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Brominated Vinyl Ketene Thioacetal, Ene- and Diene Acetals; Potential Four-Carbon Synthons

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Abstract. A novel and convenient procedure for the preparation of conjugated vinyl ketene thioacetals is described: it involves addition of CBr_4 to acrolein, followed by thioacetalization of the corresponding aldehyde **2** and double dehydrobromination of **3** under basic conditions For comparison, three *O*-acetals **4-6** were also prepared. In contrast to the reaction of dithioacetal **3**, these acetals undergo either a single or double HBr elimination with formation of mono-olefins or cumulated diene, respectively. The mechanism of formation of the reaction products is discussed, and the reactivity of the novel per-functionalized tetrasubstituted 1,3-butadiene **1** with the strongly electrophilic dienophile PTAD is presented.

Keywords: Acetals; Thioacetals; Elimination reactions; Dithiolane

Our studies in the area of synthetic pyrethroids directed our attention to the synthetic potential of more highly functionalized 1,1-dibromo-1,3-butadienes. As a specific example, we set our sights on 2-(3',3'-dibromoprop-2'-enylidene)-1,3-dithiolane **1**. This electron rich diene, whose end-groups are differently masked 1,4-dicarboxylate (or potentially dicarbonyl) functions is a vinylketene dithioacetal. Such a system is expected, in keeping with the behavior of analogous systems, to exhibit a broad spectrum of reactivities under appropriately varied conditions. *Inter alia*, it should be subject to facile electrophilic[1,2] and electrophilic free radical attack,[3-6] to 1,2-cycloadditions,[7,8] to 1,3-dipolar addition,[9] and to 1,4-cycloaddition.[1,10,11] Though **1**, being a 1,1,4,4-tetrasubstituted-1,2-diene, would not be expected, for steric reasons, to react readily in a concerted Diels-Alder reaction,[12,13] yet the possibility of 1,4-addition *via* a multistep pathway, for instance *via* a cation radical or *via* direct ET intermediates, is not to be excluded.[14,15] Even nucleophilic attack at C-4 of such compounds (albeit lacking halogens) by alkyl lithium has been demonstrated.[16]

Vinyl ketene thioacetals have been prepared by a variety of methods,[1,2,10,11,17,18] among which the Peterson olefination procedure[19] applied to α,β-unsaturated carbonyl compounds has

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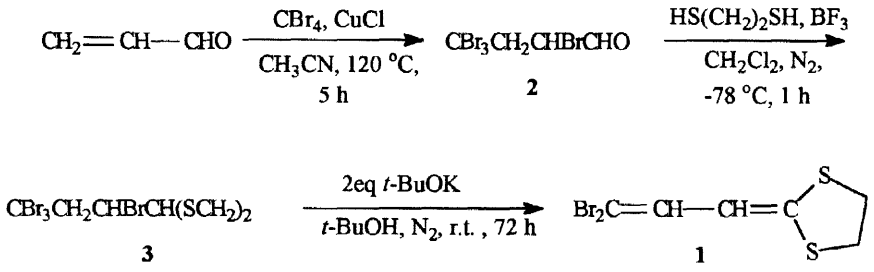
enjoyed much popularity. Dibromomethylene groups are currently generally prepared by a Wittig type procedure, reacting carbon tetrabromide and triphenylphosphine with carbonyl compounds,[20] though other routes are available. The preparative pathway we report herein is more economical and experimentally less demanding than those based on the procedures mentioned above. Cuprous chloride catalyzed addition of carbon tetrabromide to acrolein[21] yielded 2,4,4,4-tetrabromobutanal **2** which was converted to its dithioacetal **3** by the BF_3 catalyzed reaction with 1,2-ethanedithiol. Treatment of **3** with two equivalents of potassium *t*-butoxide in *t*-butanol lead to the desired diene (Scheme 1).

For purposes of comparison, three *O*-acetals of **2** were also prepared. These were 2,4,4,4-tetrabromo-1,1-di(2',2',2'-trifluoroethoxy)butane **4**, 2,4,4,4-tetrabromo-1,1-dimethoxybutane **5** and 3-(1',3',3',3'-tetrabromopropyl)-2,4-benzodioxepane **6**. In view of the expected reduced acidity of the hydrogen on the acetal carbon in these compounds, it is not surprising

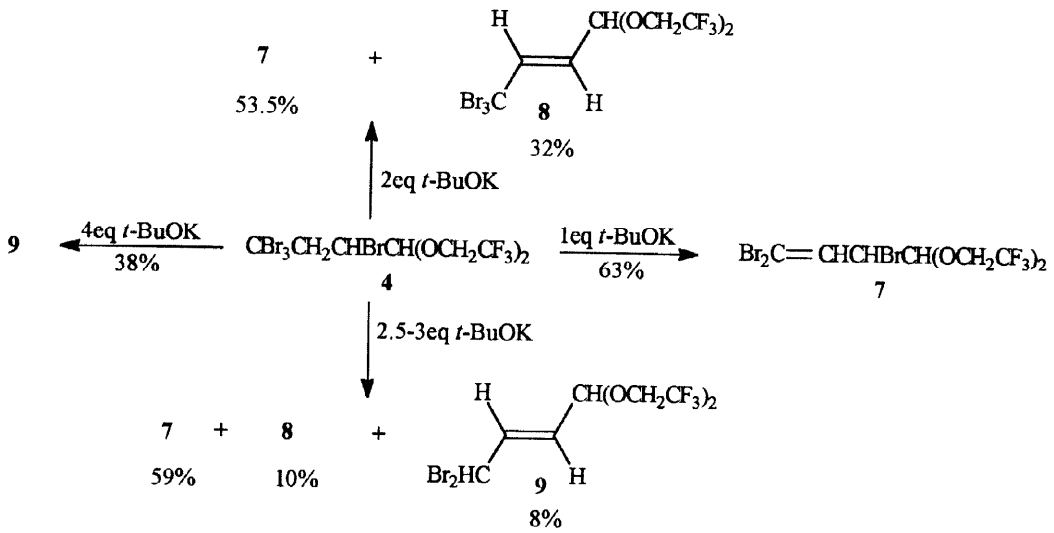
Scheme 1



that none of them yielded a 1,3-diene on treatment with base under various conditions. The treatment of **4** with one equivalent of potassium *t*-butoxide in *t*-butanol at r.t. yielded only 2,4,4-tribromo-1,1-di(2',2',2'-trifluoroethoxy)-3-butene **7** and unreacted **4** (in the ratio of ~2/1). Increasing the base to two equivalents resulted in both **7** and 4,4,4-tribromo-1,1-di(2',2',2'-trifluoroethoxy)-2*E*-butene **8** (in the ratio of 5/3), while four equivalents lead to the formation of 4,4-dibromo-1,1-di(2',2',2'-trifluoroethoxy)-2*E*-butene **9** only. 2.5 Equivalents of *t*-butoxide gave a mixture of **7**, **8** and **9** (7.4/1.25/1) (Scheme 2). These were separated by preparative tlc on silica gel. Similar results were obtained using KOH in *t*-BuOH. Only the formation of **9** is worthy of comment. Most simply, it may be viewed as proceeding *via* the removal by a nucleophile - the base or bromide ion - of an allylic bromine of the tribromomethyl group of **8**, thus yielding an allylic anion which is protonated by the solvent. Taking into consideration the activating properties of the π-bond, the suggested reaction finds reasonable precedent in the reactions of carbon tetrahalides (and some other polyhaloalkanes) with carbanions and other nucleophiles.[22-26] The possible mechanisms of such

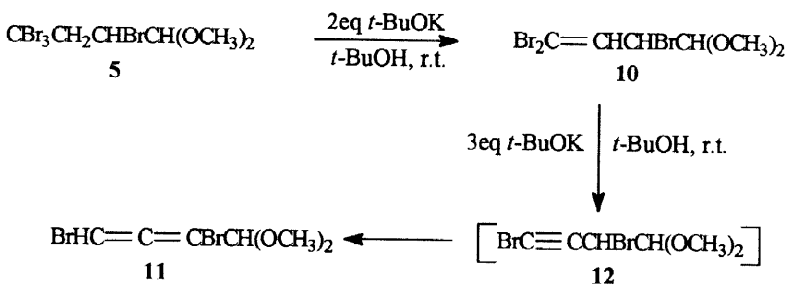
reactions, whether ionic or electron-transfer, have been investigated and discussed at length.[24-25] The allylic anion accessible as stated from **8**, would, of course, also be formed by similar nucleophile induced release of the allylic bromine of **7**.

Scheme 2



When **5** was treated at r.t. with up to two equivalents of *t*-BuOK in *t*-BuOH, the terminal olefin 2,4,4-tribromo-1,1-dimetoxy-3-butene **10** (and unreacted **5**) was the only product. Raising the amount of base to three equivalents and the reaction time to 20 h lead to the production of the allene 2,4-dibromo-1,1-dimethoxy-2,3-butadiene **11**. Among a variety of conditions tested, the ones stated were optimal for the production of **11**. The formation of **11** from **5** is in contrast to the exclusive formation of mono-olefins from **4**. It is most easily rationalized by assuming a double elimination of HBr from **5** to give 2,4-dibromo-1,1-dimethoxy-3-butyne, **12**, and a base catalyzed prototropic rearrangement of

Scheme 3

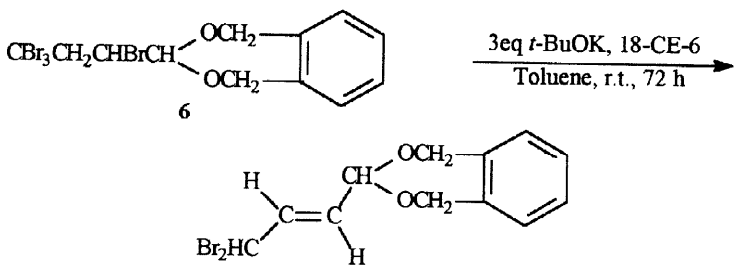


the latter to the more stable **11**[26,27] (Scheme 3). This multi-functionalized allene should also

have interesting potential as a synthon. To date only one 3-bromoallene, namely 3-bromo-1,2-nonadiene, has been reported in the literature. [28]

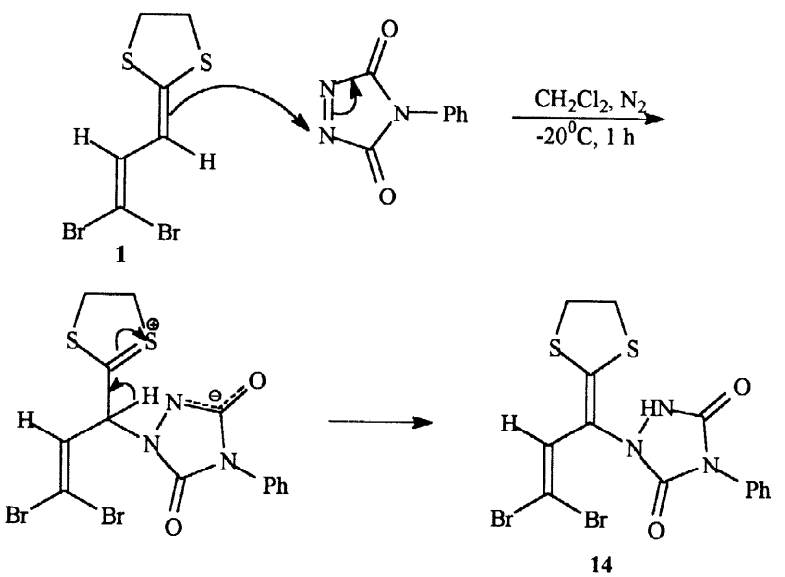
From the base treatment of **6** (see Experimental section), we isolated only a mono-olefin **13** analogous to **9** (Scheme 4), though under slightly different conditions, spectral evidence for the production of an allene was noted.

Scheme 4



Initiating the study of the reactivity spectrum of **1**, we found that to avoid extensive decomposition it was necessary to carry out its reaction with the strongly electrophilic dienophile 4-phenyl-3H-1,2,4-triazoline-3,4-dione (PTAD) at -20 °C. The spectral properties of

Scheme 5



the sole product showed it to have structure **14**, resulting from an apparent Michael-type addition of **1** to the reagent, followed by proton transfer (Scheme 5), rather than that of a

1,4-cycloaddition product. A similar finding for the reaction of a vinylketene thioacetal with PTAD was reported by Danishefsky,[1] though in that case it was the unsubstituted C-4 of the former which bonded to the nitrogen of the latter. Another relevant report is that of the reaction of PTAD with 2,5-dimethyl-2,4-hexadiene which lead to a product having only the C-3 of the hexadiene chain bonded to a nitrogen of the reagent.[12] As becomes clear from the data presented in the latter report, our compound **14** could be the end-product of a number of pathways different in detail, and in the absence of mechanistic inquiry we present Scheme 5 as an overall reaction scheme only. Finally, the utility of vinyl ketene thioacetal **1** as a synthon, with respect to the other reactions mentioned in the introduction[1-11] is now being investigated and the results will be published in due time.

Experimental Section

General. Melting points were obtained on a Thomas Hoover melting point apparatus and are uncorrected. IR spectra were recorded on a Nicolet 60 SXB FTIR. UV spectra were recorded on a Varian DMS 100S. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker AC-200, DPX-300 or DMX-600 spectrometers in $CDCl_3$ and using TMS as internal standard. Chemical shifts are reported in ppm downfield from tetramethylsilane, and coupling constants in Hz. High resolution mass spectra were obtained on a VG-Fison AutoSpec instrument and other mass spectra on a Finnigan GC/MS 4021, by using chemical ionization (CI). The atomic masses used for the exact mass calculations are as follows: $^{78.9183}Br$, $^{31.9720}S$. Column chromatography was performed with Merck silica gel 60 (230-240 mesh), and preparative thin layer chromatography was carried out in glass sheets precoated with Merck silica gel 60 F254 (2.00 mm). All solvents and reagents were obtained from Aldrich or Fluka and used without further purification with the following exceptions: acetonitrile and CH_2Cl_2 were distilled from P_2O_5 under nitrogen, toluene was distilled from Na, methanol was purified according to standard procedure [29] and acrolein was distilled prior to use.

2-(3',3'-Dibromoprop-2'-enylidene)-1,3-dithiolane (1). A solution of dithioacetal **3** (415 mg, 0.9 mmol) and potassium *t*-butoxide (220 mg, 1.96 mmol) in 4 mL of *t*-butanol was stirred under N_2 at ambient temperature for 72 h. Ether (20 mL) was added, and the ethereal solution was thrice extracted with basic (0.1 M NaOH) aqueous solution, dried over $MgSO_4$ and evaporated. The residue was crystallized from hexane: yield, 122 mg (45%), mp 80 °C. ^{1}H NMR (200 MHz): δ 3.36-3.53 (m, 4H), 6.18 (d, J 10.5, 1H), 6.99 (d, J 10.5, 1H). ^{13}C NMR (75 MHz): δ 37.61($\mathbf{C}H_2$), 38.19($\mathbf{C}H_2$), 87.27($\mathbf{C}Br_2$), 112.78($\mathbf{C}HCS_2$), 134.75($\mathbf{C}HCBr_2$), 145.60 ($\mathbf{C}S_2$). IR (KBr): 1528, 1282,1258, 1240, 813 cm^{-1}. MS-CI(CH_4) *m/z* (relative intensity) 300.8 (MH^+, 41.5), 220.9 (40.55), 194.9 (26.8), 143.0 (21.4). HRMS: calcd. for $C_6H_6BrS_2$ [MH^+ -

HBr] 220.9094; found 220.9105. UV (hexane) λ max nm (log ε): 248 (3.8), 307 (sh) (4.38), 311 (4.42), 328 (sh) (4.30).

2,4,4,4-Tetrabromobutanal (2). A magnetically stirred solution of carbon tetrabromide (19.85 g, 60 mmol), freshly distilled acrolein (4.1 mL, 60 mmol) and cuprous chloride (0.6 g, 3 mmol) in dried purified acetonitrile (15 mL) was heated in a sealed ampule at 120 °C for 5 h and then held at ambient temperature for 18 h. The solvent was removed under reduced pressure and the residue was triturated with a mixture of 50 mL of ether and saturated aqueous Na_2EDTA solution (25 mL). The ether layer was further extracted with two portions (20 mL) of the Na_2EDTA solution, dried over $MgSO_4$, and evaporated to yield 10.83 g (72.6%) of oil which was distilled under vacuum: bp 85-89 °C/0.03 mm Hg; 8.5 g of distillate **2** (42% yield). ^1H NMR (200 MHz): δ 3.62 (dd, J 3.4, 15.9, 1H), 4.26 (dd, J 7.2, 15.9, 1H), 4.60 (ddd, J 2.3, 3.4, 7.2, 1H), 9.54 (d, J 2.3, 1H). ^{13}C NMR (75 MHz): δ 34.33(**C**Br_3), 49.10(**C**HBr), 59.13(**C**H_2), 188.27(**C**HO). IR (neat): 1735, 1418, 1380, 956, 874, cm^{-1}. MS-CI: *m/z* (relative intensity) 384.7 (MH^+, 0.12), 304.8 ([MH^+ – HBr], 4.69), 224.8 (35.33), 196.8 (51.96), 116.9 (20.61). HRMS: calcd. for $C_4H_5Br_4O$ 384.7073; found 384.7057.

2-(2',3',3',3'-Tetrabromopropyl)-1,3-dithiolane (3). A solution of butanal **2** (77.5 mg, 0.2 mmol), 1,2-ethanedithiol (20 mL, 0.2 mmol) and 2 drops of boron trifluoride etherate in dichloromethane (2 mL) under a dry nitrogen atmosphere was stirred at –78 °C for 1 h, and then at ambient temperature overnight. After dilution with ether, extraction with 5% aqueous sodium hydroxide solution, drying over $MgSO_4$, and evaporation of solvent, the residue (68 mg) was chromatographed on a silica column using hexane/CH_2Cl_2 (2/1, v/v) as eluent. Recrystallization of the combined product containing fractions from CCl_4-hexane gave a 52% yield of yellow crystals of **3**, mp 67-69 °C. These were found to decompose slowly at room temperature and are best stored at < -15 °C. ^1H NMR (300 MHz): δ 3.23-3.48 (m, 4H), 3.75 (dd, J 6.5, 16.2, 1H), 3.88 (dd, J 2.7, 16.2, 1H), 4.37 (ddd, J 2.7, 5.1, 6.5, 1H), 5.11 (d, J 5.1, 1H). ^{13}C NMR (75 MHz) : δ 35.42(**C**Br_3), 38.77(**C**H_2S), 40.13(**C**H_2S), 55.03(**C**HS_2), 60.29(**C**HBr), 63.13(**C**H_2). IR (KBr): 2965, 2923, 1420, 1403, 1277, 1166, 1148, 1140, 1021, 969, 932, 719, 705 cm^{-1}. MS-CI(CH_4): *m/z* (relative intensity) 460.7 (MH^+, 4.98.), 380.7 (17.30), 300.8 (52.76), 222.9 (38.33), 196.9 (33.63), 145.0 (84.11). HRMS: calcd. for $C_6H_9Br_4S_2$ 460.6879; found 460.6855. Anal. calcd. for $C_6H_9Br_4S_2$ C, 15.53; H, 1.73; S, 13.82; found : C, 15.32; H, 1.69; S, 14.04.

2,4,4,4-Tetrabromo-1,1-di(2',2',2'-trifluoroethoxy)butane (4). Conc. sulfuric acid (1 mL) was added to a cooled (0 °C) well stirred solution of tetrabromobutanal **2** (2.304 g, 5.94 mmol) and 0.9 mL (6.5 mmol) of trifluoroethanol in 2 mL of methylene chloride. The reaction mixture was allowed to warm to ambient temperature and stirring was continued overnight. The

brown viscous mass was then poured into ice water, and extracted with methylene chloride (3 x 10 mL). The combined organic extracts were washed successively with aqueous 3% sodium bicarbonate solution and water, and the dried ($MgSO_4$) and evaporated. The residual oil was purified by flash chromatography on a silica column using hexane/EtOAc (10/1, v/v) as eluent. The yield of pure **4** was 1.9 g (62%). ^{1}H NMR (300 MHz): δ 3.60 (dd, J 6.0, 16.0, 1H), 3.87 (dd, J 2.0, 16.0, 1H), 4.11 (superposition of 2q, J_{HF} 8.8, and ddd, J_{HH} 2.0, 3.8, 6.0, 5H), 4.96 (d, J 3.8, 1H). ^{13}C NMR (75MHz): δ 35.27(**C**Br_3), 47.20(**C**HBr), 60.25(**C**H_2), 64.77(J_{CF} 35.0, CH_2O), 65.61 (J_{CF} 35.0, CH_2O), 104.63(**C**HO_2), 123.27 (J_{CF} 275, CF_3). IR (neat): 1658, 1279, 1162, 1085, 978 cm^{-1}. MS-CI(CH_4): *m/z* (relative intensity) 548.7 ([M^+ – HF], 3.32), 466.8 (23.02), 406.9 (48.81), 328.0 (31.55), 299.9 (37.06), 211.1 (76.14). Anal. calcd. for $C_8H_8Br_4F_5O_2$: C, 16.86; H, 1.41; found: C, 16.95; H, 1.39.

2,4,4,4-Tetrabromo-1,1-dimethoxybutane (5). A solution of tetrabromobutanal **2** (1.94 g, 5 mmol), trimethyl orthoformate (1.06 g, 10 mmol) and a small crystal of *p*-toluenesulfonic acid in 5 mL of anhydrous methanol was kept at ambient temperature for 72 h. The acid catalyst was then neutralized with excess of potassium carbonate, water (15 mL) and methylene chloride (20 mL) were then added, and following equilibration and separation of phases the organic solution was dried over $MgSO_4$. Evaporation of the solvent and distillation under reduced pressure yielded **5** (2.62 g, 95%) as a fraction of bp 150-155 °C/0.06 mm Hg which crystallized from hexane, mp 55-56 °C. ^{1}H NMR (200 MHz): δ 3.48 (s, 3H), 3.51 (s, 3H), 3.54 (dd, J 6.7, 16.7, 1H), 3.36 (dd, J 2.4, 16.7, 1H), 4.14 (ddd, J 2.4, 3.2, 16.7, 1H), 4.47 (d, J 3.2, 1H). ^{13}C NMR (75 MHz): δ 36.71(**C**Br_3), 48.50(**C**HBr), 55.93(**C**H_3O), 56.85(**C**H_3O), 60.52(**C**H_2), 106.38(**C**HO_2). IR (neat): 2993, 2960, 2932, 2833, 1447, 1406, 1371, 1347,1273, 1208, 1190, 1159, 1134, 1069, 1038, 968, 946, 907, 893, 740, 668, 653, 606 cm^{-1}. MS-CI (CH_4): *m/z* (relative intensity) 398.7 ([M^+ - CH_3O], 15.74), 318.8 (14.53), 270.9 (51.71), 194.0 (18.2), 169.0 (10.5). HRMS: calcd. for $C_5H_7Br_4O$ 398.7230; found 398.7251.

Reaction of dimethoxyacetal 5 with base. A solution of acetal **5** (205 mg, 0.47 mmol) in 3 mL of either *t*-butanol or methanol under an inert atmosphere was treated dropwise with a solution of 1.5 mmol of either *t*-BuOK in *t*-BuOH (5 mL) or KOH (powder) in CH_3OH (5 mL), respectively. Stirring was continued at r.t. overnight. The reaction mixture, which now contained a precipitate of KBr, was diluted with 25 mL of ether and extracted with three 10 mL portions of water. The organic layer was dried ($MgSO_4$) and evaporated, and the residue oil (66%) was purified by preparative tlc on silica using a mixture of n-hexane/methylene chloride/triethyl amine (1/1/0.025 v/v) as eluent (preparative tlc plates were pre-treated with the same eluent). Pure **2,4-dibromo-1,1-dimethoxy-2,3-butadiene 11** was isolated as an oil in 52% yield. ^{1}H NMR (600 MHz): δ 3.39 (s, 3H), 3.40 (s, 3H), 4.89 (d, J 1.2, 1H), 6.33 (d, J 1.2,

1H). ^{13}C NMR (150 MHz): δ 53.52(**C**H$_3$O), 53.57(**C**H$_3$O), 80.26(**C**-1), 96.48(**C**-2), 101.6(**C**-4), 199.87(**C**-3). IR (neat): 2936, 2833, 1960, 1448, 1338, 1193, 1108, 1065, 965, 789, 665 cm^{-1}. CI-MS(CH$_4$): *m/z* (relative intensity) 268.9 ([M – H]$^+$, 1.51), 238.9 ([M - CH$_3$O]$^+$, 44.93), 191.0 (38.10), 112.0 (100.0). HRMS: calcd. for $C_6H_7Br_2O_2$ 268.8812; found 268.8803. Using of 1 mmol of *t*-BuOK in 5 mL *t*-BuOH gave an unseparable mixture of starting acetal **5** and **2,4,4-tribromo-1,1-dimetoxy-3-butene (10)** in the ratio 1/3. ^{1}H NMR (300 MHz): δ 3.46 (s, 6H), 4.48 (d, J 5.0, 1H), 4.67 (dd, J 5.0, 10.0, 1H), 6.70 (d, J 10.0, 1H). ^{13}C NMR (75 MHz): δ 49.45(**C**HBr), 55.32(**C**H$_3$O), 55.60(**C**H$_3$O), 95.79(**C**Br$_2$), 104. 77(**C**HO$_2$), 133.76(=**C**H).

3-(1',3',3',3'-Tetrabromopropyl)-2,4-benzodioxepane (6). A solution of tetrabromobutanal **2** (3.23 g, 8.33 mmol), 1,2-benzenedimethanol (1.15 g, 8.33 mmol), and a few crystals of *p*-toluenesulfonic acid in 30 mL of toluene, containing activated molecular sieves (3 Å) was heated at reflux for 8 h. The cooled reaction mixture was diluted with Et$_2$O (70 mL), extracted with saturated aqueous NaHCO$_3$ solution (30 mL) and dried over Na$_2$SO$_4$. The residue (3.81 g) obtained by evaporation of solvent was chromatographed on a neutral alumina column using hexane-CH$_2$Cl$_2$ (9/1, v/v) as eluent. The product fraction was recrystallized twice from petroleum ether and heptane, yield 3.3 g (78%), mp 110-112 °C. ^{1}H NMR (200 MHz): δ 3.57 (dd, J 6.7,16.6, 1H), 3.92 (dd, J 2.7, 16.6, 1H), 4.24 (m, 1H), 4.96 (bs, 4H), 5.11 (d, J 3.5, 1H), 7.23 (m, 4H). ^{13}C NMR (75 MHz): δ 36.22(**C**Br$_3$), 49.44(**C**HBr), 61.18(**C**H$_2$CBr$_3$), 72.97(**C**H$_2$O), 73.11(**C**H$_2$O), 107.87(**C**HO$_2$), 127.70(**C**$_{ar}$), 127.87(**C**$_{ar}$), 138.35(**C**$_{ipso}$), 138.48(**C**$_{ipso}$). IR (KBr): 2962, 2915, 2885, 2859, 2852, 1456, 1445, 1400, 1375, 1361, 1279, 1254,1221, 1166, 1124, 1082, 1050, 1032, 1008, 999, 951, 936, 895, 887, 773, 750, 737, 698, 651, 631, 612, 603 cm^{-1}. MS-CI: *m/z* 504.8 (MH$^+$, 1.2), 241.1 (28.49), 184.9 (30.53), 149.0 (100), 119.0 (66.52), 104.0 (31.50), 91.0 (52.24). HRMS: calcd. for $C_{12}H_{13}Br_4O_2$ 504.7650; found 504.7649.

3-(3',3'-Dibromo-1*E*-propenyl)-2,4-benzodioxepane (13). A solution of acetal **6** (108 mg, 0.2 mmol), potassium *t*-butoxide (68 mg, 0.6 mmol) and a catalytic quantity of crown ether (18-CE-6, 5.5 mg, 0.02 mmol) in 2 mL of dry toluene was stirred at ambient temperature for 72 h. Following dilution with 20 mL of Et$_2$O, extraction with saturated aq.NaHCO$_3$ solution (10 mL), drying (MgSO$_4$) and evaporation, 47 mg of crude product was obtained (68% recovery). Purification was accomplished by chromatography (silica column; hexane/EtOAc eluent, 95/5 v/v) and trituration with petroleum ether, yielding 23 mg of **13** as oil. ^{1}H NMR (300 MHz): δ 4.93 and 4.88 (ABq, J_{gem} 14.5, 4H), 5.47 (ddd, J 3.2, 1.4, 0.5, 1H), 5.81 (ddd, J 15.2, 3.2, 0.7, 1H), 6.17 (ddd, J 8.5, 0.9, 0.5, 1H), 6.49 (ddd, J 15.2, 8.5, 1.4, 1H), 7.13-7.26 (m, 4H). ^{13}C NMR (75 MHz): δ 38.89(**C**HBr$_2$), 70.20(**C**H$_2$O), 101.84(**C**HO$_2$), 127.03(**C**$_{ar}$), 127.37(**C**$_{ar}$),

128.23, 134.52, 138.39(C_{ipso}). MS-CI(NH_3): *m/z* 366 (MNH_4^+, 34), 349 (MH^+, 53), 228 (32), 138 (100), 120 (32). HRMS: calcd. for $C_{12}H_{13}Br_2O_2$ 346.9281; found 346.9220.

Reaction of 4 with base: The procedure followed was that detailed for acetal **5**, except that the reaction time was reduced to 1 h. Products were purified by preparative tlc on silica gel using hexane/EtOAc (95/5, v/v) as eluent.

2,4,4-Tribromo-1,1-di(2',2',2'-trifluoroethoxy)-3-butene (7): ^{1}H NMR (300 MHz): δ 4.05 (superposition of two q, J_{HF} 8.0, 4H), 4.67 (dd, J 5.4, 10.1, 1H), 4.95 (d, J 5.4, 1H), 6.65 (d, J 10.1, 1H). ^{13}C NMR (75 MHz): δ 47.91(CHBr), 63.66 (q, J_{CF} 30, CH_2O), 65.09 (q, J_{CF} 30, CH_2O), 97.36(CBr_2), 103.20(CHO_2), 123.23 (q, J_{CF} 270,CF_3), 132.23(=CH). IR (neat): 1603, 1427, 1281, 1169, 1099, 1086, 1004, 974, 855, 822, 669 cm^{-1}. MS-CI: *m/z* 486.8 (MH^+, 1.17), 406.8 (48.75), 388.8 (52.1), 328.0 (21.5), 211.1 (54.5). HRMS: calcd. for $C_8H_8Br_3F_6O_2$ 486.7978; found 486.7930.

4,4,4-Tribromo-1,1-di(2',2',2'-trifluoroethoxy)-2*E*-butene (8): ^{1}H NMR (300 MHz): δ 3.97 (q, J_{HF} 8.0, 4H), 5.50 (dd, J 1.5, 3.0, 1H), 6.01 (dd, J 3.0, 14.5, 1H), 6.72 (dd, J 1.5, 14.5, 1H). ^{13}C NMR (75 MHz): δ 32.74(CBr_3), 62.46 (q, J_{CF} 33,CH_2), 97.91(CHO_2), 125.30 (=CH), 126.31 (q, J_{CF} 285,CF_3), 143.47(=CH). IR (neat): 1710, 1649, 1428, 1280, 1168, 1084, 1023, 971, 852, 668 cm^{-1}. MS-CI: *m/z* 406.9 ([M – HBr]$^+$, 6.36), 311.1 (16.5), 283.0 (100), 211.0 (42.4), 183.1 (82.4). HRMS: calcd. for $C_8H_7Br_2F_6O_2$ 406.8717; found 406.8710.

4,4-Dibromo-1,1-di(2',2',2'-trifluoroethoxy)-2*E*-butene (9): ^{1}H NMR (300 MHz): δ 3.93 (q, J_{HF} 8.0, 4H), 5.37 (dd, J 1.5, 3.0, 1H), 5.72 (ddd, J 1.0, 3.0, 15.0, 1H), 6.14 (dd, J 1.0, 8.0, 1H), 6.50 (ddd, J 1.5, 8.0, 15.0, 1H). ^{13}C NMR (75 MHz): δ 37.51($CHBr_2$), 62.39 (q, J_{CF} 33,CH_2), 98.32(CHO_2), 123.58 (q, J_{CF} 270, CF_3), 125.50(=CH), 136.97(=CH). IR (neat): 2962, 2860, 1430, 1285, 1175, 1089, 1013, 970 cm^{-1}. MS-CI (CH_4): *m/z* 407.9 (MH^+, 29), 327.9 (28.5), 211.1 (57.1), 183.1 (61.4). HRMS: calcd. for $C_8H_8Br_2F_6O_2$ 407.8795; found 407.8860.

1-{3',3'-Dibromo-2'-propenyl-1'-(1'',3''-dithiolane-2''-ylidene)}-4-phenyl-1,2,4-triazolidine-3,5-dione (14) : A slow stream of dry nitrogen was bubbled through a stirred mixture of diene **1** (101 mg, 0.33 mmol), 4-phenyl-3H-1,2,4-triazoline-3,5-dione (58 mg, 0.33 mmol) and 5 mL of CH_2Cl_2 kept at –20 °C. Following complete solution of the reactants (ca. 1 h) the solvent was evaporated. The ^{1}H NMR spectrum of the residue indicated an almost quantitative yield of product. Recrystallization from CH_2Cl_2-hexane yielded crystals of mp 148-150 °C. ^{1}H NMR (600 MHz): δ 3.51 (m, sym. AA'BB' pattern, 4H), 7.21 (s, 1H), 7.39 (t, J 8.2, 1H), 7.49 (m, 2H), 7.54 (d, J 7.7, 2H), 7.7 (b, 1H). ^{13}C NMR (150 MHz): δ 38.2(CH_2), 39.0(CH_2), 88.2 (CBr_2), 114.0(CN), 125.6(CH), 128.4(CH), 129.2(CH), 129.9(=CH), 131.1(C_{ipso}), 149.2 (CS_2),

153.1(CO), 155.4(CO). MS-CI(CH_4): *m/z* (relative intensity) 395.9 ([MH^+ - HBr], 11.9), 318.0 (39.9), 293.0 (10.8), 219.0 (11.0), 181.0 (10.0), 169.0 (11.8), 131.0 (9.9), 120.0 (100). HRMS: calcd. for $C_{14}H_{11}BrN_3O_2S_2$ 395.9440; found 395.9476 UV ($CHCl_3$) λ_{max} nm (log ε): 265 (4.16), 306 (4.47), 322 (4.60).

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