$M^+ - OCH_3$), 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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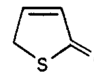
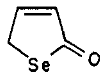
Received March 16, 1982

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



I

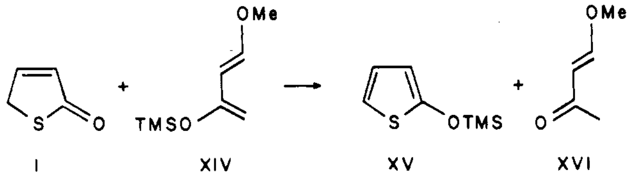


II

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



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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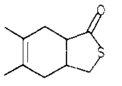
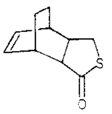
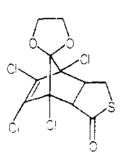
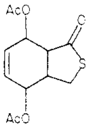
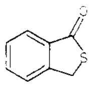
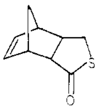
Table I. Diels-Alder Adducts of 3-Thiolen-2-one with Various Dienes

diene	adduct	% yield[a] (mp °C)	reaction conditions
2,3-dimethyl-1,3-butadiene (III)	 IV	81 (40-41)	neat sealed tube, 145-152 °C, 18 h
1,3-cyclohexadiene (V)	 VI	40 (43-44)	neat, sealed tube, 145 °C, 24 h
2′,3′,4′,5′-tetrachlorospiro-[1,3-dioxolane-2,1′-cyclopenta-2′,4′-diene] (VIII)	 VIII	99 (114-115)	toluene reflux, 14 h
(*E*,*E*)-1,4-diacetoxy-1,3-butadiene (IX)	 X	33 (85-86)	sealed tube, toluene solution, 154-155 °C, 32 h
	 XI	7 (56-57)	
cyclopentadiene (XII)	 XIII	63 (108-113)	BF_3, benzene, room temperature, 19 h

[a] Yields are of isolated, crystalline compounds and are not optimized.

centered at δ 3.26. The infrared spectrum ($CHCl_3$) showed bands at 2950 (w), 2900 (w), 1690 (vs), 1595 (m), 1445 (w), 1280–1180 (s, br), 1110 (m), 1095 (m), 1065 (m), 1030 (m), 1005 (m), 955 (m), 915 (w), and 900 cm^{-1} (m). The mass spectrum (70 eV) showed peaks at *m/e* (relative intensity) 325 (35), 327 (98), and 329 (100) [three-chlorine cluster, $M^+ - Cl$], 301 (2), 299 (4), and 297 (5) [three-chlorine cluster, $M^+ - Cl - CO$], 291 (4.0) and 289 (4.4) [two-chlorine cluster, $M^+ - 2Cl$], 285 (2), 283 (4), and 381 (4) [three-chlorine cluster, $M^+ - Cl - C_2H_4O$], 269 (4), 267 (11), and 265 (12) [three-chlorine cluster, $M^+ - Cl - CO_2$], and 255 (9), 253 (14), and 251 (13.6) [three chlorine cluster, $M^+ - Cl + C_2H_2SO$]. Exact mass calcd for $C_{11}H_8{}^{35}Cl_3SO_3$ 324.9260, found 324.9247.

3-Thiolen-2-one Adducts X and XI with (1*E*,4*E*)-1,4-Diacetoxy-1,3-butadiene (IX). A solution of 0.413 g (2.43 mmol) of 1,4-diacetoxy-1,3-butadiene (IX) and 0.365 g (3.64 mmol) of 3-thiolen-2-one (I) in 1.25 mL of dry toluene was heated under vacuum (0.010 mm) at 154–155 °C for 32 h in a heavy-walled Pyrex tube. Chromatography on silica gel yielded as the first product 0.027 g (7%) of the adduct XI: white needles; mp 55–57 °C (hexane–ether) (lit.[3] mp 56–57 °C); R_f 0.52 (4:1 hexane–ethyl acetate).

The NMR spectrum (300 MHz, $CDCl_3$) of the adduct XI showed a one-proton aromatic doublet (J = 7.68 Hz) at δ 7.84, a three-proton aromatic multiplet at δ 7.66–7.45, and a two-proton thiomethylene singlet at δ 4.48. The infrared spectrum ($CHCl_3$) showed bands at 1680 (vs), 1605 (m), 1455 (w), 1095 (w), and 905 cm^{-1} (s). The mass spectrum (15 eV) showed peaks at *m/e* (relative intensity) 150 (100, M^+), 122 (29, $M^+ - CO$), 121 (26, $M^+ - CHO$), and 105 (8).

The second product obtained from the column was the adduct X: 0.22 g (33%); pale yellow solid; mp 85–86 °C; R_f 0.21 (4b1 hexane–ethyl acetate). This material was crystallized from hexane–ether to yield 0.196 g of large, colorless primsms, mp 85–86 °C.

The NMR spectrum (300 MHz, $CDCl_3$) of adduct X showed a one-proton vinyl multiplet centered at δ 5.99, a one-proton vinyl multiplet centered at δ 5.83, a pair of one-proton allylic acetate methine multiplets centered at δ 5.67 and 5.58, a one-proton multiplet centered at δ 3.49, a complex two-proton multiplet at δ 3.26–3.10, a one-proton multiplet centered at δ 3.08, and a pair of acetate methyl singlets at δ 2.16 and 2.06. The infrared spectrum ($CHCl_3$) showed bands at 2960 (w), 1740 (vs, acetate carbonyl stretch), 1705 (s, thiocarbonyl stretch), 1375 (m), 1305 (w), 1220 (m), 1100 (m), and 950 cm^{-1} (m). The mass spectrum (70 eV) showed peaks at *m/e* (relative intensity) 270 (9, M^+), 211 (13, $M^+ - C_2H_3O$), 210 (57, $M^+ - CH_3COOH$ or $M^+ - CSO$), 168 (78, $M^+ - CH_3COO - CH_3CO$), 150 (15, $M^+ - 2CH_3COOH$ or $M^+ - CH_3COOH - CSO$), 140 (9, $M^+ - CH_3COO - CH_3CO - H_2O$), 128 (13), 123 (13, $M^+ + H - 2CH_3COOH - CO$), 122 (9, $M^+ - 2CH_3COOH - CO$), and 108 (100, $M^+ - 2\,CH_3COOH - CH_2O$). exact mass calcd for $C_{12}H_{14}SO_5$ 270.0562, found 270.0560.

3-Thiolen-2-one Adducts XIII with Cyclopentadiene. To a solution of 0.600 g (5.99 mmol) of 3-thiolen-2-one (I) in 4 mL of dry benzene cooled to 0 °C under an inert atmosphere was added 0.421 g (2.99 mmol) of boron trifluoride etherate dropwise. Stirring was continued for 15 min, and then 0.990 g (14.98 mmol) of freshly distilled cyclopentadiene was added in one portion. The reaction mixture was allowed to warm to room temperature and stirred for 19 h. The reaction mixture was poured into 20 mL of saturated aqueous sodium bicarbonate solution and extracted with 60 mL of ether. The ether layer was dried over anhydrous magnesium sulfate. Filtration and concentration gave 0.908 of a dark amber semisolid. Chromatography of the crude product on 65 g of silica gel by eluting with 9:1 hexane–ether and taking 50-mL fractions gave 0.622 g (63%) of the adduct XIII in fractions 9–14. The adduct XIII is a sticky white solid, mp 108–113 °C. Two recrystallizations from hexane–ether failed to improve the melting point.

The 300-MHz NMR spectrum is complex and may indicate the presence of more than one compound, reasonably ascribed to an endo–exo adduct mixture. The 300-MHz NMR spectrum ($CDCl_3$) of the adduct(s) XIII showed a two proton vinyl multiplet at δ 6.29, a two-proton multiplet at δ 3.45–3.33, a one-proton multiplet centered at δ 3.22, a one-proton multiplet centered at δ 3.08, a one-proton doublet of doublets, part of an ABX system (J = 3.13, 11.52 Hz), centered at δ 82.79, and a two-proton bridge AB quartet (J_{AB} = 8.49 Hz) at δ_A 1.61 and δ_B 1.45. The infrared spectrum ($CHCl_3$) showed absorbance at 2960 (m), 2945 (m), 2870 (w), 1695 (s, shoulder), 1674 (vs), 1445 (w), 1342 (m), 1130 (m), 1100 (m), 1070 (m), 962 (w), and 915 cm^{-1} (w). The mass spectrum (70 eV) showed peaks at m/e (relative intensity) 166 (100, M^+), 138 (17, $M^+ - CO$), 124 (21), 105 (17, $M^+ - CHSO$), 101 (21, $M^+ - C_5H_5$), 92 (17, $M^+ - C_2H_2SO$), 91 (21, $M^+ - 2H_3SO$), and 66 (67, $M^+ - C_4H_4SO$). Exact mass calcd for $C_9H_{10}SO$ 166.04524, found 166.0458.

2-(Trimethylsiloxy)thiophene (XV). A solution of 0.606 g (6.6 mmol) of 3-thiolen-2-one (I) and 0.918 g (9.09 mmol) of anhydrous trimethylamine in 10 mL of anhydrous ether was treated under an inert atmosphere with 0.826 g (7.575 mmol) of chlorotrimethylsilane. The resulting white suspension was stirred 5 h at room temperature. The reaction mixture was diluted with 30 mL of pentane and filtered by suction through a pad of Celite 545. The filtrate was concentrated on a rotary evaporator and then distilled bulb-to-bulb at 23 °C (0.03 mm) into a liquid nitrogen cooled trap. The product, 0.694 g (66%) of a colorless oil, was shown to be pure by NMR analysis.

The 300-MHz spectrum ($CDCl_3$) of XV showed a one-proton doublet of doublets (J = 3.64, 5.86 Hz) at δ 6.61, a one-proton doublet of doublets (J = 1.42, 5.86 Hz) at δ 6.51, a one-proton doublet of doublets (J = 1.42, 3.64 Hz) at δ 6.15, and nine-proton trimethylsilyl ether singlet at δ 0.29. The infrared spectrum ($CHCl_3$) showed bands at 2960 (w), 1540 (w), 1460 (m), 1260 (m), 1190 (s), 880 (s), 849 cm^{-1} (s). Hydrolysis of XV to the starting thiolenone is very ready and accounts for the small carbonyl doublet at 1690 and 1710 cm^{-1} observed in the infrared spectrum. The mass spectrum (70 eV) showed peaks at m/e (relative intensity) 172 (100, M^+) 100 (11, $M^+ + H - C_3H_9Si$), and 73 (11, C_3H_9Si). exact mass calcd for $C_7H_{12}OSSi$ 172.0378, found 172.0371.

Reaction of 3-Thiolen-2-one (I) with (1*E*)-1-Methoxy-3-(trimethylsiloxy)-1,3-butadiene. In an NMR tube were placed 0.047 g (0.47 mmol) of 3-thiolen-2-one (I), 0.081 g (0.47 mmol) of (1*E*)-1-methoxy-3-(trimethylsiloxy)-1,3-butadiene (XIV), and 0.50 mL of chloroform-*d*. The tube was heated at 55 °C for 50 h. At this time, the 300-MHz NMR spectrum revealed little remaining diene. In addition to small signals due to 3-thiolen-2-one, the spectrum showed 2-(trimethylsiloxy)thiophene and 4-methoxybut-3-en-2-one. Minor product peaks in the atomatic and vinyl region were observed but were not investigated further.

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

Registry No. I, 3354-32-3; III, 513-81-5; IV, 83043-39-4; V, 592-57-4; VI, 83043-40-7; VII, 2082-08-8; VIII, 83043-41-8; (*E,E*)-IX, 15910-11-9; X, 83043-42-9; XI, 1194-57-6; XII, 542-92-7; XIII, 83043-43-0; (*E*)-XIV, 54125-02-9; XV, 83043-44-1; 4-methoxybut-3-en-2-one, 4652-27-1.

Synthesis of 3,4-Bis(trifluoromethyl)pyrroles

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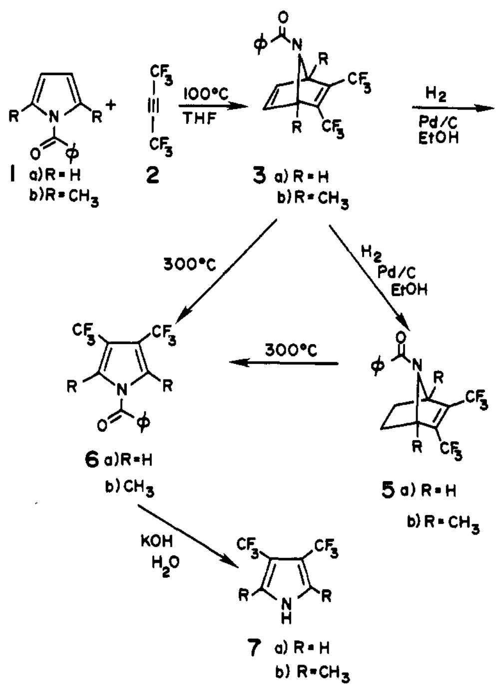
Current research directed toward the synthesis of octakis(polyfluoroalkyl)porphyrins required the preparation of 3,4-bis(trifluoromethyl)pyrroles **7a** and **7b**. The general procedure for the synthesis of these substituted pyrroles which we describe here (Scheme I) gives much higher overall yields than a method recently reported for the preparation of **7a**.[1] Heating *N*-benzoylpyrrole (**1a**) with hexafluoro-2-butyne affords a quantitative yield of the adduct **3**.[2,3] Pyrolysis of **5**, prepared by the hydrogenation of **3**, cleanly cleaves ethylene, yielding **6**. The more direct route, pyrolysis of **3**, gave mainly unreacted starting material **3**, the retro-Diels–Alder product **1**, and only a trace of **6**. Basic hydrolysis of **6** gave **7**. The overall yield for this route (**1** → **3** → **5** → **6** → **7**) is 83%.

Scheme I



Experimental Section

Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were measured on a Perkin-Elmer 237 grating spectrophotometer. Mass spectra were obtained on a Finnigan 4000 instrument at 70 eV. NMR spectra (in $CDCl_3$, Me_4Si as an internal standard) were recorded on a Varian T-60 at 60 MHz for ^1H spectra and on a Bruker WM-250 at 62.9 MHz for ^{13}C spectra. Elemental analyses were performed by Galbraith Laboratories Inc. *N*-Benzoylpyrrole and *N*-benzoyl-2,5-dimethylpyrrole were prepared as previously described.[4] Hexafluorobut-2-yne was purchased (Columbia) and used without prior purification.

***N*-Benzoyl-2,3-bis(trifluoromethyl)-7-azabicyclo[2.2.1]-2,5-heptadiene (3a).** Hexafluorobut-2-yne (**2**; 7.60 g, 46.9 mmol) was condensed at −78 °C into a heavy-walled glass tube containing *N*-benzoylpyrrole (**1a**; 4.0 g, 23.4 mmol) and THF (15 mL). The sealed tube was heated inside a steam bath for 5 h. The solvent and excess **2** were evaporated on a rotary evaporator, affording 7.79 g (100%) of **3a** as a yellow oil. This product appeared pure by NMR and TLC and was used directly in the preparation of **4** and **5a**: ^1H NMR δ 5.56 (2 H, br s, H-1 and H-4), 7.10 (2 H, m, H-5 and H-6), 7.35 (5 H, br s, aromatic); ^{13}C NMR δ 66.59, 69.76, (C-1 and C-4), 120.89 (q, J = 269.8 Hz, CF_3), 128.10, 128.86, 132.16, 132.80 (aromatic carbons), 144.48, 142.65 (C-5 and C-6), 148.98 (br, C-2 and C-3), 169.12 (C=O); mass spectrum, m/e (relative intensity) 333 (M^+, 10), 105 (100), 77 (40), 51 (13); IR (neat) 3250, 3060, 1675, 1350, 1290, 1180, 1130 cm^{-1}.

***N*-Benzoyl-2,3-bis(trifluoromethyl)-1,4-dimethyl-7-azabicyclo[2.2.1]-2,5-heptadiene (3b).** Pyrrole **3b** was prepared

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