Preparation of Medium-ring Cycloalkynes from 1-Bromo-*trans*-cycloalkene Derivatives

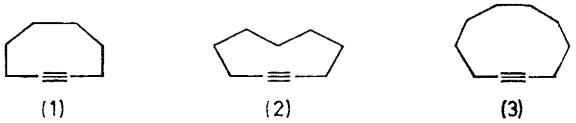
By **Colin B. Reese** *† and **Andrew Shaw**, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

2-Bromo-3-methoxy-*trans*-cycloalkenes react very rapidly with potassium t-butoxide in anhydrous dimethyl sulphoxide solution at room temperature to give the corresponding 3-methoxycycloalkynes, usually in high yields. The preparation of 3-methoxycyclo-octyne (7a), 3-methoxycyclononyne (12a), 7-methoxycyclonon-1-en-5-yne (18), and 3-methoxycyclodecyne (20) is described. 3-Methoxycyclononyne (12a) readily isomerizes in the reaction medium to give the allene (13).

2-Bromo-3-hydroxy-*trans*-cycloalkenes may similarly be converted into the corresponding 3-hydroxycycloalkynes, but protection of their hydroxy-groups by tetrahydropyranylation may be necessary before treatment with base. The preparation of cyclo-oct-2-ynol (7b) and cyclonon-2-ynol (12b) is described. The preparation, in modest yields, of the cyclodeca-1,6-diyne derivatives (23a and b) from the corresponding 2,7-dibromo-*trans,trans*-cyclodeca-1,6-dienes (22a and b) is reported. The preparation of 1-bromo-*trans*-cyclononene (28) and 1-bromo-*trans,cis*-cyclonona-1,5-diene (30c) and the conversion of the latter into cyclonon-1-en-5-yne (31) is described. The preparation of cyclononyne (2) from cyclonon-2-ynol (12b) is also described.

CYCLOALKYNES with a ring-size below nine are strained and hence exceptionally reactive.[1] Therefore comparatively mild reaction conditions are necessary for their preparation. Cyclononyne (2), cyclodecyne (3), and their derivatives readily undergo base-catalysed conversion [2] into the corresponding allenes (see below) and therefore highly basic conditions should be avoided in their preparation.

Methods available for the synthesis of medium-ring cycloalkynes have been revieved thoroughly elsewhere.[1,3]



(1) (2) (3)

The literature suggests that the most widely used method involves the oxidation of bis-hydrazones of the corres-

† *Present address:* Department of Chemistry, King's College, Strand, London WC2R 2LS.

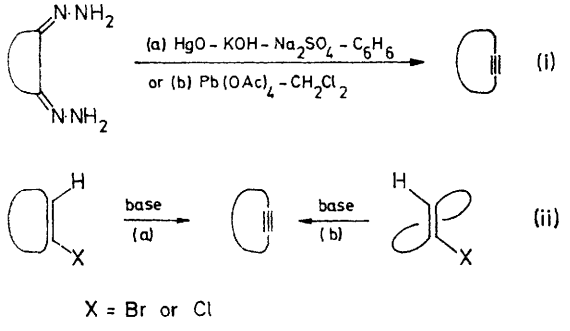
[1] A. Krebs, in ' Chemistry of Acetylenes,' ed. H. G. Viehe, Dekker, New York, 1969.

[2] W. R. Moore and H. R. Ward, *J. Amer. Chem. Soc.*, 1963, **85**, 86.

[3] (*a*) R. W. Hoffmann, ' Dehydrobenzene and Cycloalkynes,' Academic, New York and London, 1967; (*b*) H. Meier, *Synthesis*, 1972, 235.

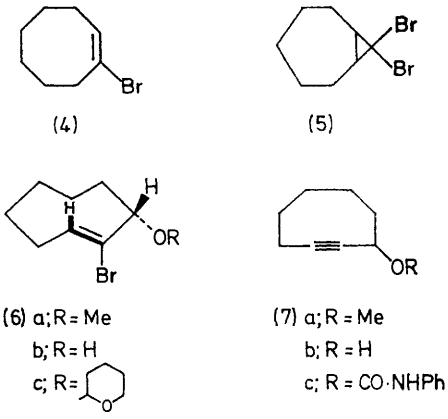
ponding cycloalkane-1,2-diones. Blomquist [4] originally used yellow mercury(II) oxide in the presence of potassium hydroxide [reaction (i), conditions (a)] as the oxidizing agent, but the yields were modest. Krebs more recently obtained [5] cyclo-octyne (1) in 52% yield by using lead tetra-acetate [reaction (i), conditions (b)] and was also able [6] to prepare the highly strained 2,2,6,6-tetramethylcycloheptyne under the same conditions.

Perhaps the most obvious approach to the synthesis of medium-ring cycloalkynes is the dehydrohalogenation of the corresponding 1-halogenocycloalkenes [reaction (ii)]. Indeed, cyclo-octyne (1) has been prepared [7] in 17% yield by the action of sodamide on 1-bromo-*cis*-cyclo-octene (4) at 200—210 °C. Despite the comparatively low yield, this represents a useful source of cyclo-octyne, as the starting material (4) is readily accessible [7] in large quantities. However, it is impracticable to prepare cyclononyne (2) and cyclodecyne (3) from the corresponding 1-halogeno-*cis*-cycloalkenes [reaction (ii)(a)] as the action of base on the latter leads [8] only to low yields of acetylenes and to much larger quantities of the isomeric



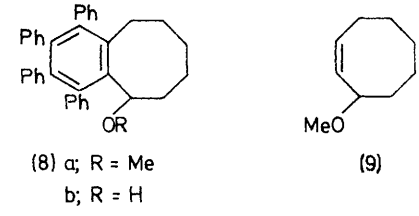
allenes. As alkenyl halides generally undergo base-catalysed *anti*- more readily [9] than *syn*-elimination, it seemed likely that medium-ring 1-bromo-*trans*-cycloalkenes would be more useful starting materials for the preparation of the corresponding cycloalkynes [reaction (ii)(b)] than their *cis*-isomers. We now report that this is indeed the case, and describe the preparation of eight-, nine-, and ten-membered cycloalkynes from the corresponding 1-bromo-*trans*-cycloalkenes, usually in good yields.[10]

Until recently, no 1-halogeno-*trans*-cyclo-octene or -cyclononene derivative had been described. However, we found [11] that when 8,8-dibromobicyclo[5.1.0]octane (5) is treated with an excess of silver perchlorate in concentrated methanolic solution at 20 °C, 2-bromo-3-methoxy-*trans*-cyclo-octene (6a) is rapidly obtained in high yield. In the same way, silver ion-assisted hydrolysis of (5) in aqueous acetone gives [11] the alcohol (6b) in high yield. Corresponding 1-bromo-*trans*-cyclo-



nonene derivatives (see below) may be prepared readily [11] in a similar way. When a solution of (6a) in anhydrous dimethyl sulphoxide is added to a vigorously stirred solution of potassium t-butoxide * in dimethyl sulphoxide at 20 °C and the reaction is quenched *within* 5—10 s by addition of acidified ice–water, 3-methoxycyclo-octyne (7a) is obtained as virtually the sole product. Compound (7a) may be isolated as a pure mobile liquid in 74% yield, following distillation; its characterization rests on physical data, its reaction with tetracyclone in benzene solution to give 5,6,7,8,9,10-hexahydro-5-methoxy-1,2,3,4-tetraphenylbenzocyclo-octene (8a) in high yield, and its reduction to 3-methoxy-*cis*-cyclo-octene [11] (9) by sodium in liquid ammonia.

It was clearly of interest to prepare cyclo-oct-2-ynol (7b), a functionalized derivative of (1). Unfortunately,



treatment of 2-bromo-*trans*-cyclo-oct-2-enol (6b) with potassium t-butoxide in dimethyl sulphoxide leads to a complex mixture. Protection of the hydroxy-function of (6b) therefore seemed necessary. Reaction between (6b) and 3,4-dihydro-2*H*-pyran in the presence of a

* In this and the related experiments described below, it is convenient to use an approximately three-fold excess of potassium t-butoxide in almost saturated solution (see Experimental section).

[4] A. T. Blomquist, R. E. Burge, jun., L. H. Liu, J. C. Bohrer, A. C. Sucsy, and J. Kleis, *J. Amer. Chem. Soc.*, 1951, **73**, 5510; A. T. Blomquist, L. H. Liu, and J. C. Bohrer, *ibid.*, 1952, **74**, 3643; A. T. Blomquist and L. H. Liu, *ibid.*, 1953, **75**, 2153.

[5] A. Krebs, unpublished results.

[6] A. Krebs and H. Kimling, *Angew. Chem. Internat. Edn.*, 1971, **10**, 509.

[7] G. Wittig and H.-L. Dorsch, *Annalen*, 1968, **711**, 46.

[8] W. J. Ball and S. R. Landor, *Proc. Chem. Soc.*, 1961, 143.

[9] S. J. Cristol and R. S. Bly, *J. Amer. Chem. Soc.*, 1961, **83**, 4027; G. Köbrich, *Angew. Chem. Internat. Edn.*, 1965, **4**, 49; D. R. Kelsey and R. G. Bergman, *J. Amer. Chem. Soc.*, 1970, **92**, 228.

[10] Preliminary reports, C. B. Reese and A. Shaw, (*a*) *Chem. Comm.*, 1970, 1172; (*b*) *J.C.S. Chem. Comm.*, 1972, 331; (*c*) *ibid.*, p. 787.

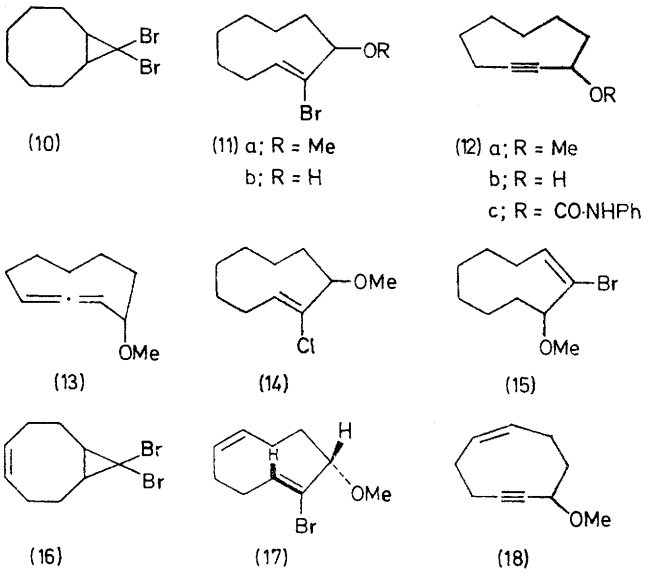
[11] C. B. Reese and A. Shaw, (*a*) *J. Amer. Chem. Soc.*, 1970, **92**, 2566; (*b*) *J.C.S. Perkin I*, 1975, 2422.

catalytic amount of toluene-*p*-sulphonic acid, in dioxan, gives its tetrahydropyranyl derivative (6c). Treatment of the latter with potassium t-butoxide under the usual conditions, and acidic hydrolysis of the products, gives cyclo-oct-2-ynol (7b), which may be isolated as an oil in 45% overall yield. Although (7b) has not been obtained crystalline, it reacts with phenyl isocyanate to give the *N*-phenylcarbamate derivative (7c), which crystallizes readily. Like its methyl ether (7a), cyclo-oct-2-ynol (7b) reacts with tetracyclone to give the expected product (8b).

The particular ease of *anti*- as opposed to *syn*-elimination of the elements of hydrogen bromide from 1-bromocyclo-octene derivatives is emphasized by the observation that 1-bromo-*cis*-cyclo-octene [7] (4) can be recovered in 86% yield after treatment with potassium t-butoxide in dimethyl sulphoxide for 15 min under the above conditions. This greater ease of *anti*-elimination is also observed in nine- and ten-membered ring systems. Thus when 2-bromo-3-methoxy-*trans*-cyclononene (11a), readily prepared [11] by the silver perchlorate-assisted methanolysis of 9,9-dibromobicyclo[6.1.0]nonane (10), is treated with potassium t-butoxide in dimethyl sulphoxide at 20 °C, 3-methoxycyclononyne (12a) is obtained almost quantitatively. Compound (12a) may be isolated by distillation as liquid in 70% yield.

If 3-methoxycyclononyne (12a) of high purity is to be obtained, it is essential that the reaction should be quenched within 5—10 s, as the compound rapidly isomerizes to 4-methoxycyclonona-1,2-diene (13) in the basic reaction medium. Indeed, if the reaction is allowed to proceed for 10 min at 20 °C before quenching, the allene (13) is obtained as virtually the sole product and may be isolated as a liquid in 69% yield. T.l.c., g.l.c., and n.m.r. spectroscopy show that the 4-methoxycyclonona-1,2-diene (13) obtained is an approximately 10 : 1 mixture of two isomers. As compound (13) has both a chiral allenic group and an asymmetric carbon atom, it may be assumed that the latter are diastereoisomers. When the major isomer, after purification, is treated with potassium t-butoxide in dimethyl sulphoxide solution, an approximately 10 : 1 mixture of the two isomers is again obtained. 3-Methoxycyclo-octyne (7a) is much more stable to base than its higher homologue (12a), and can be obtained in good yield from (6a) even if the reaction is allowed to proceed for 10 min before quenching. Cyclonon-2-ynol (12b) of fairly high purity can be prepared in good yield directly from 2-bromo-*trans*-cyclonon-2-enol (11b) without the hydroxy-group first being protected. The material obtained in this way is contaminated with a few trace impurities but can be purified by distillation, albeit with low recovery. Cyclonon-2-ynol (12b) was characterized spectroscopically and as the crystalline *N*-phenylcarbamate (12c).

The particular suitability of 1-bromo-*trans*-cycloalkenes as intermediates in the synthesis of medium-ring cycloalkyne derivatives is further emphasized by the observations that 2-chloro-3-methoxy-*trans*-cyclononene [11] (14) is incompletely converted into 3-methoxycyclononyne (12b) when treated with potassium t-butoxide in dimethyl sulphoxide for 5—10 s at 20 °C and



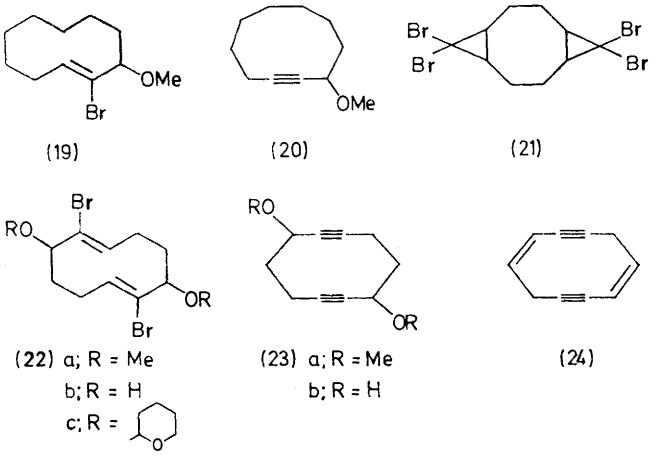
that 2-bromo-3-methoxy-*cis*-cyclononene [12] (15) may be recovered in over 80% yield after 10 min under the same conditions. The first observation suggests that the elimination of the elements of hydrogen chloride from certain 1-chloro-*trans*-cycloalkenes may occur too slowly to prevent acetylene-to-allene isomerization occurring to a significant extent, and the second observation confirms the difficulty of effecting *syn*-elimination. The value of 1-bromo-*trans*-cycloalkene intermediates is further illustrated by the preparation of 7-methoxycyclonon-1-en-5-yne (18) as a liquid in 67% yield from 2-bromo-3-methoxy-*trans*,*cis*-cyclonona-1,6-diene (17). Compound (17) is readily obtained [11b,13] in high yield by the silver perchlorate-promoted methanolysis of 9,9-dibromobicyclo[6.1.0]non-4-ene (16).

Treatment of 2-bromo-3-methoxy-*trans*-cyclodecene [11b,14] (19) with potassium t-butoxide under the usual conditions gives 3-methoxycyclodecyne (20). However, as it is difficult to prepare compound (19) free from its *cis*-isomer, it is more convenient to treat the readily available [11b] 1 : 2 mixture of 2-bromo-3-methoxy-*cis*- and -*trans*-cyclodecenes with base and then to separate the 3-methoxycyclodecyne (20) obtained from unchanged 2-bromo-3-methoxy-*cis*-cyclodecene by preparative g.l.c. It appeared to us that a more challenging objective as far as the preparation of ten-membered cycloalkynes is concerned would be the conversion of the dibromo-*trans*,*trans*-cyclodecadiene derivatives [10b,11b] (22a and b) into the corresponding cyclodeca-1,6-diynes (23a and b). Prior to the present work, no ten-membered carbocyclic system containing two acetylenic groups had been described, and further-

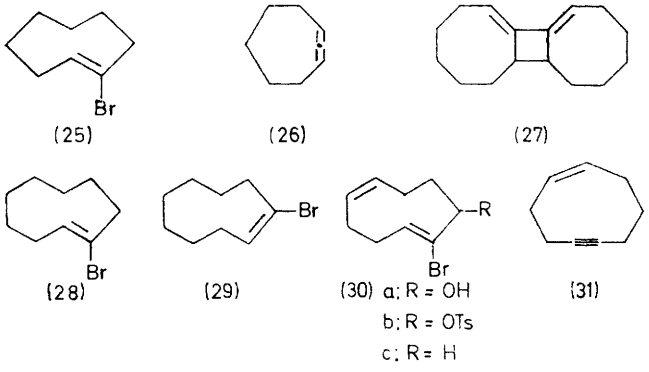
[12] M. S. Baird and C. B. Reese, *J. Chem. Soc.* (*C*), 1969, 1803.
[13] C. B. Reese and A. Shaw, *Chem. Comm.*, 1970, 1365.
[14] C. B. Reese and A. Shaw, *Chem. Comm.*, 1970, 1367.

more cyclodeca-2,7-diyne-1,6-diol (23b) is a potential precursor of *cis,cis*-cyclodeca-1,6-diene-3,8-diyne (24), which in turn is an isomer and potential precursor of didehydro[10]annulene [15] and of cyclodeca-1,2,4,6,7,9-hexaene.[16]

2,7-Dibromo-*cis*-3,8-dimethoxy-*trans,trans*-cyclodeca-1,6-diene (22a) and the corresponding diol (22b) may be prepared [10b,11b] from the tetrabromide (21) in moderate yields by silver perchlorate-promoted methanolysis and hydrolysis, respectively. When compound (22a) is treated with potassium t-butoxide in dimethyl sulphoxide solution under the usual conditions, 3,8-dimethoxycyclodeca-1,6-diyne (23a) is obtained and may be isolated crystalline in 29% yield. It is reasonable to assume that, like (22a), the diyne (23a) is a *cis*-dimethoxy-compound. Treatment of compound (22b) with base leads to a complex mixture of products; however, if its bistetrahydropyranyl derivative (22c) is treated with potassium t-butoxide in dimethyl sulphoxide and the products are submitted to acidic hydrolysis, cyclodeca-2,7-diyne-1,6-diol (23b) can be isolated crystalline in almost 20% yield. The possibility of the conversion of (23b) into (24) has not yet been investigated fully.



The generality of the present approach to cycloalkyne synthesis clearly depends on the availability of the appropriate 1-bromo-*trans*-cycloalkene precursors. Thus it is reasonable to assume that cyclo-octyne (1) itself could be prepared in good yield by the action of potassium t-butoxide on 1-bromo-*trans*-cyclo-octene (25) in dimethyl sulphoxide. In an attempt to prepare compound (25), 2-bromo-*trans*-cyclo-oct-2-enol [11] (6b) was treated with toluene-*p*-sulphonyl chloride in pyridine and the tosylate ester (6; R = Ts) obtained was treated, in ether, with an excess of lithium aluminium hydride. Unfortunately, the product was virtually pure 1-bromo-*cis*-cyclo-octene (4). Rather than examine other possible methods for the conversion of (6b) into (25), it was decided to attempt to prepare cyclo-octyne (1) from cyclo-oct-2-ynol (7b). Treatment of (7b) with methanesulphonyl chloride and triethylamine in dichloromethane solution gives the mesylate ester (7; R = SO_2Me). When the latter is treated, in ether, with lithium aluminium hydride, the allene dimer (27) is obtained in



good yield but no cyclo-octyne (1) can be detected. Thus lithium aluminium hydride appears to attack the mesylate (7; R = SO_2Me) at C-3 rather than at C-1, presumably to give the unstable cyclo-octa-1,2-diene [17] (26) which then dimerizes to give (27). There are several reports [18] of allenes being obtained by reduction of propargylic halides with lithium aluminium hydride.

The corresponding set of experiments in the nine-membered ring series are more encouraging. When 2-bromo-*trans*-cyclonon-2-enol [10] (11b) is treated with toluene-*p*-sulphonyl chloride in pyridine solution and the resulting tosylate ester (11; R = Ts) is treated with lithium aluminium hydride, an approximately 2 : 3 mixture of 1-bromo-*trans*- and -*cis*-cyclononenes [(28) and (29), respectively] is obtained. Pure 1-bromo-*trans*-cyclononene (28) can be isolated by preparative g.l.c. The corresponding brosylate ester (11; R = *p*-$BrC_6H_4{\cdot}SO_2$) is a more satisfactory intermediate in that its reduction with lithium aluminium hydride leads to an approximately 1 : 1 mixture of *trans*- and *cis*-isomers [(28) and (29), respectively]. However, even if it is prepared by the latter route, the overall yield of 1-bromo-*trans*-cyclononene (28), based on 2-bromo-*trans*-cyclonon-2-enol (11b), is too low for this to constitute a really useful approach to the synthesis of cyclononyne (2). Indeed, in the preparation of compound (2) from (11b), it is more satisfactory if the hydroxy-group is removed after rather than before the elimination reaction. Thus mesylation of cyclonon-2-ynol (12b), obtained from (11b) and not further purified, and reduction of the resulting crude mesylate (12; R = $MeSO_2$) with lithium aluminium hydride gives cyclononyne (2), which may be isolated as a liquid in *ca.* 35% overall yield, based on

[15] K. Grohmann and F. Sondheimer, *Tetrahedron Letters*, 1967, 3121.
[16] R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Verlag Chemie, Weinheim, 1970, pp. 63—64.
[17] E. T. Marquis and P. D. Gardner, *Tetrahedron Letters*, 1966, 2793.
[18] W. J. Bailey and C. R. Pfeifer, *J. Org. Chem.*, 1955, **20**, 95, 1337; T. L. Jacobs, E. G. Teach, and D. Weiss, *J. Amer. Chem. Soc.*, 1955, **77**, 6254.

(11b). This appears to be the method of choice for the preparation of cyclononyne.

Finally, deoxygenation by the tosylation–lithium aluminium hydride reduction method proceeds very smoothly in the case of 2-bromo-*trans,cis*-cyclonona-2,6-dienol [11b,13] (30a). Compound (30a) gives a crystalline tosylate (30b), which may be reduced by lithium aluminium hydride to 1-bromo-*trans,cis*-cyclonona-1,5-diene (30c), free from its *cis,cis*-isomer, in 75% yield based on the alcohol (30a). Treatment of (30c) * with potassium t-butoxide in dimethyl sulphoxide gives cyclonon-1-en-5-yne (31) in 67% yield.

In conclusion, we believe that the treatment of 1-bromo-*trans*-cycloalkenes with potassium t-butoxide in dimethyl sulphoxide for a few seconds at 20 °C is the best general method so far described for the synthesis of medium-ring cycloalkynes, and that its success is likely to depend only on the availability of the appropriate substrates.

EXPERIMENTAL

N.m.r. spectra were measured at 100 MHz with Varian HA-100 and XL-100 spectrometers; unless otherwise stated, Me_4Si was used as internal standard. U.v. spectra were measured with a Cary 14M-50 recording spectrophotometer. I.r. spectra of liquids and solids were taken for films and Nujol mulls, respectively, with a Perkin-Elmer 257 (grating) and a Unicam SP 200 spectrometer. Mass spectra were obtained with A.E.I. MS 9 and 12 spectrometers, by using a heated inlet system. Both analytical and preparative g.l.c. were carried out with an F & M 720 chromatograph (hydrogen as carrier gas); polyphenyl ether, SE 30, Carbowax 20 M, diethylene glycol adipate, and Apiezon C were used as stationary phases. T.l.c. was carried out on 20 × 5 cm glass plates coated with Merck Kieselgel GF_{254}.

Dimethyl sulphoxide was stirred with CaH_2 at room temperature and then distilled under reduced pressure; t-butyl alcohol was dried by heating it under reflux with a small quantity of potassium metal, and then distilled. Potassium t-butoxide was prepared by heating dry t-butyl alcohol with potassium metal (*ca.* 40 g l^{-1} of alcohol) under reflux; the excess of alcohol was then removed by evaporation and the residue heated for 4 h at 100° and 0.1 mmHg.

3-Methoxycyclo-octyne (7a).—A solution of 2-bromo-3-methoxy-*trans*-cyclo-octene [11] (3.67 g, 16.5 mmol) in anhydrous dimethyl sulphoxide (15 ml) was added *rapidly* to a vigorously stirred solution of potassium t-butoxide (5.5 g, 49 mmol) in anhydrous dimethyl sulphoxide (35 ml) at 20 °C. Immediately after the addition was complete (*i.e.* after *ca.* 5—10 s), ice–water (*ca.* 75 g) containing acetic acid (2.0 g, 33 mmol) was added.† The reaction medium remained colourless throughout. The products were then extracted with ether (3 × 35 ml), and the extracts washed with water (2 × 20 ml), dried ($MgSO_4$), and evaporated. Distillation of the resulting slightly yellow, mobile liquid gave *3-methoxycyclo-octyne*, b.p. 48—50° at 6 mmHg, as a colourless liquid [single component by g.l.c. (Carbowax 20 M; 110 °C)] with a penetrating odour (1.7 g, 74%); τ (CCl_4) 6.08 (1 H, m), 6.82 (3 H, s), and 7.7—8.8 (10 H, m); $\nu_{max.}$ (film) 2 260w, 2 200m, and 1 100s cm^{-1}; *m/e* 138 (M^+, 12%) and 95 (100%).

Reaction between 3-Methoxycyclo-octyne and Tetracyclone.—A solution of 3-methoxycyclo-octyne (0.15 g, 1.09 mmol) and tetracyclone (0.38 g, 0.99 mmol) in benzene (10 ml) was kept at room temperature, in darkness, for 24 h. The colourless solution was evaporated and the residue crystallized from petroleum (b.p. 60—80°) to give *5,6,7,8,9,10-hexahydro-5-methoxy-1,2,3,4-tetraphenylbenzocyclo-octene* (Found: C, 89.6; H, 7.0. $C_{37}H_{34}O$ requires C, 89.8; H, 6.9%) as a colourless solid, m.p. 228.5—229.5° (0.44 g, 81%); τ ($CDCl_3$) 2.6—3.5 (20 H, m), 5.42 (1 H, m), 6.3 (1 H, m), 6.80 (3 H, s), 7.35 (1 H, m), and 7.8—9.0 (8 H, m); $\nu_{max.}$ (Nujol) 1 600m and 1 100s cm^{-1}; *m/e* 138 (M^+, 12%) and 95 (100%).

Reduction of 3-Methoxycyclo-octyne with Sodium in Liquid Ammonia.—A solution of 3-methoxycyclo-octyne (0.8 g, 5.8 mmol) in petroleum (b.p. 30—40°) was added dropwise over 10 min to a stirred solution of sodium (0.5 g, 22 mmol) in liquid ammonia (25 ml). After the reactants had remained for a further 15 min at reflux temperature, an excess of ammonium chloride was added. The ammonia was then allowed to evaporate and the residue partitioned between petroleum (b.p. 30—40°) and water. Careful evaporation of the dried ($MgSO_4$) organic layer at atmospheric pressure gave a colourless liquid (0.8 g) which was found by g.l.c. (Carbowax M; 100 °C) and n.m.r. spectroscopy to consist of 3-methoxy-*cis*-cyclo-octene [11] (*ca.* 95%), contaminated possibly with its *trans*-isomer.

Reaction between 1-Bromo-cis-cyclo-octene and Potassium t-Butoxide in Dimethyl Sulphoxide.—1-Bromo-*cis*-cyclo-octene [7] (1.0 g, 5.3 mmol) was added to a stirred solution of potassium t-butoxide (1.8 g, 16 mmol) in dimethyl sulphoxide (12 ml) at 20 °C. After 10 min, the products were worked up as in the preparation of 3-methoxycyclo-octyne to give 1-bromo-*cis*-cyclo-octene (0.86 g, 86%), contaminated only with traces [as detected by i.r. spectroscopy and g.l.c. (SE 20; 100°)] of more volatile products.

Reaction between 2-Bromo-trans-cyclo-oct-2-enol and Potassium t-Butoxide in Dimethyl Sulphoxide.—2-Bromo-*trans*-cyclo-oct-2-enol [11] (0.5 g, 2.4 mmol) was treated with potassium t-butoxide (1.0 g, 8.9 mmol) in dimethyl sulphoxide (10 ml) as in the preparation of 3-methoxycyclo-octyne. A complex mixture was obtained and the reaction was not investigated further.

Cyclo-oct-2-ynol (7b).—3,4-Dihydro-2*H*-pyran (3.0 g, 36 mmol) was added to a stirred solution of 2-bromo-*trans*-cyclo-oct-2-enol [11] (3.76 g, 18.3 mmol) and a catalytic amount of toluene-*p*-sulphonic acid monohydrate in anhydrous dioxan (30 ml) at 20 °C. After 2 h the products were neutralized with methanolic sodium methoxide and concentrated under reduced pressure, and the residue was chromatographed on SilicAR CC7 to give the tetrahydropyranyl ether of 2-bromo-*trans*-cyclo-oct-2-enol (4.4 g, 15 mmol).

A solution of the tetrahydropyranyl ether (5.3 g, 18 mmol) in dimethyl sulphoxide (10 ml) was added rapidly to a solution of potassium t-butoxide (5.6 g, 50 mmol) in di-

* Reduction of compound (30c) with sodium in liquid ammonia gives an approximately 3 : 2 mixture of *cis,cis*-cyclonona-1,5-diene and putative *cis, trans*-isomer. Similar reductions of other 1-bromo-*trans*-cycloalkene derivatives have also shown little or no stereo-selectivity.[11b]

† In another experiment, the reaction was allowed to proceed for 10 min before addition of acidified ice–water. Again 3-methoxycyclo-octyne was obtained in good yield as the predominant product.

methyl sulphoxide (30 ml) at 20 °C. The reaction was quenched immediately and the products worked up as in the preparation of 3-methoxycyclo-octyne to give a colourless oil (4.0 g). A solution of this in dioxan (20 ml) was vigorously stirred with M-hydrochloric acid (50 ml) for 30 min at 20 °C; the products were basified with saturated aqueous sodium carbonate and the mixture was concentrated under reduced pressure (bath temperature not greater than 30°) to half-volume. The concentrate was extracted with ether (3 × 50 ml) and the dried ($MgSO_4$) combined extracts were evaporated to an oil (3.75 g), which was then dissolved in petroleum (b.p. 60—80°) and the solution applied to a column of SilicAR CC7 (50 g). Elution with petroleum (b.p. 60—80°)–benzene (85 : 15 v/v) gave *cyclo-oct-2-ynol* as a colourless oil (1.1 g, 45% based on 2-bromo-*trans*-cyclo-oct-2-enol); τ (CCl_4) 5.69 (1 H, m), 6.74 (1 H, s), and 7.7—8.9 (10 H, m); $\nu_{max.}$ (film) 3 350br,s, 2 260w, 2 220m, and 1 050s cm^{-1}.

Phenyl isocyanate (0.20 g) was added to a solution of cyclo-oct-2-ynol (0.10 g) in dry dioxan (5 ml), containing a trace of pyridine, at 20 °C. After 2 h the products were concentrated under reduced pressure and the residue was purified by chromatography on SilicAR CC7. Recrystallization from petroleum (b.p. 60—80°) gave the *N-phenylcarbamate* (Found: C, 73.8; H, 6.9; N, 5.7. $C_{15}H_{17}NO_2$ requires C, 74.1; H, 7.0; N, 5.8%) as a colourless solid (0.05 g), m.p. 98—99°; τ (CCl_4) 2.5—3.5 (6 H, m), 4.68 (1 H, m), and 7.6—8.6 (10 H, m); $\nu_{max.}$ (Nujol) 3 340m, 2 200w, and 1 700s cm^{-1}; *m/e* 243 (M^+ 10%), and 91 (100%).

Reaction between Cyclo-oct-2-ynol and Tetracyclone.—A solution of cyclo-oct-2-ynol (0.15 g, 1.24 mmol) and tetracyclone (0.40 g, 1.05 mmol) in benzene (10 ml) was kept at room temperature, in darkness, for 24 h. The products were evaporated and the residue crystallized from cyclohexane to give 5,6,7,8,9,10-*hexahydro*-1,2,3,4-*tetraphenylbenzocyclo-octen-5-ol* (Found: C, 90.1; H, 6.9. $C_{36}H_{32}O$ requires C, 90.0; H, 6.6%) as a colourless solid, m.p. 225° (0.48 g, 81%); τ ($CDCl_3$) 2.7—3.5 (20 H, m), 4.82 (1 H, m), 6.4—6.8 (1 H, m), 7.2—7.5 (1 H, m), and 8.0—9.0 (8 H, m); $\nu_{max.}$ (Nujol) 3 250br,m and 1 600m cm^{-1}; *m/e* 480 (M^+, 10%) and 461 (100%).

3-*Methoxycyclononyne* (12a).—A solution of 2-bromo-3-methoxy-*trans*-cyclononene [11] (2.87 g, 12.3 mmol) in anhydrous dimethyl sulphoxide (10 ml) was added to a vigorously stirred solution of potassium t-butoxide (3.7 g, 33 mmol) in dimethyl sulphoxide (20 ml) at 20 °C. The reaction was immediately quenched by addition of ice–water (100 g) containing acetic acid (1.2 g, 20 mmol) and worked-up as in the preparation of 3-methoxycyclo-octyne. Distillation gave 3-*methoxycyclononyne* (Found: C, 78.8; H, 10.5. $C_{10}H_{16}O$ requires C, 79.0; H, 10.5%) as a colourless liquid, b.p. 40—42° at 0.3 mmHg [mainly one component by g.l.c. (polyphenyl ether; 135°) contaminated with a shorter t_R trace component]; yield 1.31 g (70%); τ ($CDCl_3$) 6.15 (1 H, m), 6.80 (3 H, s), 7.85 (2 H, m), and 8.0—8.8 (10 H, m); $\nu_{max.}$ (film) 2 240m, 2 200m, and 1 100s cm^{-1}; *m/e* 152 (M^+, 7%) and 95.

*Reaction between 2-Chloro-3-methoxy-*trans*-cyclononene and Potassium t-Butoxide in Dimethyl Sulphoxide.*—2-Chloro-3-methoxy-*trans*-cyclononene [11] (0.3 g, 1.6 mmol), contaminated with a small amount of *cis*-isomer, was treated with potassium t-butoxide (0.45 g, 4.0 mmol) in dimethyl sulphoxide (4 ml) at 20 °C and the product was immediately worked-up as in the preparation of 3-methoxycyclo-octyne. The oily product (0.195 g) was found by g.l.c. (Carbowax 20 M; 110°) to contain starting material and 3-methoxycyclononyne in the approximate proportions 1 : 3.

*Reaction between 2-Bromo-3-methoxy-*cis*-cyclononene and Potassium t-Butoxide in Dimethyl Sulphoxide.*—2-Bromo-3-methoxy-*cis*-cyclononene [12] (0.32 g, 1.35 mmol) was treated with potassium t-butoxide (0.40 g, 3.6 mmol) in dimethyl sulphoxide (4 ml) at 20 °C and the product was worked-up as in the preparation of 3-methoxycyclo-octyne, but after 10 min. The oily product (0.28 g) was found by g.l.c. to contain starting material (at least 80%) as its major constituent.

4-*Methoxycyclonona*-1,2-*diene* (13).—A solution of 2-bromo-3-methoxy-*trans*-cyclononene [11] (2.5 g, 10.7 mmol) in anhydrous dimethyl sulphoxide (10 ml) was added to a solution of potassium t-butoxide (4.0 g, 35.8 mmol) in dimethyl sulphoxide (25 mmol) and the reactants were stirred at 20 °C. After 10 min, the reaction was quenched and worked up as in the preparation of 3-methoxycyclo-octyne. Distillation gave 4-*methoxycyclonona*-1,2-*diene* (Found: C, 78.8; H, 10.2. $C_{10}H_{16}O$ requires C, 79.0; H, 10.5%) as a mobile liquid, b.p. 55—58° at 0.8—0.9 mmHg (1.1 g, 69%); $\nu_{max.}$ (film) 1 920m and 1 110s cm^{-1}; *m/e* 152 (M^+, 2%) and 28 (100%).

T.l.c. (benzene) and g.l.c. (polyphenyl ether) of the 4-methoxycyclonona-1,2-diene obtained revealed that it contained two components in the approximate proportion 10 : 1. The minor component had the lower R_F value and higher t_R. A solution of the mixture in petroleum (b.p. 60—80°) was applied to a column of SilicAR CC7 (25 g) which was then eluted with the same solvent. Concentration of the appropriate earlier fractions gave the pure *less polar diastereoisomer* of 4-methoxycyclonona-1,2-diene (0.72 g); τ (CCl_4) 4.88 (2 H, m), 6.24 (1 H, m), 6.75 (3 H, s), and 7.5—9.0 (10 H, m); $\nu_{max.}$ (film) 1 920m and 1 110s cm^{-1}. Concentration of the appropriate later fractions gave material (0.10 g) found by g.l.c. to consist mainly (*ca.* 80%) of the more polar diastereoisomer; τ (CCl_4) 4.66 (2 H, m), 6.2—6.6 (1 H, m), 6.82 (3 H, s), and 7.5—8.9 (10 H, m).

A solution of the pure less polar diastereoisomer (0.10 g) and potassium t-butoxide (0.068 g) in anhydrous dimethyl sulphoxide was stirred at 20 °C for 10 min. The products were then worked up in the usual manner and found (g.l.c. and t.l.c.) to consist of starting material contaminated with *ca.* 10% of the more polar diastereoisomer. A solution of the above material enriched in the more polar diastereoisomer (0.10 g) was treated with potassium t-butoxide in dimethyl sulphoxide in the same way. After work-up, the products were found to consist mainly of the less polar diastereoisomer but in rather less than its equilibrium proportion.

Cyclonon-2-ynol (12b).—A solution of 2-bromo-*trans*-cyclonon-2-ynol [11] (2.19 g, 10 mmol) in anhydrous dimethyl sulphoxide (10 ml) was added to a vigorously stirred solution of potassium t-butoxide (4.5 g, 40 mmol) in dimethyl sulphoxide (30 ml) at 20 °C. The reaction was immediately quenched by addition of ice–water (60 g) containing acetic acid (1.5 g, 25 mmol) and worked-up as in the preparation of 3-methoxycyclo-octyne. T.l.c. of the viscous oil obtained (1.3 g) [benzene–ethyl acetate (19 : 1 v/v)] revealed a major component [R_F 0.3] and several higher R_F trace components; this material could be purified by distillation (b.p. 70° at 0.7 mmHg) but with a low recovery (23%); τ (CCl_4) 5.67 (1 H, m), 6.39 (1 H, s), 7.6—8.0 (2 H, m), and 8.0—9.0 (10 H, m); $\nu_{max.}$ (film) 3 440br,s, 2 240m, 2 200m, and 1 010s cm^{-1}.

Phenyl isocyanate (0.60 g) was added to a solution of distilled cyclonon-2-ynol (0.30 g) and pyridine (2 drops) in dry dioxan (3 ml) at 20 °C. After 16 h the products were filtered and the filtrate concentrated under reduced pressure. The oil so obtained was chromatographed on SilicAR CC7 (10 g). Recrystallization from petroleum (b.p. 60—80°) gave the N-*phenylcarbamate* (Found: C, 74.9; H, 7.6; N, 5.3. $C_{16}H_{19}NO_2$ requires C, 74.8; H, 7.4; N, 5.45%) as a colourless solid, m.p. 80—81°; τ (CCl_4) 2.5—3.2 (6 H, m), 4.68 (1 H, m), and 7.7—8.0 (12 H, m); $\nu_{max.}$ (Nujol) 3 340s, 2 220w, and 1 705s cm^{-1}; *m/e* 257 (M^+, 10%) and 93 (100%).

7-*Methoxy*-cis-*cyclonon*-1-*en*-5-*yne* (18).—(*a*) A solution of 2-bromo-3-methoxy-*trans,cis*-cyclonona-1,6-diene [11b,13] (2.3 g, 10 mmol) (obtained from the reaction between 9,9-dibromobicyclo[6.1.0]non-4-ene and silver perchlorate in methanol) in anhydrous dimethyl sulphoxide (10 ml) was added to a vigorously stirred solution of potassium t-butoxide (4.0 g, 35 mmol) in dimethyl sulphoxide (25 ml) at 20 °C. The reaction was immediately quenched by addition of ice–water (100 g) containing acetic acid (1.5 g, 25 mmol) and worked-up as in the preparation of 3-methoxycyclo-octyne. Distillation of the mobile yellow oil obtained gave 7-*methoxy*-cis-*cyclonon*-1-*en*-5-*yne* (Found: C, 79.8; H, 9.1. $C_{10}H_{14}O$ requires C, 80.0; H, 9.3%) as a colourless liquid, b.p. 44—46° at 0.5 mmHg (1.0 g, 67%); τ (CCl_4) 4.3—4.9 (2 H, m), 6.12 (1 H, m), 6.82 (3 H, s), and 7.5—8.3 (8 H, m); $\nu_{max.}$ (film) 2 275m, 2 220m, 1 650m, and 1 100s cm^{-1}; *m/e* 150 (M^+, 7%) and 91 (100%).

(*b*) 3-Methoxy-*cis*-cyclonon-1-en-5-yne was also prepared in good yield from the other diastereoisomer of 2-bromo-3-methoxy-*trans,cis*-cyclonona-1,6-diene [11b,13] (0.39 g, 1.7 mmol) and potassium t-butoxide (0.6 g, 5.4 mmol) in dimethyl sulphoxide (10 ml); the crude material (0.28 g) was shown by g.l.c. and i.r. spectroscopy to be virtually pure.

Reaction between the Mixture of 2-*Bromo*-3-*methoxy*-cis-*and* -trans-*cyclodecenes and Potassium t-Butoxide in Dimethyl Sulphoxide.*—A solution of an approximately 1 : 2 mixture of 2-bromo-3-methoxy-*cis*- and -*trans*-cyclodecenes [11b] (1.36 g, 5.5 mmol) in anhydrous dimethyl sulphoxide (5 ml) was added to a vigorously stirred solution of potassium t-butoxide (1.2 g, 10.7 mmol) in dimethyl sulphoxide (10 ml). The reaction was immediately quenched by addition of ice–water (50 g) containing acetic acid (0.4 g, 6.7 mmol) and worked-up as in the preparation of 3-methoxycyclo-octyne to give an oil (0.91 g), which was separated by preparative g.l.c. (diethylene glycol adipate) into two components. The major, shorter t_R component was characterized as 3-*methoxycyclodecyne* (Found: C, 77.8; H, 11.5. $C_{11}H_{18}O$ requires C, 78.0; H, 11.6%); τ (CCl_4) 6.22 (1 H, m), 6.80 (3 H, s), 7.85 (2 H, m), and 8.1—8.9 (12 H, m); $\nu_{max.}$ (film) 2 275w, 2 230m, and 1 100s cm^{-1}; *m/e* 166 (M^+, 2%) and 78 (100%).

The minor, longer t_R component was identified as unchanged 2-*bromo*-3-*methoxy*-cis-*cyclodecene* (Found: C, 53.6; H, 7.7; Br, 32.35. $C_{11}H_{19}BrO$ requires C, 53.5; H, 7.7; Br, 32.4%); τ (CCl_4) 3.92 (1 H, dd, *J* 6 and 12 Hz), 5.76 (1 H, m), 6.88 (3 H, m), and 7.3—8.9 (14 H, m); $\nu_{max.}$ (film) 1 630m and 1 100s cm^{-1}; *m/e* 246/248 (M^+, 32%) and 71 (100%).

3,8-*Dimethoxycyclodeca*-1,6-*diyne* (23a).—A solution of 2,7-dibromo-*cis*-3,8-dimethoxy-*trans,trans*-cyclodeca-1,6-diene [10b,11b] (1.0 g, 2.8 mmol) in anhydrous dimethyl sulphoxide (10 ml) was added to a vigorously stirred solution of potassium t-butoxide (1.35 g, 12 mmol) in dimethyl sulphoxide (10 ml) at 20 °C. The reaction was immediately quenched by addition of ice–water (50 g) containing acetic acid (0.4 g, 6.7 mmol) and worked up as in the preparation of 3-methoxycyclo-octyne to give a yellow oil. A solution of the latter in petroleum (b.p. 30—40°; 30 ml) was extracted with aqueous 20% silver nitrate (3 × 30 ml). The combined extracts were added slowly to a mixture of aqueous ammonia (*d* 0.88; 30 ml) and ice (20 g). The resulting mixture was extracted with ether (3 × 25 ml) and the combined extracts were dried ($MgSO_4$) and evaporated to give a yellow oil (0.28 g), which crystallized. This material was recrystallized twice from petroleum (b.p. 30—40°) to give 3,8-*dimethoxycyclodeca*-1,6-*diyne* (Found: C, 74.7; H, 8.2. $C_{12}H_{16}O_2$ requires C, 75.0; H, 8.3%) as a pale yellow solid, m.p. 63.5—65° (0.158 g, 29%); τ (CCl_4) * 6.15 (2 H, m), 6.74 (6 H, m), and 7.3—8.4 (8 H, m); $\nu_{max.}$ (Nujol) 2 260w, 2 210m, and 1 100s cm^{-1}; *m/e* 192 (M^+, 1%) and 39 (100%).

Cyclodeca-2,7-*diyne*-1,6-*diol* (23b).—A solution of 2,7-dibromo-*cis*-3,8-dihydroxy-*trans,trans*-cyclodeca-1,6-diene [10b,11b] (1.0 g, 3.08 mmol), 3,4-dihydro-2*H*-pyran (3.0 g, 36 mmol), and a catalytic amount of toluene-*p*-sulphonic acid monohydrate in anhydrous dioxan (40 ml) was stirred at 20 °C. After 90 min, an excess of solid sodium methoxide was added and the dioxan was evaporated off under reduced pressure. Chromatography of the residual oil on SilicAR CC7 gave the bistetrahydropyranyl ether as an oil (1.4 g) A solution of this in anhydrous dimethyl sulphoxide (10 ml) was added to a vigorously stirred solution of potassium t-butoxide (5.0 g, 45 mmol) in dimethyl sulphoxide (30 ml) at 20 °C. The reaction was immediately quenched by addition of ice–water (100 g) containing acetic acid (2.4 g, 40 mmol) and worked-up as in the preparation of 3-methoxy-cyclo-octyne. The product was purified by silver nitrate extraction as in the preparation of 3,8-dimethoxycyclodeca-1,6-diyne. The material obtained was dissolved in dioxan (20 ml) and M-hydrochloric acid (20 ml) was added at 20 °C. The reactants were vigorously stirred for 1 h and then carefully basified with aqueous sodium carbonate. The products were concentrated under reduced pressure to *ca.* half volume and then extracted with ethyl acetate (4 × 15 ml). The extracts were combined, dried ($MgSO_4$), and concentrated. Crystallization of the residue from ethyl acetate gave *cyclodeca*-2,7-*diyne*-1,6-*diol* (Found: C, 72.5; H, 7.3. $C_{10}H_{12}O_2$ requires C, 73.2; H, 7.3%) as a colourless powder, m.p. 154—155° (after softening at 150°) (0.098 g, 19.5%); τ (CD_3OD) 5.64 (2 H, m) and 7.2—8.4 (8 H, m); $\nu_{max.}$ (Nujol) 3 250br,s, 2 280w, 2 220m, and 1 000s cm^{-1}; *m/e* 164 (M^+, 22%) and 91 (100%).

Action of Lithium Aluminium Hydride on 2-*Bromo*-trans-*cyclo-oct*-2-*enyl Tosylate.*—A solution of 2-bromo-*trans*-cyclo-oct-2-enol [11] (2.03 g, 10.0 mmol) and toluene-*p*-sulphonyl chloride (3.0 g, 15.8 mmol) in anhydrous pyridine (50 ml) was kept at 0 °C for 18 h. The products were then poured onto ice–water (100 g) and the resulting mixture was stirred. After 30 min, the products were extracted with ether (3 × 50 ml); the combined ether layers were washed with dilute hydrochloric acid (50 ml), dried ($MgSO_4$), and evaporated. The purple oil obtained was dissolved in warm petroleum (b.p. 60—80°) and the solution was cooled. The solid (1.0 g) obtained, dissolved in anhydrous ether (20 ml), was added to a stirred, cooled (ice–water bath) slurry of

* Irradiation at τ 8.20 led to narrowing of the multiplet at τ 6.15 and to decoupling in the region of τ 7.3—7.9.

lithium aluminium hydride (0.3 g, 7.9 mmol) in ether (5 ml). After 4 h, an excess of ethyl acetate was added and the products were then treated with water and worked up in the usual way. Chromatography on SilicAR CC7 led to a colourless oil (0.40 g), found (g.l.c. and n.m.r.) to be 1-bromo-*cis*-cyclo-octene of *ca.* 95% purity.

Action of Lithium Aluminium Hydride on Arylsulphonyl Derivatives of 2-Bromocyclonon-2-enol.—(*a*) 2-Bromo-*trans*-cyclonon-2-enyl tosylate was obtained as an amorphous solid (2.48 g, 48%) by treating 2-bromo-*trans*-cyclonon-2-enol [11] (3.0 g, 13.7 mmol) with toluene-*p*-sulphonyl chloride (5.0 g, 27.3 mmol) in pyridine (70 ml) and working up the products as for the corresponding *trans*-cyclo-octene derivative. Treatment of the tosylate (2.0 g, 5.3 mmol) with lithium aluminium hydride (0.50 g, 10.3 mmol) and work-up as above gave an oil (1.0 g), found by g.l.c. (diethylene glycol adipate; 125 °C) to contain two components (*ca.* 2 : 3). The less abundant, shorter t_R component, isolated by preparative g.l.c., was 1-*bromo*-trans-*cyclononene* (Found: C, 53.4; H, 7.3; Br, 39.5. $C_{19}H_{15}Br$ requires C, 53.2; H, 7.4; Br, 39.4%); τ (CCl_4) 4.24 (1 H, dd, *J* 5.5 and 11 Hz) and 7.3—9.1 (14 H, m); $\nu_{max.}$ (film) 1 654 cm^{-1}; *m/e* 202/204 (M^+, 31%) and 81 (100%). The more abundant, higher t_R component was identified (g.l.c. and n.m.r.) as 1-bromo-*cis*-cyclononene.

(*b*) 2-Bromo-*trans*-cyclonon-2-enyl *p*-bromobenzenesulphonate was similarly obtained as a crystalline solid [from petroleum (b.p. 60—80°)], m.p. 91—93°, in 50% yield from 2-bromo-*trans*-cyclonon-2-enol [11] and *p*-bromobenzenesulphonyl chloride; when this compound (1.0 g, 2.4 mmol) was treated with lithium aluminium hydride (0.25 g, 6.6 mmol) as above, an approximately 1 : 1 mixture (as indicated by g.l.c.) of 1-bromo-*cis*- and -*trans*-cyclononenes (0.40 g) was obtained.

1-*Bromo*-trans,cis-*cyclonona*-1,5-*diene* (30c).—A solution of 2-bromo-*trans,cis*-cyclonona-2,6-dienol (6.84 g, 31.5 mmol) [obtained [11b,13] from 9,9-dibromobicyclo[6.1.0]non-4-ene and silver perchlorate in aqueous acetone] was treated with toluene-*p*-sulphonyl chloride (15.0 g, 80 mmol) in anhydrous pyridine (100 ml) at 0 °C. After 36 h, the products were poured onto ice–water (250 g) and the mixture was stirred vigorously for 30 min. The precipitate was filtered off and dried *in vacuo* to give 2-bromo-3-*trans,cis*-cyclonona-2,6-dienyl tosylate (10.5 g, 86%). Recrystallization from petroleum (b.p. 40—60°) gave colourless plates, m.p. 96—98°.

A slurry of the crude tosylate (10.5 g, 28 mmol) in anhydrous ether (100 ml) was added to a cooled slurry of lithium aluminium hydride (2.75 g, 72 mmol) in ether (50 ml). The reactants were stirred at 10 °C for 4 h and then worked up as for the corresponding *trans*-cyclo-octene derivative to give 1-*bromo*-trans,cis-*cyclonona*-1,5-*diene* (Found: C, 53.7; H, 6.2; Br, 39.7. $C_9H_{13}Br$ requires C, 53.75; H, 6.5; Br, 39.8%) as a colourless, homogeneous [t.l.c. (petroleum, b.p. 60—80°) and g.l.c. (diethylene glycol adipate; 130 °C)] oil (4.63 g, 75% based on 2-bromo-*trans,cis*-cyclonona-2,6-dienol); τ (CCl_4) 4.25—4.55 (1 H, m), 4.55—5.0 (2 H, m), and 7.4—8.6 (10 H, m); $\nu_{max.}$ (film) 1 650m cm^{-1}; *m/e* 200/202 (M^+, 1%) and 121 (100%).

Reduction of 1-*Bromo*-trans,cis-*cyclonona*-1,5-*diene with Sodium in Liquid Ammonia.*—A solution of 1-bromo-*trans,-cis*-cyclonona-1,5-diene (1.0 g, 5.0 mmol) in petroleum (b.p. 30—40°; 10 ml) was added dropwise over 10 min to a stirred solution of sodium (1.0 g, 43.5 mmol) in liquid ammonia (*ca.* 50 ml). After the reactants had been stirred for a further 10 min at reflux temperature, an excess of ammonium chloride was added. The ammonia was then allowed to evaporate and the residue was partitioned between petroleum (b.p. 30—40°) and water. Careful evaporation of the dried ($MgSO_4$) organic layer at atmospheric pressure gave a colourless liquid (0.55 g), shown by g.l.c. (diethylene glycol adipate; 105 °C) to contain two components (*ca.* 2 : 3). The more abundant component corresponded to *cis,cis*-cyclonona-1,5-diene.[19]

Cyclonon-1-*en*-5-*yne* (31).—A solution of 1-bromo-*trans,-cis*-cyclonona-1,5-diene (2.92 g, 14.5 mmol) in anhydrous dimethyl sulphoxide (5 ml) was added to a vigorously stirred solution of potassium t-butoxide (3.6 g, 32 mmol) in dimethyl sulphoxide (25 ml). The reaction was immediately quenched by addition of ice–water (60 g) containing acetic acid (1.05 g, 17.5 mmol) and worked up as in the preparation of 3-methoxycyclo-octyne. Distillation of the yellow oil obtained gave *cyclonon*-1-*en*-5-*yne* (Found: C, 89.7; H, 10.0. C_9H_{12} requires C, 90.0; H, 10.0%) as a colourless, homogeneous [g.l.c. (diethylene glycol adipate; 110 °C)] liquid (1.25 g, 67%), b.p. 86—90° at 35 mmHg; τ (CCl_4) 4.2—4.9 (2 H, m) and 7.2—8.5 (10 H, m); $\nu_{max.}$ (film) 2 280w, 2 230w, and 1 650m cm^{-1}; *m/e* 120 (M^+, 35%) and 91 (100%).

Action of Lithium Aluminium Hydride on Cyclo-oct-2-*ynyl Methanesulphonate.*—Redistilled methanesulphonyl chloride (0.92 g, 8.0 mmol) was added dropwise over 10 min to a cooled (ice–methanol), stirred solution of cyclo-oct-2-ynol (0.90 g, 7.25 mmol) and triethylamine (1.1 g, 10.9 mmol) in anhydrous dichloromethane (25 ml). After a further 10 min, the solution was washed with iced water (2 × 25 ml), cold dilute hydrochloric acid (2 × 25 ml), aqueous sodium carbonate (2 × 25 ml), and saturated aqueous sodium chloride (2 × 25 ml). The dried ($MgSO_4$) organic layer was concentrated to give a colourless oil (1.1 g), shown by t.l.c. (benzene) to be free from starting material and to consist of virtually a single component. A solution of the oil in ether (5 ml) was added to a stirred slurry of lithium aluminium hydride (1.0 g) in anhydrous ether (20 ml) at 5 °C. After 30 min, the products were worked up as in the reaction between lithium aluminium hydride and 2-bromo-*trans*-cyclo-oct-2-enyl tosylate to give an oil (0.56 g) identical [t.l.c. (petroleum, b.p. 60—80°); n.m.r. and mass spectra] with authentic cyclo-octa-1,2-diene dimer.[17]

Cyclononyne (2).—Redistilled methanesulphonyl chloride (4.2 g, 36.6 mmol) was added dropwise over 10 min to a cooled (ice–methanol), stirred solution of crude (see above) cyclonon-2-ynol (4.6 g, 33 mmol) and triethylamine (5.0 g, 50 mmol) in anhydrous dichloromethane (100 ml). After a further 10 min, the products were worked up as in the mesylation of cyclo-oct-2-ynol to give a yellow oil (6.9 g); τ (CCl_4) 4.92 (1 H, m), 7.02 (3 H, m), and 7.6—8.8 (12 H, m); $\nu_{max.}$ (film) 2 275w, 2 220m, 1 360s, and 1 180s cm^{-1}.

A solution of the oil in anhydrous ether (20 ml) was added over 10 min to a cooled (ice–water), stirred slurry of lithium aluminium hydride (1.25 g, 33 mmol) in ether (80 ml). After 4 h, the products were worked up as in the reaction between lithium aluminium hydride and 2-bromo-*trans*-cyclo-oct-2-enyl tosylate [including the chromatography step on SilicAR CC7; elution with petroleum (b.p. 60—80°)]. The mobile liquid obtained was shown by g.l.c. (polyphenyl ether; 130 °C) to contain one major and two minor, shorter

[19] R. Vaidyanathaswamy and D. Devaprabhakara, *J. Org. Chem.*, 1967, **32**, 4143.

t_R components; this material was dissolved in petroleum (b.p. 30—40°; 100 ml) and the solution was extracted with aqueous 20% silver nitrate (2 × 50 ml). The latter extract was treated with aqueous ammonia (*d* 0.88; 25 ml) and then re-extracted with ether (3 × 50 ml). Evaporation of the dried ($MgSO_4$) ethereal extracts gave *cyclononyne* of high purity (1.4 g, 35%); τ (CCl_4) 7.7—8.1 (4 H, m) and 8.2—8.8 (10 H, m); $\nu_{max.}$ (film) 2 200w cm^{-1}.

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