Mono- and Bishomobenzotropones. 2.[1] Preparation and Nuclear Magnetic Resonance Spectra of 1-Hydroxy-2,3-benzotropylium Cation, 1-Hydroxy-2,3-benzohomotropylium Cation, 1-Hydroxy-2,3-benzobishomotropylium Cation and Their Deuterated Analogues

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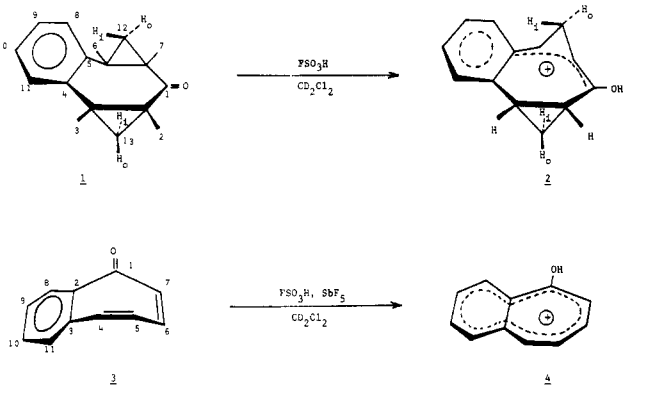
Received October 27, 1980

Protonation of 2,3-benzotropone (3), 2,3-benzo-6,7-homotropone (5) and *trans*-2,3-benzo-4,5:6,7-bishomotropone (7) using fluorosulfonic acid–antimony pentafluoride afforded a carbonium ion in each case. NMR investigation of the resulting carbonium ion formed from 5 showed it to be a monohomotropylium ion with complete electron delocalization, whereas the carbonium ion formed from 7 showed considerably less electron delocalization and is best described as a delocalized, but nonaromatic system.

Introduction

Over the past 18 years many examples of homoaromatic molecules have been observed, isolated, and studied.[2] Within the class of homoaromatic compounds, homotropones and homotropylium cations have attracted the most interest.[2] Beginning in 1962 with the work of Pettit et al.,[3a] homotropylium ions have enjoyed continuous interest to date.[2] In addition to this sustained interest in their preparation and properties, numerous types of calculations have been made[4] on these species in order to investigate the phenomenon of homoaromaticity in general and to explain the stability and properties of these homotropylium cations specifically. Throughout this continuing series of investigations, several attempts have been made to prepare homocounterparts of the tropylium cations which contain units which could possibly dampen the gain in ΔE_π due to the cyclic electron delocalization which accompanies formation of a tropylium species[5] and would thus be instructive for a further understanding of homoaromaticity.[2] Examples of these attempts have been well reviewed[2] and it is interesting that in all cases the nonclassical homoconjugative involvement of the cyclopropyl ring in cyclic electron delocalization was always observed to be substantial.

An alternative approach to the study of the gain in ΔE_π is to investigate bishomotropylium cation precursors with differing geometric arrangements of cyclopropyl groups. This approach could possibly give rise to a system where only one of the cyclopropyl rings becomes involved in homoconjugative electron delocalization and if this is observed, it would lead to the establishment of geometric limits for this type of cyclopropyl involvement. To date only one example of this type of system has been reported,[6] a monohomotropylium cation, the 1-hydroxy-4,5-benzo-2,3-cyclopropahomotropylium cation (2), made from protonation of *trans*-4,5-benzo-2,3:6,7-bishomotropone (1). We now report a second member of this series of monohomotropylium cations, the 1-hydroxy-2,3-benzo-4,5-cyclopropahomotropylium cation (8) and/or 1-hydroxy-2,3-benzo-7,7a-cyclopropahomotropylium cation (9) and its deuterated analogue (8-d_4 and 9-d_4) prepared from the protonation of *trans*-2,3-benzo-4,5:6,7-bishomotropone (7 or 7-d_4).



Our initial attempts to prepare the correct structure of the starting bishomotropone which upon protonation would afford 8 and/or 9 (and 8-d_4 and/or 9-d_4) were difficult to formulate because of the seeming disagreement in the literature as to whether the starting bishomotropone should have the two cyclopropyl groups cis or trans[1] with respect to each other. Corver and Childs[6] have found evidence that the cis arrangement of a 1,4-bishomobenzotropone upon protonation leads to substantial charge delocalization and results in a cation, best described as being bishomoaromatic, whereas protonation of *trans*-1,4-bishomotropone leads to a less charge delocalized system best described as a monohomoaromatic system. In contrast Paquette et al.,[3b] in an elegant study using ^{13}C NMR, have reported that protonation of *cis*-bicyclo-

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(5) (a) Meuche, D.; Strauss, H.; Heilbronner, E. *Helv. Chim. Acta* **1958**, *41*, 57; (b) *Ibid.* **1958**, *41*, 414. (c) Naville, G.; Strauss, H.; Heilbronner, E. *Ibid.* **1960**, *43*, 1221.

(6) Corver, H. A.; Childs, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 6201.

(7) The term "double Mobius" to describe the trans bishomoaromatic system has been rejected in one publication[6] and advanced in another.[3b] We prefer to avoid a discussion of the relative merits of this nomenclature system in this paper.

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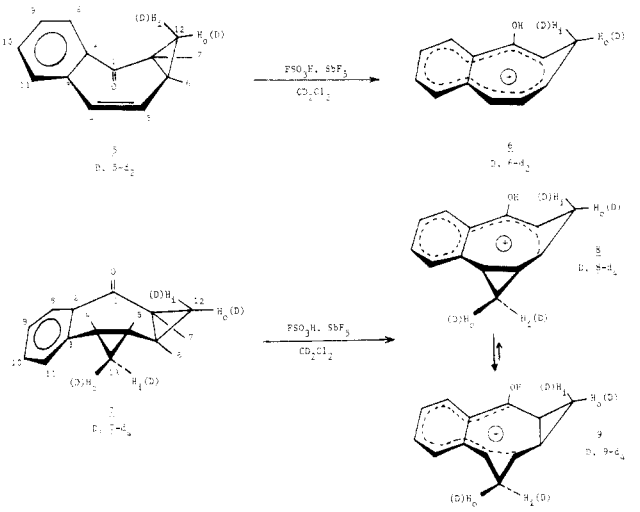

[6.1.0]nona-2,4,6-triene and its *anti*-9-methyl analogue gives rise to "initial formation of a trans cation which subsequently experiences conformational inversion of a methylene bridge." The two studies may be viewed as indicating that either more flexibility is available in the nonbenzene-fused 1,3-bishomotropylium ion studied by Paquette et al.[3b] when compared to the benzene-fused 1,4-bishomotropylium cation studied by Corver and Childs,[6] or more interestingly, that there exists fundamental differences between the π-system arrangements necessary to obtain 1,3- or 1,4-bishomotropylium cations. In view of these published results it was decided to investigate the protonation of the benzene-fused *trans*-1,3-bishomotropone **7** and to compare our findings with those already discussed.

Preparation. The synthetic approach used to prepare 2,3-benzo-6,7-homotropone (**5**), *trans*-2,3-benzo-4,5:6,7-bishomotropone (**7**) and their deuterio analogues **5**-d_2 and **7**-d_4, respectively, has been previously described.[1] Preparation of the carbonium ions of the above tropones and the 2,3-benzotropylium cation (**4**) was accomplished directly in an NMR tube by the addition of cold commercial "Magic Acid" (25% spectrograde fluorosulfonic acid–antimony pentafluoride, Aldrich) to the cold (−78 °C) tropone dissolved in methylene-d_2 chloride. The appearance of a yellow to deep reddish-purple color in all cases was indicative of the carbonium ion formation. After the NMR of the respective carbonium ions was observed and recorded, each sample was carefully quenched with water to regenerate the original tropone. In all cases, a quantitative recovery of starting material was obtained upon quenching with water and the NMR of the tropones generated in this manner was identical with the NMR of the starting material before protonation. Thus in all cases, no byproducts or skeletal reorganization was observed in going from tropone to carbonium ion and back to tropone.

NMR Spectra. The tropone derivatives **3**, **5**, and **7** and the corresponding carbonium ions **4**, **6**, and **8** (and/or **9**) were subjected to rather careful ^{1}H NMR analysis in the hope that the chemical shift and coupling constant data might shed some light on the structure of the ions. In a few cases, the spectra exhibited first-order behavior; these were analyzed directly. However, in most cases the nonfirst-order splitting required the use of spin decoupling, deuterium incorporation, and computer assistance to extract the desired information.[8] Tables I–III show the results of these analyses. Insofar as possible, the solvent was CD_2Cl_2 or $CDCl_3$. The only exceptions involve the aliphatic region of **7** and the aromatic region of **3**. Here the overlap of signals made it impossible to extract coupling constant information. However, use of C_6D_6 in **7** and Me_2SO-d_6 in **3** gave NMR signals which were well separated. Unless otherwise noted, coupling constants and chemical shifts should be accurate to ±0.3 Hz.

Table I. Chemical Shifts (δ) and Coupling Constants (Hertz) for 2,3-Benzotropone (3) and 1-Hydroxy-2,3-benzotropylium Cation (4)[a]

	3	4		3	4		3	4
δ_4	7.3	8.6	$J_{4,5}$	11.5[b]	11.1	$J_{8,9}$	8.0[c]	8.7
δ_5	6.7	7.9	$J_{4,6}$	1.1[b]	1.2	$J_{8,10}$	1.8[c]	1.1
δ_6	7.1	8.4	$J_{4,7}$	0.6	*d*	$J_{8,11}$	0.4[c]	0.0
δ_7	6.9	8.3	$J_{4,8}$	0.6	*d*	$J_{9,10}$	7.2[c]	6.9
δ_8	8.4	9.1	$J_{5,6}$	8.0[b]	9.1	$J_{9,11}$	1.6[c]	1.0
δ_9	7.6–7.7	8.2	$J_{5,7}$	1.1[b]	1.0	$J_{10,11}$	8.0[c]	8.2
δ_{10}	7.6–7.7	8.3	$J_{6,7}$	12.1	11.6			
δ_{11}	7.6–7.7	8.4						

[a] 300-MHz NMR, 5% in CD_2Cl_2, ambient temperature used for **3**; −15 to 0 °C used for **4**. Shifts are reported in parts per million relative to Me_4Si. [b] Our values are consistent with those in literature (Bertelli, D. J.; Gerig, J. T.; Herbelin, J. M. *J. Am. Chem. Soc.* **1968**, *90*, 107). [c] These values were obtained at 90 MHz, using Me_2SO as solvent. [d] Unable to measure.

Table II. Chemical Shifts (δ) and Coupling Constants (Hertz) for 2,3-Benzo-6,7-homotropone (5) and 1-Hydroxy-2,3-benzohomotropylium Cation (6) and Its Deuterio Analogue

	5[a]	6[b]	6-d_2[c]		5[a]	6[b]	6-d_2[c]
δ_4	6.1	6.9	6.8	$J_{5,7}$	0.0	0.0	0.0
δ_5	6.2	6.8	6.7	$J_{5,12i}$	0.0	0.0	
δ_6	2.0	3.7	3.6	$J_{5,12o}$	0.0	0.0	
δ_7	2.6	3.4	3.6	$J_{6,7}$	9.0	8.2	8.0
δ_8	7.6	8.1	8.2	$J_{6,12i}$	6.7	7.2	
δ_9	7.2	7.6	7.6	$J_{6,12o}$	8.6	8.6	
δ_{10}	7.4	7.9	7.9	$J_{7,12i}$	6.2	5.7	
δ_{11}	7.1	7.6	7.6	$J_{7,12o}$	8.6	8.2	
δ_{12i}	1.4	1.1		$J_{12i,12o}$	−4.5	−6.3	
δ_{12o}	1.6	3.4		$J_{8,9}$	7.6		7.8
$J_{4,5}$	11.9	11.6	11.6	$J_{8,10}$	1.1		1.1
$J_{4,6}$	0.7	0.7	*d*	$J_{8,11}$	0.5		0.5
$J_{4,7}$	0.0	0.0	0.0	$J_{9,10}$	7.7		7.4
$J_{4,12i}$	0.0	0.0	0.0	$J_{9,11}$	0.7		1.0
$J_{4,12o}$	0.0	0.0	0.0	$J_{10,11}$	7.4		8.0
$J_{5,6}$	7.1	7.0	6.9				

[a] Aryl protons, 300-MHz NMR, 5% in CD_2Cl_2, ambient temperature; remainder of molecule, 100-MHz NMR, 5% in $CDCl_3$, ambient temperature.[1] [b] 100-MHz NMR, 5% in $CDCl_2$, 0 °C. Coupling constants for aryl protons were not measured. [c] 300-MHz NMR, 5% in CD_2Cl_2, −15 to 0 °C. [d] Unable to determine.

Discussion

It has been previously observed[9–11] that although the presence of a benzene ring does not attenuate homoaromaticity, the presence of a hydroxyl function does significantly attenuate homoaromaticity and causes considerable reduction in the difference (Δ) between the position (δ) of the inside and outside protons of the homocyclopropyl group. Thus, whereas the unsubstituted homotropylium cation[3a] **10** shows a chemical shift differ-

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(11) (a) Childs, R. F.; Winstein, S. *J. Am. Chem. Soc.* **1967**, *89*, 6348. (b) Childs, R. F.; Brown, M. A.; Anet, F. A. L.; Winstein, S. *Ibid.* **1972**, *94*, 2175.

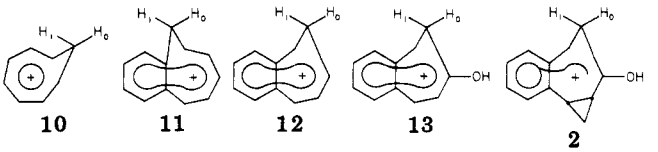
Table III. Chemical Shifts (δ) and Coupling Constants (Hertz) for *trans*-2,3-Benzo-4,5:6,7-bishomotropone (7) and 1-Hydroxy-2,3-benzo-4,5-cyclopropahomotropylium Cation (8) or 1-Hydroxy-2,3-benzo-7,7a-cyclopropahomotropylium Cation (9) and Their Deuterio Analogues[a]

	7	7-d_4	8(9)	8-d_4(9-d_4)
δ_4	1.7	1.7	1.9	1.8
δ_5	1.7	1.7	2.2	2.0
δ_6	2.1	2.1	3.5	2.9
δ_7	1.9	1.9	2.4	2.3
δ_8	7.3	7.3	7.8	7.5
δ_9	7.1	7.1	7.4	7.3
δ_{10}	7.3	7.2	7.7	7.5
δ_{11}	7.2	7.2	7.5	7.4
δ_{12i}	1.3		2.6	
δ_{12o}	1.2		2.8	
δ_{13i}	0.6		0.9	
δ_{13o}	1.3		2.0	
$J_{4,5}$	9.1[c]		9.2	9.1
$J_{4,6}$	0.4		small[b]	
$J_{4,7}$	0.1		small[b]	
$J_{4,12i}$	0.0		0.0	
$J_{4,12o}$	0.0		0.0	
$J_{4,13i}$	6.3		6.2	
$J_{4,13o}$	9.3		8.9	
$J_{5,6}$	4.5		4.1	4.3
$J_{5,7}$	0.1		small[b]	
$J_{5,12i}$	0.0		0.0	
$J_{5,12o}$	0.0		0.0	
$J_{5,13i}$	6.4		6.0	
$J_{5,13o}$	8.4		8.5	
$J_{6,7}$	10.0		9.1	
$J_{6,12i}$	7.2		9.1	
$J_{6,12o}$	8.5		8.4	
$J_{6,13i}$	0.0		0.0	
$J_{6,13o}$	0.0		0.0	
$J_{7,12i}$	5.6		4.7	
$J_{7,12o}$	8.2		7.3	
$J_{7,13i}$	0.0		0.0	
$J_{7,13o}$	0.0		0.0	
$J_{12i,12o}$	−4.6		−4.5	
$J_{12i,13i}$	0.0		0.0	
$J_{12i,13o}$	0.0		0.0	
$J_{12o,13i}$	0.0		0.0	
$J_{12o,13o}$	0.7		small[b]	
$J_{13i,13o}$	−4.8		−5.6	
$J_{8,9}$	7.9	7.8	8.1	7.9
$J_{8,10}$	1.7	1.4	0.9	1.3
$J_{8,11}$	0.1	0.3	0.4	0.3
$J_{9,10}$	7.4	7.0	7.7	7.4
$J_{9,11}$	1.3	1.2	0.8	0.8
$J_{10,11}$	7.6	7.8	7.6	7.6

[a] 300-MHz NMR, 5% in CD_2Cl_2, ambient temperature used for 7 and 7-d_4, −15 to 0 °C used for 8 and 8-d_4. Shifts are reported in parts per million relative to Me_4Si. [b] These couplings are less than 1 Hz, but clearly nonzero. [c] Coupling constants for aliphatic protons in 7 were determined in C_6D_6.[1]

ence (Δ) of 5.80 ppm (Table IV) between the inside and outside protons of the homocyclopropyl group, the benzohomotropylium cation[10] 11 with the homocyclopropyl group sharing one common carbon with the benzene ring shows a chemical shift difference (Δ) of 3.86 ppm, and the benzohomotropylium cation[6] 12 with the methylene group one carbon removed from the benzene ring shows a chemical shift difference (Δ) of 5.34 ppm between the same two protons. These differences should be contrasted with the chemical shift differences (Δ) observed for the corresponding 1-hydroxy-4,5-benzohomotropylium cation 13, where this difference is reduced to 2.41 ppm[6] or 2.15–2.35 ppm,[12] depending upon the acid used for protonation.

Table IV. Chemical Shift Differences (Δ) between Inside and Outside Homocyclopropyl Protons in Various Homotropylium Cations



10 11 12 13 2

	10	11	12	13		2
δH_o	5.20	5.36	5.02	3.57	2.75–2.95	2.32
δH_i	−0.60	1.50	−0.32	1.16	6.0	2.42
$\Delta\delta H_{oi}$	5.80	3.86	5.34	2.41	2.15–2.35	0.10
ref	3a	10	6	6	12	6

These results were reported without regard to the position of the benzene ring and the hydroxyl group with respect to each other.

In this study we have observed that in going from the parent ketone 5 to the cation 6, except for the H_{12i} proton which remains in place, all other protons experience a deshielding effect which causes them to move downfield and indicates substantial charge delocalization to exist in the cation 6. This affords a chemical shift difference (Δ) between H_{12i} and H_{12o} of 2.3 ppm for 1-hydroxy-2,3-benzohomotropylium cation (6). Two coupling constants are noteworthy. $J_{5,6}$ shows a slight decrease (7.1 to 6.9–7.0 Hz) and $J_{12i,12o}$ changes from −4.5 to −6.3 Hz when 5 is protonated. When viewed together these results indicate clearly that ion 6 is homoaromatic. The flattening of the ring upon protonation would slightly open the dihedral angle between H_5 and H_6, relative to the preferred conformation in 5, lowering the coupling constant $J_{5,6}$.[1,13] At the same time, the C_6C_7 bond lengthening will open the $C_6C_{12}C_7$ angle, causing $J_{12i,12o}$ to become more negative.[6] The chemical shift difference (Δ) between H_{12i} and H_{12o} of 2.3 ppm also suggests homoaromaticity, and it is interesting to compare its value with those for other homoaromatic ions (Table IV). It does seem that the presence of the hydroxyl group serves to reduce the ring current; however, its positioning with respect to the homocyclopropyl group has little effect on the magnitude of the current (cf. 13). Bracketing the cyclopropyl group between a benzene ring and a hydroxyl group seems to have a similar effect to placing the hydroxyl group between a benzene ring and a cyclopropyl group.

Another interesting comparison which leads to a good estimation of the reduction in ring current associated with the replacement of a delocalized double bond by a homocyclopropyl group is observed when the chemical shift differences for protons 4 and 5 in the benzotropone 3 and the 1-hydroxybenzotropylium cation 4 are compared with the chemical shift differences for the same protons in benzohomotropone 5 and the 1-hydroxybenzohomotropylium cation 6. In going from 3 to 4 the $\Delta\delta$ for protons 4 and 5 is 1.3 and 1.2 ppm, respectively, whereas conversion of 5 to 6 produces a $\Delta\delta$ for protons 4 and 5 of 0.8 and 0.6 ppm, respectively. Since these protons are common to both structures, these differences afford a good estimate of the reduction in the ring current associated with the replacement described above. These differences should be contrasted with the aromatic protons in the same molecules which all display about the same magnitude of deshielding in going from parent to cation, since the $\Delta\delta$ for the aromatic protons 8–11 ranges from 0.4 to 0.8 ppm in both systems. Thus the indication is that in these

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(13) Garbisch, E. W., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 5561.

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 (Δ) 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 π 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 (Δ) 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.

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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Received November 11, 1980

Interaction of thiourea and substituted thioureas with trifluoromethanesulfonic acid anhydride in methylene chloride results in stable dication disulfide salts $(R_2N)_2{}^+CSC^+(NR_2)_2{\cdot}2CF_3SO_3^-$. 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 ef-

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

fectively stabilize a positive charge. 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]

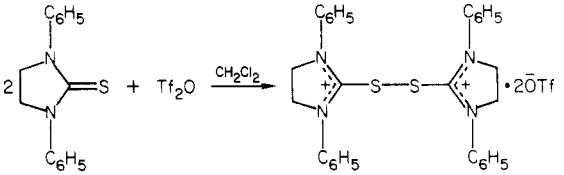
In hopes of generating the related dication thioether salts (**2**, S instead of O) we examined the interaction of thioureas with triflic anhydride. However, instead of observing the analogous thioether salts, dication disulfide salts were obtained, suggesting that triflic anhydride acts as an oxidizing 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.

(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.

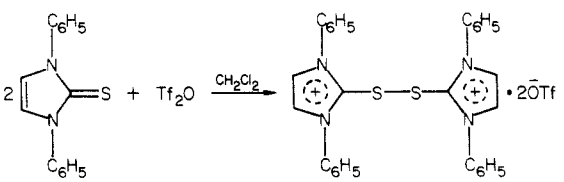
Scheme I

$$2(R_2N)_2C{=}S + Tf_2O \xrightarrow{CH_2Cl_2} (R_2N)_2\overset{+}{C}S\overset{+}{S}C(NR_2)_2{\cdot}2\overset{-}{O}Tf$$

3a, R = H; **b**, R = CH_3 — **4a**, R = H; **b**, R = CH_3



5 **6**



7 **8**

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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