slowly precipitated. The crude **33** (247 mg, 69%) was filtered, dried, and recrystallized four times from 95% ethanol. The recrystallized **33** thus obtained melted at 212–213°.

Anal. Calcd for $C_{22}H_{15}N_3O_2$: C, 74.75; H, 4.27; N, 11.89. Found: C, 74.93; H, 4.42; N, 12.11.

Alternate Synthesis of 33.—Reaction of the chalcone **34** and benzamidine according to the procedure of Dodson and Seyler gave crude **33**. The crude **33** was dissolved in hot acetonitrile and precipitated by the addition of a few drops of water. This crude purification was repeated and the **33** then recrystallized four times from 95% ethanol. The **33** so obtained melted at 212–215° and was identical with the product isolated from the reaction of **11** with sodium methoxide.

Conversion of 2,4,6-triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (10) into 2,4,6-triphenylpyrimidine (32) was analogous to the formation of **33** from **11** except that the reaction mixture was refluxed for 24 hr and the solvent evaporated. The residue was washed well with water and recrystallized three times from 95% ethanol. The recrystallized **32** obtained in 30% yield melted at 185–186° (lit.[13] mp 183.5–185°).

Conversion of 2,2-Dimethyl-4-phenyl-6-*p*-nitrophenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (15) into *trans*-2-(*p*-Nitrophenyl)-3-benzoylaziridine.—A mixture of 307 mg of **15** and 10 ml of commercial acetic acid was kept at room temperature for 3 days. The acetic acid was evaporated and the gummy residue treated with 10 ml of methanol. The 2-*p*-nitrophenyl-3-benzoylaziridine (262 mg) was recrystallized twice from 95% ethanol to give material, mp 140–141°, which was identical with an authentic sample of the aziridine. Compounds **18**, **22**, **26**, and **29** reacted analogously to give 2-*p*-nitrophenyl-3-benzoylaziridine in 41, 36, 82, and 74% yields, respectively. Cyclohexanone was also isolated in the form of its 2,4-dinitrophenylhydrazone from the acetolysis of compound **26**.

2,2-Dimethyl-4-phenyl-6-nitrophenyl-1,3-diazabicyclo[3.1.0]-hex-3-ene Hydrochloride.—Dry hydrogen chloride was bubbled through a solution of 500 mg of **15** in 75 ml of dry ether for about 5 min. The red hydrochloride was filtered and washed repeatedly with dry ether. Decomposition of the hydrochloride took place between 185–200°.

Anal. Calcd for $C_{18}H_{18}ClN_3O_2$: Cl, 10.31. Found: Cl, 10.21.

The hydrochlorides of **11** and **22** were also prepared and decomposed at 205–245° and 98–145°, respectively. The chlorine analyses for these two compounds were close to the theoretical.

***trans*-2-Phenyl-3-*p*-nitrobenzoylaziridine** was prepared by suspending 5 g of 4′-nitrochalcone dibromide in a mixture of 50 ml of 95% ethanol and 12–15 ml of concentrated ammonium hydroxide. The mixture was stirred 6.5 hr and filtered. The material was recrystallized from ethanol and melted at 122–122.5°.

Anal. Calcd for $C_{15}H_{12}N_2O_3$: C, 67.15; H, 4.51; N, 10.44. Found: C, 67.12; H, 4.83; N, 10.06.

Registry No.—**4**, 13591-54-3; **5**, 13591-55-4; **6**, 13591-56-5; **7**, 13591-57-6; **8**, 13591-58-7; **9**, 13591-59-8; **10**, 13591-60-1; **11**, 13591-61-2; **11** hydrochloride, 13591-62-3; **12**, 13591-63-4; **13**, 13746-77-5; **14**, 13591-64-5; **15**, 13591-65-6; **15** hydrochloride, 13591-66-7; **16**, 13591-67-8; **17**, 13591-68-9; **18**, 13591-69-0; **19**, 13573-32-5; **20**, 13591-70-3; **21**, 13573-33-6; **22**, 13591-71-4; **22** hydrochloride, 13591-72-5; **23**, 13591-73-6; **24**, 13591-74-7; **25**, 13591-75-8; **26**, 13591-76-9; **27**, 13591-77-0; **28**, 13591-78-1; **29**, 13591-79-2; **30**, 13591-80-5; **31**, 13639-90-2; **33**, 13573-34-7; *trans*-2-phenyl-3-*p*-nitrobenzoylaziridine, 13591-81-6; **34**, 1666-86-0.

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Cyclization Reactions of 6-Hepten-2-yl Radicals, 1-Trichloromethyl-6-hepten-2-yl Radicals, and Related Compounds[1]

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Bromotrichloromethane, carbon tetrachloride, and chloroform all react with 1,6-heptadiene to give cyclization products having a five-membered ring, contrary to published reports. An unusually clean cyclization of 6-iodo-1-heptene to *cis*- and *trans*-1-methyl-2-iodomethylcyclopentanes occurred by heating with azonitrile initiator. Model compounds were used for comparison of their infrared and nmr spectra to confirm the structures of the new compounds. Free-radical reaction of 1-iodoperfluoropropane with 1,6-heptadiyne gave little if any cyclization product, possibly because of the highly strained structure which would have resulted. Addition of carbon tetrachloride to 1,6-heptadiene by the redox-transfer method gave considerably better yield of product than azonitrile initiation.

Cyclization of certain perfluoroalkyl-substituted 6-hepten-2-yl radicals to a five-membered ring product was observed[2] in the free-radical reaction of iodoperfluoroalkane and 1,6-heptadiene. This behavior contrasts with that observed in cyclic polymerization which is reported[3,4] to give six-membered rings, but resembles that recently reported by Walling and Pearson[5] and by Lamb, Ayers, and Toney[6] for the 5-hexen-1-yl radical.[7] Julia and Maumy[8] and Cadogan, Hey, and Hock[9] have obtained both five- and six-membered ring products from free-radical cyclizations. Friedlander and Tiers,[10] in a patent which discloses many related free-radical reactions of 1,6-heptadiene and its analogs with various addenda, describe cyclization products from presumably similar radicals in terms of six-membered ring structures.[11] A detailed report of these reactions has not appeared, and it was felt that, in view of the unexpected nature of our more recent results,[2] a closer examination of this subject would be desirable.

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(1) This work was supported by the U. S. Army Research Office, Durham.

(2) N. O. Brace, *J. Org. Chem.*, **31**, 2879 (1966).

(3) C. S. Marvel and R. D. Vest, *J. Am. Chem. Soc.*, **79**, 5771 (1957); C. S. Marvel and J. K. Stille, *ibid.*, **80**, 1740 (1958).

(4) G. B. Butler and R. J. Angelo, *ibid.*, **79**, 3128 (1957).

(5) C. Walling and M. S. Pearson, *ibid.*, **86**, 2262 (1964).

(6) R. C. Lamb, P. W. Ayers, and M. K. Toney, *ibid.*, **85**, 3483 (1963).

(7) It was also noted[5] that the 5-penten-1-yl radical failed to cyclize at all under these conditions; this was attributed to an unfavorable highly strained transition state leading to cyclic product. These results also parallel our finding that 1,5-hexadiene gave no cyclic product in free-radical reactions with iodoperfluoropropane.[2]

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(9) J. I. G. Cadogan, D. H. Hey, and A. Ong Soon Hock, *Chem. Ind.* (London), 753 (1964).

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SCHEME I

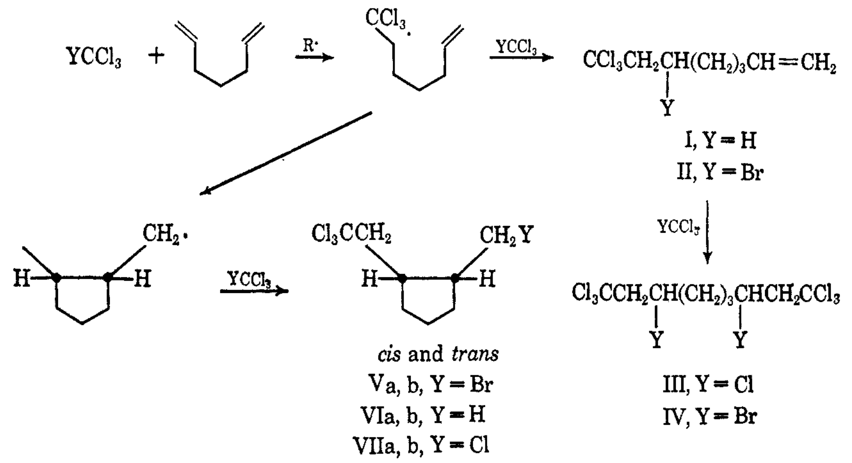


TABLE I

NUCLEAR MAGNETIC RESONANCE SPECTRA DATA FOR THE ADDUCTS FROM CARBON TETRACHLORIDE, CHLOROFORM, OR BROMOTRICHLOROMETHANE AND 1,6-HEPTADIENE

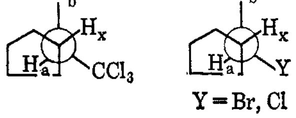
	Chemical shift, ppm			CH_2CCl_3 coupling constants, cps			
Compd	-CHY	$-CH_2CCl_3$	$-CH_2Y$	$\|J_{AB}\|$	$\|J_{AX}\|$	$\|J_{BX}\|$	ν_{AB}
II	4.25	3.30		15.5	7.2	4.8	14.5
III	4.21	3.19		14.5	11	4	13
IV	4.30	3.35		15.5	6.3	4.3	15
Va,b		2.80	3.35	15.0			
VIa,b		2.70		14.0	8.0	4.0	...
VIIa,b		2.82	3.50	15.0	6.5	7.5	15.0
VIII	4.21	3.18		14.0			

Cyclic Products from 1,6-Heptadiene and Carbon Tetrachloride, Chloroform, or Bromotrichloromethane.—In each case cyclization to a substituted *cyclopentane* occurred as the predominant process, using azonitrile or peroxide initiation. Results from several reactions are summarized in Scheme I. Clean reaction to the indicated products was observed. A small amount of olefinic compound I or II was obtained from reaction of 1,6-heptadiene with chloroform or with bromotrichloromethane, and the bisadduct III or IV was also obtained from carbon tetrachloride or from bromotrichloromethane. The effect of reaction conditions on the relative amounts of the cyclization and open-chain products was not defined. The *cis* and *trans* cyclic isomers could not be separated by fractional distillation, but gas chromatography was used to separate isomer pairs and to determine the composition of the product mixture. Analytical data and infrared and nmr spectroscopy confirmed the postulated structures for the new compounds. Identification of the cyclic isomers as five-membered ring products was demonstrated by nmr spectroscopy which showed the $-CH_2Y$ group and not the -CHY group.

Nuclear Magnetic Resonance Spectra of Adducts.—Results from a detailed analysis of nmr spectra of this series of compounds are given in Table I. 1,1,1,3-Tetrachlorononane (VIII) was prepared by the free-radical addition of carbon tetrachloride to 1-octene.[12] The structural features present in VIII are very similar to those in II, III, and IV. Chemical shifts of the protons in the -CHCl- and CCl_3CH_2- groups are those anticipated;[13-15] splitting patterns and coupling constants are consistent with these features in the new compounds. In order to facilitate study and discussion the nmr spectra of adducts IV, Va,b, VIa,b and VIIa,b are shown in Figure 1 and the spectra for the olefinic adduct II and reference compound VIII are given in Figure 2 for comparison.

The trichloroethyl group in these adducts gave rise to a characteristic ABX pattern which was analyzed by the graphical method of Bible.[13] The X portion of the spectrum is obscured in most cases by further coupling to adjacent protons, but the probable coupling constants could be evaluated from the relations between centers of the two AB quadruplets and the sum and differences of the absolute values of J_{AX} and J_{BX}. A value of J_{AX} greater than 20 cps was considered unlikely from published values for this type of system.[14,15] The splitting pattern of the $-CH_2Y$ group (in adducts Va,b and VIIa,b) appeared also to be derived from an ABX system. In VIa,b, of course, $-CH_2Y$ is a methyl group and is clearly indicated in the nmr spectrum.

The reason for the observed ABX pattern is the nonequivalence of geminal protons attached to the trichloroethyl group or the halomethyl group, respectively,



as illustrated by the Newman projection formulas.[15] The size and electronegativity of the halogen substitu-

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[14] C. N. Banwell and N. Sheppard, *Discussions Faraday Soc.*, 117 (1962). Reported values for coupling constant between geminal hydrogen nuclei of the CH_2 group in CH_3CCl_3: J = 13.0 cps; CH_3Cl, 10.8 cps; CH_3Br, 10.2 cps.

[15] J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 49.

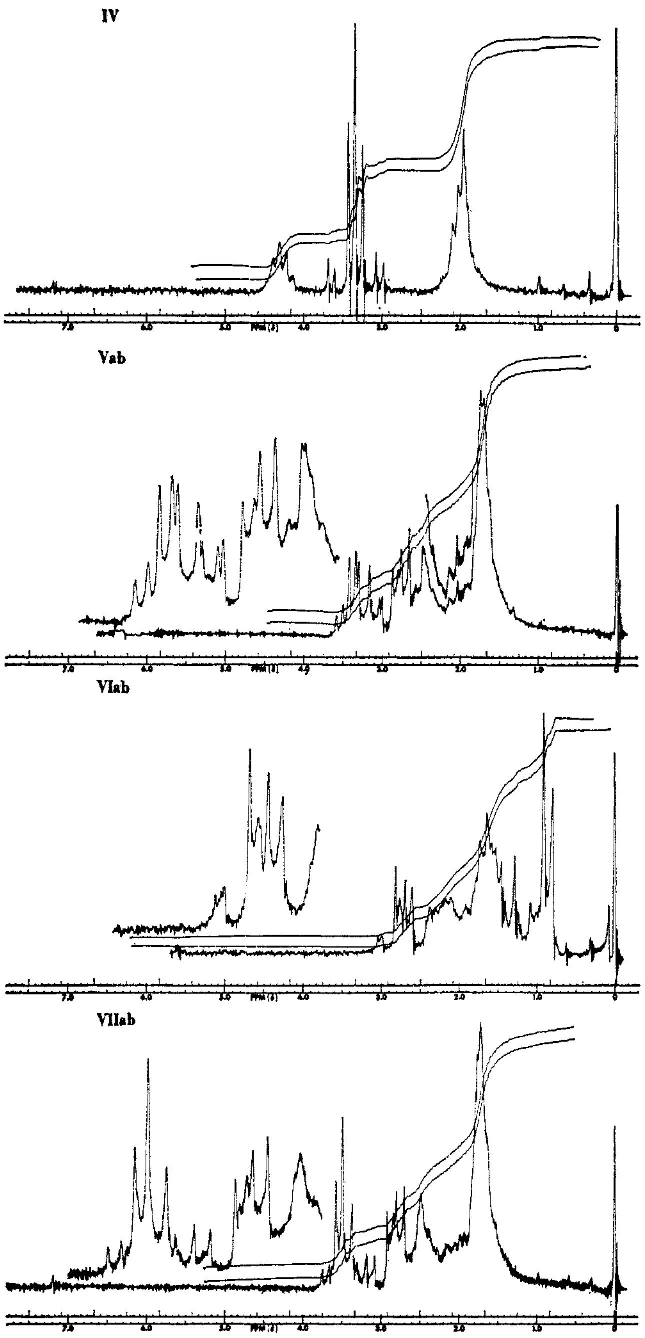


Figure 1.—Nuclear magnetic resonance spectra of adducts run at 60 Mc with tetramethylsilane internal reference at 0 ppm: IV and VIIa,b in deuteriochloroform, V in carbon disulfide solution, and VI neat at 40°. Inserts in Va,b, VIa,b, and VIIa,b were run at 250-cps sweep width.

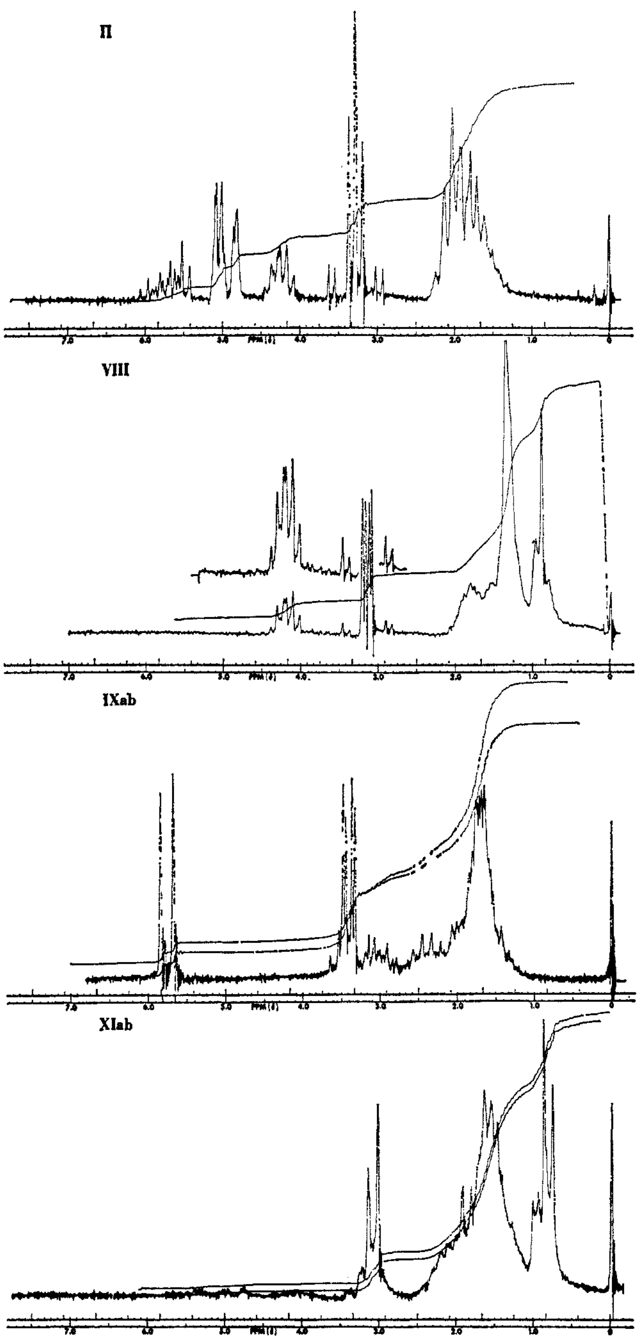


Figure 2.—Nuclear magnetic resonance spectra of adducts at 60 Mc, using tetramethylsilane as internal reference at 0 ppm; II, IXa,b (93% one isomer) and XIa,b (27:64 mixture) were run neat and VIII was run in deuteriochloroform solution at 40°.

ents also may contribute to restricted rotation of these groups attached to adjacent carbons of the five-membered ring. The result is a different average chemical environment for the geminal protons. For the -CH_2-CCl_3 group a coupling constant J_{AB} of 14.5 ± 1 cps was consistently observed, with J_{AX} and J_{BX} varying from 5 to 15 cps. For the -CH_2Y group a coupling constant J_{AB} of 10 cps was found for adducts Va,b and VIIa,b. J_{AX} and J_{BX} of -CH_2Y varied from 2 to 10.6 cps, which are reasonable values for these structures.

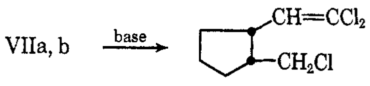
As is clearly evident from the spectra in Figures 1 and 2, the chemical shifts and areas of the proton resonances in each compound are consistent with the assigned structures. There are no unexplained or unexpected features. The influence of adjacent halogen atoms on the chemical shift of protons of the -CH_2CCl_3 group is noteworthy. In III the proton resonance is at 3.19 ppm, and this is increased to 3.35 ppm by replacing Cl by Br. In adducts VIa,b with a CH_3 group on the adjacent carbon, the -CH_2CCl_3 protons are at 2.70 ppm; the presence of a -CH_2Cl group in Va,b or VIIa,b causes a shift to 2.80 ppm.

The spectrum of VIIa,b was observed for mixtures varying in proportion from 5:95 to 35:65. There was no detectable change in resonance patterns, chemical shifts, or proton areas. This conclusively showed that the two members of the isomer pair did not differ in significant features. In particular, an alternative six-membered cyclohexane ring compound is ruled out as reaction product. In view of the similarity in the spectra of Va,b and VIIa,b, similarity in structure is evident.

The data for VIa,b are particularly compelling since only in a cyclopentane ring product would both CH_3 and CH_2CCl_3 proton resonances be present. The spectrum given in Figure 1 is of a mixture containing about 6% of I and *cis* and *trans* VIa,b (16:72). In VIa,b one CH_3 doublet (J = 7 cps) is seen at 0.90 ppm and the other methyl group doublet is at 1.05 ppm. The $(CH_2)_4$ group in I gave a sharp spike at 1.3 ppm and the $-CH{=}CH_2$ protons of I are present at 6.1 ppm.

Infrared spectra of the various adducts also were consistent with the postulated structures. In VIa,b, for example, the CH stretching band of CH_3 is at 2870 cm^{-1} and CH deformation bands of $C-CH_3$ are at 1450 and 1380 cm^{-1}.

Chemical Evidence for Adduct Structures.—Dehydrohalogenation of a 20:80 mixture of VIIa,b by 1 equiv of sodium methoxide in methanol or by potassium hydroxide in ethanol gave in 66% conversion (82% yield) a 30:70 mixture of dichlorovinyl isomers, IXa,b.



IXa, b

The infrared spectrum of IXa,b gave an absorption band for the $-CH{=}CCl_2$ group at 6.14 and bands at 10.9 and 11.3 μ. Tobler and Foster[16] reported that dichloromethylenenorbornene gave an absorption band at 6.05 and bands at 11.0–11.3 μ. The nmr spectrum of one isomer of IXa,b is shown in Figure 2. In addition to the vinyl proton resonance doublet at 5.75 ppm (J = 10 cps), the $-CH_2Cl$ pattern at 3.40 ppm appears as an ABX system, as expected. Thus, the structure is confirmed by nmr data which definitely exclude a cyclohexane product as a possibility. Dehydrohalogenation of trichloroethyl compounds to products having the dichlorovinyl structure has been previously observed.[12,16,17]

Attempts to prepare crystalline acids from VIIa,b by acid or base hydrolysis were unsuccessful. Heating of VIIa,b with barium hydroxide in ethylene glycol[17] gave mostly tar, as did reaction with perchloric acid in acetic acid.[18] Hydrolysis of VIIa,b in concentrated sulfuric acid[16] gave a black mixture which defied resolution.

Reduction of II and Va,b by lithium aluminum hydride also failed to give conclusive evidence for the hydrocarbon skeletons of the products. This procedure was successfully employed by Martin and Gleicher[19] to convert 1-phenyl-2-bromo-3,3,3-trichlorobutane to *n*-butylbenzene. With II and Va,b, however, replacement of halogen was accompanied by elimination to give *n*-octane, *cis*- and *trans*-2-octenes, and an unsaturated cyclic C_8H_{14} compound.

Free-Radical Addition by Redox-Transfer Method.—Reaction of carbon tetrachloride and 1,6-heptadiene employing the redox-transfer system developed by Asscher and Vofsi[20] gave in 69% yield a monoadduct mixture which appeared to be all cyclic and identical with that obtained by azonitrile-initiated reaction.

$$CCl_3CH_2\dot{C}H(CH_2)_3CH{=}CH_2 + MCl^+ \longrightarrow CCl_3CH_2CHCl(CH_2)_3CH{=}CH_2 + M^+ \quad (1)$$

$$CCl_3CH_2\dot{C}H(CH_2)_3CH{=}CH_2 + MCl^+ \longrightarrow \text{VIIa,b} + M^+ \quad (2)$$

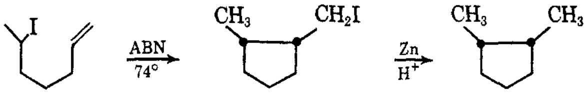
$$M^+ + CCl_4 \rightleftharpoons MCl^+ + CCl_3\cdot \quad (3)$$

$$CCl_3CH_2CHCl(CH_2)_3CH{=}CH_2 + CCl_4 \xrightarrow[\text{steps}]{2} \text{III} \quad (4)$$

This was a significantly higher conversion than the 47% given by reaction with 3 mole % of azonitrile initiator. There was also obtained from the metal chloride catalyzed reaction a 20% conversion to III (total yield 89%). In neither case was a detectable amount of olefinic adduct found in the product mixture.

It was anticipated that the transfer step (eq 1) with metal halide (MCl^+) would result in an altered proportion of olefinic and cyclic adducts because of the difference in polarity and steric requirements for carbon tetrachloride and MCl^+ in the transfer step. In free-radical reactions of this type such differences may exert a profound influence.[21,22] These and related considerations are being investigated presently.

Cyclization of 6-Iodo-1-heptene.—Further evidence for this radical cyclization process and for structures of the products was acquired from a study of the isomerization of 6-iodo-1-heptene (X). Heating X with azonitrile initiator in *n*-hexane solution at 74° for 24 hr gave isomerization to *trans*- and *cis*-1-iodomethyl-2-methylcyclopentanes (XIa,b) in a 1:2.7 ratio.



X XIa,b XIIa,b

Cyclization of X by a free-radical process evidently takes place through the intermediate 6-hexen-2-yl radical and is formally similar to the reaction observed[5,6] with the 5-hexen-1-yl radical generated by two other methods. Under the conditions studied, only with an initiator present did isomerization occur. X, itself, was a rather light-sensitive compound, but heating in dilute solution gave an unusually clean reaction.

Reduction of XIa,b gave *trans*- and *cis*-1,2-dimethylcyclopentanes, XIIa,b, having gas chromatographic (glpc) retention times identical with those of an authentic sample synthesized from 1,2-dimethyl-1-cyclopentene.[23-25] The proportion of *trans* and *cis* isomers XIIa,b formed from XIa,b was unchanged during zinc reduction, as would be expected.

In a 27:64 mixture of XIa,b shown in Figure 2 there were methyl group resonances at 0.89 and at 0.95 ppm (J = 7 cps), and the $-CH_2I$ proton resonance peak at 3.30 ppm was also split into two lines (J = 7 cps) by the adjacent ring proton.

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[17] G. Dupont, R. Dolou, and G. Clement, *Compt. Rend.*, **230**, 2027 (1950).

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Noncyclization Addition Reactions of 1,6-Unsaturated Systems.—Normal addition rather than cyclization occurred in the free-radical reaction of 1-iodoperfluoropropane with 1,6-heptadiyne. We hoped to obtain a rather unique 1,2-dimethylenecyclopentane structure which would have been quite highly strained. In previous reaction,[26] 1-hexyne gave a 95% yield of *trans*-1-perfluoropropyl-2-iodo-1-hexene and trifluoromethylacetylene also gave *trans* addition.[27] In the present case reaction occurred more slowly than with 1-hexyne and the product XIIIa,b was obtained in 44% conversion, or 71% yield based on materials consumed. The *trans* isomer XIIIa comprised the major amount

$$CF_3CF_2CF_2I + HC{\equiv}C(CH_2)_3C{\equiv}CH \longrightarrow CF_3CF_2CF_2CH{=}CI(CH_2)_3C{\equiv}CH$$

XIIIa,b

of product, and in its infrared spectrum showed the vinyl stretching band at 1632 cm^{-1} with associated bands at 985, 950, 935 and 920 cm^{-1}. The *cis* isomer XIIb was separated by glpc and gave an infrared spectrum with vinyl stretching band at 1640 cm^{-1}. Both isomers showed the CH stretching band and the triple bond stretching band of C≡CH. When this second isomer appeared in glpc analysis of the distilled product at a retention time almost twice that of the *trans* isomer, it was at first suspected that it might have been a cyclic product. Failure to obtain the radical cyclization product in this case may reasonably be attributed to the highly strained nature of the structure which would have been formed.

Cyclization reactions of other 1,6-unsaturated compounds, such as diallylcyanamide, diethyl 1,6-heptadiene-4,4-dicarboxylate, ethyl 1,6-heptadiene-4-carboxylate, and N,N-diallylacetamide, with various addenda are being currently studied. Results from these experiments will be reported before an attempt is made to define the scope of this free-radical cyclization reaction.

Experimental Section

Source and Purification of Materials.—Chloroform and carbon tetrachloride were reagent grade material. *n*-Hexane (99%) was from Phillips Petroleum Co. Bromotrichloromethane, 1,6-heptadiene, 1-methyl-2-cyclopentanone, 1,6-heptadiyne, and 1,5-hexadiene were obtained from Columbia Organic Chemicals Co. and were redistilled before use. Azobisisobutyronitrile (mp 102° dec) was supplied by Du Pont. Two Nester–Faust spinning-band columns were used; column A was fitted with a 16-in. stainless steel band and column B had a 24-in. platinum band. Infrared spectra were recorded by a Beckman IR-8 spectrophotometer, and nmr spectra were obtained at 60 Mc using a Varian A-60 instrument with tetramethylsilane as internal reference. Resonance bands are give in parts per million downfield. Areas under the peaks were integrated by the instrument. Analyses were performed by Galbraith Laboratories, Inc.

Free-Radical Reaction of Bromotrichloromethane and 1,6-Heptadiene.—In a 100-ml flask fitted with an addition funnel, Dry Ice reflux condenser, magnet stirring bar, and a nitrogen inlet, was placed 1,6-heptadiene (9.6 g, 0.10 mole) and azobisisobutyronirile (ABN; 0.16 g, 0.001 mole). Bromotrichloromethane (19.8 g, 10.0 ml, 0.10 mole) was added dropwise while the flask was being heated in an oil bath at 52–65°. After 5.0 ml had been added an exothermic reaction began. While the flask was being cooled with water, the temperature rose to 100°. At 55° the addition was resumed. Again the temperature rose to 110° after 8 ml had been added. After the mixture was cooled to 58° the remaining bromotrichloromethane was added, and the temperature was kept at 70–76° for 4-hr additional time. Gas chromatography (3-ft silicone resin, XE-60 column, 172°, 10 psi of helium carrier gas) gave peaks at 4.5, 7.0, and 12 min, but the 7.0-min peak contained unresolved cyclic isomers, as indicated by analysis below. Distillation using a total reflux, partial take-off head without a column gave the following cuts: (1) bp 106–118° (2.0 mm), 10.5 g, $n^{25}\text{D}$ 1.5143; (2) bp 120–124° (2.2–0.25 mm), 8.0 g, $n^{25}\text{D}$ 1.5261; and (3) bp 122–112° (0.2–0.15 mm), 1.0 g, $n^{25}\text{D}$ 1.5315. A residue of 8.8 g remained. The cold trap contained 1.4 g, $n^{25}\text{D}$ 1.4160 (total recovery 99%). Redistillation of cuts 1 and 2 in column A gave II, bp 94–104° (2.5 mm), 4.7 g, $n^{25}\text{D}$ 1.5010 (23% yield), with a retention time of 1.45 min (XE-60 column, 200°, 15 psi of helium), and Va, b, bp 111–113° (2.10 mm), 9.2 g, $n^{25}\text{D}$ 1.5289 (33% yield). The yield of IV amounted to 18% (based on 1,6-heptadiene). IV solidified, mp 60–64°; recrystallization from *n*-pentane gave mp 65–67°. Successive fractions had lower melting points.

Gas chromatography of redistilled Va,b, using a 6-ft column of Apiezon N (10% on Chromosorb W) at 170° and 20 psi of helium, gave peaks for II at 19.0 min (3.0%) and for Va,b at 38.5 (17.0%) and 43.6 min (80.0%).

An infrared spectrum of II (10% in CCl_4) showed vinyl unsaturation bands at 3080, 1635, 990, and 910 cm^{-1}. There was no absorption band at 965 cm^{-1} characteristic for *trans*-CH=CH–, which indicated that little if any isomeric 1,1,1-trichloro-3-bromo-6-octene was present. The infrared spectrum of Va,b showed CH_2 bands at 2960, 2875, 1470, 1450, and 1430 cm^{-1} and bands at 1240, 1100, 1050, 1030, 960, 922, 910, 700, and 640 cm^{-1}.

The nmr spectrum of II showed a six-proton resonance pattern of the methylene groups at 1.3–2.2 ppm; a two-proton AB portion of an ABX pattern[13] for the CH_2CCl_3 group (peaks at 176, 192, 198, 213, and 182, 198, 202, and 218 cps) for which J_{AB} = 15.5 cps, $|J_{AX}|$ = 7.2 cps, $|J_{BX}|$ = 4.8 cps, ν_{AB} = 14.5 cps (assuming the most probable values for J_{AX} and J_{BX}); a one-proton X portion of the ABX pattern for the –CHBr group (peaks at 245, 255, 257, 260, 262, and 268 cps) coupled to the CH_2 group on both sides; and olefinic proton resonances for the $CH_2{=}CH$– group at 3.8, 5.05, and 5.4–6.1 ppm (2.6 protons). The spectrum agrees with the structure of II and is inconsistent with an alternative structure such as 1,1,1-trichloro-3-bromo-6-octene.

An nmr spectrum of IV (20% in deuteriochloroform) gave a six-proton peak ($(CH_2)_3$) at 1.8–2.2 ppm; a two-proton, seven-line multiplet (CH_2CCl_3) at 3.35 ppm, with peaks at 178, 193.5, 200, and 215.5 cps, and 183.5, 200, 205, and 220 cps; and a one-proton multiplet (–CHBr) at 4.1–4.6 ppm. The latter showed coupling to both adjacent CH_2 groups and was not resolved. Analysis of the CH_2CCl_3 multiplet as the AB portion of an ABX system gave J_{AB} = 15.5 cps, $|J_{AX}|$ = 6.3 cps (an alternate value of 20.3 cps was rejected as being improbable), $|J_{BX}|$ = 4.3 cps, and $\Delta\nu_{AB}$ = 15 cps.

The nmr spectrum of Va,b (50% in carbon tetrachloride or in carbon disulfide) gave a six-proton resonance at 1.77 ppm (cyclic CH_2), two methinyl protons at 1.86–2.52 ppm (unresolved), a two-proton multiplet from 2.52 to 3.05 ppm (CH_2CCl_3) partly overlapped with a two-proton multiplet from 3.00 to 3.6 ppm (peaks at 180, 190, 200, and 210 cps and 188, 198, 205, and 215 cps (CH_2Cl)). An analysis[13] of the CH_2Cl multiplet as an ABX system gave the following data; J_{AB} = 10 cps, centers at 195 and 201.5 cps, $\Delta\nu_{AB}$ = 12.6 cps, $|J_{AX} + J_{BX}|$ = 13.0 cps (from separation of the two centers), $|J_{AX}|$ = 10.6 cps, $|J_{BX}|$ = 2.4 cps. The ratios of intensities to peak separations of the sets of lines were 0.35:0.33 and 0.26:0.25. The X portion of the spectrum could not be similarly analyzed because of coupling to other protons. The CH_2CCl_3 resonance gave an ABX type of pattern (J_{AB} = 10.5 cps) similar to that found in III, but a complete analysis was not attempted, since a portion of the spectrum was obscured by another resonance. The entire spectrum was consistent with structure Va,b and clearly excluded a cyclohexane-type adduct.

Anal. Calcd for $C_8H_{12}BrCl_3$: C, 32.6; H, 4.10; Cl, 36.1; Br, 26.85. Found for II: C, 33.8; H, 4.29; Cl, 35.92; Br, 27.32. Found for Va,b: C, 32.4; H, 4.08; Cl, 35.82; Br, 27.08.

Anal. Calcd for $C_9H_{12}Cl_6Br_2$: C, 21.9; H, 2.46. Found for IV: C, 22.17; H, 2.28.

Lithium Aluminum Hydride Reduction of II–Va,b Mixture.—The monoadduct mixture (11.3 g, 0.04 mole) was added to 40 ml of anhydrous ether and lithium aluminum hydride (6.15 g, 0.162 mole). Stirring by a magnet bar was continued for 2 days at

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(26) N. O. Brace, U. S. Patent 3,145,222 (Aug 18, 1964) (assigned to E. I. du Pont de Nemours and Co.).

(27) K. Leedham and R. N. Haszeldine, *J. Chem. Soc.*, 1634 (1954).

reflux (38°). Water (7.2 g) was added drop by drop over a 3-hr period, and then 10% sodium hydroxide solution (10.6 g) was added. The magnet bar was ineffective, and the slurry was stirred 2 days before the gray color had changed to white. Ether (100 ml) was added and the clear solution was decanted from white solid aluminum salts, dried over magnesium sulfate, and distilled in column A: (1) bp 44–45.5° (43 mm), 1.00 g, $n^{25}\mathrm{D}$ 1.4218; (2) an intermediate fraction, bp 47–86° (44 mm), $n^{25}\mathrm{D}$ 1.4368, 0.55 g; and (3) bp 86° (44.0 mm), $n^{25}\mathrm{D}$ 1.4586, 0.90 g. The residue of 0.4 g of viscous gum was discarded. The total yield was *ca.* 50% of theory.

Glpc of cuts 1 and 2 was attempted with several different columns. Incomplete separation occurred at 95° with a 6-ft Ucon Polar column. Best separation occurred using a 10-ft 20% Carbowax 1000 on 60–80 mesh, acid-washed, Chromosorb P column. With this column at 70° cuts 1 and 2 gave five main peaks; cut 3 gave these and also a peak at longer retention time. Cut 1 had retention time 7.2 min, 2.95%; 8.8 min, 21.6%; 9.3 min, 19.0%; 11.4 min, 53.2%; 15.3 min, 3.2%; cut 2 had retention time 7.7 min, 3.43%; 8.8 min, 6.25%; 9.3 min, 6.61%; 11.4 min, 84.0%. Mass spectrum analysis of separated components of cut 2 showed that *n*-octane, *cis-* and *trans*-2-octenes, and a C_8H_{14} compound were present. This latter may well be 1-methyl-2-vinylcyclopentane.

Chloroform and 1,6-Heptadiene.—Chloroform (35.8 g, 0.3 mole), 1,6-heptadiene (9.6 g, 0.1 mole), and ABN (0.5 g, 0.003 mole) were sealed in a glass tube which had been filled with nitrogen and evacuated twice at −70°. The mixture was heated in a bath at 70 ± 1° for 49 hr and turned orange. To remove impurities the product mixture was passed thorough 4 in. of activated alumina and 1 in. of activated carbon, the column rinsed three times with chloroform, and the eluate distilled in column B. Chloroform, 1,6-heptadiene (4.8 g, 50% recovery, $n^{25}\mathrm{D}$ 1.4120), and an adduct mixture (bp 56–58° (1.25 mm), $n^{25}\mathrm{D}$ 1.4850, 3.9 g (18% conversion; 39% yield)) were obtained; residue was 1.5 g of viscous tan oil. An infrared spectrum of the product mixture showed two weak CH out-of-plane bending bands for $CH_2{=}CH$ at 995 and 915 cm^{-1}, but strong bands for the CH stretching of CH_3 at 2870 and the CH deformation of $C{-}CH_3$ at 1450 and 1380 cm^{-1}. Glpc analysis (175°, 20 psi of helium, 6-ft column of Apiezon N, 10% on Chromosorb W) indicated two major components, and others with retention times as follows: 2 min, 1.53%; 2.2 min, 5.7%; 3.0 min, 2.9%; 3.3 min, 3.3%; 4.1 min, 16.4%; and 4.8 min, 72.3%. Traces of other substances were also present. The peak at 2.2 min (from infrared and nmr) was I, and the peaks at 4.1 and 4.8 min were VIa,b.

An nmr spectrum of the neat mixture or 50% in carbon disulfide showed proton resonances at 0.90 ppm of one methyl group split into two lines (J = 7 cps) and having a 2.3-proton area; a second methyl doublet (J = 7 cps) at 1.05 ppm, 0.8-proton area; a sharp peak at 1.3 ppm 0.76-proton area from $(CH_2)_4$ in I; broad resonances for the methylene protons from 1.0 to 2.1 ppm (5.4-proton area); a broad peak of the methinyl protons at 2.1 to 2.55 ppm (1.85-proton area); the AB portion of an ABX pattern of the CH_2CCl_3 group in VIa,b from 2.5 to 3.0 ppm (1.8-proton area); and two small peaks for protons of the $CH_2{=}CH$ group in I at 5.6 and 5.75 ppm. Analysis of the CH_2CCl_3 resonance pattern with peaks at 147, 161.5, 169, and 183 cps and at 142, 156, 166, and 180 cps in two sets gave the following data: $|J_{AB}|$ = 14 cps, $|J_{AX}|$ = 8 cps, $|J_{BX}|$ = 4 cps, which was consistent with the $-CH_2CCl_3$ parameters observed in the other compounds reported. The ratio of peak intensities to separation was 0.27:0.26, in good agreement with ABX system parameters. Correction of the CH_3 group areas for the relative amount of VIa and VIb agreed with glpc analysis.

Anal. Calcd for $C_8H_{13}Cl_3$: C, 44.6; H, 6.09; Cl, 49.4. Found: C, 44.66; H, 6.19; Cl, 49.38.

Carbon Tetrachloride and 1,6-Heptadiene.—Carbon tetrachloride (46.2 g, 0.3 mole), 1,6-heptadiene (9.6 g, 0.1 mole), and ABN (0.5 g, 0.003 mole) were heated for 24 hr at 70 ± 1° in a sealed tube as with the chloroform reaction. Distillation in column B gave a carbon tetrachloride–1,6-heptadiene mixture, bp 76°, $n^{25}\mathrm{D}$ 1.4569, 36.4 g; an adduct mixture (VIIa,b), bp 78–81° (0.18 mm), $n^{25}\mathrm{D}$ 1.5111, 11.8 g (47% conversion); and residue, 2.0 g of tan oil. A mixture of carbon tetrachloride and 1,6-heptadiene (11.8 g, $n^{25}\mathrm{D}$ 1.5551) was collected in the cold trap. Redistillation in column B of VIIa,b gave three fractions: (1) bp 100–102° (2.30 mm), $n^{23.5}\mathrm{D}$ 1.5090, 1.2 g; (2) bp 101° (1.75 mm), $n^{25}\mathrm{D}$ 1.5123; and (3) holdup pumped over, $n^{24}\mathrm{D}$ 1.5130, 1.5 g. An infrared spectrum of VIIa,b showed no $CH_2{=}CH$ bands and no CH stretching band at 2870 cm^{-1} or CH deformation band of the $C{-}CH_3$ group at 1380 cm^{-1}, but did show bands at 940 and 925 cm^{-1} which also appeared in 1-iodomethyl-2-(perfluoropropylmethyl)cyclopentane.[2] Glpc (6-ft column of Apiezon N, 10% on Chromosorb W at 180° with 30 psi of helium) showed peaks at 11.1 and at 12.8 min. The ratio of VIIa to VIIb in cuts 1–3 was 31:69, 20:80, and 7:93, respectively. Similar results were obtained with a 6-ft column of diethylene glycol succinate (20%) on Chromosorb W at 180° using 20 psi of helium pressure. An nmr spectrum (run neat or 50% in deuteriochloroform) of each cut showed proton resonances for the ring methylene protons at 1.72 ppm (6.0-proton area), the methinyl protons at 1.82–2.6 ppm (2.0-proton area), the CH_2CCl_3 protons at 2.7–3.1 ppm (2.0-proton area), with peaks at 148, 163.5, 172.5, and 187 cps and 155, 170, 177, and 193 cps; the CH_2Cl protons at 3.1–3.89 ppm (2.0-proton area), with peaks at 193, 204, 211.5, 222, and 200, 211.5, 217.5, and 228 cps in two sets of AB patterns. There were no other proton resonances resulting from other isomers. An analysis of the spectrum is consistent with the structures of VIIa,b and showed that cyclohexane products were not present. An analysis[13] of the CH_2Cl resonance as the AB portion of an ABX system gave the following data: J_{AB} = 10.5 cps, $|J_{AX}|$ = 7.5 cps (an alternate value of 21 cps was rejected as being improbable), $|J_{BX}|$ = 6.5 cps, ν_{AB} = 13 cps, and the ratio of peak intensities to separation was 0.24: 0.25 and 0.183:0.188 for the two sets of peaks. These data agree well with the anticipated parameters.

The CH_2CCl_3 resonance also appeared as an eight-line AB portion of an ABX system. The outer peaks, however, were partially obscured on one side by the overlapping methinyl proton peak. Analysis gave the following data: J_{AB} = 15.0 cps, $|J_{AX}|$ = 6.5 cps (an alternate value of 22.5 cps was rejected as being improbable), $|J_{BX}|$ = 7.5 cps, and $\Delta\nu_{AB}$ = 15 cps.

Anal. Calcd for $C_8H_{12}Cl_4$: C, 38.4; H, 4.84; Cl, 56.84. Found: C, 38.44; H, 4.93; Cl, 56.95.

1,1,1,3,7,9,9,9-Octachlorononane (III) by Redox–Transfer-Initiated Addition of Carbon Tetrachloride to 1,6-Heptadiene.—Carbon tetrachloride (46.2 g, 0.3 mole), 1,6-heptadiene (9.6 g, 0.1 mole), and a solution of ferric chloride hexahydrate (0.27 g, 0.001 mole), benzoin (0.21 g, 0.001 mole), and diethylammonium chloride (0.16 g, 0.0015 mole) in acetonitrile (8.2 g, 0.2 mole) were placed in a heavy-walled Pyrex pressure tube. The tube was cooled to −78°, evacuated and filled with nitrogen three times, sealed *in vacuo*, and heated in an oil bath at 100 ± 2° for 5 hr. Purging of air by two or three small pieces of Dry Ice was also satisfactory.[20] The products were washed with 10% hydrochloric acid, the aqueous layer was extracted with carbon tetrachloride, and the combined organic layers dried over calcium sulfate. Volatile compounds were removed under reduced pressure in column A and VIIa,b (20:80) was distilled from an oil bath heated up to 167°, bp 78–89° (0.10 mm), $n^{20}\mathrm{D}$ 1.5148, $n^{25.5}\mathrm{D}$ 1.5121, 17.3 g (69% conversion). A viscous brown oil remained, 8.15 g (20% conversion). This gave 6.0 g of III when distilled in a short-path sublimer cup still heated in an oil bath at 130–140° (0.05 mm), $n^{20}\mathrm{D}$ 1.5238. An infrared spectrum showed bands for the CH_2 group, but the $C{-}CH_3$ bands at 1450 and 1385 cm^{-1} were absent. An nmr spectrum of III gave a six-proton resonance at 1.86 ppm $(CH_2)_3$, a two-proton multiplet of CH_2CCl_3 protons at 2.8–3.6 ppm (210, 195.5, 190, and 176.5 cps, and 205.5, 192, 187, and 172 cps), and the $-CHCl-$ resonance at 3.9–4.5 ppm (center 252 cps). An analysis[13] of the eight-line CH_2CCl_3 multiplet as an ABX pattern gave the following data: J_{AB} = 14.5 cps, $|J_{AX}|$ = 11 cps; $|J_{BX}|$ = 4 cps, $\Delta\nu_{AB}$ = 13 cps; $\Delta\nu_{AX}$ = 68 cps; $\Delta\nu_{BX}$ = 54 cps. The relative ratios of peak heights and separations were 0.16:0.14 and 0.15:0.14 for the two sets.

Anal. Calcd for $C_9H_{12}Cl_8$: C, 26.76; H, 3.00; Cl, 70.24. Found: C, 26.97; H, 3.08; Cl, 70.11.

1,1,1,3-Tetrachlorononane (VIII).—Redox–transfer reaction of carbon tetrachloride and 1-octene by the method of Asscher and Vofsi[20] gave VIII, bp 108° (0.3 mm), $n^{25}\mathrm{D}$ 1.4756, in 78% yield. These values agree with those reported.[12] An nmr spectrum (50% in deuteriochloroform) showed a distorted triplet (J = 5 cps) at 0.9 ppm (CH_3), an eight-proton peak of (CH_2) at 1.4 ppm, a two-proton unresolved multiplet at 1.6–2.1 ppm (CH_2 next to CHCl), a two-proton, eight-line multiplet at 3.18 ppm, (peaks at 170, 185, 190, and 203 cps and 174, 187, 192, and 207 cps of CH_2CCl_3), and a one-proton, seven-line multiplet at 4.21 ppm ($-CHCl$) (peaks at 241, 246, 251, 253, 256, 258, and 263 cps).

The latter multiplet was distorted from the six-line pattern expected for the X portion of an ABX system, due to coupling to adjacent CH_2 protons. Analysis[13] of the $-CH_2CCl_3$ pattern at 3.18 ppm gave the following data: $J_{AB} = 14$ cps, $|J_{AX}| = 2.0$ or 15 cps, $|J_{BX}| = 2.0$ or 11 cps, and $\Delta\nu_{AX} = 6.5$ or 13 cps. Since both are reasonable values for coupling of geminal protons in each case and the X portion of the spectrum was complicated by additional couplings, no closer definition was attempted.

Hydrolysis of VIIa,b.—The adduct mixture (20:80 VIIa,b, 12.5 g, 0.05 mole) was added to a solution of sodium methoxide (2.70 g, 0.05 mole) in methanol (50 ml) at 35° and heated to reflux (68°) for 18 hr. The mixture remained alkaline and deposited sodium chloride. Methanol was distilled off, the remaining oil was poured into water (75 ml) and extracted twice with carbon tetrachloride, and the organic layer washed with water and dried. A sample was removed for glpc analysis (6-ft Apiezon N, 10% on Chromosorb W, 180°, 15 psi of helium) which showed unreacted VIIa,b, 7.6 and 12.7%; IXa,b, 12.2 and 54.0%, at 10.5 and 11.6 min; and other products at 3.1 min, 5.2%; 6.1 min, 7.8%; and 13.1 min, 1.1%. Distillation in column A gave IXa,b, bp 81–90° (1.1 mm), containing VIIa,b, 10.3 g, 82% yield; redistilled center cuts, bp 64° (0.45 mm), $n^{23}D$ 1.5148, were free from VIIa,b. Reaction of VIIa,b (12.5 g, 0.050 mole) with (2.8 g, 0.050 mole) of potassium hydroxide in 50 ml of anhydrous ethanol at 75–80° for 4 hr gave, after work-up, a 62% conversion to IXa,b (27:73). Treatment of this mixture with zinc and hydrogen chloride in ethanol in an attempt to remove halogen gave a 62% recovery of IXa,b. A separated isomer, bp 54° (0.14 mm), $n^{21}D$ 1.4141, gave the nmr spectrum shown in Figure 2.

Anal. Calcd for $C_8H_{11}Cl_3$: C, 44.99; H, 5.14; Cl, 49.81. Found: C, 44.89; H, 5.08; Cl, 49.59.

6-Iodo-1-heptene (X).—A published method[28] was modified using 1,5-hexadiene to establish conditions for reaction with a diene; the reported procedures required an excess of hydrogen iodide which would have given only diiodo compounds from 1,5-hexadiene or 1,6-heptadiene. A solution of 95% phosphoric acid was made from 174 g (1.5 mole, 102 ml) of 85% syrupy phosphoric acid added to 47 g (0.33 mole) of phosphoric anhydride while stirring the mixture and cooling to 25°. Potassium iodide (250 g, 1.5 mole) was added to the phosphoric acid in a 500-ml, three-necked flask fitted with condenser and paddle stirrer. A yellow color appeared. 1,5-Hexadiene (82.0 g, 1.0 mole, 121 ml) was added dropwise at 25–40° over a 1-hr period, and the granular brown slurry was heated to 78° for 1.5 hr at reflux. The product mixture was worked up as reported.[28] A dark purple liquid was obtained, run down a column of alumina, and distilled, bp 38–40° (5.0 mm), $n^{25}D$ 1.5100, 51.5 g (27% conversion to 5-iodo-1-hexene). The dark liquid residue (36.2 g, 11% conversion to crude 2,5-diiodohexane) was not distilled.

To decrease the conversion to a diiodo compound a 1:1 reactant ratio of 1,6-heptadiene to potassium iodide was used. Syrupy phosphoric acid (40.0 g, 0.35 mole, 23.5 ml) was added to phosphoric anhydride (10.0 g, 0.075 mole) which was then mixed with potassium iodide (41.5 g, 0.25 mole) at 25°. 1,6-Heptadiene (24.0 g, 0.25 mole, 34.6 ml at 26°) was added dropwise at 30°; the slurry was stirred, heated to 80° for 5.5 hr, and cooled, and 50 ml of water was added. The mixture was extracted with 150 ml of ether in portions, and, in turn, with 10 ml of 10% sodium bisulfite solution. After drying over magnesium sulfate, the mixture was distilled in a 10-in. packed column to give ether; 1,6-heptadiene, bp 66–67° (411 mm), $n^{24}D$ 1.4120, 4.8 g; X, bp 59–60° (6.0 mm), a red liquid, 20.5 g (36% conversion); a dark liquid residue (8.6 g); and cold trap liquid (9.5 g) estimated to contain 5.1 g of 1,6-heptadiene by the refractive index. After passing X down 4 in. of alumina, it was redistilled in column B, bp 43.5° (1.75 mm), $n^{24}D$ 1.5112. Glpc analysis (6-ft Carbowax 1500 on Chromosorb W, 172°, 25 psi of helium) gave 96% at a retention time of 7.0 min. An unknown isomeric compound (4.2%) having a retention time of 9.9 min was also present.

Anal. Calcd for $C_7H_{13}I$: C, 37.5; H, 5.83. Found: C, 37.7; H, 5.93.

Free-Radical Isomerization of X to *cis*- and *trans*-1-Iodomethyl-2-methylcyclopentane (XIa,b).—Isomerization occurred in *n*-hexane or in 1,6-heptadiene solution in sealed tubes using ABN initiator at 74 ± 1°. No reaction occurred by heating X alone at 65° for several hours in *n*-hexane solution. A mixture of ABN (0.0682 g, 0.42 mmole) and X (0.2394 g, 1.07 mole) was weighed out, but only a fraction of the solid ABN dissolved upon addition of 3.57 ml of *n*-hexane, to make a total of 4.00 ml. The solution was drawn into a syringe and placed in several tubes which were evacuated, filled with nitrogen several times, and sealed at −80°. After heating in a bath at 74° the contents were analyzed by glpc (conditions given above). Results are listed in Table II. Another set was run using a solution of ABN (0.0657 g, 0.40 mmole), 1,6-heptadiene (0.9726 g, 10.0 mmole), and X (2.247 g, 10.0 mmoles), to make a total of 3.0 ml. More, but not all, of the ABN dissolved in this mixture.

TABLE II

FREE-RADICAL ISOMERIZATION OF X

Sample	Hr	X, %	Unknown, %	XIa, %	XIb, %
Hexane	0	95	5.0		
solution	46	40	7.0	13.1	34.0
	71	41	6.5	13.7	35.5
1,6-Heptadiene	0	95	5.0		
solution	46	14.5	7.7	21.4	55.0
	69	11.1	7.0	21.4	58.3

It is apparent that in 1,6-heptadiene solution considerably more isomerization occurred. This may be principally because of the higher ABN concentration.

A preparative-scale run at 74° for 24 hr employed 7.3 g (0.0325 mole) of X, 0.21 g (0.0013 mole) of ABN, and 1.0 ml of *n*-hexane (4 mole % of initiator) weighed into a glass ampoule and sealed with nitrogen purge, *in vacuo* at −70°. The product mixture was distilled in column B. Fractions were obtained: (1) bp 43.5° (1.75 mm), 2.3 g, $n^{24}D$ 1.5112; (2) bp 43.5–47° (1.75 mm), $n^{25}D$ 1.5262, 1.8 g; (3) bp 47° (1.75 mm), 1.3 g; and pot liquid, 0.4 g. Glpc analysis (same as above, 19 psi of helium) showed that the product mixture contained 20% of X, 5% of the impurity originally present, 20% of XIa (retention time 12.6 min) 55% of XIb, retention time 15.9 min, and no other substances. Fraction 1 contained X (50.5%), XIa (28.6%), and XIb (14.0%). Fraction 2 contained X (5.63%), XIa (27.2%), and XIb (63.9%). Fraction 3 contained X (0.18%), XIa (2.88%), and XIb (96.3%). Thus, 75% of the 6-iodo-1-heptene was isomerized to a mixture of XIa,b. Infrared spectra of fraction 1 showed prominent $CH_2{=}CH$ bands at 1640, 990, and 910 cm^{-1}, fraction 2 showed only weak bands, and fraction 3, none at all. The nmr spectrum of X (neat) showed proton resonances at 1.0 ppm (3-proton area), 1.8 to 2.3 ppm (7.0-proton area (CH_2)), 4.4 ppm (1 proton of CHI), and a complex five- or six-line multiplet at 4.9–5.4 and 5.6–6.5 ppm (3-proton area of a complex set of multiplets ($CH{=}CH_2$)). The pattern resembled that of 1-perfluoropropyl-2-iodo-6-heptene.[2] The nmr spectrum of fraction 3 (1-iodomethyl-2-methylcyclopentane, XIb) gave proton resonances at 0.89 ppm (3.1-proton area, a doublet with $J = 7$ cps for the CH_3 group), 1.1–2.0 ppm (5.9-proton area for CH_2 of the ring), 2.0–2.5 ppm (2.2-proton area for CH on the ring), and at 3.10 ppm (1.9-proton area for CH_2I, a doublet with $J = 7$ cps). This last pattern also showed a small splitting of one of the pair of peaks, indicating that an additional coupling constant was present. However, the outer peaks of an ABX system could not be observed in several attempts. The CH_2I protons may be slightly different in chemical shift. The nmr spectrum of fraction 2 gave proton resonance peaks at 0.89 ppm (1.9-proton area, a doublet with $J = 7$ cps), another CH_3 group doublet at 0.95 ppm with $J = 5$ cps (0.81-proton area), a complex set of peaks at 1.1–2.0 including a 7-cps doublet at 1.85 ppm (CH_3 group in X and the $(CH_2)_3$ grouping in XIa,b (total area 6.3 protons)); the CH's of the ring at 2.0–2.8 ppm (2.3-proton area) and the CH_2I groups at 3.1 ($J = 7$ cps) and 3.2 ppm ($J = 5$ cps), total proton area of 1.94. There was also a small set of peaks at 4.0–6.0 ppm from X (0.2-proton area).

Anal. Calcd for $C_7H_{13}I$: C, 37.5; H, 5.83; I, 56.5. Found: C, 37.3; H, 5.75.

***trans*- and *cis*-1,2-Dimethylcyclopentane (XIIa,b).**—1,2-Dimethyl-1-cyclopentanol was synthesized from 1-methyl-2-cyclopentanone and methylmagnesium iodide.[23,24] Dehydration to 1,2-dimethyl-1-cyclopentene was accomplished by heating 9.4 g

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[28] H. Stone and H. Shechter in "Organic Syntheses," Coll. Vol. IV, N. Rabjohn, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, p 543.

(0.082 mole) of the alcohol with 3.0 ml of 85% phosphoric acid, using a 10-in. distillation column. The olefin distilled quickly at 140° bath temperature: 7.4 g (separated from water), 94% of theory. Fractionation in column A gave a cut, bp 102–105°, n^{24}D 1.4420, 3.4 g [lit.[23,24] bp 102.5–105.8°, n^{25}D 1.4430]; glpc analysis (10-ft Ucon Polar LB-55OX, 20% on Chromosorb W, 95°, 20 psi of helium) showed 93.6% of the olefin at 13.7 min and 6.4% of an impurity at 9.5 min. This impurity and another substance were concentrated in the forerun fraction.

Hydrogenation of 1,2-dimethyl-1-cyclopentane (5.0 g, 0.052 mole) using 0.5 g of 5% palladium on carbon in 25 ml of anhydrous ethanol at 47.6-psi hydrogen pressure in a Parr hydrogenation apparatus gave a 4.4-psi pressure drop (100%) in 0.5 hr at 22°. XIIa,b, bp 90° (745 mm), n^{24}D 1.4128, 3.1 g, separated from the filtered solution when diluted with water. Glpc (same conditions as above) showed XIIa at 7.0 min, 77%; XIIb at 9.3 min, 21%; and 1.9% of another compound at 6.0 min. An infrared spectrum was consistent. From literature values[25] for *trans*-, bp 91.9° (760 mm), n^{25}D 1.4068, and *cis*-1,2-dimethylcyclopentanes, bp 99.5° (760 mm), n^{25}D 1.4196, it is clear that XIIa is the *trans* and XIIb is the *cis* isomer.

XIIa,b from Reduction of XIa,b.—XIa,b (1.0 g, 0.0045 mole; 27.2%; at XIa, 63.9% of XIb, 5.6% of X, and 4.1% of an isomeric compound), 10 ml of anhydrous ethanol, 2.0 g (0.03 g-atom) of zinc dust, and 1.0 ml of 55% aqueous hydriodic acid were heated in a bath at 67–72° under an efficient reflux condenser. Additions of 1 ml of 55% hydriodic acid were made after 5 min and 1 hr. After 2 hr the liquid was decanted into a separatory funnel, water (25 ml) was added, and the layer of XIIa,b separated, 0.35 g, 80%. The aqueous layer was extracted three times with dichloromethane. Glpc analysis of the dried hydrocarbon layer gave peaks at 6.0 min, 0.78%; XIIa at 7.0 min, 27.4%; at 8.2 min, 3.67%; and XIIb at 9.5 min, 68%; in good agreement with the original composition of isomers. The retention times of the two main components were identical with those of XIIa,b prepared above. The dichloromethane extract combined with the hydrocarbon layer gave a glpc analysis showing 29.8% XIIa and 72.3% XIIb. From these data the original mixture was 27.2% *trans*- and 63.9% *cis*-1-iodomethyl-2-methylcyclopentanes.

Free-Radical Addition of 1-Iodoperfluoropropane to 1,6-Heptadiyne.—1-Iodoperfluoropropane (29.6 g, 0.10 mole), ABN (0.32 g, 0.0020 mole), and 1,6-heptadiyne (18.4 g, 0.20 mole) were sealed in a heavy-walled glass tube which had been filled with nitrogen and evacuated three times at −78°. The tube was heated at 71° for 22 hr in an oil bath. The contents were distilled in column B. 1-Iodoperfluoropropane (10.6 g, 36% recovery), 1,6-heptadiyne (14.1 g, 76% recovery), XIIIa,b, in 82:12 ratio (bp 78–82° (10 mm), n^{25}D 1.4250–1.4305, 14.9 g, a 44% conversion), a cut (bp 70–72° (2.0–2.5 mm), n^{24}D 1.4618, 3.2 g (probably a mixture of bisadducts)), and a residue of 3.5 g were obtained. Redistillation of the XIIIa,b mixture gave four fractions, bp 106–107° (37 mm), n^{22}D 1.4300. According to glpc analysis (6-ft Carbowax 1500 column, 150°, 30 psi of helium), the first cut was 97.7% pure XIIIa with a retention time of 9.2 min. The last cut contained 49% of this compound and 40.6% of a compound with a retention time of 18.6 min. Its much greater retention time in analogy to the products from 1,6-heptadiene suggested that the latter might be a cylic isomer, and the substances were separated by preparative-scale glpc. Infrared spectra of the two compounds showed in both the C≡CH group (CH band at 3315 cm^{-1}, C≡C at 2120 cm^{-1}) and the CH=CI group (CH of the vinyl group at 3060 cm^{-1}). In the 9.2-min isomer XIIIa a strong band at 1632 (R_FCH=CI, *trans*) and bands at 985 and 920 cm^{-1} appeared. In the 18.6-min isomer XIIIb the R_FCH=CI band appeared at 1640, and the bands at 985 and 920 cm^{-1} were absent. This is therefore probably the *cis* isomer. Both gave the same elemental analysis.

Anal. Calcd for $C_{10}H_8F_7I$: C, 30.98; H, 2.08; F, 34.35. Found for XIIIa: C, 31.0; H, 2.26; F, 34.57. Found for XIIIb: C, 30.90; H, 2.24.

Registry No.—II, 13389-25-8; III, 13389-26-9; IV, 13389-27-0; Va, 13389-28-1; Vb, 13389-29-2; VIa, 13389-30-5; VIb, 13389-31-6; VIIa, 13421-43-7; VIIb, 13389-32-7; VIII, 1070-27-5; IXa, 13389-34-9; IXb, 13389-35-0; X, 13389-36-1; XIa, 13389-37-2; XIb, 13389-38-3; XIIa, 822-50-4; XIIb, 1192-18-3; XIIIa, 13389-39-4; XIIIb, 13389-40-7; *n*-octane, 111-65-9; *cis*-2-octene, 7642-04-8; *trans*-2-octene, 13389-42-9; 1-methyl-2-vinylcyclopentane, 13389-43-0.

The Chloramine-Induced Oxidative Dimerization of Phenols[1]

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The addition of ethereal chloramine to molten phenols **1**–**6** at 120–130° resulted in the formation of oxidative coupling products. The mechanism of these transformations was investigated by varying the structure of the chloramine, by investigating the effects of solvent and added ferrous sulfate, and by performing various other pertinent experiments. The conclusion has been reached on the basis of the observed results that the chloramine-induced oxidative dimerization of these phenols probably proceeds by way of an unprecedented redox reaction involving the generation of aminium and phenoxy radicals.

The ability of phenols to undergo oxidation with a number of inorganic reagents (Ag_2O, PbO_2, MnO_2, $Pb(OAc)_4$, $K_3Fe(CN)_6$, etc.) and organic peroxides is well documented.[4–6] In fact, this propensity for oxidation has permitted the widespread use of phenols as antioxidants.[4–6] The above reagents possess in common the property that they react *via* radical processes to generate phenoxy radicals in the initial stages of the oxidation process. The ultimate fate of the phenoxy radicals generated in this manner is, in general, a function of their gross structure, the conditions of the reaction, and the nature of the oxidizing agent.

In our earlier studies, we have elaborated on the unusual ring expansions which result when hot solutions of sodio 2,6-disubstituted phenoxides in excess of the parent phenols are treated with ethereal chloramine.[7] Because of the fact that the phenols were considered relatively more readily accessible than the chloramine (especially since the excess phenol which was employed as solvent could be recovered almost

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