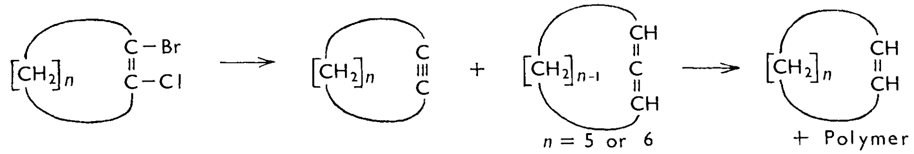
442. *Allenes. Part III.*[1] *The Synthesis of Cyclic Allenes.*

By W. J. Ball and S. R. Landor.

The action of sodium on 1-bromo-2-chloro-cycloheptene and -cyclo-octene gave cycloheptene and cyclo-octene, respectively. With sodamide in liquid ammonia 1-chlorocyclohexene gave aminated polymers, 1-chlorocycloheptene and 1-chlorocyclo-octene yielded the dimers (I) and (VI) derived from the cyclic allenes, and 1-chlorocyclononene and 1-chlorocyclodecene gave the corresponding cyclic allenes contaminated with 15% of the cyclic acetylene.

A number of attempts were made by Favorskii and Domnin [2] to prepare five-, six-, seven-, and eight-membered cyclic acetylenes and allenes by the action of sodium on 1-bromo-2-chlorocycloalkenes. Blomquist *et al.*[3] have shown that pure cyclodecyne cannot be prepared by Favorskii and Domnin's method but that a mixture of cyclodeca-1,2-diene (3 parts) and cyclodecyne (1 part) is obtained. Blomquist and Liu [4] also pointed out that the very unstable cyclo-octyne, which they prepared in 9% crude yield by pyrolysis of the bishydrazone of cyclo-octanedione with catalysis by mercuric oxide, possessed different physical properties from the product (described as cyclo-octyne) obtained by Domnin [5] by the action of sodium on 1-bromo-2-chlorocyclo-octene. Favorskii and Domnin's claim to have prepared cyclohepta-1,2-diene has, however, so far gone unchallenged. The present investigations have shown that the only volatile product obtained from the reaction of sodium (*a*) with 1-bromo-2-chlorocycloheptene is cycloheptene (30%) and (*b*) with 1-bromo-2-chlorocyclo-octene is cyclo-octene (24%). Intermolecular hydrogen transfer on the surface of the sodium, and polymerisation of the dehydrogenated product, would account for isolation of the cycloalkenes only.



Blomquist, Liu, and Bohrer [6] found that treatment of 1-chlorocyclononene with alcoholic potassium hydroxide gives a 1 : 1 mixture of cyclononyne and cyclonona-1,2-diene. We have treated 1-chlorocyclononene with sodamide in liquid ammonia and obtained mainly the corresponding cyclic allene (IX) contaminated with ~15% of the cyclic acetylene. Similarly 1-chlorocyclodecene gave cyclodeca-1,2-diene (X) containing ~15% of cyclodecyne.

As the C≡C stretching band in the infrared spectrum of medium-sized cyclic acetylenes is very weak indeed (cf. refs. 3, 4, 6) estimation of acetylene present in the cyclic allene rests mainly on the proportion of the acids isolated on ozonolysis of our products.

It is possible that the more strained cyclic acetylenes react preferentially with sodamide in liquid ammonia or rearrange by proton transfer, thus giving a higher allene : acetylene ratio than was reported by Blomquist.

Allenes could not be isolated after treatment of six-, seven-, or eight-membered 1-chlorocycloalkenes with sodamide in liquid ammonia. The only volatile fraction from the

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[1] Part II, Bhatia, Landor, and Landor, *J.*, 1959, 24; see also Ball and Landor, *Proc. Chem. Soc.*, 1961, 143.

[2] Favorskii and Domnin, *J. Gen. Chem.* (*U.S.S.R.*), 1936, **6**, 720.

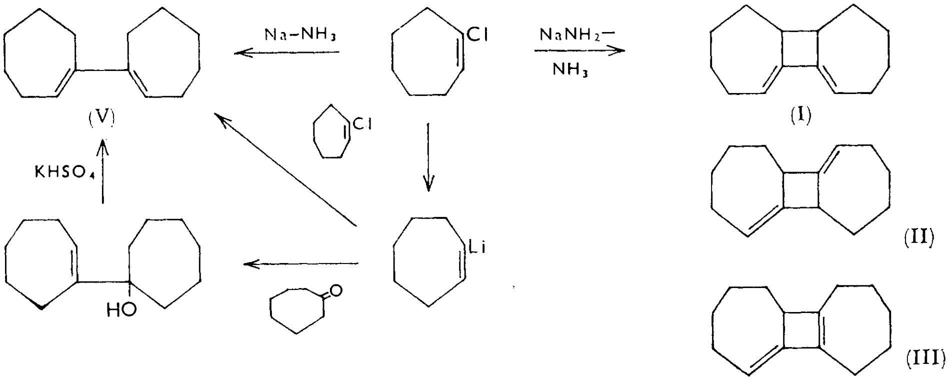
[3] Blomquist, Burge, Liu, Bohrer, Sucsy, and Kleis, *J. Amer. Chem. Soc.*, 1951, **73**, 5510; Blomquist, Burge, and Sucsy, *ibid.*, 1952, **74**, 3636.

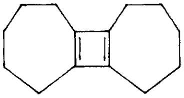
[4] Blomquist and Liu, *J. Amer. Chem. Soc.*, 1953, **75**, 2153.

[5] Domnin, *J. Gen. Chem.* (*U.S.S.R.*), 1938, **8**, 851; Domnin and Malysheva, *ibid.*, 1955, **25**, 311.

[6] Blomquist, Liu, and Bohrer, *J. Amer. Chem. Soc.*, 1952, **74**, 3643.

reaction with 1-chlorocyclohexene was recovered starting material, and no dimeric fraction could be isolated. The non-volatile residue could, however, be distilled at 0·09 mm., giving fractions of boiling range 120—190° and 190—200°. Both these fractions gave a strong positive test for nitrogen and no maxima in the ultraviolet spectrum, and undoubtedly resulted from the amination of cyclohexyne (or cyclohexa-1,2-diene). The structure of these compounds is under investigation.

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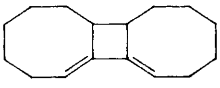
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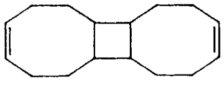
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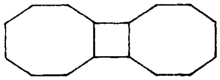
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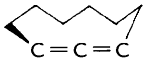
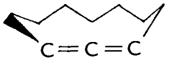


(IX)



(X)

The action of sodamide in liquid ammonia on 1-chlorocycloheptene gave a syrup, b. p. 160°/14 mm., in 32% yield, to which structure (I) is assigned. Elemental analysis and molecular-weight determination gave a molecular formula of $C_{14}H_{20}$. An infrared band at 1660m cm.$^{-1}$ and absorption of 1·98 mol. of hydrogen indicated the presence of two double bonds and a maximum at 260 mμ (ε 17750) with shoulders at 254 (ε 16,000) and 270 mμ (ε 11,100) located these double bonds in a 1,2-dimethylenecyclobutane system [Blomquist and Verdol[7] give $\lambda_{max.}$ 238 (ε 9780) and 246 mμ (ε 10,260) with a shoulder at 255 mμ for pure dimethylenecyclobutane. Caserio, Parker, Piccolini, and Roberts[8] give $\lambda_{max.}$ 223·5 mμ (ε 19,000) for 1-methyl-3-methylenecyclobut-2-ene]. Formation of a maleic anhydride diadduct (m. p. 267°) requires an *s-cis*-diene structure, as in (I), and contraindicates the *s-trans*-methylenecyclobutene structure in (II). The third possibility, the cyclobutadiene structure (IV), was dismissed on grounds of known instability and spectral evidence. Ultraviolet spectra of carefully refractionated material indicated that a non-conjugated isomer, probably (II), slightly contaminates lower-boiling fractions.

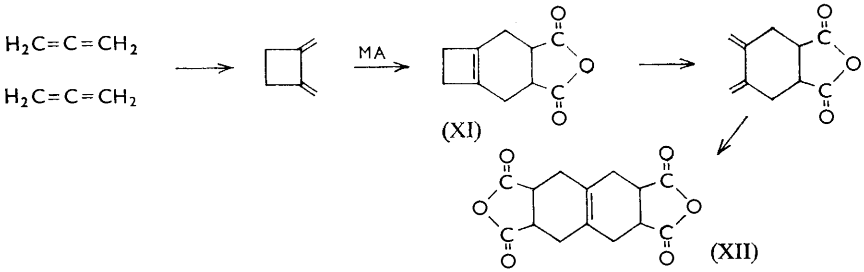
The compound (I) could not have been formed by direct Wurtz coupling of 1-chlorocycloheptene as was shown by adding sodium to 1-chlorocycloheptene in liquid ammonia, which gave 41% of bi(cyclohept-1-enyl)[9] (V) (besides 44·5% of cycloheptene) which had a different infrared spectrum and ultraviolet maxima at 242 (ε 8400) and 248 mμ (ε 8200) and gave a maleic anhydride adduct, m. p. 155°. This compound (V) was also prepared (*a*) by the action of 1-chlorocycloheptene on cycloheptenyl-lithium and (*b*) by reaction of cycloheptanone and cycloheptenyl-lithium followed by dehydration.

1-Chlorocyclo-octene with sodamide in liquid ammonia gave the tricyclohexadecadiene

[7] Blomquist and Verdol, *J. Amer. Chem. Soc.*, 1956, **78**, 109.
[8] Caserio, Parker, Piccolini, and Roberts, *J. Amer. Chem. Soc.*, 1958, **80**, 5507.
[9] Greidinger and Ginsburg, *J. Org. Chem.*, 1957, 1406.

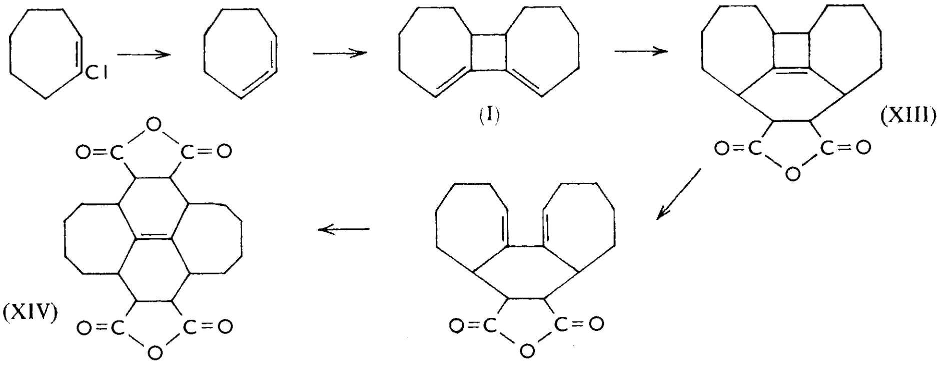
(VI), b. p. 132°/4 mm., whose infrared spectrum was similar to that of (I). This product absorbed 1·98 mol. of hydrogen, yielding the tricyclohexadecane (VIII), of unknown stereochemistry (possibly *cis-syn-cis*) and different from the tricyclohexadecane obtained by Ziegler, Sauer, Bruns, Froitzheim-Kuhlhorn, and Schneider;[10] its ultraviolet maxima were at 250 (ε 8800), 259 (ε 11,000), and 272 mμ (ε 8300) and it formed a maleic anhydride diadduct, m. p. 264°.

Lebedev[11] and more recently Blomquist and Verdol[7] have shown that allene dimerises to dimethylenecyclobutane at 140° or higher temperatures. Alder and Ackermann,[12] and Blomquist and Verdol,[7] converted dimethylenecyclobutane into a maleic anhydride diadduct of structure (XII) which was explained by the annexed reaction scheme. Blomquist and Verdol also isolated the monoadduct (XI).



(MA = maleic anhydride.)

An analogous series of reactions gives the substituted dimethylenecyclobutane (I) by spontaneous dimerisation of cyclohepta-1,2-diene which with maleic anhydride forms a maleic anhydride diadduct (XIV). We have not yet succeeded in isolating the monoadduct (XIII) although analyses show that it is the chief contaminant in impure samples of the diadduct.



Similarly cyclo-octa-1,2-diene dimerises spontaneously to compound (VI) which forms a maleic anhydride diadduct (XV).

Further work on these maleic anhydride adducts is in progress.

The ultraviolet spectrum of dimethylenecyclobutane shows abnormally low extinction coefficients, probably owing to a decrease in conjugation of the diene system held at an abnormal angle by the cyclobutane ring. It is possible that in the tricyclotetradecadiene system (I) a more normal angle is restored to the diene system, resulting in increased conjugation and the higher extinction coefficients. However, the larger eight-membered rings in compound (VI) do not restrain the dimethylcyclobutane system and this compound

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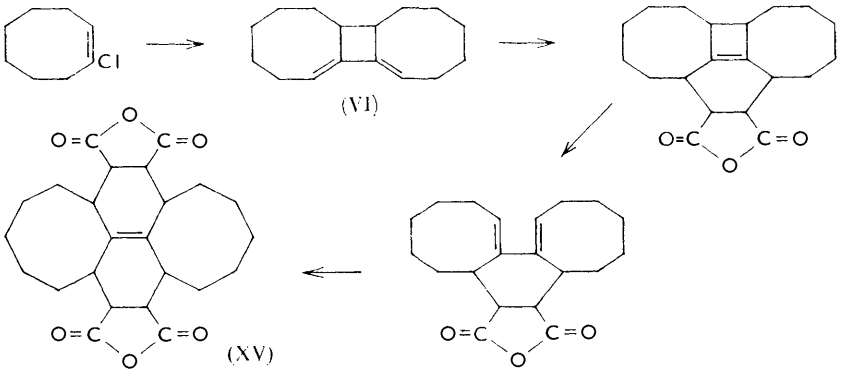
[10] Ziegler, Sauer, Bruns, Froitzheim-Kuhlhorn, and Schneider, *Annalen*, 1954, **589**, 122.

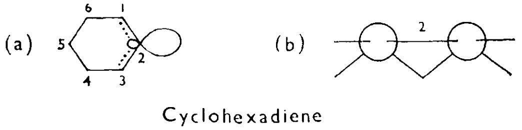
[11] Lebedev, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1357.

[12] Alder and Ackermann, *Chem. Ber.*, 1954, **87**, 1567.

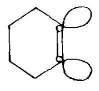
shows similar extinction coefficients to those recorded for dimethylenecyclobutane itself by Blomquist and Verdol.[7]



Examination of models shows that cyclodeca-1,2-diene and cyclonona-1,2-diene can be made in favourable conformations without involving bending of σ-bonds or twisting of π-bonds. A model of cyclo-octa-1,2-diene can only be made by twisting one of the π-bonds so that the overlap is limited, but bending of σ-bonds is not necessary (although both bending and twisting may be involved to attain the lowest energy state). It is difficult to make a model of cyclohepta-1,2-diene which leaves the linear allene system intact even by twisting one of the π-bonds and bending σ-bonds, but it is quite impossible to make a linear cyclohexa-1,2-diene, with an *sp*-hybridised central carbon atom. A more plausible structure involves sp^2-hybridisation for carbon atoms 1, 2, and 3 with an unbonded electron on carbon atom 2.*



Cyclohexadiene



Cyclohexyne

Projections: (a) perpendicular to and (b) in plane of ring.

The absence of dimer formation in the reaction of 1-chlorocyclohexene with sodamide in liquid ammonia is evidence that cyclohexyne is formed preferentially to cyclohexadiene (cf. Scardiglia and Roberts[13]).

Limited overlap of *p*-orbitals resulting from the twisting of a double bond best explains dimer formation of seven- and eight-membered allenes. Willstätter and Veraguth,[14] and more recently Ziegler and his co-workers,[10,15] reported that " labile " cyclo-octa-1,5-diene dimerises and polymerises spontaneously to give compound (VIII). Although the configuration of " labile " cyclo-octa-1,5-diene has not yet been conclusively established it is known that it contains at least one *trans*-fused double bond. Stable models of *cis-trans*- and *trans-trans*-cyclo-octa-1,5-diene can be made by twisting a *trans*-double bond, resulting in limited overlap of *p*-orbitals and therefore dimerisation.

It may be noted that cyclononanone, which was initially prepared by the standard acyloin method,[6] can be far more conveniently prepared by a Lewis acid-catalysed double ring-expansion from cycloheptanone and two equivalents of diazomethane.[16]

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* The alternative sp^3 at C-1, sp^2 at C-2 and C-3, is probably less stable.

[13] Scardiglia and Roberts, *Tetrahedron*, 1957, **1**, 343.

[14] Willstätter and Veraguth, *Ber.*, 1905, **38**, 1975; 1907, **40**, 957.

[15] Ziegler and Wilms, *Annalen*, 1950, **567**, 8.

[16] Cf. Muller, Bauer, and Rundel, *Tetrahedron Letters*, 1960, **13**, 30.

EXPERIMENTAL

Reaction of 1-*Chlorocyclohexene with Sodamide in Liquid Ammonia*.—Sodium (8 g.,) was added to liquid ammonia (0·5 l.) containing a crystal of ferric nitrate. After 3 hr. 1-chlorocyclohexene (29 g.; prepared in 66% yield by the method of Braude and Coles [17]) was added slowly and the resulting mixture was stirred for 4 days. After decomposition with ammonium chloride (18 g.), evaporation of ammonia overnight, and extraction with water and ether, the solution was dried and evaporated and the product distilled, yielding materials (i) (1 g.), b. p. 45°/2 mm., shown to be recovered 1-chlorocyclohexene by its infrared spectrum, (ii) (1·2 g.), b. p. 120—190°/0·09 mm., and (iii) (2·8 g.), b. p. 190—200°/0·09 mm. Fractions (ii) and (iii) gave a strong positive test for nitrogen and no maxima in the ultraviolet spectra.

Tricyclo[7,5,0,0 ^{2,8}]*tetradeca*-7,9-*diene* (I).—Cycloheptanone (100 g.) was added dropwise to phosphorus pentachloride (200 g.), cooled in ice and salt. After 3 hr. the product was poured on ice, extracted with ether, dried, and fractionated, to give 1-chlorocycloheptene (69 g., 53%), b. p. 54—58°/14 mm. (cf. refs. 5, 14), and 1,1-*dichlorocycloheptane* (24 g., 16%), b. p. 91°/8 mm. (Found: C, 50·6; H, 7·1; Cl, 42·3%; *M*, 162. $C_7H_{12}Cl_2$ requires C, 50·5; H, 7·2; Cl, 42·3%; *M*, 166). 1,1-Dichlorocycloheptane (16·6 g.) was converted into 1-chlorocycloheptene (9·2 g., 76·5%) by refluxing it with alcoholic potassium hydroxide.

1-Chlorocycloheptene (26 g.) was added dropwise in 1 hr. to sodamide (from sodium, 8 g.) in liquid ammonia (1 l.). After 4 days ammonium chloride (15 g.) was added, ammonia allowed to evaporate overnight, and the residue extracted with water and ether. Evaporation and fractionation gave 1-chlorocycloheptene (4·5 g.), b. p. 56°/14 mm., and *tricyclo*[7,5,0,0 ^{2,8}]-*tetradeca*-7,9-*diene* (I) (6 g., 32%), b. p. 142°/14 mm. (Found: C, 89·5; H, 10·3%; *M*, 198. $C_{14}H_{20}$ requires C, 89·3; H, 10·7%; *M*, 188), $\lambda_{max.}$ 260 (ε 17,750), shoulders at 254 (ε 16,000) and 270 mμ (ε 11,100), $\nu_{max.}$ 1660 cm.$^{-1}$ (C=C).

Compound (I) (1 g.) in ethyl acetate (30 ml.) containing platinic oxide (0·045 g.) absorbed 254 ml. of hydrogen at 19°/743 mm. (theor., 260 ml.). Ethyl acetate was evaporated and the residue distilled, yielding on fractionation material (0·69 g.) of b. p. 140—145°/12 mm.

After redistilled maleic anhydride (1 g.) and compound (I) (0·5 g.) in benzene (30 ml.) had been heated under reflux on a water-bath for 8 hr., the light brown solution was evaporated and the residue extracted with small quantities of ether. The residual solid recrystallised from benzene-light petroleum (b. p. 40—60°), yielding $\Delta^{12b,12c}$-*hexadecahydrodicyclohepta*[de : ij]-*naphthalene*-1,2,7,8-*tetracarboxylic dianhydride* (XIV) (0·6 g.), m. p. 267° (Found: C, 68·8; H, 6·1. $C_{22}H_{24}O_6$ requires C, 68·7; H, 6·3%).

This product (XIV) (0·5 g.) was dissolved in dilute sodium hydroxide solution by warming for a few minutes. After filtration, the solution was acidified, and the solid precipitate was filtered off and dried *in vacuo*. Being virtually insoluble in common solvents except ethanol from which it did not crystallise, the *tetracarboxylic acid* was reprecipitated from sodium hydroxide solution (Found: C, 62·5; H, 6·85. $C_{22}H_{28}O_8$ requires C, 62·8; H, 6·7%) and had m. p. 230° (samples were placed on a micro-Kofler block 5° below m. p.; otherwise partial anhydride formation and indefinite m. p.'s resulted).

Bi(*cyclohept*-1-*enyl*) [9] (V).—Sodium (3 g.) was added slowly to 1-chlorocycloheptene in liquid ammonia (0·5 l.) and the mixture was kept overnight. Then ammonium chloride (5 g.) was added, the mixture poured into a stainless-steel beaker, and ammonia allowed to evaporate. Extraction in ether, washing with water, drying, and distillation gave, first, cycloheptene (4·3 g., 44·5%), b. p. 112—115° (Found: C, 87·5; H, 12·5. Calc. for C_7H_{12}: C, 87·5; H, 12·5%), $\nu_{max.}$ 1646 (C=C), 690 cm.$^{-1}$ (*cis*-C=C), no ultraviolet maximum [188 ml. of H_2 absorbed at 20°/752 mm. (Calc., 194 ml.)], and then bi(cyclohept-1-enyl) (V) (3·9 g., 41%), b. p. 133°/10 mm. [Found: *M*, 181 (cryoscopic in benzene). Calc. for $C_{14}H_{22}$: *M*, 190], $\lambda_{max.}$ 242 (ε 8400), 248 mμ (ε 8200), $\nu_{max.}$ 1680 (C=C), 841s cm.$^{-1}$ (HC:C). The product (V) (1·9 g.) in ethyl acetate (65 ml.) with platinic oxide (0·41 g.) absorbed 504 ml. of hydrogen at 19°/743 mm.. (Calc., 509 ml.), and in refluxing benzene gave a maleic anhydride adduct, m. p. 155° (lit.,[9] 157—158°).

Similarly, from sodium (18 g.) and 1-chlorocycloheptene (65·5 g.), cycloheptene (25 g., 53%), and bi(cyclohept-1-enyl) (11 g., 23·6%) were obtained after 15 min.

1-Chlorocycloheptene (13 g.) was added to cycloheptenyl-lithium [18] [from lithium (1·8 g.) and 1-chlorocycloheptene (13 g.) in tetrahydrofuran (60 ml.)]. After 3 hours' refluxing, water

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[17] Braude and Coles, *J.*, 1950, 2014.

[18] Braude, Forbes, and Evans, *J.*, 1953, 2202.

was added dropwise, and the whole extracted with ether; the extract was dried and distilled, yielding bi(cycloheptenyl) (5·3 g., 28%).

Cycloheptanone (11·2 g.) in tetrahydrofuran (30 ml.) was added to cycloheptenyl-lithium [18] (from lithium, 1·8 g., and 1-chlorocycloheptene, 13 g.) in tetrahydrofuran (60 ml.). After 2 hours' refluxing and storage overnight, the product was decomposed with water and extracted with ether; the extract was dried and evaporated. The resulting cycloheptenylcycloheptanol (5·1 g.), which separated as needles, was heated with freshly fused potassium hydrogen sulphate (30 g.) for 5 hr. and distilled, yielding bi(cyclohept-1-enyl) (4·0 g., 21%).

The Action of Sodium on 1-*Bromo*-2-*chlorocycloheptene*.—1-Bromo-2-chlorocycloheptene (33·5 g.), b. p. 100—105°/4·5 mm. (prepared, in 53% yield, as described by Favorskii and Domnin [2] but without isolation of the intermediate dibromochlorocycloheptane), was added to sodium wire (12 g.) in dry ether (100 ml.) under nitrogen. After 30 min. an exothermic reaction developed which was moderated by ice-cooling. The mixture was then kept for a week. Filtration and washing of the precipitate with ether, followed by washing of the ethereal solution with water, drying, and evaporation of solvents left a viscous yellow oil. Distillation at 1 mm. gave a trap-fraction (6·6 g.) and a large non-volatile residue. Redistillation of the trap-fraction gave cycloheptene (4·6 g., 30%), b. p. 114—115°, $\nu_{\text{max.}}$ 1650m and 690s cm.$^{-1}$, the whole spectrum being superposable on that of cycloheptene.

Tricyclo[8,6,0,0^{2,9}]*hexadeca*-2,16-*diene* (VI).—1-Chlorocyclo-octene (9 g; prepared in 52% yield by the method of Braude *et al.*[19]) was added slowly to sodamide (from sodium, 2·4 g.) in liquid ammonia (0·5 l.). After 5 days ammonium chloride (3 g.) was added, ammonia allowed to evaporate overnight, the residue extracted with ether, and the ethereal solution dried and distilled, yielding *tricyclo*[8,6,0,0^{2,9}]*hexa*-2,16-*diene* (VI) (2·1 g., 32·4%), b. p. 132°/4 mm. (Found: C, 89·2; H, 11·0%; *M*, 225 $C_{16}H_{24}$ requires C, 89·9; H, 11·1%; *M*, 216), $\lambda_{\text{max.}}$ 250 (ε 8800), 259 (ε 11,000), and 269 mμ (ε 8300), $\nu_{\text{max.}}$ 1620m cm.$^{-1}$ (C=C).

The diene (VI) (0·904 g.) in ether (30 ml.) absorbed hydrogen (203 ml.) at 24°/751 mm. in the presence of platinic oxide (0·032 g.) (Calc., 206 ml.). Filtration and evaporation gave a pale yellow oil which partly crystallised on treatment with acetic anhydride. Recrystallisation from benzene gave tricyclo[8,6,0,0^{2,9}]hexadecane of low m. p.

Redistilled maleic anhydride (2 g.) and the diene (1·1 g.) were heated under reflux in dry benzene (40 ml.) for 10 hr. The mixture was then washed with water (3 × 20 ml.), dried ($MgSO_4$), and evaporated *in vacuo*. Two recrystallisations of the residue from benzene–light petroleum (b. p. 40—60°) gave $\Delta^{14b,14c}$-*octadecahydrodicyclo-octa*[de : ij]*naphthalene*-1,2,8,9-*tetracarboxylic dianhydride* (XV) (0·8 g.), m. p. 264° (Found: C, 70·2; H, 6·65. $C_{24}H_{28}O_6$ requires C, 69·9; H, 6·8%).

The Action of Sodium on 1-*Bromo*-2-*chlorocyclo-octene*.—1-Bromo-2-chlorocyclo-octene (19·5 g.; prepared, in 50·5% yield, as described by Domnin [5] but without isolation of the intermediate dibromochlorocyclo-octane) was added to sodium wire (12 g.) in dry ether (100 ml.). After gentle warming for 20 min. a vigorous reaction started and a white precipitate was formed. After 7 days the ethereal solution was filtered, washed three times with water, dried, and distilled, yielding cyclo-octene (2·3 g., 24%), b. p. 132—136°, $\nu_{\text{max.}}$ 1650m cm.$^{-1}$ (spectrum superposable on that of *cis*-cyclo-octene).

Cyclonona-1,2-*diene* (IX).—(*a*) Cyclononanone was prepared by the acyloin method [6] [2,4-dinitrophenylhydrazone, m. p. 169° (Braude *et al.*[19] report 168°)]. (*b*) An ethereal solution of diazomethane [from *N*-methyl-*N*-nitrosourea (136 g.), 50% aqueous potassium hydroxide (390 ml.), and ether (1500 ml.)] was added during 2 hr. to cycloheptanone (34 g.) and aluminium chloride (4 g.) in ether (50 ml.) kept at 0°. After 24 hr. the precipitate was filtered off, and the filtrate washed with sodium hydrogen carbonate solution and water, dried, and distilled, yielding two fractions of cyclononanone: (i) (11·6 g.), b. p. 100—107°/24 mm. (dinitrophenylhydrazone, m. p. 159°) and (ii) (15 g., 36%), b. p. 107—115°/24 mm. (2,4-dinitrophenylhydrazone m. p. and mixed m. p. 169°); fraction (i) was contaminated with cyclo-octanone (a mixture of the dinitrophenylhydrazones of cyclo-octanone and cyclononanone had m. p. 161°).

1-Chlorocyclononene (7 g.), b. p. 100°/12 mm. (prepared from cyclononanone and phosphorus pentachloride [6]), was added to sodamide (from sodium, 3 g.) in liquid ammonia (0·5 l.). After 3 hr. ammonium chloride (10 g.) was added, the ammonia allowed to evaporate overnight, and the residue extracted with ether, dried, and distilled, yielding cyclonona-1,2-diene containing

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[19] Braude, Forbes, Gofton, Houghton, and Waight, *J.*, 1957, 4711.

15% of cyclononyne (2·3 g., 43%); the mixture had b. p. 56—59°/30 mm., $\nu_{max.}$ 2380vw (C≡C) and 1960m cm.$^{-1}$ (C=C=C), no ultraviolet maximum.

The diene (0·5 g.) in ethyl acetate with platinic oxide absorbed hydrogen (179 ml.) at 18°/743 mm. (Calc., 181 ml.).

The diene (1 g.) in ethyl acetate (60 ml.) was treated with ozonised oxygen for 90 min. Thereafter, decomposition with 100-vol. hydrogen peroxide (50 ml.), refluxing, and extraction with sodium hydroxide solution, followed by acidification, extraction with ether, and evaporation of ether gave an acidic residue which recrystallised from very dilute alcohol, yielding (i) suberic acid (0·6 g.), m. p. 140·5°, mixed with an authentic sample (m. p. 142°), m. p. 140°, and (ii) azelaic acid (0·1 g.), m. p. 104°, mixed with an authentic sample (m. p. 106°), m. p. 105·5°.

Cyclodeca-1,2-*diene* (X).—Cyclodecanone (prepared by the acyloin method [3]) was converted into 1-chlorocyclodecene in 49% yield.[3]

1-Chlorocyclodecene (13 g.) in dry ether (10 ml.) was added slowly to sodamide (from sodium, 6 g.) in liquid ammonia (0·5 l.). After 4 hr. ammonium chloride was added and the ammonia allowed to evaporate overnight. The residue was extracted with ether, dried, and distilled, yielding cyclodeca-1,2-diene (X) containing 15% of cyclodecyne (4·25 g., 39%), b. p. 70—76°/12 mm., $\nu_{max.}$ 2330vw cm.$^{-1}$ (C≡C) and 1960m cm^{-1} (C=C=C), no ultraviolet maximum.

The diene (0·98 g.) in ethyl acetate (45 ml.) with platinic oxide (0·032 g.) absorbed hydrogen (352 ml.) at 21°/754 mm. (Calc., 348 ml.).

Ozonisation of the diene (1 g.) as in the preceding case gave sebacic acid (0·07 g.), m. p. and mixed m. p. 127° (from aqueous alcohol) and azelaic acid (0·45 g.), m. p. and mixed m. p. 101° (from aqueous alcohol).

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WOOLWICH POLYTECHNIC, LONDON, S.E.18.

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