The reactions were usually followed for 5 half-life times; the end point obtained after increasing the temperature for some time was 95–100% in most cases, if compared to the calculated end point on the basis of curves calibrated with TsOH. The recorded data were analyzed with suitable computer programs, indicating no deviation from fist-order kineics (see supplementary material). The alcohols used as solvents contained <0.2% water (Karl–Fischer titration) and were brought to the composition as given in the tables by adding distilled water.

Force field calculations were carried out with Allinger's MM2 program[3a] on the Siemens 7.760 of the Rechenzentrum der Universität des Saarlandes. The starting geometries for the conformers were generated by attaching substituents at the different carbon atoms, methyl usually only in (pseudo)equatorial or isoclinal positions. In a few cases the strain energies of (pseudo)axial methylcycloalkanes were also tested and found to be >2 kcal/mol less stable (e.g., with cyclooctanes, see supplementary material).

All ring systems retained their basic conformation during the energy minimization, with the exception of cyclopentanes, which therefore had to be analyzed by inspection of the full pseudorotational circle.[52]

Other calculations, such as of weighted strain energies and populations of conformers, or linear regression analyses were performed with Fortran and BASIC programs on the Siemens 7.760 or an Apple II+ computer.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support and two referees for helpful suggestions.

Registry No. Cyclobutane, 287-23-0; cyclohexane, 110-82-7; cyclooctane, 292-64-8; cyclododecane, 294-62-2; norborane, 279-23-2; 1,7,7-trimethylnorborane, 464-15-3; 1,3,3-trimethylnorborane, 6248-88-0; 2,2-dimethylbicyclo[2.2.1]heptane, 6248-85-7; 2-*exo*-methylnorbornane, 872-78-6; hydroxycyclobutane, 2919-23-5; hydroxycyclohexane, 108-93-0; hydroxycyclooctane, 696-71-9; 7-hydroxybicyclo[2.2.1]heptane, 2566-48-5; 2-*exo*-hydroxybicyclo[2.2.1]heptane, 497-37-0; 2-*endo*-hydroxybicyclo[2.2.1]heptane, 497-36-9; 2-*endo*-hydroxy-1,7,7-trimethylbicyclo[2.2.1]heptane, 507-70-0; 2-*exo*-hydroxy-1,7,7-trimethylbicyclo[2.2.1]heptane, 124-76-5; 2-*endo*-hydroxy-1,3,3-trimethylbicyclo[2.2.1]heptane, 14575-74-7; 2-*exo*-hydroxy-1,3,3-trimethylbicyclo[2.2.1]heptane, 22627-95-8; 3,3-dimethylbicyclo[2.2.1]heptan-2-*endo*-ol, 640-54-0; 2-*exo*-hydroxy-3-*exo*-methylbicyclo[2.2.1]heptane, 16745-65-6; methylcyclobutane, 598-61-8; methylcyclohexane, 108-87-2; methylcyclooctane, 1502-38-1; methylcyclododecane, 1731-43-7; 7-methylbicyclo[2.2.1]heptane, 1679-14-7; 2-*exo*-methylbicyclo[2.2.1]-heptane, 872-78-6; 2-*endo*-methylbicyclo[2.2.1]heptane, 765-90-2; 2-*endo*-methyl-1,7,7-trimethyltricyclo[2.2.1]heptane, 57905-88-1; 2-*exo*-methyl-1,7,7-trimethylbicyclo[2.2.1]heptane, 57905-87-0; 2-*endo*-methyl-1,3,3-trimethylbicyclo[2.2.1]heptane, 85283-01-8; 2-exo-methyl-1,3,3-trimethylbicyclo[2.2.1]heptane, 85283-02-9; 2-*endo*-methyl-3,3-dimethylbicyclo[2.2.1]heptane, 20536-40-7; 2-*exo*-methyl-3-*exo*-methylbicyclo[2.2.1]heptane, 20536-41-8; cyclobutanone, 1191-95-3; cyclohexanone, 108-94-1; cyclooctanone, 502-49-8; cyclododecanone, 830-13-7; bicyclo[2.2.1]heptan-7-one, 10218-02-7; bicyclo[2.2.1]heptan-2-one, 497-38-1; 1,7,7-trimethylbicyclo[2.2.1]heptan-2-one, 76-22-2; 1,3,3-trimethylbicyclo[2.2.1]heptan-2-one, 1195-79-5; 3,3-dimethylbicyclo[2.2.1]heptan-2-one, 13211-15-9; 3-*exo*-methylbicyclo[2.2.1]heptan-2-one, 3915-75-1; methylcyclopentane, 96-37-7; bromocycloheptane, 2404-35-5; methylcyclononane, 874-99-7; methylcyclodecane, 13151-43-4; methylcycloundecane, 13151-44-5; cyclopentanone, 120-92-3; cycloheptanone, 502-42-1; cyclononanone, 3350-30-9; cyclodecanone, 1502-06-3; cycloundecanone, 878-13-7; 3-pentyl tosylate, 950-25-4; cyclobutyl tosylate, 10437-85-1.

Supplementary Material Available: Strain energies of cycloalkanone and methylcycloalkane conformations, selected data on cyclohexane, cyclodecane, and cyclooctane conformations (torsional angles, strain energy distributions and populations, from MM2 calculations); kinetic data on solvolysis of cycloalkyl tosylates in ethanol/water (1:1) and trifluoroethanol (10 pages). Ordering information is given on any current masthead page.

(52) Schneider, H.-J.; Nguyen-Ba, N.; Thomas, F. *Tetrahedron* **1982**, *38*, 2337.

Diazotetrakis(trifluoromethyl)cyclopentadiene and Ylides of Electronegative Elements

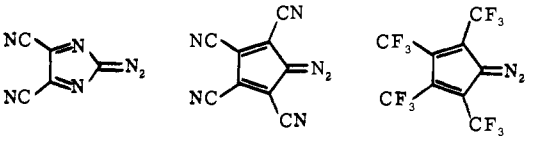
Eugene P. Janulis, Jr., and Anthony J. Arduengo III*

Contribution from the Roger Adams Laboratory, Department of Chemistry, University of Illinois, Urbana, Illinois 61801. *Received October 20, 1982*

Abstract: The synthesis of diazotetrakis(trifluoromethyl)cyclopentadiene (**1**) is described. This stable perfluorinated diazo compound undergoes a photochemical loss of nitrogen to yield a reactive intermediate which reacts with a variety of elements bearing lone pairs to give tetrakis(trifluoromethyl)cyclopentadiene ylides. The synthesis of carbonyl, thiocarbonyl, and halonium ylides is described as well as evidence for oxonium and nitrilium ylides.

Introduction

Our interest in diazocyclopentadienes bearing strong electron-attracting substituents as sources of extremely electrophilic carbenes led us to synthesize diazotetrakis(trifluoromethyl)-cyclopentadiene (**1**). Attempts to use the tetrakis(trifluoromethyl)cyclopentadienone[1] as a precursor were unsuccessful owing to the severe umpolung displayed by this molecule.[2] The recent synthesis of 5*H*-perfluoropentamethylcyclopentadiene[3] led us to attempt the synthesis of the tetrakis(trifluoromethyl)cyclopentadienide anion by a similar route. We hoped that the diazo compound **1** could be derived from this anion by one of the established techniques for such conversions. The electrophilic nature of the carbene derived from **1** should make it a good candidate for the formation of ylides with electronegative elements (e.g., the halogens or chalogens). Similar diazo compounds, for example, diazodicyanoimidazole (DDI)[4] and diazotetracyanocyclo-



1

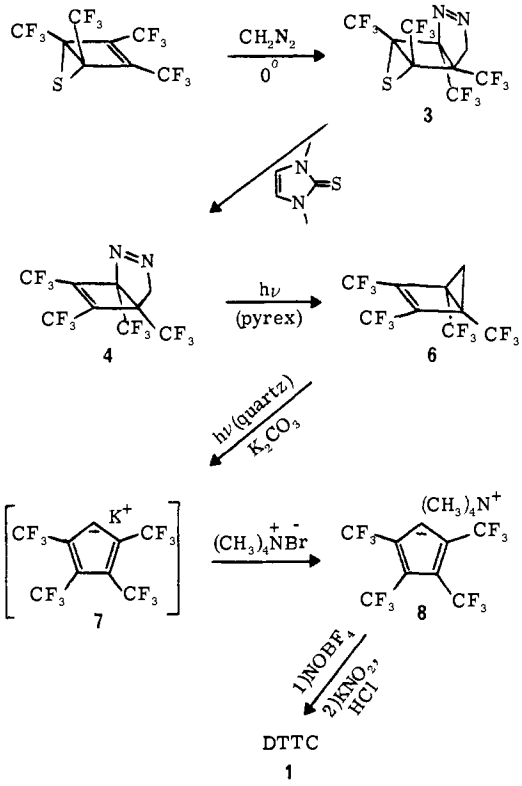
(1) We are grateful to D. M. Lemal for providing the details of his synthesis of this ketone.

(2) (a) J. L. Boston, W. A. Sharp, and G. Wilkinson, *J. Chem. Soc.*, 3488 (1962); (b) R. S. Dickson and G. Wilkinson, *ibid.*, 2699 (1964); (c) D. M. Roundhill and G. Wilkinson, *J. Org. Chem.*, **35**, 3561 (1970).

(3) E. D. Laganis and D. M. Lemal, *J. Am. Chem. Soc.*, **102**, 6633 (1980).

0002-7863/83/1505-3563$01.50/0

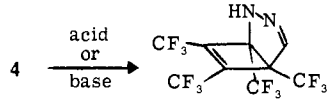
Scheme I



pentadiene (DTCC)[5], have been used as thermal precursors to carbenoid species. DDI has been used to synthesize a variety of ylides, among them a fairly stable series of chloronium, bromonium, and iodonium ylides.[4] Diazotetrakis(trifluoromethyl)-cyclopentadiene should complement DDI and DTCC by providing a stable diazo compound that has good solubility properties and a high vapor pressure, making gas-phase chemistry possible.

Discussion

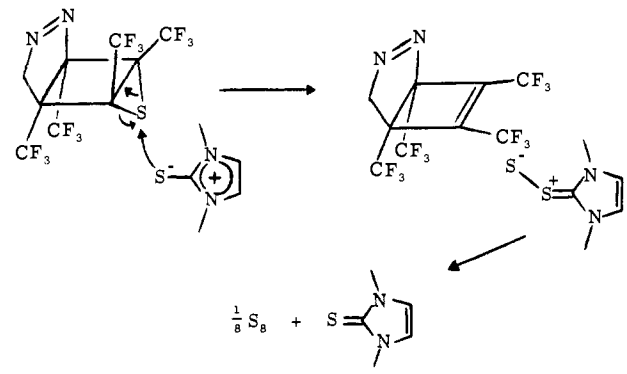
Diazotetrakis(trifluoromethyl)cyclopentadiene (DTTC) was prepared by the method outlined in Scheme I. The azothiirane **3** was obtained in high yield by the cycloaddition of diazomethane and tetrakis(trifluoromethyl)(Dewar thiophene).[6] As was reported for the synthesis of pentakis(trifluoromethyl)cyclopentadienide,[3] desulfurization of **3** without concurrent tautomerization of the azo group (to hydrazone **5**) was extremely difficult. The need



for a nonbasic thiaphile led us to try 1,3-dimethylimidazole-2-thione as a desulfurization agent. The thiirane **3** is cleanly and catalytically desulfurized by this imidazolethione without tautomerization of the azo ring. To our knowledge this is the only example of such a catalytic desulfurization. We later found that the desulfurization of **3** could also be accomplished by hydrogen sulfide, though this reaction is very slow. Scheme II shows the postulated mechanism of this unusual desulfurization.[7]

Both **3** and **4** are prone to tautomerization and great care must be exercised in handling these materials. The photoextrusion of

Scheme II

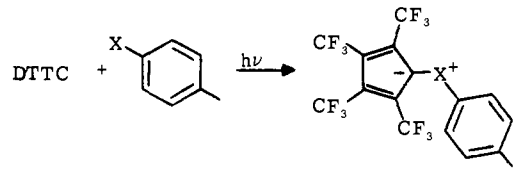


nitrogen from **4** proceeds cleanly with irradiation by a high-pressure mercury lamp through a Pyrex filter at 0 °C. The bicyclopentene **6** is quite volatile, and it was found better not to attempt its isolation, but rather to remove the Pyrex filter from the apparatus and continue the photolysis after the addition of potassium carbonate. Thus the photoisomerization of **6** to the cyclopentadiene can be easily performed. Attempts to isolate the potassium salt **7** led to extensive decomposition, and it was found necessary to convert **7** to the tetramethylammonium salt **8**, which is easily handled; the overall yield of **8** from **3** is 36%.

The nucleophilicity of **8** was not sufficient to allow diazotization by tosyl azide. Nitrosation of **8** with nitrosonium tetrafluoroborate followed by treatment with potassium nitrite/HCl gave the desired diazo compound (DTTC).

Diazotetrakis(trifluoromethyl)cyclopentadiene is a stable, colorless solid melting at 40–41 °C. It displays a strong IR absorption at 2175 cm^{-1}. The ^{19}F NMR shows two multiplets at −55.4 and −56.5 ppm upfield from $CFCl_3$ in $CDCl_3$. In acetonitrile the ^{19}F spectrum of DTTC shows only a single resonance at −55.2 ppm (spectra taken at very narrow sweep widths suggest this may really be two closely spaced resonances).

Though the DTTC is thermally stable (it is unchanged after heating to 190 °C in chlorobenzene), it undergoes a photochemical loss of nitrogen to give a highly reactive electrophile. When DTTC is irradiated with a high-pressure mercury lamp through a Pyrex filter in *p*-halotoluenes, the halonium ylides are isolated in fair yields. Both chloronium and bromonium ylides have been syn-



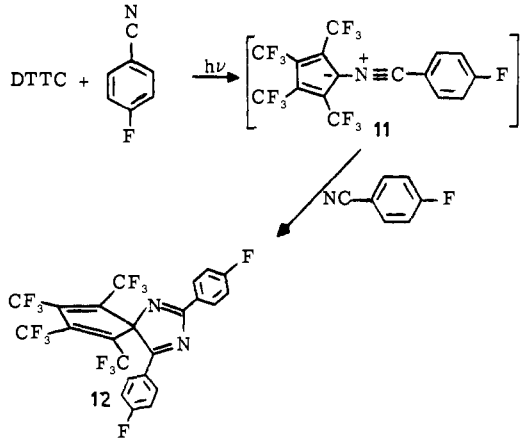
9 X = Cl
10 X = Br

thesized by this route. The iodonium ylides are not photostable under the reaction conditions and thus cannot be isolated from similar reactions. Chloronium ylide **9** shows ^{19}F resonances at −52.2 and −53.8 ppm in $CDCl_3$ while the bromonium ylide shows two resonances at −51.3 and −53.3 ppm. These ^{19}F resonances are at higher field than the many simple tetrakis(trifluoromethyl)cyclopentadienides[8] yet at lower field than the cyclopentadiene systems in which the cyclic delocalization has been disrupted (e.g., **12**; vide infra). Attempts to synthesize aryl fluoronium ylides led to complex reaction mixtures from which no products could be isolated. The aryl bromonium and chloronium ylides are quite stable and can be stored indefinitely at room temperature. The previously reported halonium ylides of Sheppard

(4) W. A. Sheppard and O. W. Webster, *J. Am. Chem. Soc.*, **95**, 2695 (1973).
(5) O. W. Webster, *J. Am. Chem. Soc.*, **88**, 4055 (1966).
(6) (a) H. A. Wiche, S. Braslavsky, and J. Heicklen, *Can. J. Chem.*, **50**, 2721 (1972); (b) Y. Kobayashi, I. Kumadaski, A. Ohsawa, Y. Sekine, and H. Mochizuki, *Chem. Pharm. Bull.*, **23**, 2773 (1975).
(7) Support for this mechanism and indeed our choice of *N,N*-dimethylimidazole-2-thione as a desulfurizing agent comes from unpublished results by E. M. Burgess and co-workers directed toward the synthesis of thione *S*-sulfides.
(8) We have now synthesized a variety of tetrakis(trifluoromethyl)cyclopentadienides of the general structure $(CF_3)_4C_5X^-$ (X = H, Cl, Br, I, F, NO_2, etc.) These anions show ^{19}F resonances in the region from δ −48 to −53 ppm from $CFCl_3$ with most falling at lower fields. The details of correlations of these shifts will be reported later.

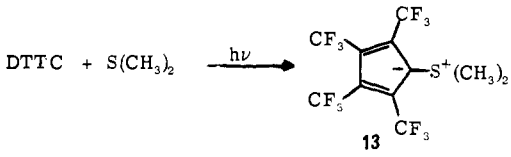
and Webster[4] are not as stable as these tetrakis(trifluoromethyl)cyclopentadienylides.

When *p*-fluorobenzonitrile is the solvent for the photolysis of DTTC, the spiro imidazole **12** is isolated. The ^{19}F NMR spectrum

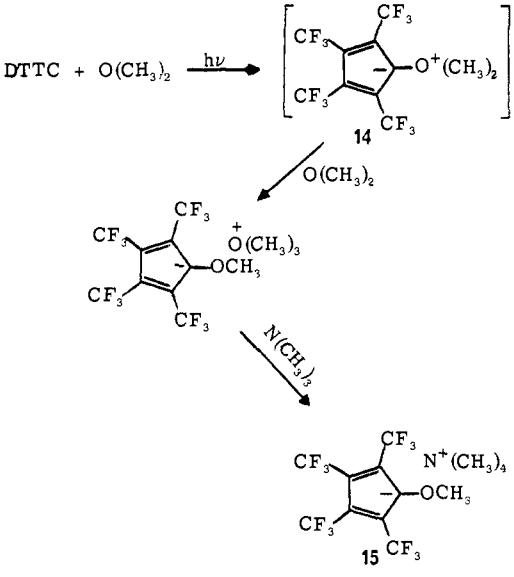


of **12** shows two high-field resonances at −59.9 and −60.7 ppm, indicating the disruption of the cyclopentadienyl delocalization by the spiro fusion. The nitrilium ylide **11** is the most likely precursor to **12**, but we have been unable to isolate or directly observe it. Acetonitrile also gives a similar reaction, and candidates for stable nitrilium ylides are currently under investigation.

As would be expected, the photolysis of DTTC in dimethyl sulfide gives the dimethylsulfonium ylide in good yield. Again this ylide showed ^{19}F resonances characteristic of the ylide-type structure at −49.78 and −53.44 ppm. The extension of this ylide

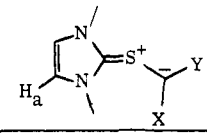


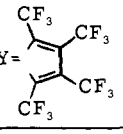
formation reaction to other chalogens led us to photolyze DTTC in dimethyl ether. This reaction provides evidence for an oxonium ylide (**14**). The crude reaction mixture exhibits ^{19}F NMR resonances at −49.17 and −50.78 ppm in dimethyl ether. Attempts to concentrate the mixture to isolate the product or substitute solvents so that the ^{1}H NMR might be observed led to complete decomposition of the material. However, when a freshly photolyzed solution of DTTC in dimethyl ether was treated with trimethylamine, tetramethylammonium methoxytetrakis(trifluoromethyl)cyclopentadienide (**15**) was easily isolated. A solution of **15** in dimethyl ether exhibited ^{19}F NMR resonances at −49.32 and −50.86 ppm (very similar to the initial reaction mixture). This



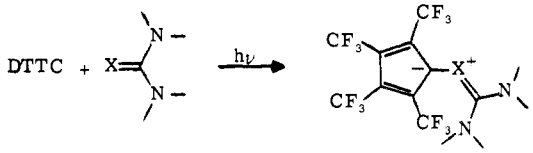
suggests that, as might be expected, **14** is a potent alkylating agent which rapidly loses a methyl group to the solvent to form trimethyloxonium methoxytetrakis(trifluoromethyl)cyclopentadienide as the first observable product. This reaction does, however, provide evidence for the oxonium methylide functionality.[9] Work is in progress to synthesize an isolable oxonium ylide and to characterize the chemistry of this unusual functional group.

Table I. Ring Proton Shifts for Various Imidazole Thione Ylides



	H_a δ
X=Y=CN	7.81
X=CN, Y=CO_2Me	7.69
X=Y=CO_2Et	7.51
X,Y= 	7.48

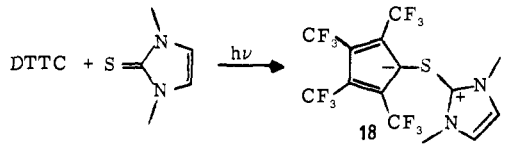
Photolysis of DTTC in THF in the presence of ureas and thioureas leads to the formation of stable carbonyl and thiocarbonyl ylides. "Push–pull" stabilized thiocarbonyl ylides have been previously reported and characterized,[10] but carbonyl ylides have not been isolated or observed directly.[11]



16 X = O
17 X = S

The carbonyl and thiocarbonyl ylides **16** and **17** exhibit ^{19}F NMR resonances of (−49.52, −51.04) and (−49.18, −51.63) ppm, respectively. These resonances are typical of the other ylides we have synthesized in this cyclopentadienyl system. Further **17** exhibits a methyl resonance at δ 3.20 which is characteristic of similar thiocarbonyl ylides.[10]

The thiocarbonyl ylide **18** is formed in moderate yield by the irradiation of DTTC in a THF solution of *N,N*-dimethylimidazole-2-thione. Comparison of the ^{1}H NMR shifts of **18** with



the same previously reported thione methylides[10b] reveals some interesting properties of the tetrakis(trifluoromethyl)cyclopentadienyl function (Table I). One might expect that the charge delocalization and the presence of the electron-demanding trifluoromethyls on the cyclopentadienyl ring would result in a ring proton shift that is comparable to the shift for the dicyanomethylide. However, the ring proton shift of **18** is the furthest upfield of the imidazolethione methylides. Using X-ray structure parameters from the previously reported imidazolethione me-

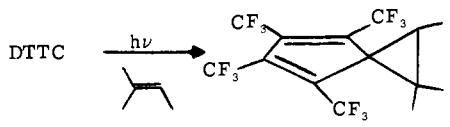
(9) The only previous mention of oxonium ylides we have found comes from the work of T. Ibata, K. Ueda, and M. Takebayashi, *Bull. Chem. Soc. Jpn*, **46**, 2897 (1973), who report an intramolecular carbene insertion into a carbon–oxygen bond which may involve the intermediacy of an oxonium ylide.

(10) (a) A. J. Arduengo and E. M. Burgess, *J. Am. Chem. Soc.*, **98**, 5020 (1976); (b) A. J. Arduengo and E. M. Burgess, *ibid.*, **98**, 5021 (1976).

(11) M. Hamaguchi and T. Ibata, *Tetrahedron Lett.* 4475 (1974), have reported the isolation of a cyclic carbonyl ylide functionality which they call an "iso-münchnon".

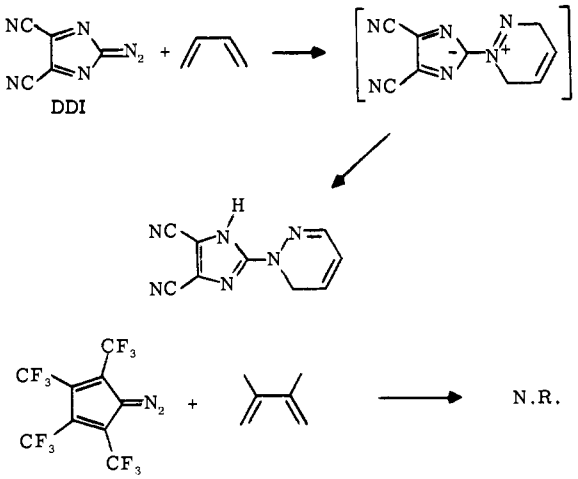
thylides[10] to construct models of **18**, it is evident that the imidazole ring protons are in the shielding region of the cyclopentadienyl ring. This diamagnetic anisotropic shielding is also observed for the methyl groups in **18** as well as for the ortho protons in aryl halonium ylides (**9** and **10**).

When DTTC is photolyzed in 2-methyl-2-butene, the spiro cyclopropane **19** is isolated in moderate yield. As would be expected, the ^{19}F NMR spectrum of **19** shows resonances at fairly high fields, similar to **12**.



19

Interestingly, unlike DDI,[4] DTTC does not form a [2 + 4]-type cycloadduct with dienes. Part of the reason for this may be the steric effect of the trifluoromethyls adjacent the diazo group in DTTC.



At present the electronic state of the carbene formed by photolysis of DTTC is unknown, but work is currently in progress to answer this question and extend the ylide formation reaction to other systems including the noble gases.

Experimental Section

General Remarks Fluorine and proton magnetic resonance spectra were recorded on a 90-MHz Varian EM-390 spectrometer. The chemical shifts are given in ppm (δ) downfield from the internal standard (fluorotrichloromethane and tetramethylsilane). Higher field NMR spectra were obtained on a Nicolet NT-360 system. Electron impact (EI) mass spectra were obtained on a Varian MAT CH-5 spectrometer. Field ionization (FI) and field desorption (FD) were obtained on a Varian MAT 731 spectrometer. High resolution electron impact mass spectra were obtained by peak matching on a Varian MAT 731 spectrometer. Infrared spectra were determined on either a Perkin-Elmer 137 or 237B spectrophotometer. Ultraviolet spectra were recorded on a Perkin-Elmer Lambda 3 UV/vis spectrophotometer. Melting points were obtained on a Thomas Hoover melting point apparatus and are uncorrected. Elemental analyses were performed by Mr. J. Nemeth, University of Illinois, Microanalytic Facility, and are within 0.37% of the theoretical values, unless otherwise indicated.

1,2,4,5-Tetrakis(trifluoromethyl)-3-thia-6,7-diazatricyclo[3.3.0.0^{2,4}]-oct-6-ene (3). To a stirred solution of tetrakis(trifluoromethyl)(Dewar thiophene) (**2**)[6] (25.0 g, 70.2 mmol) in 75 mL of dry ether at 0 °C was quickly added 350 mL of an ethereal solution of diazomethane (4.0 g, 94.7 mmol) which had been precooled to 0 °C. After 2 h the reaction mixture was warmed to room temperature. The solvent was removed under reduced pressure and the residue sublimed [42 °C (10^{-2} mm)] to afford white crystalline **3** (20.3 g, 73%): mp 80–82 °C; IR (CCl_4) 2990 (C–H), 1580 (N=N), 1350–1000 cm^{-1} (C–F); ^1H NMR ($CDCl_3$) δ 5.02 (1 H, d), 5.58 (1 H, d), J_{HH} = 21.0 Hz; ^{19}F NMR ($CDCl_3$) δ −57.52 (3 F, m), −59.21 (3 F, m), −65.37 (3 F, m), −66.42 (3 F, m); mass spectrum (FI) m/z 398 ($M^{+\cdot}$), 370 ($M^{+\cdot} - N_2$), 366 ($M^{+\cdot} - S$). Anal. ($C_9H_2N_2F_{12}S$): C, H, N, F, S.

1,5,6,7-Tetrakis(trifluoromethyl)-3,4-diazabicyclo[3.2.0]hepta-2,6-diene (5). To a stirred solution of **3** (5.15 g, 12.9 mmol) in 10 mL dry ether was added dropwise a solution of triphenylphosphine (3.33 g, 13.0 mmol) in 25 mL of dry ether. The mixture was filtered and the ether removed under reduced pressure. The oil that remained was distilled [70 °C (10^{-1} mm)] to give **5** (2.84 g, 60%): IR (neat) 3350 (N–H), 2950 (C–H), 1704 (C=C), 1570, 1400–1000 cm^{-1} (C–F); UV (CH_3OH) 254 nm, 291 (sh), 326 (sh); ^1H NMR (CCl_4) δ 5.30 (1 H, br), 6.68 (1 H, br); ^{19}F NMR (CCl_4) δ −63.35 (3 F, m), −63.98 (3 F, m), −64.42 (3 F, m), −70.72 (3 F, m); mass spectrum (FI) m/z 366 ($M^{+\cdot}$). Anal. ($C_9H_2N_2F_{12}$): C, H, N, F.

1,5,6,7-Tetrakis(trifluoromethyl)-2,3-diazabicyclo[3.2.0]hepta-2,6-diene (4). To a vigorously stirred solution of **3** (20.3 g, 51.0 mmol) in 50 mL of dry ether was added *N,N*-dimethylimidazole-2-thione (100 mg, 0.78 mmol). After 1 h the reaction mixture was filtered, and ether was removed by distillation at atmospheric pressure. Distillation of the residue at 53 °C (20 mm) gave **4** (15.5 g, 83%): IR (neat) 1715 cm^{-1} (C=C); UV (*n*-pentane) 238 nm, 292, 333; 220-MHz ^1H NMR (CD-Cl_4) δ 4.91 (1 H, d), 4.99 (1 H, d), J_{HH} = 19.79 Hz; ^{19}F NMR (CCl_4) δ −63.31 (3 F, m), −63.83 (3 F, m), −67.32 (3 F, m), −68.66 (3 F, m). Anal. ($C_9H_2N_2F_{12}$): C, H, N, F.

1,2,3,4-Tetrakis(trifluoromethyl)bicyclo[2.1.0]pent-2-ene (6). Compound **4** (13.6 g, 37.15 mmol) was dissolved in 350 mL of dry CH_3CN, and cooled to 0 °C. With vigorous stirring the solution was photolyzed by a high-pressure Hg arc lamp (450 W) through a 3-mm pyrex filter for 2 h to afford **6** in quantitative yield: IR (*n*-pentane) 1694 cm^{-1} (C=C); UV (*n*-pentane) 232 nm; ^1H NMR (CCl_4) δ 2.95 (1 H, d), 3.42 (1 H, m); ^{19}F NMR (CCl_4) δ −63.55 (6 F, s), −65.22 (6 F, s); mass spectrum (EI) m/z 338 (M^+), 69 (CF_3^+, base).

Tetramethylammonium 1,2,3,4-Tetrakis(trifluoromethyl)cyclopentadienide (8). Potassium carbonate (8.77 g, 63.5 mmol) was added to a solution of **6** maintained at 0 °C. The vigorously stirred solution was photolyzed through quartz by a high-pressure Hg arc lamp (450 W) for 9 h. To the CH_3CN reaction solution was added 450 mL CH_2Cl_2, followed by tetramethylammonium bromide (9.5 g, 62 mmol). This mixture was vigorously stirred for 30 min, divided into two equal portions, and then extracted with H_2O (3 × 300 mL). The combined organic layers were dried ($MgSO_4$) and filtered, and the solvent was removed under reduced pressure. The residue was recrystallized from CH_3CN/$CHCl_3$ to afford **8** (7.41 g, 43% from **4**) as white needles: mp 206–9 °C (d); ^1H NMR (CD_3CN) δ 3.12 (12 H, s), 6.43 (1 H, s); ^{19}F NMR (CD_3CN) δ −50.42 (6 F, m), −53.07 (6 F, m). Anal. ($C_{13}H_{13}NF_{12}$): C, H, N, F.

5-Diazo-1,2,3,4-tetrakis(trifluoromethyl)cyclopentadiene (1). Compound **8** (2.00 g, 4.86 mmol) and nitrosyl tetrafluoroborate (1.14 g, 9.73 mmol) were placed in a dried flask under dry N_2. After cooling to −78 °C, 20 mL of dry CH_3CN was slowly added with stirring. After 10 min the flask was allowed to warm to room temperature. After 10 min 20 mL of CH_2Cl_2 was added and the mixture cooled to −30 °C. Potassium nitrite (1.24 g, 14.59 mmol) in 10 mL of H_2O was added as a single portion, followed immediately by 20 mL of 0.24 M HCl. The solution was allowed to warm to room temperature. After 15 min the reaction mixture was extracted with H_2O (3 × 75 mL). The organic layer was separated, dried ($MgSO_4$), and filtered; the solvent was removed carefully at reduced pressure to afford crude DTTC (**1**) (1.3 g, 68%). Two sublimations (one through charcoal) afforded pure, colorless DTTC: mp 40–1 °C (sealed tube); IR (CH_2Cl_2) 2175 (C=N$^+$=N$^-$), 1610 (C=C), 1425, 1325, 1020–1240 cm^{-1} (C–F); UV (cyclohexane) λ_{max} 203 nm (ϵ 11 125), 298 (17 650); ^{19}F NMR ($CDCl_3$) δ −55.42 (6 F, m), −56.53 (6 F, m). Anal. ($C_9F_{12}N_2$): C, H, N, F.

***p*-Tolylchloronium Tetrakis(trifluoromethyl)cyclopentadienylide (9).** DTTC (36 mg, 0.10 mmol) was dissolved in 2 mL of *p*-chlorotoluene and the resulting solution was irradiated through quartz at room temperature with a high-pressure Hg lamp (450 W) for 15 min. The excess *p*-chlorotoluene was removed in vacuo. The residue was triturated with *n*-pentane and the resulting solid was recrystallized from *n*-pentane/$CHCl_3$ to afford **9** (10 mg, 22%): mp 117–8 °C dec; ^1H NMR ($CDCl_3$) δ 2.46 (3 H, s), 7.42 (4 H, s); ^{19}F NMR ($CDCl_3$) δ −52.24 (6 F, m), −53.77 (6 F, m); mass spectrum (EI) m/z 464 (M + 2$^+$), 462 (M^+), 126 ($C_7H_7Cl^+$, base). Anal. ($C_{16}H_7ClF_{12}$): C, H, Cl

***p*-Tolylbromonium Tetrakis(trifluoromethyl)cyclopentadienylide (10).** DTTC (25 mg, 0.07 mmol) was dissolved in 1 mL of melted *p*-bromotoluene and the resulting solution was irradiated through quartz at 35 °C with a high-pressure Hg lamp (450 W) for 15 min. The excess *p*-bromotoluene was removed in vacuo and the residue was triturated with *n*-pentane. The resulting solid was recrystallized from *n*-pentane/$CHCl_3$ to afford **10** (8 mg, 23%): mp 126–9 °C dec; ^1H NMR ($CDCl_3$) δ 2.47 (3 H, s), 7.35 (2 H, d), 7.53 (2 H, d); ^{19}F NMR ($CDCl_3$) δ −51.26 (6 F, m), −53.33 (6 F, m); mass spectrum (EI) m/z 508 (M + 2$^+$), 506 (M^+), 170 ($C_7H_7Br^+$, base).

Reaction of DTTC with *p*-Fluorobenzonitrile. DTTC (25 mg, 0.07 mmol) was dissolved in 2 mL of *p*-fluorobenzonitrile at 35 °C. The

resulting solution was irradiated through quartz for 15 min at 35 °C. The excess *p*-fluorobenzonitrile was removed in vacuo. The residue was recrystallized from *n*-pentane/$CHCl_3$ to afford **12** (3 mg, 8%): ^1H NMR ($CDCl_3$) δ 7.27 (4 H, m), 7.83 (2 H, m), 8.41 (2 H, m); ^{19}F NMR ($CDCl_3$) δ −59.93 (6 F, m), −60.65 (6 F, m), −101.74 (1 H, m), −105.32 (1 H, m); mass spectrum (EI) *m/z* 578 (M^+), 457 ($M^+ - C_7H_4FN$), 121 ($C_7H_4FN^+$).

Dimethylsulfonium Ylide 13. DTTC (9.8 mg, 0.027 mmol) was placed in a 5-mm Pyrex NMR tube and methyl sulfide (0.5 mL) was added. The resulting solution was irradiated at 0 °C for 5 min with a high-pressure Hg arc lamp (450 W). A red solution resulted. The excess methyl sulfide was removed under reduced pressure to afford 6 mg (55%) of sulfonium ylide **13**. A sample yielded mp 168–170 °C; ^1H NMR ($CDCl_3$) δ 3.16 (s); ^{19}F NMR ($CDCl_3$) δ −49.78 (6 F, m), −53.44 (6 F, m); high-resolution MS 397.9998 (calcd), 397.9996 (found).

Reaction of DTTC with Methyl Ether. DTTC (10 mg, 0.027 mmol) was placed in a 5-mm Pyrex NMR tube and evacuated. Dimethyl ether (0.5 mL) was condensed into the tube at −78 °C. The resulting solution was irradiated at −80 °C for 8 min with a high-pressure Hg arc lamp (450 W). Two new ^{19}F NMR resonances (ca. −49.17 and −50.78 ppm) were observed which disappeared upon warming to room temperature. With a second sample trimethylamine (0.25 mL) was condensed into the tube at −80 °C after irradiation and allowed to warm; a yellow solid resulted after excess ether and amine were distilled off. Recrystallization from $CHCl_3$/*n*-pentane afforded **15** as a slightly yellow solid (8 mg, 66%): mp 190–193 °C dec; ^1H NMR (CD_3CN) δ 3.58 (s, 3 H), 3.01 (s, 12 H); ^{19}F NMR (CD_3CN) δ −48.52 (6 F, m), −50.34 (6 F, m); ^{19}F NMR (CH_3OCH_3) δ −49.32 (6 F, m), −50.86 (6 F, m). Anal. ($C_{14}H_{15}NOF_{12}$): C, H, N.

1,1,3,3-Tetramethyluronium *O*-Tetrakis(trifluoromethyl)cyclopentadienylide (16). DTTC (13.9 mg, 0.038 mmol) and *N,N,N',N'*-tetramethylurea (7.7 mg, 0.066 mmol) were dissolved in 0.5 mL of dry THF. The solution was irradiated at 0 °C for 15 min in a 5-mm Pyrex NMR tube with a 250-W high-pressure Hg lamp. The THF was removed under reduced pressure and the resulting oily solid recrystallized from CH_2Cl_2/pentane at −30 °C to afford the crystalline carbonyl ylide **16**: mp 200–202 °C; ^1H NMR (CD_3CN) δ 2.97 (s); ^{19}F NMR (CD_3CN) δ −49.52 (6 F, m), −51.04 (6 F, m); high-resolution MS 452.0742 (calcd), 452.0750 (found). Anal. ($C_{14}H_{12}F_{12}N_2O$): C, H, N, F.

1,1,3,3-Tetramethyl-2-thiouronium *S*-Tetrakis(trifluoromethyl)cyclopentadienylide (17). DTTC (26.2 mg, 0.072 mmol) and *N,N,N',N'*-tetramethylthiourea (9.5 mg, 0.072 mmol) were placed in a 5-mm Pyrex NMR tube and 0.4 mL dry THF was added. A yellow solution resulted. The solution was irradiated at 0 °C for 30 min with a 250-W high-pressure Hg lamp to afford a red solution. The THF was removed under reduced pressure and the resulting solid recrystallized two times from CH_2Cl_2/pentane to afford 13.2 mg (39%) of off-white thiocarbonyl ylide: mp 138–139.5 °C; ^1H NMR (CD_3CN) δ 3.20 (s); ^{19}F NMR (CD_3CN) δ −49.18 (6 F, m), −51.63 (6 F, m); high-resolution MS 468.0479 (calcd), 468.0504 (found).

***N,N*-Dimethylimidazole-2-thione *S*-Tetrakis(trifluoromethyl)cyclopentadienylide (18).** DTTC (40 mg, 0.11 mmol) was placed in a 5-mm Pyrex NMR tube and to this were added *N,N'*-dimethylimidazolethione (14 mg, 0.11 mmol) and 2 mL of dry THF. The resulting solution was irradiated at 0 °C for 5 min with a high-pressure Hg arc lamp (450 W). The THF was removed under reduced pressure. The resulting solid was recrystallized from CH_2Cl_2/pentane (two times) to afford 12.6 mg (25%): mp 160–1 °C dec; ^1H NMR (CD_3CN) δ 3.89 (6 H, s), 7.48 (2 H, s); ^{19}F NMR (CD_3CN) δ −49.64 (6 F, m), −51.22 (6 F, m); high-resolution MS 464.0216 (calcd), 464.0213 (found).

Irradiation of DTTC in 2-Methyl-2-butene. DTTC (20 mg, 0.05 mmol) was dissolved in 1 mL of 2-methyl-2-butene and the resulting solution was irradiated in a Pyrex tube for 15 min at 0 °C with a high-pressure Hg arc lamp (450 W). The excess 2-methyl-2-butene was removed under reduced pressure to afford spiroheptadiene **19** as a slightly yellow oil: ^1H NMR ($CDCl_3$) δ 0.8–1.4 (10 H, m); ^{19}F NMR ($CDCl_3$) δ −57.0 (3 F, m), −60.4 (3 F, m), −63.5 (6 F, br m); mass spectrum (FI) *m/z* 406 (M^+).

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