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The Chemistry of 1,5,9-Cyclododecatriene and Syntheses Based on It

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The methods of synthesis and chemical properties of 1,5,9-cyclododecatriene (the butadiene cyclotrimerisation product), which is manufactured on an industrial scale, are examined; syntheses based on this interesting compound have played a major role in the development of organic chemistry of medium and large rings.
The bibliography includes 406 references.

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I. INTRODUCTION

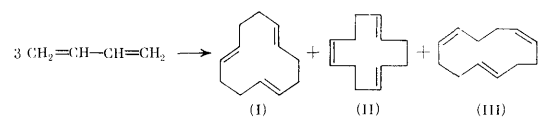
The first studies on cyclododecane and its derivatives were begun in 1926 by Ruzicka and coworkers, but the difficulty of the synthesis of these compounds and of their isolation in a pure form hindered the development of their chemistry.

In 1954, Reed reported for the first time[1] the synthesis of a cyclic butadiene trimer in the presence of bis(triphenylphosphine)nickel dicarbonyl, but it was not until Wilke's study[2] of the cyclotrimerisation of butadiene in the presence of organometallic complex catalysts that 1,5,9-cyclododecatriene (1,5,9-CDT) became readily available and vigorous development of the chemistry of this compound and its industrial use were initiated.

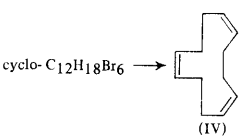
cis,trans,trans-1,5,9-CDT is manufactured at present on a large scale in many countries. The following products obtained from 1,5,9-CDT are of major technical importance: ω-dodecalactam—the monomer for the synthesis of nylon-12; decane-1,10-dicarboxylic acid—the monomer for the synthesis of polyamides and polyesters and a substitute of sebacic acid in the synthesis of plasticisers and lubricating oils; 1,12-diaminododecane—the monomer for the synthesis of polyamides; 1,2,5,6,9,10-hexabromocyclododecane, which is used as an additive to polymers in order to render them incombustible; cyclododecanone which is used as the initial compound for the synthesis of valuable perfumes—cyclopentadecanone (exaltone) and the lactone of ω-hydroxypentadecanoic acid (tibetolide).

II. SYNTHESIS AND CHEMICAL REACTIONS OF 1,5,9-CYCLODODECATRIENE ISOMERS

It has now been established that the cyclotrimerisation of butadiene to 1,5,9-CDT proceeds in catalytic systems containing the following transition metals as components: titanium, chromium, nickel, and manganese. *trans, trans,trans*-1,5,9-CDT (I), *cis,trans,trans*-1,5,9-CDT (II), and *cis,cis,trans*-1,5,9-CDT (III) have been obtained in the presence of these catalysts; the ratios of the yields of these products depend on the nature of the transition metal, the ligands in the catalytic system, and the reaction conditions:



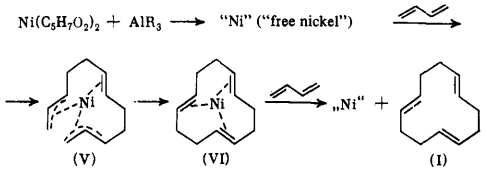
The fourth possible isomer—*cis,cis,cis*-1,5,9-CDT (IV)—is not formed in the catalytic trimerisation of butadiene. It has been obtained by the dehydrobromination of hexabromocyclododecane—the product of the addition of three bromine molecules to (I):[3]



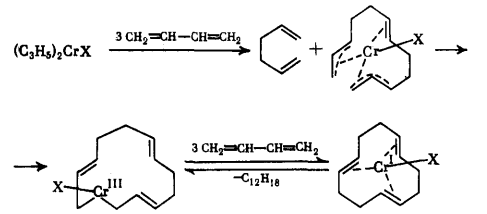
The most effective catalysts for the synthesis of 1,5,9-CDT are systems containing various titanium compounds [$TiCl_4$,[4-20] $TiBr_4$,[21] $Ti(OR)_4$,[22,23] $(RO)_2TiO$,[24] $TiCl_{4-n}(OR)_n$, $TiCl_{4-n}(OCOR)_n$,[25-28] and the complex $C_6H_6.TiCl_2.Al_2Cl_6$ [13, 29,30]] in combination with reducing agents such as trialkylaluminium or aluminium alkyl halides, calcium hydride, and dialkylaluminium hydride. The reaction proceeds only in solution in aromatic hydrocarbons with formation of 1,5,9-CDT in 80–90% yield. The 1,5,9-CDT obtained is a mixture of two isomers: 3–4% of (I) and 96–97% of (II). A mixture containing 67% of (I) and 33% of (II) is formed in the catalytic system containing poly(butyl orthotitanate) and $(C_2H_5)_2AlCl$.[31]

Catalytic systems containing chromium and manganese [$(C_5H_7O_2)_2Cr$, CrO_2Cl_2 or $CrO_3 + (C_2H_5)_3Al$,[4,5,12] $CrCl_3 + (iso\text{-}C_4H_9)_3Al$,[10-12,32,33] and $(C_5H_7O_2)_2Mn + (C_2H_5)_3Al$ [34]] lead to a mixture of approximately 60% of (I) and approximately 40% of (II). A mixture consisting of 65–80% of (I), 7–9% of (II), 9–11% of (III), 7–9% of vinylcyclohexene, and 4–6% of 1,5-cyclo-octadiene is formed in the presence of nickel catalysts [$Ni(C_5H_7O_2)_2 + C_2H_5OAl(C_2H_5)_2$,[12,35,36] $NiX_2 + (iso\text{-}C_4H_9)_3Al$,[37] $(cyclo\text{-}octadiene)_2.Ni(O)$ [30,36] and $cyclododecatriene.Ni(O)$ [35]]. The mixture composition varies with reaction temperature.

There have been numerous patents for catalytic systems containing nickel[37,38-43]. The mechanism of the reaction in the presence of nickel catalysts has been established by Wilke and coworkers[33,35,44-46]. It includes the following stages:



When $Ni(C_5H_7O_2)_2$ is reduced by an organoaluminium compound, "free" nickel is formed, which trimerises butadiene to the intermediate π-allyl complex of nickel (V); ring closure of (V) results in the formation of the π-nickel complex (VI). Treatment with butadiene leads to the displacement of 1,5,9-CDT from this complex. Complexes (V) and (VI) have been isolated and their structures have been determined by X-ray diffraction[47,48] and confirmed by certain reactions[31,35,44,45]. When complex (VI) is acted upon by *cis,cis,cis*-1,5,9-CDT (IV), *trans,trans,trans*-1,5,9-cyclododecatriene (I) is displaced from it and the complex (IV).Ni(O) is formed[45]; the latter readily reacts with carbon monoxide to give $Ni(CO)_4$ and compound (IV). A mechanism has been proposed for the trimerisation of butadiene in the presence of chromium catalysts[33] in which the valence state of chromium changes continuously from +1 to +3:



It has been shown[30,49] that in the presence of titanium catalysts the active centre for the trimerisation of butadiene is a complex in which titanium is present in the bivalent state:

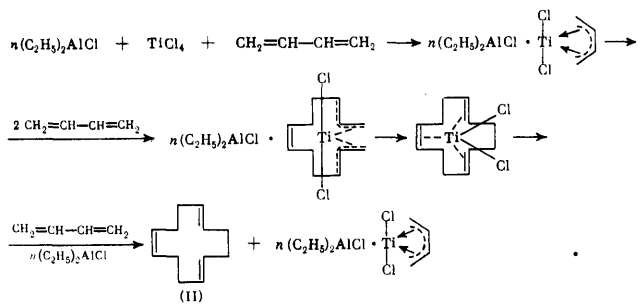


Table 1 presents the best known catalytic systems in the presence of which the trimerisation of butadiene to 1,5,9-CDT isomers takes place with a high yield.

Among the four 1,5,9-CDT isomers, the *trans,trans,trans*-isomer (I)[50] and the *cis,trans,trans*-isomer (II), which are readily obtainable in the presence of the above catalysts, have been studied in greatest detail. The presence of three non-conjugated double bonds in the 1,5,9-CDT molecule makes this system capable of undergoing many reactions. Among them the most interesting are those involving *cis–trans* isomerisation. When (II) is illuminated with ultraviolet light, a mixture of (I) and (III) is formed[51].

Table 1.

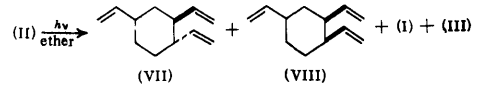
Catalytic systems	Yield of 1,5,9-CDT, %	Isomers formed (the relative percentage contents are indicated in brackets)	Refs.
$TiCl_4 + (C_2H_5)_2AlCl$	91	I (97) + II (3)	8, 9, 10
$TiCl_4 + (C_2H_5)_3Al_2Cl_3$	88	II (98) + I (2)	8, 9, 12
$CrO_2Cl_2 + (C_2H_5)_3Al$	70	I (59) + II (41)	10
$CrCl_3 + (C_2H_5)_3Al$	80	I + II	8
$CrCl_3 + (iso\text{-}C_4H_9)_3Al$	86	I (60) + II (40)	8, 9
$Ni(C_5H_7O_2)_2 + (C_2H_5)_2AlOC_2H_5$	81	I (80) + II (9) + III (11)	10
$NiX_2 + (iso\text{-}C_4H_9)_3Al$	80	I+II	37
$[(C_8H_{12})_2Ni]$	87	I+II	39

Subsequently it was shown that each of the four isomers undergoes cis–trans isomerisation giving rise to the same equilibrium mixture consisting of all four isomers (I), (II), (III), and (IV).[52] It has been established[53] that thermodynamic stability decreases in the sequence (I) > (II) > (III). Data for the photochemical isomerisation of the isomers in benzene are presented in Table 2.

Table 2. Composition of the mixture of 1,5,9-CDT isomers in photochemical isomerisation[53].

Initial olefin	Irradiation time, h	Proportions of isomers in product, %		
		(I)	(II)	(III)
(I)	17	24	43	33
(II)	17	11	55	34
(III)	100	1	21	78

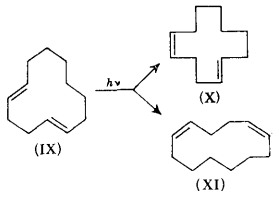
Table 2 shows that (III) isomerises much more slowly than isomers (I) and (II). The proportions of the isomers also depend on the selected sensitiser. In the presence of aromatic ketones and quinones, isomer (II) predominates in the resulting mixture, while the use of aliphatic ketones leads to isomer (III). Thus the readily available isomer (II) may be easily converted into (I) and (III) on irradiation of a benzene solution containing acetophenone or acetone. After prolonged irradiation of a mixture of (I), (II), and (III), 43% of *trans,trans*-2,6-divinyl-*cis*-bicyclo[3,3,0]octane was obtained together with 1,5,9-CDT isomers[52]. When (II) in an ethereal solution is irradiated, a mixture containing 25% of (I), 29% of (III), and isomeric 1,2,4-trivinylcyclohexanes [12% of (VII) and 1% of (VIII)] is formed[54]:



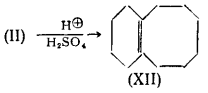
Thermal isomerisation of (II) at 450°C leads only to isomeric 1,2,4-trivinylcyclohexanes[55]. In the presence of toluene-*p*-sulphinic acid a mixture of 80–85% of (I) and 15–20% of (II) is formed from the initial (I)–(III) mixture on

heating to 90° C.[53,56] Copper salts are active catalysts of the *cis–trans* isomerisation of the double bonds in (I), (II), and (III).[53] The free-radical isomerisation of (II) to (I) takes place readily in the presence of thioglycolic acid[57], benzoyl peroxide[57], and *N*-bromosuccinimide[57,58]. The photochemical isomerisation of cyclododecenes in benzene leads to the formation of the less stable *cis*-isomer[53]. In the presence of copper salts the equilibrium is also displaced to *cis*-cyclododecene[53].

On photochemical isomerisation in benzene, *trans*, *trans*-1,5-cyclododecadiene (IX) is converted into the *cis*, *trans*-isomer (X) and the *cis*,*cis*-isomer (XI); the ratios of the isomers in the resulting mixture are (IX) : (X) : (XI) = 17 : 55 : 28[59]:

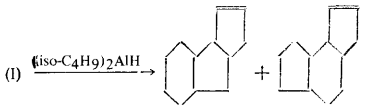


In the presence of acid reagents (II) undergoes intramolecular cyclisation, which leads to products with bicyclic and tricyclic structures. Thus a mixture of hydrocarbons in which $\Delta^{1,6}$-bicyclo[4,6,0]dodecene (XII) predominates, is formed from (II) on treatment with 80% sulphuric acid in the cold[60]:

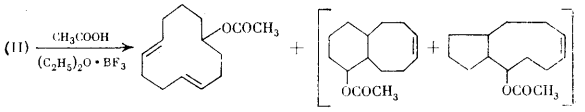


A mixture of acenaphthene and decahydroacenaphthene is formed on heating (II) with polyphosphoric acid[61].

The isomerisation of (I) takes place readily in the presence of (iso-C_4H_9)$_2$.AlH on heating to 200° C, giving an 85% yield of a mixture of tricyclo[6,4,0,$0^{3,7}$]dodec-4-ene and tricyclo[7,3,0,$0^{3,7}$]dodec-4-ene[62]:

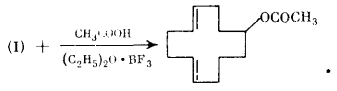


Bicyclic products were formed after the addition of acetic acid and hydrogen chloride to (II)[63]:

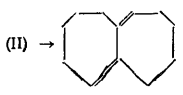


The reaction apparently proceeds both at the *cis*-double bond, giving rise to the usual addition products, and at the *trans*-double bond, giving rise to bicyclic products.

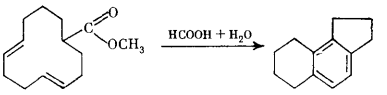
When acetic acid and hydrogen chloride react with (I), only addition products retaining the molecular skeleton are formed[63]:



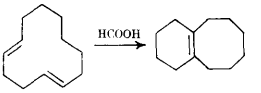
Bicyclo[5,5,0]dodeca-1,7-diene is formed from (II) in the presence of Na/Al_2O_3,[64] $Co_2(CO)_8$,[65] and the lithium derivative of ethylenediamine[66]:



When methyl *trans*,*trans*-4,8-cyclododecadiene-carboxylate is treated with 90% formic acid, 2,3,6,7,8,9-hexahydro-1H-benz[*e*]indene is produced[67].

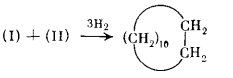


trans,*trans*-1,5-cyclododecadiene gives rise to bicyclo-[6,4,0]dodecene[67]:



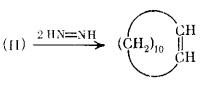
III. SYNTHESES BASED ON *cis*,*trans*,*trans*- AND *trans*, *trans*,*trans*-1,5,9-CYCLODODECATRIENES

In this section of the review we shall consider the reactions of the most readily available 1,5,9-CDT isomers—the *trans*,*trans*,*trans*-isomer (I) and the *cis*,*trans*,*trans*-isomer (II). The majority of studies on the hydrogenation of 1,5,9-CDT in cyclododecane are described in the patent literature. The two isomers (I) and (II) are quantitatively hydrogenated in the presence of platinum, palladium, and Raney nickel[68–70]:



In order to obtain large amounts of cyclododecane, (I) and (II) are hydrogenated at elevated temperatures in the presence of Ni/Al_2O_3 or Ni/Cr_2O_3.[5,68–72] Nickel, cobalt, and copper salts deposited on SiO_2 or Al_2O_3 in the presence of NaF are effective catalysts of the reduction[73,74]. The rates of hydrogenation of the two isomers are virtually the same. In the presence of these catalysts, all three double bonds are hydrogenated at virtually the same rates and one cannot therefore carry out a selective hydrogenation. When one mole of (II) is hydrogenated with two moles of hydrogen in the presence of palladium, a mixture consisting of cyclododecene, cyclododecadiene, and cyclododecanes is formed[68,75]. The hydrogenation of (I) and (II) to cyclododecane in the presence of homogeneous catalysts has been described in a number of patents: $(Ph_3As)_2(CO)RhCl$ + $AlCl_3$,[76] $Ni(C_5H_7O_2)_2$ + $LiAlH_2(OCHMeC_2H_5)_2$,[77] $Ti(OBu)_4$ + $(C_2H_5)_2AlCl$, and $Cr(C_5H_7O_2)_2$ + $(C_2H_5)_2AlCl$ + $(C_2H_5)_3Al$.[79]

The selective hydrogenation of (I) and (II) to cyclododecene, which gives rise to great possibilities for the synthesis of many products of practical importance, is of considerable interest. It has been shown that, when (II) is acted upon by di-imide, the *trans*-double bonds are reduced initially and *cis*-cyclododecene is formed in a high yield[80,81]:

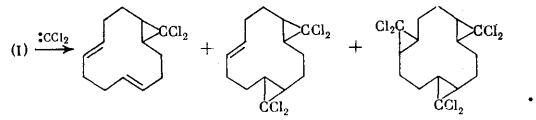


The success of the catalytic hydrogenation of (II) to cyclododecene depends primarily on the nature of the catalyst. The use of relatively inactive heterogeneous catalysts makes it possible to stop the hydrogenation at the stage corresponding to the addition of two moles of hydrogen[82–87]. Studies on a series of catalysts (Rh, Pd, and Ru on Al_2O_3)[88,89] have shown that the hydrogenation of (I) and

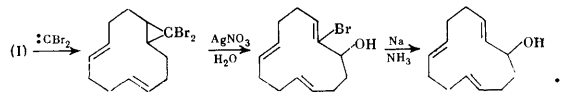
(II) to cyclododecene takes place most selectively in the presence of rhodium. The catalysts can be arranged in the following sequence in terms of decreasing yields of cyclododecene: Ph > Pd > Ru > Pt. The trichlorotripyridinerhodium +$NaBH_4$ catalytic system proved to be the most effective in the hydrogenation (II) to cyclododecene[90]. In the presence of the homogeneous catalyst $[Co(CO)_3 \cdot PR_3]_2$ [83,84,91] or $(R_3P)_2(CO)_2RuCl_2$ [92,93] (II) gives a high yield of a mixture of *cis*- and *trans*-cyclododecenes (96–98%) and in addition 1% of 1,5-cyclododecadiene and 0.5% of cyclododecane are formed. Hydrogenation of (II) in the presence of 7% $PtCl_2$ in a $(C_2H_5)_4NSnCl_2$ melt at 160°C and 100 atm of H_2 leads to 2% of (II), 10% of cyclododecadiene, and 87% of cyclododecene[94].

The addition of halogens and halogenocarbenes, oxidation, hydroboration, and carboxylation are other reactions involving double bonds in (I) and (II). When (I) and (II) are brominated, a mixture of dibromocyclododecadiene, tetrabromocyclododecene, and hexabromocyclododecane is formed[68,95,96]. However, it has been stated in patents[97,98] that, when one mole of (I) is brominated with two moles of Br_2 in the presence of sodium acetate, tetrabromocyclododecene is formed quantitatively. It has been shown[68] that hexabromocyclododecane obtained from (II) has a melting point of 194–195°C, while that obtained from (I) has a melting point of 177–178°C. These bromo-derivatives are different geometrical isomers. On recrystallisation from benzene, the hexabromocyclododecane obtained from (I) gives rise to the clathrate compound $(C_{12}H_{18}Br_6)_2C_6H_6$.[75] Hexabromocyclododecane has found an application as an additive to polymeric materials in order to render them incombustible.

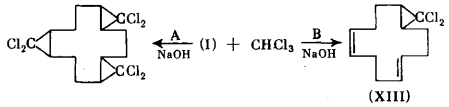
The addition of halogenocarbenes to (I) and (II) has been investigated in detail. The addition of $:CCl_2$ to (II) takes place preferentially at the *trans*-double bond[99]. When $:CHCl$ [100] and $:CCl_2$ [101] act on (I), a mixture of three products is formed:



Treatment of (I) with $:CBr_2$ gives a high yield of dibromobicyclotridecadiene[102], which on treatment with $AgNO_3$ in water is converted into bromohydroxycyclotridecatriene; on treatment with sodium in liquid ammonia, the latter is converted into hydroxycyclotridecatriene:

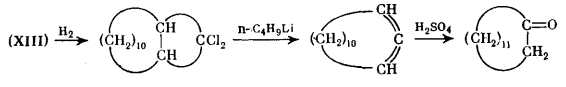


The addition of $:CCl_2$ to (II) under the conditions of phase-transfer catalysis leads to different results depending on the ammonium salt used[103]:

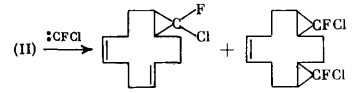


(XIII)

where A = cetyltrimethylammonium bromide and B = trialkyl-β-hydroxyethylammonium bromide. When the diene (XIII) is hydrogenated, the product is 13,13-dichlorobicyclo[10,1,0]tridecane, from which cyclotridecanone was obtained[104]:

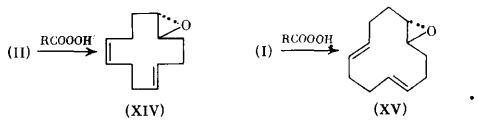


The reaction of (II) with :CFCl takes place at the *trans*-double bonds with formation of two addition products[105]:



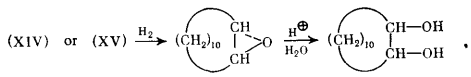
The addition of $:CHOCH_3$ to (I) entails the formation of only *trans*-13-methoxybicyclo[10,1,0]trideca-*trans*,*trans*-4,8-diene, while a mixture of diastereoisomers is formed from (II) under these conditions[106]. The reaction of $:CCl_2$ with *cis*,*trans*-1,5-cyclododecadiene takes place unambiguously, resulting in the formation of *trans*-13,13-dichlorobicyclo-[10,1,0]tridec-4-ene(*cis*).[108] A study of the rates of addition of :CHCl,[100] $:CBr_2$,[107] and $:CHOCH_3$ [106] to *cis*- and *trans*-cyclododecenes showed that the reaction involving the *trans*-double bond is faster.

The oxidation of (I) and (II) to epoxycyclododecadiene, further transformations of which lead to interesting and valuable products, is preparatively important. The epoxidation of (I) and (II) has been carried out with peracetic, perbenzoic, and perphthalic acids, as well as a mixture of H_2O_2 and CH_3COOH in the presence of a cation-exchange resin[5,11,68,109–114]. In the epoxidation of (II) the *trans*-double bond reacts first with formation of the epoxydiene (XIV)[68]:

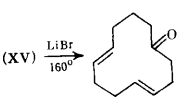


(XIV) (XV)

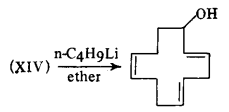
It has been established[112] that monoepoxidation of (II) results in the formation of 92% of the *trans*-epoxide and 7% of the *cis*-epoxide. The epoxidation of (I) yielded the epoxydiene (XV). The oxidation of (I) and (II) by atmospheric oxygen in the presence of boric acid or its esters leads to the formation of epoxycyclododecadiene together with 2,6,10-cyclododecatrienol[115]. The synthesis of 5,6 : 9,10-diepoxycyclododecene, 5,6 : 9,10-diepoxycyclododecane[116], 1,2 : 5,6 : 9,10-triepoxycyclododecane[117], and epoxycyclododecene[118,119] has been described in patents. The opening of the epoxy-rings of these compounds results in the formation of the corresponding diols, tetraols, and hexaols[68,74,120–122]; thus (XIV) and (XV) give rise to the corresponding *trans*-dihydroxycyclododecadienes[68]. The reduction of double bonds in (XIV) and (XV) leads to *trans*-epoxycyclododecane and subsequent opening of the epoxy-ring gives rise to *cis*-1,2-cyclododecanediol[68,123]:



In the presence of catalytic amounts of Group I and II metal halides epoxycyclododecadienes readily isomerise to the corresponding ketones[124,125]:

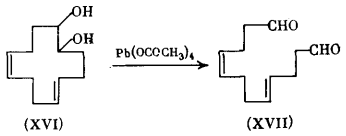


Two isomeric unsaturated ketones with different positions of the keto-group in relation to the C=C double bonds are formed from (XIV).[125] When (XIV) is acted upon by $(iso\text{-}C_4H_9)_2AlH$,[126] $n\text{-}C_4H_9Li$, or C_4H_9MgBr [127] isomerisation with formation of unsaturated alcohols takes place:

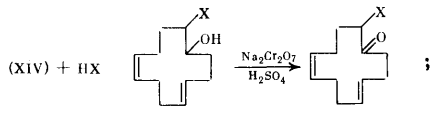


The isomerisation of the epoxide and the formation of cyclododecanone[11,75,110] together with cyclododecanol are observed in the catalytic hydrogenation of (XIV) or (XV) in the presence of nickel catalysts (Raney nickel, Ni/Al_2O_3, Ni/Cr_2O_3) at 120–150°C.

When (II) is oxidised by OsO_4 or $KMnO_4$, the reaction proceeds primarily at the *trans*-double bond with formation of the corresponding *trans*-diol and *trans,trans*-tetraol[128]. When cyclododecadienediol (XVI) was oxidised, the unsaturated dialdehyde (XVII) was obtained[129]:

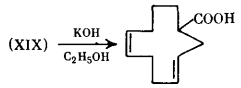


The opening of the epoxy-ring in (XIV) and (XV) takes place readily under the influence of hydrochloric and hydrobromic acids with formation of the corresponding halogenohydrins (XVIII)[114]:

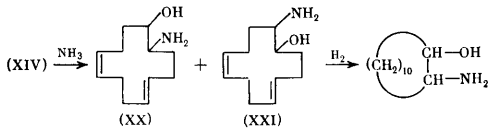


X = Cl or Br.

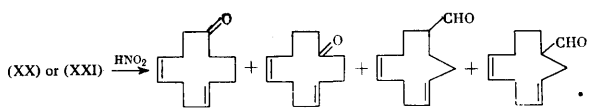
When the halogenohydrins (XVIII) are oxidised by the chromic acid mixture, it is possible to obtain high yields of the unsaturated halogeno-ketones (XIX). The halogenohydrins and the halogeno-ketones obtained from the epoxide (XIV) consist of a mixture of isomers with different positions of the OH group, the halogen atom, and the carboxy-group relative to the *cis*- and *trans*-double bonds in the ring[114]. Cycloundecadienecarboxylic acid has been obtained from the ketones (XIX) by the Favorskii reaction[114]:



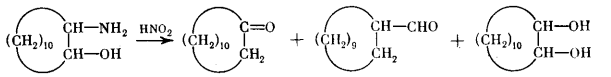
On heating with an aqueous ammonia solution, the epoxide (XIV) gives rise to a mixture of two isomeric *cis*-aminoalcohols (XX) and (XXI)[130], which form *cis*-1,2-aminocyclododecanol on hydrogenation:



When (XX) and (XXI) were deaminated, a mixture of isomeric cyclododecadienones and formylcycloundecadienes was isolated[130]:

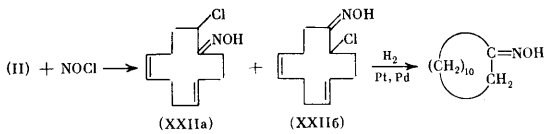


Regardless of the configuration of the initial compound, the deamination of *cis*- and *trans*-2-aminocyclododecanols leads to a mixture of cyclododecanone, formylcycloundecane and *cis*-1,2-cyclododecanediol in equal proportions[130]:

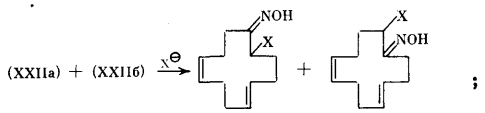


When α-aminocyclododecanecarboxylic acid is deaminated, α-hydroxycyclododecanecarboxylic acid is obtained in a quantitative yield[131].

Nitrosyl chloride readily adds to (II) at a *trans*-double bond with formation of two products (XXII, a and b)[132–140]:

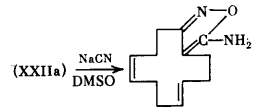


The hydrogenation of chloro-oximes at atmospheric pressure in the presence of platinum and palladium catalysts yields cyclododecanone oxime as the main product[132,133,135]. Several patents[141–144] and another communication[140] describe chlorine exchange reactions involving α-chlorocyclododecadienone oxime. When (XXIIa) and (XXIIb) are treated with nucleophiles, products resulting from the substitution of a chlorine atom are obtained in a high yield[142]:

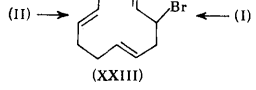


X = C_2H_5O, CH_3O, C_2H_5S, CH_3COO, or R_2N.

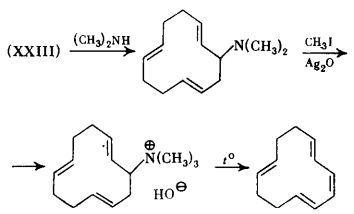
The reaction of (XXIIa) with sodium cyanide in dimethyl sulphoxide (DMSO) leads to the formation of the corresponding aminoisoxazoles[140], for example:



Allylic bromination of (II) by *N*-bromosuccinimide proceeds with isomerisation involving the *cis*-double bond and leads to bromocyclododecatriene (XXIII), which is also obtained on allylic bromination of (I)[58]:

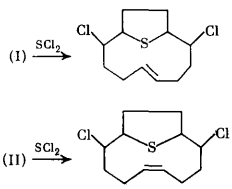


Treatment of the bromo-derivative (XXIII) with ammonia, dimethylamine, and potassium acetate gives rise to substitution products[58], for example:

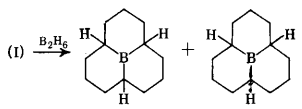


Acylation of (II) via the Kondakov reaction yields a mixture of 1-acyl-2,5-9- and 1-acyl-1,5,9-cyclododecatrienes[145]. Reactions involving the addition of sulphur

dichloride to (I) and (II) and leading to dichlorothiabicyclotridecenes are of interest[146,152]:

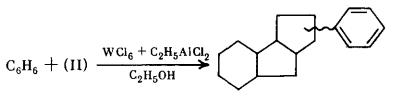


The chlorine atoms in these compounds are readily replaced by cyano- and acetoxy-groups[152]. The hydroboration of (II) gives rise to a mixture of the *cis*- and *trans*-isomers of 9*b*-boraperhydrophenalene (XXIV, a and b) together with 9*b*-boraperhydrobenzo[*ed*]azulene. The latter is converted into *cis*-9*b*-boraperhydrophenalene on heating[147,148]:



(XXIVa) (XXIVb)

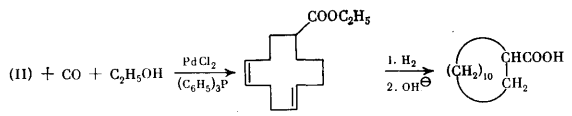
(XXIVa) readily reacts with LiH to form an addition product, which is an effective stereoselective reducing agent for cyclic ketones[149,150]. Trichlorosilane and dichloromethylsilane add to (II) preferentially at the *trans*-double bond in the presence of platinum[151]. When (II) is treated with hydrogen bromide in the presence of benzoyl peroxide, 9-halogeno-1,5-cyclododecadiene is obtained[154]. The reaction of (II) with nitrogen oxides has been described[155]. When (II) reacts with benzene in the presence of the $WCl_6 + C_2H_5AlCl_2 + C_2H_5OH$ system, phenyltricyclo[6,4,0,$0^{2,6}$]dodecane is formed[156]:



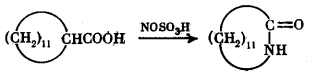
Incomplete ozonisation of (I) and (II) with subsequent cleavage of the ozonide leads to deca-3,7-diene-1,10-dicarboxylic acid and the corresponding dialdehyde[157,158]:

$$\text{(I) or (II)} \xrightarrow{O_3} \rightarrow HOOC(CH_2)_2CH{=}CH(CH_2)_2CH{=}CH(CH_2)_2COOH .$$

It has been established that ozone attacks (I) and (II) at the same rate[159]. The carbonylation of (I) and (II) under the influence of CO in the presence of metal (Ni, Co) carbonyls and palladium complexes with formation of cyclododecanecarboxylic acid has been described in several communications[160-167]. The carbonylation of (II) with the aid of palladium catalysts in alcohol gives rise to a high yield of ethyl 4,8-cyclododecadienecarboxylate[162]:

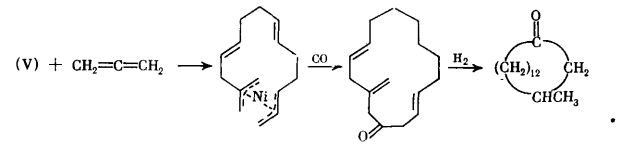


When cyclododecanecarboxylic acid is acted upon by nitrosylsulphuric acid, ω-dodecalactam is obtained in a high yield[168,169]:

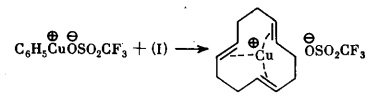


Certain other reactions of cyclododecanecarboxylic acid have been described[170,171]. (I) and (II) react on heating with maleic anhydride to form 1 : 1 adducts[172-174]. The condensation of (II) with cyclopentadiene has been described[175].

Metal complexes of (I) and (II) are known. A π-allyl complex of (V), which reacts with allene, has been described[176,177]. Subsequent reactions of the product lead to the synthesis of DL-muscone:



π-Complexes of palladium $(C_{12}H_{17-19}PdCl)_2$[178] and copper[179,180] have been obtained and a copper complex, synthesised by the reaction[181,182]



has been synthesised.

When a heptane solution of (I) is refluxed with bis(trimethylgermyl)tetracarbonylruthenium, a mixture of products with different structures is formed[183]. The reaction of (I) with dodecacarbonyltriruthenium also leads to a mixture of products having different compositions[184]:

$$\text{(I)} + Ru_3(CO)_{12} \rightarrow HRu_3(CO)_9(C_{12}H_{15}) + HRu_3(CO)_9(C_{12}H_{17}) + HRu(CO)_7(C_{24}H_{34}) + Ru_4(CO)_{10}(C_{12}H_{16}) .$$

Analogous complexes have been obtained for rhodium[185,186], iridium[187], nickel[40,48], and iron[188].

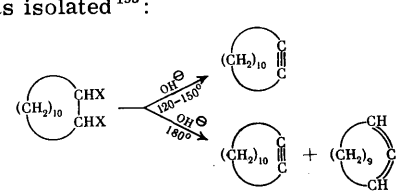
Silver nitrate forms with (I) three types of adducts in which one, two, or three *trans*-double bonds are coordinated to the silver ion[56,68,189]:

$$C_{12}H_{18} \cdot AgNO_3, \quad C_{12}H_{18} \cdot 2AgNO_3, \quad C_{12}H_{18} \cdot 3AgNO_3 .$$

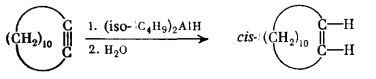
When (II) reacts with a silver ion, only the two *trans*-double bonds are coordinated, while the *cis*-double bond is unaffected[68,189].

IV. SYNTHESES BASED ON *cis*- AND *trans*-CYCLODODECENES

Several methods for the synthesis of *cis*- and *trans*-cyclododecenes (XXV) and (XXVI) are known. It was noted above that they are obtained on selective hydrogenation of (I) and (II)[83,84,91-94] in the presence of homogeneous catalysts or when (II) is acted upon by di-imide[80]. A mixture of (XXV) and (XXVI) is formed when HCl is eliminated from chlorocyclododecane in the presence of iron-containing catalysts[190]. Dehalogenation of 1,2-dichloro- or 1,2-dibromo-cyclododecane by sodionaphthalene or sodiobiphenyl gives a 90% yield of a mixture of (XXV) and (XXVI)[191]. When 1,2-dihalogenocyclododecanes are heated in the presence of alkalis at 150°C, only cyclododecyne is formed[192-194]. On raising the temperature to 180°C, a mixture of 28% of 1,2-cyclododecadiene and 72% of cyclododecyne was isolated[193]:

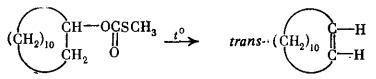


An analogous mixture was obtained after double dehydrobromination of dibromocyclododecane with alcoholic alkali [130]. When cyclododecyne is reduced by (iso-$C_4H_9)_2$.AlH, mainly 6-cyclododecene is formed [193]:



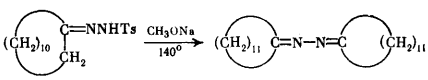
(XXV)

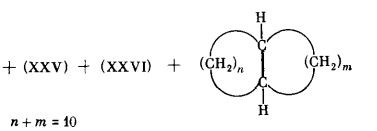
A mixture of 90% of *cis*- and 10% of *trans*-cyclododecyne is formed on decomposition of cyclododecenone semicarbazone by alkoxides at 180–240°C. [195,196] Pyrolysis of cyclododecyl acetate at 550°C leads to a mixture of isomers (XXV) and (XXVI) in proportions of 1 : 5. [197] When (XXV) or (XXVI) is heated in acetic acid at 80–130°C, *cis–trans* isomerisation takes place with formation of an equilibrium mixture containing approximately equal amounts of (XXV) and (XXVI) [197]. Contrary to the Chugaev rule, the decomposition of *O*-cyclododecyl *S*-methyl thiocarbonate gives rise to *trans*-cyclododecene [130]:



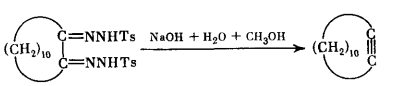
(XXVI)

When cyclododecanol was heated to 250–270°C in the presence of toluene-*p*-sulphonic acid, a high yield of cyclododecene was obtained [198]. The reaction of cyclododecene with *N*-bromosuccinimide and subsequent dehydrobromination of the product in pyridine or quinoline result in the formation of 1,3-cyclododecadiene [199]. The dehydration of 6-hydroxy- or 6-acetoxy-cyclododecanone in the presence of $Zn_3(PO_4)_2$ and Fe_2O_3, leading to cyclododec-5-en-1-one, has been described. In the presence of alkyllithium in tetrahydrofuran (THF), cyclododecanone *N*,*N*-ditosylhydrazone decomposes to form a mixture of *cis*- and *trans*-cyclododecene and cyclododecanone [201]. When cyclododecanone tosylhydrazone is heated in the presence of sodium methoxide, the decomposition leads mainly (to the extent of 60%) to cyclododecanone azine [202]:

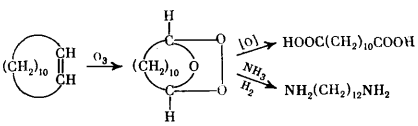




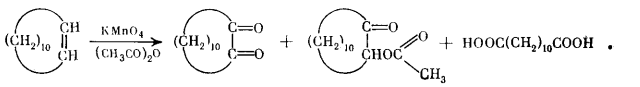
On photolysis of 1,2-cyclododecanedione bistosylhydrazone in an alkaline solution, cyclododecyne was isolated in 53% yield [203]:



Ozonisation with subsequent conversion into decane-1,10-dicarboxylic acid [204–206] and 1,12-diaminododecane [207] is an important reaction of cyclododecene:

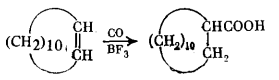


When cyclododecene is oxidised by nitric acid in the presence of ammonium vanadate, considerable amounts of nonane-1,9-dicarboxylic acid are formed together with decane-1,10-dicarboxylic acid [208]. Catalytic oxidation of cyclododecene by hydrogen peroxide in the presence of Re_2O_7 takes place with dissociation of the C=C bond and yields decane-1,10-dicarboxylic acid [209]. Oxidation with potassium permanganate in acetic anhydride leads to 1,2-cyclododecanedione (48%) and other products [210]:

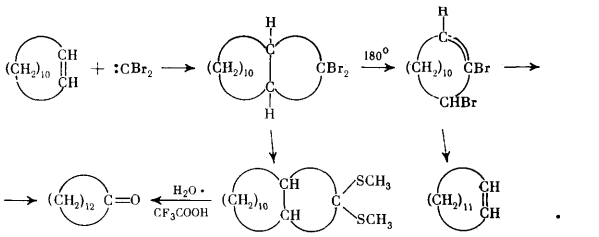


In an alkaline medium in the presence of catalytic amounts of benzyltriethylammonium chloride, *trans*-1,2-cyclododecanediol is formed in 50% yield [211].

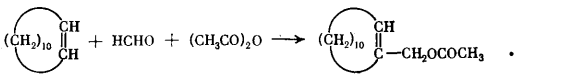
Cyclododecanecarboxylic acid has been obtained from cyclododecene by the Koch reaction [167]:



Dibromocarbene adds smoothly to cyclododecenes with formation of 13,13-dibromobicyclo[10,1,0]tridecane, from which cyclotridecanone [212,213] and cyclotridecene [212] were obtained:

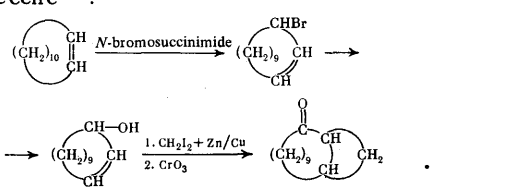


Metathesis of cyclododecene in the presence of the $WCl_5 + C_5H_5AlCl_2$ system yielded unsaturated cyclic hydrocarbons containing 24, 36, and 48 carbon atoms in the ring [214]. The condensation of cyclododecene and (II) with formaldehyde has been described [215]:

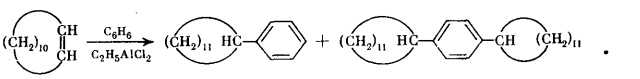


When cyclododecene reacts with paraformaldehyde, *trans*-bicyclo[10,3,0]-2-oxa-14-pentadecene is formed [216].

trans-Bicyclo[10,1,0]-2-tridecanone has been obtained from cyclododecene [217]:

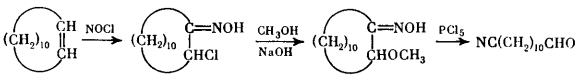


When cyclododecene is acted upon by NO in the presence of O_2, 1-nitroso-2-nitrocyclododecane is obtained. It rearranges on heating in DMF to give 2-nitrocyclododecanone oxime. 1,12-Diaminododecane and ω-nitrolauric acid were obtained from the latter [218]. Cyclododecene undergoes a Friedel–Crafts reaction with benzene and its homologues to form alkylation products [219,220]:



Pyrolysis of (XXV) and (XXVI) results in the cleavage of the ring with formation of 1,8-nonadiene and 1,11-dodecadiene and also in isomerisation involving the double bonds [221]. When cyclododecene was treated with atmospheric oxygen in t-C_4H_9OH in the presence of manganese naphthanate, 1,2,3-cyclododecanetriol was obtained [222]. Photochemical cycloaddition of the olefins (XXV) and (XXVI) to dichlorovinylene carbonate leads to three stereoisomeric carbonates of dichlorobicyclo[10,2,0]-2,3-tetradecanediols [223].

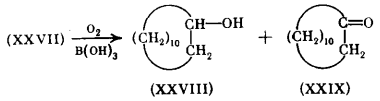
The synthesis of ω-cyanoundecanoic aldehyde from (XXV) and (XXVI) via the mechanism



is of great interest [224]. The reaction of cyclododecene with B_2H_6 yielded the corresponding tri(cyclodecyl)borane [225]. When cyclododecene was treated with nitrogen oxides and air, α-nitrocyclododecanone was obtained in a high yield [226-230]. The mechanism of the oxidation of (XXV) and (XXVI) by molybdenum peroxide has been investigated [231]. A study has been made of the kinetics of the hydrogenation of (XXV) and (XXVI) to cyclododecane in the presence of platinum and palladium blacks [232]. (XXV) and (XXVI) form π-allyl complexes with palladium chloride [233]. The structure of the complex of *trans*-cyclododecene with $AgNO_3$, having the composition (*trans*-$C_{12}H_{22})_2.AgNO_3$, has been investigated [234]. On heating with perfluorobutyne, *cis*, *trans*-1,3-cyclododecadiene gives rise to a mixture of two bicyclic products [235].

V. SYNTHESES OF CYCLODODECANE DERIVATIVES

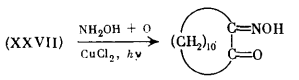
The methods of synthesis of cyclododecane derivatives are of great significance, since the preparation of the industrially important decane-1,1-dicarboxylic acid, 1,12-diaminododecane, and ω-dodecalactam is based on them. The oxidation of cyclododecane (XXVII) by atmospheric oxygen to cyclododecanol (XXVIII) and cyclododecanone (XXIX) has been studied in detail. When (XXVII) is oxidised by oxygen in the presence of boric acid or boron trioxide, a mixture of 80% of (XXVIII), 8–10% of (XXIX), and 10% of polyfunctional oxygen-containing compounds (conversion 30–35%) is formed [69,236]:



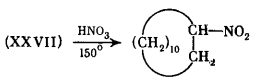
(XXVIII) (XXIX)

The high selectivity of the oxidation in the presence of boric acid has been pointed out in patents [237-239]. A greater amount of the ketone (XXIX) is formed in the presence of manganese or cobalt salts [240,241]. When (XXVII) was oxidised by oxygen in the absence of boric acid, it was found that at the beginning of the process cyclododecyl hydroperoxide, (XXIX), and (XXVIII) accumulate simultaneously [242-245]. After the attainment of the maximum, the concentration of the hydroperoxide falls owing to its thermal decomposition. This results in the formation of a mixture of 70% of (XXIX) and 30% of (XXVIII). Cyclododecane is oxidised to cyclododecyl hydroperoxide in the presence of alkali metal salts [246-248]. A study of the mechanism of the decomposition of cyclododecyl hydroperoxide showed [249] that considerable amounts of undecane and undecyl alcohol are formed in an inert medium, while in the presence of O_2 hardly any undecane is formed. The oxidation of (XXVII) by nitrogen dioxide to decane-1,10-dicarboxylic acid has been reported [250,251].

Treatment of (XXVII) by hydroxylamine and oxygen under irradiation leads to 1,2-cyclododecanedione monoxime [252]:

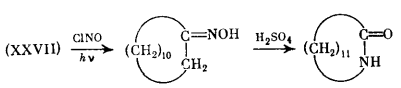


Nitrocyclododecane was obtained in the liquid-phase nitration of (XXVII) by nitric acid [168,253,254]:

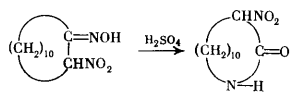


Nitrocyclododecane was also obtained on hydrogenation of 3-nitrocyclododecene [255]. When nitrocyclododecane is treated with a solution of potassium hydroxide, the potassium salt of *aci*-nitrocyclododecane is formed and is converted into *aci*-nitrocyclododecane on acidification [254,256]. This *aci*-form is stable and does not change even on recrystallisation [254]. When nitrocyclododecane was hydrogenated, aminocyclododecane and cyclododecanone oxime were obtained [254,257]. When the potassium salt of *aci*-nitrocyclododecane was treated with $H_2NOH.HCl$, cyclododecanone oxime is formed in a high yield [254].

The hydrolysis of a nitrocyclododecane salt results in the formation of cyclododecanone [254,258,259]. The conversion of nitrocyclododecane into ω-dodecalactam at a high temperature in the presence of certain metal oxides has been described [260]. Numerous studies have been devoted to the photonitrosation of (XXVII) to cyclododecanone oxime [139,153,168,261-266] and to the isomerisation of cyclododecanone oxime to ω-dodecalactam, which is the initial compound in the synthesis of polyamide-12 [261,262,267-271]:

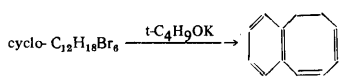


Nitrododecalactam has been obtained by treating α-nitrocyclododecanone oxime with concentrated sulphuric acid at 40-50° C:[272]



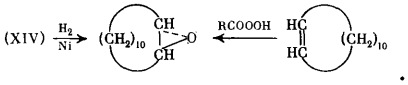
The acid or alkaline hydrolysis of ω-dodecalactam results in the formation of ω-aminododecanoic acid [11,273,274].

The photochemical chlorination of (XXVII) to monochlorocyclododecane has been investigated [75,275,276]. Monochlorocyclododecane undergoes the Friedel–Crafts reaction in benzene and toluene, forming phenyl- and tolyl-cyclododecanes [277]. Hexabromocyclododecane, obtained from (I) and (II) on dehydrobromination, undergoes an unusual transformation into benzocyclo-octatriene [278]:



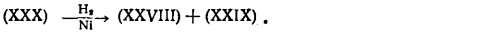
When (XXVII) is heated to 300° C in the presence of platinised charcoal, it undergoes transannular dehydrocyclisation with formation of bicyclic hydrocarbons [279].

Epoxycyclododecane (XXX) has been obtained by the hydrogenation of the double bonds in epoxycyclododecadiene[68] and by the epoxidisation of cyclododecene by peracids[75,130]:

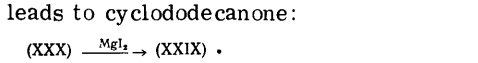


(XXX)

The *cis*- and *trans*-oxides are formed from *cis*- and *trans*-cyclododecene. Catalytic hydrogenation of (XXX) over Raney nickel[11,68,75] leads to the formation of cyclododecanol and cyclododecanone:

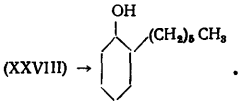


Isomerisation of the epoxide (XXX) under the influence of LiBr[125] or MgI_2[124] leads to cyclododecanone:

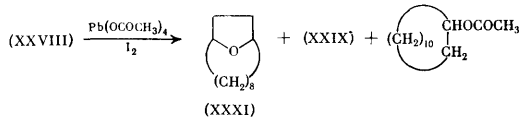


Cyclododecanol has been obtained by hydrating cyclododecene with sulphuric acid[280] and also on hydrogenation and hydrolysis of 1-acetoxy-5,9-*trans*,*trans*-cyclododecadiene[273]. Dehydrogenation of cyclododecanol at 240–250°C under the influence of catalysts (Raney nickel, Cu/Cr, Ni/Al_2O_3, Cu/SiO_2) leads to the formation of cyclododecanone in a high yield[11,70,240,281]. The synthesis of cyclododecanone by the hydrolysis of cyclododecanone oxime has been described[258,259].

Decane-1,10-dicarboxylic acid is formed in a high yield when cyclododecanol or its mixture with cyclododecanone is acted upon by nitric acid in the presence of ammonium metavanadate[11,110,282] or V_2O_5.[283] It has been stated in patents[284,285] that the oxidation of cyclododecanol is accompanied by nitration, which resulted in the isolation of ω,ω-dinitrododecanoic acid; however, the addition of copper powder to the oxidation reaction prevents the formation of nitro-acids[285]. When cyclododecanol is treated with a mixture of $FSO_3H-SbF_5-SO_2$, it isomerises to hexylcyclohexanol[286]:



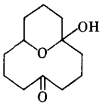
The oxidation of cyclododecanol by lead tetra-acetate in the presence of iodine gives rise to a mixture of oxygen-containing products in which 13-oxabicyclo[8,2,1]dodecane (XXXI) predominates[287]:



(XXXI)

Oxidation in the absence of iodine leads mainly to acetoxycyclododecane.

When cyclododecanediol is heated in the presence of Raney nickel, 2-hydroxycyclododecanone is formed[288], while catalytic oxidation in the presence of $[(C_6H_5)_3P]_3RuCl_2$ and benzaldehyde yields 1,2-cyclododecanedione[289]. Methods for the preparation of 2-alkoxy-1-alkylcyclododecanes[290] and cyclododecylamides[291], which exhibit pharmacological activity, have been described. 1-(Dialkylaminoalkyl)cyclododecyl carboxylates[292] and the esters of 1-(aminoalkyl)cyclododecanol possess bactericidal properties[293]. The oxidation of *cis*,*cis*,*trans*-1,5,9-cyclododecanetriol by the Brown method proceeds with a transannular interaction and leads to the hemiacetal (XXXII) and the acetal (XXXIII) in proportions of 43 : 57.[294]



(XXXII)



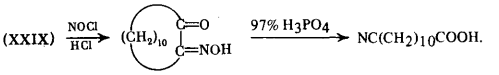
(XXXIII)

VI. SYNTHESES BASED ON CYCLODODECANONE

Numerous compounds have been synthesised on the basis of cyclododecanone (XXIX) and many interesting reactions have been carried out. As stated above, (XXIX) is obtained by the dehydrogenation of cyclododecanol (XXVIII)[11,70,240,281], the isomerisation of epoxycyclododecane (XXX)[124,125], the hydrolysis of cyclododecanone oxime[258,259], and the oxidation of cyclododecane[69,236-248] and cyclododecanol[69]. Several studies have been devoted to the synthesis of cyclododecanone oxime from (XXIX) and its conversion into ω-dodecalactam[11,70,295-297].

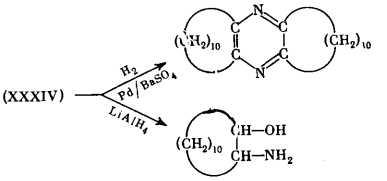
The reaction of hydroxylamine with cyclododecanone under the influence of hydroxylammonium chloride or sulphate takes place readily and in a quantitative yield in the presence of bases (ammonia, potassium or sodium carbonate)[11,70,295,296]. When industrial hydroxylammonium sulphate, containing ammonium sulphate and sodium sulphate, is used, the conversion of cyclododecanone into the oxime takes place without the addition of bases, because sulphuric acid is bound into acid ammonium and sodium salts[11,295]. The reaction with hydroxylamine is carried out in alcoholic, aqueous alcoholic, and aqueous media, a higher temperature being necessary in an aqueous medium. Cyclododecanone oxime forms a 2 : 1 complex with $SnCl_4$.[298]

The mechanism of the Beckmann rearrangement in cyclododecanone oxime has been investigated and it has been found that the process proceeds via a unimolecular mechanism[299]. α-Chlorocyclododecanone oxime is readily obtained when nitrosyl chloride adds to cyclododecene[300]. The substitution of the chlorine atom in α-chlorocyclododecanone oxime by alkoxy- and amino-groups has been described[301-304]. On treatment of (XXIX) with NOCl or $RONO_2$ in the presence of HCl or sodium alkoxide, cyclododecanedione monoxime (XXXIV) is formed in a high yield[305]; it rearranges smoothly to 11-cyanoundecanoic acid under the influence of phosphoric acid[306,307]:



(XXXIV)

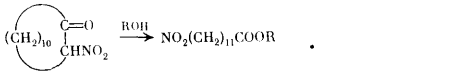
The hydrogenation of (XXXIV) yielded bis-2,3,5,6-decamethylenepyrazine[130]:



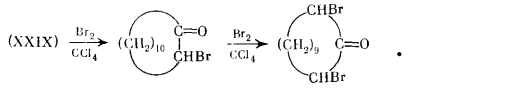
The reaction of (**XXIX**) with NOCl and ethanol in SO_2 leads to the cleavage of the ring via the mechanism[308]:

$$(XXIX) + NOCl + C_2H_5OH \xrightarrow{SO_2} HON{=}CH(CH_2)_{10}COOC_2H_5 .$$

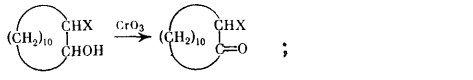
α-Nitrocyclododecanone is obtained by the hydrolysis of its oxime with hydrochloric acid[309]. The alcoholysis of α-nitrocyclododecanone results in the formation of ω-nitrododecanoate esters[310]:



When (**XXIX**) is brominated, monobromo- or dibromocyclododecanone[311] is obtained:



Monohalogenocyclododecanones are readily formed on oxidation of the corresponding halogenohydrins[114]:



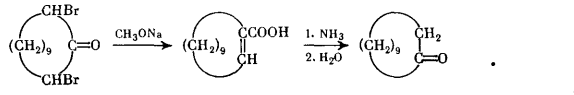
X = Cl, or Br.

The Favorskii rearrangement of α-halogenocyclododecanones under the influence of alcoholic alkali leads to the formation of cycloundecanecarboxylic acid[114]:

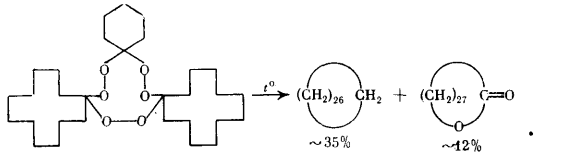


X = Cl, or Br.

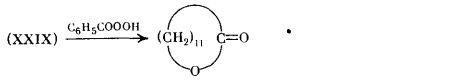
Under these conditions, α,α'-dibromocyclododecanone gives rise to cycloundecenecarboxylic acid, which has been converted into cycloundecanone[311,312]:



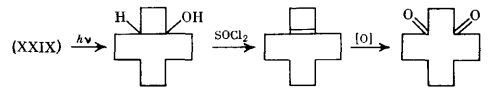
The oxidation of (**XXIX**) by hydrogen peroxide in the presence of SeO_2 leads to cycloundecanecarboxylic acid[313]. Cyclododecanone peroxide has been obtained by treating (**XXIX**) dissolved in carboxylic acids with H_2O_2.[314,315] In the presence of cyclic ketones bis(cyclododecylidene) cycloalkylidene triperoxides are formed[316] and their thermal decomposition in chlorobenzene leads to macrocyclic compounds, for example:



Perbenzoic acid[317-319], Caro's acid, and hydrogen peroxide in sulphuric acid[318] were used to oxidise (**XXIX**) to dodecanolide:



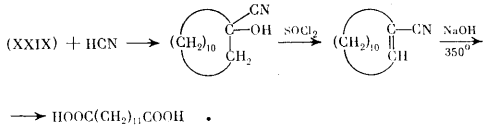
Irradiation of (**XXIX**) results in a transannular rearrangement with formation of bicyclo[8,2,0]dodecan-1-ol[320,321]:



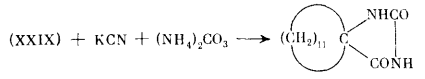
On heating cyclododecanone and cyclododecanol with alkalis to 350°C, a mixture of lauric and nonane-1,9-dicarboxylic acid is formed in 90% yield[322-324]:

$$(XXVIII) + (XXIX) \xrightarrow[350^\circ]{KOH} CH_3(CH_2)_{10}COOH + HOOC(CH_2)_9COOH .$$

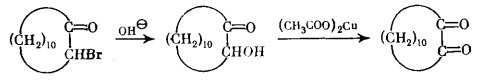
The addition of hydrocyanic acid to (**XXIX**) takes place readily in the presence of $(C_2H_5)_3N$ with formation of a cyanohydrin[325-327], from which cyclododecanecarboxylic acid[326], cyclotridecanone[327], and brassylic acid[325] were obtained:



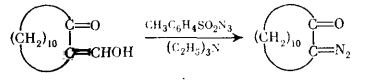
The formation of hydantoins from cyclododecanone or cyclododecenones has been described[328]:



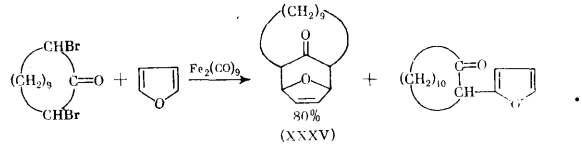
1,2-Cyclododecanedione is formed in a high yield on heating hydroxycyclododecanone with copper diacetate[329,330]:



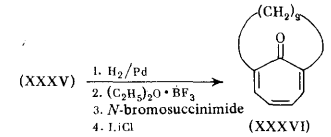
Diazocyclododecanone has been obtained by the reaction[331]:



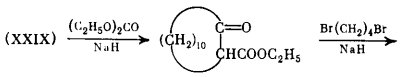
α-Halogenocyclododecanones are readily reduced to cyclododecanone in the presence of LiI and $(C_2H_5)_2O.BF_3$.[332] The reaction of α,α'-dibromocyclododecanone with furan in the presence of $Fe_2(CO)_9$ takes place in an interesting manner[333]:



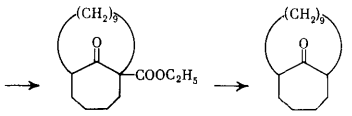
(**XXXV**) has been converted via a series of stages into tropone (**XXXVI**)[334]:



Tropone has been obtained from cyclododecanone also in accordance with another scheme via the ethoxycarbonyl derivative (**XXXVII**)[335]:

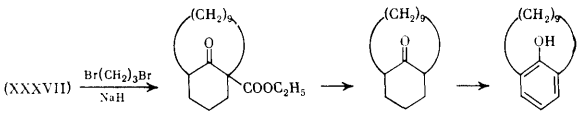


(XXXVII)



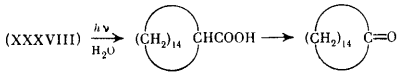
(XXXVIII)

When the ketone (**XXXVIII**) was brominated and debrominated, tropone was obtained[336]. Metacyclophane (**XXXIX**) was synthesised similarly[336]:



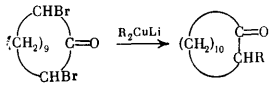
(XXXIX)

Ultraviolet irradiation of the ketone (**XXXVIII**) led to the formation of cyclopentadecanecarboxylic acid (**XL**), which was converted into cyclopentadecanone[335,337]:

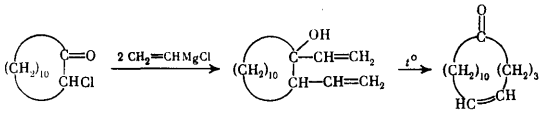


(XL)

A new method has been proposed for the alkylation of α,α'-dibromocyclododecanone with formation of α-alkylcyclododecanones[338,339]:

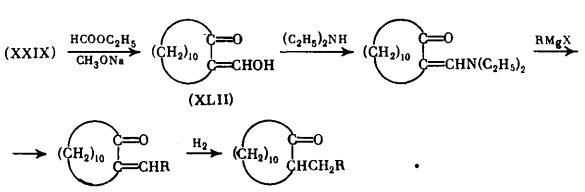


The action of a Grignard reagent on (**XXIX**) with formation of alkylcyclododecanols has been investigated[202]. Methylcyclododecanone has been obtained by the reaction of bromocyclododecanone with CH_3ZnI in DMSO[202]. The reaction of chlorocyclododecanone with two moles of vinylmagnesium chloride leads to the formation of (**XLI**), which is converted into 5-cyclohexadecenone after the Cope rearrangement[340,341]:

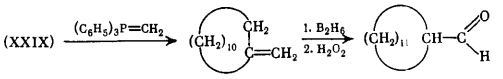


(XLI)

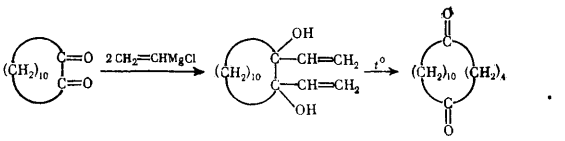
α-Alkylcyclododecanones have been obtained by the formylation of (**XXIX**) via the mechanism[342]:



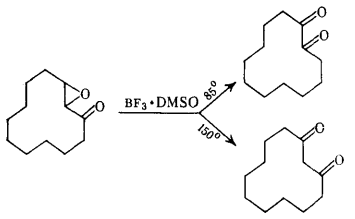
(XLII) undergoes oxidative cleavage by hydrogen peroxide, which leads to brassylic acid[325]. Formylcyclododecane was synthesised from (**XXIX**) as follows[202]:



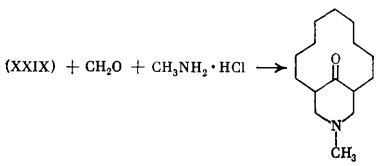
A method has been described for the synthesis of 1,6-cyclohexadecanedione by treating 1,2-cyclododecanedione with vinylmagnesium chloride and a subsequent rearrangement[343]:



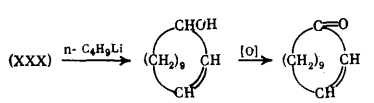
Depending on temperature, the isomerisation of 2,3-epoxycyclododecanone takes place with formation of 1,2- or 1,3-cyclododecanediones[345]:



Methods have been developed for the synthesis of [7]-metacyclophane and its bromo-derivative via the aldol condensation of 1,4-cyclododecanedione[346,347] and [7](2,6)pyridinophane derived from 1,5-cyclododecanedione[348,349]. Cyclododecanone has been made to undergo the Mannich reaction[350,351]:



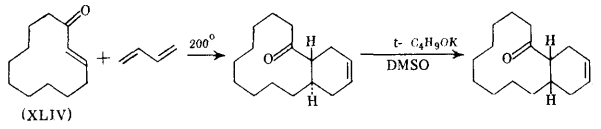
The *cis*- and *trans*-2-cyclododecenones (**XLIII**) and (**XLIV**) were obtained from epoxycyclododecane[352]:



(XLIII) (*cis*-)
(XLIV) (*trans*-).

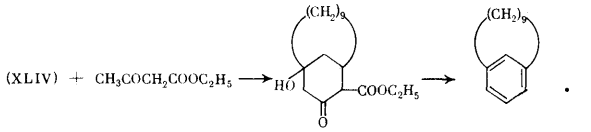
The synthesis of a mixture of *cis*- and *trans*-cyclododecenones by the bromination of cyclododecanone ethylene acetal and subsequent dehydrobromination by t-C_4H_9OK in DMSO has been proposed[353]. *cis*-Cyclododecenone (**XLIII**) is thermodynamically less stable than the *trans*-isomer (**XLIV**) and isomerises to the latter[352]. Ultraviolet irradiation of a hexane solution of (**XLIV**) leads to a mixture of (**XLIII**) and *cis*-3-cyclododecenone[352]. Diene condensation

of (XLIV) with butadiene leads to *trans*-bicyclo[10,4,0]-hexadec-14(15)-en-2-one, which wholly isomerises to the *cis*-isomer on treatment with t-C_4H_9OK.[354]

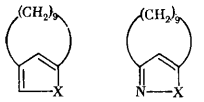


(XLIV)

The *cis*-isomer (XLIII) does not undergo diene condensation with butadiene. [9]Metacyclophane and [9](2,4)pyridinophane have been obtained by the reaction of (XLIV) with acetoacetic or cyanoacetic ester and subsequent reactions of the adducts[355]:

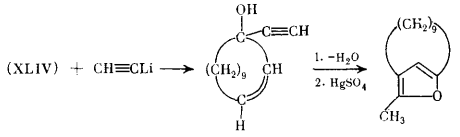


A series of [9]heterophanes have been obtained from (XLIV)[356,357]:

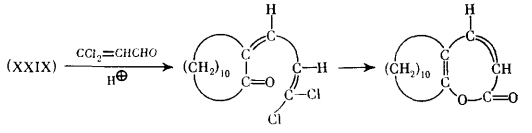


X = O or S X = O or NH

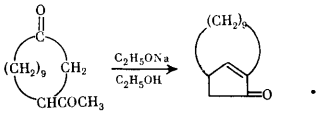
When (XLIV) reacts with hydrazine hydrate and this is followed by dehydrogenation with sulphur, [9](3,5)pyrazolophane is formed, while treatment with lithium acetylide and further cyclisation lead to 11-methyl[9](2,4)furanophane[353]:



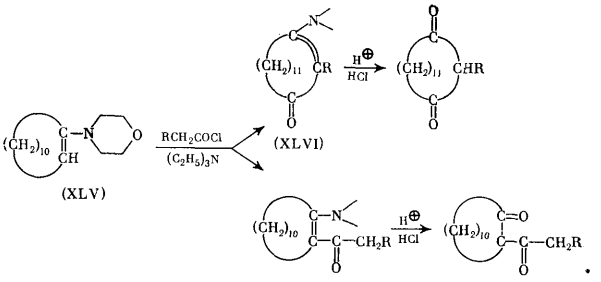
Decamethylene-α-pyrone has been obtained by the condensation of (XXIX) with dichloroacrolein and subsequent cyclisation[358]:



The product of the condensation of 1-methoxycyclododecene with 2-methylbut-3-yne-2-ol undergoes the Cope rearrangement to give 3,3-dimethylallenylcyclododecenone, which isomerises on ultraviolet irradiation to 4-isopropylidenecyclotetradecenone[359]. When 3-acetylcyclododecanone is acted upon by C_2H_5ONa, a bicyclic ketone is formed[360]:

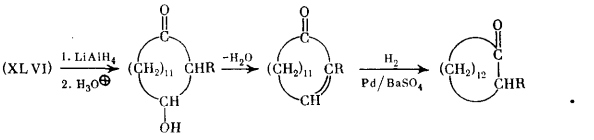


Enamines have found extensive applications in the synthesis of various cyclododecanone derivatives[361-363]. When morpholinocyclododecene (XLV) is treated with carboxylic acid chlorides in the presence of $(C_2H_5)_3N$, 2-alkyl-1,3-cyclotetradecanediones (resulting from the insertion of two carbon atoms in the ring) and acylation products are formed[364,365]:



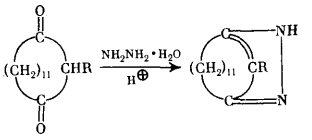
(XLV) (XLVI)

When (XLVI) was treated with lithium tetrahydroaluminate and this was followed by dehydration and hydrogenation, methyl- and ethyl-cyclotetradecanones, which have a strong musk-like scent, were obtained[366]:

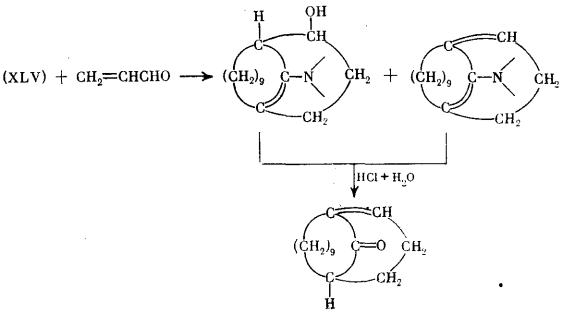


R = CH_3, C_2H_5

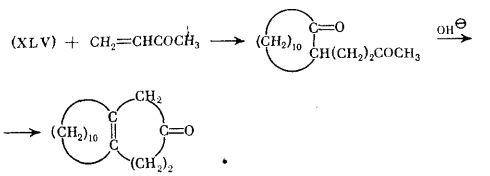
The interaction of 2-alkyl-1,3-cyclotetradecanedione with hydrazine hydrate[364] or 2,4-dinitrophenylhydrazine[366] leads to a pyrazole derivative:



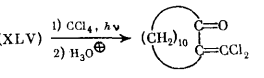
When acrolein acts on (XLV), an interesting reaction takes place[344]:



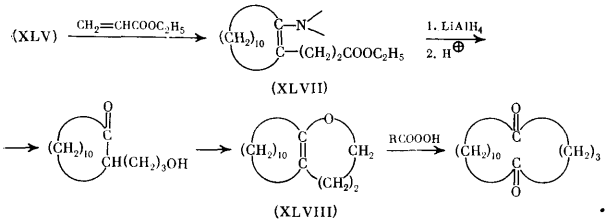
The interaction of (XLV) with methyl vinyl ketone leads to a bicyclic ketone[367]:



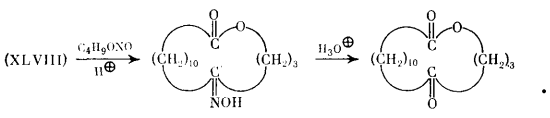
When (XLV) is irradiated with ultraviolet light in the presence of CCl_4, a dichlorovinyl ketone is formed[368]:



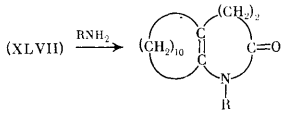
Oxopentadecanolide has been synthesised from (XLV) and ethyl acrylate via the mechanism[369]



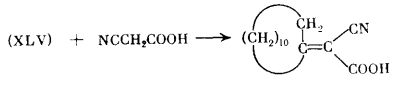
Hydrolysis of (XLVII) leads to β-(2-oxocyclododecyl)propionic acid[344,370]. Ultraviolet irradiation of this acid results in the formation of ω-formyl-4-tetradecenoic acid, whose reduction leads to ω-hydroxypentadecanoic acid[370]. Oxopentadecanolide has also been obtained from (XLVIII) by treatment with butyl nitrite and subsequent hydrolysis[371]:



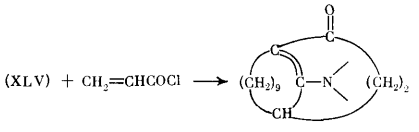
Similarly 1-acetyl-13-hydroxyimino-1-azahexadecan-2-one was obtained from 1-acetyl-2,3-decamethylene-1,4,5,6-tetrahydropyridine[372]. Treatment of the ketoester obtained from (XLVII) with alkylamines leads to the synthesis of bicyclic lactams[373]:



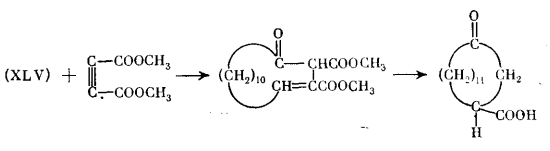
The reactions of (XLV) with a substituted cyclopropene[374] and dibromoacetone have been investigated[375]. The morpholine residue in (XLV) undergoes an exchange reaction with cyanoacetic acid[376]:



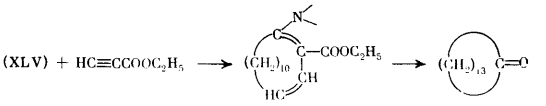
When (XLV) interacts with acryloyl chloride, a bicyclic product is formed[377]:



α-(2-Oxocyclododecyl)acetic acid has been obtained by the reaction of (XLV) with a bromoacetate ester[344]. When pyrrolidinocyclododecene condenses with an ester of acetylenedicarboxylic acid[378], ring expansion takes place with formation of a cyclotetradecenone derivative, which has been converted into 3-carboxycyclotetradecanone[376]:

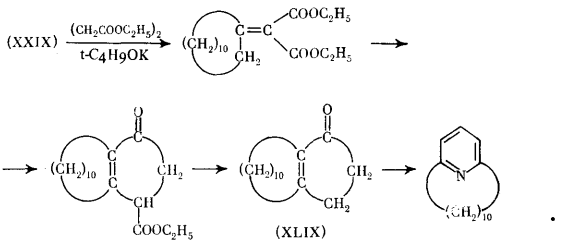


Cyclotetradecanone has been obtained by the reaction of (XLV) with ethyl propiolate[379]:

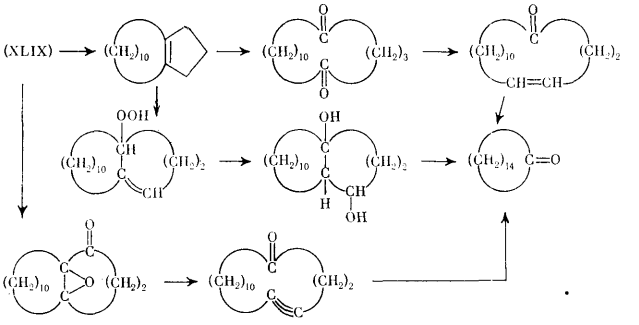


Using this reaction, it is possible to obtain the racemic muscone[380]. A series of methods of synthesis of muscone, cyclopentadecanone (exaltone), pentadecanolide (tibetolide), and methylpentadecanolide (muscolide), which are valuable perfumes, have been developed on the basis of cyclododecanone.

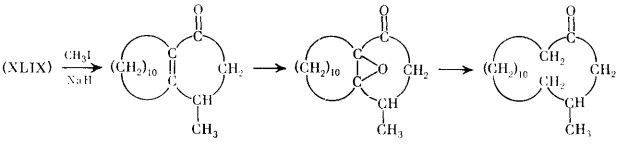
The synthesis of natural muscopyridine from cyclododecanone has been achieved by the Stobbe reaction via (XLIX)[381]:



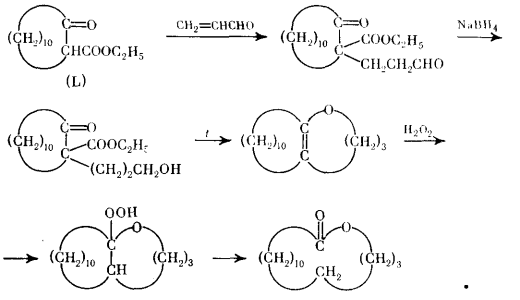
This reaction has served as the basis of a method of synthesis of cyclopentadecanone[382-385]:



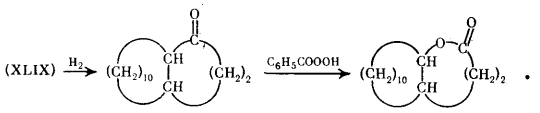
Muscone has been obtained from (XLIX) via the mechanism[383]



A convenient method of synthesis of cyclopentadecanolide via the mechanism[335,337]



has been developed. The methyl analogue of cyclopentadecanolide (muscolide) has been obtained similarly from (L) and methacrolein[328,337]. It has been reported that γ,δ-decamethylene-δ-valerolactone has a strong musk-like scent[386,387]. It has been synthesised via the mechanism



The products of the reaction of cyclododecanone with glycols[388] are components of perfumes.

During the preparation of the review for the press, studies which are of interest were published. An industrial method of synthesising compound (II) (1,5,9-CDT) by a continuous method in the presence of the $(C_2H_5)_2AlCl$–$TiCl_4$ catalytic system has been developed[389]. A mechanism has been proposed for the cyclisation of butadiene to (I) in the presence of $Ni(C_5H_7O_2)_2 + (C_2H_5)_3Al$.[390] Partial ozonolysis of (I), with subsequent reduction of the peroxy-compounds formed by dimethyl sulphide, leads to 1,12-diformyl-*trans*,*trans*-4,8-dodecadiene[391]. Conditions have been found for the selective hydrogenation of (II) to (XXVI) in the presence of $RuCl_2(PPh_3)_3$ activated by $(C_2H_5)_3N$.[392] The reaction of (XXV) and (XXVI) with *N*-bromosuccinimide in the presence of water, methanol, or acetic acid proceeds with formation of 2-bromocyclododecanol, 2-bromo-1-methoxycyclododecane, and 1-acetoxy-2-bromocyclododecane respectively[393]. Oxidation of a mixture of (XXV) and (XXVI) by Jones reagent in the presence of mercury propionate leads to cyclododecanone[394]. It was noticed for the first time that oxidation of cyclododecane by air results in the formation of 2–3% of *trans*-epoxycyclododecane[395]. The isomerisation of epoxycyclododecane to cyclododecanone proceeds with a high yield in the presence of palladium and rhodium catalysts[396]. When epoxycyclododecane is acted upon by formaldehyde in the presence of $AlCl_3$, 13,15-dioxabicyclo[10,3,0]pentadecane and 13,15,17-trioxabicyclo[10,5,0]heptadecane are formed[397]. On ultraviolet irradiation, a mixture of 36% of methyl cycloundecanecarboxylate, 17% of *cis*- and 25% of *trans*-cyclododecenones, and 9% of *cis*-3-cyclododecenone is formed on ultraviolet irradiation of α-diazocyclododecanone[398]; the reaction involving 2-methylcyclododecanone takes place with ring cleavage and the formation of 40% of formyl-12-dodecene[399]. A synthesis of bicyclo[10,3,0]pentadeca-1(12)-en-13-one and its methyl analogues from cyclododecanone has been proposed[400]. Formylcyclodecane has been obtained from cyclododecanone and ethoxymethylmagnesium chloride[401]. Treatment of 1,5-cyclododecadiene with *N*-bromosuccinimide and subsequent reduction of the product with $LiAlH_4$ lead to 13-oxabicyclo[8,2,0]dodecane[402].

A method of synthesis of cyclododecanone oxime on heating cyclododecanone with ammonia in the presence of t-butyl hydroperoxide has been described in a patent[403]. A method of synthesis of 1,3- and 1,4-cyclododecanediones from a mixture of *cis*- and *trans*-3-cyclododecenones has been discovered[404]. [10]Paracyclophane has been synthesised from cyclododecene and methyl acetylenecarboxylate[405]. [9](2,4)Pyrrolophane has been synthesised in two ways: (1) by the condensation and cyclisation of 3-formylcyclododecanone with ammonia and (2) by the condensation of chlorocyclododec-2-en-1-one with di(ethoxycarbonyl)-methylamine[406].

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