The Synthesis and Some Reactions of 1,2-Cyclononadiene and 1,2-Cyclodecadiene

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Received June 29, 1962

The preparation of 1,2-cyclononadiene by dehydrohalogenation of 1-chlorocyclononene and the preparation of 1,2-cyclodecadiene by dehydrohalogenation of 1-chlorocyclodecene are described. 1-Chlorocyclodecene has been found to be a mixture of *cis* and *trans* isomers. 1,2-Cyclononadiene and 1,2-cyclodecadiene react with 2,4-dinitrobenzenesulfenyl chloride to give adducts believed to be 3-(2,4-dinitrobenzenethio)-2-chloro-1-cycloalkenes. Upon heating with strong bases, both cyclic allenes undergo allene–acetylene interconversion. Prolonged heating of 1,2-cyclodecadiene or cyclodecyne with base gives *cis,cis*-1,3-cyclodecadiene and a 1,4-cyclodecadiene which probably has the *cis,trans* configuration.

At the outset of this work although several medium-ring carbocyclic acetylenes had been isolated and characterized, the corresponding allenes had not. The early literature contains a number of reports of the isolation of both classes of compounds but there is no question today that such reports were erroneous and reflect the difficulties encountered in isolation and characterization of labile materials without the physical techniques currently available. Several stable cyclic acetylenes have been prepared by Blomquist[1] and Prelog[2] by the oxidation of 1,2-dihydrazones with mercuric oxide; the smallest carbocyclic acetylene sufficiently stable to permit isolation is cyclooctyne.[1d] By means of isotopic labeling, Roberts has obtained results which indicate that cyclohexyne[3] and cyclopentyne[4] are intermediates in the corresponding 1-chlorocycloalkenes with phenyllithium to give 1-phenylcycloalkenes. By using 1,3-diphenylisobenzofuran and phenylazide as trapping agents, Wittig has obtained adducts from the reaction of 1,2-dibromocycloalkenes with magnesium and from the mercuric oxide oxidation of 1,2-dihydrazones which strongly suggest the transitory existence of cyclopentyne, cyclohexyne, and cycloheptyne.[5]

Blomquist and his co-workers obtained hydrocarbon mixtures in which the presence of nine- and ten-membered cyclic allenes was indicated by infrared spectra and ozonolysis[1b,c]; these workers did not report attempts to isolate the pure allenes. Recently, after the synthetic work reported in the present paper had been completed, we described the synthesis of cyclic allenes (as well as noncyclic) by treatment of *gem*-dibromocyclopropanes with alkyllithium reagents,[6] a reaction which Skatteböl[7] has also employed and which appears to be the method of choice.[8] Ball and Landor[10a] reported that they have effected the same change with high-surface sodium[9] and have also indicated[10a,b] that dehydrohalogenation of 1-chlorocycloalkenes with sodium amide in liquid ammonia yields cyclic allenes.[10c] In this paper, we report the synthesis of two medium-ring cyclic allenes by classical means and examine some aspects of the chemistry of these substances.

Results and Discussion

The method of allene synthesis involved the dehydrochlorination of 1-chlorocycloalkenes, a reaction which originally was investigated as a method for the preparation of cycloalkynes.[1b] The 1-chloroölefins were prepared from the corresponding ketones by treatment with phosphorus pentachloride followed by heating with alcoholic potassium hydroxide. 1-Chlorocyclodecene, which previously had been assigned the *cis* configuration,[1b] was found to be a mixture of approximately equal

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(1) (a) A. T. Blomquist, R. E. Burge, Jr., L. H. Liu, J. C. Bohrer, A. C. Sucsy, and J. Kleis, *J. Am. Chem. Soc.*, **73**, 5510 (1951); (b) A. T. Blomquist, R. E. Burge, Jr., and A. C. Sucsy, *ibid.*, **74**, 3636 (1952); (c) A. T. Blomquist, L. H. Liu, and J. C. Bohrer, *ibid.*, **74**, 3643 (1952); (d) A. T. Blomquist and L. H. Liu, *ibid.*, **75**, 2153 (1953).

(2) (a) V. Prelog, K. Schenker, and H. H. Günthard, *Helv. Chim. Acta*, **35**, 1598 (1952); (b) V. Prelog, K. Schenker, and W. Kueng, *ibid.*, **36**, 471 (1953).

(3) F. Scardiglia and J. D. Roberts, *Tetrahedron*, **1**, 343 (1957).

(4) L. K. Montgomery and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 4750 (1960).

(5) (a) G. Wittig, A. Krebs, and R. Pohlke, *Angew. Chem.*, **72**, 324 (1960); (b) G. Wittig and A. Krebs, *Ber.*, **94**, 3260 (1961); (c) G. Wittig and R. Pohlke, *ibid.*, **94**, 3276 (1961).

(6) (a) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960); (b) W. R. Moore and H. R. Ward, *ibid.*, **27**, 4179 (1962).

(7) L. Skatteböl, *Tetrahedron Letters*, 167 (1961).

(8) P. D. Gardner and M. Narayana, *J. Org. Chem.*, **26**, 3518 (1961), have reported the preparation of 1,2-cyclononadiene by treatment of the dibromocarbene adduct of *cis*-cycloöctene with magnesium[9]; however, see footnote 26.

(9) W. von E. Doering and P. M. LaFlamme, *Tetrahedron*, **2**, 75 (1958).

(10) (a) W. J. Ball and S. R. Landor, *Proc. Chem. Soc.*, 143 (1961); (b) W. J. Ball and S. R. Landor, *J. Chem. Soc.*, 2298 (1962); (c) Since this paper was submitted, the definitive paper by Ball and Landor has appeared (ref. 10b). These authors stated that they obtained 1,2-cyclononadiene containing 15% of cyclononyne and 1,2-cyclodecadiene containing 15% of cyclodecyne. These percentages were based upon the results of oxidative ozonolysis (the yields were not high), a method which we believe did not give an accurate indication of the composition and complexity of their hydrocarbon fractions. In a study of allene–acetylene equilibria,[22] we have found that sodamide in liquid ammonia establishes allene–acetylene equilibria fairly rapidly. Equilibrium is attained in two to three hours with 0.4 to 0.7 *M* sodamide. The equilibrium percentages are C_9, 95% allene and 5% acetylene; C_{10}, 53% allene and 47% acetylene. Moreover, in addition to allene–acetylene interconversion, isomerization to other dienes also occurs; these materials predominate with prolonged contact times. The conditions employed by Ball and Landor for dehydrohalogenation (0.2 to 0.4 *M* sodamide in *excess* for three to four hours) were such that extensive isomerization would have occurred. Since little fractionation of these isomeric hydrocarbons can be effected by distillation, we believe that their samples of allenes consisted of allenes and acetylenes in relative amounts close to the equilibrium values and in addition were seriously contaminated with other dienes as well.

amounts of two isomers. These were separated by gas chromatography and one isomer was found to show infrared absorption at 1656 cm.$^{-1}$ (C=C stretching) while the other absorbs at 1648 cm.$^{-1}$. Clearly these chloroölefins must be *cis* and *trans* isomers.

trans-4-Chloroöctene-4 has been reported[11] to absorb at 1662 cm.$^{-1}$, whereas the *cis* isomer absorbs at 1653 cm.$^{-1}$. Furthermore, in the present work it has been found that 1-chlorocycloheptene, 1-chlorocycloöctene, and 1-chlorocyclononene, all of which presumably have the *cis* configuration, show infrared absorption at 1645, 1642, and 1650 cm.$^{-1}$, respectively. In total, these data suggest that the 1656-cm.$^{-1}$ isomer is *trans*-1-chlorocyclodecene and the 1648-cm.$^{-1}$ isomer is *cis*-1-chlorocyclodecene.

Dehydrochlorination of the mixture of isomeric 1-chlorocyclodecenes by slow distillation from a melt of potassium hydroxide–ethanol afforded a hydrocarbon mixture in about 60% yield which contained 1,2-cyclodecadiene (I) and cyclodecyne (II) in a ratio of 3:2 and in addition contained a total of less than 5% of several other materials which were not identified. Similar product ratios were obtained when samples enriched in *cis* and *trans*-1-chlorocyclodecene were employed. Separation of I and II was facilitated by the observation that silver ion complexes much more strongly with the acetylene than with the allene. A 1:1 (v./v.) methanol–water mixture saturated with silver nitrate readily extracted II from a pentane solution of the hydrocarbon mixture. 1,2-Cyclodecadiene was then purified by preparative gas chromatography employing silver nitrate in tetraethylene glycol as the liquid phase.

1,2-Cyclononadiene (III) was isolated by similar means in about 15–20% over-all yield from cyclononanone. Silver nitrate in methanol–water was found to extract both III and cyclononyne (IV) from a pentane solution. Saturated aqueous silver nitrate, however, removed only IV.

1,2-Cyclononadiene and 1,2-cyclodecadiene show medium-strong absorption in the allene-stretching region of the infrared (1957 and 1962 cm.$^{-1}$, respectively) and only end absorption in the ultraviolet. Both gave the expected dibasic acids in good yield on oxidative ozonolysis and, in addition, the corresponding dialdehyde was obtained from I by reduction of the ozonide.

Partial hydrogenation of I over palladium on charcoal poisoned with pyridine resulted in the uptake of one equivalent of hydrogen to give *ca.* 82% of *cis*-cyclodecene plus 18% of *trans*-cyclodecene. Hydrogenation of III over the same catalyst gave only *cis*-cyclononene plus a small amount of cyclononane (*ca.* 3%); Gardner and Narayana[8] also reported the formation of only *cis*-cyclononene. These reactions were carried out employing conventional preparative procedures *i.e.*, no attempt was made to remove the products rapidly from contact with the catalyst to avoid isomerization of *trans* olefins.[12]

1,2-Cyclononadiene, 1,2-cyclodecadiene, cyclononyne, and cyclodecyne all react with 2,4-dinitrobenzenesulfenyl chloride to form crystalline 1:1 adducts. This reagent is known to react with acetylenes to form simple addition products,[13,14] hence the cyclic acetylene must have given 1-(2,4-dinitrobenzenethio)-2-chloro-1-cycloalkenes. It has been assumed that in analogy to the reactions with olefins, such additions to acetylenes are *trans*,[13-15] but no evidence has been presented to confirm the configurational assignments. If such additions are *trans* in the case of cyclic acetylenes, the results are of some interest since the *trans* olefins are known to be thermodynamically much less stable than the *cis*-olefins in the nine- and ten-membered systems.[16] At present, we can offer no evidence bearing upon the stereochemistry of these adducts.

The allene adducts present additional problems, since an unsymmetrical reagent potentially can add to an allene in two different ways; that is, the product could be either a 3-(2,4-dinitrobenzenethio)-2-chloro-1-cycloalkene or a 2-(2-4-dinitrobenzenethio)-3-chloro-1-cycloalkene.[17] Additionally, each mode of addition could give rise to either a *cis*- or a *trans*-cycloalkene.

Recently, Jacobs and Johnson found that hydrogen chloride reacts with allene and 1,2-butadiene to give only the products arising from addition of the proton to the terminal allenic carbon atom (C-1) but 3-methyl-1,2-butadiene gives only products resulting from addition of the proton to the central allenic carbon atom (C-2).[18] They also reported that 2,4-dinitrobenzenesulfenyl chloride adds to allene to give 2-(2,4-dinitrobenzenethio)-3-chloro-1-propene.[19] Since the reactions of this reagent can be interpreted[14] in terms of polarization as $\overset{\delta+}{\mathrm{ArS}}\text{—}\overset{\delta-}{\mathrm{Cl}}$ or in the limit fragmentation to ArS$^+$ and Cl$^-$, it is apparent that the addition of the sulfenyl halide occurred in the opposite sense to that reported for hydrogen chloride.

In the present case, the 2,4-dinitrobenzenesul-

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[11] J. T. Maynard and W. E. Mochel, *J. Poly. Sci.*, **13**, 251 (1954).

[12] Recently, we have investigated the stereochemistry of hydrogenation of these allenes and related dienes; the results will be reported elsewhere.

[13] N. Kharasch and S. J. Assony, *J. Am. Chem. Soc.*, **75**, 1081 (1953); *ibid.*, **77**, 3390 (1955).

[14] N. Kharasch, *J. Chem. Educ.*, **33**, 585 (1956), gives a review of the reactions of 2,4-dinitrobenzenesulfenyl chloride.

[15] A. J. Havlik and N. Kharasch, *J. Am. Chem. Soc.*, **78**, 1207 (1956).

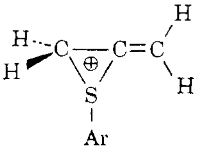
[16] A. C. Cope, P. T. Moore, and W. R. Moore, *ibid.*, **82**, 1744 (1960).

[17] With an unsymmetrically substituted olefin in which the substituents are electronically similar, in general it appears that both modes of orientation will be found and that the selectivity is not high. *Cf.* the data tabulated by R. B. Langford and D. D. Lawson, *J. Chem. Educ.*, **34**, 510 (1957).

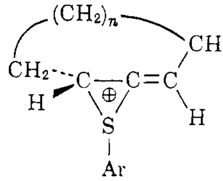
[18] T. L. Jacobs and R. N. Johnson, *J. Am. Chem. Soc.*, **82**, 6397 (1960). These authors also review the sparse literature dealing with the addition of unsymmetrical ionic reagents to allenes.

[19] 1,2-Butadiene and 3-methyl-1,2-butadiene gave mixtures.

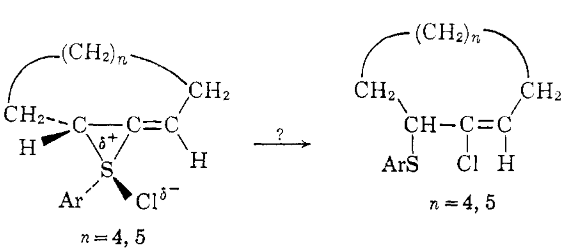
fenyl chloride adducts of both the allenes and the acetylenes were found to have chlorine atoms which were not removed by heating with silver nitrate in acetonitrile nor by heating with methanolic potassium hydroxide. This inertness of the halogen atoms is expected for the acetylene adducts which have the chlorine atoms attached to an olefinic bond. The lack of reactivity observed for the halogen atoms of the allene adducts suggests that these adducts are 3-(2,4-dinitrobenzenethio)-2-chloro-1-cycloalkenes, *i.e.* vinylic chlorides rather than allylic chlorides.[20] At this time we can offer no really satisfactory explanation for the apparent difference in the orientation of addition found for the cyclic allenes and for allene itself. Kharasch has suggested that the reaction of an olefin with 2,4-dinitrobenzenesulfenyl chloride involves formation of a cyclic sulfonium ion which subsequently undergoes attack by chloride ion. Jacobs and Johnson considered that if such a sulfonium ion formed from allene, structure V, it would undergo attack more readily at the methylene group than at the vinylic position. The formation of a cyclic sulfonium ion from a cyclic allene would be expected to occur as shown in structure VI to minimize steric repulsions. "Backside" attack by chloride ion is somewhat hindered by the methylene groups on the side opposite the thioaryl group. It is not apparent, however, why chloride ion would preferentially attack the central (vinylic) carbon atom. It is possible that the representation of a free sulfonium ion in this and other cases is an oversimplification. A more probable intermediate would be one in which the chlorine atom is still joined to the sulfur atom. The normal course of reaction could be backside attack by (external) chloride ion. But where such attack is hindered, a four-center type rearrangement might occur. If so, the product would be a *cis* olefin (whereas the backside attack on C-2 would give a *trans* olefin).[21]



V



VI. $n = 4, 5$



$n = 4, 5$

$n = 4, 5$

Isomerizations.[22]—Heating either I or II with potassium hydroxide in Diethyl Carbitol at 190° gave hydrocarbon mixtures which had allene: acetylene ratios of *ca.* 1.6. Prolonged heating led to the virtual removal of both I and II and resulted in the formation of *cis,cis*-1,3-cyclodecadiene[23] (VII) as the major product (69%–73%) as well as *ca.* 25% of a second diene, VIII, which was not any of the known cyclodecadienes. Hydrogenation of this diene over palladium on Norit resulted in the rapid uptake of two equivalents of hydrogen to give cyclodecane. Ozonolysis followed by oxidation with hydrogen peroxide and esterification with methanol gave dimethyl pimelate plus a smaller amount of dimethyl malonate, thus establishing that VIII is one of the isomeric 1,4-cyclodecadienes. The infrared spectrum of this diene is remarkably rich in the fingerprint region. It exhibits all of the bands of both *cis-* and *trans*-cyclodecene suggesting that the diene is the *cis,trans* isomer. Furthermore, molecular models indicate that the *cis,trans* isomer should be less strained due to nonbonded interactions than the *cis,cis* isomer (the *trans,trans* isomer would be exceptionally strained).

The formation of VII from I and II is not surprising since conjugated dienes are expected to be more stable than isomeric allenes or acetylenes. If *cis,trans*-1,3-cyclodecadiene[23] was formed it must have been a minor product, indicating that this diene is thermodynamically less stable than VII. As has been noted earlier,[23] the *cis,cis* diene, VII, cannot have both double bonds coplanar, a circumstance which must account for its isomerization to a nonconjugated diene which probably has fewer nonbonded interactions.

Preliminary experiments showed that heating III and IV with strong bases resulted in isomerization; but in no case was equilibrium attained. Under sufficiently drastic conditions (Diethyl Carbitol, 180°), the allene was isomerized to several other products (which have not yet been investigated) more rapidly than the acetylene was converted to allene (see Table I).

Experimental

General Procedure.—Infrared spectra were measured with a Perkin-Elmer Model 21 or a Baird Model AB spectrophotometer. Elemental analyses were performed by Dr. S. M. Nagy and associates at the Massachusetts Institute of Technology. Gas chromatography columns were 0.5 × 170–200 cm. for analytical purposes and 1 × 200 cm. for

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[20] It is possible that 2-(2,4-dinitrobenzenethio)-3-chloro-1-cycloalkenes would be somewhat less reactive than other allylic chlorides, but it is difficult to see why the former would be less reactive than typical primary or secondary halides which were found to react readily with both reagents mentioned above.

[21] In the future, we hope to be able to offer further evidence pertinent to the orientation and stereochemistry of these and related reactions.

[22] A study of the relative thermodynamic stabilities of a number of cyclic allenes and acetylenes will be presented elsewhere, W. R. Moore and H. R. Ward, *J. Am. Chem. Soc.*, in press.

[23] A. T. Blomquist and A. Goldstein, *J. Am. Chem. Soc.*, **77**, 998 (1955), first prepared this diene by pyrolysis of the *cis-* and *trans*-1,2-diacetoxycyclodecanes.

TABLE I

ISOMERIZATION OF CYCLIC ACETYLENES AND ALLENES

Isomerization conditions			Products	
Initial hydrocarbon	Solvent, catalyst[a]	Temp., time	Ratio of allene to acetylene	Other products, % of total mixture
II	DEC	190°, 48 hr.	0.0	Trace
II	E/KOH	Distillation[b]	0.13	1
II	E/KOH	Reflux, 2 hr.	1.7	54[c]
II	DEC/KOH	190°, 36 hr.	1.7	72[c]
II	DEC/KOH	Reflux, 48 hr.	...	98[d]
I	E/KOH	Distillation[b]	5.0	4
I	DEC/KOH	190°, 36 hr.	1.5	63[c]
IV	E/KOH	Distillation[b]	1.6	2
IV	DEC/KOH	180°, 48 hr.	0.05	28[e]
III	E/KOH	Distillation[b]	18	2
III	DEC/KOH	180°, 48 hr.	...	100[e]

[a] DEC, Diethyl Carbitol (diethylene glycol diethyl ether); E/KOH, ethanol–potassium hydroxide, 1:2; DEC/KOH, Diethyl Carbitol–potassium hydroxide, 4:1. [b] Distillation performed as in the dehydrohalogenation of chloroölefins. [c] Mostly VII. [d] About 70% VII and 25% VIII. [e] Products not identified.

preparative purposes. Stationary phases consisted of 25–30% by weight of the following liquids, all on 48–80 mesh firebrick: Dow-Corning No. 550 silicone oil (S-550), a saturated solution of silver nitrate in tetraethylene glycol (SN-TEG), 3-nitro-3-methylpimelonitrile (NMPN), Carbowax 1540 (C-1540), and tetrahydroxyethylethylenediamine (THEED). All melting points and boiling points are uncorrected.

Cycloalkynes.—Cyclononyne and cyclodecyne were prepared by published procedures[1,2] by mercuric oxide oxidation of the corresponding dihydrazones. Cyclodecyne was conveniently purified by extraction from pentane solution with 1:1 (v./v.) methanol-water saturated with silver nitrate followed by decomposition of the silver nitrate adduct with excess ice-cold concentrated ammonium hydroxide. The purity of II so obtained was greater than 99% (gas chromatography), b.p. 79.5° (12 mm.), $n^{25}{}_D$ 1.4882, $d^{25}{}_4$ 0.8933; reported,[1b] $n^{20}{}_D$ 1.4903, $d^{20}{}_4$ 0.8975.

Adduct of II and 2,4-Dinitrobenzenesulfenyl Chloride.—A mixture of 2.34 g. (0.010 mole) of 2,4-dinitrobenzenesulfenyl chloride and 1.36 g. (0.010 mole) of II in a solution of 20 ml. of ethylene chloride and 5 ml. of glacial acetic acid was allowed to stand at room temperature for 2 hr. After the solvents had been evaporated under reduced pressure, the residual solid obtained was recrystallized twice from carbon tetrachloride–methanol to give 2.21 g. (60%) of yellow crystals, m.p. 146.4–146.7°.

Anal. Calcd. for $C_{16}H_{19}N_2O_4SCl$: C, 51.81; H, 5.16; N, 7.56. Found: C, 52.01; H, 5.33; N, 7.65.

1-Chlorocyclodecene.—Cyclodecanone was prepared in 79% yield by the published procedure[24] (keeping the reaction temperature at 45–50°). The ketone was purified *via* its semicarbazone with 76% recovery. Cyclodecanone was treated with phosphorus pentachloride at room temperature as described by Blomquist, Burge, and Sucsy.[1b] The crude reaction mixture was poured onto ice and made basic with saturated sodium carbonate solution. The solution was extracted with petroleum ether, the solvent was evaporated from the extracts, and the residue was refluxed for 4 hr. with 20% ethanolic potassium hydroxide. Water was added to the cooled solution and the mixture was extracted with petroleum ether. The solution was washed, dried, and distilled under reduced pressure to give crude 1-chlorocyclodecene (48–55%) contaminated with cyclodecanone. This material was treated in the usual way with semicarbazide and the filtrate obtained after removal of cyclodecanone semicarbazone was extracted with petroleum ether. Distillation of the extracts gave 1-chlorocyclodecene, b.p. 98–100° (13 mm.), $n^{29}{}_D$ 1.4970; reported,[1b] b.p. 121–124° (29 mm.), $n^{20}{}_D$ 1.5038. Gas chromatography showed that this material was a mixture of two isomers which were isolated: *cis* (55%), ν_{max} 1648 cm.$^{-1}$; *trans* (45%), ν_{max} 1656 cm.$^{-1}$; relative retention times, *cis/trans* = 1.17 (C-1540, 157°). Neither material gave any precipitate with a hot solution of silver nitrate in acetonitrile.

Anal.[25] Calcd. for $C_{10}H_{17}Cl$: C, 69.55; H, 9.92; Cl, 20.52. Found: *cis;* C, 69.30; H, 9.75; Cl, 20.36. *trans;* C, 69.64; H, 9.84; Cl, 20.36.

1,2-Cyclodecadiene (I).—Equal weights of potassium hydroxide and ethanol were placed in a small distilling flask. The flask was heated strongly and shaken until approximately one half of the ethanol had distilled. The slurry was cooled and 1-chlorocyclodecene was added (about one fifth the weight of the alkali). The mixture was shaken intermittently and heated with gradually increasing temperature until all volatile material had distilled. Half-saturated aqueous sodium chloride solution was added to the distillate and the mixture was extracted with pentane. The combined extracts were washed with water, dried, and flash-distilled. Gas chromatography (S-550) separated a hydrocarbon fraction from materials with higher elution times. The hydrocarbon fraction which was generally obtained in about 55% yield, was separated into I and II by gas chromatography (SN-TEG). In some cases, preliminary separation was effected by washing a pentane solution of the hydrocarbons with 1:1 (v./v.) methanol-water saturated with silver nitrate (to remove II). The I which remained in the pentane was then purified by gas chromatography followed by short-path distillation. Dehydrohalogenation of the 55:45 mixture of *cis*- and *trans*-1-chlorocyclodecene gave a hydrocarbon mixture which consisted of about 60% I and 40% II. Similar ratios were obtained from samples enriched in *cis*- or *trans*-chloroölefin.

1,2-Cyclodecadiene had b.p. 74° (10 mm.); $n^{25}{}_D$ 1.5071; $d^{25}{}_4$ 0.8918; ν^{neat}_{max} 1962 (ms), 865 (s), 719 (m), 708 (ms), 696 (s) cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.13; H, 11.96.

Ozonolysis of I.—A solution of 162 mg. of I in 40 ml. of methanol was ozonized at −20°. To one half of the ozonide solution was added 2.0 ml. of 30% hydrogen peroxide and 0.5 ml. of acetic acid. The mixture was boiled for 30 min. and then concentrated. Water was added and the solution was chilled. The solid which formed was recrystallized from benzene to give 77 mg. of azelaic acid, m.p. 106–107.2°, which did not depress the melting point of an authentic sample.

The other half of the ozonide solution was treated with excess potassium iodide solution. The liberated iodine was titrated rapidly with sodium thiosulfate solution and excess 2,4-dinitrophenylhydrazine solution was added immediately. The precipitate which formed was recrystallized from benzene–petroleum ether to give a light tan powder, m.p. 150–151°.

The bis(N-methylanilide) of azelaic acid, prepared in 73% yield from the reaction of azeloyl chloride with N-methylaniline in pyridine, was obtained as a viscous yellow oil, b.p. 242° (0.6 mm.), $n^{27}{}_D$ 1.5446.

Anal. Calcd. for $C_{23}H_{30}N_2O_2$: C, 75.37; H, 8.25; N, 7.64. Found: C, 74.93; H, 8.31; N, 7.42.

The anilide was stirred at −10° for 2 hr. with excess lithium aluminum hydride in tetrahydrofuran. The mixture was hydrolyzed with cold hydrochloric acid and excess 2,4-dinitrophenylhydrazine reagent was added. Concentration of the solution gave a precipitate which was recrystallized from ethanol giving the bis-2,4-dinitrophenylhydrazone of azelaäldehyde, m.p. 150–151°, in nearly

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[24] A. C. Cope, J. W. Barthel, and R. D. Smith, *Org. Syn.*, **36**, 14 (1957).

[25] Analytical samples isolated by Dr. H. R. Ward.

quantitative yield. This material showed no depression of the melting point when admixed with the product obtained from the ozonolysis of I. Two more recrystallizations from ethanol gave the analytical sample, m.p. 155–155.5°.

Anal. Calcd. for $C_{21}H_{24}N_8O_8$: C, 48.83; H, 4.68; N, 21.70. Found: C, 48.33; H, 4.68; N, 21.47.

Adduct of I and 2,4-Dinitrobenzenesulfenyl Chloride.—The adduct, prepared as described for II, was obtained in 82% yield, m.p. 164.7–165°.

Anal. Calcd. for $C_{16}H_{19}N_2O_4SCl$: C, 51.81; H, 5.16; N, 7.56. Found: C, 52.14; H, 5.20; N, 7.40.

Neither this adduct nor that obtained from II showed any reaction toward a hot solution of silver nitrate in acetonitrile. When refluxed with methanolic potassium hydroxide solution, neither adduct produced any chloride ion. The infrared spectra of the adducts (chloroform solution) were different.

Partial Hydrogenation of I.—A solution of 0.287 g. of I in 6 ml. of methanol was stirred under 1 atm. of hydrogen over 100 mg. of 10% palladium on Norit poisoned with 0.05 ml. of pyridine until the uptake of hydrogen ceased (one equivalent was absorbed in *ca.* 20 min., total time in contact with the catalyst was *ca.* 80 min.). The catalyst was removed by filtration and washed with methanol. Aqueous sodium chloride solution was added to the filtrate and the mixture was extracted with pentane. The pentane solution was concentrated by distillation and the residue was gas chromatographed (S-550) to give 0.214 g. of hydrocarbon, $n^{25}D$ 1.4815, which was shown by gas chromatography (SN-TEG) and infrared spectroscopy to consist of *ca.* 82% *cis*-cyclodecene and 18% *trans*-cyclodecene.

Adduct of IV and 2,4-Dinitrobenzenesulfenyl Chloride.—This adduct was prepared as described for II, m.p. 110–111° (carbon tetrachloride–methanol).

Anal. Calcd. for $C_{15}H_{17}N_2O_4SCl$: C, 50.48; H, 4.80; N, 7.85. Found: C, 50.82; H, 4.80; N, 7.90.

1,2-Cyclononadiene (III).—1-Chlorocyclononene was prepared from cyclononanone in the manner described for 1-chlorocyclodecene except that the reaction mixture was kept at about 60° for 12 hr. The whole reaction product after removal of inorganic material was dehydrohalogenated by distillation from ethanolic potassium hydroxide. The distillate was separated by preparative gas chromatography (silicone oil) into hydrocarbon and higher boiling fractions. In a typical run, 11.7 g. (27%) of hydrocarbons and 7.8 g. of higher boiling material (shown by gas chromatography to be principally 1-chlorocyclononene) were obtained from 56 g. of cyclononanone. The hydrocarbon fraction upon gas chromatography (SN-TEG or NMPN) followed by short-path distillation gave about 50% of III, $n^{25}D$ 1.5039, d^{25}_4 0.8914, ν_{max} 1957 (ms), 856 (s), 732 (ms) and 695 (ms) cm.$^{-1}$.[26]

Anal. Calcd. for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.18; H, 11.65.

Oxidative ozonolysis gave suberic acid (59%), m.p. 141–143°, undepressed upon admixture with an authentic sample.

Adduct of III and 2,4-Dinitrobenzenesulfenyl Chloride.—This adduct was prepared in 70% yield as described for II, m.p. 146–146.4° (carbon tetrachloride–methanol).

Anal. Calcd. for $C_{15}H_{17}N_2O_4SCl$: C, 50.48; H, 4.80; N, 7.85. Found: C, 50.64; H, 4.83; N, 7.54.

Partial Hydrogenation of III.—A solution of 0.306 g. of III in 6 ml. of methanol was stirred under 1 atm. of hydrogen over 100 mg. of 10% palladium on Norit until the uptake of hydrogen ceased (one equivalent was absorbed in *ca.* 10 min.; the total time in contact with catalyst was *ca.* 30 min.). The mixture was processed as described for I. Gas chromatography (NMPN) indicated 97% of a major component and 3% of a more rapidly eluted component. The major component (g.c. recovery, 0.242 g.) was identified as *cis*-cyclononene by its infrared spectrum. The more rapidly eluted material (g.c. recovery 0.0072 g.) had $n^{28}D$ 1.4635; reported for cyclononane,[1c] $n^{20}D$ 1.4663. In subsequent runs employing the same conditions, the residue obtained after distillation of the bulk of the pentane was analyzed by gas chromatography utilizing the conditions for the separation of *cis*- and *trans*-cyclononene indicated in ref. 16 and it was established that less than 0.2% of *trans*-cyclononene could be present. Cyclononane (2–4%) obtained in these runs was identified by comparison of retention times with an authentic sample.

Isomerizations.—Samples of the hydrocarbons were heated under nitrogen in the indicated solvents, generally with added potassium hydroxide, for the times specified. Water was added to the reaction mixtures and the products were extracted with pentane. After drying and concentrating the pentane solutions the mixtures were analyzed by gas chromatography (SN-TEG, NMPN, S-550, THEED). The results are summarized in Table I. *cis,cis*-1,3-Cyclodecadiene (VII), m.p. 20–22°, $n^{25}D$ 1.4913 (reported,[23] m.p. 19–22°, $n^{25}D$ 1.4911) was isolated by gas chromatography and was found to have an infrared spectrum identical with the published spectrum.[23]

Heating II with potassium hydroxide in refluxing Diethyl Carbitol for 48 hr. (the fifth entry of Table I) yielded in addition to VII, about 25% of VIII which was isolated by gas chromatography (NMPN), $n^{28}D$ 1.4833, ν^{neat}_{max} (mw); 1680, 1655 (s); 1040, 975, 924, 868, 792, 768 (vs); 708 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 87.94; H, 12.02.

Hydrogenation of VIII over 10% palladium on Norit in methanol resulted in the absorption of two equivalents of hydrogen forming cyclodecane, m.p. 10.5–11.5° (reported,[27] m.p. 9.5°) which was identified by its infrared spectrum and gas chromatographic retention times.

The following relative retention times have been found to be useful in characterization (SN-TEG, 98°): cyclodecane, 1.0; *cis*-cyclodecene, 4.5; *trans*-cyclodecene, 13.0; VIII, 28.5.

Ozone was passed through a solution of 12 ml. of VIII in 10 ml. of methanol at −80° for 5 min. The solution was warmed to room temperature and 0.5 ml. of 30% hydrogen peroxide and 4 drops of acetic acid were added. The solution was refluxed for 0.5 hr., 4 drops of sulfuric acid was added and the mixture was refluxed overnight. A large volume of water was added; the solution was shaken with ether; the ether extract was washed with aqueous sodium bisulfite, sodium bicarbonate, and saturated sodium chloride solution and then was dried over magnesium sulfate. After the bulk of the ether had been evaporated, the residue was analyzed by programmed temperature gas chromatography employing a silicone oil column. The major product (*ca.* 85%) was found to be dimethyl pimelate, which was isolated and identified by its infrared spectrum. A smaller amount of dimethyl malonate (15%) was found along with traces (0.2 to 4%) of materials with retention times identical with those of the dimethyl esters of all of the other straight-chain dibasic acids, from oxalic to sebacic.

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[26] Gardner and Narayana[3] reported $n^{27}D$ 1.4953, indicating that their sample of III contained some other material.

[27] P. A. Plattner and J. Hulstkamp, *Helv. Chim. Acta*, **27**, 220 (1944).