separated, washed with water (20 ml), and dried ($MgSO_4$). Evaporation of the solvent gave a crystalline residue which was recrystallized (ether-pentane) to give **12-oxabicyclo[9.1.0]-dodeca-5,6-diene-3,9-dione (13)** (82 mg, 85%): mp 143–144°; mass spectrum (15 eV) *m/e* 192 (2.5%), 174, 164, 150, 120, 110, 108, 107 (100%), 94, 66, 65, 55; ir (KBr) 2980, 2930, 2880, 1965, 1700, 1467, 1438, 1418, 1390, 1340, 1300, 1270, 1249, 1200, 1112, 1090, 1027, 986, 968, 931, 886, 842, 793, and 714 cm$^{-1}$; nmr 4.44–4.80 (m, 2 H, allene), 6.40–6.64 (m, 2 H, epoxide), and 6.69–7.56 (m, 8 H, $CH_2$); electronic spectrum, see discussion.

*Anal.* Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: C, 68.42; H, 6.38.

**Registry No.**—*2*, 37709-72-1; **3**, 37709-73-2; **4**, 37780-37-3; **5**, 37709-74-3; **5** ditosylhydrazone, 37709-75-4; **6**, 37709-76-5; **6** diacetate, 37709-77-6; **7**, 37709-78-7; **8**, 37709-79-8; **9**, 37709-80-1; **9** dinitrophenylhydrazone, 37709-81-2; **10**, 37709-82-3; **10** oxime, 37709-83-4; **11**, 37709-84-5; **12**, 37709-85-6; **13**, 37709-86-7.

**Acknowledgment.**—We thank the Science Research Council, U. K., for a studentship to K. C. N.

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# Addition Reactions of *cis,trans*-1,5-Cyclodecadiene[1]

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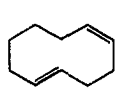
A variety of cationic, radical, and methylene reagents add selectively to *cis,trans*-1,5-cyclodecadiene. Noncyclic reagents (multistep addends), whether cationic or radical, lead to substituted *cis*-decalins, while methylene reagents give cyclopropane derivatives (preferred attack on trans C=C). The stereochemistry of the products has been established by nmr techniques and delineates to a substantial degree such mechanistic details of the addition process as position of initial attack and degree of concertedness. The stereoselectivity in product formation is usually higher with the cationic than with the radical reagents, and, in several reactions, it is sufficiently high to be useful in synthesis.

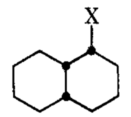
A few years ago, a report from our laboratory demonstrated the potential of *cis,trans*-1,5-cyclodecadiene (**1**) for differentiating between single-step and multistep attack of addends on the two carbons of an olefinic linkage.[3] Subsequently, several short communications showed much the same potential in the relative rates of exo addition to norbornene and to 7,7-dimethylnorbornene.[4] Both studies led to the conclusion, among others, that oxymercuration proceeds in steps rather than by a cyclic mechanism, even though cis additions are reported.

Our original investigation was limited to several reagents which add by a cyclic or single-step mechanism and to several ionic reagents. We have now extended the investigation to include radical addends as well as other ionic and methylene reagents. Additions to **1** by noncyclic reagents, whether cationic or radical, lead to substituted *cis*-decalins, usually with a substantial degree of stereoselectivity that can be useful in syntheses. This paper reports, we believe, the first examples of cycloadditions of radical reagents with the $C_{10}$ ring system. Methylenes and other reagents which add to both carbons in the olefinic linkage without forming a trivalent carbon intermediate give 5,6-disubstituted cyclodecenes, with preference for addition to the trans rather than the cis C=C.[3] Frequently the two courses of addition can be differentiated easily by monitoring the C=CH nmr absorptions by an equimolar mixture of the diene **1** and the addend. The various addends are discussed in groups according to potential synthetic usefulness as well as to mechanism.

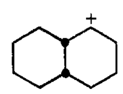
We have previously reported the photoisomerization of **1** to *cis,cis*-1,5-cyclodecadiene and the relative reactivities of the isomeric dienes toward trifluoroacetic acid and with respect to thermal isomerization to *cis*-1,2-divinylcyclohexane (**1** reacts faster than its isomer in both cases).[5]



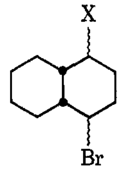
**1**



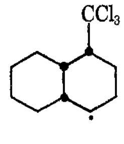
**2a**, X = $OCOCF_3$
**b**, X = $NH_2$
**c**, X = NHCOR



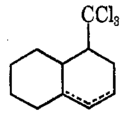
**3**



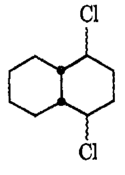
**4a**, X = $CHBr_2$
**b**, X = $CCl_3$



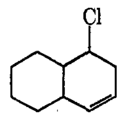
**5**



**6**



**7**



**8**

**Ionic Reagents. Trifluoroacetic Acid.**—When a sample of diene **1** is added to trifluoroacetic acid, a spontaneous, exothermic reaction produces *cis*-1-*cis*-decalyl trifluoroacetate (**2a**) in nearly quantitative yield. Saponification of the ester yields *cis*-1-*cis*-decalol, an alcohol for which several preparations have been described. We believe this preparation to be the easiest

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[1] (a) Based upon the Ph.D. dissertation of H. H. H., Louisiana State University, Baton Rouge, Aug 1970. (b) The major portion of this manuscript was prepared while J. G. T. was a NATO Senior Fellow in Science at the Institut für organische Chemie, Universität des Saarlandes, Saarbrücken, Germany; J. G. T. acknowledges with appreciation the courtesies extended to him by Professor M. Hanack and other members of the institute. (c) Supported in part by a grant from the National Science Foundation (NSF GP 8228).

[2] (a) Acknowlegment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for an American Chemical Society–Petroleum Research Fund Final Year Graduate Fellowship, 1969–1970, to H. H. H. (b) The financial assistance from the Charles E. Coates Memorial Fund, donated by George H. Coates, for preparation of the Ph.D. dissertation of H. H. H. is gratefully acknowledged.

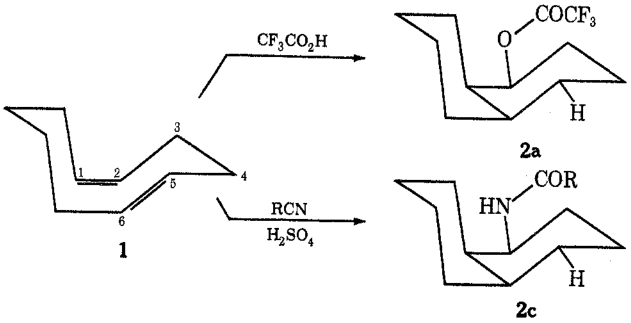
[3] J. G. Traynham, G. R. Franzen, G. A. Knesel, and D. J. Northington, Jr., *J. Org. Chem.*, **32**, 3285 (1967).

[4] H. C. Brown and K.-T. Liu, *J. Amer. Chem. Soc.*, **92**, 200, 3502 (1970); H. C. Brown and J. H. Kawakami, *ibid.*, **92**, 201 (1970); H. C. Brown and K.-T. Liu, *ibid.*, **93**, 7335 (1971).

[5] J. G. Traynham and H. H. Hsieh, *Tetrahedron Lett.*, 3905 (1969).

to use for small or large quantities of stereoisomerically pure alcohol.

The stereochemistry in this addition is not only useful for synthesis, but it is also of interest so far as details of the addition sequence are concerned. It seems unlikely that a 1-*cis*-decalyl cation (**3**) is actually formed at any time. Free 4-*tert*-butyl-1-cyclohexyl cations exhibit little regioselectivity in product formation,[6] and the neighboring methylene group in **3** would be expected to hinder rather than favor the formation of cis product. On the other hand, a process initiated by addition of a proton to the 5 position (trans C=C) and involving reasonably concerted bonding of trifluoroacetic acid at the 2 position while bridging between positions 1 and 6 is taking place accounts quite clearly for the observed stereoselectivity. Initial attack by proton at the 2 position (cis C=C) followed by a parallel sequence of events would lead to *trans*-1-*cis*-decalyl trifluoroacetate rather than the cis,cis isomer obtained. Dreiding models help significantly in picturing the alternative consequences.



**Nitriles.**—When a small amount of concentrated sulfuric acid is added to a solution of diene **1** in acetonitrile or in benzonitrile, the Ritter reaction proceeds smoothly at room temperature to form *N*-(*cis*-1-*cis*-decalyl) amides (**2c**) in moderate yield (58–64%). No evidence for the formation of an isomer (or other product) was obtained. Again, the stereoselectivity in this addition strongly implies initial protonation at C-5 in the diene followed by substantially concerted attack of the nitrile at C-2 and bond formation between C-1 and C-6.

**Mercury(II) Azide.**—An aqueous tetrahydrofuran solution of mercury(II) azide[7] reacted with diene **1** to form a mixture of products which was reduced by alkaline sodium borohydride[7] to a mixture of *cis*-1-*cis*-decalyl azide (11%), *cis*-1-*cis*-decalol (39%), and another saturated azide yet unidentified. The *cis*-1-*cis*-decalyl azide was reduced by hydrogen and platinum oxide to *cis*-1-*cis*-decalylamine (**2b**).

**Chlorine.**—Both molecular chlorine and iodobenzene dichloride react with alkenes to add the elements Cl–Cl by both polar and radical mechanisms, depending on the reaction conditions.[8a,b] An oxygen (or air) atmosphere inhibits the radical process and favors the polar one, but a nitrogen atmosphere favors the radical one. A molecular addition process (cyclic transition state; attack on both carbons of the C=C at the same time) has been proposed for the nonradical reaction of iodobenzene dichloride.[8c] We find, however, that all four reactions give only cycloaddition products; there is no evidence for the formation of substituted cyclodecenes.

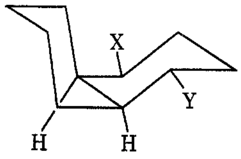
The reactions of both chlorine and iodobenzene dichloride with **1** in a nitrogen atmosphere were much more rapid than those in the presence of oxygen. The product mixtures from each reagent were similar but not identical for the two conditions. The spectra of the mixtures revealed only a little absorption for C=CH, which was identified in each case with 5-chlorobicyclo[4.4.0]dec-2-ene (**8**). The major products (~80% of the total gc area of the product mixture) are 1,4-dichloro-*cis*-decalins (**7**). Some minor products in the mixtures, particularly those from iodobenzene dichloride, have not been identified, but they do not appear to be substituted cyclodecenes or cyclodecanes.

The apparent formation of a mixture of 1,4-dichloro-*cis*-decalins (**7**) in these reactions implies that the concertedness of the additions described earlier is missing in these. Since some of the radical additions to be described below also gave stereoisomeric mixtures of substituted *cis*-decalins, the results with chlorine additions may imply that, in spite of the presence of oxygen, the (fast) radical mechanism prevailed. Alternatively, polar attack of sources of chlorine on the initially formed cationic intermediate may not accompany bridging between the 1 and 6 positions by the π electrons of the transannular C=C.[9]

In any event, it appears clear that iodobenzene dichloride does not react with diene **1** by a cyclic, molecular addition process.

**Radical Reagents. Bromoform and Bromotrichloromethane.**—Photoinitiated (3500-Å) addition of $BrCHBr_2$ to diene **1** in a nitrogen atmosphere produced a product mixture from which a single product, identified on the basis of spectral data as 1-bromo-4-dibromomethyl-*cis*-decalin (**4a**), was isolated by column chromatography in 45% yield. The minor components of the mixture were not identified. The nmr spectrum of the major product includes a triplet of doublets at δ 3.95 for HCBr, a pattern which requires vicinal coupling of an axial HCBr to two axial protons ($J$ = 9.5 Hz) and to one equatorial proton ($J$ = 2.5 Hz); that is, the ring bromine must be equatorial and trans to the ring juncture.

That same stereochemical result was obtained in the major product from photoinitiated addition of bromotrichloromethane to diene **1**. This solid adduct, identified as *trans*-1-bromo-4-trichloromethyl-*cis*-decalin (**4b**) on the basis of spectral data, was obtained in 61% yield. Its nmr spectrum included a triplet of doublets at δ 3.92 ($J$ = 9.5 and 2.5 Hz, HCBr) and a multiplet at δ 2.65 ($HCCCl_3$). The patterns require that HCBr be axial with two vicinal axial protons (that is, bromine is equatorial and trans to the ring juncture) and that



X equatorial, cis to ring fusion
Y equatorial, trans to ring fusion

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[6] S. D. Elakovich and J. G. Traynham, *Tetrahedron Lett.*, 1435 (1971).

[7] C. H. Heathcock, *Angew. Chem., Int. Ed. Engl.*, **8**, 134 (1969).

[8] (a) Molecular chlorine: M. L. Poutsma, *J. Amer. Chem. Soc.*, **87**, 2161 (1965). (b) $PhICl_2$: D. D. Tanner and G. C. Gidley, *J. Org. Chem.*, **33**, 38 (1968) and references cited therein. (c) D. H. R. Barton and E. Miller, *J. Amer. Chem. Soc.*, **72**, 370 (1950).

[9] Initial attack at either the cis or the trans C=C, followed by concerted 1,6 bridging and uptake of the second chlorine, will give the same *trans*-1,4-dichloro-*cis*-decalin.

$HCCCl_3$ be axial with one axial and two equatorial vicinal couplings (that is, trichloromethyl is also equatorial but cis to the ring juncture).

The nmr spectrum of the total reaction product mixture with no treatment other than removal of excess bromotrichloromethane at reduced pressure (25°) included absorptions for C═CH and an absorption at $\delta$ 4.46 with a pattern indicative of an equatorial HCBr vicinal to one axial and two equatorial protons. No product responsible for this absorption was ever isolated; all attempts to isolate it, as well as treatment of the original product mixture with 0.5 equiv. of base, resulted in formation of unsaturated products. We believe that these data are consistent with the structure *cis*-1-bromo-4-trichloromethyl-*cis*-decalin (**4b**), with the bromine axial and cis to the ring juncture. This compound (*ca.* 40% yield on the basis of nmr data) would be expected to lose HBr readily to form olefinic products (5-trichloromethylbicyclo[4.4.0]decenes, **6**).

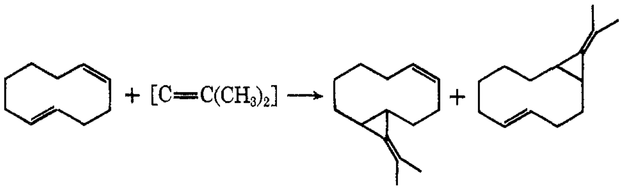
These stereochemical results have interesting implications for the details of these radical additions to **1**. One side of each alkene linkage (one lobe of each $\pi$ orbital) in **1** is substantially less accessible to attack because it is oriented toward the interior of the ring. Attack on the exposed side of each alkene linkage will, without intervening inversion, lead to equatorial bonds to the substituents in the *cis*-decalin product. In order for the ring bromines to be *both* equatorial and trans to the ring juncture, dibromomethyl or trichloromethyl attack must come on the cis rather than the trans alkene linkage. Since the cationic addition reagents appear to attack the trans alkene linkage preferentially, this contrasting behavior of the radical reagents, $\cdot CHBr_2$ and $\cdot CCl_3$, is intriguing. We have no explanation for this contrast at present.

When the reaction was carried out with molar equivalents of bromotrichloromethane and **1** in methylene chloride solution, the product mixture appeared to consist of the same compounds as were obtained in excess bromotrichloromethane, but in different proportions. The nmr spectrum included the two six-line absorptions at $\delta$ 4.46 and 3.92, but the relative intensities were 1:4 rather than 1:1.4. If we have correctly identified the $\delta$ 4.46 absorption with *cis*-1-bromo-4-trichloromethyl-*cis*-decalin, this less stable, axial bromo isomer is formed more extensively with excess bromotrichloromethane than in the moderately dilute methylene chloride solution. The fact that both stereoisomers appear to be formed from **1** and in proportions which are dependent on bromotrichloromethane concentration shows that the addition of $BrCCl_3$ is not concerted; that is, that a *cis*-4-trichloromethyl-1-*cis*-decalyl radical (**5**) is an intermediate.

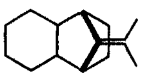
**Methylenes.**—While our work was in progress, the additions of dibromomethylene and of dichloromethylene to **1** were reported by others.[10] In each case the yield of dihalocyclopropane was about 75%, and the addition occurred preferentially at the trans-alkene linkage (about 3:1, trans:cis).[10] Our addition of dibromomethylene confirms that result, and we find quite similar results with methylene and with isopropylidenemethylene.

With methylene iodide and zinc–copper couple,[3,11] the yield of bicyclo[8.1.0]undec-4-enes was 60%, and 89% of the product was formed by attack on the trans-alkene linkage (11% on the cis C═C). When methylene was generated from diazomethane and copper, the yield of cyclopropanes was poor; the product which was formed resulted from 73% addition to the trans C═C, 27% to the cis C═C. With $C{=}C(CH_3)_2$, generated from 5,5-dimethyl-*N*-nitrosooxazalidone and lithium alkoxide,[12] we obtained a 75% yield of cyclopropanes; 70% of the addition occurred at the trans C═C (**9**) and 30% at the cis C═C (**10**).

The addition of isopropylidenemethylene was of particular interest to us, because its addition to certain acyclic olefins has been described as a sequential rather than simultaneous formation of the two bonds to the carbons in the alkene linkage.[12] The stereochemical results on which that description is based do not require that an intermediate be formed, only that bond development to the two alkene carbons occur unequally along the reaction coordinate. If a true intermediate were formed with **1**, we would expect a decalin derivative (which would presumably be 11-isopropylidenetricyclo[6.2.1.0$^{2,7}$]undecane, **11**); if no intermediate were formed, we would expect a cyclopropane (an 11-isopropylidenebicyclo[8.1.0]undec-4-ene). Since the cyclopropane product is formed exclusively, we infer that this methylene reagent does not generate a true intermediate in its addition to an alkene. The development of bonds to the two alkene carbons may well be sequential,[12] but the reaction coordinate is characterized by a single transition state between methylene reagent and cyclopropane product.



**9** **10**



**11**

## Experimental Section

Analytical gas chromatography (gc) utilized Beckman GC-5 and Hewlett-Packard Model 700 instruments equipped with flame ionization detectors and with 0.125-in. columns packed with the specified phase on 60–80 mesh solid support. Preparative gc utilized an Aerograph Autoprep Model A-700 instrument. Infrared (ir) spectra were obtained with a Beckman IR-10 instrument. Nuclear magnetic resonance (nmr) spectra were recorded on Varian Associates A-60A and HA-100 instruments with the assistance of W. Wegner; all chemical shifts are reported relative to internal tetramethylsilane. Element microanalyses were performed by R. Seab in these laboratories.

**Addition of Trifluoroacetic Acid to 1.**—To stirred trifluoroacetic acid (15 ml) was added **1**[13] (2.72 g, 20 mmol) drop by drop

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[10] J. Graefe and M. Muhlstadt, *Tetrahedron Lett.*, 3431 (1969).

[11] R. D. Smith and H. E. Simmons, *Org. Syn.*, **41**, 72 (1961).

[12] M. S. Newman and A. D. M. Okorodudu, *J. Amer. Chem. Soc.*, **90**, 4189 (1968). We acknowledge with appreciation the receipt of detailed procedures from Professor Newman in advance of publication.

[13] Prepared from butadiene, ethylene (150 psig), and bis(1,5-cyclooctadiene)nickel at room temperature: G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **2**, 105 (1963). For us, ethylene pressures below 75 psig did not lead to much cyclodecadiene formation. At 150-psig pressure, we obtained almost quantitative conversion to a mixture (approximately 1:1) of **1** and cyclododecatrienes. The boiling point of **1** is 51–53° (5 mm).

in 30 sec. The temperature of the reaction mixture rose to 58° in 1 min and began to decrease a few minutes later. After 30 min the solution, which had become brown, was poured into 100 ml of ice water. The aqueous mixture was extracted several times with ethyl ether. The ether solution was washed with 10% sodium bicarbonate solution and with water, dried (CaCl$_2$), and distilled. The ester **2a** was obtained in 80% yield: bp 99–100.5° (9 mm); ir strong absorptions at 3.38, 3.48, 5.57, 8.10, and 8.51 $\mu$, no absorptions at 10.29 (*trans*-cyclodecene) or 14.25 $\mu$ (*cis*-cyclodecene); nmr (CCl$_4$) $\delta$ 5.0 (b m, 1, HCO), 2.4–1.1 (b m, 16, decalin ring). When a portion of the ester was saponified with 2 *M* sodium hydroxide solution, *cis*-1-*cis*-decalol[3] was obtained in 93% yield, mp 90–91°.

**Addition of Nitriles. A.**—A solution of **1** (2.72 g, 20 mmol), acetonitrile (10 ml), and concentrated sulfuric acid (2 ml) was stirred overnight at room temperature and was poured into ice water (20 ml). Acetonitrile was removed by rotary evaporation under reduced pressure, and the aqueous mixture was extracted thoroughly with chloroform. The chloroform solution was washed with water, dried (MgSO$_4$), and evaporated. The white, crystalline residue (2.5 g, 68%) was purified by recrystallization from acetone and by vacuum sublimation (64%): mp 178.6–180° (lit.[14] mp 181°); nmr (CCl$_4$) $\delta$ 5.83 (b m, 1, NH), 3.90 (m, 1, HCN), 1.96 (s, 3, NCOCH$_3$), 2–1 (b m, 16, decalin ring); ir (KBr) strong absorptions at 3.06, 3.23, 6.08, and 6.41 $\mu$ (primary amide). These data are consistent with the structure *N*-(*cis*-1-*cis*-decalyl)acetamide.[14]

**B.**—When a nearly identical procedure was used with benzonitrile in place of acetonitrile, *N*-(*cis*-1-*cis*-decalyl)benzamide[15] was obtained in 58% yield: mp 205–206° (lit.[15] mp 206°); nmr (CCl$_4$) $\delta$ 7.86–7.60 (m, 5, ArH), 6.08 (m, 1, NH), 4.16 (m, 1, HCN), 2.2–1.0 (m, 16, decalin ring); ir (KBr) 2.99, 3.06, 6.12, 6.32 $\mu$ (primary amide).

**Mercury(II) Azide.**—The diene **1** (4.0 g, 30 mmol) was added to a solution[7] of mercury(II) azide in tetrahydrofuran. The two-phase mixture was stirred at room temperature for 2 hr, reduced with sodium borohydride in 15% aqueous potassium hydroxide solution,[7] and extracted three times with ethyl ether. The ether solution was dried (MgSO$_4$) and concentrated under reduced pressure. A portion (4.0 g) of the residue (5.0 g) was chromatographed on Merck alumina (150 g, acid washed); petroleum ether (bp 30–60°), petroleum ether–ethyl ether mixtures (3:1, 1:1, and 1:3), and methanol were used sequentially as eluting solvents. Only a few of the 34 30-ml fractions collected contained any solute. The first eluent was **1** (0.1 g). The second one was identified as *cis*-1-azido-*cis*-decalin: 0.6 g (11%); ir 4.75 $\mu$ (azido); nmr (CCl$_4$) $\delta$ 3.45 (m, 1, HCN$_3$), 2.1–1.0 (16, decalin ring). A sample of this azide (0.3 g) was reduced in ethanol solution with hydrogen (45 psig) and platinum oxide to the amine (**2b**), which was converted to the benzamide,[15] mp 205–206°, identical with the benzamide obtained from the benzonitrile reaction. The third eluent (1.2 g) has not been identified: ir 4.75 $\mu$ (azido) but no absorption for OH or C=C; nmr (CCl$_4$) multiplets at $\delta$ 3.36 and 2.2–1.0, ratio 1:4. The last eluent, mp 90–91°, was identified as *cis*-1-*cis*-decalol[3,14] (1.8 g, 39%) by comparison of its ir and nmr spectra with those of an authentic sample.[3]

**Molecular Chlorine Additions. Radical Conditions.**[8a]—Chlorine (2.0 g, 28 mmol), which had been condensed in a chilled finger condenser, was swept by a stream of dry nitrogen into an irradiated (300-W lamp) solution of **1** (2.72 g, 20 mmol) in carbon tetrachloride (100 ml) under a nitrogen atmosphere. The temperature of the mixture was kept below 40° by external cooling; the reaction appeared to be complete after 10 min. The mixture was washed with water, dried (MgSO$_4$), concentrated (4.3 g of residue), analyzed by gc (12-ft Carbowax 20M column) and nmr methods, and subsequently distilled (2.4 g of distillate, 1.6 g of undistilled residue). About 80% of the mixture gc trace area was contained in a peak with a small shoulder of longer retention time; the nmr spectrum showed little absorption for C=CH. The lower boiling distillate fraction [bp 44–44.5° (0.2 mm), 0.7 g] was further purified by preparative gc. Its ir and nmr spectra included absorptions for C=CH: nmr (CCl$_4$) $\delta$ 5.52 (m, 2, C=CH), 4.18 (m, 1, HCCl), 2.8–1.3 (13, remainder of H). This minor constituent appears to be 5-chloro-2-bicyclo[4.4.0]decene (**8**). The higher boiling distillate fraction [bp 70–76° (0.2 mm), 1.7 g] was shown by gc to consist of two components in about equal proportions. The ir spectrum indicated no unsaturation; nmr (CCl$_4$) $\delta$ 4.10 (m, 2, HCCl), 2.6–1.3 (14, decalin ring). When a sample of this fraction was treated with alcoholic potassium hydroxide, the elimination product obtained was readily dehydrogenated by palladium on carbon at 140° to tetralin.[16] These data show that this chlorine adduct is most probably a mixture of stereoisomeric 1,4-dichloro-*cis*-decalins (**7**).

**B. Ionic Conditions.**[8a]—The above experiment was repeated, except that air rather than nitrogen was used to sweep chlorine into the solution of **1**, and the mixture was not irradiated. Approximately 2 hr was required for the disappearance of the yellowish color of chlorine. Besides this difference in apparent reaction times, we found no other substantial differences between the nitrogen-sweep and air-sweep reactions. The major products had identical gc retention times in both cases.

**Iodobenzene Dichloride. A. Radical Conditions.**[8b]—A mixture of **1** (1.36 g, 10 mmol), iodobenzene dichloride[17] (2.75 g, 10 mmol), and carbon tetrachloride (25 ml) was degassed by a freeze–thaw method and sealed. When the mixture was warmed to room temperature, a spontaneous, exothermic reaction occurred, and the solid iodobenzene dichloride disappeared within a few seconds. The mixture was cooled to room temperature, washed with water, dried (MgSO$_4$), and analyzed by gc on a 6-ft UCON column at 160°. Six products, with relative gc trace areas of 17, 18, 17, 15, 29, and 4, in order of increasing retention time, were present in the mixture. By comparison of gc characteristics with those of products obtained from molecular chlorine additions, the first component in this mixture was identified as 5-chloro-2-bicyclo[4.4.0]decene (**8**) and the fourth and fifth components as the stereoisomeric 1,4-dichloro-*cis*-decalins (**7**). The other components in the mixture were not identified.

**B. Ionic Conditions.**[8b]—Iodobenzene dichloride (2.75 g, 10 mmol) was added in one portion to a stirred solution of **1** (1.36 g, 10 mmol) in carbon tetrachloride (25 ml). The mixture was protected from atmospheric moisture by a calcium chloride tube, but air was not excluded. After 4.5 hr, the mixture had become homogeneous. It was washed with water, dried, and analyzed by gc (6-ft UCON column, 160°). Peaks with the same six retention times as were obtained from the radical product mixture were obtained; their relative areas, in order of increasing retention times, were 23, 13, 13, 19, 27, and 5.

**Addition of Bromoform.**—A solution of **1** (5.0 g, 37 mmol) in bromoform (47 g, 190 mmol) was irradiated with 3500-Å light for 15 hr. When most of the remaining reactants had been removed at reduced pressure, 11.5 g of residue remained. The nmr and ir spectra of this residue included weak absorptions for olefin (cis), but otherwise the chemical shifts and multiplicities were identical with those in the nmr spectrum of the purified product. Elution chromatography of 3.0 g of the residue on 90 g of Florisil led to the isolation of one product (1.7 g, 45%), identified on the basis of spectral data as 1-bromo-4-dibromomethyl-*cis*-decalin (**4a**): ir (neat) 14.49 and 14.93 $\mu$ (CBr); nmr (CCl$_4$) $\delta$ 5.76 (d, $J$ = 4 Hz, 1, HCBr$_2$), 3.95 (t d, $J$ = 9.5, 2.5 Hz, 1, HCBr), 3–1 (complex m, 15, decalin ring).

*Anal.* Calcd for C$_{11}$H$_{17}$Br$_3$: C, 34.0; H, 4.4. Found: C, 34.3; H, 4.4.

**Addition of Bromotrichloromethane.**—A solution of **1** (10 g, 73.5 mmol) in bromotrichloromethane (80 g, 404 mmol) under nitrogen was irradiated for 1 hr with 3500-Å lamps in a Rayonet apparatus. The nmr spectrum of the mixture then no longer included absorptions characteristic of **1**, but it and gc analysis did show that a small amount of chloroform had formed. Removal of excess bromotrichloromethane at 25° (0.7 mm) left 25 g of residue, whose nmr spectrum included signals for C=CH and two sets of six-line signals (not identical) at $\delta$ 4.46 and 3.92 (relative intensities 0.7:1). Distillation of the concentrate gave 17 g of a slightly yellow material [bp 152–156° (0.7 mm)] which crystallized, and 3.8 g of viscous residue. The distillate was recrystallized from pentane to colorless crystals, 15 g: mp 67–69°; ir (KBr) 12.8–13.5 $\mu$ (CCl$_3$); nmr (DCCl$_3$) $\delta$ 3.92 (t d, 1, $J$ = 9.5 and 2.5 Hz, HCBr), 2.65 (b m, 1, HCCCl$_3$), 2.5–1.0 (complex, 16, decalin ring). This major product was identified as *trans*-1-bromo-4-trichloromethyl-*cis*-decalin (61% yield).

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[14] W. Hückel, R. Danneel, A. Gross, and H. Naab, *Justus Liebigs Ann. Chem.*, **502**, 99 (1933).

[15] W. Hückel, *ibid.*, **441**, 1 (1925).

[16] This dehydrochlorination–dehydrogenation experiment was performed by Dr. E. E. Green, to whom we express our appreciation.

[17] H. J. Lucas and E. R. Kennedy, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 482.

*Anal.* Calcd for $C_{11}H_{16}BrCl_3$: C, 39.5; H, 4.8. Found: C, 39.7; H, 5.0.

Several attempts to isolate the component of the original mixture responsible for the nmr signal at δ 4.46 were unsuccessful. When a portion of the original, concentrated reaction mixture was treated with 0.5 molar equiv. of potassium hydroxide in methanol–water–dimethyl sulfoxide solvent[18] at room temperature, the resulting product mixture no longer gave nmr absorptions at δ 4.46, but it did give stronger absorptions in the olefin region. We inferred that the δ 4.46 signal most likely belonged to *cis*-1-bromo-4-trichloromethyl-*cis*-decalin, the easily dehydrobrominated (axial Br) stereoisomer of the major product.

Chromatography of a portion (5 g) of an original, concentrated reaction mixture on acid-washed alumina with pentane solvent gave, in addition to the major component and some minor unidentified components which were eluted early, a small amount (0.2 g) of a component whose spectral characteristics led us to identify it tentatively as 6-bromo-5-trichloromethyl-*cis*-1-cyclodecene: ir (neat) 12.8 ($CCl_3$) and 14.0 μ (cis C=C); nmr ($CCl_4$) b m at δ 5.75–5.33 (C=CH), 4.3 (HCBr), and 3.5–0.8 ($HCCCl_3$ + $CH_2$) in an approximate ratio of 2:1:13. None of the fractions eluted from the chromatography column gave an nmr absorption at δ 4.46.

Irradiation (3500 Å) of a solution of 1 (2.72 g, 20 mmol), bromotrichloromethane (3.96 g, 20 mmol), and methylene chloride (200 ml) under a nitrogen atmosphere for 3.5 hr produced a product mixture whose nmr spectrum was quite similar to that of the mixture obtained in excess bromotrichloromethane, except for the ratio of the δ 4.46 and 3.92 absorptions and the relative intensities of the C=CH absorptions. The mixture from methylene chloride solution gave a ratio of 1:4 (δ 4.46:3.92) and less intense C=CH absorption.

**Methylenation[11] of 1.**—From a mixture of zinc–copper couple (8.6 g, 132 mmol), anhydrous ethyl ether (40 ml), 1 (18 g, 132 mmol), and methylene iodide (35 g, 130 mmol), which had been stirred at reflux temperature for 24 hr, was obtained a product mixture concentrate which contained 1, *cis*-1,2-divinylcyclohexane,[3] and the stereoisomeric methylenation products (*ca.* 60% yield) in a ratio of 89:11 (*trans*-bicyclo[8.1.0]undec-*cis*-4-ene:*cis*-bicyclo[8.1.0]undec-*trans*-4-ene). The major component was isolated by preparative gc: nmr ($CCl_4$) δ 5.40 (m, 2, C=CH), 2.5–1.3 (12, $CH_2$ in decalin ring), 0.48 (m, 2, bridgehead H), and 0.10 (m, 2, cyclopropane $CH_2$); ir 14.2 μ (strong, *cis* C=C).

A solution of diazomethane in ether (prepared from 34 mmol of *N*-methyl-*N*-nitrosourea;[19] *ca.* 24 mmol of diazomethane) and copper powder (0.5 g) were added sequentially to chilled 1 (3.5 g, 26 mmol) with stirring. With continued stirring, the mixture was kept at 0 to −5° for 3 hr and then at room temperature overnight. Addition of a few drops of acetic acid produced no gas evolution. The filtered solution was washed, dried, concentrated by rotary evaporation, and analyzed by gc. Only a small amount of methylenation had occurred. The stereoisomeric bicyclo[8.1.0]undec-4-enes were identified by the identity of their gc characteristics to those of the Simmons–Smith[11] products. The ratio of additions to the trans:cis alkene linkages was 73:27.

**Addition of Dibromomethylene.**[10]—Bromoform (8.5 g, 33 mmol) was added dropwise to a stirred, ice–salt chilled slurry of 1 (4.4 g, 32 mmol), potassium *tert*-butoxide (4.2 g, 38 mmol), and pentane (50 ml). The mixture, which became tan, was allowed to warm to room temperature and was stirred overnight. Conventional work-up and distillation led to the isolation of 70–75% yield of a mixture of addition products. Gc analysis indicated that two adducts were formed in a ratio of 3:1. The major component was isolated by preparative gc: ir (neat) 14.25 μ (strong, cis C=C); nmr ($CCl_4$) δ 5.40 (m, 2, C=CH), 2.25 (m, 8, C=C-$CH_2$ and $CHCH_2$), 1.65 (4, $CH_2CH_2CH_2$), and 1.15 (m, 2, bridgehead H). These data are consistent with the identification, 11,11-dibromo-*trans*-bicyclo[8.1.0]undec-*cis*-4-ene.

**Addition of Isopropylidenemethylene.**[12]—Lithium 2-ethoxyethoxide[12] (5.0 g, 51 mmol) was added in three portions to a stirred mixture of 5,5-dimethyl-*N*-nitrosooxazolidone[12] (5.0 g, 35 mmol) and 1 (20 ml) at 45–50°. Each addition caused vigorous gas evolution. After 30 min of stirring, the mixture was poured into ice water and extracted into ethyl ether. Conventional work-up and reduced pressure distillation gave a 75% yield of a mixture of adducts in a 7:3 ratio (gc), bp 71–73° (0.7 mm). The products were separated by preparative gc (6 ft × 0.25 in. column, 30% SE-30 silicone on Chromosorb P, 140°). The major product (shorter gc retention time) was identified by its spectral characteristics as 11-isopropylidene-*trans*-bicyclo[8.1.0]-undec-*cis*-4-ene (**9**): ir (neat) 14.20 μ (cis C=C); nmr ($CCl_4$) δ 5.40 (m, 2, C=CH), 1.70 (s, 6, $CH_3$), 2.5–1.4 (12, $CH_2$), and 0.95 (m, 2, bridgehead H). The minor product was identified by its spectral characteristics as 11-isopropylidene-*cis*-bicyclo[8.1.0]-undec-*trans*-4-ene (**10**): ir (neat) 10.4 μ (trans C=C); nmr ($CCl_4$) δ 5.55 (m, 2, C=CH), 1.66, 1.70 (2 s, $CH_3$), 2.3–0.8 (other H).

**Registry No.**—**1,** 1124-78-3; **2** (X = OH), 14759-74-1; **2** (X = $N_3$), 37710-16-0; **2a,** 37710-17-1; **2c** (R = $CH_3$), 37710-18-2; **2c** (R = Ph), 37710-19-3; ***trans*-4a,** 37710-22-8; ***cis*-4b,** 37710-23-9; ***trans*-4b,** 37710-24-0; **7,** 37710-20-6; **8,** 37710-21-7; 6-bromo-5-trichloromethyl-*cis*-1-cyclodecene, 37710-25-1; *trans*-bicyclo[8.1.0]undec-*cis*-4-ene, 24381-94-0; *cis*-bicyclo-[8.1.0]undec-*trans*-4-ene, 24315-98-8; 11,11-dibromo-*trans*-bicyclo[8.1.0]undec-*cis*-4-ene, 24315-95-5; **9,** 38821-32-8; **10,** 38821-33-9.

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[18] J. G. Traynham and T. M. Couvillon, *J. Amer. Chem. Soc.*, **87**, 5806 (1965).

[19] "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, pp 165, 461.