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530. *The Synthesis of Long-chain αω-Dihalides by Means of Acetylenic Compounds.*

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Methods are outlined whereby members of the series of straight-chain polymethylene dihalides can be synthesised through acetylenic intermediates with relative ease and in considerable quantities. Appropriate examples of previously inaccessible dihalides have been studied experimentally.

PUBLISHED methods for the preparation of straight-chain polymethylene compounds are often unsatisfactory, particularly when the chain is of considerable length or when the compound is required in quantity. Few attempts have been made to use acetylenic compounds: only recent work such as the synthesis of vaccenic acid (Ahmad and Strong, *J. Amer. Chem. Soc.*, 1948, **70**, 1699, 3391) and of linoleic acid (Raphael, *J.*, 1950, 115, 120) has employed triply-bonded intermediates (see also Taylor and Strong, *J. Amer. Chem. Soc.*, 1950, **72**, 4263; Lumb and Smith, *J.*, 1952, 5032). The present work concerns the preparation of polymethylene dihalides by various reactions involving acetylenic bonds. The reactions studied seem perfectly general and lead to any member of the series with more than six carbon atoms from readily available starting materials in workable and often excellent yields. For summaries of the synthetic methods previously used for these dihalides see von Braun and Kamp (*Ber.*, 1937, **70**, 973) and Ziegler and Weber (*ibid.*, p. 1275).

The dihalides employed as starting materials in the present work are either the commercially available lower members or are derived from naturally occurring long-chain compounds, in particular, octamethylene and decamethylene dihalides from sebacic acid. Hexamethylene dibromide has been produced commercially from propargyl alcohol through hexa-2 : 4-diyne-2 : 6-diol, a single previous use of the methods to be described:

$$2HC{\equiv}C{\cdot}CH_2{\cdot}OH \longrightarrow (HO{\cdot}CH_2{\cdot}C{\equiv}C{\cdot})_2 \longrightarrow HO{\cdot}[CH_2]_6{\cdot}OH \longrightarrow Br{\cdot}[CH_2]_6Br$$

The acetylenic condensations have followed the technique described by Vaughn *et al.* (*J. Org. Chem.*, 1937, **2**, 1) and others. In general, it has been advantageous to employ 2—2·2 times the calculated amount of sodamide in the liquid ammonia condensations, whereby the product is obtained purer and in better yield. The acetylenic ethers are hydrogenated smoothly in the presence of Adams's platinum oxide catalyst at room temperature and pressure. In the case of 1-ethoxy-9-*o*-methoxyphenoxynon-3-yne it was desirable to carry out semi-hydrogenation with a palladium catalyst first. Finally, fission was carried out in open vessels for periods which increased with the length of the carbon chain.

The general synthetic procedures are classified as follows:

(i) A halogeno-ether (II) (cf. Ziegler and Weber, *loc. cit.*; Ziegler, Weber, and Gellert, *Ber.*, 1942, **75**, 1715) is treated with sodium acetylide, to give an ω-(methoxyphenoxy)acetylene (III) which is treated as the sodium salt with a further halogeno-ether, to give the acetylenic diether (IV) which is finally hydrogenated to (V) and converted into the dihalide:

$$\underset{\text{(II)}}{RO{\cdot}[CH_2]_n{\cdot}Br} \longrightarrow \underset{\text{(III)}}{RO{\cdot}[CH_2]_n{\cdot}C{:}CH} \xrightarrow{RO{\cdot}[CH_2]_m{\cdot}Br} \underset{\text{(IV)}}{RO{\cdot}[CH_2]_n{\cdot}C{:}C{\cdot}[CH_2]_m{\cdot}OR} \longrightarrow$$

$$\underset{\text{(V)}}{RO{\cdot}[CH_2]_{n+m+2}{\cdot}OR} \longrightarrow Br{\cdot}[CH_2]_{n+m+2}{\cdot}Br \qquad (R = o\text{- or } p\text{-methoxyphenyl})$$

The procedure has been illustrated for $n = m = 5$, to give dodecamethylene dibromide and di-iodide, and for $n = 2$, $m = 5$, to give nonamethylene di-iodide. An ethoxy-group was used for protection in the latter case because 2-ethoxyethyl bromide was available, but certain precautions became necessary during hydrogenation. An attempt to prepare 4-*o*-methoxyphenoxybutyne from 2-*o*-methoxyphenoxyethyl bromide and sodium acetylide gave only *o*-methoxyphenyl vinyl ether (cf. Summers and Larson, *J. Amer. Chem. Soc.*, 1952, **74**, 4498).

(ii) When the required dihalide contains $2n$ methylene groups and the dihalide with

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$n - 2$ methylene groups is available, the acetylene (VI) can be coupled with itself in the presence of an oxidising agent to give a diacetylenic diether (VII), which is then hydrogenated and hydrolysed as before:

$$\underset{\text{(VI)}}{2RO\cdot[CH_2]_{n-2}\cdot C{\vdots}CH} \longrightarrow \underset{\text{(VII)}}{(RO\cdot[CH_2]_{n-2}\cdot C{\vdots})_2} \longrightarrow RO\cdot[CH_2]_{2n}\cdot OR \longrightarrow Br\cdot[CH_2]_{2n}\cdot Br$$

Several of the coupling methods described in the literature were applied to 7-*o*-methoxyphenoxyhept-1-yne. When the cuprous salt was heated with aqueous cupric chloride for some hours, 1 : 14-di-*o*-methoxyphenoxytetradeca-6 : 8-diyne was obtained (cf. Strauss and Kollek, *Ber.*, 1926, **59**, 1680), but shaking the acetylene in oxygen with aqueous alcoholic cuprous chloride and ammonium chloride (Bowden, Heilbron, Jones, and Sargent, *J.*, 1947, 1579) was not effective, perhaps owing to the very low solubility of the acetylene in the medium. No diyne was detected in an attempt to couple two molecules of 7-*o*-methoxyphenoxyhept-1-ynylmagnesium bromide with iodine, but 19% of a product, in which the acetylenic hydrogen had been replaced by iodine, was obtained.

(iii) Di-iodides and two mols. of sodium acetylide give αω-diacetylenes (VIII), which with two mols. of ω-bromoalkyl ethers give diacetylenes (IX), which are then treated in the usual way:

$$I\cdot[CH_2]_n\cdot I + 2HC{\vdots}CNa \longrightarrow \underset{\text{(VIII)}}{HC{\vdots}C\cdot[CH_2]_n\cdot C{\vdots}CH} \xrightarrow[NaNH_2]{Br\cdot[CH_2]_m\cdot OR}$$

$$\underset{\text{(IX)}}{RO\cdot[CH_2]_m\cdot C{\vdots}C\cdot[CH_2]_n C{\vdots}C\cdot[CH_2]_m\cdot OR} \xrightarrow{\text{2 Steps}} Br\cdot[CH_2]_{2m+n+4}\cdot Br$$

This method is useful in the preparation of higher members of the series. For example, octamethylene dibromide was converted into octadecamethylene dibromide.

(iv) The converse procedure of (iii) was also used, in which two mols. of the sodium salt of an acetylenic ether were condensed with a polymethylene di-iodide, and the diacetylene resulting hydrogenated as usual:

$$2RO\cdot[CH_2]_n\cdot C{\vdots}CH + I\cdot[CH_2]_m\cdot I \longrightarrow RO\cdot[CH_2]_n\cdot C{\vdots}C\cdot[CH_2]_m\cdot C{\vdots}C\cdot[CH_2]_n\cdot OR \xrightarrow{\text{2 Steps}} Br\cdot[CH_2]_{2n+m+4}\cdot Br$$

In this way, pentamethylene di-iodide and 7-*o*-methoxyphenoxyheptyne were converted into pentadecamethylene dibromide. An improved preparation of pentamethylene di-iodide is also described.

It will be seen that syntheses embodying one of these four procedures can easily be devised for any polymethylene compound from seven methylene groups upwards. Taylor and Strong (*loc. cit.*), however, discovered unexpected limitations in an analogous attempted synthesis of petroselinic acid.

Larger-scale working has been realised without difficulty in the preparation of 500 g. of dodecamethylene di-iodide.

Dithiuronium picrates obtainable from various dihalides are listed on p. 2606.

EXPERIMENTAL

5-o-*Methoxyphenoxypentyl Bromide*.—Pentamethylene dibromide (920 g., 4 mols.), guaiacol (124 g., 1 mol.) and methanolic 2·7N-potassium hydroxide (380 c.c.) were heated on a steam-bath for 2 hr. The potassium bromide which crystallised was filtered off and the methanol distilled off at atmospheric pressure, followed by excess of pentamethylene dibromide at 120°/10 mm. The remaining oil was decanted from further potassium bromide which had separated, and was distilled in a high vacuum, giving 5-o-*methoxyphenoxypentyl bromide*, b. p. 125—128°/0·4 mm., n_D^{20} 1·541 (206 g., 76% based on the guaiacol used). A refractionated portion of the product, b. p. 130—131°/0·45 mm., was analysed (Found: Br, 29·0. $C_{12}H_{17}O_2Br$ requires Br, 29·3%). The compound was characterised as the *thiuronium picrate*, obtained by heating 1 c.c. under reflux with thiourea (2 g.) in ethanol for 3 hr. and treating the hot solution with picric acid (1 g.) in ethanol (10 c.c.); the picrate crystallised in bright yellow prisms, m. p. 146° (Found: N, 14·1; S, 6·6. $C_{19}H_{23}O_9N_5S$ required N, 14·1; S, 6·4%).

7-o-*Methoxyphenoxyhept*-1-*yne*.—Sodium (50 g., >2 mols.) was converted into a suspension of sodium acetylide in liquid ammonia (2 l.) in the presence of a little ferric nitrate (cf. *inter al.*, Heilbron, Jones, and Weedon, *J.*, 1945, 83), and the stirred suspension was treated dropwise during 1½ hr. with 5-*o*-methoxyphenoxypentyl bromide (276 g., 1 mol.) in twice its bulk of dry

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ether. Ether was added to replace the liquid ammonia lost by evaporation and the whole allowed to warm to room temperature overnight. It was finally heated gently under reflux on the steam-bath for 1½ hr., filtered, and washed with ether, and the solvent was evaporated, to give a thick oil, which gave fractions boiling at 130—152°/1 mm., and at 153—165°/1 mm. The main (lower-boiling) fraction solidified to a waxy *ether* which crystallised (141 g.) from light petroleum (b. p. 40—60°), m. p. 33°. The purer material distilled at 120—130°/0·2 mm. (Found: C, 76·9; H, 8·3; OMe, 14·4. $C_{14}H_{18}O_2$ requires C, 77·1; H, 8·2; OMe, 14·2%) and gave a silver salt on admixture with ammoniacal silver nitrate solution. The higher-boiling fraction, redistilled through a Vigreux column, gave 95 g. of 5-*o*-methoxyphenoxypentyl bromide. The average yield of a number of runs was 93%. The *mercury* salt was obtained by adding an alcoholic solution to potassium mercuri-iodide solution. It crystallised from benzene containing a little light petroleum (b. p. 40—60°) in colourless plates, m. p. 91—92° (Found: Hg, 31·6. $C_{28}H_{34}O_4Hg$ requires Hg, 31·6%).

1 : 12-*Di*-o-*methoxyphenoxydodec*-6-*yne*.—Sodamide (from 14 g. of sodium) in liquid ammonia (1·5 l.) was treated with 7-*o*-methoxyphenoxyhept-1-yne (125 g. in twice its bulk of dry ether) during 1 hr., with stirring, which was continued for a further hour, and then 5-*o*-methoxyphenoxypentyl bromide (157 g. in twice its volume of dry ether) was run in during 30 min. The reactants were stirred overnight and then the suspension was heated under reflux for 4 hr. After filtration, the ether was removed. The solid residue, crystallised from ethanol, gave 1 : 12-*di*-o-*methoxyphenoxydodec*-6-*yne* (245 g., 100%) as plates, m. p. 82·5—83°, showing no reaction for halogen or a free ethynyl group (Found: C, 75·8; H, 8·2; OMe, 15·0. $C_{26}H_{34}O_4$ requires C, 76·1; H, 8·3; OMe, 15·2%).

1 : 12-*Di*-o-*methoxyphenoxydodecane*.—1 : 12-Di-*o*-methoxyphenoxydodec-6-yne (226·5 g.) in ethyl acetate (800 c.c.) was shaken with Adams's platinum oxide (4 g.) in hydrogen at 4 atm. (theoretical uptake in 84 min.). The solution was filtered and evaporated. 1 : 12-*Di*-o-*methoxyphenoxydodecane* (186 g., 82%) was obtained as needles, m. p. 84—85°, after two recrystallisations of the residue from ethanol (Found: C, 75·1; H, 9·3. $C_{26}H_{38}O_4$ requires C, 75·4; H, 9·2%).

Dodecamethylene Dibromide.—1 : 12-Di-*o*-methoxyphenoxydodecane (5 g.) was heated under reflux with 50% aqueous hydrobromic acid (15 c.c.) for 48 hr. The cooled dark solution was made alkaline to litmus, extracted with benzene, black humus-like material being filtered off ("Hyflo supercel"), and the extract was dried and evaporated. The resulting oil solidified on trituration with a little very cold methanol and was then crystallised twice from methanol. Colourless waxy crystals of dodecamethylene dibromide (3·4 g., 86%), m. p. 38·5° (lit., m. p. 40·5—41°), were obtained (Found: C, 44·4; H, 7·6. Calc. for $C_{12}H_{24}Br_2$: C, 43·9; H, 7·3%).

Dodecamethylene Di-iodide.—This was prepared by heating the above diether for 16 hr. with 55% hydriodic acid, and the crude oil, in chloroform solution, was washed with solutions of sodium hydrogen sulphite and sodium hydroxide and dried before distillation. The product, b. p. 192—198°/0·5 mm., solidified. Crystallised from ethanol, it had m. p. 41° (90%) (lit., m. p. 41°).

1 : 14-*Di*-o-*methoxyphenoxytetradeca*-6 : 8-*diyne*.—(i) A solution of 7-*o*-methoxyphenoxyhept-1-yne (28·3 g. 0·13 mol.) in methanol (100 c.c.) was added to freshly prepared cuprous chloride (26 g.) in 50% ammonia solution (*d* 0·88; 50 c.c.) with stirring. A thick pea-green flocculent precipitate of the copper salt was formed, which was kept for 5 min., then filtered through sintered glass and washed with water, ethanol, and ether. The damp solid (32 g.) was suspended in aqueous ethanol (1 : 1) and heated on the steam-bath with cupric chloride (18 g.) in water (40 c.c.) for 48 hr. Another 5 g. of cupric chloride were added after 24 hr. The mixture was filtered, the residue was extracted thoroughly with hot methanol; the combined aqueous-alcoholic solutions crystallised on cooling. The residue was further digested with chloroform, and the dried chloroform solution was evaporated; the resulting oil partly crystallised; these crystals were added to the main product which was recrystallised from methanol. 1 : 14-*Di*-o-*methoxyphenoxytetradeca*-6 : 8-*diyne* (12·4 g., 71% calc. on the hept-1-yne not recovered) was obtained in colourless needles, m. p. 71°, which slowly assumed a deep violet colour, removed by recrystallisation [Found: C, 77·4; H, 7·9; OMe, 14·3%; *M* (in acetone), 405. $C_{28}H_{34}O_4$ requires C, 77·4; H, 7·8; OMe, 14·3%; *M*, 434]. The residual oil from the chloroform extract yielded 10·8 g. of 7-*o*-methoxyphenoxyhept-1-yne, b. p. 140—145°/0·4 mm.

(ii) Shaking a suspension of the copper salt of 7-*o*-methoxyphenoxyhept-1-yne and ammonium chloride in aqueous acetone in a hydrogenation apparatus filled with oxygen led to no uptake of oxygen, and an almost quantitative recovery of starting material.

(iii) Ethylmagnesium bromide solution, prepared from magnesium (2·4 g., 0·1 mol.),

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ethyl bromide (10 c.c.), and dry ether (100 c.c.), was treated dropwise with 7-*o*-methoxyphenoxyhept-1-yne (21·8 g., 0·1 mol.) in dry ether (100 c.c.). After a few min., a colourless precipitate began to separate, and ethane was evolved. When the reaction was over, dry benzene (100 c.c.) was added, the ether distilled off, and the suspension of partly dissolved Grignard complex treated with iodine (12·7 g., 0·05 mol.) in benzene (100 c.c.), and stirring continued subsequently for a few min. The solution was kept overnight and decomposed with 1% sulphuric acid. The benzene layer was washed with sodium hydrogen carbonate solution and water, dried, and evaporated. The residual oil was distilled, giving fractions, b. p. 110—115°/0·01 mm. and 130—150°/0·01 mm. The former solidified on trituration with light petroleum (b. p. 40—60°) cooled in solid carbon dioxide and proved to be starting material (12·3 g.). The second fraction solidified on trituration with methanol similarly cooled and recrystallised from methanol in colourless prisms, m. p. 62° (6·6 g.). It appeared from the analytical data and the absence of any precipitate with ammoniacal silver nitrate solution, to be 1-*iodo*-7-o-*methoxyphenoxyhept*-1-*yne* [Found: C, 48·7; H, 5·1; I, 37·2; OMe, 9·5%; *M* (in acetone), 318. $C_{14}H_{17}O_2I$ requires C, 48·8; H, 4·9; I, 36·9; OMe, 9·1; *M*, 344].

1 : 14-*Di*-o-*methoxyphenoxytetradecane*.—1 : 14-Di-*o*-methoxyphenoxytetradeca-6 : 8-diyne (5·75 g.) was hydrogenated in dry ethyl acetate (50 c.c.) with Adams's platinum oxide (0·5 g.) at room temperature and pressure (100% uptake in 8 hr.). The solution was filtered hot, and colourless 1 : 14-*di*-o-*methoxyphenoxytetradecane* (5·3 g., 92%) crystallised, having m. p. 81—82° (from ethanol) (Found: C, 76·0; H, 9·2; OMe, 13·8. $C_{28}H_{42}O_4$ requires C, 76·0; H, 9·5; OMe, 14·0%).

Tetradecamethylene Dibromide.—This was obtained as a colourless wax (40%), m. p. 48°, (from methanol) (lit., m. p. 49—49·5°), after the above diether had been heated with 50% hydrobromic acid and acetic anhydride for 70 hr.

Tetradecamethylene Di-iodide.—Treatment of 1 : 14-di-*o*-methoxyphenoxytetradecane (10 g.) with 55% hydriodic acid (100 c.c.) for 24 hr. (as above) gave an oil, b. p. 200—220°/0·8 mm., which solidified, giving *tetradecamethylene di-iodide*, plates (from methanol), m. p. 50—51° (8·5 g., 82%) (Found: I, 56·0. $C_{14}H_{28}I_2$ requires I, 56·3%).

4-*Ethoxybutyne*.—2-Ethoxyethyl bromide (*Org. Synth.*, 1943, **23**, 32) was treated with sodium acetylide according to Kroeger and McCusker (*J. Amer. Chem. Soc.*, 1937, **59**, 213). It was characterised as the mercury salt, colourless prisms (from ethanol), m. p. 100·5° (lit., m. p. 99·5°) (Found: Hg, 50·8. Calc. for $C_{12}H_{18}O_2Hg$: Hg, 50·8%).

1-*Ethoxy*-9-o-*methoxyphenoxynon*-3-*yne*.—4-Ethoxybutyne (45 g., 0·45 mol.) in ether (100 c.c.) was run into a suspension of sodamide in liquid ammonia (1 l.) prepared from sodium (18 g., 0·8 mol.) and stirred for 1 hr. The suspended sodium salt was then treated with 5-*o*-methoxyphenoxypentyl bromide (93 g., 0·35 mol.) in ether (200 c.c.) during 2 hr. and the ammonia allowed to evaporate with stirring overnight. After 1 hour's heating under reflux the ethereal solution was filtered, the ether removed, and the residue distilled, first at the water-pump, and then in a high vacuum, giving fractions, (*a*) b. p. 40—50°/12 mm., 4-ethoxybutyne, (*b*) b. p. 150—180°/12 mm. (15 g.), (*c*) b. p. 200—210°/11 mm. (17 g.), and (*d*) b. p. 180—185°/0·1 mm. (45 g.). Redistillation of fractions (*b*), (*c*), and (*d*) through a short Vigreux column gave finally 53 g. (55%) of 1-*ethoxy*-9-o-*methoxyphenoxynon*-3-*yne* (b. p. 145—150°/0·05 mm., n_D^{20} 1·516) which solidified at about 10—12°. A redistilled portion, b. p. 147—150°/0·05 mm., was analysed (Found: C, 75·0; H, 9·1; alkoxy-O, 11·6. $C_{18}H_{26}O_3$ requires C, 74·5; H, 9·0; alkoxy-O, 11·0%).

1-*Ethoxy*-9-o-*methoxyphenoxynonane*.—Some difficulty was experienced in hydrogenation of the above acetylene because of the tendency to hydrogenolysis of the ethoxy-group. Adams's platinum oxide in ethyl acetate, and 5% palladised barium sulphate in ethyl acetate, caused some dealkylation. Raney iron produced no hydrogen uptake. 1-Ethoxy-9-*o*-methoxyphenoxynon-3-yne (33 g.) in ethyl acetate (100 c.c.) was shaken in an atmosphere of hydrogen with 10% palladised calcium carbonate (1 g.) at room temperature and pressure. Hydrogen uptake was 47% after 2 hr. and then almost ceased. The catalyst was filtered off, Adams's platinum oxide (1 g.) added, and hydrogenation continued. A rapid uptake of another 43% occurred. The solution was filtered, the solvent evaporated, and the residue distilled, to give 1-*ethoxy*-9-o-*methoxyphenoxynonane* (30 g., 91%), as a viscous colourless oil, b. p. 210—214°/9 mm., which slowly crystallised (Found: C, 73·6; H, 9·8. $C_{18}H_{30}O_3$ requires C, 73·5; H, 10·1%). When the acetylene compound was hydrogenated in the presence of 5% palladised barium sulphate, 50% of the theoretical uptake of hydrogen was observed. After being worked up as before, the product distilled at 210—215°/16 mm., and analysis indicated that it was 1-*ethoxy*-9-o-*methoxyphenoxynon*-6-*ene*, which was confirmed by the strong colour reaction

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with tetranitromethane, absent from tests with both the starting material and the fully reduced compound (Found: C, 74·1; H, 9·0. $C_{18}H_{28}O_3$ requires C, 74·0; H, 9·0%).

Nonamethylene Di-iodide.—1-Ethoxy-9-*o*-methoxyphenoxynonane (30 g.) was treated for 30 hr., with stirring, with 55% hydriodic acid (200 c.c.) and worked up in the usual way, giving *nonamethylene di-iodide*, b. p. 123°/0·2 mm., n_D^{15} 1·560 (19·8 g., 74%), solidifying to a colourless wax, m. p. *ca.* 12—15° (Found: I, 66·1. $C_9H_{18}I_2$ requires I, 66·8%).

Hydrolysis for 24 hr. without stirring gave about 45% of nonamethylene di-iodide and about 50% of an oil, b. p. 185—187°/0·5 mm., probably 9-*o*-hydroxyphenoxynonyl iodide (Found: I, 36·7. Calc. for $C_{15}H_{23}O_2I$: I, 35·1%).

When an attempt to prepare 4-*o*-methoxyphenoxybutyne from sodium acetylide in liquid ammonia and 2-*o*-methoxyphenoxyethyl bromide was made (Di Boscogrande, *Atti R. Accad. Lincei*, 1897, [v], **6**, II, 33), the product, apart from some recovered starting material, appeared to be *o*-methoxyphenyl vinyl ether, b. p. 95—100°/10 mm., 200—202°/760 mm. (Found: C, 71·4; H, 6·9. Calc. for $C_9H_{10}O_2$: C, 71·9; H, 6·9%). No acetylenic reactions were observed.

3-p-*Methoxyphenoxypropyl Bromide.*—(*a*) By the procedure indicated for 5-*o*-methoxyphenoxypentyl bromide, 3-p-*methoxyphenoxypropyl bromide* was obtained as a colourless oil (64%), b. p. 178—180°/20 mm., 156—159°/10 mm., n_D^{20} 1·5459 (Found: C, 49·8; H, 5·5; OMe, 12·9. $C_{10}H_{13}O_2Br$ requires C, 49·0; H, 5·3; OMe, 12·6%). Some fore-run, b. p. 157—175°/20 mm., m. p. 51—52°, was also obtained, identified as dimethylquinol, an impurity in the starting material. The residue from the distillation solidified and crystallised from methanol; 1 : 3-di-*o*-methoxyphenoxypropane was thereby obtained as colourless plates, m. p. 87° (lit., m. p. 88°) (Found: C, 71·3; H, 7·0; OMe, 22·0. Calc. for $C_{17}H_{20}O_4$: C, 70·8; H, 7·0; OMe, 21·5%).

(*b*) When *p*-methoxyphenol, trimethylene dibromide and aqueous sodium hydroxide were heated together overnight, only 36% of the pure product was obtained.

The halide was characterised by conversion into the *thiuronium picrate* which crystallised from ethanol in flat yellow plates or prisms, m. p. 147°, and sometimes in a mixture of yellow prisms and scarlet needles. The scarlet form, m. p. 148°, was also formed by cooling the yellow melt and appeared to be the metastable form since it reverted to the other after about two weeks (Found: N, 14·8; S, 7·0. $C_{17}H_{19}O_9N_5S$ requires N, 14·9; S, 6·8%).

5-p-*Methoxyphenoxypent*-1-*yne.*—3-*p*-Methoxyphenoxypropyl bromide (175 g.) was treated as already described with sodium acetylide (prepared from 40 g. of sodium in 1½ l. of liquid ammonia), and the resulting yellow oil was distilled. After a few drops of fore-run, b. p. 140—160°/19 mm., 5-p-*methoxyphenoxypent*-1-*yne* (131 g., 97%) was collected at 163—166°/19 mm. Redistilled through a 12-cm. Vigreux column, it had b. p. 151—155°/11 mm., m. p. 24° (Found: C, 75·5; H, 7·6; OMe, 16·8. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4; OMe, 16·3%). The residue from the first distillation gave a small amount of an unidentified *substance*, colourless plates (from methanol), m. p. 65°, depressed in m. p. in admixture with 1 : 3-di-*p*-methoxyphenoxypropane (m. p. 84°) (Found: C, 66·9; H, 8·0; OMe, 18·6%). 5-*p*-Methoxyphenoxyprop-1-yne was characterised as its *mercury* salt, crystallising from benzene in plates, m. p. 109—111° (Found: Hg, 34·7. $C_{24}H_{26}O_4Hg$ requires Hg, 34·7%).

1 : 15-*Di*-p-*methoxyphenoxypentadeca*-4 : 11-*diyne.*—Pentamethylene di-iodide was obtained by refluxing tetrahydropyran (250 c.c.) with 55% hydriodic acid (300 c.c.) for 8 hr., the lower layer being separated and washed with aqueous sodium hydrogen sulphite, sodium hydroxide, and water, and dried. After recovery of 70 c.c. of tetrahydropyran, the di-iodide, b. p. 155—157°/24 mm. (119 g.), was collected (lit., b. p. 149°/20 mm.).

5-*p*-Methoxyphenoxypent-1-yne (38 g.) was converted into the sodium salt in liquid ammonia (100 c.c.) and treated with redistilled pentamethylene di-iodide (25 g.) in ether (50 c.c.). After being stirred overnight, the ethereal suspension was refluxed for 6 hr. and then worked up as before. The red oil left after the removal of ether was distilled and after a fore-run of the acetylenic starting material (b. p. 160—165°/20 mm.) the residue was distilled in a high vacuum, and a thick oil, b. p. 220—240°/0·1 mm., was collected. This solidified. The 1 : 15-*di*-p-*methoxyphenoxypentadeca*-4 : 11-*diyne* (12·6 g., 40% based on the pentyne not recovered) recrystallised in prisms, m. p. 44·5° (Found: C, 77·9; H, 8·0; OMe, 14·2. $C_{29}H_{36}O_4$ requires C, 77·6; H, 8·0; OMe, 13·8%).

An alternative preparation in which pentamethylene dibromide was used led to the same product (mixed m. p.) but in very inferior yield. Compounds containing a small percentage of bromine were isolated from middle fractions of the distilled product in this case.

1 : 15-*Di*-p-*methoxyphenoxypentadecane.*—1 : 15-Di-*p*-methoxyphenoxypentadeca-4 : 11-diyne (12·6 g.) in ethyl acetate (50 c.c.) was hydrogenated at room temperature and pressure with Adams's platinum oxide (1 g.) (86% uptake in 2 hr.). The solution was filtered hot and

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1 : 15-*di*-p-*methoxyphenoxypentadecane* crystallised. It recrystallised from methanol in needles, m. p. 87—88° (11·3 g., 90%) (Found : C, 75·7; H, 9·5; OMe, 14·1. $C_{29}H_{44}O_4$ requires C, 76·3; H, 9·6; OMe, 13·5%).

Pentadecamethylene Dibromide.—1 : 15-Di-*p*-methoxyphenoxypentadecane (4·6 g., 0·01 mol.) was refluxed in acetic anhydride (20 c.c.), after addition of 50% hydrobromic acid (20 c.c.), for 32 hr. After being worked up in the usual way, the oil was distilled, giving pentadecamethylene dibromide, b. p. 175—190°/14 mm., m. p. 26·5—27° (3·2 g., 87%) (Found : Br, 42·2. Calc. for $C_{15}H_{30}Br_2$: Br, 43·2%), and a small amount of starting material, b. p. 235—240°/14 mm.

Dodeca-1 : 10-*diyne.*—To sodium acetylide, prepared from sodium (23 g., 1 atom) in liquid ammonia (1 l.), octamethylene dibromide (Luttringhaus and Schade, *Ber.*, 1941, **74**, 1565) (133 g., 0·5 mol.) was added in ether (100 c.c.) during 1 hr. with stirring. Ammonia was removed by stirring overnight, more ether (250 c.c.) was added, and the mixture heated under reflux for 3 hr. The filtered ethereal solution was washed with water, dried, and evaporated. The remaining oil was fractionated through a 5-cm. Vigreux column, giving fractions, (i) b. p. 110—114°/19 mm. and (ii) b. p. 114—150°/20 mm. Fraction (ii) appeared to be a mixture of brominated compounds. Fraction (i) was redistilled at 110°/19 mm. This product (45·5 g.) was slightly contaminated with halogenated material, but on being kept for some days at 0—10° crystallised, giving pure *dodeca*-1 : 10-*diyne*, m. p. 27°, very soluble in all organic solvents (Found : C, 87·8; H, 11·0. $C_{12}H_{18}$ requires C, 88·8; H, 11·2%).

In an attempt made to prepare the mercury salt, an amorphous white solid was obtained, which slowly darkened on heating and decomposed without melting between 150° and 250°. This was insoluble in most organic solvents except chloroform and carbon tetrachloride, in which it dissolved freely, and benzene, in which it dissolved with great difficulty and only separated again, during several days, after the addition of light petroleum (b. p. 40—60°). It was still amorphous and was dried in a vacuum-desiccator for a week. Analyses for mercury failed to give consistent values and it appeared that the product was non-homogeneous and possibly polymeric.

1 : 18-*Di*-p-*methoxyphenoxyoctadeca*-4 : 14-*diyne.*—Dodecadiyne (19·0 g.) in ether (50 c.c.) was run slowly into a suspension of sodamide [from sodium (5·4 g.) in liquid ammonia (500 c.c.)] and then stirred for 30 min. 3-*p*-Methoxyphenoxypropyl bromide (60 g.) in ether (100 c.c.) was then added dropwise with stirring, and the mixture stirred overnight whilst the ammonia evaporated. After 1½ hours' refluxing, the product was decomposed with dilute sulphuric acid, and the ethereal extract was separated, washed with aqueous sodium hydrogen carbonate and water and dried. After the removal of the ether, the residue partly solidified; it was triturated with methanol, giving 1 : 18-*di*-p-*methoxyphenoxyoctadeca*-4 : 14-*diyne* (14·3 g., 36%), m. p. 62·5—63·5° (from methanol) (Found : C, 78·6; H, 8·3; OMe, 12·9. $C_{32}H_{42}O_4$ requires C, 78·4; H, 8·6; OMe, 12·6%). The residual oil from the methanolic mother-liquors was distilled to give fractions, b. p. 117—119°/15 mm. (6·0 g.; dodecadiyne), 120—140°/15 mm., and 155—170°/15 mm. (*p*-methoxyphenoxypropyl bromide). The residue (2·2 g.) had m. p. 85—87° after crystallisation from light petroleum (b. p. 60—80°) and analysis and a mixed m. p. determination confirmed that this was 1 : 3-di-*p*-methoxyphenoxypropane.

1 : 18-*Di*-p-*methoxyphenoxyoctadecane.*—1 : 18-Di-*p*-methoxyphenoxyoctadeca-4 : 14-diyne (10 g.) in dry ethyl acetate (150 c.c.) in the presence of Adams's platinum oxide (1 g.) was hydrogenated at room temperature and pressure (100% uptake in 20 min.). The solution was

$NH_2\cdot(NH\colon)C\cdot S\cdot[CH_2]_n\cdot S\cdot C(\colon NH)\cdot NH_2,2C_6H_3O_7N_3$

				Found (%)				Required (%)			
n	Solvent	M. p.	Formula	C	H	N	S	C	H	N	S
4	A	240—242° *	$C_{18}H_{20}O_{14}N_{10}S_2$	33·2	3·2	20·8	—	32·5	3·0	21·1	—
5	B	227—228	$C_{19}H_{22}O_{14}N_{10}S_2$	33·8	3·3	20·0	—	33·7	3·3	20·6	—
6	C	243—245 *	$C_{20}H_{24}O_{14}N_{10}S_2$	34·8	3·9	—	—	34·6	3·5	—	—
7	B	228—229 *	$C_{21}H_{26}O_{14}N_{10}S_2$	35·2	3·8	19·4	—	34·8	3·8	19·4	—
8	B	206	$C_{22}H_{28}O_{14}N_{10}S_2$	36·7	3·9	19·4	—	36·8	4·2	19·2	—
9	D	202—204	$C_{23}H_{30}O_{14}N_{10}S_2$	—	—	19·0	9·0	—	—	19·0	8·7
10	E	211—212 *	$C_{24}H_{32}O_{14}N_{10}S_2$	39·2	4·5	18·4	—	38·5	4·3	18·7	—
12	F	183·5—184	$C_{26}H_{36}O_{14}N_{10}S_2$	40·2	4·8	17·5	8·5	40·2	4·7	18·0	8·3
14	B	175—175·5	$C_{28}H_{40}O_{14}N_{10}S_2$	—	—	17·1	8·0	—	—	17·4	8·0
15	G	143—145	$C_{29}H_{42}O_{14}N_{10}S_2$	—	—	16·9	—	—	—	17·1	—
18	B	151·5—152·5	$C_{32}H_{48}O_{14}N_{10}S_2$	44·8	5·7	16·2	7·4	44·7	5·6	16·3	7·4

* With decomp. A, Propylene glycol. B, Ethanol. C, Methanol. D, *iso*Propanol. E, Aqueous acetone (1 : 1). F, Aqueous methanol (3 : 1). G, Benzene.

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filtered hot, and, on cooling, 1 : 18-*di*-p-*methoxyphenoxyoctadecane* (10·1 g., 99%) crystallised in plates, m. p. 123° (Found : C, 77·4; H, 10·1; OMe, 12·2. $C_{32}H_{50}O_4$ requires C, 77·1; H, 10·0; OMe, 12·4%).

Octadecamethylene Dibromide.—1 : 18-Di-*p*-methoxyphenoxyoctadecane (2·5 g.) was heated for 24 hr. under reflux with acetic anhydride (25 c.c.) after admixture with 50% hydrobromic acid (25 c.c.). After the usual working up, the residue solidified, giving octadecamethylene dibromide (1·82 g., 88%), m. p. 60·5—62·5° (from ethanol) (lit., m. p. 63·5—64°), which was characterised in the usual way.

Dithiuronium Salts.—The *alkylenedithiuronium picrates* (see Table), prepared in the usual way, formed yellow prisms, except that when $n = 6$ or 9 needles were obtained, and when $n = 18$ the crystal form was not identified.

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