molecules the reduction in the ring current in going from parent to cation occurs mainly in the seven-membered ring where the cyclopropyl for double bond replacement actually occurs, not in the aromatic portion of the molecule which is essentially unaffected.

The chemical shift differences ($\Delta$) observed in going from *trans*-2,3-benzo-4,5:6,7-bishomotropone (**7**) to its cation **8** and/or **9** present a different story. Although the downfield shift in all protons in going from **7** to **8** and/or **9** again indicates charge delocalization in the cation, the magnitude of the chemical shift differences between the inside and outside protons of the methylene groups indicates that the resulting ring current is minimal. Note that the downfield shifts of $H_6$, $H_{12i}$, and $H_{12o}$ are of comparable magnitude. This is consistent with charge delocalization into the $C_6C_{12}C_7$ ring. The fact that proton 12i is shifted the least of these three is consistent with its location, which overhangs this delocalized $\pi$ system. In a similar manner, the downfield shifts of $H_5$, $H_{13i}$, and $H_{13o}$ indicate charge delocalization into the second cyclopropyl ring. As with $H_{12i}$, the shift for $H_{13i}$ is somewhat smaller than the other two, consistent with its position overhanging the delocalized electron cloud. The extent of delocalization into the $C_4C_{13}C_5$ ring (**9**) is probably greater than that involving the $C_6C_{12}C_7$ ring (**8**), for the chemical shift difference ($\Delta$) between $H_{13i}$ and $H_{13o}$ is greater than that for the $H_{12i}$–$H_{12o}$ pair. Also, the change in $J_{13i,13o}$ from −4.8 to −5.6 Hz indicates an opening of the $C_4C_{13}C_5$ angle, whereas the 12i–12o coupling remains unchanged.[6]

A bishomoaromatic structure for **8** would also have delocalization across the $C_5$–$C_6$ bond. As was already mentioned, the NMR data do not support such a structure. Presumably the trans stereochemistry prohibits this extended conjugation. Therefore protonated **7** is best represented as two ions in rapid equilibrium, one with delocalization through $C_6$, $C_7$, and $C_{12}$, (**8**) and the other with delocalization through $C_4$, $C_5$, and $C_{13}$ (**9**). Further comments and comparisons must be left until the cis isomer of **7** is prepared and protonated. This study is currently under way.

**Registry No. 3**, 485-46-1; **4**, 76529-69-6; **5**, 68001-02-5; **5**-$d_2$, 76529-27-6; **6**, 76612-96-9; **6**-$d_2$, 76612-95-8; **7**, 70812-14-5; **7**-$d_4$, 70775-43-8; **8**, 76613-00-8; **8**-$d_4$, 76612-98-1; **9**, 76612-99-2; **9**-$d_4$, 76612-97-0.

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# Dication Disulfides by Reaction of Thioureas and Related Compounds with Trifluoromethanesulfonic Anhydride. The Role of Triflic Anhydride as an Oxidizing Agent

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Interaction of thiourea and substituted thioureas with trifluoromethanesulfonic acid anhydride in methylene chloride results in stable dication disulfide salts $(R_2N)_2{}^+CSSC^+(NR_2)_2{\cdot}2CF_3SO_3{}^-$. These results indicate that triflic anhydride is acting as an oxidizing agent toward thioureas. The most likely mechanism for the formation of these dication disulfides is an ionic pathway with initial formation of a monocation which is attacked on sulfur by a second molecule of thiourea. These results are discussed in detail.

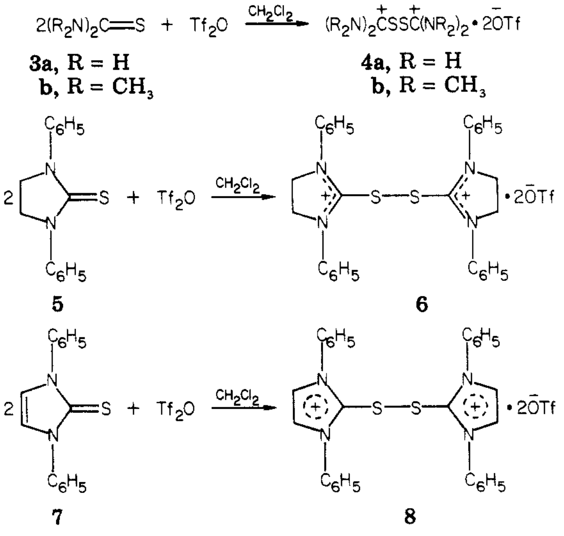
Reaction of trifluoromethanesulfonic anhydride ($CF_3SO_2OSO_2CF_3$, $Tf_2O$) with certain ketones, such as cyclopropenone, tropone, and pyridone, leads to novel dication ether salts[1] **2**, where R is a residue that can effectively stabilize a positive charge.

$$R_2C{=}O \xrightarrow{Tf_2O} \underset{\mathbf{1}}{R_2\overset{+}{C}OTf{\cdot}\overset{-}{O}Tf} \xrightarrow{R_2C=O} \underset{\mathbf{2}}{R_2\overset{+}{C}O\overset{+}{C}R_2{\cdot}2\overset{-}{O}Tf}$$

The formation of these ether salts **2** was readily explained via a triflated ketone **1**, followed by a nucleophilic displacement of the triflate ion, $CF_3SO_3{}^-$, by a second mole of ketone.[1]

In hopes of generating the related dication thioether salts (**2**, S instead of O) we examined the interaction of thioureas with triflic anhydride. However, instead of observing the analogous thioether salts, dication disulfide salts were obtained, suggesting that triflic anhydride acts as an oxidizing agent toward thioureas. Hence in this paper we report the formation and characterization of dication disulfide salts and propose a plausible mechanism for their formation.

Scheme I



## Results and Discussion

Reaction of 1 mol of triflic anhydride with 2 mol of the appropriate thiourea, **3**, **5**, and **7**, in $CH_2Cl_2$ gave the re-

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(1) Stang, P. J.; Maas, G.; Fisk, T. E. *J. Am. Chem. Soc.* **1980**, *102*, 6361. Stang, P. J.; Maas, G.; Smith, D. A.; McCloskey, J. A. *Ibid.* **1981**, *103*, in press.

0022-3263/81/1946-1606$01.25/0

Table I. Spectral Data of Dication Disulfide Salts 4, 6, and 8

| compd | FD mass spectra, $m/z$ (intensity)[a] | $^1$H NMR,[b] $\delta$ | $^{19}$F[c] NMR, ppm | IR,[d] cm$^{-1}$ | | |
|---|---|---|---|---|---|---|
| | | | | $C \doteq N$ | $CF_3SO_3$[e] | others |
| **4a** | 751 (3), 526 (8), 333 (12), 317 (9), 303 (8), 302 (19), 301 (100), 285 (20), 269 (6), 177 (18), 145 (79) | 8.72[f] | 87.3 | 1670 (s) | 1249 (s), 1225 (s), 1180, 1034 (s) | 3350-3100 (br, s, $NH_2$), 1420 (m) |
| **4b** | 695 (0.3), 693 (1), 563 (0.3), 561 (0.6), 445 (4), 415 (17), 414 (17), 413 (100), 233 (6), 201 (18), 147 (3), 133 (4), 132.5 (2), 132 (12), 131 (47) | 3.41 (s) [3.14 (s)] | 87.6 | 1620 (s) | 1280 (s), 1255 (s), 1223 (s), 1168 (s), 1154 (s), 1145 (sh), 1036 (s), 1029 (s) | 1496, 1463, 1395 (all m) |
| **6** | 659 (3), 657 (3), 571 (5), 509 (5), 493 (3), 270 (4), 257 (52), 256 (98), 255 (100), 254.5 (0.45), 254 (3.2) | 4.43 (s, 8 H), 7.18-7.56 (m, 20 H) [4.24 (s)] | 87.3 | 1555 (s) | 1297, 1273, 1257 (s), 1223, 1158 (m), 1031 (s) | |
| **8** | 654 (50), 653 (9), 321 (20), 254 (4), 253 (12), 252 (100), 251 (29), 222 (9.5), 221 (50) | 7.14-7.32 (m, 8 H), 7.58-7.76 (m, 12 H), 7.96 (s, 4 H) [7.13 (s)] | 87.8 | | 1285-1245 (br, s), 1228 (s), 1158 (s), 1036 (s) | 1592, 1545 (m), 1499, 1461 (s) |

[a] Field-desorption mass spectra at 6 mA for **4a**, 5 mA for **4b**, 0 mA for **6**, and 17 mA for **8**. [b] Value in brackets is signal of nonaromatic H in neutral precursor thiourea. In $CD_3CN$, internal $Me_4Si$. [c] In $CD_3CN$, internal $C_6F_6$. [d] KBr pellets. [e] Absorption characteristic of and in the range expected for the $CF_3SO_3$ group but due to the complexity of the spectrum may also be due to other vibrations. [f] Strongly concentration dependent.

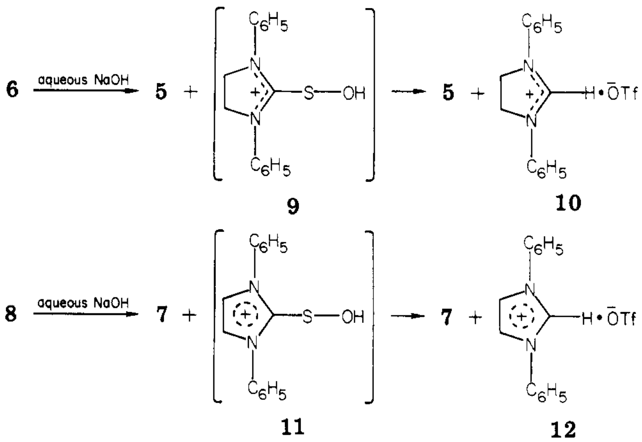
spective dication disulfides **4**, **6**, and **8** as stable crystalline salts, shown in Scheme I.

These dication disulfides were characterized by spectral as well as chemical means. The spectral data are summarized in Table I and discussed in detail below. The disulfide rather than thioether character of these salts is indicated by the elemental analyses (see the Experimental Section) and confirmed by the field-desorption (FD) mass spectra.

FD mass spectra have proven to be particularly useful tools for the determination of molecular weights and other characteristics of organic salts.[2] In the present case compound **4a** shows peaks at $m/z$ 301 (base peak), corresponding to the cation plus one anion, and 526 ($M^+$ + thiourea) and another ion at $m/z$ 751 (2 cations plus 3 anions). The fragment ions at $m/z$ 285, 269, and 145 are more difficult to explain but $m/z$ 285 and 269 might correspond to loss of one and two amino groups, respectively, from the dications. The spectrum at an anode current of ~0 mA is similar. Ion **4b** shows a base peak at $m/z$ 413 corresponding to the dication plus one anion. The peaks at $m/z$ 563/562 correspond to the molecular ion and gain of a proton by $M^+$, respectively, whereas the peaks at $m/z$ 693/695 are cluster ions of the molecular ion plus a fragment ion (tetramethylthiourea). For dication **6** the dication plus one anion ($m/z$ 657/659) shows up along with the dication plus H ($m/z$ 509) as well as the S–S cleaved protonated thiourea ($m/z$ 255–257). The $m/z$ 254 peak could be the thiourea radical cation or as indicated by the $^{13}$C isotope peak at $m/z$ 254.5 the doubly charged, cation portion itself. Similarly for salt **8** the $m/z$ 653 peak corresponds to the dication plus one anion. The base peak at $m/z$ 252 is due to the cation portion after S–S cleavage and the $m/z$ 221 peak corresponds to the imidazole ring plus a hydrogen. Hence in all four spectra the fragment corresponding to the dication plus one triflate anion is a prominent peak and provides good evidence for the dication disulfide nature of these species.

The cationic nature of these salts is indicated by the 0.2–0.4 ppm downfield shift of the nonaromatic and the ortho and para protons in the ions compared to the neutral thiourea in the proton NMR. The $^{19}$F spectra show a single signal (see discussion below) in the region expected for ionic $CF_3SO_3^-$ (i.e., $KOSO_2CF_3$ in $CH_3CN$ appears at 87.4 ppm whereas covalent triflate in $Tf_2O$ appears at 95.0 ppm). The infrared spectra, besides the absorptions expected for the triflate, show a strong band between 1555 and 1670 cm$^{-1}$ characteristic of $C \doteq N$.

Scheme II



Chemically, all salts are remarkably stable to water, in contrast to the extreme moisture sensitivity of the ether salts **2**.[1] However, they are readily hydrolized by dilute NaOH to give the starting thiourea and the corresponding formamidinium salts as shown in Scheme II. In base, $^-$OH initially attacks sulfur to give 1 mol of the starting thiourea and the unstable salts **9** or **11** which disproportionate to give more starting thiourea and the formamidinium salts **10** and **12**. Compounds **10** and **12** were independently synthesized and found to be identical with the products of the above hydrolyses. A similar mechanism has been previously proposed for the alkaline hydrolysis of **4a** (Cl instead of OTf), resulting in thiourea, sulfur, and cyanamide.[3]

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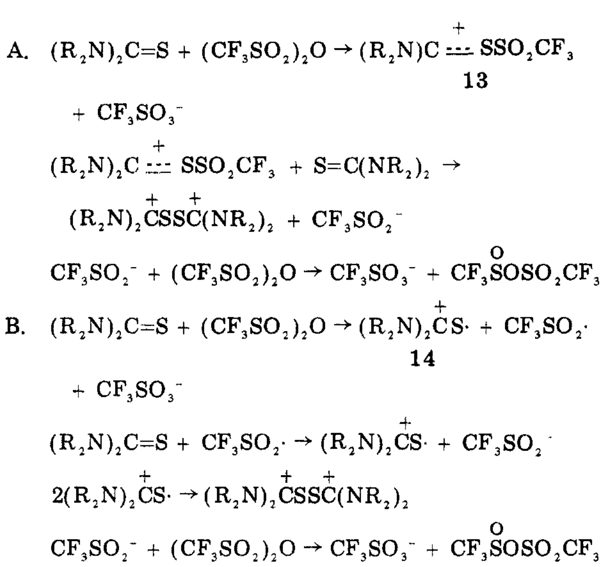
(2) Schulten, H.-R.; Röllgen, F. W. *Org. Mass Spectrom.* **1975**, *10*, 649.

(3) Toennies, G. *J. Biol. Chem.* **1937**, *120*, 297.

Scheme III



$$\text{A.}\quad (R_2N)_2C{=}S + (CF_3SO_2)_2O \rightarrow \underset{\mathbf{13}}{(R_2N)C\overset{+}{\cdots}SSO_2CF_3} + CF_3SO_3^-$$

$$(R_2N)_2C\overset{+}{\cdots}SSO_2CF_3 + S{=}C(NR_2)_2 \rightarrow (R_2N)_2\overset{+}{C}S S\overset{+}{C}(NR_2)_2 + CF_3SO_2^-$$

$$CF_3SO_2^- + (CF_3SO_2)_2O \rightarrow CF_3SO_3^- + CF_3\overset{O}{S}OSO_2CF_3$$

$$\text{B.}\quad (R_2N)_2C{=}S + (CF_3SO_2)_2O \rightarrow \underset{\mathbf{14}}{(R_2N)_2\overset{+}{C}S\cdot} + CF_3SO_2\cdot + CF_3SO_3^-$$

$$(R_2N)_2C{=}S + CF_3SO_2\cdot \rightarrow (R_2N)_2\overset{+}{C}S\cdot + CF_3SO_2^-$$

$$2(R_2N)_2\overset{+}{C}S\cdot \rightarrow (R_2N)_2\overset{+}{C}SS\overset{+}{C}(NR_2)_2$$

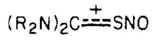
$$CF_3SO_2^- + (CF_3SO_2)_2O \rightarrow CF_3SO_3^- + CF_3\overset{O}{S}OSO_2CF_3$$

The oxidative coupling of thioureas has precedents in the transformation, by a variety of oxidizing agents, of thiourea,[4] substituted thioureas,[5] and some thioketones[6] into dication disulfides analogous to compounds **4**, **6**, and **8**. The mechanism of the electrochemical oxidation has recently been established as a two-fold one-electron transfer.[6b] However, the oxidizing properties of triflic anhydride have only recently been recognized through its ability to convert Grignard reagents into alkyl halides.[7]

Two reasonable mechanisms may be proposed for the reaction of thioureas with triflic anhydride as shown in Scheme III. Mechanism A corresponds to the one proposed for the formation of dication ether salts **2** by reaction of $Tf_2O$ with activated ketones.[1] In the first step, electrophilic attack of the $Tf_2O$ on the sulfur of the thiocarbonyl occurs, forming monocation **13**. Contrary to the formation of dication ethers **2**, the second mole of thiourea attacks monocation **13** on sulfur, rather than on the partially positive carbon, forming the dication disulfides by displacement of the triflinate ($CF_3SO_2^-$) anion. The triflinate anion is known to be a good leaving group.[8] However, as the $^{19}F$ data in Table I indicate, only one fluorine signal, that corresponding to $CF_3SO_3^-$, was observed for all disulfide salts. This is readily explained by the anion-exchange reaction shown in the last step. That such an anion exchange occurs can be independently confirmed by reacting an equimolar amount of $Tf_2O$ with a suspension of $KOSOCF_3$ in methylene chloride that results in the complete conversion of $KOSOCF_3$ into $KOSO_2CF_3$ and probably the mixed anhydride of trifluoromethanesulfinic and trifluoromethanesulfonic acids. However, the actual mechanism must be more complicated than shown as that mechanism requires a 1:1 molar ratio of thiourea and triflic anhydride, yet a 1:~0.6 ratio was found sufficient, suggesting the involvement of another oxidizing agent, perhaps the mixed anhydride, besides triflic anhydride itself.

Mechanism B involves an electron transfer between thiourea and triflic anhydride, forming a radical cation **14** which subsequently dimerizes to give the observed dication disulfides. The initially formed $CF_3SO_2\cdot$ radical may be oxidized to the triflinate ($CF_3SO_2^-$) anion by a second molecule of thiourea. This triflinate anion undergoes the same anion-exchange reaction mentioned above. However, without an additional oxidizing agent (once again perhaps the mixed anhydride) this mechanism also fails to fully account for the actual stoichiometry of 1:~0.6 thiourea to triflic anhydride. Furthermore, $CF_3SO_2\cdot$ would be expected to readily fall apart to $SO_2$ and $CF_3\cdot$. We have not seen any evidence for such $SO_2$ or $CF_3\cdot$ radical formation.

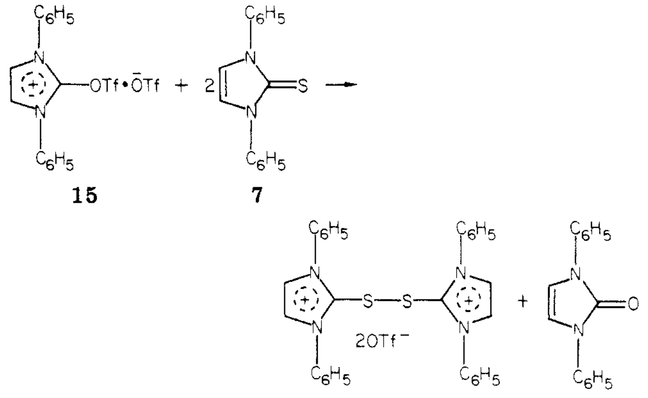
At the moment we cannot distinguish between the two possible mechanisms; however, we think the ionic path A to be more likely. As the nitrosyl cation (I) is almost



$$(R_2N)_2C\overset{+}{\cdots}SNO$$

I

certainly involved in the oxidative coupling of thioureas by $HNO_2$[5,9] or by *N*-nitroso-*N*-methylaniline,[10] it is likely that $Tf_2O$ acts in a similar manner, resulting in the initial formation of monocation **13**. Such ionic behavior of $Tf_2O$ is consistent with its known electrophilic properties[11] as well as with its behavior toward carbonyls.[1,12] Formation of monocations is further aided by the superior leaving ability of the triflate group.[13] Likewise, trifloxy salt **15**[1b] reacts with thiourea **7** to give dication **8** in accordance with the expected behavior of $Tf_2O$, the leaving group in this case being the neutral imidazolone **16**.



**8** **16**

Subsequent attack of a second molecule of thiourea upon monocation **13** is favored by the strong electrophilicity of the sulfur in **13**. This electrophilicity is of course a consequence of the powerful electron-withdrawing effect of the cation as well as the $CF_3SO_2$ group attached to sulfur in the monocation. In fact the triflinate group $CF_3SO_2$, besides being an excellent leaving group, is one of the most powerful neutral electron-withdrawing groups known.[14] Formation of dication disulfide salts in the case of thioureas and dication ether salts **2** in the case of carbonyls is also understandable on thermodynamic grounds. Formation of analogous dications in the case of carbonyls[1] would result in peroxides with an O–O bond strength of

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(4) Foss, O.; Johnsen, J.; Tvedten, O. *Acta Chem. Scand.* **1958**, *12*, 1782 and references therein.

(5) Collings, P.; Al-Mallah, K.; Stedman, G. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1734.

(6) (a) Doyle, M. P.; Hedstrand, D. M. *J. Chem. Soc., Chem. Commun.* **1977**, 643. (b) Doyle, M. P.; Hedstrand, D. M.; Tamblyn, W. N.; Blankespoor, R. L. "Abstracts of Papers", 2nd North American Chemical Congress, Las Vegas, NV, Aug 1980; American Chemical Society: Washington, DC, 1980; ORG-269.

(7) Creary, X. *J. Org. Chem.* **1980**, *45*, 2727.

(8) Hendrickson, J. B.; Giga, A.; Wareing, J. *J. Am. Chem. Soc.* **1974**, *96*, 2275.

(9) Al-Mallah, K.; Collings, P.; Stedman, G. *J. Chem. Soc., Dalton Trans.* **1974**, 2469.

(10) Williams, D. L. *J. Chem. Soc., Perkin Trans. 2* **1977**, 128.

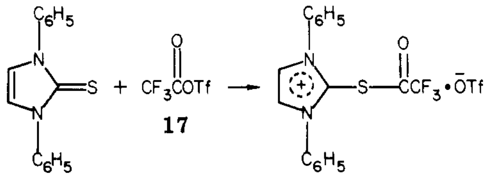
(11) (a) Howells, R. D.; McCown, J. D. *Chem. Rev.* **1977**, *77*, 69. (b) Hendrickson, J. B.; Sternbach, D. D.; Bair, K. W. *Acc. Chem. Res.* **1977**, *10*, 306.

(12) Stang, P. J.; Treptow, W. L. *Synthesis* **1980**, 283.

(13) Stang, P. J. *Acc. Chem. Res.* **1978**, *11*, 107.

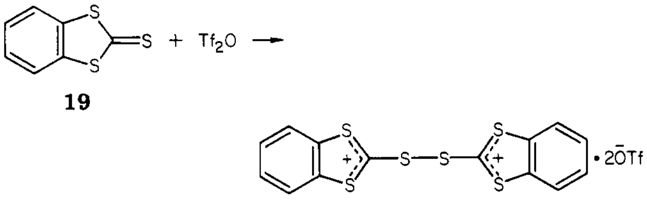
(14) Stang, P. J.; Anderson, A. G. *J. Org. Chem.* **1976**, *41*, 781.

only approximately 146 kJ/mol whereas formation of the disulfides in the present case results in the more stable S–S bond with a bond energy of 226 kJ/mol.[15] That the leaving ability of $CF_3SO_2$ is important in the subsequent reaction of monocation **13** is indicated by the fact that trifluoroacetyl triflate **17**[16] readily acylates thiourea **7** to form monocation **18**. However, the lack of a leaving group in cation **18** prevents a second molecule of thiourea from attacking the partially positive sulfur in **18**.



**7** **17** **18**

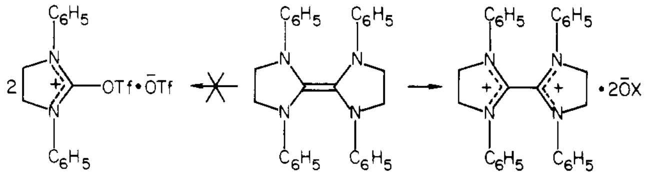
Thiocarbonyls other than those of thioureas may also be oxidatively coupled by $Tf_2O$. Thus, reaction of trithiocarbonate **19** with $Tf_2O$ yields the dication salt **20**.



**19** **20**

However, unlike the stable dication disulfide salts **4**, **6**, and **8**, resulting from thioureas, the yellow salt **20**, similar to the known[6a] 2,2′-dithiobis(1,3-dithiolanium) dication, is air and moisture sensitive.

Finally, we have reacted $Tf_2O$ with the electron-rich olefin **21**. As expected, not the electrophilic but the oxidizing properties of $Tf_2O$ dominate in this reaction. No



**22** **21** **23a**, X = $CF_3SO_2$
**b**, X = $CF_3CO$

monocation **22** but only the dication **23a** was observed in this reaction. The easy oxidation of **21**, like that of other electron-rich olefins, is well documented,[17] including oxidation by halogenated compounds that normally act as electrophiles.[18] Presumably the $CF_3$ group in $Tf_2O$ facilitates such behavior, as trifluoroacetic anhydride reacts in the same manner with **21** to give **23b**. On the other hand, trifluoroacetic anhydride failed to react with thiourea **7** under conditions employed for reaction with $Tf_2O$, pointing out the unique ability of $Tf_2O$ to act as an oxidizing agent.

In summary, we have shown that in certain cases triflic anhydride can act as an oxidizing agent. Its interaction with thioureas yields stable crystalline dication disulfide salts **4**, **6**, and **8**. This oxidative coupling of the thioureas most likely occurs via an ionic mechanism (path A, Scheme III) rather than a free-radical process although the latter cannot be ruled out.

## Experimental Section

All melting points are uncorrected and were taken on a Mel-Temp melting-point apparatus. Infrared spectra were recorded on a Beckman IR 5A. NMR spectra were obtained on a Varian EM-390 spectrometer and values are reported in parts per million downfield from the standard. Field-desorption mass spectra were obtained on a Varian Mat 731 spectrometer.[1b] All solvents employed were purified and dried by standard procedures immediately prior to use. All reactions with $Tf_2O$ were carried out under an argon atmosphere.

**Materials.** Triflic anhydride,[19] 1,3-diphenylimidazoline-2-thione (**5**),[20] 1,3-diphenylimidazole-2-thione (**7**),[21] and 1,1′,3,3′-tetraphenyl-2,2′-biimidazolidine (**21**)[22] were prepared by literature procedures. Thioureas and tetramethylthiourea were commercial products and 1,3-benzodithiol-2-thione (**19**)[23] was kindly provided by Dr. R. D. Miller, IBM Research Laboratories, San Jose, CA.

***C,C′*-Dithiobisformamidinium Ditriflate, 4a. General Procedure.** In a three-neck round-bottom flask, equipped with an argon inlet and outlet, a magnetic stirring bar, and a serum cap, was added 1.52 g (20 mmol) of thiourea in 20 mL of $CH_2Cl_2$ followed by 2 mL (12 mmol) of triflic anhydride via a syringe. The mixture was stirred at room temperature for 24 h. The precipitate (3.77 g) was filtered and recrystallized three times from $THF/CH_2Cl_2$, yielding 2.79 g (62%) of **4a**, mp 167–169 °C. Anal. Calcd for $C_4H_8F_6N_4O_6S_4$ (mol wt 450.4): C, 10.67; H, 1.79; N, 12.44. Found: C, 10.6; H, 1.70; N, 12.6. All spectral properties of these new dication disulfides are reported in Table I.

***C,C′*-Dithiobis(tetramethylformamidinium) Ditriflate, 4b.** To a solution of 1.32 g (20 mmol) of thiourea **3b** in 10 mL of $CH_2Cl_2$ at 0 °C was added dropwise 1.02 mL (6 mmol) of triflic anhydride. The initial yellow color disappeared at the end of the addition. After addition of 5 mL of $CH_3CN$ and 75 mL of ether the precipitate was filtered and recrystallized from $CH_3CN$/ether, yielding 2.26 g (80%) of colorless white **4b**, mp 109–111 °C. Anal. Calcd for $C_{12}H_{24}F_6N_4O_6S_4$ (mol wt 562.6): C, 25.61; H, 4.30; N, 9.95. Found: C, 25.5; H, 4.15; N, 9.9.

**2,2′-Dithiobis(1,3-diphenyl-2-imidazolinium) Ditriflate, 6.** To a solution of 763 mg (3 mmol) of thione **5** in 10 mL of $CH_2Cl_2$ was added 0.31 mL (1.8 mmol) of triflic anhydride. After the mixture was stirred at room temperature for 10 min, 10 mL of ether was slowly added, precipitating 905 mg (75%) of pale yellow crystalline **6**, mp 158–159 °C. Anal. Calcd for $C_{32}H_{28}F_6N_4O_6S_4$ (mol wt 806.8): C, 47.64; H, 3.50; N, 6.94. Found: C, 47.1; H, 3.47; N, 6.9.

**2,2′-Dithiobis(1,3-diphenyl-2-imidazolium) Ditriflate, 8.** To a solution of 505 mg (2 mmol) of thione **7** in 5 mL of $CH_2Cl_2$ was added 0.17 mL (1 mmol) of triflic anhydride. After addition of 5 mL of ether to the pale yellow solution 625 mg (78%) of pure **8** was obtained, mp 212–213 °C. Anal. Calcd for $C_{32}H_{24}N_4F_6O_6S_4$ (mol wt 802.8): C, 47.88; H, 3.01; N, 6.98. Found: C, 47.6; H, 3.05; N, 6,7.

This compound can also be made from **15** and **7** as follows. A solution of **15** in $CH_2Cl_2$ was prepared by addition of 0.17 mL (1 mmol) of triflic anhydride to 236 mg (1 mmol) of 1,3-diphenylimidazol-2-one in 5 mL of $CH_2Cl_2$.[1b] After the mixture was stirred for 15 min, 505 mg (2 mmol) of thione **7** in 5 mL of $CH_2Cl_2$ was added. Crystallization of **8** was immediate and was completed by adding 15 mL of ether, yielding 710 mg (88%) of pale yellow **8** identical in all respects with the above material. The solvent from the filtrate was evaporated at 14 torr and the solid residue washed with ether, yielding 182 mg (77% based on **15**) of 1,3-diphenylimidazol-2-one, **16**.

**Alkaline Hydrolysis of 6.** To the yellow solution of 301 mg (0.37 mmol) of **6** in 5 mL of $CH_3CN$ was added sufficient ($\sim$2.8 mL) 0.05 N NaOH to discharge all color. To this solution was added 100 mL of distilled water whereupon 145 mg (0.57 mmol) of thione **5** crystallized (containing a 10% impurity by NMR).

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After filtration, the aqueous filtrate was evaporated to dryness and the residue extracted twice with 20 mL of $CH_2Cl_2$. After removal of the $CH_2Cl_2$ and washing with ether, 19 mg (0.05 mmol) of colorless 1,3-diphenyl-2-imidazolinium triflate (**10**) was obtained: mp 208–209 °C; $^1$H NMR ($CH_3CN$, internal $Me_4Si$) 4.59 (s, 4 H), 7.51 (m, 10 H), 9.09 (br s, 1 H); IR (KBr) 1625, 1593, 1298, 1275, 1254, 1229, 1169, 1155, 1040 $cm^{-1}$ (all strong). Anal. Calcd for $C_{16}H_{15}F_3N_2O_3S$ (mol wt 372.36): C, 51.61; H, 4.06; N, 7.52. Found: C, 50.8; H, 4.06; N, 7.4.

**Independent Synthesis of 10.** This procedure is based upon the preparation of the analogous chloride[24] (**10**, Cl instead of OTf). A 500-mg sample of *N*-formyldianilinoethane[25] was dissolved in 10 mL of 4 N $CF_3SO_3H$ and stirred for 1 h at room temperature. The crude precipitate was filtered (270 mg of impure **10**, mp 203 °C), and 20 mL of $H_2O$ was added to the filtrate. Overnight 210 mg of pure **10** crystallized (mp 215 °C) that was identical in all respects with the above material.

**Alkaline Hydrolysis of 8.** To 297 mg (0.37 mmol) of **8** in 6 mL of $CH_3CN$ was added 17 mL of 0.05 N NaOH whereupon the yellow color of the solution disappeared. On addition of 100 mL of distilled $H_2O$, 129 mg (0.51 mmol) of thione **7** was precipitated. After filtration the aqueous filtrate was evaporated to dryness and the residue was stirred with 100 mL of $CH_2Cl_2$. After filtration the $CH_2Cl_2$ was evaporated and the residue dissolved in 50 mL of ether. When the mixture was allowed to stand, 34 mg (0.09 mmol) of white needles of 1,3-diphenylimidazolium triflate (**12**) was obtained, mp 213–214 °C. Anal. Calcd for $C_{16}H_{13}F_3N_2O_3S$ (mol wt 370.35): C, 51.89; H, 3.54; N, 7.56. Found: C, 51.6; H, 3.60; N, 7.6. The spectral data are in general agreement with the independently synthesized material.

**Preparation of Authentic 12.** To a solution of 159 mg (0.5 mmol) of 1,3-diphenylimidazolium hydrogensulfate[21] in 3 mL of $H_2O$ was added 218 mg (0.5 mmol) of $Ba(OTf)_2$ in 3 mL of $H_2O$. After the mixture stood overnight, the $BaSO_4$ was centrifuged off and the water layer evaporated to dryness. The residue was stirred with $CH_2Cl_2$ and filtered. After addition of ether **12** precipitated out as colorless crystals: mp 212–213 °C; IR (KBr) 1590, 1547, 1484, 1410 (all m), 1274, 1255, 1223, 1161, 1150, 1035 $cm^{-1}$ (all s); $^1$H NMR ($CH_3CN$, internal $Me_4Si$) $\delta$ 7.9 (m, 10 H), 8.19 (d, $J \simeq 2$ Hz, 2 H), 9.59 (t, $J \simeq 2$ Hz, 1 H).

**Reaction of $K^+CF_3SO_2^-$ with $Tf_2O$.** To a suspension of 172 mg (1 mmol) of $K^+CF_3SO_2^-$[26] in 10 mL of $CH_2Cl_2$ was added 0.17 mL (1 mmol) of triflic anhydride. After being stirred for 30 min the mixture was filtered to yield 188 mg (100%) of $KOSO_2CF_3$ [IR (KBr) 1260, 1250, 1177, 1034 $cm^{-1}$ (all s)] identical with authentic $KOSO_2CF_3$. The $^{19}$F NMR of the filtrate showed signals at 93.6 (excess $Tf_2O$), 87.3, and 82.5 ppm relative to internal $C_6F_6$.

**1,3-Diphenyl-2-(trifluoroacetyl)thio-1,3-imidazolium Triflate, 18.** To 505 mg (2 mmol) of **7** in 10 mL of $CH_2Cl_2$ was added 0.31 mL (2 mmol) of trifluoroacetyl triflate.[16] After the mixture was stirred for 20 min at room temperature, 20 mL of ether was added and the precipitate was filtered off in a closed funnel, yielding 940 mg (94%) of moisture-sensitive white crystalline **18**: mp 136–139 °C; IR (Nujol) 1745 (m, C=O), 1590 (w), 1495 (s), 1256 (vs), 1216, 1168, 1180, 1034 $cm^{-1}$ (all s); $^1$H NMR ($CH_3CN$, internal $Me_4Si$) $\delta$ 7.92 (m, 10 H), 8.40 (s, 2 H); $^{19}$F NMR ($CH_3CN$, internal $C_6F_6$) 87.3 (OTf), 91.3 ($COCF_3$). Anal. Calcd for $C_{16}H_{12}F_6N_2O_4S_2$ (mol wt 498.4): C, 43.28; H, 2.43; N, 5.62. Found: C, 43.2; H, 2.48; N, 5.7.

**2,2′-Dithiobis(1,3-benzodithiolium) Ditriflate, 20.** A solution of 0.46 g (2.5 mmol) of **19** and 0.42 mL (2.5 mmol) of triflic anhydride in 25 mL of $CH_2Cl$ was stirred for 5 h, then 25 mL of ether was added, and the mixture was stirred for an additional 30 min. Filtration in a closed funnel and drying at 0.5 mm gave 620 mg (74%) of **20** as a very moisture-sensitive yellow powder: mp >105 °C dec; IR (Nujol) 1446 (w) 1270, 1242, 1228 (all s), 1178, 1151 (m), 1036 $cm^{-1}$ (s); $^1$H NMR ($CH_3CN$, internal $Me_4Si$) $\delta$ 9.14 and 8.71 (both m, AA′BB′), impurity at $\delta$ 7.5–7.9; $^{19}$F NMR ($CH_3CN$, internal $C_6F_6$) 87.2 ppm. Anal. Calcd for $C_{16}H_8F_6O_6S_8$ (mol wt 666.7): C, 28.82; H, 1.21. Found: C, 28.3; H, 1.31.

**1,1′,3,3′-Tetraphenyl-2,2′-biimidazolinium Ditriflate, 23a.** To a suspension of 444 mg (1 mmol) of **21** in 20 mL of $C_6H_6$ was added 0.34 mL (2 mmol) of triflic anhydride. After the mixture was stirred at room temperature for 2 h the precipitate was filtered and recrystallized from $CH_3CN$/ether, yielding 530 mg (71%) of yellow powder **23a**: mp 303 °C dec; IR (KBr) 1574 (sh at 1593), 1491, 1305, 1265, 1225, 1152, 1032 $cm^{-1}$ (all, s); $^1$H NMR ($CH_3CN$, internal $Me_4Si$) $\delta$ 4.73 (s, 4 H), 6.93–7.13 (m, 8 H), 7.23–7.63 (m, 12 H); $^{19}$F NMR ($CH_3CN$, internal $C_6F_6$) 87.2 ppm. Anal. Calcd for $C_{32}H_{28}N_4F_6O_6S_2$ (mol wt 742.7): C, 51.75; H, 3.80; N, 7.54. Found: C, 51.6; H, 3.77; N, 7.6.

**1,1′,3,3′-Tetraphenyl,-2,2′-biimidazolinium Bistrifluoroacetate, 23b.** This compound was prepared analogous to **23a** from 444 mg (1 mmol) of **21** and 0.28 mL (2 mmol) of trifluoroacetic anhydride. **23b**: 460 mg (69%); mp 185–187 °C; IR (KBr) 1683 (s, $COO^-$) 1563 (s), 1295, 1280 (m), 1200 (m), 1167/1156 (m), 1114, 1100 (m) $cm^{-1}$; $^1$H NMR ($CH_3CN$, internal $Me_4Si$) $\delta$ 5.00 (s, 4 H), 7.26–7.46 (m, 8 H), 7.60–7.82 (m, 12 H); $^{19}$F NMR ($CH_3CN$, internal $C_6F_6$) 91.6 ppm. Anal. Calcd for $C_{34}H_{28}F_6N_4O_4$ (mol wt 670.6): C, 60.89; H, 4.21; N, 8.35. Found: C, 59.7; H, 4.22; N, 8.3.

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