721. *Researches on Acetylenic Compounds. Part XXVII. The Preparation and Properties of the Toluene-*p*-sulphonates of Acetylenic Alcohols.*

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Treatment of βγ- and γδ-acetylenic alcohols with toluene-*p*-sulphonyl chloride gives esters, often in excellent yield, which in their properties closely resemble the corresponding halides. Indeed the latter are most readily obtained from these toluene-*p*-sulphonates, which are also convertible, in the case of the βγ-acetylenic alcohols, into vinylacetylenes on treatment with alkaline reagents.

The conversion of αβ-acetylenic alcohols into the corresponding halides by treatment with thionyl chloride, phosphorus halides, etc., is a well-known and widely applicable reaction (see, *inter alia*, Henry, *Ber.*, 1873, **6**, 728; 1875, **8**, 398; 1884, **17**, 1133; Newman and Wotiz, *J. Amer. Chem. Soc.*, 1949, **71**, 1296). The present work originated in an attempt to extend this reaction to βγ- and γδ-acetylenic alcohols possessing a free ethynyl group :

$$HC{\equiv}C{\cdot}[CH_2]_n{\cdot}CH_2{\cdot}OH \longrightarrow HC{\equiv}C{\cdot}[CH_2]_n{\cdot}CH_2Br$$

The halides so obtained were required for the synthesis of a series of acetylenic compounds in which the triple bond is situated at the end of a carbon chain farthest from the functional group. The availability of such compounds would do much to increase the value of acetylenic compounds in synthetic work.

Direct treatment of the βγ- and γδ-acetylenic alcohols, but-3-yn-1-ol and pent-4-yn-1-ol, with inorganic acid halides was found to give the corresponding acetylenic halides, but only in small yield. From but-3-yn-1-ol and phosphorus tribromide in the presence of a little pyridine, for example, considerable quantities of high-boiling material containing phosphorus and bromine, and also a fraction apparently consisting largely of dibromobutenes, were obtained in addition to only 7% of the acetylenic bromide, the purification of which was troublesome. Apparently, considerable quantities of phosphite were formed, the hydrogen bromide produced then adding both to the phosphite and to the desired acetylenic bromide. [Since this work was begun, Newman and Wotiz (*J. Amer. Chem. Soc.*, 1949, **71**, 1296) have described the preparation of the corresponding bromide from a βγ-acetylenic alcohol not possessing a free ethynyl group, the yield being much lower than those recorded for similar alcohols in which the acetylenic bond is in the αβ-position. Very recently Schlubach and Wolf (*Annalen*, 1950, **568**, 142) have described the preparation of 4-bromobut-1-yne from but-3-yn-1-ol and phosphorus tribromide.]

It was considered likely that, although improvements in these yields obtained could doubtless be achieved, βγ- and γδ-acetylenic halides would never be obtainable, in a state of purity and in good yield, from the corresponding alcohols by direct treatment with inorganic acid halides. As an alternative route to reactive derivatives of these alcohols attention was then directed to the preparation of the corresponding toluene-*p*-sulphonates. It was found that toluene-*p*-sulphonyl chloride and pyridine converted but-3-yn-1-ol and pent-4-yn-1-ol into the corresponding esters in about 85% yield, and that pent-4-yn-2-ol, a secondary alcohol, gave a 92% yield of ester. These esters could be distilled at 10^{-4} mm., or on a small scale at 0·02 mm., without decomposition, but were normally used without purification.

Various by-products were formed in the reaction : (*a*) A small quantity of 5-chloropent-1-yne was isolated from a preparation of the corresponding toluene-*p*-sulphonate; it was probably formed by a reaction between the latter and pyridine hydrochloride (see Hess and Stenzel, *Ber.*, 1935, **68**, 981). (*b*) When in the preparation of but-3-yn-1-yl toluene-*p*-sulphonate the pyridine was incompletely removed before isolating the ester, but-3-yn-1-ylpyridinium toluene-*p*-sulphonate was obtained (cf. Sekara and Marvel, *J. Amer. Chem. Soc.*, 1933, **55**, 345). Some quaternisation probably occurred during the preparation of the esters of primary alcohols by this method. (*c*) A very inert by-product containing sulphur and chlorine, of unknown structure, was obtained when chloroform was used in the isolation of pent-4-yn-2-yl toluene-*p*-sulphonate. Its empirical formula corresponded to the addition of HOCl or $H_2O + HCl$ to the molecule of the toluene-*p*-sulphonate.

Treatment of the αβ-acetylenic alcohol, ethynylpropylcarbinol, with toluene-*p*-sulphonyl chloride and pyridine gave the corresponding ester in 70% yield, though in this case the conditions were more critical, presumably because of the more ready quaternisation of the pyridine (cf. the reactivity of allyl benzenesulphonate; Matheson and McCombie, *J.*, 1931, 1103). Applied to the di-primary αβ-acetylenic glycol, but-2-yne-1 : 4-diol, the method failed completely, no non-volatile material being obtained. Phenylethynylcarbinol also failed to yield a toluene-*p*-sulphonate under these conditions: the carbinol was not recovered, presumably because it was converted into a water-soluble quaternary salt. When the tertiary αβ-acetylenic alcohol, 1-ethynyl*cyclo*hexanol, was treated with toluene-*p*-sulphonyl chloride and pyridine a slow dehydration reaction took place and 1-ethynyl*cyclo*hexene was formed in 40% yield.

Since the toluene-*p*-sulphonates of but-2-yne-1 : 4-diol and of phenylethynylcarbinol were required for further work attention was turned to the condensation of the alcohols with toluene-*p*-sulphonyl chloride in the presence of sodium hydroxide, which had been used successfully by Schlichting and Klager (U.S.P. 2,340,701; *Chem. Abstr.*, 1944, **38**, 4269) in the cases of propargyl alcohol and methylethynylcarbinol. The glycol readily gave the corresponding ditoluene-*p*-sulphonate in 50—60% yield; this was found to react readily with pyridine and with triethylamine or diethylaniline, even at room temperature, to give syrupy quaternary salts. The failure of the pyridine method in this case is thus explained. Phenylethynylcarbinol, however, was recovered unchanged after treatment with toluene-*p*-sulphonyl chloride and sodium hydroxide, probably because its ester is rapidly hydrolysed by sodium hydroxide. Attempts to substitute calcium or magnesium hydroxide proved ineffectual.

Treatment of but-3-yn-1-yl toluene-*p*-sulphonate with sodium iodide in acetone gave the corresponding iodide in 64% yield, and reactions with lithium chloride and anhydrous calcium bromide [using 2-ethoxyethanol and 2-(2-ethoxyethoxy)ethanol, respectively, as solvents] gave the corresponding halides in 90 and 80% yields. Similar results were obtained from pent-4-yn-1-yl toluene-*p*-sulphonate; this method is thus clearly preferable to direct treatment with halogenating reagents as a method of preparing βγ- and γδ-acetylenic halides, especially since the products thus obtained were very readily purified. In many cases, however, this conversion is unnecessary since the toluene-*p*-sulphonates themselves undergo reactions similar to those of the halides (see below; also Jones, Whiting, and Eglinton, forthcoming publication).

Since the preparation of 1 : 4-dibromobut-2-yne from but-2-yne-1 : 4-diol by treatment with phosphorus tribromide (Johnson, *J.*, 1946, 1009) has been found to give a somewhat inhomogeneous product (Henbest, Jones, and Walls, private communication), the reaction between the corresponding toluene-*p*-sulphonate and calcium bromide was examined. A 75% yield of the halide was obtained; it proved to be homogeneous and had physical constants in agreement with those recorded by Valette (*Ann. Chim.*, 1948, **3**, 646).

On treatment with strongly alkaline reagents, *e.g.*, sodium hydroxide, sodium *n*-butoxide, and potassium cyanide, the toluene-*p*-sulphonates of the two βγ-acetylenic alcohols were found to lose toluene-*p*-sulphonic acid, with the formation of the corresponding vinylacetylenes. If this reaction is generally applicable it constitutes a useful synthesis of monosubstituted vinylacetylenes not otherwise easily accessible, since the βγ-acetylenic alcohols can readily be obtained from the corresponding aldehydes by a Reformatsky reaction with propargyl bromide (Henbest, Jones, and Walls, *J.*, 1949, 2696) :

$$\mathrm{R{\cdot}CHO} \longrightarrow \mathrm{R{\cdot}CH(OH){\cdot}CH_2{\cdot}C{\equiv}CH} \longrightarrow \mathrm{R{\cdot}CH{=}CH{\cdot}C{\equiv}CH}$$

In this way, treatment of but-3-yn-1-yl toluene-*p*-sulphonate with alcoholic potassium hydroxide readily gave vinylacetylene (77% overall yield from but-3-yn-1-ol). Indeed this is a very useful method of preparing small quantities of vinylacetylene of assured purity, since vinylacetylene prepared by dimerisation of acetylene requires rigorous purification to free it from higher polymers, vinyl chloride, etc. When the dehydroacylation was effected with sodamide (2 moles) in liquid ammonia, the sodio-derivative of vinylacetylene was formed, and addition of paraformaldehyde and isolation of the product then gave pent-4-en-2-yn-1-ol, albeit in small yield. A convenient method for the prepartion of vinylacetylenic carbinols is thus indicated.

Potassium hydroxide (a 30% aqueous solution at 100° was convenient) reacted with pent-4-yn-2-yl toluene-*p*-sulphonate to give a volatile hydrocarbon, b. p. 46—48°, n_{D}^{19} 1·4356. From its method of formation and its light absorption, that of a typical vinylacetylene, it is evidently pent-2-en-4-yne, though because of its volatility accurate analytical data could not be obtained. The overall yield from pent-4-yn-2-ol was about 90% when a suitable technique was employed; careful fractionation showed it to be homogeneous, and condensation through its Grignard reagent with *cyclo*hexanone gave a 73% yield of the expected carbinol which analysed correctly, gave crystalline derivatives, and showed light-absorption similar to that of the parent hydrocarbon (Hamlet, Henbest, and Jones, forthcoming publication). Its structure is therefore established; however, a hydrocarbon, b. p. 62°, n_{D}^{20} 1·438, was obtained by Lespieau and Journaud (*Bull. Soc. chim.*, 1931, **49**, 423) and tentatively formulated by them as pent-4-en-2-yne. The two hydrocarbons are clearly not identical. Lespieau and Journaud investigated the action of allyl chloride on sodium acetylide, and obtained this hydrocarbon only in the first of several experiments; no proof of homogeneity was given, but it formed a silver salt, and its high boiling point was considered to prove that it could not be allylacetylene. It is possible that this hydrocarbon consisted essentially of pent-1-en-3-yne [for which Jacobsen and Carothers (*J. Amer. Chem. Soc.*, 1933, **55**, 1622) give b. p. 59°/760 mm., n_{D}^{20} 1·4496] admixed with allylacetylene; the presence of the latter would account for the silver salt and the lower refractive index, and the reaction by which the former was obtained (migration of the triple, instead of the double, bond) would then be analogous to the formation of 1-phenylprop-1-yne from benzyl chloride and sodium acetylide (Lespieau and Journaud, *loc. cit.*) and of penta-1 : 3-diyne from propargyl bromide and sodium acetylide (Schlubach and Wolf, *loc. cit.*).

Treatment of the toluene-*p*-sulphonate of propylethynylcarbinol with sodium ethoxide gave the corresponding ethyl ether in 55% yield. Whilst this is a more general route to αβ-acetylenic ethers than published methods, the easily accessible αβ-acetylenic carbinyl bromides would probably be equally satisfactory in this reaction. As was expected but-2-yne-1 : 4-diol ditoluene-*p*-sulphonate apparently behaved toward ethanolic sodium ethoxide in the same way as the corresponding dichloride (Johnson, *loc. cit.*), diacetylene being formed rapidly and converted by alcohol addition more slowly into 1-ethoxybut-1-en-3-yne. The toluene-*p*-sulphonate of pent-4-yn-1-ol was converted by sodium ethoxide solution into the corresponding ethyl ether.

EXPERIMENTAL.

*But-3-yn-1-yl Toluene-*p*-sulphonate.*—A solution of toluene-*p*-sulphonyl chloride (42·6 g.) in warm pyridine (20·5 g.) was cooled rapidly to obtain small crystals, and but-3-yn-1-ol (14 g.) was added slowly during 30 minutes with mechanical stirring. The temperature of the mixture was kept below 25° by external cooling; after the exothermic reaction had subsided the mixture was set aside at 20° for 18 hours. Water (30 c.c.) was then added with cooling, and when the exothermic reaction had ceased the mixture was poured into water and extracted with ether. After repeated washing with sulphuric acid to remove the pyridine, then with sodium hydrogen carbonate solution, evaporation of the dried solution and removal of more volatile material at 100°/0·01 mm. gave the crude *ester* (37 g., 84%), n_D^{22} 1·5252. A small portion was distilled with slight decomposition at 128°/0·01 mm. and another at 90° (bath temp.)/10^{-4} mm. to give the purest specimen obtained, n_D^{19} 1·5262 (Found : C, 57·6, 58·1; H, 5·05, 4·95. $C_{11}H_{12}O_3S$ requires C, 58·9; H, 5·4%). Attempted distillation of *ca.* 40 g. at 0·5 mm. resulted in explosive decomposition.

The yield in this reaction and in similar acylations fell considerably when the temperature was allowed to exceed 35° or was kept below 5°. It also fell slightly when the amount of pyridine was increased in order to obtain a homogeneous solution. When 2 : 6-lutidine was substituted for pyridine no heat was evolved on mixing of the reagents; 1·5% by volume of pyridine was then added, whereupon the reaction took place rather slowly, the temperature being kept at about 40°. The yield was 84%, but the decomposition of the excess of toluene-*p*-sulphonyl chloride was sluggish and appeared to be incomplete, some being present in the crude product.

On one occasion when the pyridine was not adequately removed by washing with acid, a crude product was obtained which solidified partly on cooling. By treatment with ether the solid was separated; after recrystallisation from *iso*propanol 1-(*but-3-yn-1-yl*)*pyridinium toluene-*p*-sulphonate* formed deliquescent needles, m. p. 129—130° (Found : C, 63·1; H, 5·65. $C_{16}H_{17}O_3NS$ requires C, 63·35; H, 5·65%). The same salt was obtained when the ester was heated with pyridine. When a solution of this salt was treated with cupric sulphate and hydrazine sulphate a clear brown solution, presumably containing a water-soluble cuprous derivative, was obtained.

*Pent-4-yn-2-yl Toluene-*p*-sulphonate.*—This ester was prepared as above from pent-4-yn-2-ol (Kreimeier, U.S.P. 2,106,182) (42 g.), toluene-*p*-sulphonyl chloride (103·5 g.), and pyridine (70 c.c.) at 20—25°, the mixture being set aside for 20 hours after the end of the exothermic reaction. Isolation with ether gave the crude *ester* (109 g., 92%). After distillation at 70° (bath-temp.)/10^{-4} mm. it had n_D^{23} 1·5142; on cooling to −30° a portion crystallised. Recrystallisation from ether–light petroleum at −40° gave the pure ester as prisms, m. p. 31° (Found : C, 60·4; H, 5·95. $C_{12}H_{14}O_3S$ requires C, 60·45; H, 5·9%).

*Pent-4-yn-1-yl Toluene-*p*-sulphonate.*—Prepared by the method described above, from pent-4-yn-1-ol (Eglinton, Jones, and Whiting, forthcoming publication) (42 g.), toluene-*p*-sulphonyl chloride (110 g.), and pyridine (60 g.), the crude *ester* (98 g., 83%) had n_D^{13} 1·5215. A small portion, distilled for analysis, had b. p. 70—80° (bath-temp.)/10^{-5} mm., n_D^{15} 1·5229, m. p. 15° (Found : C, 60·25; H, 5·65%). During the removal of more volatile material a small quantity (*ca.* 2 g.) of liquid collected in a liquid-air trap. On redistillation it had b. p. 86°/280 mm., n_D^{15} 1·4460, and contained chlorine but not sulphur. It yielded an insoluble silver derivative with ammoniacal silver nitrate and presumably consisted essentially of 5-chloropent-1-yne (see below) (Found : C, 59·3; H, 6·8. Calc. for C_5H_7Cl : C, 58·5; H, 6·9%).

*Hex-1-yn-3-yl Toluene-*p*-sulphonate.*—Hex-1-yn-3-ol (Bowden, Heilbron, Jones, and Weedon, *J.*, 1946, 39) (20 g.), toluene-*p*-sulphonyl chloride (40 g.), and pyridine (22 c.c.) were allowed to react for 30 minutes at 10—20° with cooling, then for 40 minutes at 20°. Isolation of the neutral fraction gave the crude *ester* (34·6 g., 70%), n_D^{20} 1·5075. After distillation at 90° (bath-temp.)/10^{-4} mm. it had n_D^{21} 1·5113 (Found : C, 62·1; H, 6·55. $C_{13}H_{16}O_3S$ requires C, 61·9; H, 6·4%).

*But-2-yne-*1 : 4-*diol Ditoluene-*p*-sulphonate.*—But-2-yne-1 : 4-diol (21·6 g.) and toluene-*p*-sulphonyl chloride (111 g.) were dissolved in acetonitrile (190 c.c.), and the resultant solution was stirred and cooled while a solution of potassium hydroxide (28 g.) in water (50 c.c.) was added slowly, the temperature being kept at 10—20°. The mixture was then stirred without cooling for 18 hours, water (300 c.c.) and ether (200 c.c.) were added, and the phases were separated. The aqueous layer was extracted with ether, and the combined extracts were washed with water, dried, and evaporated. The residue readily solidified and was crystallised from methanol to give a solid (58 g., 60%), m. p. 92—93°. After recrystallisation from methanol or benzene–light petroleum (b. p. 60—80°) the *ester* formed long, stout needles, m. p. 94—95°, which after several days in contact with a saturated solution were converted into compact prisms with the same melting point, undepressed on admixture with the previously obtained form (Found : C, 54·7; H, 4·75. $C_{18}H_{18}O_6S_2$ requires C, 54·8; H, 4·6%). Similar (54, 58%) yields were obtained when tetrahydrofuran and acetone, respectively, were used as solvents.

1-*Ethynyl*cyclo*hexene*.—A mixture of 1-ethynyl*cyclo*hexanol (28 g.), toluene-*p*-sulphonyl chloride (48 g.), and pyridine (80 c.c.) was heated to 58° in a thermostatically controlled water-bath for 24 hours. After cooling, and decomposing the excess of chloride with water, isolation of the neutral fraction followed by careful fractional distillation gave (i) 1-ethynyl*cyclo*hexene (9·45 g., 40%), b. p. 34—37°/14 mm., n_D^{17} 1·4962, and (ii) recovered 1-ethynyl*cyclo*hexanol (7·75 g., 25%) (Milas, MacDonald, and Black, *J. Amer. Chem. Soc.*, 1948, **70**, 1829, give b. p. 52—53°/30 mm., n_D^{25} 1·4934 for a specimen of the hydrocarbon regenerated from the silver derivative). Unlike the crude hydrocarbon obtained by aluminium phosphate pyrolysis (Milas *et al.*, *loc. cit.*; Heilbron, Jones, and Richardson, *J.*, 1949, 287), material made by this route appeared to be free from *cyclo*hexanone; it did, however, contain a trace of a chlorine-containing substance responsible for a faint positive Beilstein test and probably also for a tendency to darken considerably on storage.

4-*Chlorobut*-1-*yne*.—A solution of lithium chloride (25·6 g.; somewhat moist) in 2-ethoxyethanol (170 c.c.) was distilled slowly through an 8″ Dufton column until the boiling point of the distillate reached 127° (80 c.c., containing much water, had then distilled). But-3-yn-1-yl toluene-*p*-sulphonate (88·9 g.) was added to the residual solution after the latter had cooled to about 50° and the mixture was homogenised by shaking. An exothermic reaction took place on warming, and careful distillation was resumed and continued until a boiling point of 124° was reached; most of the product distilled at 85—90°. The distillate was dried ($CaCl_2$) and fractionated; practically all boiled at 86—88·5°, giving the *chloride* (31·5 g., 90%), b. p. 86°/762 mm., n_D^{22} 1·4383 (Found: C, 54·4; H, 5·95. C_4H_5Cl requires C, 54·25; H, 5·7%).

4-*Bromobut*-1-*yne*.—(*a*) Essentially the above method was employed using the toluene-*p*-sulphonate (56·65 g.), anhydrous calcium bromide (30 g.), and 2-(2-ethoxyethoxy)ethanol (200 c.c.). It was necessary to moderate the reaction temperature by effecting the distillation at about 170 mm. pressure; much trouble was caused by bumping and frothing which made it impossible to volatilise the last traces of the bromide by distilling over a little of the solvent. Redistillation of the crude product, after drying ($CaBr_2$), gave the bromide (25·4 g., 82%), b. p. 107°/740 mm., n_D^{20} 1·4817 (Found: C, 36·35; H, 3·9. Calc. for C_4H_5Br: C, 36·1; H, 3·8%). Schlubach and Wolf, *loc. cit.*, give b. p. 109—110°/760 mm. It is probable that a better yield would be obtained by using as solvent an alcohol, b. p. *ca.* 160—170°, and distilling at atmospheric pressure; however, an attempt to employ *cyclo*hexanol failed, dehydration to *cyclo*hexene taking place.

(*b*) A solution of phosphorus tribromide (48 g.) in ether (20 c.c.) was added to a stirred mixture of but-3-yn-1-ol (35 g.) and pyridine (4 c.c.), the temperature being kept at between −20° and −10°. After the addition was complete the mixture was stirred at −20° for 30 minutes. Little heat was evolved until the mixture was allowed to warm to room temperature, whereupon an exothermic reaction set in; the temperature was then kept below 35° by gentle cooling. After it had subsided, water was added and the neutral fraction was isolated with ether. The almost colourless product was distilled at atmospheric pressure, fractions, b. p. 80—120° (15·2 g.), being collected. These on redistillation gave crude 4-bromobut-1-yne (8 g.), b. p. 104·5—109°/772 mm., n_D^{23} 1·4682—1·4721. The residue from the first distillation gave two further fractions: one (16·8 g.), b. p. 53—56°/12 mm., n_D^{21} *ca.* 1·52, appeared to consist largely of dibromobutenes, while the other (7·6 g.), b. p. 130—142°/0·1 mm., n_D^{21} *ca.* 1·49, contained both phosphorus and bromine. Both proved heterogeneous on redistillation.

4-*Iodobut*-1-*yne*.—A solution of butynyl toluene-*p*-sulphonate (15 g.) and sodium iodide (10 g.) in acetone (50 c.c.) was kept for 24 hours at 20°, then cooled to 0°. The separated sodium toluene-*p*-sulphonate was removed by filtration, and evaporation of the solvent through an 8″ Dufton column followed by fractionation gave the *iodide* (7·6 g., 64%), b. p. 61°/80 mm., n_D^{19} 1·5504 (Found: C, 26·95; H, 2·7. C_4H_5I requires C, 26·7; H, 2·8%).

5-*Chloropent*-1-*yne*.—A solution of pent-4-yn-1-ol (Eglinton, Jones, and Whiting, forthcoming publication) (8·5 g.) in dry pyridine (8·0 g.) was cooled strongly (solid carbon dioxide–alcohol) while thionyl chloride (14·6 c.c.) was added slowly, with stirring, the temperature being kept below 20°. After 2 hours at 20° the mixture was warmed slowly to 80° and kept at that temperature for 15 minutes, then cooled. Addition of water, followed by isolation of the neutral fraction with ether, evaporation through a 10-cm. Fenske column and fractionation gave crude chloride (3·0 g., 29%), b. p. 110—118°, and higher-boiling material which did not give a precipitate with ammoniacal silver nitrate solution. Redistillation of the first fraction gave the chloride, b. p. 88°/350 mm., n_D^{20} 1·4422 (Found: C, 58·85; H, 6·9. Calc. for C_5H_7Cl: C, 58·5; H, 6·9%). (Henne and Greenlee, *J. Amer. Chem. Soc.*, 1945, **67**, 484, give b. p. 67—69°/145 mm., n_D^{20} 1·445.) This substance could probably be more conveniently prepared from the toluene-*p*-sulphonate and lithium or calcium chloride.

5-*Bromopent*-1-*yne*.—(*a*) To a solution of pent-4-yn-1-ol (8·4 g.) and pyridine (2 g.) in dry ether (10 c.c.), phosphorus tribromide (10·8 g.) in ether (10 c.c.) was added slowly with stirring, the temperature being kept below −10°. After 1 hour at 20° the neutral fraction was isolated with ether. Distillation gave the crude bromide (4·2 g., 28%), b. p. below 85°/100 mm., which after redistillation had b. p. 82°/100 mm., n_D^{13} 1·4803 (Found: C, 42·3; H, 5·25; Br, 48·65. C_5H_7Br requires C, 40·8; H, 4·8; Br, 54·35%). It probably contained about 10% of pent-4-yn-1-ol. A considerable amount of higher-boiling material, probably dibromopentenes, was formed in this reaction.

(*b*) Pent-4-yn-1-yl toluene-*p*-sulphonate (24 g.) was added to a solution of calcium bromide (15 g.) in 2-(2-ethoxyethoxy)ethanol (150 c.c.) (previously dried by distillation of low-boiling material at 100 mm.). The mixture was homogenised and distilled till the boiling point reached 130°/100 mm.; the distillate was washed with water, dried, and redistilled to give the *bromide* (11 g., 75%), b. p. 134°/763 mm., n_D^{22} 1·4772 (Found: C, 41·0; H, 4·5. C_5H_7Br requires C, 40·8; H, 4·8%).

5-*Iodopent*-1-*yne*.—A mixture of pent-4-yn-1-yl toluene-*p*-sulphonate (46 g.), sodium iodide (31 g.), and acetone (230 c.c.) was heated under reflux for 3½ hours, cooled to room temperature, and filtered, the residue being washed with ether. The filtrate was evaporated through a 10-cm. Fenske column, whereupon an additional small quantity of sodium toluene-*p*-sulphonate separated and was removed by filtration; the total yield was 37·5 g. (theoretical). Distillation of the residue gave, after a small fore-run, 5-*iodopent*-1-*yne* (26·2 g., 70%), b. p. 84—89°/43 mm., n_D^{17} 1·5351 (Found: C, 31·25; H, 3·65. C_5H_7I requires C, 30·95; H, 3·65%). The fore-run appeared to consist largely of pent-4-yn-1-ol, the formation of which could probably have been prevented by using dried acetone. When the reaction period was 3 hours at 20°, the yield was 57%, about 15% of the toluene-*p*-sulphonate being recovered. An experiment in which 2-(2-ethoxyethoxy)ethanol was used as solvent, the technique being similar to that employed for 4-bromobut-1-yne (*a*), gave a yield of only 40%, apparently because of thermal decomposition and the difficulty of separating the product from the solvent.

1 : 4-*Dibromobut*-2-*yne*.—A solution of but-2-yne-1 : 4-diol ditoluene-*p*-sulphonate (19·7 g.) in dry chloroform (50 c.c.) was added to a solution of anhydrous calcium bromide (13 g.) in ethanol (50 c.c.; dried over magnesium ethoxide). After 20 hours at 20° water was added, the phases were separated, the aqueous layer was extracted with light petroleum (b. p. 40—60°), and the combined chloroform and petroleum layers were washed with water and dried ($CaBr_2$). Evaporation of the solvent followed by distillation of the residue gave the strongly lachrymatory dibromobutyne (7·75 g., 75%), b. p. 42°/0·1 mm., n_D^{20} 1·5877 (Valette, *Ann. Chim.*, 1948, **3**, 646, gives b. p. 92°/15 mm., n_D^{18} 1·588). Light absorption: rising absorption, ε = 4600, 3900, and 2700 at 2170, 2250, and 2350 A. respectively.

Vinylacetylene.—But-3-yn-1-yl toluene-*p*-sulphonate (85 g.) in ethanol (50 c.c.) was added dropwise to a solution of potassium hydroxide (25 g.) in water (30 c.c.) and ethanol (25 c.c.) containing a trace of "Teepol" and maintained at 60°. A steady evolution of gas was observed; the vapours evolved were passed up a reflux condenser, through a tube containing anhydrous calcium chloride, and into two traps cooled to about −25° in a solid carbon dioxide–carbon tetrachloride mixture. After the completion of the reaction the vinylacetylene was redistilled by allowing the traps to warm to 15° and collecting the distillate at −25° after pasage through a calcium chloride drying-tube; the yield was 18·2 g. (92%).

Pent-2-*en*-4-*yne*.—(*a*) Pent-4-yn-2-yl toluene-*p*-sulphonate (109 g.) was added slowly to a solution of potassium hydroxide (30 g.) in water (100 c.c.) containing a few drops of "Teepol," at 110° with mechanical stirring. A vigorous reaction took place, and the vapours evolved were passed into two traps cooled in solid carbon dioxide–carbon tetrachloride to −25°. When the reaction was complete the contents of the trap were warmed to melt the ice, and the layers were separated; the upper layer was dried ($CaCl_2$) and distilled to give *pent*-2-*en*-4-*yne* (29·9 g., 91% from pent-4-yn-2-ol), b. p. 46—48°, n_D^{19} 1·4356. Analytical results on this hydrocarbon were erratic, presumably because of its volatility (Found: C, 85·35; H, 9·0. C_5H_6 requires C, 90·85; H, 9·15%).

The presence of "Teepol" was essential for a high yield; in its absence the reaction was difficult to control.

(*b*) Pent-4-yn-2-yl toluene-*p*-sulphonate (33 g.) was added to a solution of sodium *n*-butoxide, prepared from sodium (3·5 g.) and *n*-butanol (150 c.c.) at 60°. A precipitate of sodium toluene-*p*-sulphonate formed immediately. Water (50 c.c.) was then added, and the mixture was heated to 100° in a distilling-flask, the side-arm being inserted into a test-tube cooled in carbon dioxide–alcohol. Slow evaporation of a very volatile substance took place, water distilling simultaneously. When the latter alone was collecting in the receiver the distillation was stopped, the layers were separated, and the upper was distilled, fractions boiling below 47° (3·0 g.) and at about 116° (butanol) being obtained. The former was redistilled, giving the hydrocarbon, b. p. 45—48°, n_D^{22} 1·4312. Light absorption: maximum, 2195 A.; inflexion, 2270 A.; ε = 9000 and 7000 respectively. No higher-boiling material was obtained from the residue in the flask.

After experiments [method (*a*)] in which the pent-4-yn-2-yl toluene-*p*-sulphonate used had been isolated with chloroform, dilution of the aqueous solution obtained after distillation of the pent-2-en-4-yne gave a turbidity and, on ether-extraction and distillation of the residue, a *by-product* was isolated (yield about 5% of the crude ester used). This appeared to be homogeneous; it had b. p. 124°/0·01 mm., n_D^{19} 1·5222, constants indistinguishable from those of the toluene-*p*-sulphonate. Analytical data (Found: C, 48·8, 49·25, 49·4; H, 5·2, 5·35, 5·3; S, 11·25, 12·44, 11·8; Cl, 13·75, 13·4. $C_{12}H_{15}O_4SCl$ requires C, 49·7; H, 5·2; S, 11·05; Cl, 12·25. $C_{12}H_{17}O_4SCl$ requires C, 49·2; H, 5·9; S, 10·95; Cl, 12·05%) were indecisive, and further investigations were frustrated by the extreme inertness of the compound.

Pent-4-*en*-2-*yn*-1-*ol*.—But-3-yn-1-yl toluene-*p*-sulphonate (22·4 g.) in ether (20 c.c.) was added to a suspension of sodamide, prepared from sodium (4·6 g.) and liquid ammonia (150 c.c.) in a Dewar vessel. The resulting solution was treated with paraformaldehyde (3 g.; dried for three days over phosphoric oxide). Evaporation of the ammonia after 40 hours and isolation in the usual way gave the alcohol (0·9 g., 11%), b. p. 64°/23 mm., n_D^{22} 1·4961 (Gverdtsiteli, *Doklady Akad. Nauk. S.S.S.R.*, 1948, **60**, 57, gives b. p. 55—58°/10 mm., n_D^{20} 1·4988). Light absorption: maximum, 2320 A., ε = 9500, and rising absorption below 2260 A. The product gave a *phenylurethane*, which formed long needles, m. p. 82° (corr.), from light petroleum (Found: C, 71·65; H, 5·6. $C_{12}H_{11}O_2N$ requires C, 71·65; H, 5·5%).

3-*Ethoxyhex*-1-*yne*.—To a solution of sodium ethoxide, obtained from sodium (2·1 g.) and dried ethanol (60 c.c.), hex-1-yn-3-yl toluene-*p*-sulphonate (19·5 g.) was added with ice-cooling. The temperature reached 45°, a precipitate of sodium toluene-*p*-sulphonate appearing. After 1½ hours at 20° the mixture was treated with water in excess and extracted with pentane. Evaporation of the solvent through a Widmer column and distillation gave the *ether* (5·75 g., 59%) (Found: C, 74·3; H, 11·5. $C_8H_{14}O$ requires C, 76·15; H, 11·2%). Analytical results with this compound varied widely, although it appeared to be homogeneous.

5-*Ethoxypent*-1-*yne*.—To a solution of sodium ethoxide, obtained from sodium (0·6 g.) and dried ethanol (15 c.c.), pent-4-yn-1-yl toluene-*p*-sulphonate (4·8 g.) in ethanol (5 c.c.) was added. A copious precipitate of sodium toluene-*p*-sulphonate separated immediately. After the initial reaction had subsided, the mixture was refluxed for 30 minutes. On cooling, the paste was treated with water and extracted with light petroleum (b. p. 40—60°). The solvent was removed through a 10-cm. Fenske column and distillation of the residue gave the *ether* (0·75 g., 34%), b. p. 38°/25 mm., n_D^{20} 1·4189 (Found : C, 74·25; H, 10·8. $C_7H_{12}O$ requires C, 74·9; H, 10·8%).

Mr. J. C. Hamlet was responsible for considerable improvements in the technique of both stages in the preparation of pent-3-en-1-yne.

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