was mainly 1-iodobuta-1,2-diene (2·45 g., 35%). G.l.c. (dinonyl phthalate, 80°, N_2 2·0 l./hr.) showed two peaks, 3-iodobut-1-yne (3%) and 1-iodobuta-1,2-diene (97%).

1-Iodopenta-1,2-diene.—*Method* A. Triphenyl phosphite methiodide (64 g., 0·14 mole) dissolved in *NN*-dimethylformamide (71 ml.) with pent-1-yn-3-ol (10·1 g., 0·12 mole) at 80° for 2 hr. gave 1-iodopenta-1,2-diene (12·6 g., 54%), $\nu_{max.}$ 3280w (≡CH), 1940s (C=C=C), 870m (−CH=), 840vs cm.$^{-1}$ (=CHI). A band at 1680s cm.$^{-1}$ (C=O), also present in the acetylenic carbinol, showed that carbonyl impurities were carried over into the halide fraction. G.l.c. (silicone oil, 100°, N_2 2 l./hr.) showed one major peak, 1-iodopenta-1,2-diene (95%) (*t*, 17 min.), and six minor peaks the total proportions of which was less than 5%.

Method B. Pent-1-yn-3-ol (4·2 g., 0·05 mole) and triphenyl phosphite methiodide (30 g.) gave, after the product had been washed with 2% ice-cold aqueous sodium hydroxide to remove phenol, extracted into ether, dried ($MgSO_4$), and distilled, a mixture of 1-iodopenta-1,2-diene and 3-iodopent-1-yne (2 g., 21%), b. p. 55—62°/80 mm.

1-Iodohexa-1,2-diene.—*Method* A. Triphenyl phosphite methiodide (72 g., 0·16 mole)

* 10% of 10% aqueous acetic acid.

dissolved in *NN*-dimethylformamide (80 ml.) with hex-1-yn-3-ol (13 g., 0·19 mole) at 80° for 2 hr. gave 1-iodohexa-1,2-diene (16·5 g., 60%), $\nu_{max.}$ 3280w (≡CH), 1940s (C=C=C), 870m (–CH=), 830s cm.$^{-1}$ (=CHI). G.l.c. (dinonyl phthalate, 104°, N_2 2 l./hr.) showed one major peak (98%) of 1-iodohexa-1,2-diene (*t*, 47 min.) and two minor peaks the proportion of which was less than 2%.

Method B. Hex-1-yn-3-ol (9·8 g., 0·1 mole) and triphenyl phosphite methiodide (54·5 g., 0·12 mole) at 90° for 0·5 hr. gave, after washing with 2% ice-cold aqueous sodium hydroxide, 1-*iodohexa*-1,2-*diene* (9·3 g., 45%), b. p. 39—41°/0·3 mm. (Found: C, 35·8; H, 4·5; I, 59·6. C_6H_9I requires C, 34·6; H, 4·4; I, 61·0%). The i.r. spectrum was identical with that of the previous sample.

1-*Iodohepta*-1,2-*diene*.—*Method* B. Hept-1-yn-3-ol (10 g., 0·09 mole) and triphenyl phosphite methiodide (50 g., 0·11 mole) gave, after washing with 2% ice-cold aqueous sodium hydroxide, 1-*iodohepta*-1,2-*diene* (4 g., 20%), b. p. 55—56°/1·5 mm. (Found: C, 38·4; H, 5·4; I, 56·0. $C_7H_{11}I$ requires C, 37·8; H, 5·0; I, 57·2%), $\nu_{max.}$ 3300vw (≡CH), 1940m (C=C=C), 840s cm.$^{-1}$ (=CHI).

1-*Iodo-octa*-1,2-*diene*.—*Method* B. Oct-1-yn-3-ol (10 g., 0·08 mole) and triphenyl phosphite methiodide (50 g., 0·11 mole) gave, after washing with 2% ice-cold aqueous sodium hydroxide, 1-*iodo-octa*-1,2-*diene* (7·6 g., 43%), b. p. 62—65°/1·5 mm. (Found: C, 41·5; H, 5·8; I, 53·2. $C_8H_{13}I$ requires: C, 40·6; H, 5·9; I, 53·5%), $\nu_{max.}$ 3300 vw (≡CH), 1940m (C=C=C), 850s cm.$^{-1}$ (=CHI).

1-*Iodo*-4-*methylpenta*-1,2-*diene*.—*Method* A. To triphenyl phosphite methiodide (352 g., 0·78 mole) dissolved in *NN*-dimethylformamide (390 ml.) 4-methylpent-1-yn-3-ol (49 g., 0·50 mole) was added dropwise with stirring, the temperature being kept at 15—25° by cooling in an ice-bath. The mixture was stirred under nitrogen at room temperature for a further 5 hr. and then left for 2 days. Working up gave fractions (i) b. p. 72—74°/48 mm. (4·7 g., 5%), $\nu_{max.}$ 3300m (≡CH), 1940vw (C=C=C), 1740vs cm.$^{-1}$ (C=O), g.l.c. (dinonyl phthalate, 81°, N_2 2 l./hr.) showed two major peaks, 1-iodo-4-methylpenta-1,4-diene (70%), (*t*, 62 min.) and 1-iodo-4-methylpenta-1,2-diene (20%) (*t*, 78 min.), and 10% of three other impurities; (ii) b. p. 74—78°/48 mm. (19·0 g., 18%), $\nu_{max.}$ 3280w (≡CH), 1940w (C=C=C), 1650 and 1610s (C=C), 895vs (CH_2=), 845vs cm.$^{-1}$ (=CHI), g.l.c. showed two major peaks, 1-iodo-4-methylpenta-1,2-diene (40%) (*t*, 81 min.) 1-iodo-4-methylpenta-1,4-diene (60%) (*t*, 63 min.), and 5% of two other impurities; (iii) b. p. 78—80°/48 mm. (18·2 g., 17·5%), $\nu_{max.}$ 3280vw (≡CH), 1940m (C=C=C), 1640 and 1610m (C=C), 895s (CH_2=), 845vs cm.$^{-1}$ (=CHI), g.l.c. showed two major peaks, 1-iodo-4-methylpenta-1,4-diene (25%) (*t*, 61 min.) and 1-iodo-4-methylpenta-1,2-diene (70%) (*t*, 75 min.), and 5% of two other impurities.

Method B. 4-Methylpent-1-yn-3-ol (9·0 g., 0·09 mole) was treated with triphenyl phosphite methiodide as described for hex-1-yn-3-ol (method B). Distillation at 35—38°/3 mm. gave impure 1-*iodo*-4-*methylpenta*-1,2-*diene* (8·0 g., 44%) (Found: C, 34·8; H, 4·4; I, 61·2. C_6H_9I requires C, 34·6; H, 4·4; I, 61·0%), $\nu_{max.}$ 3280vw (≡CH), 1940m (C=C=C), 1640 and 1610m (C=C), 895s (CH_2=), 845vs cm.$^{-1}$ (=CHI). There was no maximum in the ultraviolet spectrum.

1-*Iodo*-4,4-*dimethylpenta*-1,2-*diene*.—*Method* A. Triphenyl phosphite methiodide (103 g., 0·33 mole) dissolved in *NN*-dimethylformamide (150 ml.) with 4,4-dimethylpent-1-yn-3-ol at 80° for 2 hr. gave 1-iodo-4,4-dimethylpenta-1,2-diene (26·7 g., 67%), $\nu_{max.}$ 3300vw (≡CH), 1940m (C=C=C), 885m (–CH=), 845s cm.$^{-1}$ (=CHI).

1-*Iodo*-3-*phenylpropa*-1,2-*diene*.—*Method* A. Triphenyl phosphite methiodide (70 g., 0·15 mole) dissolved in *NN*-dimethylformamide (78 ml.) with 3-phenylprop-1-yne-3-ol (13·2 g., 0·1 mole) at room temperature with shaking gave, after extraction with light petroleum (40—60°, 200 ml.) and washing with water, 1-iodo-3-phenylpropa-1,2-diene (5·2 g., 21·5%), $\nu_{max.}$ 3280w (≡CH), 1930w (C=C=C), 1600m (C=C aromatic), 756 and 700s cm.$^{-1}$ (–CH aromatic), $\lambda_{max.}$ 282 mμ (ε 11,800).

Method B. 3-Phenylprop-1-yn-3-ol (13·2 g., 0·1 mole) was added to triphenyl phosphite methiodide (54·5 g., 0·12 mole) and warmed slightly on a water-bath to complete the reaction. The mixture became very dark and polymerised rapidly on attempted distillation.

Action of Triphenyl Phosphite Methiodide on 3-*Methylpent*-1-*yn*-3-*ol*.—3-Methylpent-1-yn-3-ol (9·8 g., 0·1 mole) was treated with triphenyl phosphite methiodide (54·5 g., 0·12 mole) and the product distilled at 28—40°/4 mm. to give a mixture of dehydration products and recovered 3-methylpent-1-yn-3-ol (6·9 g.), $\nu_{max.}$ 3400vs (OH), 3300vs (≡CH), 1620m (C=C), 890m (C=CH_2), and no band at 1950 cm.$^{-1}$ (C=C=C), $\lambda_{max.}$ 226 and 245 mμ (ε 4810 and 5280).

1-*Iodopenta*-1,2-*dien*-4-*yne*.—*Method* A (with E. S. PEPPER). Triphenyl phosphite, methiodide (27·1 g., 0·06 mole) dissolved in *NN*-dimethylformamide (30 ml.) with penta-1,4-diyn-3-ol (4·0 g., 0·05 mole) at 100° for 0·5 hr. gave 1-iodopenta-1,2-dien-4-yne (4·0 g., 42%), $\nu_{max.}$ 3350s (≡CH), 1940m (C=C=C), 835vs cm.$^{-1}$ (=CHI), $\lambda_{max.}$ 212·5 and 258 mμ (ε 6500 and 5000).

Method B. Penta-1,4-diyn-3-ol (2·4 g., 0·026 mole) was added to triphenyl phosphite methiodide (22·6 g., 0·05 mole) and heated to 80° until the mixture became liquid. Distillation at 24—30°/0·04 mm. gave 1-iodopenta-1,2-dien-4-yne (2·2 g., 37%), $\nu_{max.}$ 3300s (≡CH), 1940m (C=C=C), 1600 cm.$^{-1}$ (aromatic C=C due to phenolic impurity). Attempts to remove traces of phenol by washing with 2% ice-cold aqueous sodium hydroxide were unsuccessul and the allenic iodide was hydrolysed.

Action of Triphenyl Phosphite Methiodide on 6,6-*Dimethylhepta*-1,4-*diyn*-3-*ol*.—6,6-Dimethylhepta-1,4-diyn-3-ol (7 g., 0·05 mole) was treated with triphenyl phosphite methiodide (30 g., 0·067 mole) and the product distilled at 20—40°/0·05 mm. to give 1-iodo-6,6-dimethylhepta-1,2-diene-4-yne containing some 3-iodo-6,6-dimethylhepta-1,4-diyne and phenol (5 g., 41·3%), $\nu_{max.}$ 3400vw (OH), 3300m (≡CH), 1940m (C=C=C), 1600 (aromatic C=C i.p. vib.), 845s cm.$^{-1}$ (=CHI), $\lambda_{max.}$ 215, 240, and 244 mμ (ε 4120, 1490, and 1550).

Action of Triphenyl Phosphite Methiodide on Pent-4-*en*-1-*yn*-3-*ol*—*Method* B (with W. J. BALL). Pent-4-en-1-yn-3-ol (12·3 g., 0·15 mole) and triphenyl phosphite methiodide (87·5 g., 0·18 mole) at 40° for 15 min. gave, after washing with ice-cold 2% sodium hydroxide, a mixture of *cis*- and *trans*-1-iodopent-2-en-4-yne containing a trace of 1-iodopenta-1,2,4-triene (13·2 g., 46%), b. p. 42°/4 mm., $\nu_{max.}$ 3300s (≡CH), 2100w (C≡H), 1940vw (C=C=C), 960s (−CH=CH *trans*), 765s cm.$^{-1}$ (−CH=CH− *cis*), $\lambda_{max.}$ 242 mμ (ε 10,000), infl. 220 mμ (ε 8000).

Reactions with Trisnonylphenyl Phosphite.—*Trisnonylphenyl Phosphite Methiodide*. Trisnonylphenyl phosphite (69 g., 0·1 mole) refluxed (70 hr.) with methyl iodide (21 g., 0·15 mole) gave, on cooling, crystalline, trisnonylphenyl phosphite methiodide. The methiodide was washed several times with dry light petroleum (b. p. 40—60°), the solvent decanted, and the last traces removed *in vacuo* to give hygroscopic, yellow crystals of trisnonylphenyl phosphite methiodide (54 g., 65%) (m. p. 90—100°).

3-*Iodoprop*-1-*yne*. *Method* C. Trisnonylphenyl phosphite methiodide (130 g., 0·16 mole) dissolved in methylene chloride (78 ml.) with prop-2-ynol (7·3 g., 0·13 mole) for 3 hr. at 0° and overnight at room temperature gave 3-iodoprop-1-yne (14·7 g., 68%). The i.r. spectrum and g.l.c. showed 10% 1-iodopropa-1,2-diene and 90% 3-iodoprop-1-yne.

3-*Iodobut*-1-*yne*. *Method* C. Trisnonylphenyl phosphite methiodide (43 g., 0·052 mole) dissolved in methylene chloride (26 ml.) with but-3-yn-2-ol (2·9 g., 0·041 mole) at 0° for 3 hr. and then at room temperature overnight gave 3-iodobut-1-yne and 1-iodobuta-1,2-diene containing some unreacted but-3-yn-2-ol (2·0 g., 27%). G.l.c. (dinonyl phthalate, 40°, N_2 4 l./hr.) showed three peaks, but-3-yn-2-ol (10%) (*t*, 17 min.), 3-iodobut-1-yne (67%) (*t*, 42 min.), and 1-iodobuta-1,2-diene (22%) (*t*, 70 min.).

1-*Iodobuta*-1,2-*diene*. *Method* B. But-3-yn-2-ol (5·2 g., 0·074 mole) and trisnonylphenyl phosphite methiodide (74 g., 0·089 mole) at 80° gave 1-iodobuta-1,2-diene (10·0 g., 75%). G.l.c. (dinonyl phthalate, 80°, N_2 2 l./hr.) showed one major peak of 1-iodobuta-1,2-diene (99%) (*t*, 32 min.) and <1% of 3-iodobut-1-yne (*t*, 22 min.).

1-*Iodo*-4-*methylpenta*-1,2-*diene*. *Method* C. Trisnonylphenyl phosphite methiodide (46 g., 0·055 mole) dissolved in methylene chloride (28 ml.) and 4-methylpent-1-yn-3-ol (4·5 g., 0·046 mole) at 0° for 4 hr. and then at room temperature overnight gave 1-iodo-4-methylpenta-1,2-diene and other dienes (7·4 g., 77·5%). G.l.c. (dinonyl phthalate, 82°, N_2 1·9 l./hr.) showed four peaks. The major peak was 1-iodo-4-methylpenta-1,2-diene (80%) (*t*, 95 min.), and the three minor peaks, *t*, 34, 38, and 78 min., totalled 20%.

Method B. 4-Methylpent-1-yn-ol (4·1 g., 0·042 mole) and trisnonylphenyl phosphite methiodide (42 g., 0·052 mole) at room temperature gave a mixture of 1-iodo-4-methylpenta-1,2-diene, other dienes, and unreacted 4-methylpent-1-yn-3-ol (4·5 g., 52%), $\nu_{max.}$ 3500m (OH), 3260vs (≡CH), 2100w (C≡CH), 1940w (C=C=C), 1730s (C=O), 1650m and 1660m cm.$^{-1}$ (C=C). Chromatography on deactivated alumina (10% of 10% acetic acid solution) with light petroleum (b. p. 40—60°) as eluent yielded 1-iodo-4-methylpenta-1,2-diene (3·7 g., 43%); and g.l.c. (dinonyl phthalate, 100°, N_2 2 l./hr.) showed two peaks, 1-iodo-4-methylpenta-1,2-diene (75%) (*t*, 42 min.) and a second peak (*ca.* 25%) with two shoulders (*t*, 36 min.).

1-*Iodohexa*-1,2-*diene*. *Method* C. Trisnonylphenyl phosphite methiodide (155 g., 0·19 mole) dissolved in methylene chloride (93 ml.) and hex-1-yn-3-ol (11·8 g., 0·12 mole) at room

temperature gave 1-iodohexa-1,2-diene (11·3 g., 45%). The i.r. spectrum and g.l.c. showed 98% of 1-iodohexa-1,2-diene.

Method B. Hex-1-yn-3-ol (2·7 g., 0·028 mole) and trisnonylphenyl phosphite methiodide (28 g., 0·034 mole) at 80° for 1·5 hr. gave a mixture of 1-iodohexa-1,2-diene and unreacted hex-1-yn-3-ol (3·6 g., 63%). Chromatography on deactivated alumina (10% of 10% acetic acid) using n-pentane as eluent yielded 1-iodohexa-1,2-diene (2·0 g., 35%) free from unreacted alcohol. G.l.c. (dinonyl phthalate, 100°, N_2 1·8 l./hr.) showed only one peak (*t*, 90 min.).

Resolution of But-3-yn-2-ol.[8]—*But-3-yn-2-yl-hydrogen phthalate.* To but-3-yn-2-ol (28 g., 0·40 mole) and phthalic anhydride (88·8 g., 0·60 mole; recrystallised from chloroform) ice-cold 10% sodium hydroxide solution (240 ml., 0·60 mole) was added in three parts with vigorous shaking. The mixture became warm, was shaken for a further 5 min., then carefully rendered acid by the addition of 5N-hydrochloric acid. The oily crude phthalate was extracted with chloroform (200 ml.), phthalic acid (12 g.) filtered off, the solution evaporated, and the product recrystallised from chloroform–light petroleum (b. p. 40—60°), giving but-3-yn-2-yl hydrogen phthalate (67 g., 77%), m. p. 90°. Five experiments gave between 75 and 82% of recrystallised hydrogen phthalate.

Brucine salt of but-3-yn-2-yl hydrogen phthalate. Anhydrous brucine (315 g., 0·80 mole) and but-3-yn-2-yl hydrogen phthalate (175 g., 0·80 mole) in acetone (2·3 l.), were refluxed for 3 hr. and allowed to cool. Acetone (500 ml.) was distilled off and, after cooling, 338 g. (69% of total) slightly positive isomer crystallised. This was refluxed with acteone (1 l.) for 2 hr. and allowed to cool. Filtration gave the brucine salt (230 g., 47%) which, on debasification of a sample, gave hydrogen phthalate, $[\alpha]_D^{20}$ +6·6°.

Decomposition of the brucine salt of (+)-but-3-yn-2-yl hydrogen phthalate. The brucine salt of the (+)-but-3-yn-2-yl hydrogen phthalate (230 g., 0·375 mole) was shaken with 2·5N-hydrochloric acid (400 ml., 1·0 mole) and ether (1 l.), and the ether layer separated and dried ($MgSO_4$). The solvent was removed *in vacuo* on a rotary evaporator, and the crude but-3-yn-2-yl hydrogen phthalate recrystallised from chloroform–light petroleum (b. p. 40—60°) giving a small residue of phthalic acid and *(+)-but-3-yn-2-yl hydrogen phthalate* (38·5 g., 47%), m. p. 84°, $[\alpha]_D^{20}$ +7·9° (Found: C, 66·2; H, 4·8. $C_{12}H_{10}O_4$ requires C, 66·0; H, 4·6%).

(−)-But-3-yn-2-ol from (+)-but-3-yn-2-yl hydrogen phthalate. (+)-But-3-yn-2-yl hydrogen phthalate (52 g., 0·24 mole) $[\alpha]_D^{20}$ +7·7°, was dissolved in a 40% sodium hydroxide solution (50 ml., 0·5 mole) and continuously extracted with ether for 20 hr. The ethereal layer was separated, dried ($MgSO_4$), and the solvent carefully removed *in vacuo*, giving residual crude (−)-but-3-yn-2-ol (11·1 g., 66·5%). Redistillation gave one fraction, b. p. 46—49°/120 mm. (8·25 g., 50%), $[\alpha]_D^{20}$ −17·4°, $\nu_{max.}$ 3400vs (−OH hydrogen bonded), 3300vs (≡CH), 2130w cm.$^{-1}$ (C≡CH). The spectrum was superimposable on that of authentic specimen.

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[8] A preliminary account of a resolution of but-3-yn-2-ol *via* the brucine salt of the hydrogen phthalate was described by E. R. H. Jones, J. D. Loder, and M. C. Whiting, *Proc. Chem. Soc.*, 1960, 180. They state that they are " relating the butynol $[\alpha]_D^{20}$ −12·6° (homogeneous, l = 1 dm.) to the corresponding hydrogen phthalate, $[\alpha]_D^{23}$ −6·6° (*c.* 10·0 in $CHCl_3$)." In our hands (+)-but-3-yn-2-yl hydrogen phthalate, $[\alpha]_D^{20}$ +7·7°, gave (−)-but-3-yn-2-ol, $[\alpha]_D^{20}$ −17·4°.