

Cycloadditions. XVI. Addition of 1,1-Dichloro-2,2-difluoroethylene and the Stereoisomeric 1,2-Dichloro-1,2-difluoroethylenes to *trans*-Cyclooctene

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Abstract: *trans*-Cyclooctene reacts thermally with 1,1-dichloro-2,2-difluoroethylene at 120–130° to yield a cycloadduct in which 99% of the *trans* configuration is retained (yield 69%). *cis*-Cyclooctene at 185° affords a 3% yield of cycloadduct showing 96% retention of the *cis* configuration. That the reaction is nevertheless unconcerted is shown by the behavior of 1,2-dichloro-1,2-difluoroethylene: four cycloadduct isomers are produced representing, from the *trans*-haloalkene, 20.2% loss of relative configuration of the halogens with only 3.4% loss of the ring configuration and, from the *cis*-haloalkene, 33% loss of halogen configuration and 1.4% loss of ring configuration. This independent, uncorrelated stereoisomerization in the two moieties undergoing cycloaddition is best explained by way of a biradical intermediate in which transannular interference hinders the stereoequilibration of the cyclic portion but not that of the open halogen-bearing end.

Among simple alkenes the ability to enter into (2 + 2) cycloaddition varies more critically with structure than does the common ability to act as a dienophile in (2 + 4) cycloaddition.¹ Cyclobutane formation may be brought into the observable range by structural features which either raise the energy of the initial reactants through double bond destabilization² or lower the energy of the biradical, and hence of the transition state for its formation, by providing a mechanism for electron delocalization at one end of the double bond.^{1,3} Both favorable effects may be counteracted by substitution hindering the formation of the new covalent bond in the biradical.^{2,4} The favorable effects appear to be energetically additive in the two reacting partners. Thus the rates of (2 + 2) cycloaddition increase in the order: tetrafluoroethylene (TFE) + ethylene, TFE + butadiene, 1,1-dichloro-2,2-difluoroethylene ("1122") + butadiene.

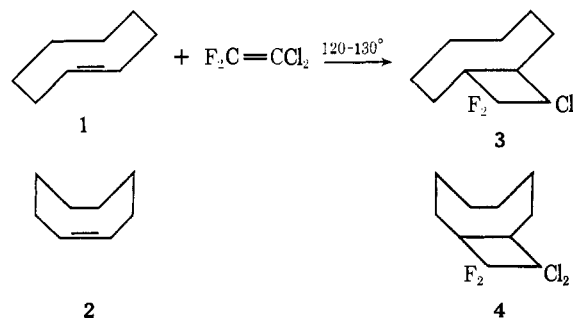
Cyclooctene is of interest in comparison with these compounds. Toward the reactive ketenes⁵ both *cis*- and *trans*-cyclooctene react readily with retention of configuration. The greater strain of about 9 kcal/mol⁶ in *trans*-cyclooctene is reflected in a reactivity much greater than that of the *cis* isomer. The strained compound *trans*-bicyclo[4.2.2]deca-3,7,9-triene is reported⁷ to dimerize at room temperature with retention of configuration in one reacting molecule and inversion in the other, suggesting a concerted 2_s + 2_a mechanism. However, the much slower dimerization of *trans*-cyclooctene at 150° yields the "2_s + 2_a" dimer as only two-thirds of a mixture containing also two dimers of retained ring configuration.⁸ The room-temperature dimerization at the *trans* double bond of *cis,trans*-1,3-cyclooctadiene⁸ yields a product mixture of which

more than two-thirds has the *trans* configuration fully retained.

Thus the cross cycloaddition of *trans*-cyclooctene to other alkenes is of interest from several viewpoints. (1) Will the special type of strain which it exemplifies result in strongly preferred 2_s + 2_a cycloaddition with dissimilar reagents? (2) How great will the difference be between the behavior of *cis*- and of *trans*-cyclooctene? (3) In the event that the result is not pure retention or pure inversion on the part of the cyclooctene, how may a concerted 2_a + 2_a mechanism, with the cyclooctene functioning in part suprafacially and in part antarafacially, be distinguished from a biradical mechanism?

Results and Discussion

***trans*-Cyclooctene and 1,1-Dichloro-2,2-difluoroethylene.** Two tubes, each containing 4 g of 99% *trans*-cyclooctene⁹ (1) and 16 g of 1122, were sealed in nitrogen and placed in a preheated oven at 120–130° for 3 hr. The tubes were opened and gave 26 g of recovered 1122. By a combination of distillation and vapor chromatography, the product was found to contain the *trans* cycloadduct 3 and the *cis* cycloadduct 4 in a total yield of 69% and in the ratio of 99:1.



In this experiment, 8% of *cis*-cyclooctene (2) was also recovered. In other experiments, the amount of *cis*-cyclooctene was never constant enough to eliminate the possibility that it arose from the presence of adventitious catalysts, although the concerted (2 + 4)

(1) See, for example, P. D. Bartlett, *Science*, **159**, 833 (1968), Table V.

(2) P. D. Bartlett and R. Wheland, *J. Amer. Chem. Soc.*, **94**, 2145 (1972).

(3) L. E. Walker and P. D. Bartlett, *ibid.*, **95**, 150 (1973).

(4) J. Marchand-Brynaert and L. Ghosez, *ibid.*, **94**, 2870 (1972).

(5) R. Montaigne and L. Ghosez, *Angew. Chem., Int. Ed. Engl.*, **7**, 221 (1968).

(6) R. B. Turner and W. R. Meador, *J. Amer. Chem. Soc.*, **79**, 4133 (1957).

(7) K. Kraft and G. Koltzenburg, *Tetrahedron Lett.*, 4357 (1967).

(8) J. Leitch, *Angew. Chem., Int. Ed. Engl.*, **8**, 909 (1969).

(9) A. C. Cope, R. A. Pyle, and C. S. Spencer, *J. Amer. Chem. Soc.*, **75**, 3212 (1953).

Table I. Cycloaddition of *trans*-Cyclooctene to ClFC=CFCl (172°, 14 hr)

Configuration of initial ClFC=CFCl	Configuration of recovered ClFC=CFCl	Relative areas in glpc trace of adducts			
		5	6	7	8
99.3% <i>trans</i>	99.0% <i>trans</i>	27.2	20.2	49.2	3.4
95.4% <i>cis</i>	94.2% <i>cis</i>	10.2	67.0	21.4	1.4
51.3% <i>cis</i>	50.0% <i>cis</i>	17.8	46.9	33.8	1.5

Table II. Stereochemical Course of Thermal Addition of *trans*-Cyclooctene to *cis*- and *trans*-1,2-Dichloro-1,2-difluoroethylene

1212 Isomer	Configuration in product				Biradical configuration for 5 and 7	
	Ring junction		1212 portion		% erythro	% threo
	% retained	% inverted	% retained	% inverted		
Trans (99.3%)	96.6	3.4	79.8	20.2	64	36
Cis (95.4%)	98.6	1.4	67	33	68	32
Cis and trans	98.5	1.5			66	34

cycloaddition of butadiene to *trans*-cyclooctene results in no generation of *cis*-cyclooctene. The establishment of the structures of these and other new cycloadducts is described in a later section. Control experiments established that the cycloadducts 3 and 4, under conditions more vigorous than those of the cycloaddition, were neither interconverted nor cleaved to cyclooctene.

No detectable cycloadduct was formed when *cis*-cyclooctene (2) was heated with 1122 under the same conditions. In a sealed tube held at 185° for 16 hr, *cis*-cyclooctene reacted with 1122 to give a 3% yield of a cycloadduct from which 4 could be isolated as the main product. Vapor chromatography showed that this cycloadduct was accompanied by 3–4% as much of the *trans*-fused cycloadduct 3. A few milligrams of this component was isolated having the right ir spectrum and a mass spectrum appropriate for not quite pure 3. Since the control experiments show that the *cis* cycloadduct 4 from *trans*-cyclooctene could not have arisen by way of isomerization and cycloaddition, it is evident that the cycloaddition to *trans*-cyclooctene occurs with 99% but not 100% retention of configuration, while the very much slower cycloaddition to *cis*-cyclooctene, at a temperature 60° higher, occurs with about 96% retention of configuration. It also appears from the yields of these reactions that *trans*-cyclooctene at 125° is more than 100 times as reactive toward 1122 as *cis*-cyclooctene at 185°.

It is a familiar property of cyclooctane that the transannular steric interactions of the hydrogen atoms are strong and that rotation about any single bond in the ring requires cooperative movements of many other bonds with resultant strong hindrance. There is thus an obvious reason why the biradical involved in cycloaddition to cyclooctene should close with less configuration loss than a biradical whose rotation is not similarly constrained. However, in view of the apparent propensity of *trans*-cyclooctenes to undergo $2_s + 2_a$ dimerization,⁷ the possibility must be examined that this is also occurring in the cross cycloaddition between the cyclooctenes and 1122. Such a mechanism would require that every cycloaddition that is supra-

facial in a cyclooctene molecule be antarafacial with respect to the molecule of 1122 entering into the cycloaddition. In the case of 1122, it is not possible to test for this predicted inversion of configuration, but its isomer 1212 (1,2-dichloro-1,2-difluoroethylene) exists in *cis* and *trans* isomers and is well suited to the test.

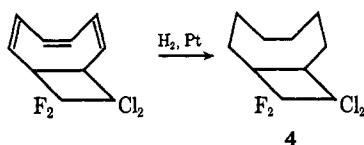
***trans*-Cyclooctene and 1212.** 1212, in comparison with its isomer 1122, is characterized by a stronger preference for 1,4-cycloaddition to cyclopentadiene in competition with the 1,2 mode.¹⁰ With similar degrees of destabilization of the double bond, the 1122 isomer has a location where a free radical can be stabilized to the extent of about 8 kcal by two chlorine atoms, while the best free radical site available on 1212 has a stabilization of only 4 kcal from a single chlorine atom (the effect of a fluorine atom on radical stabilization is zero or slightly negative). Accordingly, the cycloaddition of *trans*-cyclooctene to 1212 was carried out at 172° for 14 hr to achieve about the same rate as that found with 1122 at 125° in 3 hr. Table I summarizes the compositions of the cycloadducts found from the *cis* and *trans* isomers of 1212 and from a mixture of the isomers. Of the six stereoisomeric 9,10-dichloro-9,10-difluorobicyclo[6.2.0]decenes, only four were found in detectable amounts. A summary of the stereochemical course of the reaction based upon the structural assignments described in the next section is contained in Table II. There is seen to be no correlation between retention at the ring and inversion in the haloalkene. On the contrary, the *trans* configuration of the cyclooctene ring is maintained to the extent of 98.5, 98.6, and 96.6% in the three cycloadditions, while the configuration of the 1212 is inverted 20.2 and 33% of the time from the *trans*- and *cis*-haloalkenes, respectively. This is almost the same degree of configuration loss as was observed¹⁰ in the (2 + 2) cycloaddition of these isomers to cyclopentadiene (19 and 31%, respectively). The amount of configuration loss within each reacting moiety is a function of its own local hindrance to rotation in the free radical and not of any variance in the electronic

(10) R. Wheland and P. D. Bartlett, *J. Amer. Chem. Soc.*, **92**, 3822 (1970).

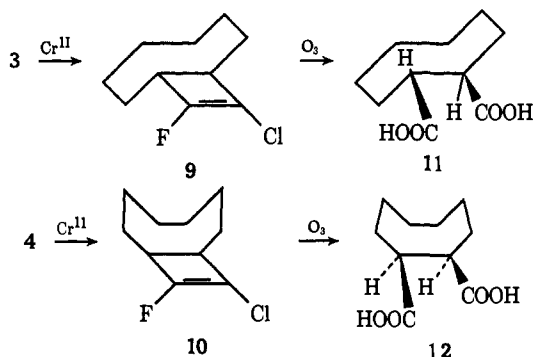
interaction between reactants from one reacting pair to another.^{11,12}

Cycloadduct isomers **6** and **8** might each have arisen from either an erythro or a threo biradical, depending upon which bond was formed first. Isomer **5**, however, clearly belongs to the threo series and isomer **7** to the erythro series. The relative amounts of these isomers are similar from both cis and trans 1212 (Table II). With respect to the material leading to these two products, there seems to have been about a 2 to 1 preference for the formation of erythro biradical.

Structures of the Cycloadducts 3 to 8. The cis adduct **4** of 1122 was prepared by hydrogenation of the known cis adduct of 1122 and cyclooctatetraene.¹⁷



Each cycloadduct was converted to the corresponding cyclooctane-1,2-dicarboxylic acid (**3** \rightarrow **11** and **4** \rightarrow **12**) by dehalogenation with chromous sulfate and zinc,¹⁸ and ozonization of the resulting chlorofluorobicyclo[6.2.0]decene, **9** and **10**.



Since these results showed that dehalogenation occurred without effect upon the geometry of the ring fusion, it was possible to gain information on the 1212 cycloadducts **5**–**8** by dehalogenation performed on the unseparated mixture whose isomeric composition was known. The mixed adduct of Table I was subjected to the dehalogenating reagent for 40 hr at 95–100°. About 58% of the sample was accounted for

(11) This reacting pair does not show the behavior of the AD-like type in the sense of N. D. Epiotis [*J. Amer. Chem. Soc.*, **94**, 1924 (1972)], in which inversion in A is accompanied by retention in B and *vice versa*. On the other hand, if this were an AX-like reactant pair, the extent of inversion in the 1212 should not be the same with two such different donors as cyclooctene and cyclopentadiene.

(12) *trans*-Cyclooctene appears to present an unusual degree of retention of configuration under conditions of stepwise cycloaddition. Thus, although this olefin has been used to discriminate between concerted and stepwise mechanisms,^{6,7,13,14} it is a far less sensitive agent for this purpose than 2,4-hexadiene¹⁵ or even 2-butene.¹⁶

(13) P. G. Gassman and H. P. Benecke, *Tetrahedron Lett.*, 1089 (1969).

(14) W. Weyler, Jr., L. R. Byrd, M. C. Caserio, and H. W. Moore, *J. Amer. Chem. Soc.*, **94**, 1027 (1972).

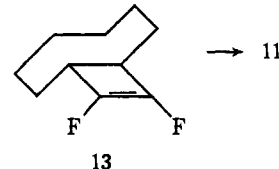
(15) L. K. Montgomery, K. E. Schueller, and P. D. Bartlett, *ibid.*, **86**, 622 (1964).

(16) P. D. Bartlett, K. Hummel, S. P. Elliott, and R. A. Minns, *ibid.*, **94**, 2898 (1972).

(17) G. Schröder and Th. Martini, *Angew. Chem., Int. Ed. Engl.*, **6**, 806 (1967).

(18) (a) D. M. Singleton and J. K. Kochi, *J. Amer. Chem. Soc.*, **89**, 6547 (1967); (b) J. K. Kochi and D. M. Singleton, *ibid.*, **90**, 1582 (1968); (c) J. R. Hanson and E. Premuzic, *Angew. Chem., Int. Ed. Engl.*, **7**, 247 (1968).

as recovered starting material and dehalogenation product, in the ratio of about 16:84. The dehalogenation product had entirely trans ring fusion, containing 1% of the known **9** and 99% of the corresponding difluoro compound **13**, whose configuration was established by ozonization to **11**.



The incomplete recovery of dehalogenation products (yield about 50%) from the mixture of **5**–**8** leaves room for two possible interpretations. On the one hand, as much as half of the cycloadducts may be resistant to the dehalogenating conditions, and might include substantial amounts of cis-fused bicyclodecanes. In our previous experience with this dehalogenating technique,^{10,19} the only one of the six hydrogenated cycloadducts of 1212 to cyclopentadiene that failed to undergo quantitative dehalogenation under these conditions was the norbornane with both chlorine atoms endo, and this isomer yielded 50.5% of dehalogenation products under the standard conditions. From this it appears likely that every isomer present in substantial amount in the **5**–**8** mixture is represented by a dehalogenation product, and if this is so, then the principal cycloadducts **5**, **6**, and **7** must all have the trans ring fusion and **8** must have the cis ring fusion. A combination of its small amount in the mixture with nonquantitative dehalogenation would then account for the absence of any cis product in the dehalogenation mixture.

This assignment is strongly supported by the combined evidence of ¹⁹F nmr and product composition. The AA'XX' spectra have not been fully resolved, but **5** and **7** show single main signals (**5**: ϕ 128, separation of outer lines 19 Hz; **7**: ϕ 97, doublet, 12 Hz), while **6** and **8** show two main signals each (**6**: quartets at ϕ 108 and 137; **8**: doublets at ϕ 97 and 117) corresponding to nonequivalent fluorine nuclei (Table III).

Table III. ¹⁹F Chemical Shifts and Major Splittings

Compd	Chemical shift (ϕ), ^a multiplicity, splitting (Hz)
3	98, d, 8; 100, d, 8; 120, q, 15, 3; 122, q, 15, 3
4	95, q, 12, 6; 97, q, 12, 6; 110, d, 9; 112, d, 9
5	128, m, main splitting 19
6	108, q; 137, q
7	97, d, 12
8	97, d; 117, d
9	105, q, 11, 5
10	106, q, 14, 5
13	128, q

^a Parts per million upfield from CCl₄ internal standard.

This assignment has the further element of consistency that *trans*-1212 always leads to a greater predominance of trans chlorine in the cycloadduct than does *cis*-1212, in common with most thermal cycloadditions of simple olefins.^{16,20} In Table I, the indicated as-

(19) R. Wheland, Ph.D. Thesis, Harvard University, 1970, Table I, p 36.

(20) P. D. Bartlett, 23rd International Congress of Pure and Applied Chemistry, Vol. 4, Butterworths, London, 1971, p 281.

signments correspond to a PQ^{15} of 8.0 for the halogen configuration.

It should be noted that whereas Table I indicates predominant retention in 1212 and strongly predominant retention in the *trans*-cyclooctene, any altered assignment permitted by the ^{19}F nmr spectra would now correspond to predominant inversion in *both* reacting components, which would be at least as inconsistent with a concerted reaction mechanism as the present assignments. We conclude that the assignments of Table I are a uniquely self-consistent set.

The erythro-threo assignments of 5 and 7 are made in accord with the generalization that *cis* vicinal alkyl groups, including a ring member, are more shielding to the fluorine nucleus than *cis* vicinal hydrogen atoms. On this basis the erythro configuration is preferred by about 2:1 from both *cis*- and *trans*-1212, compared with about 0.8 and 0.9, respectively, in the addition of *cis*- and *trans*-1212, to cyclopentadiene.¹⁰ Models show that fusion with a cyclooctane ring has no distorting effect on the cyclobutane ring whether the fusion be *cis* or *trans*, and the members of the eight-membered ring may therefore have effects on the ^{19}F nmr similar to those of acyclic substituents.

Experimental Section

Fluorine and proton nmr spectra were taken on a Varian HA-100 spectrometer at 94.1 MHz. Mass spectra were determined on an Associated Electrical Industries MS-9, ir spectra on a Perkin-Elmer 137B Infracord, and vapor chromatography was carried out on an Aerograph Autoprep Model A-700 and on F&M Scientific Models 300, 609, and 700. Molecular formulas of cycloadducts were established by parent peak masses (Table IV).

Table IV. Parent Peak Masses for Cycloadducts and Dehalogenation Products

Compd	Parent m/e		$(P + 2)/P$	
	Obsd	Calcd	Obsd	Calcd
3	242.0434	242.0441	0.64	0.65
4	242.0452	242.0441	0.63	0.65
5	242.0439	242.0441	0.65	0.65
6	242.0444	242.0441	0.67	0.65
7	242.0433	242.0441	0.60	0.65
8	242.0466	242.0441	0.65	0.65
9	188.0768	188.0768	0.35	0.33
10	188.0762	188.0768	0.33	0.33

Thermal Cycloaddition of 1122 to *trans*-Cyclooctene. Two tubes, each containing 4 g of 99% pure *trans*-cyclooctene²¹ and 16 g of 1122, were sealed under nitrogen and placed in a preheated oven at 120–130° for 3 hr. The tubes were opened and gave 26 g of recovered 1122. The remaining material was subjected to a vacuum of 10 mm while heating gently. About 0.5 g of material was collected in a flask cooled in Dry Ice-acetone. This low boiling fraction was subjected to preparative vpc with a 4 m × 0.25 in., 25% TCEP on 60–80P AW column at 125°. The major components in an 88:12 ratio gave the ir spectra of *cis*-cyclooctene and *trans*-cyclooctene, respectively. Continuing the distillation gave 6.1 g (69%) of colorless oil bp 106–108° (11 mm). Vpc analysis on Carbowax 20M indicated that this fraction was 99% 3 and 1% 4. Use of a preparative Carbowax 20M column resulted in 5.6 g (63%) of 3 and 35 mg (0.5%) of 4. This sample of 3 gave the mass spectrum, 1H nmr, ^{19}F nmr, and ir spectrum hereafter considered standard for 3. The sample of 4 on a second pass through Carbowax 20M gave about 20 mg of material with 1H nmr and ir identical with those for a genuine sample of 4. In order to put these results in their proper perspective a number of controls were run.

(21) (a) A. C. Cope, R. A. Pile, and C. F. Spencer, *J. Amer. Chem. Soc.*, **75**, 3213 (1953); (b) J. L. Coke and M. C. Mourning, *ibid.*, **90**, 5561 (1968).

Control Experiments. About 50 μ l of *cis*-cyclooctene was heated under nitrogen at 120–130° for 28 hr with 0.3–0.5 g of 1122. At the end of this period no *cis*-fused adduct 4 could be detected. Thus, the 4 detected above truly arose in the reaction of *trans*-cyclooctene with 1122 rather than from a competing cycloaddition of *cis*-cyclooctene of 1122.

About 25 μ l of pure 3 in 0.2–0.4 g of 1122 was heated under nitrogen for 11 hr at 185°. No *cis*-fused adduct could be detected in the reaction mixture on recovery. Approximately 30 μ l of pure *cis*-fused adduct 4 in 0.4–0.6 g of 1122 was heated under nitrogen for 25 hr at 185°. No *trans*-fused adduct 3 could be detected in the reaction mixture on recovery. The distribution of the adducts 3 and 4 on cycloaddition of 1122 to *trans*-cyclooctene thus did not reflect any interconversion under the reaction conditions.

In a sealed Pyrex tube 30 μ l of pure *cis*-fused adduct 4 was heated under nitrogen in 0.4–0.6 g of 1122 for 25 hr at 185°. No *cis*-cyclooctene could be detected in the recovered reaction mixture. The heating of a 0.2–0.3-g sample of pure *trans*-fused adduct 3 in 0.2–0.3 g of 1122 under nitrogen for 3 hr at 155° also failed to produce any *cis*-cyclooctene. The *cis*-cyclooctene in the product mixture from the cycloaddition of 1122 to *trans*-cyclooctene thus could not be accounted for by decomposition of either cycloadduct.

On heating 50 μ l of *trans*-cyclooctene in 0.5 g of pentane for 3 hr at 125°, there resulted 3% isomerization to *cis*-cyclooctene, whereas use of acetonitrile in the place of pentane resulted in 7% isomerization. Concerted cycloaddition of *trans*-cyclooctene to butadiene resulted in little if any isomerization of *trans*-cyclooctene to *cis*-cyclooctene (see below).

About 50 μ l of 99% *trans*-cyclooctene and 0.3–0.5 g of 1122 were heated under nitrogen at 120–130° for 3 hr. The tube was opened and its contents analyzed by vpc without any work-up: 4 (1), 3 (99), and *cis*-cyclooctene (9). With correction for the 1% *cis* impurity in the starting *trans*-cyclooctene, the relative quantities were readjusted to 4 (1), 3 (99), and *cis*-cyclooctene (8). This correction for the *cis*-cyclooctene in the starting *trans*-cyclooctene assumed that the areas of cyclooctene and adduct peaks were directly proportional to their mole per cents. This assumption was checked by preparing a solution of 35 mg of *cis*-cyclooctene (16.7 mol %) in 386 mg of 3 (83.3 mol %). Injection of this standard solution gave 83.8 area per cent for 3 and 16.2 area per cent for *cis*-cyclooctene on a Carbowax 20M column in an F&M Scientific Model 700 thermal conductivity vpc.

For the distribution of cyclooctene between *cis* and *trans* isomers a 4 m × 0.25 in., 25% TCEP, 60–80P AW column was used. For the distribution of cyclooctene relative to adducts or for the distribution of adducts relative to one another a 3 m × 0.25 in., 20% Carbowax 20M, 30–60W AW DMCS column was used.

Thermal Cycloaddition of *cis*-Cyclooctene to 1122. Preparation of 4. In a sealed tube, 10 g of *cis*-cyclooctene and 37 g of 1122 were heated under nitrogen for 16 hr at 185°. Vpc analysis of the resulting yellow solution suggested that the major product was *cis*-fused adduct 4 with a peak area some 3% as great as that of unreacted *cis*-cyclooctene. Distillation gave a large fraction, bp 60–70° (60 mm), and 1.7 g of residue. The bp 60–70° (60 mm) fraction afforded a pure (ir) sample of *cis*-cyclooctene after a single pass on a 3 m × 0.25 in., 20% Carbowax 20M, 30–60W AW DMCS column at 160°. Passage of the 1.7 g of residue through the same Carbowax 20M column produced 0.3 g (1.4%) of clear oil with the correct ir, 1H , and ^{19}F spectra for the *cis*-fused adduct 4.

A study of the initial vpc trace revealed a minor product of 3–4% of the area of 4 and with the retention time of 3. Preparative vpc first on Carbowax 20M and then on a 4 m × 0.25 in., 25% TCEP column produced several milligrams of material. The ir spectrum obtained was weak but remarkably like that of 3. The mass spectrum of this material showed a number of extraneous peaks in addition to the parent peaks expected for a genuine sample of 3.

Independent Synthesis of *Cis*-Fused Adduct 4. A solution of 6.0 g of *cis*-9,9-dichloro-10,10-difluorobicyclo[6.2.0]deca-2,4,6-triene¹⁷ in 60 ml of methanol was hydrogenated at atmospheric pressure with $PtO_2 \cdot nH_2O$ as catalyst. When virtually no hydrogen was absorbed during the first day, the reaction mixture was treated with Norit and filtered. New $PtO_2 \cdot nH_2O$ was added, permitting exhaustive hydrogenation to proceed readily. Methanol was removed by distillation at atmospheric pressure. Further distillation gave 0.2 g of colorless oil, bp 108–113° (11 mm), and 4.8 g of colorless oil, bp 113–116° (11 mm). The bp 113–116° (11 mm) fraction was at least 70% a single product which was collected off Carbowax 20M. The mass, ir, 1H , and ^{19}F spectra of this product were taken as standard for 4.

Chromous Ion Dehalogenation of Adduct 4. Preparation of 10. *Cis*-fused adduct 4 (3.0 g), 6 g of zinc dust, 3 g of $Cr_2(SO_4)_3 \cdot nH_2O$,

0.6 g of HgCl_2 , 30 ml of dimethylformamide, 30 ml of water, and a stirring bar were sealed under nitrogen in a 300-ml Kjeldahl flask. The lower portion of the flask was suspended for 1 day in a 95–100° oil bath while its contents were stirred vigorously. When the flask was opened, 100 ml of water was added. Then 15 ml of pentane was added and shaken vigorously with the contents of the flask. The flask was sealed on Dry Ice, freezing the aqueous layer and allowing the pentane layer to be decanted. This pentane extract was combined with two later ones and concentrated by distillation at atmospheric pressure to an oil. Preparative separation on Carbowax 20M allowed 1.6 g (69%) of the major product **10** to be isolated.

Chromous Ion Dehalogenation of 3. Preparation of 9. Thermal *trans*-cyclooctene adducts (4 g) with 1122 (99% **3**, 1% **4**), 8 g of zinc dust, 4 g of $\text{Cr}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$, 0.8 g of HgCl_2 , 40 ml of water, 40 ml of dimethylformamide, and a stirring bar were sealed under nitrogen in a Kjeldahl flask, treated and worked up as in the dehalogenation of **4**. Distillation of the residue gave 2.0 g (62%) of clear colorless **9**, bp 110–114° (25 mm). Final purification was effected on a 3 m \times 0.25 in., 20% Carbowax 20M, 30–60W AW DMCS column at 165°.

Ozonolysis of 9 and 10. Preparation of 11 and 12. **10** (1 g) was dissolved in 20 ml of ethyl acetate. Ozone was bubbled through the solution in a Dry Ice-acetone bath until the reaction mixture turned blue. The reaction mixture was washed into a 125-ml round-bottom flask. Most of the ethyl acetate was removed on a rotary evaporator at high vacuum so as to keep the flask below room temperature. To the resulting heavy oil 20 ml of 90% formic acid and 7 ml of 30% hydrogen peroxide were added. The flask was fitted with a reflux condenser and magnetic stirrer. After about 20 hr the reaction mixture was heated under reflux briskly for 1 hr. Norit was added to the solution which was filtered hot by gravity. Evaporation of the filtrate on a rotary evaporator gave 0.8 g of solid which was washed onto a vacuum filter with ice-water. Once dry the crystals were dissolved in a refluxing methylcyclohexane-ether mixture. The resulting solution was treated with Norit and filtered. After concentration and cooling, the filtrate gave 0.26 g of white solid (23%). This material had the ir spectrum of a carboxylic acid, mp 159–161° (reported²² mp 161–162°), and hence was assigned the structure **12**.

Similar ozonolysis of **9** afforded 36% of **11**, mp 144–146° (reported²² mp 145–147°).

Thermal Cycloaddition of 1212 to *trans*-Cyclooctene. About 42 g of 1212 and 15 g of 60% *trans*-, 40% *cis*-cyclooctene were heated under nitrogen in a sealed tube for 14 hr at 170°. Distillation at atmospheric pressure gave 33 g of recovered 1212. Further distillation gave about 10 ml of impure *cis*-cyclooctene, bp 60–70° (50 mm); 0.7 g bp <40° (10 mm); 0.3 g bp 110–112° (10 mm); and 10.1 g (51%) of adducts bp 112–115° (10 mm). No evidence could be found for the cycloaddition of 1212 to *cis*-cyclooctene under these conditions.

The separation of the individual adducts by vpc was rather difficult. Separation was accomplished with various combinations of passes on a 4 m \times 0.25 in., 25% TCEP, 60–80P column (referred to as column I) and on a 3 m \times 0.25 in., 20% Carbowax 20M, 30–60W AW DMCS column (referred to as column II). It was found empirically that adducts collected off TCEP were considerably cleaner if they were first mixed with an equal volume of pentane before injection.

Adduct 5. Injections (20 μl) of the pentane solution of adducts bp 112–115° (10 mm) were passed on column I at 165°. The material collected was remixed with pentane and put through column I a second time at 142° in 30- μl injections.

Adduct 6. Injections (20 μl) of the pentane solution of adducts were passed on column I at 165°. The material collected was remixed with pentane and put through column I at 142° in 15- μl injections. This material was in turn put through column II at 150° in 15- μl injections.

Adduct 7. When the bp 112–115° (10 mm) fraction was cooled, crystals formed that were separable by vacuum filtration. Three recrystallizations from methanol gave white crystals rich in **7**, mp 69–71°. The remaining impurities were removed by a single pass through column II at 150°.

Adduct 8. The original filtrate from which the adduct **7** had been first crystallized was now somewhat richer in **8** than the original mixture and was more suitable for vpc separation since the peak immediately preceding **8** on the vpc was the one partially removed by

crystallization. This filtrate was mixed with pentane and put through column I at 150° in 100- μl injections. After a second pass on column I the ir and nmr spectra of **8** were taken. Its fluorine nmr revealed no extraneous compounds. The nmr sample was then given a single pass on column II with the material collected being used to determine the mass spectrum of **8**. This pass on the vpc vindicated the previous assumption that **8** had indeed been separated entirely from the other adducts.

Thermal Stability of 1212 Adducts with *trans*-Cyclooctene. A. Stability of 6. Purified adduct **6** (10 μl) was heated in 0.2–0.4 g of 1212 for 16 hr at 172°. At the end of this period the tube was opened and its contents were allowed to evaporate to a heavy oil. This residue was chromatographed on a 10 m \times $\frac{1}{8}$ in., 20% Carbowax 20M, 60–80 W column at 165°. Only a single material with the retention time of starting **6** was apparent. No rearranged or additional materials were detected.

B. Stability of a 5–8 Mixture. An adduct mixture (18.2% **5**, 47.4% **6**, 32.4% **7**, and 2.0% **8**) was heated at 172° for 18 hr in about 0.4 g of 1212. On recovery the mixture analyzed as 17.9% **5**, 45.4% **6**, 34.0% **7**, and 2.7% **8**.

Cycloaddition of *trans*- and *cis*-1212 to *trans*-Cyclooctene. All the runs contributing to Table I were performed simultaneously in an identical manner. Pure *trans*-cyclooctene (30 μl , 99%) and 1.2 g of 99.3% pure *trans*-1212 were separately bulb-to-bulb distilled into a thick-walled Pyrex tube. The tube was sealed under high vacuum while cooling its contents in liquid nitrogen. After heating for 14 hr at 172 \pm 5°, the tube was opened and its contents were poured into a 14/20 flask which was then refrigerated. Analysis on a 1.25 m \times $\frac{1}{8}$ in., 5% DMSO, 80–100 alumina column at 0° indicated that the recovered 1212 was 99.0% *trans* and 1.0% *cis*. The 1212 was removed by bulb-to-bulb distillation giving a residue which was analyzed on a 10 m \times $\frac{1}{8}$ in., 20% Carbowax 20M, 60–80W column at 165°: 27.2% **5**, 20.2% **6**, 49.2% **7**, and 3.4% **8**. The results starting with 95.4% *cis*-1212 and 51.3% *cis*-1212 are shown in Table I together with those for the 99.3% *trans*-1212 just described.

The necessity of using *cis*-1212 which was only 95% pure raises the question of how different may be the rates of cycloaddition of *cis*- and *trans*-1212 to *trans*-cyclooctene. Since the 1212 was present in great excess during these runs, both *cis*- and *trans*-1212 in the mixed run (line 3 of Table I) may be regarded as present at constant concentrations. It is then possible to calculate *F*, the fraction of adducts formed from *trans*-1212 in this run, by comparing the amount of a particular component in the product mixture with that arising from pure *cis*- or *trans*-1212, according to eq 1, where (5)_t, (5)_c, and (5)_m are the percentages of adduct **5** resulting from pure *trans*, from pure *cis*, and from the mixed 1212 isomers, respectively. Equation 1 is (5)_m = (5)_t*F* + (5)_c(1 – *F*); by substitution of the values from Table I, 17.8 = 27.2*F* + 10.2(1 – *F*) and *F* = 0.45. Since the mole fraction of *trans*-1212 in the mixed isomers is 0.487, and since the average value of *F* from adducts **5**, **6**, and **7** is 0.44, it appears that *cis*-1212 is 1.2 times as reactive as *trans* in cycloaddition to *trans*-cyclooctene. Therefore, small amounts of isomeric impurity will not produce gross distortions in the adduct compositions by determining greatly more than their share of the products.

Preparative Chromous Ion Dehalogenation of the 1212 Adduct Mixture with *trans*-Cyclooctene. Preparation of 13. About 10 g of adduct mixture (18% **5**, 47% **6**, 34% **7**, 1% **8**), 20 g of zinc dust, 10 g of $\text{Cr}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$, 2 g of HgCl_2 , 100 ml of water, and 100 ml of dimethylformamide were stirred magnetically under nitrogen in a sealed 500-ml Kjeldahl flask. After 40 hr in a 95–100° oil bath, the flask was cooled with Dry Ice and placed behind a safety shield and opened. The contents were shaken with 25 ml of pentane and 200 ml of water. After cooling with Dry Ice in order to refreeze the aqueous layer, the pentane was decanted. Two more such pentane extracts were combined with the first. Distillation at atmospheric pressure removed the pentane. Rapid distillation of the residue gave the following fractions; 1, bp 98–110° (45 mm), 3.25 g; 2, bp 110–135° (45 mm), 0.7 g; 3, bp 135–152° (45 mm), 1.3 g. Fraction 1 was at least 95% **13**, fraction 2 at least 85% **13**, and fraction 3 about 74% starting material with the largest proportion of **9** of any fraction.

Preparative vpc of fraction 3 on a 3 m \times 0.25 in., 20% Carbowax 20M, 30–60W AW DMCS column allowed separation of impure **9**. A second pass on a 4 m \times 0.25 in., 20% DIDP, 60–80P column at 155° gave pure **9** except for some stripping on the part of the column packing. A third pass on Carbowax 20M gave pure **9** identified by ir and mass spectral comparison to a genuine sample.

On slower, more careful distillation fraction 1 was redistilled,

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bp 89–92° (32 mm). For degradative and nmr spectral purposes a middle cut, bp 90–91° (32 mm), was employed. This middle cut was quite pure except for a small 1–2% material that showed up on the tail of **13** when subjected to vpc analysis on a 10 m × 1/8 in., 20% Carbowax 20M, 60–80W column at 140°. Similarly, there was a small blip in the baseline of the ¹⁹F nmr of **13**. It was not unreasonable to assume that this small impurity corresponded to the *cis* ring fused isomer of **13** that may arise from dehalogenation of the 1–2% of **8** in the starting adduct mixture. Preparative vpc was employed for ir and mass spectral samples of **13** where purity was more critical and smaller samples were practical. The first part of 2–3- μ l injections of the fraction, bp 90–91° (32 mm), coming through a 10 m × 0.25 in., 20% Carbowax 20M, 30–60W AW DMCS column at 155° gave **13** free of this minor impurity.

Running a somewhat small scale dehalogenation on the same adduct mixture for 60 hr caused the reaction to go to completion. The product distribution before distillation and separation into fractions was 1% **9** and 97–99% **13** depending upon whether 0–2% of material was hidden under the tail end of the **13** peak. On isolation **13** proved identical with that isolated above.

Ozonolysis of 13. Ozone was bubbled through a Dry Ice–2-propanol cooled solution of 0.9 g of freshly bulb-to-bulb distilled **13** in 10 ml of ethyl acetate until the solution turned blue. Excess ozone was blown out with nitrogen. The ethyl acetate solution was transferred to a rotary evaporator operating under high vacuum. When the temperature rose above 0°, the flask containing the residue was transferred to a Dry Ice–2-propanol bath. To the chilled residue, 20 ml of 88% formic acid and 7 ml of 30% hydrogen peroxide were added. The solution was stirred magnetically at room temperature for 3.5 days after which time the gradual oxygen evolution perceptibly slowed. The reaction mixture was refluxed for 1 hr after which it was treated with Norit and filtered. Addition of methylcyclohexane–ether and extended evaporation on a rotary evaporator produced an oil that eventually changed to a sticky solid. The solid was washed onto a vacuum filter with water. Repeated washings with ice–water followed by sucking dry overnight gave 0.48 g of sweet-smelling, greenish-yellow crystals. The crystals were dissolved in refluxing ether, treated with Norit, and

filtered. Addition of methylcyclohexane and cooling produced 0.16 g of white crystals, mp 146–148° (lit.²² 145–147°), corresponding to acid **11**.

Cycloaddition of *trans*-Cyclooctene to Butadiene. About 20 g of butadiene, 5 g of 60% *trans*-, 40% *cis*-cyclooctene, and a trace of hydroquinone were heated for 2 hr at 125° in a sealed tube under nitrogen. Fractional distillation of the product was carried out in a large flask on account of a tendency to foam strongly. There was obtained 2.7 ml bp 55–61° (43 mm), 0.5 ml bp 61–142° (43 mm), and 3.4 ml bp 142–143° (43 mm). For ¹H and mass spectral purposes the bp 142–143° (43 mm) fraction was distilled a second time giving 2 g (45%) of bicyclo[6.4.0]dodec-10-ene, bp 102–103° (10 mm). This material gave a single vpc peak on a 3 m × 0.25 in., 20% Carbowax 20M, 30–60W AW DMCS column at 162° with a 29-min retention time.

Mass spectrum: exact mass parent 164.156 (calcd 164.157); P + 2/P = 0.13 (calcd 0.13); peak at mass 110 (cyclooctene)⁺; peak at mass 54 (butadiene)⁺. Nmr: 2 vinyl protons, 18 alkyl protons.

A small scale control reaction was run in order to determine the extent of isomerization of *trans*- to *cis*-cyclooctene under the reaction conditions. About 50 μ l of 98.6% pure *trans*-cyclooctene and 0.25 g of butadiene were heated under nitrogen for 2 hr at 125°. Vpc analysis at the end of this period gave the following uncorrected trace areas on TCEP: 4-vinylcyclohexene (8.3), *cis*-cyclooctene (1.0), *trans*-cyclooctene (1.1), and adduct (97.9). Vpc areas were left uncorrected on the basis of a sample of 114.8 mg of adduct (76.9 mol %) mixed with 23.2 mg of *cis*-cyclooctene (23.1 mol %) which showed relative vpc trace areas of 78.6 for adduct and 21.4 for *cis*-cyclooctene.

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Bimolecular Self-Reaction of Peroxy Radicals. An Oxygen-18 Isotope Study

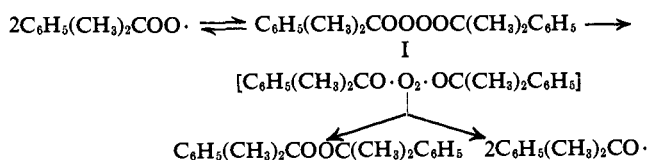
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Abstract: A technique using electron spin resonance spectroscopy has been developed to determine the isotopic distribution of the oxygen evolved from the decomposition of an equimolar mixture of the peroxy radicals R¹⁶O¹⁶O· and R¹⁸O¹⁸O· (where R was a primary, secondary, or tertiary alkyl, acetyl, or 2-pyridyl group) in an inert solvent. In each case the mixed isotope, ¹⁶O¹⁸O, was observed in the oxygen that was evolved in the termination reaction. These results provide additional evidence that the rate controlling termination reaction for the liquid phase autoxidation of hydrocarbons with labile primary, secondary, and tertiary hydrogens involves a head-to-head reaction of two alkylperoxy radicals.

There is at the present time considerable interest in the kinetics and mechanisms of the bimolecular self-reactions of alkylperoxy radicals.² The self-reaction of tertiary alkylperoxy radicals is fairly well understood³ and is believed to occur *via* a tetroxide interme-

diante, I. For example



The oxygen molecule formed in this reaction is produced by the elimination of the terminal oxygen atom from each radical. This has been confirmed by the detection of ³⁴O₂ during the oxidation of cumene (ini-

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