arabino-tetraacetoxybutyl)-5-methylpyrazine[7] (δ 8.38, s, 2 H) and fructosazine octaacetate[2] (δ 8.53, s, 2 H).

Thus, the most probable structure for the acetylated compound **4** is the 2-(D-*arabino*-tetraacetoxybutyl)-5-(3,4-diacetoxy-2-sulfobutyl)pyrazine pyridinium salt, and the structure of the principal product of this condensation reaction is the hydroxy derivative of **4** (**5**).

Experimental Section

^{1}H NMR spectra were recorded at 60 MHz with a Hitachi R-24 spectrometer. Measurements were made in $CDCl_3$ solution containing tetramethylsilane as an internal standard and in D_2O with the sodium salt of 3-(trimethylsilyl)propanesulfonic acid (DSS) as the internal standard. IR spectra were measured as KBr pellets and recorded on an IR-27 Shimadzu spectrophotometer. UV spectra were measured with Hitachi spectrometer, Model 124. Analytical paper chromatography was performed with the solvent systems (A) pyridine/isoamyl alcohol/water (40:35:30) and (B) ethyl acetate/pyridine/acetic acid/water (5:5:1:3). Spots on the paper chromatogram were developed with $FeSO_4$ solution[8] and permanganate-periodate solution.[9] All melting points were determined with a Yanaco micro melting point apparatus and are uncorrected.

Condensation Products of 2-Amino-2-deoxy-D-glucose in the Presence of Sodium Bisulfite. 2-Amino-2-deoxy-D-glucose hydrochloride (17.2 g) was dissolved in 80 mL of water containing 0.08 mol of sodium bisulfite (8.32 g) and sodium hydroxide (3.2 g, 0.08 mol). The mixture was heated at 80 °C for 5 h, and during the reaction air was bubbled through the mixture. After the reaction mixture had been passed through a column of Amberlite IR-120 (H^+), its acidic effluent was concentrated to syrup in vacuo. Paper chromatography (system A) of this syrup showed that it contained four components: the main product (**5**, R_f 0.34) and small amount of other three components (R_f 0.43, 0.21, 0.10). Methanol was added to produce a precipitate which, after filtration and a washing with methanol, gave a hygroscopic solid weighing 3 g.

2-(D-*arabino*-Tetraacetoxybutyl)-5-(3,4-diacetoxy-2-sulfobutyl)pyrazine (4). Acetylation was carried out according to the method of Taha.[10] A mixture of 6 g of the hygroscopic solid, 300 mL of acetic anhydride, and 300 mL of pyridine was stirred overnight at room temperature. This reaction mixture was poured into ice-water and treated with chloroform. The chloroform layer formed was washed successively with 0.3 N hydrogen chloride solution and water, dried with anhydrous sodium sulfate, and concentrated in vacuo to give crystals. After three recrystallizations from methanol, the yield was 252 mg of **4**: mp 179 °C; $[\alpha]^{15}{}_{\mathrm{D}}$ 0° (*c* 0.1, MeOH); UV (MeOH) λ_{max} 206, 256, 263, 269, 275 nm; IR (KBr) ν_{max} 3030 (CH_2), 1750 (C=O), 1640 (C=N), 1380, 1230 (SO_3H) cm^{-1}; NMR ($CDCl_3$), Table I. Anal. Calcd for $C_{29}H_{37}N_3O_{15}S$: C, 49.78; H, 5.33; N, 6.01; S, 4.58. Found: C, 49.82; H, 5.30; N, 5.90; S, 4.20.

2-(D-*arabino*-Tetrahydroxybutyl)-5-(3,4-dihydroxy-2-sulfobutyl)pyrazine (5). Ten grams of **4** was suspended in 400 mL of ethanol after which hydrogenchloride gas was passed through it to produce the gelatinous precipitate. After filtration, the precipitate was washed several times with ethanol and then reprecipitated from water and ethanol which gave an amorphous mass: 4.1 g; mp 115 °C; $[\alpha]^{15}{}_{\mathrm{D}}$ −53.6° (*c* 1.0, H_2O); UV (H_2O) λ_{max} 276 nm (ϵ 7360); IR (KBr) ν_{max} 1620 (C=N), 1170 (SO_3H), 1030 cm^{-1}. Anal. Calcd for $C_{12}H_{20}N_2O_9S$: C, 39.13; H, 5.47; N, 7.60; S, 8.70. Found: C, 39.32; H, 5.14; N, 7.16; S, 8.37.

Pyrazine-2,5-dicarboxylic Acid (6). One gram of **5** in 150 mL of water was neutralized with 2 N potassium hydroxide solution. Another 0.7 g of potassium hydroxide was added to bring the pH to 11.6. Enough potassium permanganate was added to this solution in portions under continuous stirring to oxidize compound **6**. The slight excess of potassium permanganate was digested with ethanol. The precipitated manganese oxide was filtered and its filtrate passed through a column of Amberlite IR-120 (H^+). Condensation in vacuo of this solution gave white crystals. Recrystallization from water produced 130 mg of the product, yield 28%. This crystal had an IR spectrum, R_f value and color development in solvent system A and $FeSO_4$ identical with those found for **6** derived from **3**.

Hydrogenolysis of Compound 5 and 1-Amino-1,3,4-trideoxy-4-sulfo-2-hexulose (7). Hydrogenolysis of **5** was performed according to the method of Kuhn et al.[3] A 674.4-mg sample of **5** was dissolved in 10 mL of 2 N hydrochloric acid, and then palladium oxide (50 mg) was added to this solution. This solution was treated for 16 h under a slightly increased atmosphere of hydrogen. After sufficient hydrogen had been consumed, the reaction mixture was filtered, and its filtrate was concentrated in vacuo to give the crystals. After recrystallization from water, the yield was 38 mg of **7**: mp 151 °C; IR (KBr) 3400 (OH), 2900 (CH_2), 1620 (NH_2), 1520 cm^{-1}; NMR (D_2O) δ 3.28 (2 H, s, H-1a and H-1b), 2.48 (2 H, m, H-3a and H-3b), 3.4–3.9 (4 H, m, H-4, H-5, H-6a, and H-6b). Anal. Calcd for $C_6H_{13}NO_6S{\cdot}0.25H_2O$: C, 31.10; H, 5.87; N, 6.04; S, 13.84. Found: C, 31.05; H, 5.82; N, 6.01; S, 13.78.

The filtrate also was concentrated to give 7.5 mg of other crystals (**8**). These crystals had an IR spectrum and an R_f value (0.28 in solvent system B) identical with those for the 1-amino-1-deoxy-D-fructose hydrochloride prepared from deoxyfructosazine (**3**).

Registry No. 1, 3416-24-8; **4**, 82995-49-1; **5**, 82995-50-4; **6**, 122-05-4; **7**, 82995-51-5; **8**, 4429-04-3; $NaHSO_3$, 7631-90-5.

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Preparation and Diels-Alder Reaction of (1*E*)-1,3-Dimethoxybutadiene

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Received March 16, 1982

A high degree of synthetic utility has been demonstrated for the 1,3-dioxygenated butadienes by Danishefsky and his collegues.[1] Their synthesis and development of 1-methoxy-3-[(trimethylsilyl)oxy]-1,3-butadiene (I), as well as other electron-rich dienes, has made possible wide-ranging synthetic advanes.[1]

We recently encountered an innstance in which the (trimethylsilyl)oxy group of I suffered intermolecular transfer to the oxygen atom of thiolen-2-one in preference to the anticipated Diels-Alder reaction.[2] Accordingly, it appeared that a 1,3-dialkoxybutadiene might provide a useful alternative for those rare instances in which intramolecular silyloxy group transfer intervenes in the Diels-Alder reaction of I.

The literature contains one report[3] of 1,3-diethoxy-1,3-butadiene. Other 1,3-dialkoxybutadienes, including 1,3-dimethoxybutadiene, are unknown.

We intended to prepare 1,3-dimethoxy-1,3-butadiene (II) by pyrolysis of the acetal 1,1,3-trimethoxybut-2-ene (III). The latter is ordinarily prepared by addition of sodium methoxide in methanol[4] to 1,1-dimethoxybut-2-yne (IV) (the prepartion of IV is described in the Experimental Section) at 150 °C in a sealed tube.

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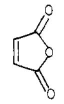
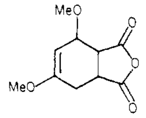
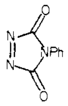
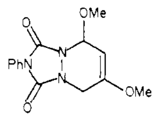
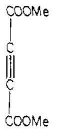
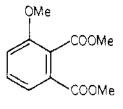
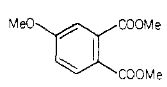
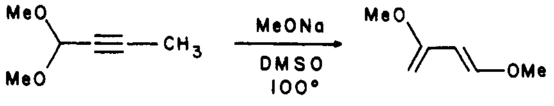
Table I. Diels–Alder Reaction of (1*E*)-1,3-Dimethoxybutadiene (II) with Dienophiles

dienophile	product (% yield)
	 V (98)
	 VI (82)
	 VIII (44)  VII (19)

As an alternative to the sealed-tube reaction above, the acetylenic acetal IV was heated with sodium methoxide



IV II

in dimethyl sulfoxide at 100 °C for 2.75 h. The product was not the expected acetal III. Instead, the desired diene II was isolated in 20–30% yield following distillation. Although the yield of the diene II is modest, the starting material is readily available, and the procedure is straightforward.

The spectral properties of the diene II are in good agreement with expectation. The NMR spectrum (300 MHz) shows the expected vinyl AB quartet at δ 6.93 and 5.32 with J_{AB} = 12.53 Hz, indicating the presence of the trans double bond. The terminal methylene group also appears as an AB quartet at δ 3.93 and 3.91 with J_{AB} = 1.82 Hz. The two methoxy groups appear as singlets at δ 3.59 and 3.61. The NMR spectrum also showed a small but persistent impurity which was not entirely removed by conventional (Vigreaux column) distillation. The impurity did not interfere with the Diel–Alder reactions of the diene II.

Reaction of 1,3-dimethoxy-1,3-butadiene (II) with maleic anydride, *N*-phenyltriazolinedione, and dimethyl acetylenedicarboxylate yielded the adducts V– VIII (Table I) whose properties are described in the Experimental Section.

The 1,3-dimethoxybutadiene (II) appears to be somewhat less stable than the Danishefsky diene I. For example, the diene II decomposes quite rapidly on heating. For this reason, it is advantageous to include a small amount of 2,6-di-*tert*-butyl-4-methylphenol (BHT) in all preparations and distillations of II.

Experimental Section

Preparation of 1,1-Dimethoxybut-2-yne (IV). **α-Bromocrotonaldehyde.** In a 500-mL, three-necked, round-bottomed flask equipped with a Trubore mechanical stirrer, dropping funnel, and glass stopper was placed 86.2 g (1.23 mol) of distilled crotonaldehyde. The dropping funnel was charged with 206.3 g (1.29 mol) of bromine. The stirrer was started and the bromine added dropwise over a period of 90 min while the reaction was cooled at 0 °C. After the addition was complete, 7.0 g (0.10 mol) of crotonaldehyde was added to consume the excess bromine. Mechanical stirring and ice cooling were continued while 121.1 g (1.48 mol) of anhydrous sodium acetate was added in 10–20-g portions over a 40-min period. The resulting thick, white suspension was stirred for 1 h at 0 °C, and then 150 mL of deionized water was added. To the resulting two-phase mixture was added 124.0 g (1.48 mol) of sodium bicarbonate. The reaction mixture was then diluted with 300 mL of water and extracted with three 500-mL portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate, filtered, and concentrated to yield 160.0 g (81%) of α-bromocrotonaldehyde as a light yellow oil.

The 60-MHz NMR spectrum (CCl_4) of the aldehyde showed a one-proton aldehydic singlet at δ 9.13, a one-proton vinyl quartet (J = 7.0 Hz) at δ 7.07, and a three-proton methyl doublet (J = 7.0 Hz) at δ 2.03. The IR spectrum (film) showed bands at 3010 (w), 2850 (m), 2750 (w), 1710 (s), 1700 (s), 1635 (s), 1450 (m), 1390 (m), 1380 (m), 1300 (m), 1175 (s), 1080 (m), 970 (m), and 830 cm^{-1} (m).

α-Bromocrotonaldehyde Dimethyl Acetal. In a 1000-mL, round-bottomed, single-necked flask equipped with a magnetic stirring bar and a reflux condenser were placed 160.0 g (1.08 mol) of α-bromocrotonaldehyde, 126.7 g (1.19 mol) of trimethyl orthoformate, and 190.0 mL of absolute methanol. The stirrer was started, and 1.56 mL (0.019 mol) of concentrated hydrochloric acid was added. The reaction started within 1 min, with the temperature rising to reflux. After 4 h, the reaction was complete as shown by NMR analysis of an aliquot, which showed disappearance of the aldehyde singlet at δ 9.13. Sodium bicarbonate (3.0 g, 0.035 mol) was added, and the volatile material was removed on a rotary evaporator. The resulting oil was diluted with 150 mL of water. The layers were separated. The aqueous layer was extracted with two 100-mL portions of ether. The organic layers were combined, dried over anhydrous potassium carbonate, filtered, and concentrated to yield 224.3 g of α-bromocrotonaldehyde dimethyl acetal of sufficient purity for use in the next reaction.

The 60-MHz NMR spectrum (CCl_4) of the acetal showed a one-proton vinyl doublet of quartets (J = 1, 6 Hz) at δ 6.25, a one-proton acetal multiplet centered at δ 4.67, a six-proton methyl acetal singlet at δ 3.20, and a three-proton methyl doublet of doublets (J = 1, 6 Hz) at δ 1.81. The IR spectrum (film) showed bands at 2990 (s), 2955 (s), 2945 (s), 2830 (s), 1660 (s), 1445 (s), 1380 (s), 1360 (s), 1275 (s), 1220 (s), 1190 (s), 1100 (s, br), 990 (s), 839 (m), and 765 cm^{-1} (m).

1,1-Dimethoxybut-2-yne (IV). In a 100-mL, single-necked, round-bottomed flask equipped with a reflux condenser, a drying tube charged with calcium sulfate (Drierite), and a magnetic stirring bar were placed 224.3 g (1.15 mol) of α-bromocrotonaldehyde dimethyl acetal, 152.0 g (2.30 mol) of 85% potassium h'hydroxide, and 250 mL of absolute methanol. The resulting heterogeneous mixture was stirred at reflux for 2 h. After this time, the reflux condenser was replaced with a 6-cm Vigreaux distillation apparatus, and 260 mL of methanol was distilled from the reaction flask. The reaction mixture was cooled to room temperature, and 150 mL of deionized water was added. The resulting two-phase mixture was filtered under reduced pressure through a pad of Celite 545. The layers of the filtrate were separated. The aqueous layer was extracted with two 200-mL portions of 1:1 pentane–ether. The combined organic layers were dried over anhydrous sodium sulfate, filtered, and partially concentrated at room temperature on the rotary evaporator. The remaining solvent was removed by distillation through a 12-cm Vigreaux distilling apparatus at 25 °C and 45–50 mmHg. The pressure was then lowered, and the product was distilled, yielding 78.0 g (59%) of 1,1-dimethoxybut-2-yne (IV) as a colorless liquid, bp 50–52 °C (20–22 mm) [lit.[4] bp 144–145 °C (760 mm)]. The overall yield from crotonaldehyde was 51%.

The NMR spectrum (60 mHz, CCl_4) of the acetal IV showed a one-proton acetylenic acetal quartet (J = 1.7 Hz) at δ 4.88, a six-proton methyl acetal singlet at δ 3.23, and a three-proton acetylenic methyl doublet (J = 1.7 Hz) at δ 1.86. The IR spectrum (CCl_4) showed bands at 3000 (me), 2960 (s), 2940 (s), 2900 (s), 2830 (s), 2310 (w), 2260 (m), 2135 (w), 2125 (m), 1360 (s), 1195 (s), 1155 (s), 1090 (s), 1050 (s), 960 (s), and 905 cm^{-1} (s). The mass spectrum (15 eV) showed peaks at m/e (relative intensity) 113 (8, $M^+ - H$), 99 (8, $M^+ - OCH_3$), and 100, ($M^+ - OCH_3$).

(1*E*)-1,3-Dimethoxy-1,3-butadiene (II). In a 500-mL round-bottomed flask equipped with serum stopper, magnetic stirring bar, reflux condenser, and nitrogen inlet was placed 10.50 g (0.22 mol, 50% dispersion in mineral oil) of sodium hydride. The system was evacuated and flushed three times with nitrogen. The sodium hydride was washed with two 40 mL portions of pentane to remove the mineral oil. The residual pentane was evaporated in vacuo, and the system was flushed again with nitrogen. Dimethyl sulfoxide (100 mL, freshly distilled from calcium hydride) was added. The resulting gray suspension was stirred, and then 7.03 g (0.22 mol) of absolute methanol was added dropwise by using a syringe. The resulting white suspension was stirred for 30 min at room temperature, and then 25.00 g (0.22 mol) of 1,1-dimethoxybut-2-yne (IV) containing 1.50 g (0.0068 mol, 3.1 mol %) of 2,6-di-*tert*-butyl-4-methylphenol (BHT) was added in one portion by using a syringe. The resulting brown suspension was heated at 100–102 °C (oil bath temperature) for 2.75 h.

After cooling to room temperature, the dark brown mixture was slowly poured into 200 mL of pentane and 200 mL of saturated aqueous sodium bicarbonate. The layers were separated, and the aqueous phase was extracted with two 100-mL portions of pentane. The combined pentane extracts were washed with four 50-mL portions of saturated aqueous sodium bicarbonate solution and dried over anhydrous sodium sulfate. Filtration followed by concentration at room temperature yielded 18.4 g of crude product as a dark amber oil. The crude product was distilled under reduced pressure through a base-washed 6-cm Vigreaux column. Four fractions covering a 4.5 °C boiling range were taken. The fractions were nearly equivalent in purity as judged by NMR analysis. A total of 10.90 g of colorless liquid [bp 53–57.5 °C (21–23 mm)] was collected. The diene II obtained in this way contained small amounts of impurities. Distillation of the crude product through a 28-cm Vigreux column followed by immediate redistillation failed to give completely pure material but did not reduce the impurity to an acceptably low level.

The 300-MHz NMR spectrum ($CDCl_3$) of the diene II showed a two-proton vinyl AB quartet ($J = 12.53$ Hz) at δ 6.93 and 5.32, a two-proton vinyl methylene AB quartet ($J_{AB} = 1.82$ Hz) at δ 3.91 and 3.93, and a pair of three-proton enol methyl ether singlets at δ 3.61 and 3.59. The infrared spectrum (neat) showed bands at 3000 (m), 2960 (s), 2940 (s), 2830 (s), 1660 (vs), 1610 (s), 1465 (m), 1450 (m), 1320 (vs), 1210 (vs), 1160 (vs), 1130 (vs), 1080 (vs), and 940 cm^{-1} (s). The mass spectrum (15 eV) showed peaks at *m/e* (relative intensity) 114 (100, M^+), 99 (55, M − CH_3), and 83 (72, M − OCH_3). Exact mass (calcd for $C_6H_{10}O_2$ 114.0680, found 114.0680.

An impurity is evident in the NMR spectrum as a series of singlets at δ 3.55–3.33. The impurity is estimated to constitute approximately 10% of the material and does not interfere with subsequent reactions of the diene.

1,3-Dimethoxy-1,3-butadiene Adduct V with Maleic Anhydride. In a 50-mL, single-necked, round-bottomed flask equipped with a magnetic stirring bar was placed 0.426 g (4.34 mmol) of maleic anhydride. The system was evacuated and flushed three times with nitrogen, and 5 mL of dry THF was added by using a syringe. This was followed by 0.044 g (0.435 mmol) of dry triethylamine. The resulting solution was stirred and cooled in an ice–water bath, and then 0.545 g (4.78 mmol) of 1,3-dimethoxy-1,3-butadiene (II) was added dropwise, by using a syringe, over a 15-min period. The reslting pale yellow solution was stirred for an additional 15 min at 0 °C. The solvent was removed in vacuo at 0 °C (0.010 mm) for 1.5 h. The cooling bath was removed, and concentration was allowed to proceed under vacuum for 10 h to give 0.902 g (98%) of the adduct V as a light yellow oil.

The 300-MHz NMR spectrum ($CDCl_3$) of the adduct V showed the enol ether vinyl proton as a doublet of doublets ($J = 2.22$, 6.37 Hz) at δ 4.95, the adjacent methine proton as a doublet of doublets ($J = 3.94$, 6.37 Hz) at δ 4.37, a three-proton methyl enol ether singlet at δ 3.61, a one-proton multiplet centered at δ 3.47, a three-proton methyl ether singlet at δ 3.20, a one-proton multiplet centered at δ 3.19, and the allylic methylene group as the AB part of an ABX spin system with the A proton showing allylic coupling ($J = 2.22$ Hz, $J_{AX} = 5.76$ Hz, $J_{AB} = 16.98$ Hz) at δ_A 2.80 and the B proton ($J_{BX} = 10.71$ Hz, $J_{AB} = 16.98$ Hz) at δ_B 2.51. The infrared spectrum ($CHCl_3$) showed bands at 2930 (s), 2980 (w), 2820 (w), 1850 (w), 1785 (vs), and 1645 cm^{-1} (m). The mass spectrum (15 eV) showed peaks at *m/e* (relative intensity) 213 (22, $M^+ + H$), 212 (53, M^+), 168 (47, $M^+ - CO_2 - CO$), and 109 (100, $M^+ - CO_2 - CO - OCH_3$).

1,3-Dimethoxy-1,3-butadiene Adduct VI with 4-Phenyl-1,2,4-triazoline-3,5-dione. To a solution of 0.066 g (0.377 mmol) of 4-phenyl-1,2,4-triazoline-3,5-dione in 1.0 mL of anhydrous dichloromethane under an inert atmosphere was added crude 1,3-dimethoxy-1,3-butadiene (II) dropwise by using a syringe. The red color of the solution was discharged after 0.059 g of the diene II had been added. The solvent was removed, yielding 0.115 g of the adduct VI as a white solid, mp 124–127 °C. Recrystallization from hexane–dichloromethane gave 0.039 g (82%) of fine white needles, mp 127–130 °C.

The 300-MHz NMR spectrum ($CDCl_3$) of the adduct VI showed a five-proton aromatic multiplet at δ 7.52, a one-proton doublet ($J = 4.7$ Hz) at δ 5.78, a one-proton doublet ($J = 4.7$ Hz) at δ 5.00, a two-proton AB quartet ($J_{AB} = 15.4$ Hz) at δ_A 4.33 and δ_B 3.95, and two three-proton methyl ether singlets at δ 3.69 and 3.58. The infrared spectrum ($CHCl_3$) of VI showed bands at 1785 (w), 1670 (w), 1600 (w), and 1410 cm^{-1} (m). The mass spectrum (15 eV) showed peaks at *m/e* (relative intensity) 289 (100, M^+), 258 (59, $M^+ - OCH_3$), 155 (9, $M^+ - CH_3 - CONPh$), 142 (14, $M^+ - PhNCO - CO$), 139 (16, $M^+ - PhNCO - OCH_3$), 119 (18, PhNCO), and 114 (32, dimethoxybutadiene).

1,3-Dimethoxy-1,3-butadiene Adducts VII and VIII with Dimethyl Acetylenedicarboxylate. A solution of 2.82 g (24.71 mmol) of 1,3-dimethoxy-1,3-butadiene (II) in 6 mL of anhydrous benzene was added over a period of 3 h to a solution of 1.75 g (12.31 mmol) of dimethyl acetylenedicarboxylate in 6.0 mL of anhydrous benzene containing 0.125 g (1.24 mmol) of triethylamine and 0.050 g (0.127) of 4,4′-thiobis[6-*tert*-butyl-*o*-cresol] held at 75 °C under an inert atmosphere. The resulting dark amber solution was heated an additional 13.5 h at 75 °C and then cooled to room temperature. Concentration on a rotary evaporator yielded 4.426 g of amber oil. Thin-layer chromatographic analysis (3:2 hexane–ethyl acetate) showed two products at R_f 0.54 and 0.43. The crude product was distilled bulb-to-bulb at 25 °C (0.03 mm). The volatile products were collected in a liquid nitrogen cooled trap and weighed 1.212 g. NMR analysis of the distillate showed a complex mixture of starting diene II and ester and diene decomposition products. The nonvolatile residue, 3.214 g of a dark amber oil, was passed through a 15-g column of silica gel and eluted with dichloromethane, yielding 2.512 g of a light yellow oil. This material was rechromatographed on 250 g of silica gel and eluted with 4:1 hexane-ethyl acetate. Thirty 50-mL fractions were taken. Fractions 9–15 with R_f 0.54 (3:2) hexane–ethyl acetate) were combined and concentrated to give 1.213 g (44%) of the dimethyl 4-methoxyphthalate (VIII).

The 300-MHz NMR spectrum ($CDCl_3$) of (VII) showed a one-proton doublet ($J = 8.49$ Hz) at δ 7.81, a one-proton doublet ($J = 2.63$ Hz) at δ 7.07, a one-proton doublet of doublets ($J =$ 2.63, 8.49 Hz) at δ 6.99, a three-proton methyl ether singlet at δ 3.86, and two three-proton methyl ester singlets as δ 3.87 and 3.92. The infrared spectrum ($CDCl_3$) showed bands at 2960 (w), 2860 (w), 1730 (vs), 1610 (m), 1585 (w), 1438 (w), 1295 (vs), 1130 (s), 1075 (s), and 1035 cm^{-1} (w). The mass spectrum (15 eV) showed peaks at *m/e* (relative intensity) 224 (7, M^+) and (100, $M^+ - OCH_3$). The spectral properties are in good agreement with those reported.[5]

Fractions 16–25 were combined to yield 0.538 g of product with R_f 0.43 (3:2 hexane–ethyl acetate) as a pale yellow oil which solidifed on standing. Crystallization from hexane–ether gave 0.485 (19%) of white needles [mp 74–75 °C (lit.[6] mp 77–78 °C)] of dimethyl 3-methoxyphthalate (VIII).

The 300-MHz spectrum ($CDCl_3$) of VIII showed a one-proton doublet ($J = 7.88$ Hz) at δ 7.57, a one-proton doublet of doublets ($J = 8.29$, 7.88 Hz) at 7.39, a one-proton doublet ($J = 8.29$ Hz) at δ 7.10, a three-proton aryl methyl ether singlet at δ 3.83, and two three-proton methyl ester singlets at δ 3.90 and 3.83. The infrared spectrum ($CDCl_3$) showed bands at 2950 (w), 2845 (w), 1735 (vs), 1595 (m), 1470 (m), 1430 (m), 1790 (vs), 1109 (m), 0165 (vs), 965 (w), and 885 cm^{-1} (w). The mass spectrum (15 eV) showed peaks at *m/e* (relative intensity) 224 (62, M^+), 193 (100,

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[5] Neunhoeffer, H.; Werner, G. *Justus Liebigs Ann. Chem.* **1973**, 1955.

$M^+ - OCH_3$), 161 (19, $M^+ - OCH_3 - CH_2O$), and 134 (14, $M^+ - COOCH_3 - OCH_3$). The spectral properties compare favorably with those reported.[6]

Acknowledgment. This work was generously supported by the National Institute for General Medical Sciences under Grant GM 27667.

Registry No. II, 83027-08-1; IV, 22022-34-0; V, 83027-09-2; VI, 83027-10-5; VII, 22895-19-8; VIII, 32136-52-0; crotonaldehyde, 4170-30-3; α-bromocrotonaldehyde, 24247-53-8; α-bromocrotonaldehyde dimethyl acetal, 83027-11-6; maleic anhydride, 108-31-6; 4-phenyl-1,2,4-triazoline-3,5-dione, 4233-33-4; dimethyl acetylenedicarboxylate, 762-42-5.

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3-Thiolen-2-one. A Useful Dienophile

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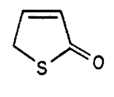
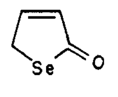
Received March 16, 1982

Although 3-thiolen-2-one (I) and 3-selenolen-2-one (II)



I

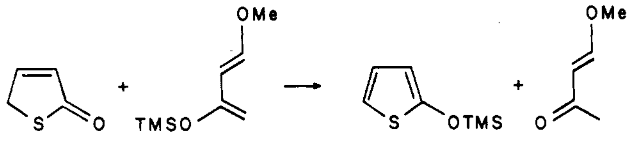


II

were prepared a number of years ago and are quite readily available,[1] their potential as dienophiles has not been explored. Not only would they afford an unusual series of heterocyclic compounds but they also comprise *cis*-crotonate equivalents since Raney nickel desulfurization of unsaturated substances is a well-established procedure.

Thus, Diels–Alder reaction of the thiolactone I with 2,3-dimethyl-1,3-butadiene (III) yields the adduct IV (table I). Likewise, reaction with cyclohexadiene V, 1,1-(ethylenedioxy)-2,3,4,5-tetrachlorocyclopentadiene (VII), and 1,4-diacetoxy-1,3-butadiene (IX) led to the adducts VI, VIII, X, and XI (Table I) identified by their spectral properties (see the Experimental Section).

An exception to this sequence was revealed when the reaction was attempted with the dienophile I and 1-methoxy-3-[(trimethylsilyl)oxy]butadiene XIV.[4] In this



I XIV XV XVI

instance, silyl group transfer dominated the reaction; no evidence for Diels–Alder reaction products was found. The identity of the silyl-transfer products XV and XVI was confirmed by comparison with authentic samples.

The thiolactone I responds to catalysis by Lewis acids. The reaction of the thiolactone I with 1,3-cyclopentadiene (XII) proceeded rapidly at room temperature in the presence of $BF_3 \cdot Et_2O$, yielding the adduct XIII (Table I).

Experimental Section

3-Thiolen-2-one (I) was prepared according to Hurd and Krenz and Hawkins.[1] The 60-MHz NMR spectrum (CCl_4) showed a one-proton vinyl multiplet at δ 7.61, a one-proton vinyl multiplet at δ 6.40, and a two-proton allylic triplet (J = 2 Hz) at δ 4.16: IR (film) 1675 (vs), 1405 (w), 1335 (w), 1130 (m), 1070 cm^{-1} (m); mass spectrum (15 eV), m/e (relative intensity) 100 (100), 72 (66, $M^+ - CO$).

8-Thio-3,4-dimethylbicyclo[4.3.0^{1,6}]non-3-en-7-one (IV). In a heavy-walled Pyrex tube was placed 5.00 g (0.050 mol) of 3-thiolen-2-one (I) and 8.20 g (0.10 mole) of 2,3-dimethyl-1,3-butadiene (III). The solution was flushed with nitrogen and cooled in a dichloromethane/dry-ice bath. The tube was sealed, then heated in a Carius oven at 145–152 °C for 18 h. After cooling to room temperature, the tube was opened and the product, a light yellow oil, was dissolved in 50 mL of hexane. Overnight cooling at −12 °C gave 3.85 g of small white needles: mp 39–40 °C; R_f 0.54 (9:1 hexane–ethyl acetate). Concentration of the mother liquor followed by seeding gave 2.56 g of small white needles, mp 38–39 °C. The remaining mother liquor, 4.10 g of a dark amber oil, was chromatographed on 80 g of silica gel. The column was eluted with 9:1 hexane–ethyl acetate. Five 75-mL fractions followed by five 50-mL fractions were taken. Fractions 5–9 were combined and concentrated to yield 1.30 g of a pale, yellow oil which gave 0.981 of white needles (mp 39–40 °C) upon crystallization. A 0.150-g sample of the preceeding material was recrystallized from ether–pentane, giving 0.122 g of fine white needles, mp 40–41 °C. the combined yield of chromatographically pure adduct (mp 38–41 °C) was 7.39 g (81%).

The 300-MHz NMR spectrum ($CDCl_3$) of IV showed the thiomethyl protons as the AB part of an ABX system with H_A as a one-proton doublet of doublets (J = 5.15, 11.0 Hz) at δ 3.44 and H_B as a one-proton doublet of doublets (J = 3.84, 1.00 Hz) at δ 3.08, the ring junction protons as a complex two-proton multiplet at δ 2.80–2.70, an allylic proton as a broad doublet (J = 18.19 Hz) at δ 2.37, a three-proton allylic multiplet at δ 2.22–2.09, a three-proton broad methyl singlet at δ 1.63, and a three-proton broad methyl singlet at δ 1.61. The infrared spectrum ($CHCl_3$) showed bands at 3025 (w), 2890 (m), 2850 (m), 2825 (m), 1690 cm^{-1} (vs). The mass spectrum (15 eV) showed peaks at m/e (relative intensity) 182 (15, M^+), 154 (35, $M^+ - CO$), 121 (26, $M^+ - C_2H_5S$), 107 (100, $M^+ - C_2H_2SO$), and 91 (60, $M^+ - C_3H_7SO$). Exact mass calcd for $C_{10}H_{14}OS$ 182.0765, found 182.0766.

4-Thiotricyclo[5.2.2.0^{2,6}]undec-8-en-3-one (VI). In similar fashion, 0.988 g (9.87 mmol) of 3-thiolen-2-one (I) and 1.58 g (19.73 mmol) of 1,3-cyclohexadiene (V) were converted to 0.709 g (40%) of the adduct VI: white needles (from ether–hexane); mp 43–44 °C.

The 300-MHz NMR spectrum ($CDCl_3$) of the adduct VI showed a two-proton vinyl multiplet at δ 6.29, a one-proton thiomethyl doublet of doublets (J = 8.89, 10.51 Hz) at δ 3.48, a one-proton multiplet centered at δ 3.04, a complex four-proton multiplet at δ 2.95–2.77, a one-proton multiplet centered at δ 2.73, a two-proton multiplet centered at δ 1.51, and a two-proton multiplet centered at δ 1.30. The infrared spectrum ($CHCl_3$) showed bands at 2935 (m), 2860 (w), and 1680 cm¯1 (vs). The mass spectrum (15 eV) showed peaks at m/e (relative intensity) 180 (100, M^+), 152 (39, $M^+ - CO$), and 146 (20, $M^+ - H_2S$). Exact mass calcd for $C_{10}H_{12}SO$ 180.0609, found 180.0605.

3-Thiolen-2-one Adduct VIII with 2′,3′,4′,5′-Tetrachlorospiro[1,3-dioxolane-2,1′-cyclopenta-2′,4′-diene] (VII). Similarly, 3.209 g (12.3 mmol) of VII and 0.841 g (8.4 mmol) of 3-thiolen-2-one (I) in 4 mL of dry toluene heated at reflux for 14 h yielded 2.948 g (97%) of the adduct VIII. Following silica gel chromatography, white prisms were obtained: mp 114.0–115.0 °C; R_f 0.35 (4:1 hexane–ethyl acetate).

The 300-MHz NMR spectrum ($CDCl_3$) of the adduct VIII showed the ketal protons as a complex four-proton multiplet from δ 4.31 to 4.19, a complex three-proton multiplet from δ 3.68 to 3.48, and a one-proton doublet of doublets (J = 2.02, 12.13 Hz)

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