the earlier conclusion[11] that the γ effect is at least partially steric in nature, because the steric interactions of sp^2- and sp-hybridized carbons must surely be different. Except for the alkanes, the γ effect remains an important but poorly rationalized phenomenon. Further research into the mechanism of this effect is underway.[20]

Regardless of the origin of the γ effect, its identification has allowed us to assign the sp resonances uniquely in the spectra of 3-alkynes. In previous work, the unsaturated carbon resonances of such alkynes as 3-octyne were incorrectly assigned, or left unassigned.[6a] The derivation of the γ parameter, however, allows specific assignment in such examples. Alkynes which possess triple bonds which are removed by more than three sp^3-hybridized carbons from the end of a linear chain cannot, however, be assigned using our method. Fortunately, the chemical shifts of the sp-hybridized carbons in such systems are frequently so similar as to preclude the resolution of the peaks.[6a]

The similarities of the α' shifts of alkenes and alkynes tends to confirm the hypothesis[11] that this effect is derived in part from polarizations of the π electrons. Certainly, large chemical-shift differences have been demonstrated for unsaturated species and, where mesomeric polarizations can be expected, these lead to very large polarizations of both double[21,22] and triple[23] bonds. In the hydrocarbons, in which the polarizing effect can be due only to inductive and hyperconjugative effects, the polarizations lead to much smaller differences in the shifts of the unsaturated carbons. Thus, the chemical shifts of carbons 1 and 2 of ethoxyethyne are 104.6 and 170.8 ppm,[23] respectively. These shifts may be directly compared to those of 1-pentyne, in which the chemical shifts of the sp-hybridized carbons differ by only 15.4 ppm.

Both the β' and γ' shifts are small and negative. Furthermore, the lower F levels[9] indicate that these parameters are less important to the regressional analysis. In the alkenes,[11] the analogous β' effect was found to be approximately +2 ppm, and its origin was considered to be of a steric nature. The present results are consistent with such a formulation. In the rigidly linear alkynes, the β' carbon is precluded from coming into the proximity of the more distant sp-hybridized carbon and a steric effect would therefore be suppressed. Without such an influence, the presence of the β' effect becomes less important.

With the present analysis of the ^{13}C nmr spectra of alkynes, procedures are now available for the prediction of the spectra of all three major groups of acyclic hydrocarbons. We are therefore prepared to establish a set of rules through which the interpretation of carbon-13 chemical-shift data can lead to elucidation of structures. The development of such rules and their applications to compounds other than hydrocarbons are currently under investigation in these laboratories and will be reported later.[7]

Registry No.—^{13}C, 14762-74-4.

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[20] C. Marzin, D. E. Dorman, and J. D. Roberts, unpublished results.

[21] G. E. Maciel, *J. Phys. Chem.*, **69**, 1947 (1965).

[22] T. Higashimura, S. Okamura, I. Morishima, and T. Yonezawa, *J. Polym. Sci., Part B*, **7**, 23 (1969).

[23] D. Rosenberg, J. W. deHaan, and W. Drenth, *Recl. Trav. chim. Pays-Bas*, **87**, 1387 (1968).

Cycloaddition. XV. Competing Mechanisms in the Reaction of Cyclopentadiene with Trifluoroethylene and 2-Chloro-1,1-difluoroethylene

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Thermal cycloaddition of trifluoroethylene to cyclopentadiene competes unfavorably with diene dimerization (about 1:600 at 8°). At 210°, where the dimer dissociates thermally, a cross-cycloadduct is obtained consisting of about 99% of the two norbornenes (exo H/endo H, 2:1). 2-Chloro-1,1-difluoroethylene appears to be about four times as reactive a dienophile as trifluoroethylene, yielding a cycloadduct at 170° that is 99.5% norbornenes (exo H/endo H, 5:3). Photosensitized cycloaddition of trifluoroethylene to cyclopentadiene yields mixtures of six cross-cycloadducts, whose structures and configurations were established by proton and fluorine nmr spectroscopy and by independent synthesis. The product composition did not depend on the nature or triplet excitation energy of the sensitizer, but reflected competition, even at 2°, between slow thermal cycloaddition and the relatively inefficient photosensitized process. When thermal reaction was minimized, the photosensitized product consisted of 15.5% norbornenes and 84.5% bicyclo[3.2.0]heptenes from (2 + 2) cycloaddition. The latter showed major/minor regioselectivity of about 2.3, and in the major orientation the ratio of endo H/exo H was ~ 2. The photosensitized adduct of 2-chloro-1,1-difluoroethylene to cyclopentadiene differed from that of trifluoroethylene chiefly in showing a much greater regioselectivity in the bicyclo[3.2.0]-heptenes: the major/minor orientation = 42 and endo H/exo H = 3.2–3.4. These results are consistent in detail with competition in the thermal cycloaddition such that about 98.5% is concerted in the case of trifluoroethylene and 99.4% in the case of 2-chloro-1,1-difluoroethylene. The endo preference of halogen in the concerted (2 + 4) cycloaddition mechanism is absent or slightly reversed in the (2 + 4) products of the photosensitized reaction and is strongly reversed in the (2 + 2) product.

Photosensitized cycloadditions, proceeding through an excited triplet state of one of the reactants, have been used successfully as models indicating what may be expected of a *bona fide* biradical mechanism.[1,2] When one of the reactants is a conjugated diene and the other is unsymmetrically substituted, the product mixture is characterized by its relative content of

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[1] Part XIII: P. D. Bartlett, B. M. Jacobson, and L. E. Walker, *J. Amer. Chem. Soc.*, in press.

[2] P. D. Bartlett, XXIIIrd International Congress of Pure and Applied Chemistry, Boston, Mass., July 26–30, 1971, Vol. 4, Butterworths, London, 1971, pp 281–305.

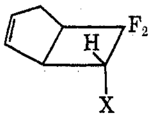
cyclobutanes and cyclohexenes, resulting respectively from (2 + 2) and (2 + 4) addition, and by the orientation of the reactant molecules in the former (regioselectivity). If, in addition, there is geometrical configuration in either or both of the reactants, wide variations are possible in the extent of configurational loss, retention, or inversion during the cycloaddition. In the reaction between cyclopentadiene and 1,2-dichloroethylene,[3] on going from photosensitized to thermal reaction the four (2 + 2) cycloadducts disappear from the product and one observes only the Diels–Alder product (two isomers from the cis alkene and one from the trans) formed with retention of configuration, indicating that the thermal reaction is a concerted one with no biradical behavior. On the other hand, the cycloaddition of trifluoroethylene to butadiene photosensitized with biacetyl yields a mixture of the same four stereoisomeric vinyltrifluorocyclobutanes plus trifluorocyclohexene as is obtained by thermal cycloaddition, the only difference between these two mixtures being a regioselectivity factor of 1.35 for the photosensitized reaction and 2.16 for the thermal.[1] By detailed study of the dependence of product composition upon the triplet energy of the sensitizer it was possible to conclude that the thermal addition of trifluoroethylene to butadiene is chiefly a biradical reaction, but with about 9% occurring by a competing concerted mechanism.

If trifluoroethylene represents a compound in which the capabilities for biradical formation and for concerted Diels–Alder reaction are delicately balanced, the behavior of this olefin should be subject to variation as it reacts with dienes differing in their predisposition to be Diels–Alder donors or to yield biradicals. Accordingly we have, in the present study, compared the thermal and photosensitized cycloaddition of trifluoroethylene to cyclopentadiene, previously shown to be more than 1000 times as reactive as butadiene toward maleic anhydride in a concerted mechanism, but less reactive by a factor of 8 than butadiene toward the stepwise reagent 1,1-dichloro-2,2-difluoroethylene.[4]

Results

Thermal Cycloadditions.—Although it was possible to obtain appreciable amounts of cycloadducts by protracted thermal reactions at temperatures as low as 8°, these preparations were made very inefficient by the strongly competing dimerization of cyclopentadiene. Thus, with a sixfold excess of trifluoroethylene over diene, after 30% reaction of the diene only 0.9% of the product was cross-cycloadduct, the rest being dicyclopentadiene. This indicates that the bimolecular rate constant for dimerization of cyclopentadiene must be at least 600 times as great as that for its cycloaddition with trifluoroethylene. For the practical purpose of obtaining higher yields of cross-cycloadducts, advantage was taken of the reversibility of cyclopentadiene dimerization; when the reaction was run with an excess of trifluoroethylene at 210° dicyclopentadiene was formed only temporarily and eventually the whole of the diene was converted into cross-cycloadducts.

With only cis ring juncture being considered, the possible cross-cycloadducts are **1**-F to **6**-F. The characterization and establishment of structure for these isomers and the corresponding ones where X = Cl are described below. Table I shows the product compositions indicated by vapor chromatography for the thermal cycloadditions. None of **3**-F or **4**-F could be detected in these mixtures; although there is interference from the overlapping of the relatively large peaks of **5**-F and **6**-F, we know from the butadiene adducts[1] and from the photosensitized products from cyclo-



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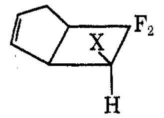

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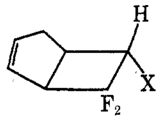

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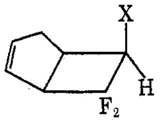

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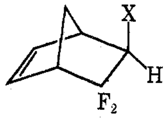

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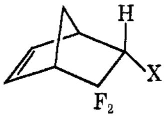

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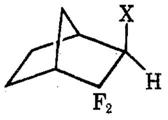

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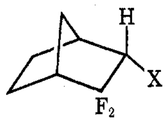

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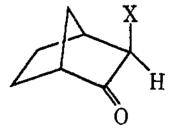

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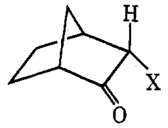

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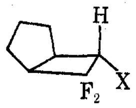

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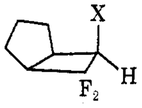

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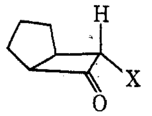

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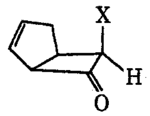

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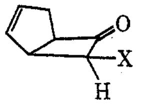

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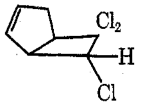

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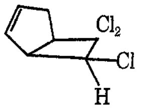

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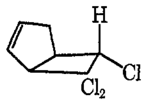

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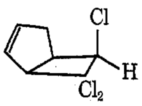

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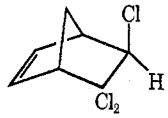

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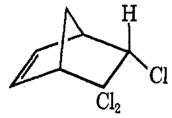

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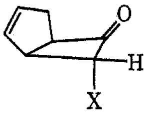

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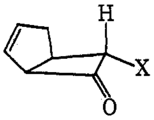

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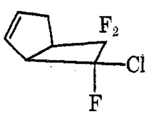

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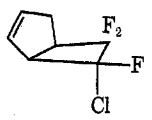

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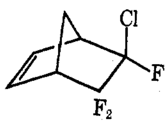

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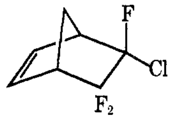

27

X = F or Cl

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(3) P. D. Bartlett, R. Helgeson, and O. A. Wersel, *Pure Appl. Chem.*, **16**, 187 (1968).

(4) P. D. Bartlett and L. K. Montgomery, *J. Amer. Chem. Soc.*, **86**, 628 (1964).

TABLE I

PRODUCTS OF THE THERMAL REACTION OF TRIFLUOROETHYLENE AND CYCLOPENTADIENE

Temp, °C	Ratio of C_2F_3H/diene	1-F	2-F	5-F	6-F	Dicyclopentadiene yield, %	Diene converted, %
8 ± 3	6.0	<0.01	<0.01	0.2	0.7	99+	30
29.2 ± 0.1	4.0	<0.01	<0.01	1.1	3.0	96	55
64.5 ± 0.1	5.2	<0.01	<0.01	2.8	6.4	91	65
121.7 ± 0.1	4.9	<0.01	<0.01	5.0	10.0	85	95
210 ± 5	2.0	0.6	0.3	39.0	60.1		100

TABLE II

PRODUCTS OF THE THERMAL REACTION OF 2-CHLORO-1,1-DIFLUOROETHYLENE AND CYCLOPENTADIENE

Temp, °C	Ratio of C_2F_2ClH/diene	1-Cl	2-Cl	5-Cl	6-Cl	Dicyclopentadiene yield, %	Diene converted, %
8 ± 3	2.4	~0.02	~0.01	0.6	1.1	98	30
29.2 ± 0.1	6.0	~0.02	~0.01	1.8	3.1	95	55
64.5 ± 0.1	3.7	~0.02	~0.01	3.1	5.0	92	70
121.7 ± 0.1	3.9	~0.09	~0.05	9.5	15.6	75	95
170 ± 5	2.0	0.3	0.2	38.0	61.5		100

TABLE III

CROSS-ADDUCT DISTRIBUTIONS FROM THE PHOTOSENSITIZED REACTION OF CYCLOPENTADIENE AND TRIFLUOROETHYLENE

Sensitizer	1-F	2-F	3-F	4-F	5-F	6-F	Yield of all cross-adducts, %
None[a]	~1	<1	?	?	24	75	~0.5
None[b]	28	13	12	4	18	25	1.3
2-Acetonaphthone or benzophenone	42	19.5	20.5	5.0	6.5	6.5	6–12

[a] Cyclopentadiene treated with lithium aluminum hydride before use, all transfers done under vacuum. [b] No precautions taken to prevent oxidation of the cyclopentadiene.

pentadiene that the orientation of **1** and **2** is preferred over that of **3** and **4** by at least 2:1, which sets an upper limit of 0.45% for (**3** + **4**) in the product at 210° having the most (2 + 2) cycloadducts. This very strong preference for (2 + 4) cycloaddition by trifluoroethylene, when compared with the formation of 67% (2 + 2) product[5] by tetrafluoroethylene at 470–480° and of 16% (2 + 2) product[6] by 1122 at 80°, confirms the position of trifluoroethylene as a reagent in which the concerted mechanism competes strongly with the stepwise.

Table II shows that the thermal cycloaddition of 2-chloro-1,1-difluoroethylene to cyclopentadiene is similar to that of trifluoroethylene, with the small difference that the detectable (2 + 2) cycloadducts now represent only 0.5% of the whole. The regioselectivity introduced by a single chlorine atom in the alkene will reduce the products **3**-Cl and **4**-Cl to negligible proportions (see the photosensitized results in Table IV). Table II shows that 170° is a sufficient temperature to eliminate the cyclopentadiene dimer through its thermal dissociation and recapture of the cyclopentadiene by the halo olefin. There is a hint that the endo/exo ratio in the norbornenes, which favors endo halogen, chlorine somewhat more than fluorine, is determined by the secondary orbital-overlap effects often seen in the concerted Diels–Alder mechanism. This selectivity, amounting to as much as 2:1, is reversed in the (2 + 2) adducts, and also in all the products of photosensitized addition, indicating that secondary orbital overlap does not control the isomer distribution in the stepwise mechanism.

Photosensitized Cycloadditions.—After a few photosensitized cycloadditions had been run, it became apparent that the reactivity of cyclopentadiene in thermal dimerization and cross-cycloaddition was high enough to necessitate correction for competing thermal reaction even at 0°. In a series of reactions with seven different sensitizers it was noted that, as the total yield of cross adducts rose from 2 to 12%, the fraction of **5**-F and **6**-F in the product declined from 31 to 15.5%. Photochemical runs without sensitizer sometimes gave as much **1** + **2** as **5** + **6** and some of the (2 + 2) as well as (2 + 4) dimers of cyclopentadiene, but, if oxidation products were removed from the starting diene and air was excluded, only **5**, **6**, and the thermal diene dimer were formed. The absence of the tetracyclic dimer[3] showed that the reaction occurring under these conditions was thermal and not initiated by excited cyclopentadiene singlets. This conclusion is supported by the dark control in Table IV. Increasing the concentration of the sensitizer (using a little ether to increase sensitizer solubility) and using sensitizers of higher absorbance helped to increase the photosensitized reaction and decrease the correction for competing thermal reaction. There was no dependence of the composition of cyclopentadiene cycloadducts on the triplet energy of the sensitizer within the limits of those used here (biacetyl, E_T 54.9, to acetone >78 kcal/mol). Good photosensitized rates and reproducible product compositions were obtained with benzophenone or 2-acetonaphthone (Table III) at concentrations of about 15 mol %.

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[5] J. J. Drysdale, W. W. Gilbert, H. K. Sinclair, and W. H. Sharkey, *J. Amer. Chem. Soc.*, **80**, 3672 (1958).

[6] P. D. Bartlett, L. K. Montgomery, and B. Seidel, *ibid.*, **86**, 616 (1964).

TABLE IV

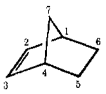
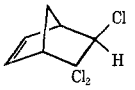
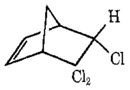
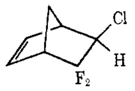
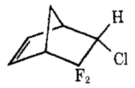
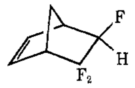
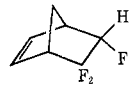
CROSS-ADDUCT DISTRIBUTIONS FROM THE PHOTOSENSITIZED REACTION OF CYCLOPENTADIENE AND 2-CHLORO-1,1-DIFLUOROETHYLENE

Sensitizer	1-Cl	2-Cl	3-Cl	4-Cl	5-Cl	6-Cl	Yield of all cross-adducts, %
None[a]	5	6	?	?	42	47	0.8
None[b]	37	12	?	?	25	18	2.5
None, no light	<1	?	?	?	36	63	0.8
Acetophenone, benzophenone, 2-acetonaphthone	66	19.5	1.4	0.6	7.5	4.5	15–20

[a] No precautions taken to prevent air oxidation of the cyclopentadiene. [b] Cyclopentadiene treated with lithium aluminum hydride before use, all transfers done under vacuum.

TABLE V

PROTON NMR DATA FOR SOME 5,5,6-TRIHALOBICYCLO[2.2.1]HEPTENE-2 COMPOUNDS

		δ_{H_1}	δ_{H_4}	δ_{H_6}	δ_{H_2}, δ_{H_3}	δ_{H_7} (2 H)	$\Delta\delta_{H_6}$
20		3.03	3.48	4.20	6.32 (2 H)	1.95, 2.3	0.57
21		3.25	3.53	4.77	6.28 (2 H)	2.0 (2 H)	
5-Cl		2.96	2.96	3.80	6.2, 6.2	1.95, 2.15	0.44
6-Cl		3.10	3.10	4.24	6.2, 6.3	1.9 (2 H)	
5-F		2.9	2.9	4.33	6.2 (2 H)	2.0, 2.15	0.52
6-F		3.0	3.0	4.85	6.22 (2 H)	1.7, 1.8	

The photosensitized cycloaddition of 2-chloro-1,1-difluoroethylene to cyclopentadiene is similar to that of trifluoroethylene. Table IV shows that the main difference between the two cases is the much smaller fraction of **3** and **4** in the chlorodifluoroethylene adduct where these isomers together amount to only 2% of the product, as compared to 25.5% in the trifluoroethylene photoadducts. This difference is obviously appropriate to a biradical mechanism, where the high preference for forming an allylic radical from the diene and an α-chloroalkyl radical from the haloalkene produces a high regioselectivity in the reactant having a chlorine atom at one end. It is also noticeable that, between the two principal products, the less hindered stereoisomer is more highly favored where the disposition of a chlorine atom rather than a fluorine atom is involved (**1**-F/**2**-F 42:19.5, **1**-Cl/**2**-Cl 66:19.5).

Identification of Products.—The analyses and preparative separations were accomplished by vapor chromatography as described in the Experimental Section. The proton nmr spectra of 5,5,6-trihalonorbornenes form a consistent pattern, as shown in Table V where the chemical shifts of **5** and **6** are compared with those of the trichloronorbornenes.[7] The assignments are consistent with the generalization that an endo hydrogen is shielded relative to a similarly situated exo hydrogen, and that hydrogen is shielded by an eclipsing chlorine atom.[8–11] The nmr spectra of the hydrogenated compounds shown in Table VI further illustrate the effect of endo or exo configuration and show that the effect can be as large in norbornanes (*e.g.*, **9**-Cl and **10**-Cl) as in the corresponding norbornenes.

The availability of all the cycloadducts from photosensitized cycloaddition made possible the nmr observations summarized in Tables VII, VIII and IX. The ethylenic proton absorptions of the bicyclo[3.2.0]-heptenes examined here fell in the range δ 5.7–6.0

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(7) J. A. Berson, Z. Hamlet, and W. A. Mueller, *J. Amer. Chem. Soc.*, **84**, 297 (1962).

(8) P. M. Subramanian, M. T. Emerson, and N. A. LeBel, *J. Org. Chem.*, **30**, 2624 (1965).

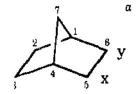
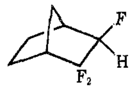
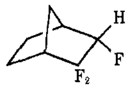
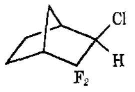
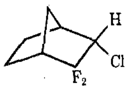
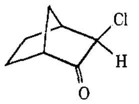
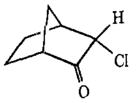
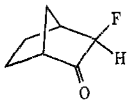
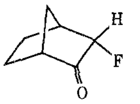
(9) W. D. Kumler, J. N. Shoolery, and F. V. Brutcher, Jr., *J. Amer. Chem. Soc.*, **80**, 2533 (1958).

(10) R. B. Fraser, *Can. J. Chem.*, **40**, 78 (1962).

(11) T. J. Flautt and W. F. Erman, *J. Amer. Chem. Soc.*, **85**, 3212 (1963).

Table VI

Proton Nmr Data from Some 2,2,3-Trihalonorbornanes and Related Compounds

	 [a]	δ_{H_1}	δ_{H_4}	δ_{H_6}	$\Delta\delta_{H_6}$	δ_{H_6} of dehydro compounds
7-F		2.1	2.4	4.28	0.27	4.33
8-F		2.5	2.5	4.55		4.85
7-Cl				3.80	0.31	3.80
8-Cl				4.11		4.24
9-Cl		2.65	2.65	3.75	0.54	3.75
10-Cl				4.29		4.28
9-F		2.6	2.6	4.17	0.48	
10-F		2.2	2.2	4.65		

[a] The numbering is made to correspond with that of the norbornenes to simplify comparisons to values in Table V.

ppm, while those of the norbornenes were at 6.2–6.3 ppm. The exo and endo assignments based on the hydrogen chemical shifts are confirmed by the ^{19}F chemical shifts, which also show fluorine more shielded when in the endo than in the exo position (Table X). The structural and configurational assignments based on the nmr spectra were made in a consistent manner by comparison with analogous compounds.[12] These assignments were confirmed by synthesis of several of the adducts or derivatives as well as of analogous compounds.

The trichloroethylene cycloadducts **16**, **17**, and **18** were prepared as shown in Scheme I. **15**-Cl was identical with the known main product of cycloaddition of monochloroketene to cyclopentadiene. The known endo configuration[13–16] of **15**-Cl establishes the exo configuration of the major and minor products, **22**-Cl and **23**-Cl, which yield a common hydrogenation product (**13**-Cl) whereas **15**-Cl yields a different one (**14**-Cl). The three unsaturated chloro ketones were converted by phosphorus pentachloride into the corresponding trichlorobicyclo[3.2.0]heptenes without loss of configuration.

Of the reactions used in approaching the bicyclo[3.2.0]heptene ring system, the addition of ketenes is more regio- and stereoselective than the addition of nitrosyl chloride. Compound **17**, accessible by both paths and almost the sole product by the ketene approach, is the isomer missing in the previous[3] photosensitized cycloaddition of trichloroethylene and cyclopentadiene. In a reexamination of such a cycloadduct mixture, a small peak was observed in the vapor chromatogram having the retention time of 17; it represented 0.3% of the mixture.

The configurations of the 2-chloro-1,1-difluoroethylene cycloadducts **1**-Cl, **2**-Cl, and **5**-Cl were independently established through their hydrogenation products **11**-Cl, **12**-Cl, and **7**-Cl which were prepared from the ketones **13**-Cl, **14**-Cl, and **9**-Cl, respectively, by reaction with sulfur tetrafluoride, the yield in the last case being 95% of a single product. The reaction of **13**-Cl, catalyzed with a few mole per cent of HF, and that of **14**-Cl, catalyzed by 30–40 mol % HF, gave 25% yields and neither the **11**-Cl nor the **12**-Cl was contaminated with the other.

An attempt to synthesize the trifluoroethylene cycloadducts **1**-F to **6**-F by way of the corresponding fluoro

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[12] B. M. Jacobson, Thesis, Harvard University, 1970.

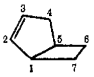
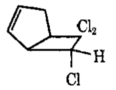
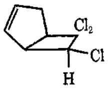
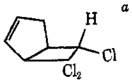
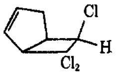
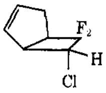
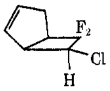
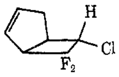
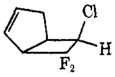
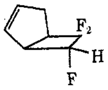
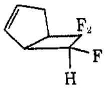
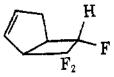
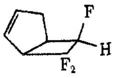
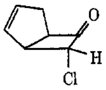
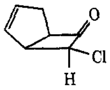
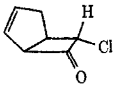
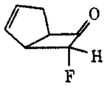
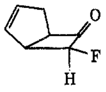
[13] W. T. Brady and E. F. Hoff, Jr., *J. Amer. Chem. Soc.*, **90**, 6256 (1968).

[14] W. T. Brady, E. F. Hoff, Jr., R. R. Roe, Jr., and F. H. Parry, III, *ibid.*, **91**, 5679 (1969).

[15] P. R. Brook, A. J. Duke, and J. C. R. Duke, *Chem. Commun.*, 574 (1970).

[16] P. R. Brook, J. M. Harrison, and A. J. Duke, *ibid.*, 589 (1970).

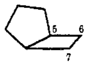
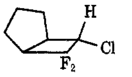
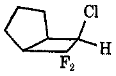
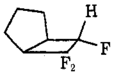
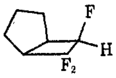
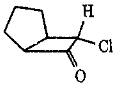
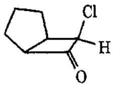
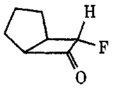
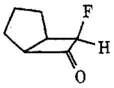
TABLE VII
PROTON NMR ABSORPTIONS FOR SOME HALOBICYCLO[3.2.0]HEPT-2-ENES

		δ_{H_1}	δ_{H_5}	$\delta_{H_1} - \delta_{H_5}$	δ_{H_6} or δ_{H_7}	$\Delta(\delta_{H_6}$ or $_{H_7})$
16	 [a]	3.34[b]	3.64	−0.30	4.28	0.73
17		3.81[b]	3.60	0.21	5.01	
18	 [a]	3.98	3.06[c]	0.92	4.30	0.69
19	 [a]	4.01	3.50[c]	0.51	4.99	
1-Cl		3.16	3.50	−0.34	4.00	0.65
2-Cl		3.55	3.24[d]	0.31	4.65	
3-Cl		3.8	2.7	1.1	4.02	0.65
4-Cl		3.80	3.15	0.65	4.67	
1-F		3.3	3.3	0.0	4.65	0.43
2-F		3.58	3.00	0.58	5.08	
3-F		3.68	2.75	0.93	4.65	0.34
4-F		3.63	2.90	0.73	4.99	
22-Cl		3.52	4.15	−0.63	4.32	0.93
15-Cl		3.92	3.90	0.02	5.25	
23-Cl		4.30	2.92	1.38	4.52	
22-F		3.54	3.96	−0.42	4.86	0.07
15-F		3.84	3.48	0.36	5.56	

[a] Reference 3. [b] Assigned by decoupling H-7. [c] Assigned by decoupling H-6. [d] Assigned by decoupling H-4.

TABLE VIII

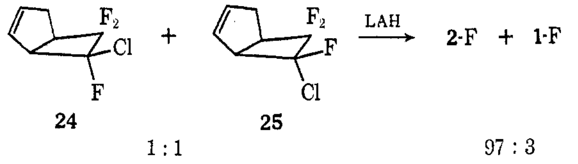
PROTON NMR ABSORPTIONS FOR SOME HALOKETO- AND TRIHALOBICYCLO[3.2.0]HEPTANES

		δ_{H_1}	δ_{H_5}	δ_{H_6}	$\Delta\delta_{H_6}$	δ_{H_6} of dehydro compounds
11-Cl		2.64	3.18	3.92	0.67	4.0, 4.2
12-Cl		2.22	2.90	4.59		4.65, 4.67
11-F		2.6 to	3.0	4.53	0.43	4.65, 4.65
12-F		2.1	2.9	4.96		4.99, 5.08
13-Cl		2.88	3.70	4.45	0.67	4.32, 4.52
14-Cl		3.28	3.72	5.12		5.25
13-F		2.8	3.5	4.98	0.44	4.86
14-F		3.3	3.3	5.42		5.56

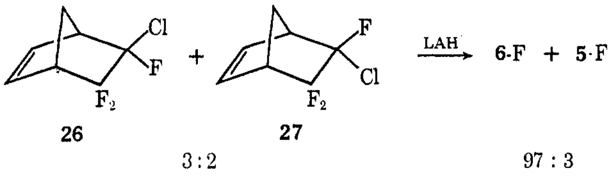
ketones was unsuccessful. Sulfur tetrafluoride converted *exo*-3-fluoro-2-norbornanone (**9**-F) into an almost equal mixture of the stereoisomeric dihydro products **7**-F and **8**-F, offering no check on the configurations of the single fluorine atoms. In the case of **14**-F, sulfur tetrafluoride did not yield either **11**-F or **12**-F, but instead an isomer containing a $-CF_2H$ group and a single ethylenic hydrogen atom, evidently resulting from opening of the four-membered ring.

Incidentally to the preparation of the fluoro ketone **15**-F, we observed that the cycloadduct of fluoroketene and cyclopentadiene contains not only the endo isomer, recognized by Brady and Hoff,[13] but actually 14% of the exo isomer **22**-F, which is enough more water soluble than the endo to be easily lost in water washing during work-up unless special precautions are taken. A comparison of the endo/exo ratios in the cycloadducts of fluoroketene (6.1), chloroketene (24), methylketene (99),[17] and *tert*-butylketene (>99)[17] extends by about a log unit the field of plottable points in the correlation[18] between Taft's E_S and the endo/exo ratio in cycloaddition of substituted ketenes. The new points maintain the Brady–Roe slope of 1.5 within the limited precision of the relationship. The $(2_s + 2_a)$ mechanism provides the only general "masochistic steric effect" of which we are aware—one in which the requirements of the transition state and product are so completely reversed that a product predominates in direct proportion to its steric strain.

To establish the orientation of the major and minor pairs of the (2 + 2) products of trifluoroethylene with butadiene,[1] advantage had been taken of the high regiospecificity in cycloaddition of trifluorovinyl chloride. The same was now done with the cyclopentadiene adducts; a mixture of **24** and **25** in a 1:1 ratio was



completely dechlorinated by lithium aluminum hydride to yield a 97:3 mixture of **2**-F and **1**-F. Exactly the same endo/exo ratio was seen in the trifluoronorbornenes resulting from the LAH dechlorination of a 3:2 mixture of **26** and **27** after 80 and 100% reaction.



The mechanism of the LAH dechlorination, in cases where SN2 displacement is not favored, is not known, but the predominant delivery of the hydrogen on the exo side is in accord with any of the possible two-step mechanisms proceeding through an ionic or radical intermediate. The assignment of the orientations **1** and **2** to the major 1,2 adducts of trifluoroethylene

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(17) L. A. Hull, unpublished work.

(18) W. T. Brady and R. Roe, Jr., *J. Amer. Chem. Soc.*, **93**, 1662 (1971).

Table IX

Coupling Constants in the Bicyclo[3.2.0]heptene-2 System as Determined by Double Irradiation

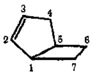
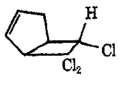
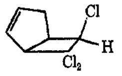
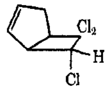
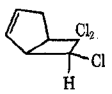
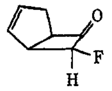
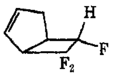
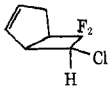
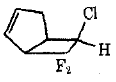
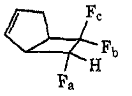
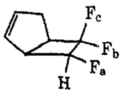
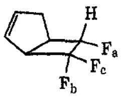
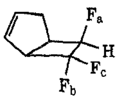
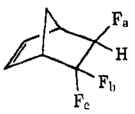
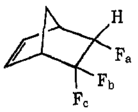
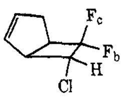
		$J_{1,7}$ or $J_{5,6}$, cps	$J_{5,7}$ or $J_{1,6}$, cps	$J_{4,5}$, cps
18		7	1	
19		8	3	
16		5	1	
17		8	<1	
15-F		8	3	
3-F		7	<1	
2-Cl				7
4-Cl				9

Table X

^{19}F Nmr Data for the Cyclopentadiene–Trifluoroethylene Adducts

		δ_{F_a}[a]	δ_{F_b}	δ_{F_c}	$J_{b,c}$, cps	J_{H,F_a}, cps
1-F		176	101	102	210	52
2-F		186	84	117	200	51
3-F		181	93	110	200	51
4-F		195	91	109	210	52
5-F		178	95	105	230	53
6-F		178	93	105	230	53
1-Cl			88	91	190	

[a] In parts per million upfield from $CFCl_3$ internal standard.

confirms the assignments made on the basis of nmr spectra.

Finally, **3-F** and **4-F** are assigned their configurations by hydrogenation, **1-F** and **3-F** both yielding the same product (**11-F**) while **2-F** and **4-F** yield **12-F**.

Discussion

The characteristics of typical thermal concerted cycloadditions (such as maleic anhydride and cyclopentadiene) and of typical thermal biradical cycloadditions (such as 1122 and butadienes) have been explored in detail and found to form two self-consistent patterns.

For (2 + 4) cycloaddition, both concerted and biradical mechanisms are equally "allowed." We first raised the question of possible biradical pathways for certain (2 + 4) cycloadditions when it was found that substitution of bulky groups in the 2 position of butadiene[19,20] made cyclohexenes prominent reaction products of 1122, which with butadiene gave 99% vinylcyclobutanes. A consistent explanation of this steric effect was that the 2 substituents forced a larger fraction of the dienes into the s-cis or the skew conformation, resulting in the kind of cis-allylic radical which was compatible with closure to a six-membered ring. It was found, however,[21] that the cis-fixed diene, 1,2-dimethylenecyclobutane, gave entirely (2 + 2) cycloaddition of 1122, and it was noted that two discernible differences between it and cyclopentadiene—C_1–C_4 distance and strain in the double bond of the (2 + 4) adduct—would operate similarly whether the mechanism of the cycloaddition were concerted or stepwise. Therefore other criteria of mechanism would be needed if any assignment to competing modes of (2 + 4) cycloaddition in such cases were to be made.

Our first attempt to resolve the cycloaddition of a borderline reagent into simultaneous competing pathways[22] was based on the stereochemistry of thermal addition of *cis*- and *trans*-1,2-dichloro-1,2-difluoroethylene ("1212") to cyclopentadiene. The (2 + 4) cycloadduct showed retained configuration with retention index[2,23] PQ > 10^4, while the (2 + 2) cycloadduct lost configuration to an extent normal (PQ = 9.5) for the stepwise mechanism. The ratio of rate constants for (2 + 4) and (2 + 2) addition was found to be 16 for *cis*- and 36 for *trans*-1212, and the rate constant ratio for the two mechanisms is presumably not far from this value.

For alkenes, such as trifluoroethylene, having no geometrical configuration to serve as an indicator of stepwise mechanism, a detailed comparison between thermal and photosensitized cycloaddition[1] to butadiene has indicated that the ratio k_{2+4}/k_{2+2} of 0.15 in thermal cycloaddition corresponds to $k_{\text{concerted}}/$

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[19] P. D. Bartlett, *Science*, **159**, 833 (1968).

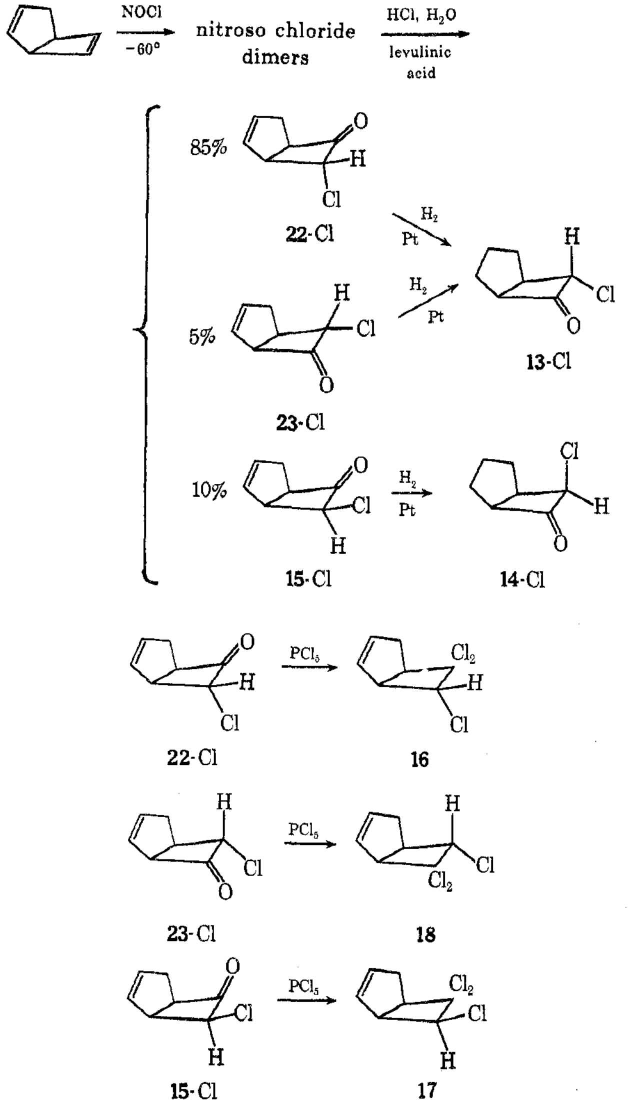
[20] P. D. Bartlett, G. E. H. Wallbillich, A. S. Wingrove, J. S. Swenton, L. K. Montgomery, and B. D. Kramer, *J. Amer. Chem. Soc.*, **90**, 2049 (1968).

[21] P. D. Bartlett, A. S. Wingrove, and R. Owyang, *ibid.*, **90**, 6067 (1968).

[22] R. Wheland and P. D. Bartlett, *ibid.*, **92**, 3822 (1970).

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

SCHEME I



k_{stepwise} of 0.12, reflecting a mechanism that is mostly by the biradical path. The present results reflect the large preference of cyclopentadiene for the concerted process. The (2 + 4)/(2 + 2) ratio of 110 observed in the thermal reaction of trifluoroethylene at 210° should probably be corrected by assuming that the undetected **3**-F and **4**-F were formed thermally in a proportion to (**1**-F and **2**-F) no greater than that (0.41) seen in the photosensitized reaction where all the (2 + 2) isomers are more abundant. This would make the ratio of (2 + 4)/(2 + 2) for trifluoroethylene greater than 78, and for 2-chloro-1,1-difluoroethylene about 195. To determine the ratio of concerted to stepwise mechanism we need to transfer from the numerator of this fraction to the denominator that part of the (2 + 4) adduct which arose from biradicals, as indicated by the photosensitized results. If N_C = amount of norbornenes in the thermal product from concerted reaction, N_R = amount of norbornenes in the thermal product from biradicals, and B = amount of bicyclo[3.2.0]heptanes in the thermal product, then for trifluoroethylene $(N_C + N_R)/B = (2 + 4)/(2 + 2) = 78$; $N_C + N_R = 78B$; $N_R/B = 13/87 = 0.15$; $N_R = 0.15B$; $N_C = 77.85B$; (concerted)/(stepwise) = $N_C/(N_R + B) = 77.85B/(0.15B + B) = 68$. Similarly for 2,2-difluoro-1-chloroethylene, (concerted)/(stepwise) = $N_C/(N_R + B) = (195 - 0.136)B/(0.136B + B) = 172$. These figures show that the 500-fold preference of cyclopentadiene for (2 + 4) rather than (2 + 2) cycloaddition, as compared to butadiene, is a matter of a strong predisposition to react by the concerted mechanism.

If we assume that the lack of a primary end to the conjugated system of cyclopentadiene leads to the same eightfold retardation for biradical formation with trifluoroethylene as with 1122, the concerted mechanism must be faster for cyclopentadiene by a factor of 566/8 or 71, corresponding to a $\Delta\Delta F^{\ddagger}$ of 4 kcal/mol. The ionization potential of cyclopentadiene is 0.10 V lower than that of butadiene,[24] which would account for a $\Delta\Delta F^{\ddagger}$ of 2.3 kcal in a reaction controlled by donor-acceptor interactions. The remaining 1.7 kcal could be provided as a $T\Delta\Delta S^{\ddagger}$ term, since to react concertedly butadiene must be brought into the s-cis conformation in which cyclopentadiene is permanently fixed. (Toward benzoquinone in benzene, the $\Delta S^{\ddagger}$ of reaction with cyclopentadiene is 5.9 eu more favorable than is that with butadiene.[25])

The results to date support the following generalizations. (1) The tendency to react *via* biradicals changes more rapidly with structure of the alkene than does the capacity for concerted Diels-Alder reaction.[19] (2) Geminal substitution on the double bond by fluorine or by a cyclopropane ring[26] increases the proneness to biradical formation. (3) Accommodation of an odd electron in a biradical is favored in the descending order: $-CCl_2 > -CHCl > -CHF > CF_2$. Regioselectivity is the greater, the farther apart the two ends of the alkene are in this series. (4) Relative to hydrogen or fluorine, most other substituents on a carbon-carbon double bond are favorable to the formation of a radical site, but unfavorable to initial bond formation at that position, in the biradical mechanism.[27] (5) Regioselectivity is the same in direction, and somewhat reduced in magnitude, when biradicals are formed in reaction of an excited triplet state of a diene compared to its ground state. (6) Despite incomplete correction for thermal effects, alkenes in photosensitized reaction with cyclopentadiene all yield ratios of k_{2+4}/k_{2+2} within the limits 0.15–0.78, even though the k_{2+4}/k_{2+2} ratios for thermal reaction vary in the same series from 5 to over 100. (7) The structural features predisposing alkenes and dienes to undergo cycloaddition thermally by concerted mechanisms are largely independent of those predisposing to biradical mechanisms. Nevertheless, the widely varying behavior of the borderline fluorinated alkenes in this regard is a predictable function of the structure of the diene.

Experimental Section

Thermal Reaction of Cyclopentadiene and Trifluoroethylene.—A 0.75-g sample of freshly cracked cyclopentadiene was placed

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[24] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Positive Ions," National Standard Reference Data System.

[25] A. Wassermann, "Diels-Alder Reactions," Elsevier, Amsterdam, 1965, p 52, Table 14.

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

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

in a heavy walled (2 mm) tube, and 2–2.5 g of trifluoroethylene was condensed into the tube, which was then degassed and sealed. The tube was heated in the appropriately thermostated water or oil bath or tube oven. Reaction times for complete consumption of the diene were several weeks at or below 30°, 1 week at 65°, 2 days at 120°, and 36 hr above the cracking temperature of the diene dimer.

After being cooled in liquid nitrogen and opened, the tube was transferred to a Dry Ice–acetone bath with immersion as complete as possible. *n*-Decane (100 mg) was washed into the tube with ether, and the contents of the tube were poured into a flask previously cooled in a Dry Ice–acetone bath. The flask was allowed to warm to room temperature with vigorous stirring. The residue left after the excess trifluoroethylene had been removed was distilled trap-to-trap and analyzed on column K (Table XI) with flame detector response factor of 1.7 for the adducts. Preparative separation was carried out using column E. The first material eluted from the column other than solvent was **5-F**, mp 74.5–75.5°, a volatile waxy material (exact mass for $C_7H_7F_3$: calcd, 148.04998; found, 148.04964.) Compound **6-F** follows **5-F**, mp 73–75°, also a waxy volatile solid (exact mass found, 148.04935).

TABLE XI

GAS-LIQUID PARTITION CHROMATOGRAPHY COLUMNS USED[a]

Index no.	Column[b]	Machine[c]
A	Apiezon J, 20 ft × $^1/_4$ in. 45/60 Chromosorb P	90P-3
B	Carbowax 20M, 24 ft × $^1/_4$ in. 60/80 acid-washed Chromosorb P	700
C	Tricresyl phosphate, 30 ft × $^1/_4$ in. 60/80 Chromosorb P	700
D	1,2,3-Tris(2-cyanoethoxy)propane, 25 ft × $^1/_4$ in. 60/80 Chromosorb P	700
E	Carbowax 20M, 20 ft × $^3/_8$ in. 60/80 Chromosorb W	90P-3
F	β,β'-Oxydipropionitrile, 25 ft × $^1/_4$ in. 45/60 Chromosorb P	90P-3
G	Carbowax 20M, 9 ft × $^1/_4$ in. 60/80 Chromosorb W	1520
H	10% tricresyl phosphate, 30 ft × $^1/_8$ in. 60/80 Chromosorb P	609, 7620A
J	10% 1,2,3-tris(2-cyanoethoxy)propane, 30 ft × $^1/_8$ in. 60/80 Chromosorb P	609, 7620A
K	11% Carbowax 20M, 30 ft × $^1/_8$ in. 60/80 Chromosorb P	609
L	10% β,β'-oxydipropionitrile, 30 ft × $^1/_8$ in. 45/60 Chromosorb P	609

[a] Flow rates: 110 ml/min for $^3/_8$ in. diameter columns; 75 ml/min for $^1/_4$ in. diameter columns; 20–25 ml/min for $^1/_8$ in. diameter columns. [b] 20% liquid phase unless noted otherwise. [c] Machines: F & M 700, T. C. detector, dual columns; F & M 609, flame detector, single column; F & M 7620A, flame detector, dual columns; Varian Aerograph 90P-3, T. C. detector, single column.

Precautions.—The glass tubing used for the thermal reaction was always annealed in an annealing oven before use (with a neck for the final seal already made) and the final seal annealed carefully. Tubes were not filled more than one-quarter full and tube diameters of more than 12 mm were avoided. A weak or over-full tube may explode violently upon heating.

Thermal Reaction of Cyclopentadiene and 2-Chloro-1,1-difluoroethylene.—The procedure, work-up, and analysis were the same ones used for the reaction of cyclopentadiene and trifluoroethylene. Compound **5-Cl**, *exo*-6-chloro-5,5-difluoronorbornene, a waxy material melting slightly below room temperature (exact mass for $C_7H_7F_2Cl$: calcd, 164.02035; found, 164.02071) was eluted from the column before the endo-chloro compound, **6-Cl**, a waxy solid, mp 34–36° (exact mass found, 164.0206). Both materials have retention times greater than that of cyclopentadiene dimer. The flame response factor is 1.7.

Photosensitized Reaction of Cyclopentadiene and Trifluoroethylene. Materials.—Acetophenone and biacetyl were distilled before use. Fluorene (Eastman White Label) was recrystallized before use from 95% ethanol. Benzophenone (Eastman White Label), acetone (Fisher reagent), and 2-acetonaphthone (Matheson Coleman and Bell) were all used as received. Triphenylene (Aldrich Chemical Co.) was recrystallized from CH_2Cl_2–pentane and phenanthrene was purified by heating with maleic anhydride in triglyme and recrystallization from 95% ethanol. Trifluoroethylene (Peninsular Chem-Research Co.) was used as received. Cyclopentadiene was freshly cracked or distilled before use, but in the blanks, additional purification was required. This consisted of placing the freshly cracked cyclopentadiene over a few grams of lithium aluminum hydride in a flask attached to a vacuum line. The flask was degassed and the mixture was stirred at room temperature for 2 hr. The cyclopentadiene was then distilled through the line into the previously prepared and degassed reaction tube which was then sealed *in vacuo*.

Irradiation.—This was performed in sealed heavy walled (2 or 3 mm) Pyrex tubes. The tube was charged with 0.5–2 g of cyclopentadiene, depending on its diameter (9 to 19 mm), a 3- to 15-fold excess of trifluoroethylene, and the sensitizer (1–15 mol % based on diene, with 2 or 3 ml of ethyl ether if more than 3 mol % of sensitizer was used, since trifluoroethylene is a very poor solvent and the sensitizer would fail to dissolve in most cases without added ether). The tube was given a final degassing and sealed under vacuum. Tubes were strapped to an immersion well placed in a water bath cooled to 3 ± 2° by a Lauda Ultra Kryomat TK-30 circulating methanol cooled to −10°. Irradiation was performed with a 450-W Hanovia medium pressure mercury lamp. Irradiation in analytical runs was from 10 to 100 hr. In preparative runs 72 hr of irradiation was used.

Analysis.—Following irradiation, the tubes were cooled in liquid nitrogen, opened, and transferred to Dry Ice and 100 mg of *n*-decane was washed into each tube. Each tube was immersed as deeply as possible in Dry Ice; the contents were then poured into a previously cooled flask. The excess trifluoroethylene was distilled off with vigorous stirring and the residue distilled trap-to-trap at 0.1 mm pressure. Glpc analysis of the distillate was carried out using column K at 90°. The order of elution of cross-adducts was **1-F**, **3-F**, **5-F**, **4-F**, **6-F**, and **2-F**. Retention times are 20, 23, 24, 27, 30, and 32 min, respectively.

Preparative Scale Reaction.—Following removal of the excess trifluoroethylene and trap-to-trap distillation, the distillate was injected 0.5 ml at a time on column A to yield a mixture of the six cross-adducts (retention time 20–30 min at 125°) free of the cyclopentadiene dimers (retention time approximately 2 hr, three spaced injections of distillate are made before clearing the column of dimers). The mixture of cross-adducts was then injected 30 μl at a time on column B at 90°. Collection at this stage yielded **1-F** and **2-F** in greater than 99% purity, and almost pure **6-F**. **5-F**, **3-F**, and **4-F** were not completely separated by one pass and a second pass of each of these materials, injected 10 μl at a time, was necessary. Nmr spectra of the separated adducts were taken in 50% $CFCl_3$ (both H and ^{19}F). Ir spectra were taken in CCl_4. Samples for mass spectra were collected by the method of Burson and Kenner[28] [exact masses for $C_7H_7F_3$: calcd, 148.04998; found, 148.04949 (for **1-F**), 148.04949 (for **2-F**), 148.05049 (for **3-F**)].

Photosensitized Reaction of Cyclopentadiene and 2-Chloro-1,1-difluoroethylene.—Materials and irradiation procedure were as for trifluoroethylene except that no added ethyl ether solvent was required.

Analysis.—The work-up used is the same used for the trifluoroethylene case. Column K at 110° or L at 90° may be used for glpc. The order of retention times is (for column K): **1-Cl**, 55 min; **3-Cl**, 61 min; **5-Cl**, 65 min; **6-Cl**, 77 min; **4-Cl**, 84 min; **2-Cl**, 98 min.

Preparative Scale Reaction.—Following the trap-to-trap distillation of the crude photoproducts, the distillate was injected 0.5 ml at a time on column A (retention time of cross-adduct mixture 40–55 min at 125°) yielding the six cross-adducts together freed from diene dimers. The adduct mixture was injected 50 μl at a time on column B at 110°. **5-Cl**, **6-Cl**, **1-Cl**, and **2-Cl** were collected essentially pure (99 +%). Fractions containing about 50% pure **3-Cl** contaminated with **1-Cl** and **5-Cl** and 50% pure **4-Cl** contaminated with **6-Cl** were reinjected to give 90% pure **3-Cl** and 99% pure **4-Cl**. Since the total yield

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[28] K. R. Burson and C. T. Kenner, *J. Chromatogr.*, **7**, 63 (1969).

of **3**-Cl at this point (200 hr of collecting time) was 19 mg, no further purification was attempted. The 10% impurity remaining is compound **5**-Cl.

Nmr spectra were taken in 50% CCl_4. Ir spectra were also in CCl_4. Samples for mass spectra were collected in capillary tubes by the method of Burson and Kenner[27] [exact masses for $C_7H_7F_2Cl$: calcd, 164.02035; found, 164.02038 (for **1**-C), 164.02055 (for **2**-Cl)].

Hydrogenation of Trifluoro- and 2-Chloro-1,1-difluoroethylene–Cyclopentadiene Adducts. Hydrogenation of *exo*-5,5,6-Trifluoronorbornene (5-F).—A 150-mg sample of **5**-F and 10 mg of PtO_2 in 500 μl of ethyl acetate were placed in a 5-ml flask with magnetic stirring bar, degassed with one freeze–thaw pumping cycle, and then stirred under hydrogen at atmospheric pressure until the calculated amount of hydrogen had been absorbed (approximately 30 ml). The mixture was then distilled trap-to-trap and injected 150 μl at a time on column B or G at 100°; 120 mg of *exo*-2,2,3-trifluoronorbornane was collected (80% yield).

Hydrogenation of the 11 other cross-adducts was done in the same manner, except that for **3**-Cl only 15 mg of adduct and 2 mg of PtO_2 were used yielding 10 mg of product while 8 mg of **4**-Cl and 2 mg of PtO_2 were used yielding 5 mg of hydrogenation product. In these two cases, the product was transferred from the collection trap in a minimum of CCl_4 to a 0.2-mm ir cell for the ir spectrum to be taken and then transferred, with a drop of tetramethylsilane added, to an nmr probe.

Reaction of Nitrosyl Chloride and Bicyclo[3.2.0]heptadiene-2,6. Preparation of Ketones 15-Cl, 22-Cl, and 23-Cl.—A 7.5-g sample of bicyclo[3.2.0]heptadiene-2,6[29] dissolved in 75 ml of chloroform was cooled in a Dry Ice–acetone bath. Nitrosyl chloride (Matheson) was bubbled in with rapid stirring until the deep blue-green solution turned a definite yellow-brown and remained so colored when the NOCl addition was stopped. The mixture, containing a thick semicrystalline precipitate, was allowed to warm to room temperature. The chloroform was removed on a rotary evaporator, and this residue was stirred with 200 g of levulinic acid (Aldrich Chemical Co., freshly distilled) and 17 ml of 2 *N* hydrochloric acid at 70° overnight. The cooled mixture was poured into 600 ml of water and the aqueous layer extracted ten times with 30-ml portions of ethyl ether. The original organic layer and combined ether fractions were washed once with 200 ml water, twice with 200 ml of saturated $NaHCO_3$ solution, and once with saturated NaCl solution, and dried over anhydrous $MgSO_4$; the ether was evaporated. The crude product was distilled through a 6-in. column of glass helices. The fraction, bp 80–90° (8 mm), 5.5 g (48% yield), consisted of nearly pure chloro ketones **15**-Cl, **22**-Cl, and **23**-Cl and a few per cent of ethyl levulinate. All are separated on column E at 150°. The first ketone eluted from the column is **22**-Cl, *exo*-7-chlorobicyclo[3.2.0]hepta-2-en-6-one. **23**-Cl follows, then ethyl levulinate and then **15**-Cl. The proportions of the three ketones were 17:1:2.

Preparation of *exo*-6,6,7-Trichlorobicyclo[3.2.0]heptene-2 (16).—A 1.0-g sample of **22**-Cl was placed in 4.0 ml of PCl_3, and 3 g of PCl_5 was added. The mixture was stirred at room temperature for 8 days. It was poured on ice, a few milliliters of CH_2Cl_2 were added, and the solution was extracted with $KHCO_3$ solution, dried, and distilled trap-to-trap. Analytical glpc on column K indicates the presence of **16** and the absence of **17**, **18**, and **19**. Preparative glpc on column E at 160° yielded 0.1 g of pure **16** having nmr and ir spectra matching those of material isolated from the photosensitized reaction of cyclopentadiene and trichloroethylene.[3]

Preparation of *endo*-6,6,7-Trichlorobicyclo[3.2.0]heptene-2 (17).—A 0.6-g sample of *endo*-7-chlorobicyclo[3.2.0]hept-2-en-6-one (**15**-Cl) was placed in 3 ml of PCl_3 containing 2 g of PCl_5 and stirred at room temperature for 2 weeks. It was poured onto ice and a few milliliters of CH_2Cl_2 were added. The organic layer was extracted with aqueous $KHCO_3$, washed once with water and once with saturated NaCl, dried over anhydrous $MgSO_4$, and filtered, and the CH_2Cl_2 was evaporated. The residue was distilled trap-to-trap. Analytical glpc indicated the absence of **16**, **18**, and **19**. The major peak occurred with the retention time assigned to the previously unisolated **17** from the photosensitized reaction of cyclopentadiene and trichloroethylene. The photoreaction was repeated and preparative glpc using column E at 160° (two passes) allowed isolation of a few milligrams of **17**. Nmr and ir spectra of the adduct collected in this way matched those at the product from the reaction with PCl_5.

Preparation of *exo*-6,7,7-Trichlorobicyclo[3.2.0]heptene-2 (18).—A 0.1-g sample of *exo*-6-chlorobicyclo[3.2.0]hept-2-en-7-one (**23**-Cl) was placed in 0.4 ml of PCl_3 containing 300 mg of PCl_5 and stirred at room temperature for 8 days. The product was worked up as in the case of **17**. Analytical glpc on column K indicated a low yield of **18** and the absence of **16**, **17**, and **19**. Preparative separation on column G at 150° afforded 10 mg of **18**, with nmr and ir matching authentic samples obtained from the cyclopentadiene–trichloroethylene photoreaction.

Hydrogenation of 22-Cl and 23-Cl. Preparation of *exo*-7-Chlorobicyclo[3.2.0]heptanone-6 (13-Cl).—A 1-g sample of **22**-Cl (or 100 mg of **23**-Cl) with 5 mg of PtO_2 per 100 mg was hydrogenated at atmospheric pressure in ethyl acetate as solvent. Following absorption of 1 equiv of H_2, the mixture was filtered and distilled to yield 0.9 g (85 mg from **23**-Cl) of **13**-Cl.

Preparation of *exo*-3-Chloro-2,2-difluoronorbornane (7-Cl).—A 2.5-g sample of *exo*-3-chloronorcamphor[30] in 30 ml of CH_2Cl_2 and 0.35 g of water was cooled in a stainless steel pressure vessel to −70°. SF_4 (30 g, Matheson) was condensed into the vessel through Teflon tubing; the vessel was sealed and shaken overnight at 70°. After venting (through aqueous KOH), the solution was washed with aqueous $KHCO_3$, filtered, dried, and distilled trap-to-trap to give 2.6 g (95%) of *exo*-3-chloro-2,2-difluoronorbornane (**7**-Cl) after removal of the CH_2Cl_2.

Hydrogenation of 100 mg of **5**-Cl (PtO_2, ethyl acetate) yielded the same material. Hydrogenation of the endo adduct **6**-Cl (PtO_2, ethyl acetate) indicated that no detectable (on column K as well as by nmr) endo compound was produced in the reaction with SF_4.

Preparation of *exo*-7-Chloro-6,6-difluorobicyclo[3.2.0]heptane (11-Cl).—The reaction vessel used was a 20-cm length of ¹/₄ in. o.d. stainless steel tubing capped at each end by Swagelok fittings, union and plug, all 316-stainless steel. The internal volume of the vessel is approximately 7 ml.

A 200-mg portion of *exo*-7-chlorobicyclo[3.2.0]heptanone-6 (**13**-Cl) in 1 ml of CH_2Cl_2 was placed in the vessel. The volume of water appropriate to yield the desired amount of HF upon reaction with SF_4 was added, and the vessel was cooled in Dry Ice. Through Teflon tubing, 1 ml of SF_4 was condensed into the vessel (transferred from a calibrated polyethylene tube) and the vessel was sealed. It was placed in a water bath held at 39 ± 2° for 48 hr. It was inverted to mix the contents several times a day during this period. Upon removal from the bath, the vessel was cooled in Dry Ice and opened, 50 mg of *n*-decane was added as an internal standard, and the vessel was allowed to warm to room temperature, with all effluent gases being passed through a KOH solution. The remaining contents of the vessel were washed out with more CH_2Cl_2 into a dilute K_2CO_3 solution, washed twice with water, dried, and distilled trap-to-trap. Analysis was done on column K at 110°. There were several products besides the desired materal **11**-Cl but no endo chloride **12**-Cl was present. The yields ran up to 26% with 20 mol % HF catalyst. Preparative separation on column G yielded 20 mg of **11**-Cl with ir and nmr matching those produced by the product of hydrogenation of adducts **1**-Cl and **3**-Cl (PtO_2, ethyl acetate).

Preparation of *endo*-7-Chloro-6,6-difluorobicyclo[3.2.0]heptane (12-Cl).—A 200-mg sample of *endo*-7-chlorobicyclo[3.2.0]-heptanone-6 (**14**-Cl) in 1 ml of CH_2Cl_2 was placed in the reaction vessel previously described, and the vessel was cooled in Dry Ice. SF_4 (1 ml) was condensed into the vessel after addition of the desired amount of water, and the vessel was sealed. It was placed in a water bath at 35 ± 2° for 48 hr with occasional inversion to mix the contents. Upon removal from the bath, the vessel was cooled in Dry Ice, opened, and allowed to warm to room temperature with all effluent gases being passed through a KOH solution. *n*-Decane (50 mg) was added; the contents of the vessel were washed into dilute K_2CO_3 solution with a few milliliters of CH_2Cl_2, washed with water twice, dried, filtered, and distilled. Analysis on column K indicated a maximum yield of **12**-Cl with 40 mol % of HF present, and with no exo compound, **11**-Cl, detectable. The highest yield attained was 13%. Separation using column G at 100° yielded enough material for ir and nmr spectra, which were found to match those of the hydrogenation product of **2**-Cl as well as of **4**-Cl.

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(29) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961).

(30) J. Meinwald, Y. C. Meinwald, and T. N. Baker, *J. Amer. Chem. Soc.*, **86**, 4074 (1964).

Reaction of Monochloroketene with Cyclopentadiene.—Freshly distilled chloroacetyl chloride (10 g) and 100 ml of ethyl ether (dried over sodium wire) were placed in a 500-ml three-neck flask. Freshly cracked cyclopentadiene (100 ml) was added, and the flask was cooled with Dry Ice–acetone. An 8.5-g sample (slightly less than the equivalent amount needed to react quantitatively with the acid chloride) of freshly distilled triethylamine was dripped in slowly with vigorous stirring. The flask was allowed to warm to room temperature over several hours while stirring continued. A stream of dry nitrogen was passed over the solution throughout the reaction. After stirring 1 day at room temperature, the mixture was poured into 100 ml of water; the organic layer was washed once with dilute $KHCO_3$, once with saturated NaCl solution, and dried over anhydrous $MgSO_4$ and the ether evaporated. Distillation affords 6 g of material boiling at 94–96° (8 mm). Glpc on column G at 140° indicates that the product is 96% *endo*-7-chlorobicyclo[3.2.0]-hept-2-en-6-one (**15**-Cl) and 4% its exo epimer **22**-Cl. Separation using column E at 150° yields pure compounds whose spectra (ir, nmr) match those of the compounds prepared *via* the reaction of NOCl and bicyclo[3.2.0]heptadiene-2,6.

Reaction of Monofluoroketene and Cyclopentadiene.—A 1.0-g sample of fluoroacetyl chloride[31] in 10 ml of sodium-dried ethyl ether, 5 g of freshly cracked cyclopentadiene, and 100 mg of decane was cooled under a dry nitrogen atmosphere to −78°. Freshly distilled triethylamine (1 g) was added dropwise over a 5-min period with vigorous stirring. The flask was allowed to warm to 0° and stirred at this temperature for 6 hr. A 1-ml sample was withdrawn and quenched in water (1 ml); the organic phase was checked, with no further purification, by glpc on column K. A ratio of 14:86 was observed for the two ketones produced, and the size of the peaks relative to the decane standard was noted. The flask with the remaining reactants was allowed to warm to room temperature and stirring continued for 2 days. The contents were then poured into 5 ml of water and shaken, the organic phase was separated and dried over anhydrous $MgSO_4$, and the ether was removed. Glpc on column K at the same temperature used before, 140°, indicated that the product ratio had remained constant at 14:86 and that the earlier sample had been withdrawn at approximately 1% of complete reaction. If the volume of water used in the quench is increased or an additional water wash is used, the ratio of the two ketones changes markedly, with the minor component decreasing relative to the major. Isolation of the ketones free of cyclopentadiene dimer may be accomplished by chromatography on Florisil: elution with 95% petroleum ether–5% ethyl ether until cyclopentadiene dimer is completely eluted, then changing to 30% petroleum ether–70% ethyl ether to elute the ketone mixture. Preparative glpc is accomplished on column E at 150°. The first (the minor) ketone from the column is *exo*-7-fluorobicyclo-[3.2.0]hept-2-en-6-one, **22**-F (exact mass for C_7H_7OF: calcd, 126.04809; found, 126.04776). The second ketone is the endo epimer found by Brady and Hoff.[13] Identical results are achieved using fluoroacetyl bromide[32] in place of the chloride. If triethylamine is replaced with tributylamine, no precipitate is formed in the reaction and the yield of cross-adduct is very low. However, if the solvent is changed to tetrahydrofuran and 2 g of fresh cyclopentadiene is added to the refluxing reaction mixture every 12 hr for 2 days, a 70% yield of ketones in a 12:88 ratio is isolated. If the reaction using triethylamine is filtered before warming above 0° and the solid residue treated with cyclopentadiene in ether, the yield of ketones from the filtrate is found to be 1% or less—while the yield from the residue is 50–60%, indicating that the precipitate is not triethylamine hydrochloride, but a precursor to the ketene. Replacing triethylamine with ethyldiisopropylamine, which is nearly immune to alkylation[33] resulted in no significant difference in the rate of the reaction. A precipitate also formed immediately in this case, indicating that the intermediate may be an enolate rather than an acylammonium ion.[34]

Preparation of *exo*- and *endo*-3-Fluoronorcamphor (9-F and 10-F).—A 4.5-g sample of norbornene in 100 ml of $CHCl_3$ which had been freed of ethanol by elution through an alumina column was cooled to −60°. Approximately 3 g (2.2 ml) of nitrosyl fluoride (Ozark-Mahoning Co.) previously measured into a polyethylene tube was transferred into the cold solution with vigorous stirring over a 10-min period. (All vessels or tubing coming into contact with the FNO should be of Teflon or polyethylene since glass will be etched.) The reaction vessel was then allowed to warm to room temperature, the chloroform evaporated away, and the residue treated with 60 g of levulinic acid and 7 ml of 2 *N* HCl with stirring for several days. The mixture was poured into 300 ml of water and extracted 15 times with 25-ml portions of ether; the ether extracts were washed once with water, once with $NaHCO_3$ solution, and dried. The ether was then removed on a rotary evaporator. The residue was distilled and the distillate injected 150 μl at a time on column E at 150°. The major product (600 mg) was *exo*-3-fluoronorcamphor (**9**-F) followed by ethyl levulinate and then (60 mg) impure *endo*-3-fluoronorcamphor (**10**-F) (exac mass for **9**-F: calcd 128.0637; found, 128.0628).

Preparation of *endo*-6,6,7-Trifluorobicyclo[3.2.0]hept-2-ene (2-F). Reduction of the Chlorotrifluoroethylene–Cyclopentadiene Adducts.—To 0.31 g (32 mequiv) of lithium aluminum hydride in 10 ml of freshly purified tetrahydrofuran (distilled from lithium aluminum hydride) was added 1.2 g (6.2 mequiv) of a 1:1 mixture of *endo*- and *exo*-7-chloro-6,6,7-trifluorobicyclo-[3.2.0]heptene-2 (**24** and **25**), and the mixture was refluxed at least 15 hr. The excess hydride was then destroyed by addition of 5 ml of ethyl acetate followed by dilute H_2SO_4. The organic phase was washed with water and dried over anhydrous $MgSO_4$. It was then distilled and injected 100 μl at a time on column B at 90°. The collected yield of **2**-F was 35%. If the reaction was quenched after 6 hr of reflux and 100 mg of decane added as internal standard, the reaction was found to be 65% complete with a 3:1 ratio of **24**/**25** and a 60% yield based on reacted material. In neither case does the *exo*-trifluoro compound **1**-F appear in more than 4% of the yield of the endo compound **2**-F.

Preparation of *endo*-5,5,6-Trifluorobicyclo[2.2.1]hept-2-ene (6-F).—To 0.3 g of lithium aluminum hydride in 10 ml of freshly purified tetrahydrofuran was added 1.2 g of a 3:2 mixture of *exo*- and *endo*-6-chloro-5,5,6-trifluorobicyclo[2.2.1]heptene-2 (**27** and **26**), and the mixture was refluxed at least 15 hr. The excess hydride was then destroyed by addition of 5 ml of ethyl acetate followed by dilute H_2SO_4. It was then dried over $MgSO_4$ and distilled. The distillate was injected 100 μl at a time on column B at 90°. The collected yield of **6**-F was 40%. Quenching of the reaction after 6 hr and addition of decane standard indicated 80% of the reaction was complete at that time with a 1:1 ratio of recovered starting materials and a 40% yield of products based on consumed material. In both the 6- and 16-hr reactions, the exo adduct **5**-F produced does not exceed 3% of the endo (**6**-F).

Registry No.—**1**-Cl, 37579-89-8; **1**-F, 37579-90-1; **2**-Cl, 37579-91-2; **2**-F, 37579-92-3; **3**-Cl, 37579-93-4; **3**-F, 37579-94-5; **4**-Cl, 37579-95-6; **4**-F, 37579-96-7; **5**-Cl, 37579-97-8; **5**-F, 37579-98-9; **6**-Cl, 37579-99-0; **6**-F, 37580-00-0; **7**-Cl, 37580-01-1; **7**-F, 37580-02-2; **8**-Cl, 37580-04-4; **8**-F, 37580-03-3; **9**-Cl, 10464-71-8; **9**-F, 37580-06-6; **10**-Cl, 30860-22-1; **10**-F, 37580-07-7; **11**-Cl, 37580-08-8; **11**-F, 37580-09-9; **12**-Cl, 37580-10-2; **12**-F, 37580-11-3; **13**-Cl, 37580-12-4; **13**-F, 37580-13-5; **14**-Cl, 37580-14-6; **14**-F, 37580-15-7; **15**-Cl, 25169-61-3; **15**-F, 25975-83-1; **16**, 37580-18-0; **17**, 37580-19-1; **18**, 37580-20-4; **19**, 37580-21-5; **20**, 37580-22-6; **21**, 37580-23-7; **22**-Cl, 37573-87-8; **22**-F, 37573-88-9; **23**-Cl, 37573-89-0; **24**, 37573-83-4; **25**, 37573-84-5; **26**, 37573-85-6; **27**, 37573-86-7; cyclopentadiene, 542-92-7; trifluoroethylene, 359-11-5; 2-chloro-1,1-difluoroethylene, 359-10-4; monochloroketene, 29804-89-5; monofluoroketene, 37580-39-5; norbornene, 498-66-8.

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[31] W. E. Truce, *J. Amer. Chem. Soc.*, **70**, 2828 (1948).

[32] M. M. E. Gryszkiewicz-Trochimowski, A. Sporzynski, and J. Wnuk, *Recl. Trav. Chim. Pays-Bas*, **66**, 423 (1947).

[33] S. Hünig and M. Kiessel, *Chem. Ber.*, **91**, 380 (1958).

[34] B. M. Jacobson, manuscript in preparation.