Notes

Synthesis and Fragmentation Reactions of 7,7-Dimethoxy-1,2,3,4-Tetrachlorobenznorbornadiene. A Convenient Route to 7-Benznorbornenone

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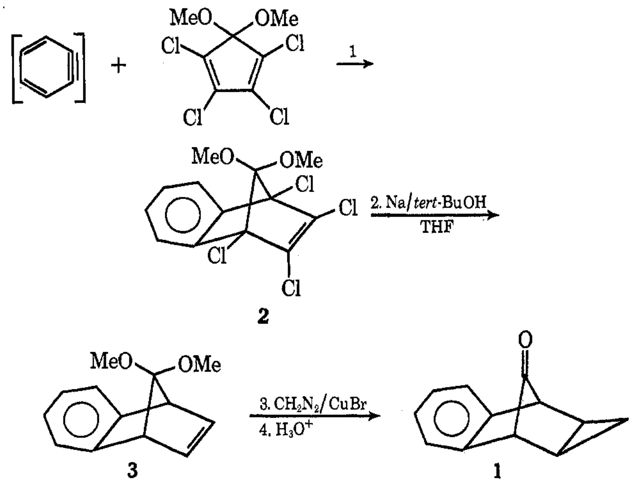
Current investigations in our laboratory of the homoconjugative reinforcing effects of favorably disposed cyclopropyl groups have required the facile synthesis of benznorbornadiene derivatives bearing oxygenated substituents at the bridge carbon. Previous work[2] utilizing the Cu(I)-catalyzed reaction of benzoyl peroxide or *tert*-butyl perbenzoate with benznorbornadiene afforded such derivatives, albeit not without difficulties. The reaction sequence illustrated in Scheme I appeared to offer an attractive alternative approach to the tricyclo[3.2.1.0^{2,4}]octenone **1**,[3] and this report describes the initial results of an attempted application of this synthetic scheme (steps 1 and 2) as well as some interesting thermal and electron impact induced fragmentations of 7,7-dimethoxy-1,2,3,4-tetrachlorobenznorbornadiene (**2**).

Scheme I



The adduction of benzyne with 5,5-dimethoxy-1,2,3,-4-tetrachlorocyclopentadiene[4] afforded adduct **2** in 49% yield.[5] Mass spectral examination (70 eV) of **2** failed to reveal a molecular ion (*m/e* 338); however, an intense peak (base peak) was observed at *m/e* 303 corresponding to the loss of chloride. The isotopic peak ratios (*m/e* 305, 307, and 309) were in accord with that predicted for a fragment ion containing three chlorine atoms. The remaining fragment ions of major interest and their relative abundance are recorded in Table I.

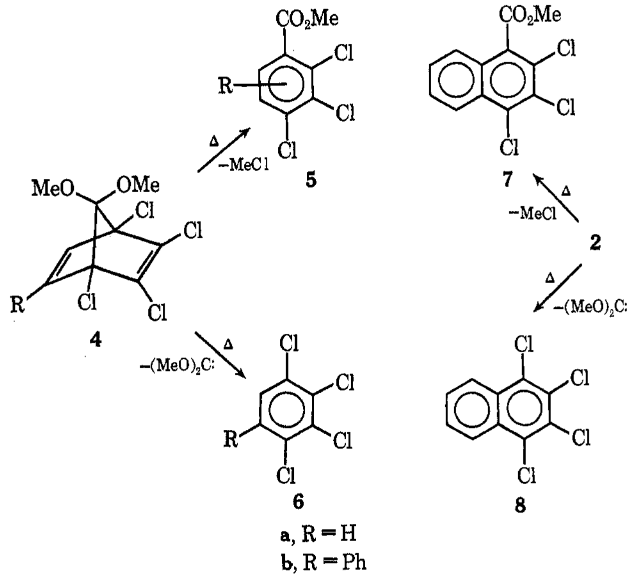
Table I

Relative Abundances of the Major Ions in the Mass Spectra (70 eV) of **2** and **4a**

	2		**4a**	
Ion	*m/e*	Relative abundance	*m/e*	Relative abundance
M$^+$ − Cl	303	100	253	100
M$^+$ − CH$_3$Cl	288	15	238	3
M$^+$ − C$_3$H$_6$O$_2$	264	20	214	8
M$^+$ − C$_2$H$_6$O$_2$Cl	257	43	207	100
M$^+$ − C$_3$H$_6$O$_2$Cl	229	17	179	28
C$_2$H$_3$O$_2$	59	30	59	100

The facile loss of chloride from **2** on electron impact appears related mechanistically to thermal fragmentation of the chlorinated norbornadienone ketals **4a**[6] and **4b**[7,8] to the corresponding trichlorobenzoates **5a** and **5b** and methyl chloride (Scheme II). Furthermore, on electron impact ketal **4a** displays an identical assortment of fragment ions (Table I) with the highest mass ion (*m/e* 253, base peak) again formed by loss of chloride. On this basis we formulate the M − 35 ion from **2** as the trichloroaryldimethoxycarbinyl cation a as shown in Scheme III.[9] Subsequent loss of dimethyl

Scheme II



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[1] (a) National Science Foundation Cooperative Predoctoral Fellow, 1966–1970; (b) Alfred P. Sloan Foundation Fellow.

[2] M. E. Brennan and M. A. Battiste, *J. Org. Chem.*, **33**, 324 (1968).

[3] M. A. Battiste and M. E. Brennan, *Tetrahedron Lett.*, 5857 (1966).

[4] J. S. Newcomer and E. T. McBee, *J. Amer. Chem. Soc.*, **71**, 946 (1949).

[5] See J. W. Wilt and E. Vasiliauskas, *J. Org. Chem.*, **35**, 2410 (1970), for a similar preparation of **2** reported while our study was in progress.

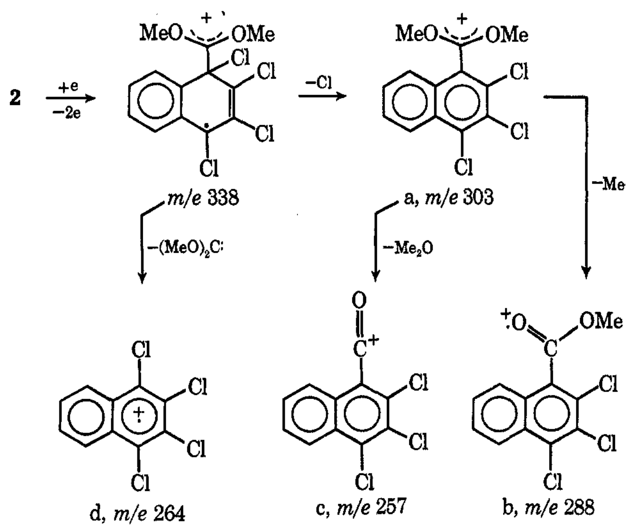
[6] K. McKenzie, *J. Chem. Soc.*, 5710 (1964).

[7] R. W. Hoffman and H. Hauser, *Tetrahedron Lett.*, 197 (1964).

[8] (a) D. M. Lemal, E. P. Gosselink, and A. Ault, *ibid.*, 579, (1964); (b) D. M. Lemal, E. P. Gosselink, and S. D. McGregor, *J. Amer. Chem. Soc.*, **88**, 582 (1966).

[9] Since the molecular ion of **2** was unobserved it is perhaps unreasonable to discuss the structure of this ion, as loss of chloride or dimethoxycarbene may be nearly simultaneous with electron impact. It is therefore purely for the sake of convenience that we represent the structure of this ion in Scheme III as that of the bridge-opened cation radical.

SCHEME III



ether or methyl from this ion leads to ions b (*m/e* 288) and c (*m/e* 257) respectively. Similar structures may be accorded to fragment ions *m/e* 253, *m/e* 238, and *m/e* 207 analogously derived from **4a**.

Complete scission of the dimethoxymethano bridge on electron impact is seen to be a relatively less important process than chloride loss at least for the annelated ketal **2**. Though the $M^+ - C_3H_6O_2$ ion from **4a** is even less intense than that from **2** the larger intensity for the *m/e* 59 ion, presumably derived from the bridge fragment, complicates the picture for **4a**, while suggesting that bridge scission and chloride loss from the molecular ion (*m/e* 288) are competitive. The latter conclusion compares favorably with the reported[6] product distribution (Table II) from thermal decomposition (85°) of neat **4a**. By varying the solvent polarity, however, either process, extrusion of dimethoxycarbene or loss of methyl chloride, may become the predominant reaction course[10] as clearly revealed by the two entries for **4b** in Table II.

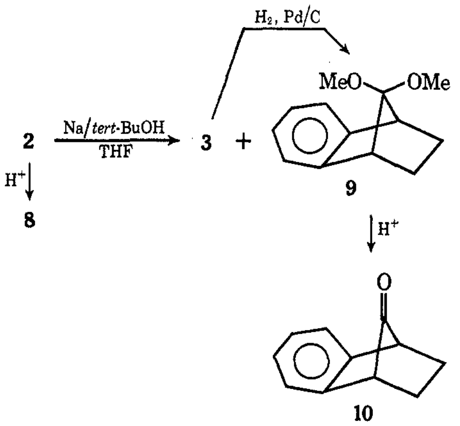
TABLE II
AROMATIZATION OF SOME 7-NORBORNADIENONE KETALS.
PRODUCT DISTRIBUTION

Ketal	Solvent	T, °C	Rel wt % —aromatic products— Ester[a]	Chloro-aromatic[b]
4a[c]	Neat	85	56.7	43.3
4b[d]	Cyclohexane	145	7.1	92.9
4b[d]	Acetonitrile	115	87.5	12.5
2[e]	Decalin	193	6.5	93.6
2[e]	Acetonitrile	145–155[f]	85	15

[a] Refers to the corresponding ester **5a**, **5b**, or **7**. [b] Refers to the corresponding chloroaromatic **6a**, **6b**, or **8**. [c] Reference 6. [d] Reference 8b. [e] This work. [f] See Experimental Section.

For comparison, the thermal fragmentation of **2** was examined in two solvents, decalin and acetonitrile, of widely differing polarity. While the distribution of the expected products **7** and **8** in the two solvents was very similar to that found for **4b**, the enhanced stability of **2** as revealed by the higher decomposition temperatures was surprising. Thus **2** was essentially unchanged after 14 hr at 100° in hexachlorobutadiene, conditions which far exceed that required for decomposition of **4a** (see Experimental Section). Furthermore, a crude rate determination in acetonitrile at 115° revealed that bridge cleavage in **2** was slower than that found for **4b**[8b] by a factor of *ca.* $10^{2.6}$. Although more precise kinetic data may be desirable, the magnitude of the observed annelation effect is sufficient to warrant reopening of the question of simultaneity of the requisite bond fragmentations.[11]

Dechlorination of **2** using sodium in *tert*-BuOH/THF[12] resulted in partial reduction of the olefinic moiety to yield a nearly 1:1 mixture of **3** and the corresponding saturated ketal **9**. Attempted separation of the two ketals by a variety of techniques proved unyielding. Monitoring of the dechlorinated products by glpc during the course of reaction indicated that **3** and **9** are formed simultaneously, thus ruling out further reduction of **3** under the reaction conditions. Identification of **9** in the reaction mixture was achieved by nmr analysis and subsequent catalytic hydrogenation of the dechlorinated mixture to pure **9**. Acid hydrolysis of **9** yielded the known[13] 7-benznorbornenone (**10**) in good yield. The overall yield of **10** by this process (*ca.* 27%) compares favorably with that reported[14] for a recently improved synthetic route to **10**. Thus, although an improved route to cyclopropyl ketone **1** was not realized, a convenient alternate synthesis of **10** has been developed inadvertently.



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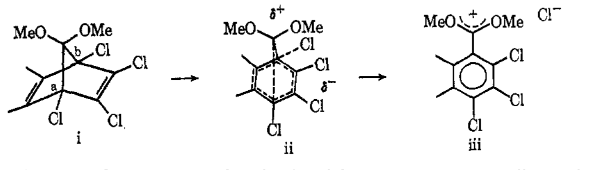
[10] See ref 8b for an excellent discussion of the mechanistic alternatives suggested by these solvent effects. Homopolar or heteropolar one-bond cleavages, depending on solvent, are postulated for the rate-determining step.

[11] Lemal and coworkers had earlier[8b] ruled out the possibility of concerted fragmentation of **4b** to **6b** in nonpolar solvents on the basis of poor overlap of the bridge orbitals with the 1,4-diene system. However, while this may be partially true for the ground state, the geometry of the transition state may be sufficiently altered so as to allow six-center orbital overlap that begins to approach that for the fully aromatized ring. Furthermore, without too severely stretching the theme of the latter argument, one can visualize an unsymmetrical transition state for formation of ion pair iii that likewise has a high degree of concertedness. Thus, if the breaking of bond a in i results in a flattening of the ring, a concomittant loosening of bond b may occur leading smoothly to transition state ii in which the breaking of bond a is considerably advanced over that for bond b. Transition state ii permits some cyclic delocalization while at the same time allowing for appreciable charge dispersal which may help to explain the rather small rate enhancements observed for this process in going from a nonpolar to polar solvent.



[12] P. G. Gassman and J. L. Marshall, *Org. Syn.*, **48**, 68 (1968).

[13] P. D. Bartlett and W. P. Giddings, *J. Amer. Chem. Soc.*, **82**, 1240 (1960).

[14] R. Muneyuki and H. Tanida, *J. Org. Chem.*, **31**, 1988 (1968).

Experimental Section[15]

7,7-Dimethoxy-1,2,3,4-tetrachlorobenznorbornadiene (**2**).—A mixture of 24.3 g (0.092 mol) of 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene,[4] 5.67 g (0.031 mol) of 2-carboxybenzenediazonium chloride, 250 ml of 1,2-dichloroethane, and 7 ml of propylene oxide was stirred at reflux for 2 hr. The solvent was removed on a rotary evaporator and the residue was chilled until crystalline. Recrystallization from isooctane gave 2.1 g of **2**, mp 121–123°; a second crop, 0.3 g, mp 110–114° was obtained. Distillation of the mother liquor at 85–92° (2–3 mm) afforded 6.93 g of starting material. Chromatography of the residue on standard alumina using 20% benzene–hexane followed by treatment as before gave 2.7 g of product (5.1 g overall, 49% based on diazonium salt) and 7.64 g of starting material. Three recrystallizations from isooctane gave analytically pure **2** as white crystals: mp 123–124°; nmr (CCl_4) τ 6.82 (3, s), 6.42 (3, s), 2.5–2.9 (4, m).

Anal. Calcd for $C_{13}H_{10}O_2Cl_4$: C, 45.89; H, 2.96; Cl, 41.73. Found: C, 46.12; H, 3.02; Cl, 41.75.

Thermal Fragmentation of 7,7-Dimethoxy-1,2,3,4-tetrachlorobenznorbornadiene (**2**). **A. Nonpolar Solvent.**—A quantity of **2** was dissolved in hexachlorobutadiene, placed in an nmr tube, and immersed in a constant-temperature bath. Periodic analysis revealed no change in the spectrum up to 14 hr at 100°. After 20 hr at 150–160°, *ca.* 25% of the starting ketal still remained. Immersion of the tube in boiling decalin (bp 193°) for 2 hr resulted in the formation of crystalline material which negated further nmr examination. On the preparative scale 0.300 g (0.882 mmol) of **2** and 4 ml of freshly distilled decalin (bp 193°) were refluxed for 2 hr. At the end of this time, the reaction was cooled to room temperature and 0.123 g of white needles, mp 195–197°, was collected by filtration and washed with hexane. Chromatography of the combined filtrate on silica gel using hexane afforded decalin and another component. Elution with benzene gave 0.030 g of a heavy yellow oil, the major portion of which (55%) consisted of methyl 2,3,4-trichloro-1-naphthoate (**7**): nmr (CCl_4) τ 6.00 (3, s), 2.40 (3, m), 1.75 (1, m); $\nu_{C=O}$ 1725 cm^{-1}. Elution with ether gave 0.023 g of a heavy yellow oil whose nmr suggested it contained products originating from the extruded dimethoxymethano bridge. Rechromatography of the hexane fraction on alumina to remove decalin gave on elution with benzene 0.097 g of white solid, identical with the initially isolated white needles and with authentic 1,2,3,4-tetrachloronaphthalene (**8**) prepared by the acid hydrolysis of **2**. The overall yield of **8** from thermolysis of **2** was 0.220 g (93.6%): nmr ($CDCl_3$) τ 2.4 (2, m) and 1.8 (2, m).

B. Polar Solvent.—A mixture of 75 mg of **2** (0.22 mmol) and 1 ml of acetonitrile was sealed in a nmr tube and immersed in a constant-temperature bath at 115°. Periodic analysis of the nmr spectrum revealed the formation of a new singlet at τ 6.00. Determination of the relative integral ratios of the original methyl absorptions of **2** and that of the new singlet with time provided an approximate rearrangement rate of 3×10^{-6} sec^{-1}. After 44 hr (0.7 half-lives), the contents of the nmr tube were sealed in a thick-walled Carius tube and heated in an oil bath at 145–155° for 14 hr. Removal of solvent gave 52 mg of yellow-white crystals whose nmr spectrum indicated that the material was predominantly methyl ester **7**. Chromatography on silica gel with hexane afforded 8 mg of white solid whose ir spectrum was identical with that of authentic **8**. Further elution with benzene afforded 41 mg of yellow-white crystals, mp 90–92°. Recrystallization from *n*-hexane gave mp 96.5–97.5°. Analysis of the nmr and ir spectra confirmed that the product was methyl 2,3,4-trichloro-1-naphthoate (**7**).

Anal. Calcd for $C_{12}H_7O_2Cl_3$: C, 49.78; H, 2.42. Found: C, 49.99; H, 2.51.

Thermal Fragmentation of 7,7-Dimethoxy-1,2,3,4-tetrachloronorbornadiene (**4a**).—A quantity of **4a**[6] was dissolved in hexachlorobutadiene, placed in an nmr tube, and immersed in a constant-temperature bath at 100°. Analysis of the spectrum after 3 hr revealed complete disappearance of the vinylic protons for **4a**.

Dechlorination of 2.—To a vigorously stirred mixture of 6.0 g (0.018 mol) of **2**, 14.7 g of *tert*-butyl alcohol (distilled from sodium) and 105 ml of tetrahydrofuran (distilled from lithium aluminum hydride), there was added, in an argon atmosphere, 10.9 g (0.471 g-atom) of freshly cut sodium metal. The mixture was stirred at reflux for 8.5 hr and methanol then added cautiously to destroy excess sodium. The reaction was poured onto 200 g of ice and the reaction flask was washed with 200 ml of water. The mixture was extracted with three 100-ml portions of ether and the combined extracts were washed with three portions of water and one portion of saturated NaCl solution. The ethereal solution was dried over $MgSO_4$ and filtered. Removal of solvent on a rotary evaporator gave a yellow oil which, upon chilling, gave 0.4 g of white crystals, mp 43–45°, after thorough washing with hexane. Distillation of the mother liquor at 83–86° (1.5–2.0 mm) gave 2.6 g (3.0 g overall, 84%) of a colorless oil whose nmr spectrum was identical with that of the white crystals. Glpc analysis at 150° (5 ft × $^1/_8$ in. 5% SE-30 column) indicated the presence of two components in *ca.* equal proportions, data consistent with nmr integral ratios. Attempted separations by column chromatography and $AgNO_3$ partition extraction were only partially successful. The nmr (CCl_4) spectrum of 7,7-dimethoxybenznorbornadiene showed the methoxy protons as singlets at τ 7.08 and 6.88, two bridgehead protons as a triplet at 6.17, two olefinic protons as a triplet at 3.45, and four aromatic protons as an A_2B_2 multiplet at 3.01.

7,7-Dimethoxybenznorbornene (**9**).—A 3.28-g sample of the dechlorinated ketal mixture (estimated to contain 1.64 g, 8.1 mmol, of unsaturated ketal) in 30 ml of methanol was hydrogenated at room temperature with 150 mg of 10% Pd/C as catalyst. Hydrogenation was complete in about 35 min with an uptake of about 225 ml (*ca.* 10 mmol) of hydrogen. The solution was filtered through a pad of Celite, and, on removal of solvent, a brownish oil was obtained. Chromatography on standard alumina with hexane gave 2.5 g (76%) of a colorless oil which solidified upon standing, mp 45–48°. Two recrystallizations from petroleum ether (bp 20–40°) gave 7,7-dimethoxybenznorbornene (**9**): mp 54–54.8°; nmr ($CDCl_3$) τ 8.86 (2, m), 7.90 (2, m), 6.91 (3, s), 6.81 (5, broad singlet), 2.96 (4, s).

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.54; H, 7.98.

7-Benznorbornenone (**10**).—A mixture of 150 mg (0.735 mmol) of ketal **9**, 4 ml of tetrahydrofuran, and 2 ml of concentrated H_2SO_4 was stirred at room temperature for 2 hr. At the end of this time, the dark red solution was poured into water and the aqueous mixture was extracted three times with ether. The combined extracts were dried and filtered, and the solvent was removed on a rotary evaporator to give a dark yellow oil which was percolated through a column of standard alumina with ether. Removal of solvent gave 0.101 g (87%) of 7-benznorbornenone (**10**) [nmr (CCl_4) τ 2.83 (4, s), 6.75 (2, t), 7.87 (2, m), 8.68 (2, m)], identical with an authentic sample prepared by chromium trioxide oxidation of *anti*-7-benznorbornenol, mp 101–103° (lit.[13] mp 103–104°), obtained from catalytic hydrogenation of *anti*-7-benznorbornadienol.[3] The 2,4-dinitrophenylhydrazone of **10** gave yellow crystals from ethanol, mp 152–152.5° (lit.[13] mp 143.6–146.4°).

Registry No.—**2**, 24472-15-9; **7**, 29261-09-4; **9**, 29370-70-5; **10**, 6165-88-4.

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Synthesis of Dithienothiophenes

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Recently we reported the synthesis of four of the six possible dithienothiophene isomers.[1] The two remain-

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[15] Melting points were determined with a Thomas-Hoover apparatus. All melting and boiling points were uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and Atlantic Microlab, Inc., Atlanta, Ga. Vapor phase chromatographic analyses were performed with an Aerograph Model 600-D instrument equipped with a hydrogen flame ionization detector. Infrared spectra were recorded on either a Perkin-Elmer 137 or Beckman IR-10 instrument. Solid samples were examined as Nujol mulls while liquid samples were examined neat on sodium chloride plates. Nmr spectra were obtained on a Varian A-60A instrument using tetramethylsilane as an internal reference. Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6E instrument.

[1] F. de Jong and M. J. Janssen, *J. Org. Chem.*, **36**, 1645 (1971).