Experimental

Materials.—All the materials were reagent grade, freshly distilled with care taken to separate water in the forerun as an azeotrope. Benzyl isocyanide was prepared by the method of Corey[18] from benzylformamide; b.p. 92° (10 mm.),[19] strong infrared band at 2140 cm.$^{-1}$ characteristics of isocyanides.

Infrared Spectra.—Most of the spectra were measured on a Perkin–Elmer model 21 using a lithium fluoride prism under high resolution conditions with a chart speed of 10 inches/micron. Either 0.1-mm. or 1-mm. NaCl cells were used to maintain absorbances of about 0.2 to 0.7. Intensities were reproducible to about ±2%; wave numbers were reproducible to about ±3 cm.$^{-1}$, recording the water vapor band at 3566 cm.$^{-1}$ as an internal reference[20] for each critical spectrum. All measurements were made at 26 ± 1.0°.

The solutions were prepared using calibrated pipets and volumetric flasks. The *n*-amyl alcohol concentration was either 0.25 or 0.50 volume % introduced, for accuracy, as a more concentrated solution in carbon tetrachloride. The base concentrations varied from 20 to 60 volume %, the remainder being carbon tetrachloride. The solutions used in the reference beam were identical with the sample except that alcohol was omitted.

N.m.r. Spectra.—The n.m.r. spectra were measured using a Varian A-60. All n.m.r. values quoted are relative to tetramethylsilane at 60 mc./sec. Most runs were at room temperatures. The runs quoted at 0 and 55° were made with the samples initially at these temperatures but reverting slowly to room temperature while spectra were hastily determined.

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[18] W. R. Hertler and E. J. Corey, *J. Org. Chem.*, **23**, 1221 (1958).

[19] I. Ugi and R. Meyr, *Ber.*, **93**, 239 (1960).

[20] A. R. Downie, M. C. Magoon, T. Purcell and B. Crawford, Jr. *J. Opt. Soc. Am.*, **43**, 941 (1953).

[Contribution from the Department of Chemistry, Purdue University, Lafayette, Ind.]

Nucleophilic Displacement Reactions of Polyhalogenated Cyclopentadienes and Cyclopentenes. I[1,2]

By E. T. McBee, D. L. Crain, R. D. Crain, L. R. Belohlav and H. P. Braendlin

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The reaction of hexachlorocyclopentadiene with methanolic base has been studied. The bimolecular reaction, first order both in halide and in base, led to the formation of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene exclusively. No monomethoxy derivative was obtained. Further reaction with base yielded 1,2,3-trichloro-4,5,5-trimethoxycyclopentadiene which, upon isolation and continued exposure to base, underwent two simultaneous reactions to give 1,2,5-trichloro-3,3,4,4-tetramethoxycyclopentene and a compound believed to be 1,4,5,5-tetramethoxy-2,3-dichlorocyclopentadiene. Octachlorocyclopentene reacted with methanolic base to give 1,2,4,4,5,5-hexachloro-3,3-dimethoxycyclopentene. The product did not undergo further substitution, whereas the isomeric 1,2,3,3,5,5-hexachloro-4,4-dimethoxycyclopentene yielded 1,2,4,4-tetrachloro-3,3,5,5-tetramethoxycyclopentene. The reaction of 1-methoxy-2-chloro-3,3,4,4,5,5-hexafluorocyclopentene with base gave mainly 1,3,3-trimethoxy-2-chloro-4,4,5,5-tetrafluorocyclopentene and a dimethoxy derivative believed to be 1,4,4,5,5-pentafluoro-2-chloro-3,3-dimethoxycyclopentene. Mechanistic aspects of these nucleophilic displacement reactions are discussed.

Reaction of hexachlorocyclopentadiene (I) with alcoholate or thiolate ion is known to give ketals[3] or thioketals[4] of 2,3,4,5-tetrachlorocyclopentadienone. However, beyond subjection of the products to subsequent reactions of different nature, no extensions or elucidations of this remarkable reactivity have been reported in the literature, and a closer investigation was attempted.

Results.—The reaction of I with equimolar quantities of potassium hydroxide in methanol, both at reflux and in the cold, gave II exclusively, with recovery of nearly 50% of I. Vapor phase chromatography of the reaction mixture showed the presence of I and II only. No intermediate, such as a monomethoxy derivative, $C_5Cl_5OCH_3$, could be detected. A kinetic investigation revealed the rate-determining step to be bimolecular in the cold, first order both in I and in base. Hence, the second chlorine atom is displaced in a fast step, unmeasurable by comparison with the first displacement. The ketal II, after further reaction with base, yielded the trimethoxy compound III which, after isolation and continued exposure to methoxide ion, underwent two simultaneous reactions. The main product isolated, resulting from alcohol addition, was the tetramethoxytrichlorocyclopentene IV, whose structure was proved by hydrolysis to the known[5] 3,4,5-trichloro-3-cyclopentene-1,2-dione (VI); nucleophilic displacement of chlorine in III yielded a tetramethoxy derivative to which the diene structure V was assigned. The reaction III → IV is base catalyzed; no reaction occurred on treating III with refluxing methanol in the absence of base. The sequence may be compared to the base-catalyzed addition of ethanol to ethoxyacetylene, where the only product isolated was ethyl orthoacetate.[6]

The trimethoxy derivative III gave 1:1 adducts with styrene and maleic anhydride and its ultraviolet spectrum showed characteristic absorption of a cyclopentadiene derivative: λ_{max} 310 mμ, log ϵ 3.282 (*viz.* for I: λ_{max} 322 mμ, log ϵ 3.170[7]; for II: λ_{max} 307 mμ, log ϵ 3.412). The ultraviolet spectrum of IV was consistent with that of a cyclopentene structure, λ_{max} 212 mμ, log ϵ 3.916, whereas

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[1] Part of a paper presented by E. T. McBee, R. D. Crain, D. L. Crain, J. O. Stoffer, L. R. Belohlav and H. P. Braendlin, 137th Meeting, Am. Chem. Soc., Cleveland, O., April, 1960, p. 31-O.

[2] This paper is based in part on portions of the theses submitted by Ronald D. Crain and Donald L. Crain to the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

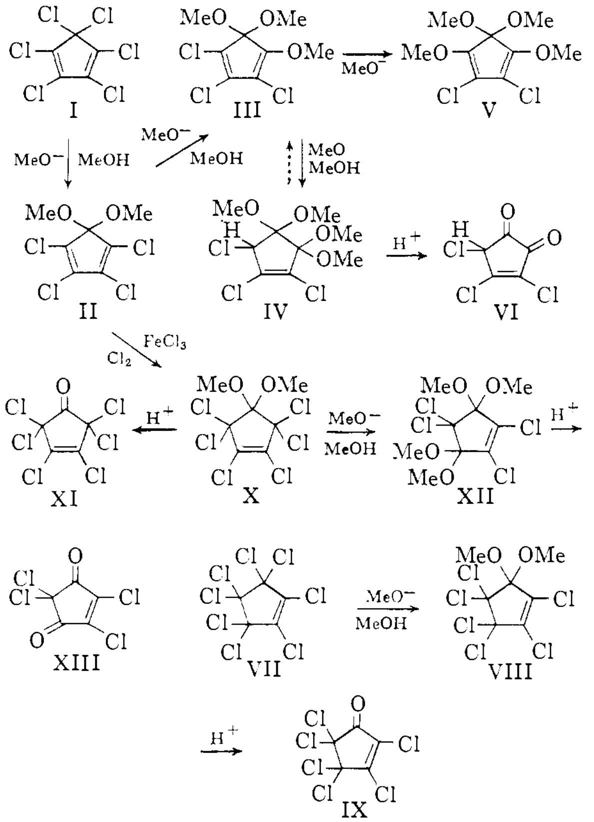
[3] (a) J. A. Krynitsky and R. W. Bost, *J. Am. Chem. Soc.*, **69**, 1918 (1947); (b) J. S. Newcomer and E. T. McBee, *ibid.*, **71**, 946, 952 (1949); (c) J. W. Dawson and W. J. Croxall, U. S. Patent 2,562,893 (1952); *C. A.*, **46**, 1587 (1952).

[4] E. P. Ordas, U. S. Patent 2,697,102 (1954); *C. A.*, **49**, 15956 (1955).

[5] H. J. Prins, *Rec. trav. chim.*, **65**, 455 (1946).

[6] H. C. Volger and J. F. Arens, *ibid.*, **76**, 847 (1957).

[7] E. T. McBee, J. D. Idol, Jr., and C. W. Roberts, *J. Am. Chem. Soc.*, **77**, 4375 (1955).

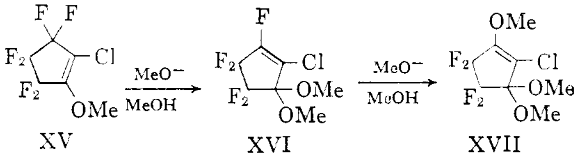


V again showed cyclopentadiene absorption, λ_{max} 304 mμ, log ϵ 3.242. Of interest is the shift of the double bond absorption to shorter wave lengths in the infrared: for I, with two —CCl=CCl— units, the double bond absorptions were at 6.17 and 6.30 μ; for II, also with two —CCl=CCl— units, at 6.20 and 6.32 μ; however; for III, with one —CCl=CCl— and one —CCl=COR— unit, they were found at 6.20 and 6.05 μ; V absorbed at 6.10 and 5.96 μ; the absorption shifts of both double bonds constitute support for the presence of two —CCl=COR— units, as anticipated in V.[8]

Octachlorocyclopentene (VII) was converted in methanolic base to 1,2,4,4,5,5-hexachloro-3,3-dimethoxycyclopentene (VIII), whose structure was proved by hydrolysis to the known[9] ketone IX. The ketal VIII did not react further on vigorous treatment with base for 48 hours. On the other hand, 1,2,3,3,5,5-hexachloro-4,4-dimethoxycyclopentene (X), isomeric to VIII, which was prepared by chlorination of II with ferric chloride catalyst[10] and identified by hydrolysis to the known[11] ketone XI, readily reacted with methanolic base to give the tetramethoxy derivative XII, whose structure was proved by hydrolysis to the known[11] diketone XIII.

1,2-Dichloroperfluorocyclopentene is known[12] to react rapidly with alcoholic base, yielding monoalkoxy and, on further treatment, trialkoxy derivatives. With careful addition of methoxide ion to the monomethoxy derivative XV, we succeeded in isolating a dimethoxychloropentafluorocyclopentene. The latter upon further reaction yielded the trimethoxy derivative which is usually obtained on treatment of XV and to which the structure XVII has been assigned.[12c]

For the dimethoxy compound the only reasonably possible structures are that of 1,4,4,5,5-pentafluoro-2-chloro-3 3-dimethoxycyclopentene (XVI) or of 1-chloro-2,5-dimethoxy- and 1-chloro-2,3-dimethoxypentafluorocyclopentene, both α-fluoroethers. Little is known about the latter type of compound and no decision can be made about stability in base.[13] However, good supporting evidence for structure XVI was obtained from infrared spectral data. The double bond absorptions of XV and XVII were observed at 6.00 and 6.02 μ, respectively, *i.e.*, in the region of —CCl=COR absorption. The dimethoxy derivative XVI, on the other hand, absorbed at 5.87 μ: this shift to a shorter wave length cannot be explained by the α-fluoroether structures, but agrees with what would be expected from the —CCl=CF— unit.[14] Moreover, XVI can be readily visualized as a precursor to XVII, since nucleophilic displacement of vinyl fluorine is known to occur quite easily.[15]



Discussion.—Bimolecular nucleophilic displacement of chlorine in I can occur on three positions, carbon atoms 1, 2 and 5, of the cyclopentadiene nucleus. Attack on the "5"-position, the direct displacement of an allylic chlorine atom by an S_N2 mechanism, is unlikely due to the excessive crowding the molecule would be subjected to in the transition state. The inability of VIII to react further is in agreement with this supposition. If displacement took place on one of the two allylic centers in VII, the other should react also, with the reasonable assumption that the dimethoxy-

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[8] Attempts to prepare a Diels–Alder adduct of V with maleic anhydride led to the loss of carbon monoxide and the formation of an unidentified solid. Upon standing, V decomposed to give a dark liquid with a pungent odor.

[9] E. B. Towne and H. M. Hill, U. S. Patent 2,588,977 (1952); *C. A.*, **46**, 4728 (1952).

[10] Chlorination of II under actinic light gave a product, $C_7H_4O_2Cl_8$ (XIV), which hydrolyzed to the ketone XI. Hence, XIV is a ketal of XI wherein two methoxy hydrogen atoms are substituted by chlorine. Based on results obtained in the chlorination of ethers (E. M. Letterscheid, *Ann.*, **330**, 114 (1903), and H. S. Booth, U. S. Patent 2,066,905 (1937); *C. A.*, **31**, 1037 (1937)) the two additional chlorine atoms are assumed to be situated on one methyl group each.

[11] J. S. Newcomer, U. S. Patent 2,722,497 (1955); *C. A.*, **50**, 8128 (1956).

[12] (a) A. L. Henne and K. A. Latif, *J. Indian Chem. Soc.*, **30**, 809 (1953); (b) R. A. Shepare, H. Lessoff, J. D. Domijan, D. B. Hilton and T. F. Finnegan, *J. Org. Chem.*, **23**, 2011 (1958); (c) C. O. Parker, *J. Am. Chem. Soc.*, **81**, 2183 (1959).

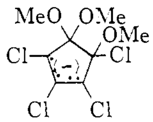
[13] Hydrolysis of XVI with 85% sulfuric acid gave a material difficult to purify. Much inorganic fluorine was detected; hence, reaction went beyond ketal hydrolysis and thus was unsuitable for structural elucidation.

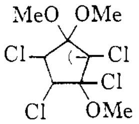
[14] The only 1,2-chlorofluoroethylenic absorptions apparently reported in the literature are those of 1-chloro-2-fluoropropenes, with bands in the 5.9 μ region (L. F. Hatch and D. W. McDonald, *J. Am. Chem. Soc.*, **74**, 2911 (1952).

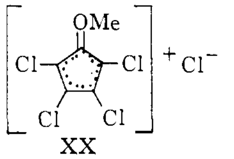
[15] (a) J. T. Barr, K. E. Rapp, R. L. Pruett, C. T. Bahner, J. D. Gibson and R. H. Lafferty, *ibid.*, **72**, 4480 (1950); (b) E. F. Silversmith and J. D. Roberts, *ibid.*, **80**, 4083 (1959); (c) E. F. Silversmith and D. Smith, *J. Org. Chem.*, **23**, 427 (1958); (d) A. T. Blomquist and E. A. LaLancette, Abstracts of Papers, 135th Meeting, Am. Chem. Soc., Boston, Mass., April, 1959, p. 54-O.

methylene group in VIII does not deactivate the remaining allylic dichloromethylene group. This points to the vinyl positions as centers of attack. That vinyl attack can take place in these systems was evident from the reactivities of II, III and X.

The conversion of II to III constitutes nucleophilic displacement of vinyl chlorine by base. This type of reaction is not uncommon in polyhalogenated systems where chlorine is situated either at the extremity of a conjugated diene,[16] or adjacent to an allylic difluoromethylene group.[12,17] In view of the inertness[18] otherwise displayed by vinyl chlorine toward base, these results may be explained by the following. In contrast to aliphatic bimolecular nucleophilic displacement reactions, aromatic and vinyl SN2 reactions can proceed by an alternate one-step mechanism, wherein the rate is controlled by the formation of a discrete intermediate. Rate control by bond forming increases when k_{-1} is negligible in comparison to k_2 in the equation, $Y^- + R\text{-}X \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [Y\text{-}R\text{-}X]^- \xrightarrow{k_2} R\text{-}Y + X^-$. In reactions of this type the affinity for nucleophiles, of the species undergoing displacement, is of major importance, rather than the polarizability of the leaving group.[19] This rate control by bond forming is then dependent on the relative stability of the charged intermediate, which thus would be the driving force of the reaction. Such increase in intermediate stability may be achieved by charge distribution and/or by imparting a partial positive charge on the allylic carbon atom with an electron-withdrawing substituent. In the case of cyclic 1,2-dichloroperfluoroalkenes, electron withdrawal by the inductive effect and by hyperconjugation of allylic fluorine[20] probably has a twofold effect: reduction of electron density at the double bond, promoting attack of the nucleophile, and stabilization of the intermediate. In the case of II, there are two types of vinyl chlorine atoms susceptible to displacement, giving rise to either of the charged intermediates XVIII or XIX. Following the reasoning above, however, it can be seen that XVIII would be favored because of additional charge distribution. Hence, the formation of III from II is not surprising. Moreover, the assignment of structure V to the tetramethoxydichlorocyclopentadiene isolated subsequently would then appear logical. The formation of V, in addition to IV, may be due to nearly equal reactivity of the two extreme diene centers in III or to reversibility of reaction III ⇄ IV, permitting reaction III → V to take place.


XVIII


XIX


XX

The ketal X can form the diketal XII only on nucleophilic displacement with allylic shift. This would also be necessary to explain the formation of II from I if, as expected, a vinyl position is involved in the reaction.[21] In a recent publication, Roberts and co-workers have demonstrated such vinyl attack with allylic shift in a similarly reactive cyclobutene.[22]

Regardless of the manner with which the first chlorine atom in I undergoes bimolecular displacement, the rapidity of the second displacement step would be plausible because any intermediate of the formula cyclo-C_5Cl_5OMe is subject to unimolecular exchange of allylic chlorine *via* a carbonium ion, XX, in which the methoxy group provides additional resonance stabilization. The extreme sensitivity of, for instance, α-chloroethers to base is well known.[23]

Experimental[24]

Rate of Reaction between Hexachlorocyclopentadiene (I) and Sodium Methoxide in Methanol.—A solution of I (0.04 *N*, purified by chromatography on an acid-washed alumina column and subsequent distillation) in 50 ml. of dry methanol was placed in a 150-ml. stoppered round-bottomed flask and immersed in a constant temperature bath kept at 17.0 ± 0.1°. After approximately 30 min., 50 ml. of a solution of sodium methoxide in methanol, chilled to about 10°, was added. Samples (5 ml.) of the combined solution were removed at zero time, to establish the initial base concentration, and after given intervals. They were placed in chilled erlenmeyer flasks and titrated with dilute hydrochloric acid (2.9×10^{-3} *N*), with phenolphthalein indicator.

Table I lists a typical set of data from one run, with a = initial concentration of I, b = concentration of base, Δb = amount of base consumed after time t, and the amount of II formed = $x = \Delta b/2$. The rate was defined by the equation $dx/dt = k(a - x)(b - 2x)$ and the second-order constant k calculated from the integral $k = 1/t(2a - b) \times \ln [b(a-x)/a(b - 2x)]$, in liter mole^{-1} sec.$^{-1}$.

Table II lists the average rate constants with their standard deviations obtained from five runs, wherein 70% reaction of halide, on one extreme, and 78% reaction of base, on the other, are represented, with initial halide:base concentrations of 1:3, 2:3, 1:1, 2:1 and 3:1, approximately. The

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[16] A. Roedig and P. Bernemann, *Ann.*, **600**, 1 (1956).

[17] (a) J. D. Park, C. M. Snow and J. R. Lacher, *J. Am. Chem. Soc.*, **73**, 2342 (1951); (b) E. T. McBee, D. K. Smith and H. E. Ungnade, *ibid.*, **77**, 387 (1955); (c) W. T. Miller, Jr., and J. Fried, Abstracts of Papers, 132nd Meeting, Am. Chem. Soc., New York, N. Y., September, 1957, p. 29-M.

[18] This excludes elimination–addition reactions promoted by vicinal hydrogen.

[19] (a) C. W. L. Bevan, *J. Chem. Soc.*, 2340 (1951); (b) G. S. Hammond and L. R. Parks, *J. Am. Chem. Soc.*, **77**, 340 (1955); (c) J. D. Loudon and T. D. Robson, *J. Chem. Soc.*, 242 (1937).

[20] (a) J. D. Roberts, R. L. Webb and E. A. McElhill, *J. Am. Chem. Soc.*, **72**, 408 (1950); (b) A. L. Henne and S. Kaye, *ibid.*, **72**, 3369 (1950); (c) R. N. Haszeldine, *J. Chem. Soc.*, 3559 (1953).

[21] Examples of abnormal SN2 reactions are known: (a) M. M. Runde, E. W. Scott and J. R. Johnson, *J. Am. Chem. Soc.*, **52**, 1284 (1930); (b) T. Reichstein, *Ber.*, **63**, 749 (1930); (c) T. Reichstein and G. Trivelli, *Helv. Chim. Acta*, **15**, 254 (1932); (d) E. L. Eliel and P. E. Peckham, *J. Am. Chem. Soc.*, **72**, 1209 (1950); (e) M. J. Kland-English and C. L. Wilson, Abstract of Papers, 119th Meeting, Am. Chem. Soc., New York, N. Y., April, 1951, p. 48-M; (f) O. Moldenhauer, G. Trautmann and R. Pfluger, *Ann.*, **583**, 61 (1953).

[22] Y. Kitahara, M. C. Caserio, F. Scardiglia and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 3106 (1960).

[23] (a) M. F. Shostakovskii and F. P. Sidel'kavoskaya, *Zhur. Obshchei Khim.*, **20**, 620 (1950); (b) C. T. Mason, C. W. R. Wade and H. W. Pouncy, *J. Am. Chem. Soc.*, **76**, 2255 (1954); (c) P. Ballinger P. B. D. de la Mare, G. Kohnstam and B. M. Pruett, *J. Chem. Soc.*, 3641 (1955).

[24] Analyses were performed by Dr. C. S. Yeh, Purdue University. Miss Marjory Haley and Mrs. W. Dilling, Purdue University, furnished the infrared spectra, using a Perkin-Elmer recording infrared spectrophotometer, model 21. Ultraviolet spectra were determined with a Cary recording spectrophotometer with ethanol as solvent. Vapor phase chromatography was accomplished with a Perkin-Elmer model 154-B fractometer, containing a Celite-C column; a Leeds and Northrup Speedomax type G recorder was used. All melting points and boiling points are uncorrected.

TABLE I

THE KINETICS OF THE REACTION C_5Cl_6 (I) + $2MeO^- \rightarrow C_5Cl_4(OMe)_2$ (II) IN METHANOL AT 17.0 ± 0.1°

Time, sec. $\times 10^2$	Base concn. $b \times 10^{-5}$	Base concn. $\Delta b \times 10^{-5}$	Concn. of II, $x \times 10^{-5}$	$k \times 10^{-4}$
0	3248			
36	3084	164	82	3.57
72	2946	304	152	3.57
108	2822	426	213	3.44
144	2692	556	278	3.53
180	2566	682	341	3.62
216	2474	774	387	3.52
288	2300	948	474	3.45
360	2090	1158	579	3.67
432	1952	1296	648	3.62
504	1856	1392	696	3.48
864	1358	1890	945	3.59
1008	1204	2004	1002	3.49
1152	1128	2120	1060	3.50

Initial concn. of $C_5Cl_6 = 2 \times 10^{-2}$ k_{av} 3.55 ± 0.08

amounts of base consumed at 72×10^2 sec. in any two runs listed consecutively, constituting less than 10% of initial base concentration in each case, were used to calculate the order in base according to the formula $n = \log(x_1/x_2)/\log(b_1/b_2)$.[25]

TABLE II

SUMMARY KINETICS FROM FIVE RUNS OF THE REACTION C_5Cl_6 (I) + $2MeO^- \rightarrow C_5Cl_4(OMe)_2$ (II) IN METHANOL AT 17.0 ± 0.1°

Init. base concn. $\times 10^{-5}$	% Reaction of C_5Cl_6	base	At sec. $\times 10^2$	k_{av}, l. mole^{-1} sec.$^{-1}$ $\times 10^{-4}$	Order in Base n
6224	70	45	864	3.57 ± 0.07	
3248	53	65	1152	3.55 ± .08	1.004
2109	36	69	1152	3.46 ± .10	0.993
0927	18	78	1152	3.53 ± .16	1.001
0656	12	70	864	3.44 ± .14	0.979

Initial concn. of C_5Cl_6 =
2×10^{-2} (mean) k_{av} 3.51 ± 0.11 n_{av} 0.994

1,2,3,4-Tetrachloro-5,5-dimethoxycyclopentadiene (II).—A solution of potassium hydroxide (448 g., 8.0 moles) in 1200 ml. of methanol was added dropwise to a solution of I (819 g., 3.0 moles) in 1500 ml. of methanol. The base was added rapidly at first until the reaction mixture was at gentle reflux. The temperature was maintained at reflux by controlling the rate of base addition. On complete addition, the mixture was stirred for 12 hr. without heating. The salt (487 g.) was filtered, 2 l. of methanol was distilled from the filtrate and the remainder poured into water. The crude product was washed with water and dried over anhydrous calcium sulfate. Distillation gave 512.4 g., b.p. 82–84° (2 mm.), of a pale yellow liquid which was diluted with 250 ml. of dry methanol and cooled on Dry Ice until crystals formed. Continued crystallization at −6° gave 454.6 g. of a colorless solid,[26] m.p. 27–28°. An additional 35.4 g. of product was obtained from the mother liquors. The product was then distilled at 82–83° (2 mm.) to remove traces of methanol and gave pure II, $n^{20}D$ 1.5250, total yield 62%.

Anal. Calcd. for $C_7H_6O_2Cl_4$: C, 31.84; H, 2.29; Cl, 53.71. Found: C, 31.76; H, 2.74; Cl, 53.59.

The reaction was repeated twice with 1.12 g. (0.02 mole) of potassium hydroxide and 5.46 g. (0.02 mole) of I in a total of 20 ml. of methanol, once under reflux as before, and the other time at 0° in an ice–salt-bath. Both crude products, washed and dried and subjected to vapor phase chromatography, revealed the presence of binary mixture of I and II only.

1,2,3-Trichloro-4,5,5-trimethoxycyclopentadiene (III).—A solution of potassium hydroxide (84.0 g., 1.5 moles) in 450 ml. of methanol was added dropwise to a stirred and refluxing solution of II (275.8 g., 1.05 moles) in 600 ml. of methanol. On complete addition, the mixture was stirred at reflux for 6 hr. The salt was filtered and the methanol distilled from the solution. The crude product was dried by azeotropic distillation with benzene. Vacuum rectification afforded 174.4 g. (79%) of colorless III, b.p. 102–103° (2.5 mm.), $n^{20}D$ 1.5170.

Anal. Calcd. for $C_8H_9O_3Cl_3$: C, 37.00; H, 3.47; Cl, 41.05. Found: C, 37.16; H, 3.56; Cl, 40.86.

Diels-Alder Adducts of III. 1. With Maleic Anhydride.—A solution of III (9.5 g., 0.37 mole) and maleic anhydride (4.0 g., 0.04 mole) in 40 ml. of benzene was heated at reflux while protected by a drying tube. After 20 hr., the solution was cooled and poured into 200 ml. of petroleum ether (90–100°). After concentration and cooling, 12.5 g. (95%) of crystalline 1,7,7-trimethoxy-4,5-trichlorobicyclo[2.2.1]-hept-5-ene-2,3-dicarboxylic acid anhydride was obtained, m.p. 163–165°.

Anal. Calcd. for $C_{12}H_{11}O_6Cl_3$: C, 40.03; H, 3.10; Cl, 29.79; neut. equiv., 178. Found: C, 40.07; H, 3.02; Cl, 29.68; neut. equiv., 181.

2. With Styrene.—A solution of III (66.1 g., 0.25 mole) and styrene (26.0 g., 0.25 mole) in 200 ml. of benzene was heated under reflux for 42 hr. Approximately 80 ml. of benzene was distilled from the mixture, the cooled remainder was carefully diluted with methanol until crystallization commenced (about 100 ml.), and methanol was added slowly as crystallization proceeded. The colorless adduct, 77.1 g., was filtered and dried, m.p. 137–139°. An additional 6.1 g. was recovered from the mother liquors; total yield 83%. Recrystallization from benzene–methanol raised the melting point to 139–140°.[27]

Anal. Calcd. for $C_{16}H_{17}O_3Cl_3$: C, 52.84; H, 4.98; Cl, 29.25. Found: C, 52.64; H, 4.79; Cl, 29.41.

Reaction of III with Potassium Methoxide.—A solution of potassium methoxide was prepared by dissolving potassium (14.9 g., 0.38 g. atom) in dry methanol (300 ml.). To this solution, III (91.7 g., 0.35 mole) in 200 ml. of methanol was added and the resulting solution stirred at reflux for 19 hr. under exclusion of moisture. The cooled reaction mixture was filtered and the salt (17.2 g.) washed with methanol. The methanol was evaporated, the residue dissolved in benzene and the resulting solution filtered. The benzene was evaporated and the residue subjected to vacuum distillation. A total of 74.4 g. was obtained, b.p. 97–104° (1 mm.); a residue of 8.0 g. remained in the flask. Rectification of the distillate at 1.5 mm. pressure through a 30 × 1 cm. column, packed with 2.3 mm. glass helices, gave 22.3 g. of starting material and a higher boiling distillate, b.p. 99–106° (1.5 mm.), consisting of mixed 1,2,5-trichloro-3,3,4,4-tetramethoxycyclopentene (IV) and 1,4,5,5-tetramethoxy-2,3-dichlorocyclopentadiene (V).

Compound IV could be isolated by treating the mixture with maleic anhydride to remove V. The unreacted IV was then purified by distillation and recrystallization. However, separation was more easily effected by seeding the mixture with IV and allowing it to stand at 20° for one week. The liquid was decanted from the solid and the latter recrystallized from pentane at −6° to give pure IV, m.p. 60–61°, total yield 20%.

Anal. Calcd. for $C_9H_{13}O_4Cl_3$: C, 37.06; H, 4.49; Cl, 36.48. Found: C, 36.83; H, 4.44; Cl, 36.60.

The decanted liquid solidified upon cooling to −6°. After nine recrystallizations from pentane, a 3.8-g. (5.6%) sample of pure V was obtained, m.p. 54–55°.

Anal. Calcd. for $C_9H_{12}O_4Cl_2$: C, 42.38; H, 4.74; Cl, 27.81. Found: C, 42.62; H, 5.00; Cl, 27.82.

Acid Hydrolysis of IV.—A solution of IV (10 g.) in concentrated sulfuric acid (40 ml.) was warmed on a steam-bath for 30 min. After cooling to 20°, the solution was poured onto crushed ice and the resulting mixture extracted with four 50-ml. portions of chloroform. The combined extracts

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(25) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd Ed., J. Wiley and Sons, Inc., New York, N. Y., 1961, p. 45.

(26) It is necessary to obtain $C_5Cl_4(OCH_3)_2$ as a colorless material. Subsequent reactions of II with methanolic potassium hydroxide will yield yellow colored products if this precaution is not taken.

(27) No attempts were made at elucidation of the adduct structure. Two isomers are possible, 2-phenyl- or 3-phenyl-1,7,7-trimethoxy-4,5,6-trichlorobicyclo[2.2.1]hept-5-ene.

were repeatedly washed with water until a violet color developed in the aqueous layer (Note: failure to do this causes difficulty in obtaining a pure product.) The chloroform was evaporated, the residue dissolved in 10 ml. of dry methylene chloride and the solution carefully diluted with pentane. The product crystallized slowly and after 24 hr. was filtered and dried, m.p. 58–59°. One recrystallization from the same solvent system raised the melting point to 68–69°. Admixture of authentic 3,4,5-trichloro-3-cyclopentene-1,2-dione (VI) showed no depression; also, the infrared spectra of prepared and authentic material were superimposable.

1,2,4,4,5,5-Hexachloro-3,3-dimethoxycyclopentene (VIII). A solution of 145.6 g. (2.6 moles) of potassium hydroxide in 500 ml. of methanol was added dropwise, with stirring, to a refluxing solution of VII (344 g., 1.0 mole) in 1 l. of methanol. The addition was completed in 2 hr. and the mixture refluxed for a total of 12 hr. The solution was poured into water and the organic layer separated and washed twice with water. The solid was dissolved in methanol, the solution treated with charcoal, filtered, and the filtrate cooled to give 210 g. of white crystalline VIII, m.p. 41–42°. After concentration of the mother liquor to half its volume and cooling, an additional 50 g. of product was obtained; total yield 78%.

Anal. Calcd. for $C_7H_6O_2Cl_6$: C, 25.11; H, 1.81; Cl, 63.53. Found: C, 24.92; H, 2.04; Cl, 63.83.

Acid Hydrolysis of VIII.—A mixture of VIII (30 g., 0.087 mole) and 30 ml. of concentrated sulfuric acid was stirred for 40 min. at 45°, poured onto crushed ice and extracted with 100 ml. of ether. The ether solution was washed with water until the water was neutral to litmus. After drying over Drierite, the ether was removed and pentane added. After cooling on Dry Ice, 22.2 g. of white 2,3,4,4,5,5-hexachlorocyclopentenone (IX), m.p. 27–28°, was obtained. The solvent was completely removed under reduced pressure and the residue crystallized from pentane to give an additional 1.5 g. of the product; total yield 94%.

1,2,3,3,5,5-Hexachloro-4,4-dimethoxycyclopentene (X).—A mixture of II (200 g., 0.757 mole) and 0.2 g. of anhydrous ferric chloride was cooled to 0–5° in an ice-bath and chlorine was passed through a gas dispersion tube while stirring. A solid formed which was filtered after 2 hr. and washed with methanol to give 101.5 g. of X, m.p. 68.5–69°. After cooling of the mother liquor, an additional 40.2 g. of product was obtained; total yield 65%.

Anal. Calcd. for $C_7H_6O_2Cl_6$: C, 25.11; H, 1.81; Cl, 63.53. Found: C, 25.05; H, 2.08; Cl, 63.24.

Dilution of the methanol solution with water, extraction of the aqueous solution with pentane and distillation of the extract gave 73 g. of a material, b.p. 98–109° (1 mm.). This was fractionated to give 67.4 g. (24%) of VIII, b.p. 107–109° (1 mm.), n^{20}D 1.5445. Addition of a seed crystal resulted in solidification, m.p. 42°.

1,2,3,3,5,5-Hexachloro-4,4-bis-(chloromethoxy)-cyclopentene (XIV).—Through a solution of II (50 g., 0.189 mole) and 150 ml. of carbon tetrachloride, chlorine gas was passed *via* a gas dispersion tube for 2.5 hr. while irradiating with a 400 watt mercury vapor lamp. Excess chlorine was removed with solvent by distillation. Rapid distillation at 0.4 mm. and cooling of the distillate at −6° for 1 week gave a solid which was recrystallized from methanol to yield 5.2 g. (7%) of XIV, m.p. 57.5–58.5°.

Anal. Calcd. for $C_7H_4O_2Cl_8$: C. 20.82; H, 1.00; Cl, 70.25. Found: C, 20.89; H, 1.11; Cl, 70.50.

Acid Hydrolysis of X.—A mixture of X (10 g., 0.0298 mole) and 20 ml. of concentrated sulfuric acid was shaken for 20 min. at 70°. After pouring onto crushed ice and extracting with 50 ml. of ether, the ether solution was washed with water until the water was neutral to litmus and then dried over Drierite. The ether was removed and the residue crystallized from hexane to give a 37% yield of 2,2,3,4,5,5-hexachlorocyclopentenone (IX), m.p. 87.5–88.5°.

Acid Hydrolysis of XIV.—The above procedure was used for the hydrolysis of 3 g. of XI. The ketone had m.p. 87.5–88.5°.

1,2,4,4-Tetrachloro-3,3,5,5-tetramethoxycyclopentene (XII).—All equipment was dried by flaming under a stream of dry nitrogen. A solution of sodium (18.4 g. 0.8 g. atom) in 250 ml. of dry methanol was added dropwise to a stirred solution of X (100 g., 0.298 mole) in 200 ml. of methanol at reflux. After a total reflux time of 18 hr. and removal of *ca.* 200 ml. of methanol by distillation, water was added and the precipitate filtered on a sintered glass funnel. After washing thoroughly with water, the solid was dried in a vacuum desiccator to give 89.6 g. of XII, m.p. 94–98°. Recrystallization from hexane gave 62.5 g. (64%) of pure product, m.p. 108–109.

Anal. Calcd. for $C_9H_{12}O_4Cl_4$: C, 33.15; H, 3.71; Cl, 43.51. Found: C, 33.30; H, 3.50; Cl, 43.42.

Acid Hydrolysis of XII.—A mixture of XII (10 g., 0.03 mole) and 20 ml. of concentrated sulfuric acid was shaken for 20 min. on a steam-bath. After pouring onto crushed ice and extracting with ether, the ether solution was washed with water until the water was neutral to litmus. After drying with Drierite and removal of ether the residue was crystallized from hexane to give 5.1 g. of 2,3,5,5-tetrachloro-2-cyclopentene-1,4-dione (XIII), m.p. 65–66°. After concentration of the mother liquor and cooling, an additional 0.8 g. of the product was obtained; total yield 84%. No depression of melting point was observed on admixture of an authentic sample of XIII.

Reaction of 1-Methoxy-2-chloro-3,3,4,4,5,5-hexafluorocyclopentene (XV) with Potassium Hydroxide in Methanol.—A solution of XV (100 g., 0.41 mole), prepared according to the procedure of Henne and Latif,[13a] in 200 ml. of methanol was cooled to 5–10° in an ice-water-bath. A solution of potassium hydroxide (22.4 g., 0.40 mole) in 200 ml. of methanol was added dropwise, with stirring, over a period of 5 hr. After continued stirring in the cold for 3 hr., the mixture was poured into water, the organic portion washed twice with water and the aqueous portions extracted with ether. The combined organic portions were dried over Drierite and the solvent removed. Distillation of the residue gave, in addition to 1,3,3-trimethoxy-2-chloro-4,4,5,5-tetrafluorocyclopentene (XVII) and starting material XV, two fractions, b.p. 51–53° (17 mm.) (6.0 g.) and b.p. 53° (17 mm.) (4.7 g.), respectively. Vapor phase chromatography revealed the first fraction to contain 10% XV and 90% 1,4,4,5,5-pentafluoro-2-chloro-3,3-dimethoxycyclopentene (XVI) and the second fraction to be pure XVI.

Anal. Calcd. for $C_7H_6O_2ClF_5$: C, 33.28; H, 2.40; Cl, 14.04. Found: C, 33.06; H, 2.65; Cl, 13.75.

1,3,3-Trimethoxy-2-chloro-4,4,5,5-tetrafluorocyclopentene (XVII).—A solution of XVI (5 g., 0.02 mole), 2.24 g. (0.04 mole) of potassium hydroxide and 20 ml. of methanol was refluxed on the steam-bath for 15 min. and then allowed to stand at room temperature for 2 hr. After pouring into water and extracting with three 20-ml. portions of ether, the combined ether extracts were washed with water and dried over Drierite. The ether was evaporated and the residue distilled to give 4.9 g. (93%) of XVII, b.p. 97–98.5° (17 mm.), n^{20}D 1.4224.

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