

ppm; mass spectrum, m/e 371 (M^+); high-resolution mass spectrum, calcd for C_9HNSF_{12} m/e 370.9638, found m/e 370.9626; ^{13}C NMR ($CDCl_3$) δ 159.7 (q, $J_{CF} = 36.7$ 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, $J_{CF} = 35$ 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_9HNSF_{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

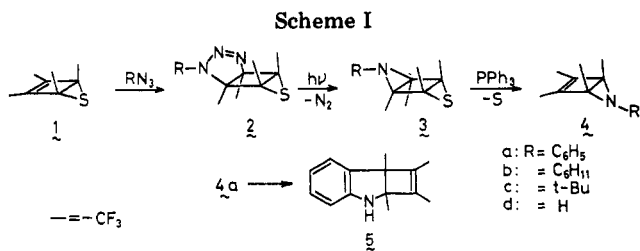
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The 1,3-dipolar cycloadducts of tetrakis(trifluoromethyl)(Dewar thiophene) with azides were photochemically denitrogenated to 2-thia-5-azatricyclo[3.1.0.0^{2,5}]hexanes which were desulfurized with triphenylphosphine, affording tetrakis(trifluoromethyl)(Dewar 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 ($\sigma_2 + \sigma_2$) 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.

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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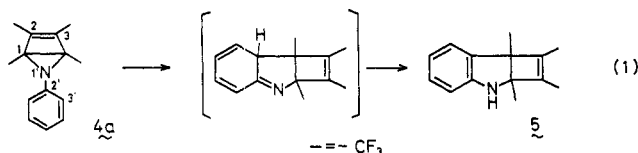
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on the substituents on the nitrogen atom. Thus, *N*-phenyl compound **4a** spontaneously rearranged to the dihydrocyclobut[b]indole **5**, possibly by a [3.3] sigmatropic reaction, as shown in eq 1. This rearrangement was followed

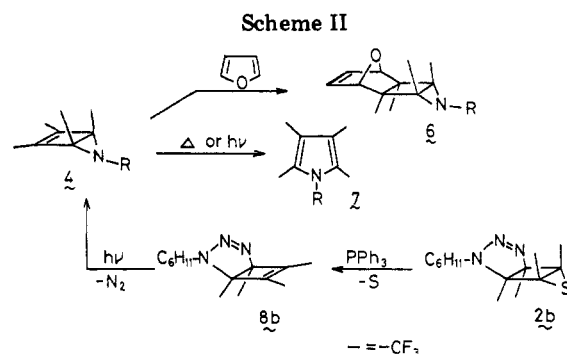


by ^{19}F NMR and ESR, but no radicals were detected. Thus, it must be a concerted process. Other Dewar pyrroles (**4b,c,d**) are stable at room temperature. The structures of compounds **4** were established by high symmetry in the ^{19}F NMR spectra and an absorption near 1700 cm^{-1} due to the cyclobutenic double bond. The compound **4a** was rearranged so rapidly to **5** that it was only observed by ^{19}F NMR and IR spectroscopy. Reaction of **4b,d** with furan gave the Diels–Alder adducts **6b,d**, which supported the Dewar structure of **4** by analogy with the reaction of Dewar thiophene 1.^{3,4,9,10} The structures of **6b,d** were considered to be *exo-anti* by analogy with the structure of the adduct of 1 with furan. Small coupling constants between the CF_3 fluorines support the *anti* structure. The high stability of these Dewar pyrroles, especially *N*-H compound **4d**, is remarkable, since, in the latter case, prototropy could readily cause isomerization. These stabilities might be due to the electron-withdrawing effect of the trifluoromethyl groups.¹¹ The compounds **4b,d** isomerized thermally to the corresponding pyrrole compounds **7b,d**. Lemal et al.¹² reported that automerization was observed on thermal isomerization of 1. Day et al.¹³ postulated a Dewar pyrrole intermediate and a “walk” of its nitrogen atom during the photoisomerization of 2-cyanopyrrole. Therefore, we followed this thermal isomerization of **4b** with ^{19}F NMR, but no automerization was observed: the isomerization to the pyrrole was much faster than the automerization, if any, or otherwise the automerization occurred too slowly to be observed to an appreciable extent by ^{19}F NMR. Irradiation of **4b** with a high-pressure mercury lamp also caused its isomerization to **7b**.

The cycloadduct **2b** was desulfurized with triphenylphosphine to the cyclobutatriazoline **8b**, irradiation of which gave **4b**. Therefore, the order of desulfurization and denitrogenation was not essential, but the photochemical denitrogenation was crucial for the formation of the aziridine ring. The same reactions did not follow with **2a**, since the desulfurized product **8a** isomerized rapidly to a diazo imine compound, as shown in the previous paper. These results are summarized in Scheme II.

Conclusion

Tetrakis(trifluoromethyl)(Dewar pyrroles) **4a–d** were synthesized from tetrakis(trifluoromethyl)(Dewar thiophene) (1) through reaction of 1,3-dipolar cycloadducts **2** with azides. Photochemical denitrogenation of triazoline compounds to aziridine compounds was the essential step in



this synthesis. *N*-Phenyl isomer **4a** isomerized spontaneously to cyclobutindole compound **5**, while the other isomers **4b–d** isomerized thermally or photochemically to the pyrrole **7**. Reaction of **4b,d** with furan gave the Diels–Alder adducts **6**.

Experimental Section

Photolysis of 1,3-Dipolar Cycloadducts 2. Denitrogenation of 2a. 6-Phenyl-1,2,4,5-tetrakis(trifluoromethyl)-6-aza-3-thiatricyclo[3.1.0.0^{2,4}]hexane (**2a**). A degassed solution of **2a** (500 mg, 1.05 mmol) in *n*-pentane (10 mL) was irradiated with a high-pressure mercury lamp for 4 h. After evaporation of the solvent on a vacuum line, the residue was worked up by column chromatography (SiO_2 , *n*-pentane). **3a** was obtained as a colorless oil: 358.4 mg (76.2% yield); IR (CHCl_3) 3040, 1600, 1290, 1170 (CF) cm^{-1} ; ^1H NMR (CDCl_3) δ 7.18 (PhH); ^{19}F NMR (CDCl_3)¹⁴ δ -5.6 (6 F, br s), 2.8 (6 F, br s) ppm; mass spectrum, *m/e* 447 (M^+); high-resolution mass spectrum, calcd for $\text{C}_{14}\text{H}_5\text{NF}_{12}\text{S}$ *m/e* 446.9951, found *m/e* 446.9966.

6-Cyclohexyl-1,2,4,5-tetrakis(trifluoromethyl)-6-aza-3-thiatricyclo[3.1.0.0^{2,4}]hexane (2b**).** A solution of **2b** (995.8 mg, 2.07 mmol) in *n*-pentane (30 mL) sealed in a quartz tube under vacuum was irradiated with a low-pressure mercury lamp for 6.5 h. The solvent was removed on a vacuum line, and the residue was passed through an SiO_2 column with *n*-pentane as eluent. The effluent was purified by bulb-to-bulb distillation (96–98 °C, 18 mmHg) to give **3b** (862.1 mg, 91.9% yield) as a colorless oil: IR (CHCl_3) 2940, 2860, 1160 (CF) cm^{-1} ; ^1H NMR (CDCl_3) δ 2.93 (1 H, CH–N, m), 1.03–2.1 (10 H, CH_2 , m); ^{19}F NMR (CDCl_3) δ -2.4 (6 F, s), 2.8 (6 F, s) ppm; mass spectrum, *m/e* 453 (M^+ , w). Anal. Calcd for $\text{C}_{14}\text{H}_{11}\text{NF}_{12}\text{S}$: C, 37.08; H, 2.46; N, 3.09; F, 50.31; S, 7.07. Found: C, 36.78; H, 2.36; N, 3.32; F, 50.57; S, 6.95.

6-tert-Butyl-1,2,4,5-tetrakis(trifluoromethyl)-6-aza-3-thiatricyclo[3.1.0.0^{2,4}]hexane (2c**).** A solution of **2c** (569.5 mg, 1.25 mmol) in perfluoro-*n*-hexane (5 mL) sealed in a Pyrex tube fitted with a cold finger under vacuum was irradiated with a high-pressure mercury lamp for 28 h. After concentration of the mixture, the residue was worked up by column chromatography on silica gel. The product was recrystallized from *n*-pentane (at dry-ice acetone temperature) to give **3c** (194.4 mg, 36.3% yield) as highly sublimable colorless prisms: mp 115–119 °C; IR (CCl_4) 2970, 1260–1280, 1160–1200 (CF) cm^{-1} ; ^1H NMR (CDCl_3) δ 1.36 ($\text{C}(\text{CH}_3)_3$, s); ^{19}F NMR (CDCl_3) δ -6.12 (6 F, s), 1.68 (6 F, s) ppm; mass spectrum, *m/e* 412 ($\text{M}^+ - \text{CH}_3$), 339 (412 – $\text{C}_3\text{H}_5 - \text{S}$); high-resolution mass spectrum, calcd for $\text{C}_{11}\text{H}_6\text{NF}_{12}\text{S}$ [*m/e* 412 ($\text{M}^+ - \text{CH}_3$)] *m/e* 412.0029, found *m/e* 412.0011.

1,2,4,5-Tetrakis(trifluoromethyl)-6-aza-3-thiatricyclo[3.1.0.0^{2,4}]hexane (2d**).** A solution of **2d** (432 mg, 1.08 mmol) in ether (5 mL) was placed in a degassed quartz reaction vessel equipped with a cold finger. The solution was irradiated with a low-pressure mercury lamp for 3 days after concentration of the mixture on a vacuum line, and the crude product was purified by preparative GLC (SE-30, 50 °C) to give **3d** (177.2 mg, 44.1% yield) as a colorless oil: IR (CCl_4) 3310 (NH), 1150–1210 (CF) cm^{-1} ; ^1H NMR (CDCl_3) δ 4.75 (NH, m); ^{19}F NMR (CDCl_3) δ 0 (6 F, s), 3.8 (6 F, s) ppm; mass spectrum, *m/e* 371 (M^+); high-resolution mass spectrum, calcd for $\text{C}_8\text{HNF}_{12}\text{S}$ *m/e* 370.9638, found *m/e* 370.9648.

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

Synthesis of Dewar Pyrroles 4. **5-Phenyl-1,2,3,4-tetrakis(trifluoromethyl)-5-azabicyclo[2.1.0]pent-2-ene [N-Phenyl(Dewar Pyrrole)] (4a).** To an ice-cold solution of **3a** (49.6 mg, 0.111 mmol) in *n*-pentane (0.3 mL) was added triphenylphosphine (29.1 mg, 0.111 mmol). At this time, the ^{19}F NMR spectrum of the reaction mixture showed signals different from those of **3a**. In the IR spectrum, the absorption at 1700 cm^{-1} ascribable to a cyclobutenic double bond appeared. But the reaction proceeded further, and **4a** changed to another product, **5**, at room temperature. The solvent was removed, and the residue was worked up by preparative TLC. **5** was obtained in a yield of 16.4 mg (35.6%) as a colorless oil: IR (*n*-pentane) 3430 (NH), 1715 (cyclobutenic double bond), 1618, 1210, (CF) cm^{-1} ; ^1H NMR (CCl_4) δ 4.72 (NH, 1 H, br), 7.2–7.5, 6.75–7.04 (aromatic H, 4 H, m); ^{19}F NMR (CDCl_3) δ -0.8 (3 F, m), 0 (3 F, m), 5.2 (3 F, m), 10.8 (3 F, m) ppm; mass spectrum, m/e 415 (M^+); high-resolution mass spectrum, calcd for $\text{C}_{14}\text{H}_8\text{NF}_{12}$ m/e 415.0230, found m/e 415.0243.

5-Cyclohexyl-1,2,3,4-tetrakis(trifluoromethyl)-5-azabicyclo[2.1.0]pent-2-ene [N-Cyclohexyl(Dewar Pyrrole)] (4b). After irradiation of **2b** (785 mg, 1.73 mmol) in *n*-pentane (30 mL) for 6 h with a low-pressure mercury lamp, the reaction mixture was treated with triphenylphosphine (454.0 mg, 1.73 mmol). The precipitated sulfide was filtered off, the filtrate was concentrated, and the residue was worked up by preparative TLC to give **4b** (544.7 mg, 79.3% yield) as a colorless oil: bp 65°C (7 mmHg); IR (CCl_4) 2940, 2860, 1700 (cyclobutenic double bond), 1160 (CF) cm^{-1} ; ^1H NMR (CCl_4) δ 2.63 (CH–N, 1 H, m), 1.15–1.95 (CH_2 , 10 H, m); ^{19}F NMR (CCl_4) 1.52 (6 F, s), 2.72 (6 F, s) ppm; ^{13}C NMR (CDCl_3) δ 140.4 (sp^2 , q, $J_{\text{CF}} = 45$ Hz), 121.2 (sp^3 , q, $J_{\text{CF}} = 274$ Hz), 118.1 (sp^3 , q, $J_{\text{CF}} = 272$ Hz), 55.1 (sp^3 , d, $J_{\text{CH}} = 134$ Hz), 50.0 (sp^3 , q, $J_{\text{CF}} = 45$ Hz), 32.0, 25.9, and 23.8 (sp^3 , t, $J_{\text{CH}} = 127$ Hz); mass spectrum, m/e 421 (M^+ , w); high-resolution mass spectrum, calcd for $\text{C}_{14}\text{H}_{11}\text{NF}_{12}$ m/e 421.0700, found m/e 421.0681.

5-tert-Butyl-1,2,3,4-tetrakis(trifluoromethyl)-5-azabicyclo[2.1.0]pent-2-ene [N-tert-Butyl(Dewar Pyrrole)] (4c). To a solution of **3c** (325 mg, 0.761 mmol) in *n*-pentane (3 mL) was added triphenylphosphine (excess). The solution was stirred at room temperature for 30 min. By use of a vacuum line, low-boiling materials were separated from triphenylphosphine and the sulfide. The separated solution was worked up by preparative GLC (SE-30, 3 m, 70°C). **4c** was isolated as a colorless oil: 235.2 mg (78.2% yield); IR (CCl_4) 2970, 1710 (cyclobutenic double bond), 1255–1275, 1190–1210, 1170 (CF) cm^{-1} ; ^1H NMR (CDCl_3) δ 1.25 ($\text{C}(\text{CH}_3)_3$, s); ^{19}F NMR (CDCl_3) 0.2 (6 F, s), 2.4 (6 F, s); mass spectrum, m/e 339 ($\text{M}^+ - \text{C}_4\text{H}_8$), 56 (C_4H_8). *N*-tert-Butyl(Dewar pyrrole) (**4c**) was comparatively stable at room temperature, but it decomposed slowly to give tetrakis(trifluoromethyl)pyrrole over several weeks at room temperature. This fact is consistent with the evidence that the mass spectrum showed not a parent peak but an $\text{M}^+ - \text{C}_4\text{H}_8$ peak [$(\text{CH}_3)_2\text{C}=\text{CH}_2$].

1,2,3,4-Tetrakis(trifluoromethyl)-5-azabicyclo[2.1.0]pent-2-ene (N-Unsubstituted Dewar Pyrrole) (4d). A solution of **2d** (2.0 g, 5.01 mmol) in Et_2O (30 mL) was placed in the quartz vessel equipped with a cold finger and irradiated with a low-

pressure mercury lamp under vacuum for ca. 20 h. The reaction mixture was concentrated on a vacuum line. To the residue was added *n*-pentane, and undissolved starting material (**2d**) was recovered by filtration (175.5 mg after purification). The filtrate was treated with triphenylphosphine (excess). Then, the product and solvent were separated from the phosphine sulfide on a vacuum line. The solution was worked up by preparative GLC (SE-30, 6 m, 38°C) to give **4d** (634.9 mg, 40.9% yield) as a light yellow oil: IR (CCl_4) 3300 (NH), 1700 (cyclobutenic double bond), 1290, 1250, 1160–1230 (CF) cm^{-1} ; ^1H NMR (CDCl_3) δ 6.16 (NH, m); ^{19}F NMR (CDCl_3) 1.6 (br s, 6 F), 2.4 (br s, 6 F) ppm; mass spectrum, m/e 339 (M^+); high-resolution mass spectrum, calcd for $\text{C}_8\text{HNF}_{12}$ m/e 338.9917, found m/e 338.9910; ^{13}C NMR (CDCl_3) δ 148.7 (sp^2 , q, $J_{\text{CF}} = 47.6$ Hz), 120.8 (sp^3 , q, $J_{\text{CF}} = 272.2$ Hz), 117.5 (sp^3 , q, $J_{\text{CF}} = 272.2$ Hz), 44.5 (sp^3 , q, $J_{\text{CF}} = 48.8$ Hz).

Transformation of 8b to 4b. A solution of **8b** (200.8 mg, 0.447 mmol) in *n*-pentane (5 mL), obtained by desulfurization of **2b**, was irradiated with a high-pressure mercury lamp for 12 h. The reaction mixture was concentrated on a vacuum line, and the residue was worked up by preparative TLC. The yield of **4b** was 122.2 mg (64.9%). The **4b** obtained was identical with the product obtained by denitrogenation and desulfurization.

Diels-Alder Reaction of 4b,d with Furan. **4-Cyclohexyl-2,3,5,6-tetrakis(trifluoromethyl)-4-aza-10-oxatetracyclo[5.2.1.0^{2,6}.0^{3,5}]dec-8-ene (6b).** *N*-Cyclohexyl(Dewar pyrrole) (**4b**; 205 mg, 0.487 mmol) was dissolved in CHCl_3 (3 mL), and furan (excess) was added. After the mixture was stirred at room temperature for 30 min, the solvent and furan were evaporated, and the residue was recrystallized from CH_3OH to give **6b** (212.9 mg, 89.4% yield) as colorless crystals. The mother liquor was worked up to give **6b** (14 mg) by evaporation and sublimation: mp $123\text{--}125^\circ\text{C}$; IR (CCl_4) 2940, 2860, 1210, 1170 (CF) cm^{-1} ; ^1H NMR (CCl_4) δ 6.6 ($=\text{CH}$, 2 H, br s), 5.31 (CH–O, 2 H, s), 3.0 (N–CH, 1 H, m), 1.0–2.1 (CH_2 , 10 H, m); ^{19}F NMR (CCl_4) δ -0.4 (6 F, s), -0.4 (6 F, s) ppm; mass spectrum, m/e 421 ($\text{M}^+ - \text{furan}$), 68 (furan). Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{NOF}_{12}$: C, 44.18; H, 3.09; N, 2.86; F, 46.60. Found: C, 43.79; H, 3.22; N, 2.90; F, 46.51.

2,3,5,6-Tetrakis(trifluoromethyl)-4-aza-10-oxatetracyclo[5.2.1.0^{2,6}.0^{3,5}]dec-8-ene (6d). Compound **3d** (84.5 mg, 0.249 mmol) obtained by denitrogenation of **2d** was dissolved in *n*-pentane (3 mL). To this solution was added triphenylphosphine (78.1 mg, 0.298 mmol), and the sulfide was filtered off. Then, furan (37.1 mg, 0.546 mmol) was added to this filtrate and the mixture stirred for 30 min at room temperature. Solvent was evaporated off and the residue was sublimed to give **6d** (57.4 mg, 61.9% yield) as colorless crystals: mp $61\text{--}64^\circ\text{C}$; IR (CCl_4) 3370 (NH), 1140–1220 (CF) cm^{-1} ; ^1H NMR (CCl_4) δ 6.62 ($=\text{CH}$, 2 H, s), 5.35 (CH–O, 2 H, s), 3.72 (NH, 1 H, m); ^{19}F NMR (CCl_4) δ -0.8 (6 F, s), 2.8 (6 F, s) ppm; mass spectrum, m/e 387 ($\text{M}^+ - \text{HF}$).

Registry No. **2a**, 64724-54-5; **2b**, 64724-55-6; **2c**, 73688-02-5; **2d**, 68318-50-3; **3a**, 64724-56-7; **3b**, 64724-57-8; **3c**, 73688-03-6; **3d**, 73688-04-7; **4b**, 64724-58-9; **4c**, 73688-05-8; **4d**, 68318-51-4; **5**, 64747-38-2; **6b**, 64724-59-0; **6d**, 68318-52-5; **8b**, 73688-06-9.

Organic Fluorine Compounds. 34.¹ Some Reactions of Valence-Bond Isomers of Tetrakis(trifluoromethyl)pyrroles

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By use of the valence-bond isomers of trifluoromethylated pyrrole compounds, the mechanism of photochemical transformation of five-membered aromatic compounds was studied. The formerly postulated intermediates, Dewar pyrroles or cyclopropenyl imines, did not give pyrroles in thermal reactions, while only the Dewar pyrroles rearranged to pyrroles on photolysis. Although the reaction of trifluoromethylated Dewar thiophene with aniline gave the corresponding pyrrole, neither the Dewar pyrrole nor the cyclopropenyl imine is the intermediate, as postulated previously.

In the previous papers, we described some valence-bond isomers of pyrroles. These compounds appeared useful

for studies on the mechanism of photochemical transformations of five-membered heterocyclic compounds.