72448-16-9; **22**, 72524-41-5; **23**, 14370-25-3; **24**, 72524-42-6; **25**, 72524-43-7; **26**, 72524-44-8; **27**, 72524-45-9; **28**, 72524-46-0; **29**, 72524-47-1; **30**, 72524-48-2; **31**, 72524-49-3; **32**, 72524-50-6; **33**, 72524-51-7; **34**, 72524-52-8; **35**, 72524-53-9; **36**, 72524-54-0; **37**, 72524-55-1; **38**, 72524-56-2; **39**, 72524-57-3; **40**, 72524-58-4; **41**, 72524-59-5; **42**, 72581-28-3; **43**, 72524-60-8; **44**, 72524-61-9; **45**, 72524-62-0; **46**, 72524-63-1; **47**, 72524-64-2; **48**, 72524-65-3; **49**, 72541-92-5; **50**, 72524-66-4; **51a**, 72541-93-6; **51b**, 72524-67-5; **51c**, 72524-68-6; **52**, 72524-69-7; **53**, 72541-94-7; **55**, 72541-95-8; **56a**, 72524-70-0; **56b**, 72524-71-1; **56b** 1,1-dioxide, 72524-72-2; **57a**, 72524-73-3; **57b**, 72524-74-4; **58**, 72524-75-5; **59**, 72524-76-6; **61a**, 72541-96-9; **61b**, 72524-77-7; **61c**, 72524-78-8; **61d**, 72524-79-9; **61e**, 72524-80-2; **61f**, 72524-81-3; **61g**, 72524-82-4; **61g**·HCl, 72524-83-5; **61h**, 72524-84-6; **61i**, 72524-85-7; **62**, 18517-93-6; **63**, 72524-86-8; **64**, 72524-87-9; **65**, 72524-88-0; **66**, 72524-89-1; tetrachlorothiophene, 6012-97-1; tetrachlorothiophene 1,1-dioxide, 72448-17-0; tetrabromothiophene 1,1-dioxide, 72524-90-4; 1,2,3,4-tetrachloro-5,6,7,8-tetrahydronaphthalene, 1203-38-9; 2,3,4,5-tetrachlorotoluene, 1006-32-2; 3,4-dichlorothiophene, 17249-76-2; hexachloro-1,3-butadiene, 87-68-3; tetrabromothiophene, 3958-03-0; 1,1,2,4-tetrachloro-1-buten-3-yne, 5658-91-3; cyclopentadiene, 542-92-7; 2,3-dimethylbutadiene, 513-81-5; 1,5-hexadiene, 592-42-7; *cis*-1,5-heptadiene, 7736-34-7; *trans*-1,5-heptadiene, 7736-22-3; 2,6-octadiene (*E,E* isomer), 18152-32-4; 2,6-octadiene (*E,Z* isomer), 29801-67-0; 2,6-octadiene (*Z,Z* isomer), 18680-11-0; 1,2-divinylbenzene, 105-06-6; allyl vinyl ether, 3917-15-5; allyl vinyl sulfide, 41049-25-6; vinyl acrylate, 2177-18-6; vinyl methacrylate, 4245-37-8; 1,6-heptadiene, 3070-53-9; diallyl ether, 557-40-4; diallyl sulfide, 592-88-1; *N,N*-diallylacetamide, 6296-61-3; diallylcyanamide, 538-08-9; (*N,N*-diallylamino)acetonitrile, 72524-91-5; 1,5-cyclooctadiene, 111-78-4; tetrachloro-α-pyrone, 10269-62-2; dibenzo[*a,e*]cyclooctene, 262-89-5; 1,5-cyclononadiene, 57357-81-0; sodium 2,4,5-trichlorobenzoate, 72524-92-6; CH_2=CH_2, 74-85-1; cyclopentene, 142-29-0; cyclohexene, 110-83-8; cycloheptene, 628-92-2; cyclooctene, 931-88-4; cyclododecene, 1501-82-2; 1,4-cyclohexadiene, 628-41-1; *cis*-1,*trans*-5-cyclodecadiene, 1124-78-3; methylenecyclobutane, 1120-56-5; methylenecyclohexane, 1192-37-6; 1,4-dimethylenecyclohexane, 4982-20-1; (−)-β-pinene, 18172-67-3; methyleneadamantane, 875-72-9; indene, 95-13-6; acenaphthylene, 208-96-8; *endo*-dicyclopentadiene, 1755-01-7; PhC≡CH, 536-74-3; 1-hexen-5-yne, 14548-31-3; 1-dodecene, 112-41-4; 1,7-octadiene, 3710-30-3; 1,8-nonadiene, 4900-30-5; CH_2=CHCOOH, 79-10-7; CH_2=CHCOOMe, 96-33-3; CH_2=CHCN, 107-13-1; CH_2=$CHCH_2COOH$, 625-38-7; CH_2=$CH(CH_2)_8COOH$, 112-38-9; dimethyl maleate, 624-48-6; maleic anhydride, 108-31-6; maleimide, 541-59-3; *N*-methylmaleimide, 930-88-1; CH_2=C(Me)COPh, 769-60-8; CH_2=$CHCH_2Br$, 106-95-6; CH_2=$CHCH_2NCS$, 57-06-7; safrole, 94-59-7; 1,4-benzoquinone, 106-51-4; 1,4-naphthoquinone, 130-15-4; 2-vinylpyridine, 100-69-6; *N*-vinylpyrrolidone, 88-12-0; *N*-vinylsuccinimide, 2372-96-5; *N*-methylpyrrole, 96-54-8; indole, 120-72-9; diethyl 2,3-diazanorbornene-2,3-dicarboxylate, 14011-60-0; thiophene, 110-02-1; precocene II, 644-06-4.

Addition-Rearrangement Reactions of Halogenated Thiophene Dioxides with Furans

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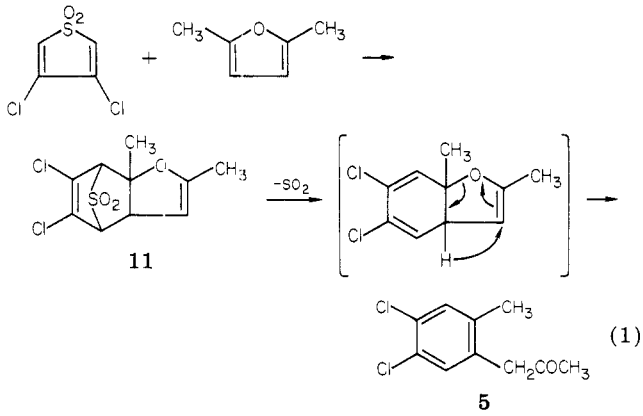
Received October 22, 1979

Dichloro-, tetrachloro-, and tetrabromothiophene dioxides undergo novel addition–rearrangement reactions with furans to form halobenzyl carbonyl compounds.

Halogenated thiophene 1,1-dioxides undergo addition–rearrangement reactions with furans to form halobenzyl carbonyl compounds (**1–10**, Table I). No precedent for this rearrangement has been found in furan chemistry. In the case of 2,5-dimethylfuran and 3,4-dichlorothiophene dioxide,[2] the primary adduct **11** precipitates from solution



11 (1) 5

and can be isolated if the reaction is stopped after 1–2 min. Warming the reaction results in loss of sulfur dioxide and rearrangement of the annelation product to yield the benzyl ketone **5** (eq 1).

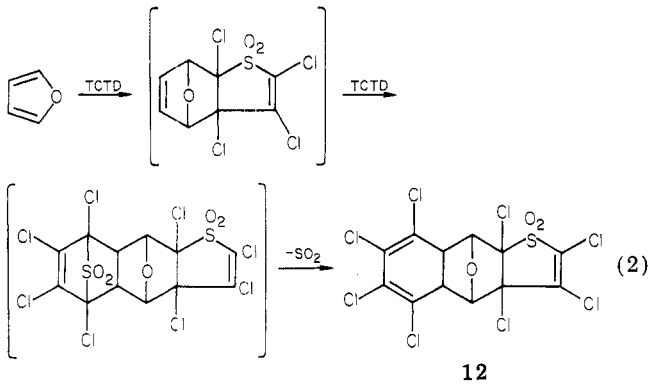
The reaction and rearrangement also proceed with tetrachloro- and tetrabromothiophene dioxides[3a] to give products corresponding to **5**. Intermediates corresponding to **11** have not been observed, however. A variety of substituted furans has been employed to give the halogenated benzyl ketones listed in Table I (compounds **1–10**). The products (**8, 9**) from tetrachlorothiophene dioxide and methyl 2-furoate or 2-acetylfuran exist in the enolic form, as shown, rather than the ketonic form (NMR and IR data are detailed in the Experimental Section). Hydrolysis of **8** gives the corresponding tetrachloro-α-hydroxycinnamic acid.

The reactions with the substituted furans listed in Table I generally proceed in high yield. Reaction of furan itself, however, differs from these examples. The normal rearrangement product, (2,3,4,5-tetrachlorophenyl)acetaldehyde, has been isolated in 8% yield. A second product (**12**, 27% yield) results from furan acting as a 1,3-diene accepting one double bond of tetrachlorothiophene dioxide (TCTD), and the resulting intermediate acting as a donor

(1) Contribution No. 2725.
(2) Bluestone, H.; Bimber, R.; Berkey, R.; Mandel, Z. *J. Org. Chem.* **1961**, *26*, 346–351.
(3) (a) Raasch, M. S. *J. Org. Chem.* **1980**, *45*, 000. (b) Raasch, M. S.; Smart, B. E. *J. Am. Chem. Soc.* **1979**, *101*, 7733–7734.

0022-3263/80/1945-0867$01.00/0

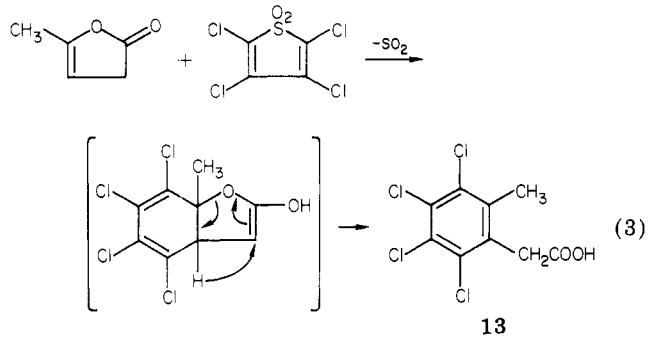
of one double bond to another molecule of the thiophene dioxide which acts as a diene (eq 2).



(2)

12

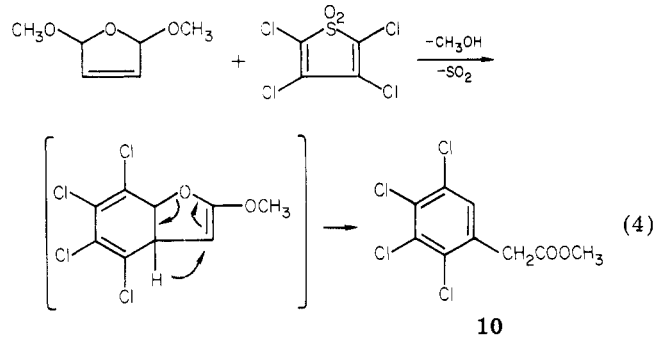
α-Angelica lactone functions like 2-hydroxy-5-methylfuran. Thus, with tetrachlorothiophene dioxide it forms (2,3,4,5-tetrachloro-6-methylphenyl)acetic acid (**13**) in 62% yield (eq 3).



(3)

13

More surprisingly, 1:2 *cis*-:*trans*-2,5-dimethoxy-2,5-dihydrofuran functions like 2-methoxyfuran by loss of methanol in the reaction, and methyl (2,3,4,5-tetrachlorophenyl)acetate (**10**) is produced in 51% yield (eq 4). The same compound is produced from 2-methoxyfuran (Table I).



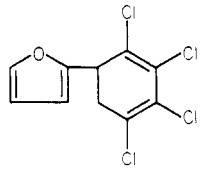
(4)

10

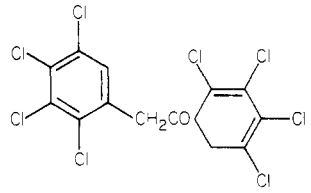
2-Methoxyfuran has been made by the acid-catalyzed pyrolysis at 220–250 °C of 2,5-dimethoxy-2,5-dihydrofuran,[4] and evidently some forms under the above reaction conditions. However, none was detected by NMR after passing sulfur dioxide into 2,5-dimethoxy-2,5-dihydrofuran at 100 °C.

2-Vinylfuran did not yield a benzyl vinyl ketone as the vinyl group proved to be more reactive than the furan ring. Thus, tetrachlorothiophene dioxide annelated 2-vinylfuran to form **14**. Reaction of **14** with another mole of tetrachlorothiophene dioxide produced the benzyl ketone **15**.

The retention of the sulfone bridge in the primary reaction product of thiophene dioxides with olefinic compounds, as illustrated by **11**, is a rare occurrence. Usually,



14



15

sulfur dioxide is lost with the formation of a 1,3-cyclohexadiene derivative.[2,3] The primary adduct of thiophene dioxide with diethyl acetylenedicarboxylate containing the sulfone bridge has been reported,[5] but later investigators, following the reaction by NMR, were unable to detect the presence of the primary adduct.[6] The Diels–Alder addition of 2,5-dimethylthiophene dioxide to 1,4-benzoquinone with retention of sulfur dioxide has been reported.[7]

Experimental Section

The ^1H NMR spectra were determined with a Varian A-60 instrument using Me_4Si as internal reference. A Perkin-Elmer Model 21 spectrometer was used for IR spectra (KBr wafers). Melting and boiling points are uncorrected.

Compounds of Table I. The reactions were run on a 0.01–0.02-mol scale and are exothermic. *Any scale-up should make provisions for controlling the heat of reaction.* 2-Methyl- and 2,5-dimethylfuran were used in sufficient excess to serve as solvents. The other furans were used in 10% excess. Solvents and excess volatile furans were removed at the end of the reaction and the residues were recrystallized as indicated.

NMR (ppm, $CDCl_3$ unless noted) and IR data: **1**: NMR 2.23 (s, CH_3), 3.82 (s, CH_2), 7.16 (aromatic H); IR 3086 (=CH), 2967 (CH), 1718 (C=O), 1575, 1538 cm^{-1} (aromatic C=C). **2**: NMR 0.8–1.8 (m, C_3H_7), 2.57 (t, $C_3H_7CH_2$), 3.86 (s, $ArCH_2$), 7.32 (s, 1 H, aromatic). **3**: NMR 2.30 (s, CH_3), 2.36 (s, CH_3), 4.07 (s, CH_2); IR 2959 (CH), 1712 cm^{-1} (C=O), no band for C=C as is the case for hexasubstituted benzenes, but long-wavelength bands are consistent for an aromatic ring. **4**: IR 2915 (CH), 1704 cm^{-1} (C=O). **5**: NMR 2.17 (s, 2 CH_3), 3.67 (s, CH_2), 7.18 (s, aromatic H), 7.26 (s, aromatic H); NMR [$(CD_3)_2SO$] 2.17 (s, 2 CH_3), 3.83 (s, CH_2), 7.33 (2 H, aromatic); IR 3077 (=CH), 2941 (CH), 1709 (C=O), 1592, 1481 cm^{-1} (C=C). **6**: NMR 2.17 (s, CH_3), 3.88 (s, CH_2CO), 4.75 (s, CH_2O), 7.25 (s, aromatic H). **7**: NMR [$(CD_3)_2SO$] 1.89 (s, CH_3), 4.03 (s, benzylic CH_2), 4.08 (d, J = 5.5 Hz, converted to s by D_2O, CH_2NH), 7.62 (s, aromatic H), 8.18 (t, J = 5.5 Hz, removed by D_2O, NH). **8**: NMR 3.98 (s, CH_3), 6.81 (s, CH + OH, reduced to CH by D_2O), 8.30 (s, aromatic H); IR 3356 (OH), 3125 (=CH), 2967 (CH), 1706 (C=O), 1650 (C=C), 1520 cm^{-1} (w, aromatic C=C). **9**: NMR 2.62 (s, CH_3), 6.78 (d, J = 1.2 Hz, converted to s by D_2O, CH), 7.53 (d, J = 1.2 Hz, removed by D_2O, OH), 8.38 (s, aromatic H); IR 3257 (OH), 1672 (C=O, broadness on high wavelength side may mask olefinic C=C), 1522 cm^{-1} (aromatic C=C). **10**: NMR 3.77 (s, CH_3), 3.80 (s, CH_2), 7.43 (s, 1 H, aromatic); NMR [$(CD_3)_2CO$] 3.82 (s, CH_3), 3.92 (s, CH_2), 7.68 (s, 1 H, aromatic); IR 3077 (=CH), 2959 (CH), 1724 (C=O), 1575, 1534 (aromatic C=C), 1205 cm^{-1} (C=O).

Addition of 3,4-Dichlorothiophene Dioxide to 2,5-Dimethylfuran. 3,4-Dichlorothiophene dioxide[2] (2.78 g, 0.015 mol) and 5 mL of 2,5-dimethylfuran were warmed slightly to bring the sulfone into solution and initiate the reaction. The temperature was kept at 50 °C by cooling. Compound **11** separated. After 2 min, the reaction mixture was cooled and the product was filtered off and washed with methanol to give 2.87 g (68%) of **11**. Recrystallization from acetone left 2.18 g (52%) of 5,6-dichloro-3a,4,7,7a-tetrahydro-2,7a-dimethyl-4,7-epithiobenzofuran 8,8-dioxide: mp 113–114 °C; NMR ($CDCl_3$) 1.73 (s, 2 CH_3), 3.98 (s, 3a-H), 6.17–6.50 (3 H); IR 3058 (CH, bridgehead CH), 2985, 2941 (CH), 1626 shoulder, 1603 (C=C), 1307, 1147 cm^{-1} (SO_2). After

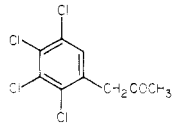
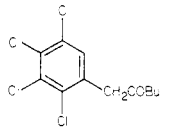
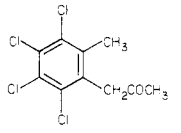
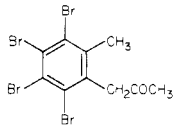
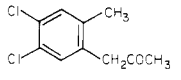
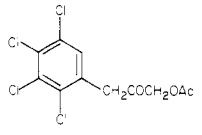
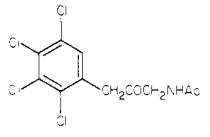
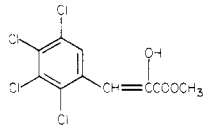
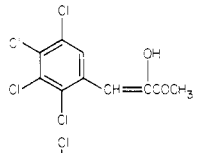
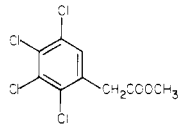
(4) D'Alelio, G. F.; Williams, C. J., Jr.; Wilson, C. L. *J. Org. Chem.* **1960**, *25*, 1028–1030.

(5) Bailey, W. J.; Cummins, E. W. *J. Am. Chem. Soc.* **1954**, *76*, 1940–1942.

(6) Van Tilborg, W. J. M.; Smael, P.; Visser, J. P.; Kouwenhoven, C. G.; Reinhoudt, D. N. *Recl. Trav. Chim. Pays-Bas* **1975**, *94*, 85–88.

(7) Torssell, K. *Acta Chem. Scand.* **1976**, *30B*, 353–357.

Table I.[a,d] Halogenated Benzyl Ketones and Related Compounds from Thiophene Dioxides and Furans

compd	substituted furan	halogenated thiophene dioxide	reaction conditions	product	recrystn solvent	mp, °C	yield, %
1	2-methyl	tetrachloro	hexane, 65 °C, 0.5 h		EtOH	85.5-86.5	92
2	2-*n*-butyl[b]	tetrachloro	hexane, 65 °C, 0.5 h		hexane	78-79	93
3	2,5-dimethyl	tetrachloro	93 °C, 0.5 h		EtOH	128-129	90
4	2,5-dimethyl	tetrabromo	93 °C, 0.5 h		EtOH	173-174	90
5	2,5-dimethyl	2,5-dichloro	93 °C, 0.5 h		hexane	50-51	77
6	2-acetoxymethyl	tetrachloro	$ClCH_2CH_2Cl$, 83 °C, 1 h		*n*-BuCl	132-132.5	74
7	2-acetamidomethyl[c]	tetrachloro	$ClCH_2CH_2Cl$, 83 °C, 1 h		EtOH	197-198.2	84
8	2-carbomethoxy	tetrachloro	100 °C, 22 h		glyme	166-167	62
9	2-acetyl	tetrachloro	125 °C, 1 h		hexane	149-152	37
10	2-methoxy	tetrachloro	CH_2Cl_2, 30 °C, cooled		MeOH	88-89	77

[a] NMR and IR data are given in the Experimental Section. [b] Chemsampco, Columbus, OH. [c] Clauson-Kaas, N.; Tyle, Z. *Acta Chem. Scand.* **1952**, *6*, 667-670. Schlesinger, A. H.; Prill, K. J. *J. Am. Chem. Soc.* **1956**, *78*, 6123-6127. [d] Satisfactory analytical data (±0.4%) for C, H, and Cl or Br were obtained for all products in the table except **8** (Cl: calcd, 44.88; found, 44.44).

15 h, the $CDCl_3$ solution contained 9% of **5** formed by decomposition of **11**.

Anal. Calcd for $C_{10}H_{10}Cl_2O_3S$: C, 42.72; H, 3.59; Cl, 25.22. Found: C, 42.97; H, 3.63; Cl, 25.32.

The original filtrate and methanol wash were allowed to evaporate to give 0.7 g (22%) of **5**. This was obtained as the main product by heating the above reactants on a steam bath for 30 min. Excess dimethylfuran was removed and the residue was recrystallized from hexane to give 2.52 g (77%) of (4,5-dichloro-2-methylphenyl)-2-propanone (**5**, Table I).

Reaction of Tetrachlorothiophene Dioxide with Furan. Furan (10 mL) and 5.08 g (0.02 mol) of tetrachlorothiophene dioxide[3a] were heated under reflux for 2 h. Excess furan was removed to leave a residue of crystals and syrup. A little acetone was added and the crystals were filtered off and recrystallized from chloroform to give 1.38 g (27%) of **12**: mp 262 °C; NMR ($CDCl_3$) 4.01 (s, 2 H, cyclohexadiene ring), 5.05 (m, 1 H), 5.55 (m, 1 H nearest SO_2); IR 3049, 2976 (CH), 1618, 1600 shoulder (C=C), 1342, 1164 cm^{-1} (SO_2).

Anal. Calcd for $C_{12}H_4Cl_8O_3S$: C, 28.15; H, 0.79; Cl, 55.42. Found: C, 28.24; H, 0.87; Cl, 55.35.

The filtrate from the above product was heated at 0.5 mm in a short-path still to distill a solid from the resin. This was recrystallized from hexane to give 0.42 g (8%) of (2,3,4,5-tetrachlorophenyl)acetaldehyde: mp 84.5–85 °C; NMR ($CDCl_3$) 3.88 (d, J = 1 Hz, CH_2), 7.33 (s, CH), 9.77 (t, J = 1 Hz, CHO); IR 2857 (CH of CHO), 1715 cm^{-1} (C=O).

Anal. Calcd for $C_8H_4Cl_4O$: C, 37.25; H, 1.56; Cl, 54.98. Found: C, 37.25; H, 1.78; Cl, 55.32.

Hydrolysis of 8. To 2.21 g (0.007 mol) of methyl 2-hydroxy-3-(2,3,4,5-tetrachlorophenyl)acrylate (**8**) suspended in 10 mL of ethanol was added 0.46 g (0.007 mol) of potassium

hydroxide in 5 mL of ethanol. The compound dissolved. The ethanol was evaporated, the residue was dissolved in water, and the free acid was precipitated by adding hydrochloric acid. The acid was filtered off and recrystallized from acetone to give 1.80 g (80%) of 2-hydroxy-3-(2,3,4,5-tetrachlorophenyl)acrylic acid in two crops: mp 209.5–210 °C; NMR (DMF-d_7) 6.69 (s, removed by D_2O, CH), 8.40 (s, aromatic H), 10.30 (OH + COOH).

Anal. Calcd for $C_9H_4Cl_4O_3$: C, 35.80; H, 1.34; Cl, 46.97. Found: C, 36.12; H, 1.28; Cl, 46.65.

Reaction of Tetrachlorothiophene Dioxide with α-Angelica Lactone. α-Angelica lactone[8] (1.18 g, 0.012 mol) and 2.54 g (0.01 mol) of tetrachlorothiophene dioxide were heated on a steam bath for 1.5 h. The reaction product solidified and was recrystallized from acetone to give 1.80 g (62%) of (2,3,4,5-tetrachloro-6-methylphenyl)acetic acid (**13**) in two crops: mp 245.5–247 °C; NMR [$(CD_3)_2SO$] 2.43 (s, CH_3), 3.93 (s, CH_2), 11.5 (br, low peak, OH); IR 3333 (OH), 1695 cm^{-1} (C=O); mass spectrum, m/z 285.9091 (parent), 250.9417 (-Cl), 240.9067 (-C-OOH).

Anal. Calcd for $C_9H_6Cl_4O_2$: C, 37.53; H, 2.10; Cl, 49.24. Found: C, 37.46; H, 2.16; Cl, 48.69.

Synthesis of 10 from 2,5-Dimethoxy-2,5-dihydrofuran. 2,5-Dimethoxy-2,5-dihydrofuran[8] (1.95 g, 0.015 mol, 1:2 cis-trans mixture) and 2.54 g (0.01 mol) of tetrachlorothiophene dioxide were warmed together. The temperature rose to 120 °C and was moderated by cooling. After the reaction subsided, excess 2,5-dimethoxy-2,5-dihydrofuran was removed under vacuum. The residue was rinsed with cold methanol to give 1.62 g (51%) of product. Recrystallization from hexane left 1.45 g (45%) of methyl (2,3,4,5-tetrachlorophenyl)acetate (**10**, Table I), mp 88–89 °C.

Addition of Tetrachlorothiophene Dioxide to 2-Vinylfuran. 2-Vinylfuran[9] (4 mL), 10 mL of 1,2-dichloroethane, and 5.08 g (0.02 mol) of tetrachlorothiophene dioxide were warmed in a flask with a reflux condenser and then cooled to moderate the vigorous reaction. The mixture was heated on a steam bath for 1 h after the reaction subsided. Distillation gave 3.65 g, bp 92–100 °C (0.4 mm), and 2.15 g of residue. The distillate was recrystallized from absolute ethanol to give 3.2 g (56%) of 2-(2,3,4,5-tetrachloro-2,4-cyclohexadienyl)furan (**14**): mp 67–68.2 °C; NMR ($CDCl_3$) 3.1 (m, CH_2), 3.97 (dd, CH of cyclohexadiene ring), 6.23 (m, 3-H and 4-H), 7.35 (m, 5-H).

Anal. Calcd for $C_{10}H_6Cl_4O$: C, 42.30; H, 2.13; Cl, 49.94. Found: C, 42.52; H, 2.34; Cl, 49.67.

Synthesis of 15. Tetrachlorothiophene dioxide (2.54 g, 0.01 mol), 10 mL of 1,2-dichloroethane, and 2.84 g (0.01 mol) of **14** were heated on a steam bath under reflux for 1 h. The solvent was removed and the residue was recrystallized from CCl_4 to give 3.18 g (69%) of **15**: mp 128–129 °C; NMR ($CDCl_3$) 3.12–3.72 (ABC, CH_2 + CH of cyclohexadiene ring), 4.07 (AB, CH_2CO), 7.27 (aromatic H); IR 3077 (=CH), 2933 (CH), 1715 (C=O), 1600, 1527 cm^{-1} (C=C).

Anal. Calcd for $C_{14}H_6Cl_8O$: C, 35.49; H, 1.28; Cl, 59.86. Found: C, 35.69; H, 1.52; Cl, 59.62.

Acknowledgment. I am indebted to F. A. Blissick for technical assistance and to E. W. Matthews for IR spectral interpretations.

Registry No. 1, 72541-70-9; **2**, 72541-71-0; **3**, 72541-72-1; **4**, 72541-73-2; **5**, 72541-74-3; **6**, 72541-75-4; **7**, 72541-76-5; **8**, 72541-77-6; **9**, 72541-78-7; **10**, 72541-79-8; **11**, 72541-80-1; **12**, 72541-81-2; **13**, 72541-82-3; **14**, 72541-83-4; **15**, 72541-84-5; 3,4-dichlorothiophene dioxide, 52819-14-4; furan, 110-00-9; (2,3,4,5-tetrachlorophenyl)-acetaldehyde, 72541-85-6; 2-hydroxy-3-(2,3,4,5-tetrachlorophenyl)-acrylic acid, 72541-86-7; *cis*-2,5-dimethoxy-2,5-dihydrofuran, 5143-07-7; *trans*-2,5-dimethoxy-2,5-dihydrofuran, 5143-08-8; 2-vinylfuran, 1487-18-9; 2-methylfuran, 534-22-5; 2-butylfuran, 4466-24-4; 2,5-dimethylfuran, 625-86-5; 2-(acetoxymethyl)furan, 623-17-6; 2-(acetamidomethyl)furan, 5663-62-7; 2-(carbomethoxy)furan, 611-13-2; 2-acetylfuran, 1192-62-7; 2-methoxyfuran, 25414-22-6; tetrachlorothiophene dioxide, 72448-17-0; tetrabromothiophene dioxide, 72524-90-4; 2,5-dichlorothiophene dioxide, 72541-87-8; 2-angelica lactone, 591-12-8.

(8) Aldrich Chemical Co., Milwaukee, WI.
(9) Polysciences, Inc., Warrington, PA.

Preparation and Selected Reactions of 2,3-Bis(bromomethyl)-1,3-butadiene[1]

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Received May 19, 1979

2,3-Bis(bromomethyl)-1,3-butadiene (**1**) was prepared by zinc-induced debromination of 1,4-dibromo-2,3-bis(bromomethyl)-2-butene (**2**). The versatility of **1** as a synthetic intermediate was demonstrated through consecutive use of its allylic bromides and conjugated diene functions, with eventual further modification of the primary reaction products. Coupling of **1** with vinylmagnesium chloride or ethynylmagnesium bromide gave highly unsaturated hydrocarbons (**8–11**). Reaction of **1** with nucleophiles such as sodium methoxide, sodium azide, sodium acetate, or potassium cyanide gave symmetrically disubstituted 1,3-butadienes (**12a–d**) which could in some cases be modified at the level of the substituent into other analogous dienes (**12e–f**). Five-membered heterocycles with exocyclic cis-fixed dienes, namely, the thiolane **13**, oxolane **14**, and pyrrolidines **15a–e** were obtained from **1** by reaction with sodium sulfide, with potassium hydroxide, or with secondary amines, respectively. Two of the pyrrolidines (**15a,c**) were photolytically cyclized into the corresponding 3-azabicyclo[3.2.0]heptene derivatives (**24a,b**). Dimethylenehexahydropyridazine derivatives (**28, 29**) were obtained from **1** by reaction with dimethyl azodicarboxylate and subsequent elimination of bromine. These unstable compounds could be stabilized as diene–iron tricarbonyl complexes (**31–34**). Carbocyclic systems were obtained from **1** by various Diels–Alder additions, such as the addition of dimethyl acetylenedicarboxylate which was followed by debromination and addition of a second molecule of the acetylenic ester to give a tetrahydronaphthalene derivative (**35** → **36** → **37**). Reaction of **1** with diiron nonacarbonyl produced three binuclear π complexes: the known 2,2′-bis(π-allyl) complex (**38**) and two isomeric trimethylenemethane-type complexes (**39, 40**) deriving from dimerization of **1**. The structure of the latter was proven by isomerization into bis(diene) complexes (**41, 42**) and oxidation to known hydrocarbons.

During the last few years we have been exploring the chemistry of the title compound, 2,3-bis(bromomethyl)-1,3-butadiene (**1**), a versatile reactive synthetic intermediate which was readily available by a zinc-induced de-

0022-3263/80/1945-0870$01.00/0