tograph (Aerograph, 5-ft 20% Carbowax 20M on a 35–80-mesh Chrom P column). The benzene fraction was collected (~15 mg) and was found to contain 73% C_6H_5D by mass spectrometry.

Isolation of Hydrazobenzene and Diphenyl. Acetonitrile (5 ml) was added to the yellow residue from a (0.2 *M*) phenyldiazene decomposition reaction after distillation to dryness. Thin layer chromatography showed four spots after developing with $CHCl_3$–pentane, 23:19 v/v. The main component (R_f 0.86) was shown to be hydrazobenzene by uv spectrum and formation of benzidine on treatment with 0.1% $HClO_4$ in CH_3CN.

Thick layer chromatography of the solution of the yellow residue gave nine distinct zones after development with $CHCl_3$–pentane, 25:75 v/v. The component with the greatest R_f value (0.63) was colorless and was shown to be diphenyl by its uv spectrum.

Isolation of Azobenzene. The solution from a phenyldiazene decomposition (0.0135*M*) was evaporated to dryness. The residue (in *n*-pentane) was chromatographed on an alumina (acid, Woelm) column (3 mm diameter, 3 cm long). Elution with *n*-pentane saturated with acetonitrile (2 ml) yielded a solution of azobenzene (by uv spectrum).

Reaction with Hydroxide Ion. Distilled phenyldiazene solution in acetonitrile (10.4 ml, $(1.97 \pm 0.08) \times 10^{-4}$ *M*) was mixed with degassed phosphate buffer (10 ml, pH 7.1, 0.05 *M*) introduced through a breakseal. A spectrum indicated (a) little change in the concentration of **3** and (b) only a trace of benzene. Sodium hydroxide solution (2.5 ml, 1 *M*) was introduced through a second breakseal. Sodium phosphate crystallized as a white solid. A spectrum showed that all of the phenyldiazene had reacted. Benzene was extracted with *n*-pentane (5 ml, two times) after opening to air and adding water (6 ml). The extract was distilled and analyzed by uv spectroscopy. After correcting for incomplete recovery (measured with controls), the yield of benzene was found to be 79 ± 8%.

Reaction with Perchloric Acid. Six milliliters of phenyldiazene solution (1.4×10^{-4} *M*) was mixed with 1.5 µl of degassed 70% aqueous perchloric acid (11.8 *N*). Changes in the spectrum of the reaction solution were followed (Figure 7).

Reaction with Benzenesulfonyl Chloride and Methyl Chloroformate. Phenyldiazene solution (1.4×10^{-4} *M*, 4.6 ml) was mixed with 0.35 ml of benzenesulfonyl chloride in acetonitrile (1.83×10^{-3} *M*). The reaction was followed by spectroscopic means. Degassed triethylamine solution in acetonitrile (5×10^{-2} *M*, 0.5 ml) was introduced after 24 hr.

Phenyldiazene solution (1.4×10^{-4} *M*, 4.2 ml) was mixed with 0.1 ml of degassed methyl chloroformate solution in acetonitrile (0.59 *M*). After five spectra of the reaction solution had been taken, 5 µl of degassed triethylamine (3.6×10^{-2} mmole) was introduced (1 hr after mixing). Other than the normal bimolecular disappearance of **3**, no reaction was observed in either case.

Reaction with Azobenzene. Phenyldiazene solution (1.7×10^{-4} *M*, 4.4 ml) was mixed with 0.25 ml of azobenzene solution in acetonitrile (1.34×10^{-3} *M*). The reaction was followed for 24 hr. The change in the concentration of **3** was that expected for bimolecular decomposition.

Acknowledgment. The authors are grateful to Dr. Melvin B. Robin, Bell Telephone Laboratories, for some very valuable discussion.

Diels–Alder Reactions of Tetrahalocyclopropenes[1a]

David C. F. Law[1b] and Stephen W. Tobey

Contribution from The Dow Chemical Company, Eastern Research Laboratory, Wayland, Massachusetts 01778. *Received November 20, 1967*

Abstract: Tetrahalocyclopropenes undergo facile 1,4 addition to 1,3-dienes and 2,6 addition to bicyclo[2.2.1]heptadiene. Certain of the highly strained adducts undergo rearrangement involving stereospecific ionization of labile halide. The relative rate-enhancing effect of halogen substituents in the 3 position on cyclopropene reactivity toward furan is Br > Cl > F. Infrared and H^1 and F^{19} nmr data are reported on all new compounds.

Wiberg and Bartley[2a] have described the high velocity and *endo* stereospecificity of the Diels–Alder reaction between cyclopropene and cyclopentadiene. Battiste[2b] and Closs, *et al.*,[2c] have investigated the reactions of alkyl- and aryl-substituted cyclopropenes with cyclic and open-chain 1,3-dienes and have shown that open-chain dienes react sluggishly, that cyclopropenes monosubstituted in the methylene position give *endo-syn* hydrogen adducts exclusively, and that 3,3-disubstituted cyclopropenes fail totally to form Diels–Alder adducts with *any* diene.[2d] These results have until quite recently[2e] been plausibly ascribed to a strong but unexplained preference for cyclopropene *endo* adduction, along with extreme sensitivity of the *transition state* to the *steric* size of the cyclopropene 3 substituent which must lie *syn* to the diene.[2d]

That such "steric" effects on the transition state *do not* by themselves adequately explain the success or failure of the cyclopropene Diels–Alder reaction is demonstrated by the work reported herein in which we find that *all* tetrahalocyclopropenes[3] undergo facile 1,4 addition to cyclopentadiene, furan, and 1,3-butadiene in spite of the obvious large size of the halogen substituents. Furthermore, competition experiments with furan show clearly that although tetrahalocyclopropenes are less reactive than cyclopropene, tetra*bromo*cyclopropene reacts more readily than tetra*chloro*cyclopropene, and that both these cyclopropenes are more reactive than their counterparts having 3,3-difluoro substituents! Thus, the observed relative rate enhancing effect of halogen substituents in the 3 position on cyclopropene reactivity toward furan is Br > Cl > F, an order directly oppositive to that predicted on steric grounds.

In addition to affecting the rates of Diels–Alder adduct formation, the halogen substituents permit

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(1) (a) Presented at the Symposium International sur la Chimie des Petit Cycles et ses Applications, Louvain, Belgium, Sept 12–15, 1967. (b) Eastern Research Laboratory postdoctoral fellow, 1966–1967.

(2) (a) K. B. Wiberg and W. J. Bartley, *J. Am. Chem. Soc.*, **82**, 6375 (1960); (b) M. A. Battiste, *Tetrahedron Letters*, 3795 (1964); (c) G. L. Closs, L. E. Closs, and W. A. Böll, *J. Am. Chem. Soc.*, **85**, 3796 (1963); (d) G. L. Closs in "Advances in Alicyclic Chemistry," Vol. I, H. Hart and G. J. Karabatsos, Ed., Academic Press Inc., New York, N. Y., 1966, Chapter 2, particularly pp 78–80; (e) W. C. Herndon and L. H. Hall, *Tetrahedron Letters*, 3095 (1967).

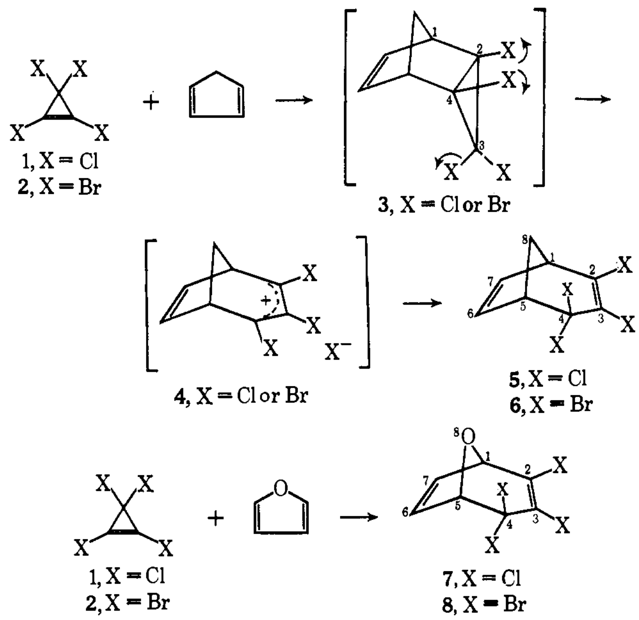
(3) (a) S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **88**, 2481 (1966); (b) D. C. F. Law, Ph.D. Thesis, University of Wisconsin, 1967, and Abstracts of Papers, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, Paper S52.

certain of the highly strained tricyclic cyclopropyl adducts to undergo skeletal rearrangement involving stereospecific ionization of the labile halide. These reactions presumably involve concerted ionization and ring opening, since their permissibility and course are unerringly predicted by the applicable Woodward–Hoffmann electrocyclic reaction rules.[4]

Finally, the presence of allylic halogens in the rearranged products provides ready access to a number of bicyclic β-diketones, whose keto–enol equilibria are described.

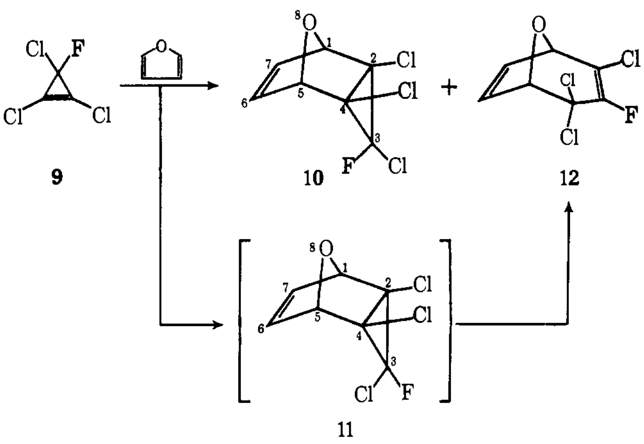
1,4 Addition with Subsequent Ring-Opening Rearrangement. Tetrachlorocyclopropene (**1**) and tetrabromocyclopropene react readily with excess cyclopentadiene at room temperature to give the bicyclic adducts **5** and **6**, respectively, in nearly quantitative yield. This process is conceived as involving an intermediate, the unstable tricyclic Diels–Alder adduct **3**, which spontaneously rearranges *via* the ion **4** to form the bicyclic allylic products **5** and **6**. Compounds **1** and **2** likewise react with furan at 80° to give the bicyclic products **7** and **8**, respectively, in good yield (Chart I).

Chart I



According to theoretical considerations[4] concerning electrocyclic transformations, rearrangement of **3** should involve disrotatory (outward) rotation of the halogen substituents at C_2 and C_4, accompanied by stereospecific ionization of the halogen at C_3 which is *syn* to the double bond. The reaction products obtained when 1,2,3-trichloro-3-fluorocyclopropene (**9**) is treated with furan clearly illustrate the validity of these predictions. Diels–Alder addition of **9** to furan can conceivably lead to two adducts, **10** and **11**, differing only in the configurations at C_3 (Chart II).

Chart II

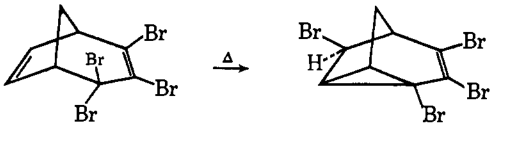


Concerted ring-opening isomerization of **10** requires ionization of the fluorine. This process is energetically unfavorable due to the strength of the C–F bond. On the other hand, analogous rearrangement of **11** should involve ionization of the *chlorine* at C_3, a process so facile that compounds like **3** rearrange as soon as they form. On this basis we would expect **10** to be stable and that **11** would rearrange spontaneously to the bicyclic structure **12**. Indeed, these predictions are borne out by our experimental results. Reaction of **9** with furan at 80° leads to a mixture of the tricyclic compound **10** and the rearranged bicyclic product **12** in the ratio 1.5:1.[5]

The structures of the bicyclic rearranged adducts **5**, **6**, **7**, **8**, and **12** are clearly indicated by their nmr spectra, as summarized in Table I. These unsymmetrical compounds all show two nonequivalent vinylic protons and two nonequivalent bridgehead protons.

The ir spectra of the structurally related bicyclic compounds **5**, **6**, **7**, and **8** are similar in many aspects, as shown in Table II. Besides the C–H stretching bands in the 3000-cm^{-1} region and a multitude of strong to medium bands between 1450 and 550 cm^{-1}, only one C=C stretching band is observed. This band is of strong intensity and lies between 1600 and 1570 cm^{-1}. The band is apparently due to the halogen-substituted C_2=C_3 bond since it shifts from 1600 cm^{-1} in the chlorinated compounds **5** and **7** to 1570 cm^{-1} in the brominated compounds **6** and **8**. It is interesting to note that vibration of the C_6=C_7 bond in these compounds is infrared inactive, although bicyclo[3.2.1]-octadiene itself shows two bands at 1625 and 1587 cm^{-1}.[6]

Further Reaction Products Obtained from the Bicyclic Compounds. The chlorinated bicyclic compound **5** is unaffected by heating to 180° for 15 min. However the bromo analog **6** undergoes quantitative rearrangement to the tricyclic isomer **13** when heated to 80° in CCl_4. Moore, Moser, and LaPrade[6] have reported the analogous conversion of the mixture **14**



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[4] (a) C. H. DePuy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *J. Am. Chem. Soc.*, **87**, 4006 (1965); (b) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965); (c) S. J. Cristol, R. M. Sequeira, and C. H. DePuy, *ibid.*, **87**, 4007 (1965).

[5] Ghosez, *et al.*, and Jefford, *et al.*, have described in detail the ring-opening rearrangements of cyclopropyl halides in *exo*-tricyclo[3.2.1.0^{2,4}]-octane systems. See (a) L. Ghosez, P. Laroche, and S. Slinckx, *Tetrahedron Letters*, 2767 (1967); (b) L. Ghosez, G. Slinckx, M. Glineur, P. Hoet, and P. Laroche, *ibid.*, 2773 (1967); (c) C. W. Jefford and R. T. Medary, *Tetrahedron*, **23**, 4123 (1967); and (d) C. W. Jefford, S. Mahajan, J. Waslyn, and B. Waegell, *J. Am. Chem. Soc.*, **87**, 2183 (1965).

[6] W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, **28**, 2200 (1963).

Table I. Nmr Data on Tetrahalocyclopropene Addition Products and Derivatives[a]

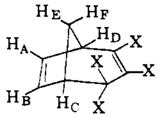
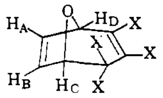
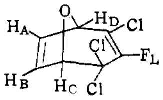
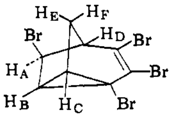
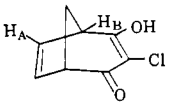
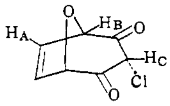
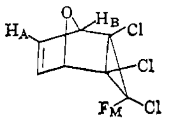
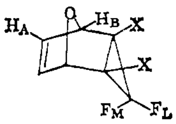
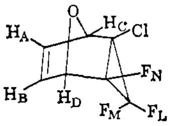
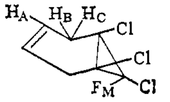
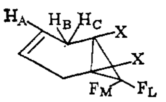
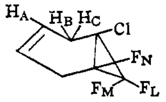
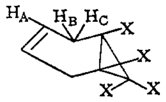
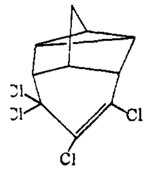
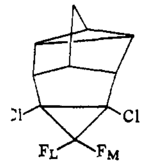
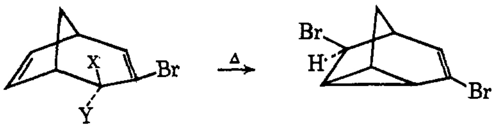
Structure	Compound	Vinyl	Methine	Methylene	F	Coupling constants
	**5**, X = Cl	(B) 6.13 q (A) 6.62 q	(C) 3.13 t (D) 3.72 t	(F) 2.22 d (E) 2.48 m		AB = 5 AD = BC = 3 CE = DE = 3 EF = 10
	6, X = Br	(B) 6.23 q (A) 6.73 q	(C) 3.33 t (D) 4.01 t	(F) 2.18 d (E) 2.64 m		AB = 5.5 AD = BC = 3 CE = DE = 3 EF = 11
	**7**, X = Cl	(B) 6.42 q (A) 6.88 q	(C) 4.86 d (D) 5.35 d			AB = 5.5 AD = BC = 2
	8, X = Br	(B) 6.49 q (A) 6.92 q	(C) 4.92 d (D) 5.57 d			AB = 6 AD = BC = 2
	**12**	(B) 6.31 m (A) 6 83 m	(C) 4.80 m (D) 5.23 m		127.6 t	AB = 6 AD = BC = 2 CL = DL = 7
	**13**		(D) 3.07 m (A) 3.87 s (B, C, and E) 2.22–2.55 complex	(F) 1.47 d		EF = 12
	**17**	(2) 6.50 s	(2) 3.52 s	(2) 2.52 m		
	**18**	(2) 6.39 d	(2) 5.47 d (C) 5.89 s			AB = 1
	**10**	(2) 6.83 s	(2) 5.30 d		138.4 t	BM = 2.5
	**26**, X = Cl	(2) 6.87 s	(2) 5.26 d		(L) 103.7 d (M) 136.7 dt	LM = 147.5 BM = 2.5
	27, X = Br	(2) 6.81 s	(2) 5.29 d		(L) 92.0 d (M) 136.5 dt	LM = 144 BM = 2
	**28**	(2) 6.98 m	(2) 5.26 m		(L) 115.2 q (M) 135.1 qt (N) 222 6 qm	LM = 160 MN = 23 LN = 7 CM = DM = 2
	**29**	(2) 5.48 m		(4) 2.90 s	145.4 s	AB = AC = 1
	**30**, X = Cl	(2) 5.59 t		(4) 2.89 m	(L) 130.8 dp (M) 143.6 d	LM = 156 BL = CL = 4 AB = AC = 1.5
	31, X = Br	(2) 5.50 t		(4) 2.99 m	(L) 117.1 dp (M) 142.7 d	LM = 152 BL = CL = 3 AB = AC = 1
	**32**	(2) 5.52 m		(4) 2.87 m	(L) 142.0 dm (M) 146.8 q (N) 192.6 m	LM = 170 NM = 4 LN < 3 BL $\simeq$ CL < 3
	**33**, X = Cl	(2) 5.50 t		(4) 2.98 d		AB = AC = 1
	34, X = Br	(2) 5.46 m		(4) 3.22 m		

Table I (*Continued*)

Structure	Compound	Vinyl	Methine	Methylene	F	Coupling Constants
	**35**		(2) 2.58 s (1) 3.06 s (5) 1.58–1.92 complex			
	**36**		(2) 2.66 t (6) 1.4–1.8 complex		(1) 121.6 d (1) 132.0 d	LM = 158

[a] Proton chemical shifts are given in parts per million (ppm) downfield from internal TMS. Fluorine chemical shifts are given in ppm upfield from internal trichlorofluoromethane. The chemical shift values are prefixed by a number in parentheses which denotes the number of atoms, or by a capital letter which denotes a specific atom where assignment is unambiguous. Coupling constants are given in cycles per second and are preceded by capital letters denoting the interacting nuclei. The postscripts are: s, singlet; d, doublet: t, triplet: q, quartet; p, pentuplet; m, unresolved multiplet.

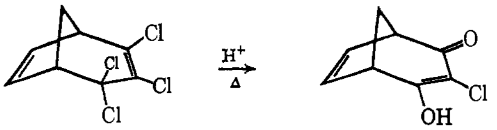
and **15** to **16** under similar conditions and have speculated on the mechanism. Exclusive formation of the *exo*-Br epimers **13** and **16** seems to be characteristic of these rearrangements, and further investigation of this reaction is in progress. Compound **8**, the 8-oxa analog of **6**, is thermally stable to at least 120°.



14, X = Br; Y = H
15, X = H; Y = Br

16

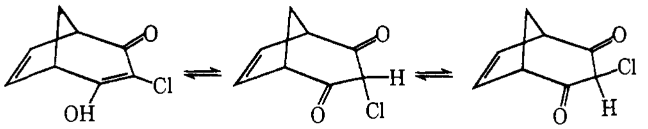
The structure assigned to **13** is clearly indicated by its ir and nmr spectra. **13** shows strong ir absorption at 1580 cm^{-1} (Table II), indicative of its brominated double bond (*vide supra*). In sharp contrast to its precursor **6**, which has two vinylic protons, **13** shows *no* vinylic proton in its nmr spectrum (Table I). A molecular model of **13** shows that if H_A has an *endo* configuration the dihedral angles between H_A and its vicinal protons H_B and H_D are nearly 90°. This stereochemistry should lead to minimal spin–spin coupling between H_A and these adjacent protons.[7a] In fact, H_A, strongly deshielded by geminal bromine, appears as a downfield *singlet* at δ 3.87. The methylene proton *syn* to the double bond, H_F, appears as a high-field doublet at δ 1.47 with J_{EF} = 12 cps, characteristic of geminal H-H coupling in this system.[7b] The other methylene proton, H_E, and the two cyclopropyl protons, H_B and H_C, appear as a complex multiplet ranging from δ 2.22 to 2.55. The allylic bridgehead proton, H_D, appears as an unresolved multiplet at δ 3.07.



5

17a

Acid hydrolysis of **5** provides a solid $C_8H_7ClO_2$ isomer **17**, mp 137°, whose Nujol mull ir shows bands indicative only of the enol ketone **17a**.[8] These absorptions include a broad hydrogen-bonded -OH band from 3300 to 2400 cm^{-1} with a hump at 2580 cm^{-1}, strong sharp bands at 1650 and 1590 cm^{-1} for the conjugated C=O and C=C groups, plus a broader band at 1570 cm^{-1} characteristic of nonchelating β-OH-conjugated carbonyl compounds.[8]



17a 17b 17c

Infrared and nmr evidence both indicate that, in *solution*, **17a** is in delicate equilibrium with *both* possible diketo tautomers **17b** and **17c**. A dilute CH_2Cl_2 solution of **18** shows strong sharp bands at 3460 (free -OH), 1670 (conjugated carbonyl), and 1595 cm^{-1} (conjugated C=C), all characteristics of **17a**. However, this same solution simultaneously shows strong sharp carbonyl absorption at 1720 cm^{-1}, indicating the presence of one (or both) of the β-diketones **17b** and **17c**. Both **17b** and **17c** can exist in two flip forms, one of which places the chlorine in the carbonyl plane and the proton at 90° to it, and the other of which reverses this placement. The observed location of the carbonyl absorption at 1720 cm^{-1} suggests that **17b** and **17c** exist in solution preferentially with the chlorine perpendicular to the carbonyl plane.[8]

That **17b** and **17c** are *both* present in tautomeric equilibrium with **17a** is shown by the nmr of a $CHCl_3$ solution of **17**. Such a solution contains primarily **17a**, since the most intense nmr peaks (Table I) are characteristic of this tautomer. A strong band for the -OH group in **17a** is seen at δ 7.65, the location and shape of which are temperature dependent. This indicates fast hydroxyl proton exchange. This rapid proton exchange renders the vinyl protons in **17a** symmetry equivalent, and they are seen as a broadened

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(7) (a) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. I, Pergamon Press, Oxford, 1965, pp 166–170. (b) The analogous proton in compound **16** appears as a doublet (J = 12 cps) at δ 1.04. See W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, **28**, 2202 (1963).

(8) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen & Co., Ltd., London, 1964, pp 38–39.

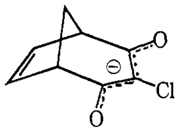
Table II. Infrared Data on Tetrahalocyclopropene Addition Products and Derivatives

Compd	Solvent	C—H, cm^{-1}	C=C, cm^{-1}	Other,[a] cm^{-1}
5	CCl_4	3060 w 2970 m 2940 sh 2860 w 1450 m[b]	1600 s	1328, 1214, 1200, 1132, 1052, 988, 888, 722, 708, 616, 556
6	CCl_4	3060 w 2970 m 2940 m 2860 w 1450 m[b]	1570 s	1325, 1192, 1120, 1038, 940, 928, 876, 712, 662, 585
7	CCl_4	3100 w 2980 m	1604 s	1304, 1285, 1154, 1060, 1004, 936, 924, 844 (800, 760 Nujol mull), 719, 619, 600, 568
8	CCl_4	2980 m	1580 s	1300, 1130, 1060, 1038, 939, 925, 918, 836 (760, 730 Nujol mull), 706, 589, 560
13	CCl_4	3060 w 2970 (m) 2940 m 2860 w 1450 m[b]	1580 s	1330, 1305, 1290, 1240, 1190, 1168, 1088, 1010, 962, 925, 875, 840, 830, 712, 664, 586
17a	Nujol mull		1590 s 1570 s	3300–2400 (OH), 1650 (CO), 1350, 1245, 1172, 1135, 1048, 1008, 955, 888, 805, 772, 759, 704, 679, 600, 587, 529, 453
18a	Nujol mull	3090 w		1770, 1740 (C=O), 1143, 1083, 1067, 940, 825, 730, 655, 590, 565
26	CCl_4	3020 m		1430, 1400, 1300, 1215, 1200, 1047, 1030, 920, 834 (780, 740, 722 liquid film), 674, 559
27	CCl_4	3020 m		1380, 1295, 1215, 1200, 1020, 1000, 917, 829, 710, 670, 550
28	Lf[c]	3020 m		1450, 1300, 1260, 1210, 1190, 1126, 1070, 1030, 914, 830, 802, 740, 728, 636
29	Lf[c]	3040 m 2920 m 2840 m 1430 s[b]	1670 m	1360, 1320, 1230, 1188, 1148, 1125, 1012, 974, 940, 898, 890, 676
30	L	3040 m 2920 m 2830 m 1445 s[b]	1670 m	1420, 1410, 1325, 1238, 1206, 1190, 1160, 1108, 990, 935, 900, 870, 730, 706, 650
31	Lf	3040 m 2920 m 2830 m 1445 s[b]	1670 m	1410, 1320, 1236, 1190, 1152, 1100, 972, 920, 886, 870, 785, 730, 680, 650
32	Lf	3040 m 2920 m 2830 m 1470 s[b]	1660 m	1420, 1340, 1240, 1215, 1192, 1148, 1122, 1028, 908, 870, 740, 654
33	CCl_4	3030 m 2900 m 2825 m 1425 s[b]	1670 m	1340, 1228, 1137, 998, 952, 938, 865, 846, 662, 640, 538
34	CCl_4	3030 m 2880 m 2820 w 1420 s[b]	1670 m	1330, 1225, 1120, 982, 950, 930, 898 (770 Nujol mull), 652, 598, 550
35	CCl_4	3060 w 2990 w 2945 s 2870 m	1610 s	1380, 1288, 1230, 1204, 1187, 1094, 1020, 825 (802, 778–758 Nujol mull), 650, 592, 562
36	Lf	3060 w 2940 m 2870 m		1420, 1182, 1020, 765

[a] All bands listed in this category have either medium or strong intensities. [b] CH_2 deformation vibration. [c] Liquid film.

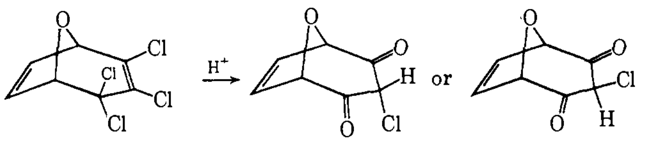
singlet at δ 6.50 (half-width 3 cps). Likewise, the bridgehead protons become equivalent, and they appear as a singlet of equal area (half-width 6 cps) at δ 3.52. The methylene protons in **17a** produce a multiplet of the same area at δ 2.52. In addition to these bands, the solution shows two lower intensity band *sets* (singlets, area ratio 2:1) at δ 6.12 and 5.38, and δ 6.40 and 5.60, the former set being twice as intense as the latter. Since it is most unlikely that the two flip forms of either **17b** or **17c** would fail to be rapidly interconverting on the nmr time scale, it follows that to account for the observed spectra *both* **17b** and **17c** must be present. The δ 6.12 and 6.40 absorptions are assigned to the vinyl protons in **17b** and **c** and the δ 5.38, 5.60 resonances to the diketone-flanked CHCl protons. The bridgehead and methylene protons of **17b** and **c** are lumped at δ 3.75 and 2.65. The relative areas of the various peaks indicate that in $CHCl_3$, **17** consists of a 70:20:10 mixture of **17a**, **b**, and **c** at room temperature.

The concentration of **17a** in the equilibrium tautomer mixture can be increased readily by dissolution of **17** in a more polar, better hydrogen-bonding solvent. For example, the ir of a tetrahydrofuran solution of **17** shows sharp intense peaks at 1670 and 1590 cm^{-1} for the conjugated carbonyl and double bond of **17a**, whereas the β-diketone peak for **17b** and **c**, now at 1710 cm^{-1}, is very weak. In line with its preferred enolic character **17** is quite soluble in H_2O but essentially insoluble in CCl_4. **17** gives a negative ferric chloride test.



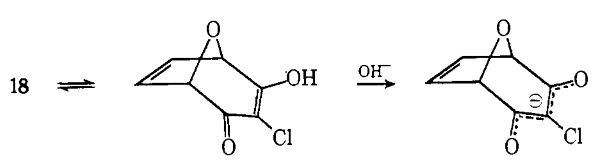
17d

In aqueous base, **17** is completely converted to the enol anion **17d** which shows nmr singlets at δ 6.55 (half-width 3 cps) for the vinyl protons and δ 3.37 (half-width 6 cps) for the bridgehead protons, plus a multiplet centered at δ 2.42 for the bridging methylene group.



7 **18a** **18b**

Acid hydrolysis of **7**, the 8-oxa analog of **5**, provides a solid $C_7H_5ClO_3$, **18**, mp 140°, which, in contrast to **17**, appears to exist preferentially as a 2,4-diketone **18a** or **b** (*vide infra*). The Nujol mull ir spectrum of **18** shows no absorption in the —OH or C═C regions, but only an intense C═O band at 1735 cm^{-1} with a minor satellite at 1765 cm^{-1}. In $CHCl_3$ solution **18** remains almost exclusively in *one* of the diketone forms **18a** or **18b**. The nmr of this solution (Table I) shows *only* a sharp doublet at δ 6.39 (J = 1 cps) for two equivalent vinyl protons, a doublet with 1-cps splitting at δ 5.47 for two equivalent bridgehead protons, plus a singlet at δ 5.89 for a lone diketone-flanked CHCl proton. The ir of this same solution shows a strong carbonyl band at 1770 cm^{-1} plus an intense carbonyl band at 1740 cm^{-1} suggesting that in this β-diketone the chlorine is *in* the carbonyl plane, rather than perpendicular to it as was the case with **17**.[8]

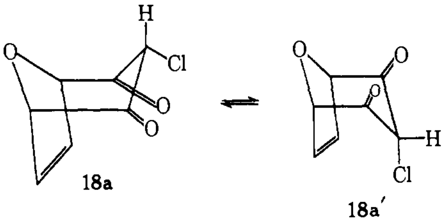


18c **18d**

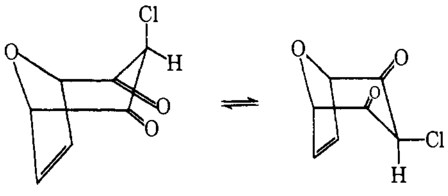
The $CHCl_3$ ir of **18** *does* show a weak bulge at 3470 cm^{-1} plus weak C═C conjugated carbonyl absorptions at 1685 and 1600 cm^{-1}, indicating the presence of at least a minor equilibrium amount of the enol **18c**. This enol content can be increased considerably by adding a small amount of tetrahydrofuran to the $CHCl_3$ solution. In straight THF **18** maintains strong carbonyl absorption at 1740 cm^{-1} diagnostic for **18a** or **b**, but also shows intense conjugated C═O and C═C bands at 1685 and 1595 cm^{-1} plus strong broad hydrogen-bonded -OH absorption around 3470 cm^{-1}, establishing that the tautomeric equilibrium has now shifted toward the enol ketone form **18c**. The nmr of the THF solution supports this interpretation. In addition to the doublets for **18a** (or **b**) at δ 5.42 and 6.55, the solution shows doublets at δ 6.80 and 5.04 (J = 0.5 cps) which can be assigned to the vinyl and bridgehead protons in the rapidly equilibrating enol **18c**. The relative peak areas indicate a 50:50 mixture of enol and keto forms of **18**.

The resonance position of the -CHCl- proton in the β-diketone form of **18** present is now found at δ 6.33, shifted downfield 0.44 ppm from its δ 5.89 location in $CHCl_3$ solution. In mixtures of $CHCl_3$ and THF this resonance lies at intermediate values.

From the ir evidence that the equilibrium β-diketone form of **18** has its chlorine in the carbonyl plane, and the fact that the -CHCl- proton in this isomer is in a location highly accessible to solvent interaction, **18a** (chlorine *endo*, with the six-membered ring in a pseudo-boat conformation) is assigned as the β-diketone tautomer actually present in solution. If it is assumed that dipole–dipole interactions are the crucial factor in determining the relative thermodynamic stabilities of the diketones, it is clear why **18a** is so strongly favored. This tautomer is shown below along with its flip form **18a′** and the two flip forms of the *exo*-chlorine isomer **18b** and **18b′**. **18a** is readily seen to be the only conformer in which the bridging oxygen C–O–C dipoles are effectively canceled by the carbonyl and halogen dipoles



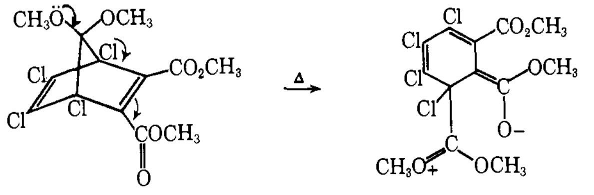
18a **18a′**



18b **18b′**

The greater ability of **18** than **17** to assume a β-diketone structure is evidenced by the fact that **18**, unlike **17**, is quite soluble in CCl_4. **18** is, however, readily converted to its enol anion **18d** in basic solution. In D_2O, this anion shows narrow singlet absorptions at δ 6.82 and 5.10 for the vinyl and bridgehead protons. **18** gives a negative ferric chloride test.

Attempted Condensation of Tetrahalocyclopropenes with Chlorinated 1,3-Dienes. Both tetrachlorocyclopropene (**1**) and 1,2-dichloro-3,3-difluorocyclopropene (**23**) react with 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene[9a] at 90–110° to give an identical product,



37 **38**

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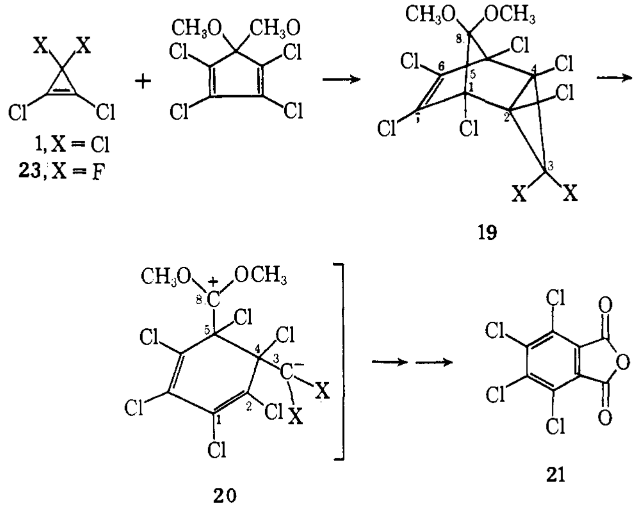
(9) (a) J. S. Newcomber and E. T. McBee, *J. Am. Chem. Soc.*, **71**, 946 (1949). (b) Thermal decomposition of **37** *via* the intermediate **38** has been reported by D. M. Lemal, E. P. Gosselink, and S. D. McGregor, *ibid.*, **88**, 582 (1966).

tetrachlorophthalic anhydride (**21**), in moderate yield. This process can be rationalized assuming the pathway outlined in Chart III. The cyclopentadiene reacts with the cyclopropene to form the Diels–Alder adduct **19**. This adduct spontaneously undergoes an intramolecular *trans*-elimination reaction by concertedly breaking the C_1–C_8 and C_2–C_3 bonds. This forms a C_1=C_2 double bond and gives the zwitterion **20**.[9b] The driving force for the "abnormal" transformation of the Diels–Alder adduct to the zwitterion is presumably the stabilization of the positive and negative charges in the zwitterion by the dimethoxy and dihalocarbinyl groups, respectively. Although the subsequent steps are not entirely understood, it is clear that **20** has the appropriate skeleton for subsequent transformation to tetrachlorophthalic anhydride (**21**).

Chart III



1, X = Cl
23, X = F

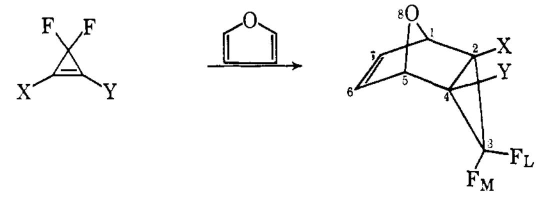
19

20

21

Tetrachlorocyclopropene (**1**) did not condense with hexachlorobutadiene upon heating at 180° for 48 hr. However, **1** did react with hexachlorocyclopentadiene under similar conditions to give a mixture of chlorocarbons, from which a C_8Cl_{10} isomer **22**, mp 105°, could be isolated in low yield. This crystalline solid has mass spectral peaks corresponding to the molecular ion $C_8Cl_{10}^+$ with the proper chlorine isotope distribution. **22** shows ir C=C absorption at 1650 cm⁻¹. Its uv spectrum (in isooctane) shows a maximum at 223 mμ (log ε 4.4). No structure has been assigned to **22**.

Stable Diels–Alder Adducts. As mentioned in the first section, 1,2,3-trichloro-3-fluorocyclopropene (**9**) reacts with furan at 80° to give a mixture of stable Diels–Alder adduct **10** and rearranged product **12** in the ratio 1.5:1 according to nmr analysis. 1,2-Dichloro-3,3-difluorocyclopropene (**23**), 1,2-dibromo-3,3-difluorocyclopropene (**24**), and 1-chloro-2,3,3-trifluorocyclopropene (**25**) likewise react with furan at 80° to give exclusively the stable Diels–Alder adducts **26**, **27**, and **28**, respectively. Further heating of these adducts at 100° produces no change. Since the cyclopropane → propene rearrangements of all these adducts would require breaking a C–F bond, the rearrangements simply do not occur under the reaction conditions.[4,5]



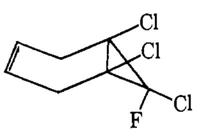
23, X = Y = Cl
24, X = Y = Br
25, X = Cl; Y = F

26, X = Y = Cl
27, X = Y = Br
28, X = Cl; Y = F

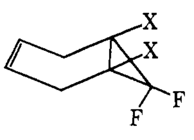
The ir spectra of the tricyclic Diels–Alder adducts **26**, **27**, and **28** are similar to each other in many aspects, but different from those of the bicyclic products **5**, **6**, **7**, and **8** (Table II). One of the notable differences is in the frequency of the most intense band in the C–H stretching region. In the bicyclic products, this band lies at 2970–2980 cm⁻¹, whereas in the tricyclic adducts, it shifts to a higher frequency range, 3010–3020 cm⁻¹. Another notable difference is the absence of any band in the 1600-cm⁻¹ region in the spectra of **26**, **27**, and **28** whereas the bicyclic products **5**, **6**, **7**, and **8** show *one* band in the 1600-cm⁻¹ region due to the *halogenated* C_2=C_3 bond (*vide supra*). We therefore conclude that the C_6=C_7 stretching vibration is infrared inactive in *both* the tricyclic and the bicyclic products due to the local symmetry of the C=C bond.[10]

In their H¹ nmr spectra (Table I), the tricyclic adducts **10**, **26**, **27**, and **28** all show a single peak at δ 6.81–6.98 for the two vinylic protons and a band at δ 5.26–5.30 for the two bridgehead protons. There are three possible kinds of fluorine atoms in these adducts (Table I). F_M appears in the F¹⁹ nmr spectra within the narrow range 135.1–138.4 ppm and is attributed to the C_3 fluorine which is *syn* to the double bond. F_L, attached to C_3 and *anti* to the double bond, appears over the wider range 92–115.2 ppm, depending on the nature of the halogens *cis* to it on the three-membered ring.[11a] F_M is coupled to F_L by 144–160 cps, diagnostic for geminal nonequivalent fluorines in cyclopropane systems.[11b] In **28**, F_N, attached to C_2 and *cis* to F_L, appears at *very* high field (222.6 ppm). F_N is coupled to the *cis* adjacent fluorine, F_L, by 7 cps, and is coupled to the *trans* adjacent fluorine, F_M, by 23 cps. In all the tricyclic adducts the bridgehead protons interact with F_M, the coupling constant being 2–2.5 cps, but *not* with F_L.

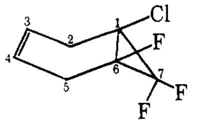
As anticipated, the fluorocyclopropenes **9**, **23**, **24**, and **25** were found to react smoothly with 1,3-butadiene at 100° to form the stable Diels–Alder adducts **29**,



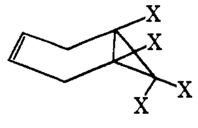
29



30, X = Cl
31, X = Br



32



33, X = Cl
34, X = Br

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(10) Reference 8, pp 132–144.

(11) (a) See K. L. Williamson and B. A. Braman, *J. Am. Chem. Soc.*, **89**, 6183 (1967), for an explanation of this effect. (b) *J* = 157 cps for the geminal F–F coupling in 1-methyl-2,2-difluorocyclopropane. See J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 333–334.

30, 31, and **32**. Unexpectedly, tetrachlorocyclopropene (**1**) and tetrabromocyclopropene (**2**) were also found to give the unrearranged Diels–Alder adducts **33** and **34** under the same conditions. The instability of intermediates **3** and **11** must therefore be due to the high ground-state strain built into these adducts *via* the methylene or oxygen bridges.[5] These bridges distort the Diels–Alder adducts precisely in the direction required to initiate disrotatory opening[4] of their cyclopropane rings.

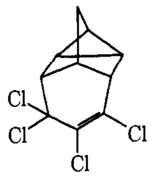
Attention should be drawn to the fact that whereas reaction of **9** with furan presumably provides *both* isomers **10** and **11** in the ratio of 1.5:1 (*vide supra*), **9** gives *exclusively* adduct **29** with 1,3-butadiene. This implies that 1,3-butadiene discriminates more effectively between possible approach orientations of **9** than does furan in going to the Diels–Alder transition state, but the mechanism of discrimination requires further study.

The ir spectral data of the butadiene adducts **29**, **30**, **31**, **32**, **33**, and **43** are summarized in Table II. In contrast to the furan adducts **26**, **27**, and **28**, in which the C=C stretching vibration is entirely inactive, the butadiene adducts all show an infrared band of medium intensity for the symmetrically substituted $C_1{=}C_2$ bond over the very narrow range 1660–1670 cm^{-1}. Evidently the greater flexibility of these structures results in a measurable dipole moment change during C=C vibration.[10]

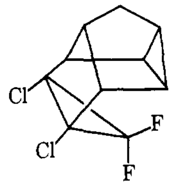
The nmr data of the butadiene adducts **29**, **30**, **31**, **32**, **33**, and **34** are summarized in Table I. In the H^1 nmr, these compounds show two vinylic protons at δ 5.48–5.59 and four methylene protons at δ 2.87–3.22. These methylene protons are now observed to be coupled by 3–4 cps to the fluorine atom, F_L, at C_7 which is *anti* to the double bond. F_L can confidently be assigned this location since the F^{19} resonance appears over the relatively wide range of 117–142 ppm and depends on the nature of the *cis*-halogens.[11a] F_M, appearing over the very narrow range 142.7–146.8 ppm, can therefore be assigned as the fluorine attached to C_5 *syn* to the double bond. The observed F_L–F_M coupling constants of 152–170 cps are again characteristic of geminal F–F coupling in the cyclopropane systems.[11] In adduct **32**, F_N, attached to C_6 and *cis* to F_L, again appears at the rather high field of 192.6 ppm. F_N is coupled to the adjacent *cis*-fluorine F_L by *ca.* 3 cps and to the adjacent *trans*-fluorine F_M by 4 cps.

The marked difference between vicinal F–F coupling constants in adducts **28** and **32** is undoubtedly a reflection of the rather different geometry of these adducts. In **26**, **27**, and **28** the bridgehead protons are found to be coupled to F_M, not F_L. In **30**, **31**, and **32** the analogous methylene protons are coupled to F_L but not to F_M. This suggests that the butadiene adducts exist as indicated, that is, predominantly in flip forms *opposite* to those *required* in the furan adducts. The indicated conformations of the adducts **29** through **32** are the ones with minimum steric interactions.

2,6 Addition to Bicyclo[2.2.1]heptadiene. Like many other dienophiles,[12] tetrachlorocyclopropene (**1**) and 1,2-dichloro-3,3-difluorocyclopropene (**19**) undergo 2,6 addition to bicyclo[2.2.1]heptadiene at 100° to give the adducts **35** and **36**, respectively. **35** is a colorless crystalline solid melting at 62–63°. It shows a C=C stretching vibration at 1610 cm^{-1} due to the chlorinated double bond (Table II). The nmr spectrum of **35** (Table I) shows a singlet (width at half-height 4 cps) at δ 3.06 for one proton, a singlet (width at half-height 5 cps) at δ 2.58 for two protons, and a complex multiplet for five protons which includes peaks at δ 1.58, 1.66, 1.74, 1.82, and 1.92. **36** is a colorless liquid. It shows no C=C stretching vibration in the infrared spectrum (Table II). The H^1 nmr spectrum of **36** (Table I) shows a triplet (J = 2 cps) at δ 2.66 for two protons and an unresolved complex for six protons ranging from δ 1.4 to 1.8. The F^{19} nmr spectrum of **36** shows a pair of doublets centered at 121.6 and 132.0 ppm, respectively, for the two geminal fluorine atoms. The F–F coupling constant of 158 cps indicates an intact cyclopropane ring (*vide supra*).[11b] The high-field doublet (at 132.0 ppm) shows additional fine splitting due to long-range H–F coupling ($J \simeq$ 3 cps). **36** is presumed to have an *endo* configuration, based on an examination of molecular models.

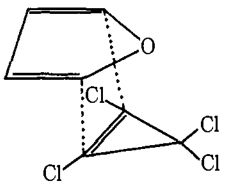


35

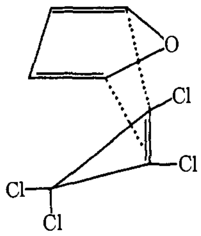


36

Stereochemistries of the Diels–Alder Adducts. As stated at the outset, cyclopropene and its alkyl- and phenyl-substituted derivatives have all been shown to form exclusively *endo* adducts with cyclopentadiene.[2] That *endo* adduction should also be highly favored over *exo* for the tetrahalocyclopropenes is made absolutely clear if one accepts the structures recently proposed[2e] for the transition states in the two processes. Herndon and Hall[2e] showed that the entropies of activation for the decompositions of both *exo*- and *endo*-dicyclopentadiene are essentially zero.[2e] From this they conclude that in the transition states the (still planar) reacting molecules can be pictured as being oriented to each other in a geometry closely resembling the carbon skeleton of the corresponding dimer. Presuming, as suggested by these authors,[2e] that this situation applies in general, the following pictures can be drawn for the two possible transition states in the reactions of tetrahalocyclopropenes with furan.



exo



endo

In the *exo* transition state, essential superposition of one of the cyclopropyl methylene substituents with the furan oxygen is implied! Although this situation could not actually be so bad in the real case, the implication is

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[12] (a) R. C. Cookson, J. Dance and J. Hudec, *J. Chem. Soc.*, 5416 (1964), and references therein; (b) P. D. Bartlett, G. E. H. Wallbillich, and L. K. Montgomery, *J. Org. Chem.*, 32, 1293 (1967).

clearly most unfavorable. On the other hand, the *endo* transition state looks entirely reasonable. Furthermore, the fact that the axis of the cyclopropene methylene substituent *syn* to the diene lies parallel to the diene suggests that reasonably sized substituents at this position should show *at best* modest steric interference with the developing transition state. The results outlined previously in this paper and those given below are all readily explained if the Diels–Alder adducts are assumed to be *endo*.

Relative Reactivity of Tetrahalocyclopropenes. The relative dienophilic reactivities of the various cyclopropenes, as measured by allowing mixtures of cyclopropenes to compete for a deficient amount of furan at 79° (see Experimental Section), are summarized in Table III.

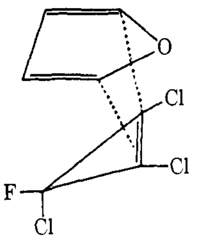
Table III. Relative Reaction Rates of Tetrahalocyclopropenes[a] in Diels–Alder Reactions with Furan at 79°

Compound	Rel rate	Prodt
C_3Br_4 (**2**)	1.42 ± 0.05	**8**
C_3Cl_4 (**1**)	1.00[d]	**7**
C_3Cl_3F (**9**)	0.48[b]	**10**
$C_3Br_2F_2$ (**24**)	0.45[d]	**27**
C_3Cl_3F (**9**)	0.31[c]	**12**
$C_3Cl_2F_2$ (**23**)	0.29[d]	**26**

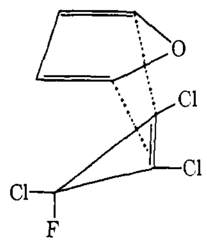
[a] Except for tetrachlorocyclopropene (**1**) all the other fluoro and bromocyclopropenes produce tar along with 1:1 adducts during their reactions with furan. The bulk of this tar presumably arises *via* acid-catalyzed ring opening and resinification of the *furan*, since the analogous reactions of the cyclopropenes with butadiene give much cleaner products and the furan adducts are demonstrably stable to the reaction conditions. The tar-producing side reaction of furan has no serious effect on the competitive rate results, since simply decreasing the furan concentration has no effect on the validity of the competitive rate equation: W. von E. Doering and W. A. Henderson, Jr., *J. Am. Chem. Soc.*, **80**, 5274 (1958). [b] *Via* transition state A. [c] *Via* transition state B. [d] Internal consistency checked by separate competition experiments between all three possible pairs of these cyclopropenes.

Taking the relative reaction rate of tetrachlorocyclopropene (**1**) as a standard, it is immediately apparent that replacing Cl with Br at any position on the cyclopropene system *enhances* the cyclopropene reactivity, and that replacing Cl or Br with F at the methylene position *decreases* the cyclopropene reactivity. Evidently, the electronic effect exerted by the halogen substituents is more important than the steric effect, because steric effects alone predict a reactivity order opposite to that observed. The reactions of 1,2,3-trichloro-3-fluorocyclopropene (**9**) with furan clearly demonstrate that some steric selectivity *is* involved; in this case furan prefers to approach the cyclopropene from the less hindered side (transition state A, leading to product **10**) rather than from the more hindered side (transition state B, leading to intermediate **11**). However the selectivity is slight, only by a factor of 1.5:1.

The observed trend in substituent effects on the dienophilic reactivity of the tetrahalocyclopropenes (*i.e.*, Br > Cl > F in the order of decreasing reactivity) found in this study is opposite to that predicted by the "Alder rule,"[13] which states that Diels–Alder reaction rates should be increased by electron-donating substituents in the diene and electron-withdrawing substituents in the dienophile. As can be seen from Table III, increased substitution of the cyclopropene with sterically smaller, more electronegative fluorines actually leads to a *diminution* in reactivity.



transition state A



transition state B

To rationalize the observed reactivity order we suggest that the most important effect of replacing Br or Cl with F at the methylene position in a cyclopropene is to change the bonding properties of the methylene carbon so that the internal ring σ bond strain is diminished[2d] and the over-all cyclopropene thermodynamic ground-state energy is lowered. Although the details of the mechanism by which this ultimate effect is achieved may be quite different, Closs, *et al.*,[2c,d] do suggest that replacement of H by an *alkyl* group at the 3 position has a similar stabilizing effect on cyclopropenes.

Since all parts of the cyclopropene carbon skeleton are involved in and altered by the Diels–Alder reaction the over-all cyclopropene thermodynamic stability will be of fundamental importance. This situation must be distinguished from that obtaining where a highly strained part of a molecule does not directly participate in a reaction. In this latter case the over-all thermodynamic stability of the molecule can be totally irrelevent; strain in the reactant simply shows up as *unaltered* strain in the product.

Closs has pointed out that the angle strain at the cyclopropene methylene position exceeds that in cyclopropane by about 5°, and that the thermodynamic ring strain in cyclopropene exceeds that in cyclopropane by about 27 kcal/mol.[2d] Given that cyclopropenes are intrinsically more strained than cyclopropanes, any structural alteration at the methylene position which can diminish ring angle strain should show a greater stabilizing effect on the cyclopropene than on a cyclopropane product derived from it.

Since the Diels–Alder reaction in question here involves conversion of a cyclopropene to a cyclopropane, it follows that the geometry of the three-membered ring in the intervening transition state must be *somewhere between* the two. This implies that stabilizing structural changes in the original cyclopropene should have a greater effect *there* than on the Diels–Alder transition state. Thus, in comparing the reactions of two cyclopropenes with a common diene, the transition states should be more similar than the starting states, and a thermodynamically more stable cyclopropene should react more sluggishly than a less stable one.

Based on these assertions, we feel that the total failure of 3,3-dimethyl-substituted cyclopropenes to undergo Diels–Alder adduction,[2] and the lowered activity of 3,3-

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(13) (a) J. Sauer, *Angew. Chem. Intern. Ed. Engl.*, **6**, 24 (1967). (b) From its known reactivity,[13c] furan must be considered to be a normal "electron-rich" diene, not an "electron-poor" diene exhibiting "inverse" electron demand.[13d] (c) See A. S. Onishchenko, "Diene Synthesis," L. Mandel, Trans., Daniel Davey and Co., Inc., New York, N. Y., 1964, Chapter VII. (d) See J. Sauer and H. Wiest, *Angew. Chem. Intern. Ed. Engl.*, **1**, 269 (1962).

difluoro-substituted cyclopropenes observed here, should *not* be ascribed primarily to "steric interferences" with the *endo* transition state, but rather to differences in the ground-state energies of the cyclopropene reactants involved.

Although the origin of the effect varies, preferential stabilization of small ring systems by F relative to Cl does show up elsewhere in three- and four-membered ring chemistry. Hexachlorocyclopropane[14a] undergoes ring opening at about 250°,[14d,e] whereas hexafluorocyclopropene is evidently stable to 1000°![14b] Perfluorocyclobutene is thermodynamically favored over perfluorobutadiene at 200°,[14c] whereas at this temperature perchlorocyclobutene rearranges to hexachlorobutadiene.[14f]

Experimental Section

General. Ir spectra were recorded on a Perkin-Elmer 337 grating infrared spectrophotometer. Uv spectra were recorded on a Perkin-Elmer 202 ultraviolet-visible spectrophotometer. Nmr spectra were recorded on a Varian Associates A-56/60A combination H^1 and F^{19} nmr spectrometer. The nmr and ir data are summarized in Tables I and II. Elemental analyses were performed by Dr. Carol K. Fitz, Needham Heights, Mass.

Tetrahalocyclopropenes. Compounds **1**, **2**, **9**, **23**, and **24** were prepared according to procedures given in ref 3a. 1-Chloro-2,3,3-trifluorocyclopropene (**25**) was prepared by the method given in ref 3c.

2,3,4,4-Tetrachlorobicyclo[3.2.1]octa-2,6-diene (5). Tetrachlorocyclopropene (**1**) (1.5 g, 8.4 mmol) and freshly distilled cyclopentadiene (1.1 g, 16 mmol) in 2 ml of CCl_4 were allowed to react at room temperature over 2 days. The solvent and unreacted cyclopentadiene were removed *in vacuo*. The solid residue was recrystallized from petroleum ether, bp 30–60°, to give colorless crystals of **5**, mp 90° (1.95 g, 95% yield based on **1**). The uv spectrum in isooctane showed end absorption with shoulders at 215 and 245 mμ (log ϵ 4).

Anal. Calcd for $C_8H_6Cl_4$: C, 39.3; H, 2.48; Cl, 58.2. Found: C, 39.4; H, 2.4; Cl, 58.0.

2,3,4,4-Tetrabromobicyclo[3.2.1]octa-2,6-diene (6). Tetrabromocyclopropene (**2**) (1.5 g, 4.2 mmol) and freshly distilled cyclopentadiene (0.5 g, 8 mmol) in 2 ml of CCl_4 were allowed to react at room temperature for 2 days. The volatile materials were removed *in vacuo*. The dark solid residue was repeatedly recrystallized from petroleum ether, bp 30–60°, to give colorless crystals of **6**, mp 134–135° (1.6 g, 90% yield based on **2**). The uv spectrum in isooctane showed end absorption with shoulders at 215 and 240 mμ (log ϵ 4).

Anal. Calcd for $C_8H_6Br_4$: C, 22.8; H, 1.47; Br, 75.8. Found: C, 22.6; H, 1.4; Br, 75.6.

2,3,4,4-Tetrachloro-8-oxabicyclo[3.2.1]octa-2,6-diene (7). Tetrachlorocyclopropene (**1**) (1.5 g, 8.4 mmol), furan (1.1 g, 16 mmol), and 2 ml of CCl_4 were heated in a sealed tube at 80° for 18 hr. The volatile materials were removed *in vacuo*. The residue, a viscous oil, solidified upon trituration with petroleum ether. The solid was recrystallized from petroleum ether to give colorless crystals of **7**, mp 59–60° (1.9 g, 92% yield based on **1**). The uv spectrum in isooctane showed a broad shoulder from 215 to 245 mμ (log ϵ 4).

Anal. Calcd for $C_7H_4OCl_4$: C, 34.2; H, 1.63; Cl, 57.8. Found: C, 34.3; H, 1.7; Cl, 57.7.

2,3,4,4-Tetrabromo-8-oxabicyclo[3.2.1]octa-2,6-diene (8). Tetrabromocyclopropene (**2**) (1.5 g, 4.2 mmol), furan (0.5 g, 8 mmol), and 2 ml of CCl_4 were heated in a sealed tube at 80° for 18 hr. The reaction mixture, consisting of a tan solution and some black precipitate, was filtered and the filtrate evaporated *in vacuo*. The residue, a tan oil, solidified upon trituration with petroleum ether. This solid, recrystallized from petroleum ether, gave colorless crystals of **8**, mp 121–122° (1.4 g, 80% yield based on **2**).

Anal. Calcd for $C_7H_4OBr_4$: C, 19.8; H, 0.95; Br, 75.5. Found: C, 19.6; H, 1.0; Br, 75.6.

2,3,4-Trichloro-3-fluoro-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene (10) and 2,4,4-Trichloro-3-fluoro-8-oxabicyclo[3.2.1]octa-2,6-diene (12). 1,2,3-Trichloro-3-fluorocyclopropene (**9**) (1.5 g, 9.3 mmol), furan (1.5 g, 22 mmol), and 2 ml of CCl_4 were heated in a sealed tube at 80° for 18 hr. The dark reaction mixture was filtered. The filtrate was evaporated *in vacuo*. The residue, a tan oil, was analyzed by H^1 and F^{19} nmr (Table I) and found to be composed of **10** and **12** in the ratio 1.5:1.

2,3,4,7-Tetrabromotricyclo[3.2.1.0^{4,6}]oct-2-ene (13). A solution of **6** in CCl_4 was refluxed for 1 hr. **13**, a colorless liquid, was obtained after the solvent was removed *in vacuo*. The uv spectrum in isooctane showed a shoulder at 230 mμ (log ϵ 3.8).

Anal. Calcd for $C_8H_6Br_4$: C, 22.8; H, 1.47; Br, 75.8. Found: C, 22.5; H, 1.5; Br, 75.4.

2-Hydroxy-3-chlorobicyclo[3.2.1]octa-2,6-dien-4-one (17). Finely powdered **5** (0.5 g, 2.5 mmol) was treated with concentrated H_2SO_4. An orange-yellow color developed with evolution of gas. The mixture was gently warmed over a steam bath with stirring for 15 min, then poured on crushed ice. A colorless solid appeared which was extracted with two portions of $CHCl_3$. The organic layer was dried over Linde Molecular Sieve and evaporated *in vacuo*. The oily residue solidified upon trituration with petroleum ether. This solid was recrystallized from CCl_4 to give colorless crystals of **17**, mp 135–157° (0.14 g, 40% yield).

Anal. Calcd for $C_8H_7O_2Cl$: C, 56.3; H, 4.1; Cl, 20.8. Found: C, 56.0; H, 4.1; Cl, 21.1.

3-Chloro-8-oxabicyclo[3.2.1]oct-6-ene-2,4-dione (18). Finely powdered **7** (0.5 g, 2.0 mmol) was treated with concentrated H_2SO_4 over a steam bath for 5 min with stirring. The resulting yellow solution was cooled and poured on crushed ice. Extraction with $CHCl_3$, drying, and then evaporation of the solvent provided colorless crystals of **18**, mp 139–140° (0.15 g, 42% yield).

Anal. Calcd for $C_7H_5O_3Cl$: C, 48.6; H, 2.9; Cl, 20.6. Found: C, 48.0; H, 2.8; Cl, 21.1.

Condensation of 1,2,3,4-Tetrachloro-5,5-dimethoxycyclopentadiene with Tetrachlorocyclopropene (1) or with 1,2-Dichloro-3,3-difluorocyclopropene (23). The cyclopentadiene (0.5 g, 1.9 mmol)[9a] and an excess of **1** (1.5 g, 8.4 mmol) or of **23** (1.5 g, 10 mmol) were dissolved in 3 ml of CCl_4. The solutions were refluxed under a nitrogen atmosphere for 2 days, and volatile materials were removed *in vacuo*. The remaining solids were repeatedly recrystallized from CCl_4 to give colorless crystals of tetrachlorophthalic anhydride, mp 255° (lit.[15] 255–6.5°). The ir and mass spectra of the product were identical with those of an authentic sample.

Condensation of Hexachlorocyclopentadiene with Tetrachlorocyclopropene (1). Hexachlorocyclopentadiene (1.7 g, 6.2 mmol) and an excess of **1** (6 g, 33.7 mmol) were heated in a sealed tube at 180° for 3 days. When the brown-red solution was triturated with petroleum ether a solid appeared. Fractional crystallization of this solid provided a colorless crystalline material, **22**, mp 105°. The mass spectrum of **22** showed peaks corresponding to $C_8Cl_{10}^+$, $C_8Cl_9^+$, $C_8Cl_8^+$, C_8Cl_7,$^+$ $C_8Cl_6^+$ (base peak), etc.; ir (CCl_4): 1650, 1575, 1202, 1165, 960, 832, 815, 650, 638, 618, and 592 cm^{-1}; $\lambda_{\max}^{\text{isooctane}}$ 223 mμ (log ϵ 4.4).

2,4-Dichloro-3,3-difluoro-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene (26). **23** (1.5 g, 10.3 mmol), excess furan (1.5 g, 22 mmol), and 2 ml of CCl_4 were heated in a sealed tube at 80° for 18 hr. The volatile materials were removed *in vacuo*. The remaining viscous liquid was short-path vacuum distilled (pot temperature, *ca.* 100°) to give **26** as a colorless liquid (1.1 g, 50% yield based on **23**).

Anal. Calcd for $C_7H_4OCl_2F_2$: C, 39.5; H, 1.9; Cl, 33.3; F, 17.8. Found: C, 39.2; H, 1.9; Cl, 34.2; F, 18.0.

2,4-Dibromo-3,3-difluoro-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene (27). **24** (1.5 g, 6.4 mmol), excess furan (1.5 g, 22 mmol), and 2 ml of CCl_4 were heated in a sealed tube at 80° for 18 hr. The dark mixture was filtered and the filtrate evaporated *in vacuo*. The residue was short-path vacuum distilled (pot temperature, *ca.* 100°) to give **27**, a colorless liquid, which on cooling provided a solid, mp 95° (0.9 g, 46% yield based on **24**).

Anal. Calcd for $C_7H_4OBr_2F_2$: C, 27.8; H, 1.3; Br, 53.0. Found: C, 27.7; H, 1.3; Br, 53.4.

2-Chloro-3,3,4-trifluoro-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene (28). **25** (1 g, 7.8 mmol), excess furan (1.5 g, 22 mmol), and 2 ml of CCl_4 were heated in a sealed tube at 80° for 18 hr. The dark reaction mixture was filtered and the filtrate evaporated *in vacuo*. The resi-

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(14) (a) S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **86**, 56 (1964); (b) J. Harmon, U. S. Patent 2,404,374 (1946); *cf. Chem. Abstr.*, **40**, 7234^3 (1946); (c) M. Prober and W. T. Miller, Jr., *J. Am. Chem. Soc.*, **71**, 598 (1949); (d) W. R. Moore, S. E. Krikorian, and J. E. LaPrade, *J. Org. Chem.*, **28**, 1404 (1963); (e) E. K. Fields and S. Meyerson, *ibid.*, **28**, 1915 (1963); (f) G. Maahs and P. Hegenberg, *Angew. Chem. Intern. Ed. Engl.*, **5**, 800 (1966).

(15) D. S. Pratt and G. A. Perkins, *J. Am. Chem. Soc.*, **40**, 203 (1918).

due was short-path vacuum distilled (pot temperature, *ca.* 100°) to give **28**, a colorless liquid (0.8 g, 52% yield based on **25**).

Anal. Calcd for $C_7H_4OClF_3$: C, 42.7; H, 2.0; Cl, 18.0; F, 29.0. Found: C, 42.3; H, 2.0; Cl, 18.5; F, 29.0.

1,6,7-Trichloro-7-fluorobicyclo[4.1.0]hept-3-ene (29). **9** (1.5 g, 9.3 mmol), excess 1,3-butadiene (2 ml, 22 mmol), and 2 ml of CCl_4 were heated in a sealed tube over a steam bath for 18 hr. The dark reaction mixture was filtered and the filtrate evaporated *in vacuo.* The residue was short-path vacuum distilled (pot temperature, *ca.* 100°) to give a colorless liquid, **29** (0.8 g, 40% yield based on **9**).

Anal. Calcd for $C_7H_6Cl_3F$: C, 39.0; H, 2.8; Cl, 49.5. Found: C, 38.7; H, 2.7; Cl, 49.8.

1,6-Dichloro-7,7-difluorobicyclo[4.1.0]hept-3-ene (30). **23** (1.5 g, 10.3 mmol), excess 1,3-butadiene (2 ml, 22 mmol), and 2 ml of CCl_4 were heated in a sealed tube over a steam bath for 18 hr. The usual work-up (*vide supra*) provided a colorless liquid, **30** (0.9 g, 43% yield based on **23**).

Anal. Calcd for $C_7H_6Cl_2F_2$: C, 42.2; H, 3.0; Cl, 35.6. Found: C, 42.3; H, 2.7; Cl, 35.2.

1,6-Dibromo-7,7-difluorobicyclo[4.1.0]hept-3-ene (31). **24** (1.5 g, 6.4 mmol), excess 1,3-butadiene (2 ml, 22 mmol), and 2 ml of CCl_4 were heated in a sealed tube over a steam bath for 18 hr. The usual work-up (*vide supra*) provided a colorless liquid, **31**, which solidified on standing (0.7 g, 38% yield based on **24**).

Anal. Calcd for $C_7H_6Br_2F_2$: C, 29.2; H, 2.1; Br, 55.6. Found: C, 28.7; H, 2.1; Br, 55.4.

1-Chloro-6,7,7-trifluorobicyclo[4.1.0]hept-3-ene (32). **25** (1 g, 7.8 mmol), excess 1,3-butadiene (2 ml, 22 mmol), and 2 ml of CCl_4 were heated in a sealed tube over a steam bath for 18 hr. The usual work-up (*vide supra*) provided a colorless liquid, **32** (0.5 g, 35% yield based on **25**).

Anal. Calcd for $C_7H_6ClF_3$: C, 46.0; H, 3.3; Cl, 19.5; F, 31.2. Found: C, 46.4; H, 3.4; Cl, 20.0; F, 31.5.

1,6,7,7-Tetrachlorobicyclo[4.1.0]hept-3-ene (33). **1** (1.5 g, 8.4 mmol), excess 1,3-butadiene (2 ml, 22 mmol), and 2 ml of CCl_4 were heated in a sealed tube over a steam bath for 18 hr. The reaction solution was evaporated *in vacuo.* The residue solidified on standing and was recrystallized from petroleum ether to give colorless crystals of **33**, mp 50–51° (1.8 g, 92% yield based on **1**).

Anal. Calcd for $C_7H_6Cl_4$: C, 36.2; H, 2.6; Cl, 61.2. Found: C, 36.4; H, 2.8; Cl, 59.6.

1,6,7,7-Tetrabromobicyclo[4.1.0]hept-3-ene (34). **2** (1.5 g, 4.2 mmol), excess 1,3-butadiene (2 ml, 22 mmol), and 2 ml of CCl_4 were heated in a sealed tube over a steam bath for 18 hr. The dark reaction mixture was filtered. The filtrate was evaporated *in vacuo.* The residual solid was recrystallized from petroleum ether to give colorless crystals of **34**, mp 81–82° (1.5 g, 87% yield based on **2**).

Anal. Calcd for $C_7H_6Br_4$: C, 20.5; H, 1.5; Br, 78.1. Found: C, 21.3; H, 1.3; Br, 77.6.

4,4,5,6-Tetrachlorotetracyclo[5.3.0.0^{2,10}.0^{3,8}]dec-5-ene (35). Tetrachlorocyclopropene (**1**) (1.5 g, 8.4 mmol), bicyclo[2.2.1]heptadiene (0.8 g, 8.7 mmol), and 2 ml of CCl_4 were heated in a sealed tube over a steam bath for 3 days. The volatile materials were removed *in vacuo.* The remaining solid was recrystallized from petroleum ether to give colorless crystals of **35**, mp 62–63° (1.8 g, 79% yield).

Anal. Calcd for $C_{10}H_8Cl_4$: C, 44.5; H, 3.0; Cl, 52.6. Found: C, 44.4; H, 3.0; Cl, 52.4.

4,6-Dichloro-5,5-difluoropentacyclo[5.3.0.0^{2,10}.0^{3,8}.0^{4,6}]decane (36). 1,2-Dichloro-3,3-difluorocyclopropene (**23**) (1.5 g, 10.3 mmol), bicyclo[2.2.1]heptadiene (1 g, 11 mmol), and 2 ml of CCl_4 were heated in a sealed tube over a steam bath for 2 days. The reaction mixture was filtered and the filtrate evaporated *in vacuo.* The residue was short-path vacuum distilled (pot temperature, *ca.* 100°) to give a colorless liquid, **36** (0.8 g, 33% yield).

Anal. Calcd for $C_{10}H_8Cl_2F_2$: C, 50.7; H, 3.4; Cl, 29.9. Found: C, 51.0; H, 3.6; Cl, 30.0.

Relative Reactivity of Tetrahalocyclopropenes. A mixture of two different cyclopropenes, typically 6 mmol each, a deficient amount of furan (usually in the ratio 3:3:1), and an equal volume of CCl_4 were heated in a sealed tube at 79 ± 1° for 18 hr. The reaction mixtures were filtered and concentrated by flashing off part of the volatiles. The product ratios were then determined by either H^1 nmr or F^{19} nmr or both. The nmr's of the concentrates showed *exclusively* peaks characteristic of unreacted starting materials and Diels–Alder adducts or their bicyclic rearrangement products. The reaction rate ratios were calculated using the expression $k_a/k_b = P_aC_b/P_bC_a$, where P is the mole per cent of the product and C is the initial mole per cent of the cyclopropene.[16] Competition experiments in which the cyclopropene–furan ratio was increased to 10:10:1 gave relative rate data entirely comparable to that shown in Table III.

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(16) See von E. Doering and Henderson, footnote *a*, Table III.