4-Methyl-1,3-dithiol-2-one (5a). This compound was obtained pure by evaporative distillation (kugelrohr) at 90 °C (12 mmHg): ^{1}H NMR ($CDCl_3$) δ 6.3 (q, J = 1.4 Hz, 1 H), 2.3 (d, J = 1.4 Hz, 3 H); IR (neat) 1740, 1670, 1640 cm^{-1}; UV (EtOH) 269 (3.38), 238 (3.39), 212 (3.37) nm (log ϵ).

Anal. Calcd for $C_4H_4OS_2$: C, 36.4; H, 3.0; S, 48.5. Found: C, 36.5; H, 3.1; S, 48.4.

4-Ethyl-1,3-dithiol-2-one (5b). This compound was obtained pure by evaporative distillation (kugelrohr) at 60 °C (0.10 mmHg): ^{1}H NMR ($CDCl_3$) δ 6.2 (t, J = 1.8 Hz, 1 H), 2.6 (q of d, J = 9, J = 1.8 Hz, 2 H), 1.2 (t, J = 9 Hz, 3 H); IR (neat) 1739, 1653, 1563, 870 cm^{-1}.

Anal. Calcd for $C_5H_6OS_2$: C, 41.1; H, 4.1; S, 43.9. Found: C, 41.3; H, 4.1; S, 43.6.

4-Isopropyl-1,3-dithiol-2-one (5c). This compound was obtained pure by evaporative distillation at 70 °C (0.10 mmHg): ^{1}H NMR ($CHCl_3$) δ 6.4 (d, J = 1.5 Hz, 1 H), 2.9 (septet of doublets, J = 1.5, J = 6.7 Hz, 1 H), 1.3 (d, J = 6.7 Hz, 6 H); IR (neat) 1754, 1653, 1574, 869 cm^{-1}; mass spectrum, m/e 160 (M^+), 145, 132, 117, 99, 87, 53, 45, 41, 39.

Anal. Calcd for $C_6H_8OS_2$: C, 45.0; H, 5.0; S, 40.0. Found: C, 45.1; H, 4.9; S, 39.7.

4-*n*-Hexyl-1,3-dithiol-2-one (5d). This compound was obtained pure by evaporative distillation (kugelrohr) at 85 °C (0.15 mmHg): ^{1}H NMR ($CDCl_3$) δ 6.3 (t, J = 1.2 Hz, 1 H), 2.6 (t of d, J = 1.2, J = 6.6 Hz, 2 H), 1.4–0.9 (m, 11 H).

Anal. Calcd for $C_9H_{14}OS_2$: C, 53.5; H, 6.9; S, 31.7. Found: C, 53.4; H, 6.9; S, 32.0.

4-Benzyl-1,3-dithiol-2-one (5e). This compound was obtained pure by evaporative distillation (kugelrohr) at 195 °C (20 mmHg); mp (EtOH) 38–40 °C; ^{1}H NMR ($CDCl_3$) δ 7.2 (m, 5 H), 6.3 (t, J = 1.2 Hz, 1 H), 3.8 (d, J = 1.2 Hz, 2 H); UV (EtOH) 265 (3.52), 242 (3.60) nm (log ϵ); IR (neat) 1724, 1645, 1563, 1493, 1449, 862, 760, 690 cm^{-1}; mass spectrum, m/e 208, 180, 179, 147, 135, 117, 115, 91.

Anal. Calcd for $C_{10}H_8OS_2$: C, 57.7; H, 3.8; S, 30.8. Found: C, 58.0; H, 3.8; S, 30.9.

4-Benzyl-1,3-dithiole-2-thione (5d). This compound was obtained by evaporative distillation at 195 °C (0.1 mmHg): ^{1}H NMR ($CDCl_3$) δ 7.1 (m, 5 H), 6.4 (t, J = 1 Hz, 1 H), 3.8 (d, J = 1 Hz, 2 H). In contrast, 4-benzylidene-1,3-dithiolane-2-thione had ^{1}H NMR ($CDCl_3$) δ 7.3 (m, 5 H), 6.7 (t, J = 2 Hz, 1 H), 4.7 (d, J = 2 Hz, 2 H).

Anal. Calcd for $C_{10}H_8S_3$: C, 53.6; H, 3.5; S, 42.9. Found: C, 53.2; H, 3.4; S, 43.1.

Cyclohexano[*d*]-1,3-dithiol-2-one (5g). This compound was obtained by evaporative distillation at 90 °C (0.05 mmHg). NMR and IR spectra were identical with those of a known sample.[3a]

4-Methyl-1,3-dithiole-2-thione (5h). This compound was obtained by distillation: bp 90–93 °C (0.05 mmHg); mp 28–30 °C (lit.[14] 30 °C); ^{1}H NMR ($CDCl_3$) δ 6.7 (q, J = 1.2 Hz, 1 H), 2.3 (d, J = 1.2 Hz, 3 H).

4-Isopropyl-1,3-dithiole-2-thione (5i). This compound was obtained by distillation: bp 89–91 °C (0.05 mmHg); ^{1}H NMR ($CDCl_3$) δ 6.7 (d, J = 1.2 Hz, 1 H), 3.0 (septet of d, J = 1.2, J = 7.0 Hz, 1 H), 1.3 (d, J = 7.0 Hz, 6 H).

Anal. Calcd for $C_6H_8S_3$: C, 40.9; H, 4.5; S, 54.6. Found: C, 41.2; H, 4.9; S, 54.2.

Registry No. 3a, 73872-16-9; **3b**, 73872-17-0; **3d**, 73872-18-1; **3g**, 73872-19-2; **3i**, 73872-20-5; **5a**, 42574-01-6; **5b**, 73872-21-6; **5c**, 73872-22-7; **5d**, 73872-23-8; **5e**, 73872-24-9; **5f**, 6136-08-9; **5g**, 698-41-9; **5h**, 3608-38-6; **5i**, 73872-25-0; *S*-allyl *O*-ethyl dithiocarbonate, 7124-50-7; potassium ethyl xanthate, 140-89-6; 3-bromo-1-propene, 106-95-6; *S*-buten-2-yl *O*-ethyl dithiocarbonate, 73872-26-1; 1-bromo-2-butene, 4784-77-4; *S*-cinnamyl *O*-ethyl dithiocarbonate, 73872-27-2; cinnamyl bromide, 4392-24-9; *S*-cyclohexen-3-yl *O*-ethyl dithiocarbonate, 73872-28-3; 3-bromocyclohexene, 3540-84-9; *S*-(3-methyl-2-buten-1-yl) *O*-ethyl dithiocarbonate, 73872-29-4; 1-bromo-3-methyl-2-butene, 870-63-3; *S*-(2-octen-1-yl) *O*-ethyl dithiocarbonate, 73872-30-7; 1-bromo-2-octene, 25466-54-0; 3-bromo-1-octene, 40906-92-1; *S*-(3β-(benzoyloxy)-5-cholesten-7β-yl) *O*-ethyl dithiocarbonate, 73872-31-8; 7α-bromocholesterol, 26048-46-4; cinnamyl *tert*-butyl trithiocarbonate, 73872-32-9; sodium *tert*-butyl trithiocarbonate, 71127-42-9.

Organic Fluorine Compounds. 32.[1] A 1,3-Dipolar Cycloaddition Reaction of Tetrakis(trifluoromethyl)(Dewar Thiophene) and Some Reactions of the Cycloadducts[2]

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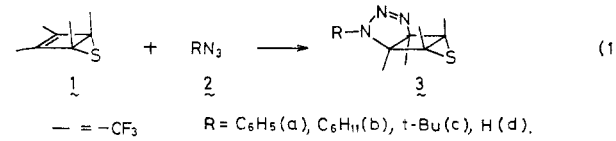
The reaction of tetrakis(trifluoromethyl)(Dewar thiophene) (**1**) with azide compounds **2**, including hydrogen azide, gave high yields of 1,3-dipolar cycloadducts **3**. Compounds **3a–d** were desulfurized with triphenylphosphine to afford cyclobutatriazoline compounds **4a–d**, which were converted thermally to the diazo imine compounds **5a–d** by a retro-1,3-dipolar reaction. Compounds **5a–d** were denitrogenated to pyrrole compounds **7a,b,d** and/or cyclopropenylimines **8b,c** on thermolysis. The adducts **2a–d** were ring opened thermally to diazothiirane compounds **9a–d**, which were further converted to thiete compounds **10a–d**.

Tetrakis(trifluoromethyl)(Dewar thiophene) (**1**) has a strained double bond substituted with highly electronegative trifluoromethyl groups and is known to be a good dienophile in Diels–Alder reactions.[3] We have now found that **1** undergoes 1,3-dipolar cycloaddition with azides. The 4,5-dihydro-1,2,3-triazoles formed in this way were thermally cleaved to diazo imines.

Results and Discussion

Treatment of **1** with azides **2a–d** at room temperature gave the corresponding 1,3-dipolar cycloadducts **3a–d** in good yield[2a,b] (eq 1). The isolated cycloadducts are stable



(1)

1 — = —CF_3 **2** R = C_6H_5(a), C_6H_{11}(b), t-Bu(c), H(d). **3**

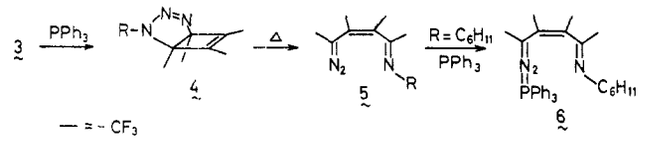
(1) Part 31: Kobayashi, Y.; Taguchi, T.; Morikawa, T.: Tokuno, E.; Sekiguchi, S. *Chem. Pharm. Bull.* **1980**, *28*, 262.

(2) Part of this work was published in preliminary form: (a) Kobayashi, Y.; Ando, A.; Kumadaki, I. *J. Chem. Soc., Chem Commun.* **1978**, 509. (b) Kobayashi, Y.; Kumadaki, I.; Ohsawa, A.; Ando, A. *J. Am. Chem. Soc.* **1977**, *99*, 7350.

(3) Kobayashi, Y.; Kumadaki, I.; Ohsawa, A.; Sekine, Y.; Ando, A. *J. Chem. Soc., Perkin Trans. 1* **1977**, 2355.

0022-3263/80/1945-2962$01.00/0

Scheme I

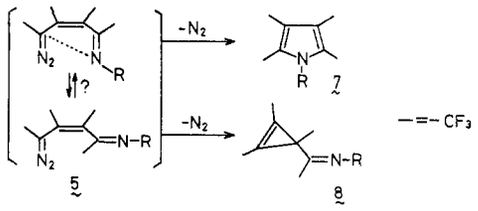


in the dark below room temperature, but they decompose slowly in solution and on exposure to daylight. The structures of **3a–d** were determined by elemental analysis and ^1H and ^{19}F NMR. Thus, four kinds of trifluoromethyl groups were observed in the ^{19}F NMR of **3a–c**, while **3d** showed only two kinds of trifluoromethyl groups, presumably owing to rapid tautomerism. The four peaks of **3a** are tentatively named as A, B, C, and D in increasing order in the magnetic field. The coupling constants are J_{AC} = 5.35 Hz, J_{BD} = 6.90 Hz, J_{AD} = 2.82 Hz, and J_{BC} = 1.83 Hz, showing that A, C, B, and D form a circle in this order and that A, C and B, D are cis to each other, while C, B and A, D are trans. The ^{19}F NMR spectra of **3b** and **3c** show similar patterns of coupling, and that of **3d** shows very small coupling between two pairs. Therefore, **3a–d** must be anti. Mass spectra showed no parent peaks but showed an $M^+ - 28$ ($M^+ - N_2$) peak instead. The most interesting in the above results is the reaction with hydrogen azide, which is known to undergo 1,3-dipolar cycloaddition only with active acetylenes like dimethyl acetylenedicarboxylate but not with any olefinic compounds.[4] This must mean that **1** is an extremely good dipolarophile. Cycloadducts **3a–d** were desulfurized smoothly with triphenylphosphine to give cyclobutatriazolines **4a–d**. Compounds **4a–d** are valence bond isomers of triazepines; they are rather unstable, especially the *N*-phenyl isomer **4a**. The thermolysis of **4a–d** was followed by IR spectroscopy. Thus, the IR absorption near 1700 cm^{-1} ascribable to the cyclobutenic double bond disappeared gradually as a new absorption at 2100 cm^{-1} ascribable to the diazo group grew stronger. These results suggest that a thermal retro-1,3-dipolar cycloaddition has occurred (Scheme I), although it is not clear whether this reaction is a stepwise or a concerted one.

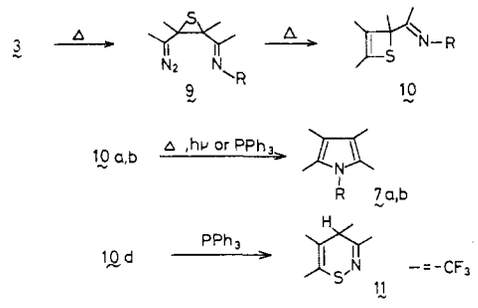
Further evidence supporting the retro-1,3-dipolar cycloaddition of Scheme I includes ^{19}F NMR spectra and the fact that the *N*-cyclohexyl compound **5b** reacted with triphenylphosphine to give phosphazine **6**.[5] Baldwin et al.[6] and Gassman et al.[7] have proposed a diazo imine intermediate for the thermolysis of an *exo*-triazoline into an *endo*-aziridine. Our result, however, is the first example of an isolable intramolecular diazo imine compound. This might be due to the high electronegativity of the trifluoromethyl group, which makes both parts electron deficient, thus disfavoring a potential intramolecular 1,3-dipolar cycloaddition reaction.

Pyrolysis of the diazo imine compounds **5a–d** gave pyrroles **7a,b,d** and/or cyclopropenylimines **8b,c**, depending on the substituents on the nitrogen atom: the *N*-phenyl isomer **5a** gave only **7a**, and the *N*-*tert*-butyl isomer **5c** gave only **8c**, while the *N*-cyclohexyl isomer **5b** gave a mixture of **7b** and **8b** in a 1:3 ratio (Scheme II). These results leading to different products must be explained by the stereoisomerism of **5**. Compounds **5a** and **5d** show four trifluoromethyl groups in ^{19}F NMR, while **5b** shows two pairs of four trifluoromethyl groups. Thus, **5a** consists of one stereoisomer and **5c** the other, while **5b** is a mixture of both. This isomerism might be *E*/*Z* isomerism around the C=N bond or *S*-cisoid/*S*-transoid around the C–C bond. As the ^{19}F NMR of **5b** was independent of temperature, the latter seemed more probable. However, if so, **5c** must be the *E* form due to the large steric requirement of the *tert*-butyl group, and **5a** must be the *Z* form. For the formation of **7a**, **5a** must take the *S*-cisoid form, but this is highly improbable due to the steric repulsion. The *S*-cisoid/*S*-transoid isomerism of *E* compounds **5a–c** seems to explain the results more easily. *S*-Cisoid isomer **5a** gives pyrrole **7a**, and *S*-transoid isomer **5c** gives cyclopropenyl imine **8c**, while a mixture of both isomers, **5b**, gives **7b** and **8b**.

Scheme II



Scheme III



Treatment of **8b** under the same reaction conditions did not give **7b**. Therefore, **8b** is not an intermediate in the reaction affording **7b**. Photolysis of **5b** gave only **8b** and no **7b**. These results are very interesting, since a cyclopropenyl imine compound similar to **8** was proposed as an intermediate for the photolytic conversion of a furan into a pyrrole in the presence of an amine.[8]

The thermolysis of 1,3-dipolar adducts **3a–d** was found to give the thietimine compounds **10a–d**.[9] In the case of the *N*-phenyl derivative **3a**, the intermediate, diazothiiranimine **9a**,[9] was isolated. Compound **9a** was smoothly converted to **10a** on prolonged heating. The structure of **9a** was deduced from its IR spectrum which showed an absorption at 2100 cm^{-1} (=N_2), with its mass spectrum showing a peak at *m*/*e* 447 ($M^+ - N_2$) and ^{19}F NMR spectrum showing four different trifluoromethyl absorptions. Compound **10** gave no diazo absorption in the IR but did show an absorption at 1700 cm^{-1} which was attributed to a tetrasubstituted double bond. Therefore, the triazoline ring of **3a–d** was thermally cleaved to a diazo imino group in the same manner as for desulfurized com-

(4) Benson, F. R.; Savell, V. L. *Chem. Rev.* **1950**, *46*, 1.
(5) Carpenter and his co-workers have reported that a fluorinated triazoline decomposes to an aziridine on glass beads, while it decomposes to an alkene and an imine on a nickel surface. The latter process is somewhat analogous to the formation of the diazo imine. Carpenter, W.; Haymaker, A.; Moore, D. W. *J. Org. Chem.* **1966**, *31*, 789.
(6) Baldwin, J. E.; Kaiser, G. V.; Romersberger, J. A. *J. Am. Chem. Soc.* **1965**, *87*, 4114 and references cited therein.
(7) Gassman, P. G.; Schaffhausen, J. G. *J. Org. Chem.* **1978**, *43*, 3214.
(8) A detailed discussion of the mechanism will be presented in the following paper. See also: (a) Couture, A.; Delevallee, A.; Lablache-Combier, A.; Parkanyl, C. *Tetrahedron* **1975**, *31*, 785; (b) Couture, A.; Lablache-Combier, A. *J. Chem. Soc., Chem. Commun.* **1969**, 524; (c) Couture, A.; Lablache-Combier, A. *Tetrahedron* **1971**, *27*, 1059.
(9) According to a private communication from Professor Lemal, the same type of product was supposed in the thermolysis of a 1,3-dipolar cycloadduct of **1** and a diazomethane compound.

pounds **4a–d**. The compounds **9a** lost nitrogen readily, and the ensuing carbene added to the C–S bond intramolecularly to form the thietimine compounds **10a–d**. The high stability of these thietimine compounds was remarkable, since thietes have been reported to be relatively unstable.[10] This surprising stability of **10a–d** is also attributed to the effect of the trifluoromethyl group.

Compounds **10a,b** were converted to the pyrrole compounds **7a,b** thermally, photochemically, or by treatment with triphenylphosphine. Compound **10d** was isomerized to the 1,2-thiazine **11** by treatment with triphenylphosphine. These results are shown in Scheme III.

Conclusion

Tetrakis(trifluoromethyl)(Dewar thiophene) (**1**) was found to be a good dipolarophile in cycloaddition reactions with azides. The adducts **3a–d** and their desulfurization products **4a–d** were cleaved thermally to intramolecular diazo imine compounds **9a–d** and **5a–d**, respectively. Compound **9a** was isolated, but the others (**9b,c,d**) lost nitrogen quickly, affording the thietimines **10b–d**. Compounds **5a–d** were thermally converted to the pyrroles **7a,b,d** and/or cyclopropenyl imine compounds **8b,c**. The stability of these peculiar ring systems (**3–5**, **9**, and **10**) has been ascribed at least in part to the electronic effect of the trifluoromethyl groups.

Experimental Section

1,3-Dipolar Cycloaddition of Dewar Thiophene 1 with Azides 2. 8-Phenyl-1,2,4,5-tetrakis(trifluoromethyl)-3-thia-6,7,8-triazatricyclo[3.3.0.0^{2,4}]oct-6-ene (3a). To a solution of **1** (4.36 g, 12.2 mmol) in 20 mL of CH_2Cl_2 was added phenyl azide[11] (**2a**; 2.18 g, 18.3 mmol). The mixture was stirred at room temperature for 2–3 days in the dark. The solvent and excess **2a** were removed on a vacuum line. The residue was recrystallized from *n*-pentane and sublimed to give 4.63 g (79.6% yield) of **3a** as colorless prisms: mp 64–65 °C; IR ($CHCl_3$) 3040, 1600, 1300, 1185 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.43 (PhH, br s); ^{19}F NMR ($CDCl_3$) –3.6 (3 F, m), –2.6 (3 F, m), –2.0 (3 F, m), 7.4 (3 F, m) ppm;[12] mass spectrum, *m/e* 447 ($M^+ - N_2$). Anal.[13] Calcd for $C_{14}H_5N_3F_{12}S$: C, 35.36; H, 1.06; N, 8.84; F, 47.98; S, 6.78. Found: C, 35.09; H, 1.01; N, 8.96; F, 48.14; S, 6.81.

8-Cyclohexyl-1,2,4,5-tetrakis(trifluoromethyl)-3-thia-6,7,8-triazatricyclo[3.3.0.0^{2,4}]oct-6-ene (3b). Cyclohexyl azide[14] (**2b**; 1.57 g 12.6 mmol) was added to a solution of **1** (4.02 g 11.3 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred at room temperature for 1 day in the dark and then was concentrated under vacuum to remove CH_2Cl_2 and excess **2b**. The residue was recrystallized from *n*-pentane to give 4.39 g (80.5% yield) of **3b** as colorless prisms; mp 59–60 °C; IR ($CHCl_3$) 2940, 2860, 1300, 1180, 1165 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.68 (1 H, m, CH–N), 1.2–2.36 (10 H, m, CH_2); ^{19}F NMR ($CDCl_3$) –4.6 (3 F, m), –2.4 (3 F, m), 1.6 (3 F, m), 6.8 (3 F, m) ppm; mass spectrum, *m/e* 453 ($M^+ - N_2$). Anal.[13] Calcd for $C_{14}H_{11}N_3F_{12}S$: C, 34.92; H, 2.30; N, 8.73; F, 47.38; S, 6.66. Found: C, 34.70; H, 2.42; N, 8.82; F, 47.44; S, 6.64.

8-*tert*-Butyl-1,2,4,5-tetrakis(trifluoromethyl)-3-thia-6,7,8-triazatricyclo[3,3.0.0^{2,4}]oct-6-ene (3c). To a solution of **1** (1 g 2.81 mmol) in CCl_4 (10 mL) was added *tert*-butyl azide[15] (**2c**; 278 mg 2.81 mmol). The mixture was stirred at room temperature for several days in the dark, and then CCl_4 and **2c** were removed in vacuo. The residue was triturated with *n*-pentane and filtered. The filtrate was evaporated under vacuum and the residue purified by column chromatography (SiO_2, *n*-pentane). Recrystallization from *n*-pentane gave colorless prisms of **3c**: 629.7 mg (49.3% yield); mp 52–53 °C; IR (CCl_4) 2980, 1220, 1200 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.66 ($C(CH_3)_3$, s); ^{19}F NMR (CCl_4) –5.6 (3 F, m), –3.88 (3 F, m), –2.12 (3 F, m), 7.08 (3 F, m) ppm; mass spectrum, *m/e* 412 ($M^+ - N_2 - CH_3$). Anal. Calcd for $C_{12}H_9N_3F_{12}S$: C, 31.64; H, 1.99; N, 9.23; F, 50.09. Found: C, 30.58; H, 1.92; N, 9.18; F, 49.80. The sample **3c** could not be purified completely from contaminants, mainly **3d**, since **3c** decomposed to **3d** in the course of purification. The residue from *n*-pentane trituration was sublimed to give colorless prisms (445.9 mg). This material was identical with the adduct **3d** of Dewar thiophene with HN_3.

1,2,4,5-Tetrakis(trifluoromethyl)-3-thia-6,7,8-triazatricyclo[3.3.0.0^{2,4}]oct-6-ene (3d). To a solution of HN_3[16] (**2d**) in $CHCl_3$ obtained by reaction of NaN_3 (6.5 g, 0.1 mol) with concentrated H_2SO_4 (5.4 mL) was added a solution of **1** (6.25 g, 17.6 mmol). When the mixture was kept at room temperature for 1–2 days in the dark, crystalline material precipitated. The mixture was concentrated under vacuum, and the residue was washed with *n*-pentane and sublimed to give colorless prisms of **3d**: 6.58 g (94% yield); mp 140–144 °C dec; IR (KBr) 3140 (NH), 1180 (CF) cm^{-1}; ^{1}H NMR (CD_3COCD_3)[17] δ 3.77 (NH, m); ^{19}F NMR (Et_2O) –3.2 (6 F, m), 5.6 (6 F, m)[18] ppm; mass spectrum, *m/e* 371 ($M^+ - N_2$). Anal. Calcd for $C_8HN_3F_{12}S$: C, 24.07; H, 0.25; N, 10.53; F, 57.12; S, 8.03. Found: C, 23.93; H, 0.29; N, 10.77; F, 57.39; S, 7.87.

Desulfurization of 3 with Triphenylphosphine. 4-Phenyl-1,5,6,7-tetrakis(trifluoromethyl)-2,3,4-triazabicyclo[3.2.0]hepta-2,6-diene (4a). Triphenylphosphine (23.4 mg, 0.0893 mmol) was added to an ice-cold solution of **3a** (42.7 mg, 0.0899 mmol) in *n*-pentane (3 mL). The precipitated sulfide was filtered and the filtrate concentrated under vacuum. The unstable crude product[19] **4a** was obtained (36 mg) as a yellow oil: IR (CCl_4) 3060, 1698 (cyclobutenic double bond), 1155–1280 (CF) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.0 (PhH, m); ^{19}F NMR ($CDCl_3$) –1.2 (3 F, m), –0.68 (3 F, m), 4.0 (3 F, m), 6.6 (3 F, m) ppm.

4-Cyclohexyl-1,5,6,7-tetrakis(trifluoromethyl)-2,3,4-triazabicyclo[3.2.0]hepta-2,6-diene (4b). Treatment of **3b** (600 mg, 1.25 mmol) in *n*-pentane (5 mL) with triphenylphosphine (359.5 mg, 1.37 mmol) as in the preceding experiment gave **4b**. After evaporation of the solvent, the residue was purified by column chromatography or preparative TLC. Compound **4b** (469.7 mg, 83.9% yield) was obtained as a pale yellow oil: IR (CCl_4) 2940, 2860, 1700 (cyclobutenic double bond), 1280, 1220, 1180 (CF) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.3–3.9 (1 H, CH–N, m), 1.1–2.33 (10 H, CH_2, m); ^{19}F NMR ($CDCl_3$) –0.8 (6 F, m), 6.0 (3 F, m), 7.6 (3 F, m) ppm; mass spectrum, *m/e* 421 ($M^+ - N_2$).

4-*tert*-Butyl-1,5,6,7-tetrakis(trifluoromethyl)-2,3,4-triazabicyclo[3.2.0]hepta-2,6-diene (4c). After a solution of **3c** (204 mg, 0.448 mmol) in *n*-pentane (3 mL) was treated with triphenylphosphine (117.5 mg, 0.448 mmol) as in the preparation of **4c**, the sulfide was filtered off. The filtrate was concentrated under vacuum and the residue purified by preparative TLC to afford 117.6 mg of **4c** (61% yield) as a yellow oil: IR (CCl_4) 2980, 1698 (cyclobutenic double bond), 1160–1280 (CF) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.6 ($C(CH_3)_3$, s); ^{19}F NMR ($CDCl_3$) –2.4 (3 F, m), –1.0 (3 F, m), 1.8 (3 F, m), 6.4 (3 F, m) ppm; mass spectrum, *m/e* 395 ($M^+ - N_2$).

1,5,6,7-Tetrakis(trifluoromethyl)-2,3,4-triazabicyclo-[3.2.0]hepta-2,6-diene (4d). To a suspension of **3d** (518.6 mg, 1.30 mmol) in CH_2Cl_2 was added triphenylphosphine (340.5 mg, 1.30 mmol). The reaction mixture was concentrated under vacuum and the residue sublimed at 20–25 °C (5 mmHg) to give **4d** (392.1 mg, 82.2% yield) as colorless crystals: mp 65–68 °C dec; IR (CH_2Cl_2) 3380 (NH), 1705 (cyclobutenic double bond), 1170 (CF) cm^{-1}; ^{1}H NMR ($CDCl_3$) not observed; ^{19}F NMR($CDCl_3$) –0.8 (6 F, m), 7.6 (6 F, m) ppm; mass spectrum, *m/e* 339 ($M^+ - N_2$).

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(12) Benzotrifluoride (BTF) as an internal standard.

(13) Analytical samples of **3a–c** were purified by sublimation.

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(17) Compound **3d** decomposed slowly in CD_3COCD_3.

(18) The ^{19}F NMR spectrum shows only two kinds of signals, owing to rapid tautomerism.

(19) Further purification caused decomposition to the diazo imine and *N*-phenylpyrrole.

Thermolysis of 4. General Procedure. A solution of 4 in *n*-pentane was sealed in a 4-mm Pyrex tube under vacuum and was heated at 60–65 °C. The reaction was followed spectroscopically. In the ^{19}F NMR spectrum, the signals of 4 changed gradually to those of 5. In the IR, absorption near 1700 cm^{-1} ascribable to a cyclobutenic double bond disappeared gradually, as a new absorption at 2100 cm^{-1} ascribable to the diazo group of 5 increased in intensity.

***N*-Phenyldiazo Imine Compound 5a.** After the signal of **4a** disappeared at room temperature, the reaction mixture was evaporated and the residue purified by preparative TLC to give **5a** as an unstable oil: IR (CCl_4) 3060, 2095 (=N_2), 1600, 1160–1280 (CF) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.8–7.7 (PhH, m); ^{19}F NMR ($CDCl_3$) –6.2 (3 F, m), –5.6 (3 F, m), –2.2 (3 F, m), 4.28 (3 F, m) ppm. Compound **5a** was contaminated by a trace of *N*-phenylpyrrole (**7a**) which formed by further decomposition during isolation.

***N*-Cyclohexyldiazo Imine Compound 5b.** After **4b** (224.3 mg, 0.50 mmol) was heated for 8.5 h at 60–65 °C, the mixture was evaporated and purified by preparative TLC to afford **5b** (64.3 mg) as a yellow oil which was a mixture of two isomers: IR (*n*-C_5H_{12}) 2100 (=N_2), 1250, 1180 (CF) cm^{-1}; ^1H NMR (CCl_4) δ 3.23, 3.83 (CH–N, m, intensity ratio ca. 3:2), 1.6 (CH_2, m); ^{19}F NMR (CCl_4) for isomer A –6.8 (3 F, m), –5.6 (3 F, m), –2.8 (3 F, m), 4.6 (3 F, m) ppm; for isomer B –6.0 (3 F, m), –4.4 (3 F, m), –2.0 (3 F, m), –0.2 (3 F, m) ppm. In this spectrum, the intensity ratio of component A to B was about 3:2.

***N*-Cyclohexylphosphazine 6.** To a solution of *N*-cyclohexyldiazo imine **5b** in *n*-pentane obtained by the thermolysis of **4b** at 60–70 °C (bath temperature) was added triphenylphosphine. The reaction mixture was concentrated under vacuum to remove the solvent, affording a yellow resinous oil which could not be purified due to decomposition on preparative TLC and/or column chromatography (SiO_2): IR (CCl_4) 3050, 2930, 2850, 1660, 1260, 1140–1220 cm^{-1}; ^1H NMR (CCl_4) δ 7.1–7.8 (5 H, PhH, m), 3.3 (1 H, CH–N, m), 1.2 (10 H, CH_2, m); ^{19}F NMR (CCl_4) –5.6 (3 F, m), –4.2 (3 F, m), –0.4 (3 F, m), 4.4 (3 F, m); mass spectrum, *m/e* 711 (M^+), 692 (M^+ – F), 672 (692 – HF), 642 (M^+ – CF_3).

***N*-*tert*-Butyldiazo Imine Compound 5c.** Compound **4c** was heated in pentane at 45 °C to give **5c** (quantitative by ^{19}F NMR). Compound **5c** was purified by preparative TLC (SiO_2, *n*-pentane) to afford a yellow oil: IR (CCl_4) 2980, 2100 (=N_2), 1680, 1175–1220 (CF) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 ($C(CH_3)_3$, s); ^{19}F NMR ($CDCl_3$) –7.2 (6 F, m), –2.6 (3 F, m), 5.0 (3 F, m).

***N*-Hydrodiazo Imine Compound 5d.** Compound **4d** was heated at 55 °C for 1 h. The absorption at 2100 cm^{-1} ascribable to a diazo group was observed in the IR spectrum of the reaction mixture. However, isolation of **5d** was unsuccessful because of rapid decomposition to 2,3,4,5-tetrakis(trifluoromethyl)pyrrole (**7d**).

Thermolysis of 4. *N*-Phenyl-2,3,4,5-tetrakis(trifluoromethyl)pyrrole (7a). Compound **4a** (36 mg, 0.0812 mmol) obtained by desulfurization of **3a** in *n*-pentane was heated[20] at 60 °C in a sealed tube and the reaction mixture evaporated under vacuum. The residue was purified by preparative TLC to give **7a** (32 mg) as colorless prisms: mp 98–99 °C; IR ($CHCl_3$) 1600, 1160 (CF) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.16–7.66 (PhH, m); ^{19}F NMR ($CDCl_3$) –9.6 (12 F, m); mass spectrum, *m/e* 415 (M^+); high-resolution mass spectrum, calcd for $C_{14}H_5NF_{12}$ *m/e* 415.023, found *m/e* 415.021.

***N*-Cyclohexyl-2,3,4,5-tetrakis(trifluoromethyl)pyrrole (7b) and *N*-Cyclohexylcyclopropenyl Imine 8b.** A solution of **4b** (300 mg, 0.668 mmol) in *n*-pentane (0.3 mL) was sealed in a 4-mm Pyrex tube under vacuum and heated at 80–85 °C for 10–20 h. The mixture was evaporated under reduced pressure to remove solvent, and the residue was distilled by trap-to-trap distillation to give **8b** (110 mg, 39.1% yield). The residue was sublimed at 50–60 °C (760 mmHg) to give **7b**: 31.5 mg (11.2% yield); mp 63.5–64 °C; colorless prisms; IR (CCl_4) 2930, 2850, 1180, 1220 cm^{-1}; ^1H NMR (CCl_4) δ 4.56 (1 H, CH–N, m), 1.03–2.31 (10 H, CH_2, m); ^{19}F NMR (CCl_4) –9.4 (12 F, m); mass spectrum, *m/e* 421 (M^+); high-resolution mass spectrum, calcd for $C_{14}H_{11}NF_{12}$ *m/e* 421.0700, found *m/e* 421.0681. Compound **8b** was obtained as a colorless oil containing two isomers: IR (CCl_4) 2945, 2860, 1905 (cyclopropenyl double bond), 1675, 1290, 1175 (CF) cm^{-1}; ^1H NMR (CCl_4) δ 3.76 (1 H, CH–N, m), 1.2–2.0 (10 H, CH_2, m); ^{19}F NMR ($CDCl_3$)[21] for isomer A –3.0 (6 F, br s), 0.6 (3 F, m), 3.8 (3 F, m) ppm; for isomer B –3.4 (6 F, br s), 4.4 (3 F, m), 7.4 (3 F, m) ppm; mass spectrum, *m/e* 421 (M^+); high-resolution mass spectrum, calcd for $C_{14}H_{11}NF_{12}$ *m/e* 421.0700, found *m/e* 421.0681.

***N*-*tert*-Butylcyclopropenyl Imine 8c.** The thermolysis of a pentane solution of **4c** at 80 °C for 9.5 h in a sealed tube gave only one product. The reaction mixture was evaporated under vacuum and the crude product purified by bulb-to-bulb distillation (70–80 °C, 760 mmHg): IR (CCl_4) 2980, 1900 (cyclopropenyl double bond), 1680, 1180–1220 (CF) cm^{-1}, ^1H NMR (CCl_4) δ 1.35 ($C(CH_3)_3$, s); ^{19}F NMR (CCl_4) –3.6 (6 F, br s), –1.88 (3 F, m), 4.0 (3 F, m); mass spectrum, *m/e* 395 (M^+), 380 (M^+ – CH_3). **8c** was identical with the product obtained by the reaction of the cyclopropenyl ketone with *tert*-butyl amine in the presence of $TiCl_4$.[22]

2,3,4,5-Tetrakis(trifluoromethyl)pyrrole (7d). Compound **4d** (386.2 mg, 1.05 mmol) was sealed in a 4-mm Pyrex tube without a solvent and heated at 50–60 °C until the color of the reaction mixture faded. The reaction mixture was distilled by bulb-to-bulb distillation at 130-134 °C (760 mmHg) to give **7d**: 298.6 mg (83.7% yield); IR (CCl_4) 3400 (NH), 1290, 1250 and 1170 (CF) cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.2 (NH, br); ^{19}F NMR ($CDCl_3$) –6.6 (6 F, m), –3.2 (6 F, m); mass spectrum, *m/e* 339 (M^+); high-resolution mass spectrum, calcd for C_8HNF_{12} *m/e* 338.9917, found *m/e* 338.9910.

Pyrolysis of 1,3-Dipolar Cycloadducts 3. Thermal Decomposition of 3a to Thietimine 10a via Diazo Imine Episulfide 9a. After a solution of **3a** (1 g 2.11 mmol) in cyclohexane (20 mL) was refluxed for 7.5 h, the solvent was removed by a vacuum line. The residue was distilled by bulb-to-bulb distillation at 93 °C (9 mmHg) to give **10a** (876.5 mg, 93.1% yield) as a pale yellow oil: IR (CCl_4) 3060, 1675, 1600, 1165–1215 (CF) cm^{-1}; ^1H NMR (CCl_4) δ 6.73–7.6 (PhH, m); ^{19}F NMR (CCl_4) –4.0 (3 F, q, J = 7.2 Hz), –3.4 (3 F, septet, J = 4.5 Hz), 2.4 (3 F, q, J = 4.5 Hz), 3.6 (3 F, qq, J = 7.2, 4.5 Hz) ppm; mass spectrum, *m/e* 447 (M^+); high-resolution mass spectrum, calcd for $C_{14}H_5NSF_{12}$ *m/e* 446.9951, found *m/e* 446.9981.

Isolation of 9a during the Thermolysis of 3a. After a solution of **3a** (1 g, 2.11 mmol) in cyclohexane (20 mL) was heated at 60–65 °C for 16 h, the solvent was removed on a vacuum line, and the residue was column chromatographed (SiO_2, *n*-pentane). From the workup of the first fraction was obtained **9a** (365.6 mg). The spectra of **9a** differred from those of **10a**: IR 2100 cm^{-1}; ^{19}F NMR –9.6–6.4 ppm. Compound **9a** was converted quantitatively to **10a** on heating at 80 °C in cyclohexane (^{19}F NMR).

Pyrolysis of 3b in Cyclohexane or without a Solvent. A solution of **3b** (500 mg, 1.04 mmol) in cyclohexane (20 mL) was refluxed for 40–50 h, and then the solvent was removed on a vacuum line. The residue was purified by column chromatography (SiO_2, *n*-pentane), affording 401.4 mg (85.2% yield) of **10b** as a yellow oil. Compound **10b** was also obtained without solvent in 94% yield: IR (CCl_4) 2950, 2870, 1680, 1460, 1160 cm^{-1}; ^1H NMR (CCl_4) δ 3.5–4.16 (1 H, CH–N, m), 1–2 (10 H, CH_2, m); ^{19}F NMR (CCl_4) –3.8 (3 F, septet), –1.8 (3 F, qq), 2.4 (3 F, q), 3.6 (3 F, m); mass spectrum, *m/e* 453 (M^+). Anal. Calcd for $C_{14}H_{11}NSF_{12}$: C, 37.08; H, 2.45; N, 3.09; S, 7.07. Found: C, 36.68; H, 2.38; N, 3.41; S, 6.78.

Pyrolysis of 3c without a Solvent. Compound **3c** (143.5 mg, 0.315 mmol) was sealed in a Pyrex tube and heated at 100 °C for 4 h. The crude product was purified by preparative TLC to give **10c** (84.4 mg, 62.7% yield) as a yellow oil: IR (CCl_4) 2970, 1670, 1115 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.4 ($C(CH_3)_3$, s); ^{19}F NMR ($CDCl_3$) –4.6 (3 F, m), –4.4 (3 F, m), 2.4 (3 F, q), 3.4 (3 F, m); mass spectrum, *m/e* 412 (M^+ – CH_3).

Pyrolysis of 3d without a Solvent. Compound **3d** (1.23 g, 3.08 mmol) was sealed in a Pyrex tube and heated for several hours at 95–100 °C. The crude product was distilled to give **10d** (945.8 mg, 82.8%) as a colorless oil: bp 106 °C; IR (CCl_4) 3280 (NH), 1680, 1650, 1170 cm^{-1}; ^1H NMR ($CDCl_3$) δ 11.3 (NH, br); ^{19}F NMR ($CDCl_3$) –2.6 (3 F, septet), 2.2 (3 F, q), 4.2 (3 F, qq), 7.2 (3 F, q)

(20) The decomposition of **4a** occurred at 60 °C and/or at room temperature for 1–2 weeks.

(21) Compound **8b** existed as two isomers, the syn and anti forms, or as conformational isomers around the C–C bond.

(22) In the same way, **8a** and **8b** were synthesized. Kobayashi, Y.; et al., to be submitted for publication.

ppm; mass spectrum, m/e 371 (M^+); high-resolution mass spectrum, calcd for C_8HNSF_{12} m/e 370.9638, found m/e 370.9626; ^{13}C NMR ($CDCl_3$) δ 159.7 (q, J_{CCF} = 36.7 Hz), 143.6, 124.6. 122.3 (q, J_{CF} = 281.2 Hz), 117.5 (q, J_{CF} = 282.3 Hz), 117.4 (q, J_{CF} = 272.5 Hz), 116.9 (q, J_{CF} = 271.6 Hz), 58.2 (q, J_{CCF} = 35 Hz).

Reaction of 10a,b,d. Conversion of 10a to *N*-Phenylpyrrole 7a. A. To a solution of **10a** (500 mg, 1.12 mmol) in *n*-hexane (10 mL) was added triphenylphosphine (293 mg, 1.12 mmol) at room temperature. The precipitated sulfide was filtered off, and the solvent was removed on a vacuum line.

The residue was purified by column chromatography (SiO_2, *n*-pentane elution) to give **7a** (441.3 mg, 95% yield). Compound **7a** obtained by this method was identical with the product of thermolysis of **4a**.

B. A solution of **10a** (71.2 mg, 0.159 mmol) in *n*-pentane (0.4 mL) was sealed in a 4-mm Pyrex tube and heated at 140 °C for 1 h. The reaction mixture was evaporated under vacuum to remove the solvent, and the residue was purified by preparative TLC to give **7a** (47.7 mg, 72.1% yield).

C. A solution of **10a** in *n*-pentane was sealed in a Pyrex tube and irradiated with a high-pressure mercury lamp for several hours. By ^{19}F NMR, **10a** was converted to **7a** quantitatively.

Conversion of 10b to 7b. To a solution of **10b** (200 mg, 0.442 mmol) in *n*-pentane (5 mL) was added triphenylphosphine (115.7 mg, 0.442 mmol), and the mixture was refluxed for several hours. The reaction mixture was concentrated under vacuum and the residue purified by column chromatography (SiO_2, *n*-pentane) to give **7b** (119 mg, 64% yield). Compound **10b** was also converted quantitatively to **7b** by irradiation with a low-pressure mercury lamp and by thermolysis at 160 °C. Compound **7b** obtained by these methods was identical with the product of thermolysis of **4b**.

Reaction of 10d with Triphenylphosphine, 4*H*-3,4,5,6-tetrakis(trifluoromethyl)-1,2-thiazine (11). To a solution of **10d** (518 mg, 1.40 mmol) in *n*-pentane (5 mL) was added triphenylphosphine (365.8 mg, 1.40 mmol) at room temperature. The reaction mixture was carefully concentrated under vacuum, and the crude product was purified by column chromatography (SiO_2, *n*-pentane), followed by bulb-to-bulb distillation (55–60 °C, 95 mmHg) to give **11**: 254.5 mg (49.1%); IR (CCl_4) 2980, 1720, 1610, 1353, 1305, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.9 (1 H, q, J = ca. 8 Hz); ^{19}F NMR ($CDCl_3$) −3.7 (3 F, q, J = 11.3 Hz), −1.8 (3 F, qq, J = 11.3, 2.8 Hz), 4.4 (3 F, qqd, J = 4.5, 2.8, 8 Hz), 6.6 (3 F, q, J = 4.5 Hz) ppm; mass spectrum, m/e 371 (M^+); high-resolution mass spectrum, calcd for C_8HNSF_{12} m/e 370.9638, found m/e 370.9626; ^{13}C NMR ($CDCl_3$) δ 142.9 (q, J = 31.7 Hz), 123.29, 120.2, 120.0, 119.8, 118.1, 110.2, 38.6.

Registry No. **1**, 39091-73-1; **2a**, 622-37-7; **2b**, 19573-22-9; **2c**, 13686-33-4; **2d**, 7782-79-8; **3a**, 64724-54-5; **3b**, 64724-55-6; **3c**, 73688-02-5; **3d**, 68318-50-3; **4a**, 73697-47-9; **4b**, 73688-06-9; **4c**, 73688-33-2; **4d**, 73688-34-3; **5a**, 73688-35-4; **5b**, 73688-36-5; **5c**, 73688-37-6; **5d**, 73688-38-7; **6**, 73688-39-8; **7a**, 73679-97-7; **7b**, 73688-40-1; **7d**, 73688-41-2; **8b**, 73688-42-3; **8c**, 73688-43-4; **9a**, 73697-48-0; **10a**, 73688-44-5; **10b**, 73688-45-6; **10c**, 73688-46-7; **10d**, 73688-47-8; **11**, 73688-48-9; triphenylphosphine, 603-35-0.

Organic Fluorine Compounds. 33.[1] Derivation of Tetrakis(trifluoromethyl)(Dewar Pyrroles) from Tetrakis(trifluoromethyl)(Dewar Thiophene)[2]

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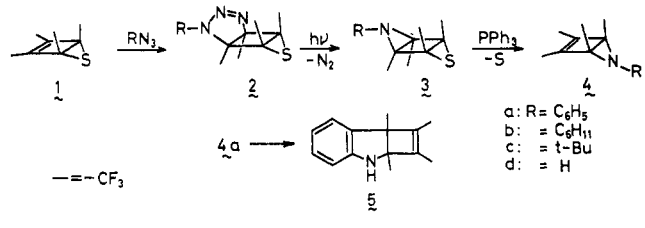
The 1,3-dipolar cycloadducts of tetrakis(trifluoromethyl)(Dewar thiophene) with azides were photochemically denitrogenated to 2-thia-5-azatricyclo[3.1.0.0^{2,5}]hexanes which were desulfurized with triphenylphosphine, affording tetrakis(trifluoromethyl)(Dewar pyrroles). The Dewar pyrroles reacted with cyclic dienes to give Diels–Alder adducts.

In the course of our studies on valence-bond isomers of aromatic compounds stabilized with trifluoromethyl groups,[3,4] a new type of valence-bond isomer, "Dewar" pyrroles, has been synthesized. Thus, as shown in the previous paper,[1] tetrakis(trifluoromethyl)(Dewar thiophene) (1) reacted with azide compounds to give 1,3-dipolar cycloadducts **2a–d**. These cycloadducts as well as their desulfurized products were thermally ring opened to diazo imino compounds by a retro-1,3-dipolar mechanism. Here we describe the denitrogenation of the dihydrotriazole part of **2** that might occur on photolysis, by a ($_\sigma 2_s + _\sigma 2_s$) process; several examples of the photolysis of triazolines to aziridine compounds are known.[5-8] In the event, photolysis of **2** gave compounds **3** of a new condensed ring system, 2-thia-5-azatricyclo[3.1.0.0^{2,5}]hexane, which may be considered as a valence-bond isomer of 1,4-thiazine. The structure of **3** was determined by spectral data; the ^{19}F NMR showed only one pair of trifluoromethyl groups, indicating the high symmetry of these compounds.

Scheme I



The compounds **3** were desulfurized with triphenylphosphine to give compounds **4**, another new ring system, 5-azabicyclo[2.1.0]pent-2-ene, or "Dewar" pyrrole. These results are shown in Scheme I. Compounds **3** are thermally stable, while the stability of compounds **4** depends

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