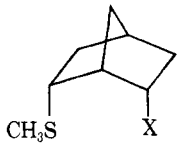
Communications to the Editor

Facilitation of Dialkyl Sulfide Oxidation by Neighboring Groups

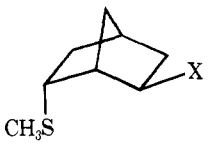
Sir:

The oxidation of dialkyl sulfides to the corresponding cation radical or dication is generally regarded as difficult. Thus Cottrell and Mann[1] reported the peak potentials for oxidation of a variety of dialkyl sulfides in anhydrous acetonitrile using cyclic voltammetry to be considerably more anodic than 1 V[2] and usually between 1.4 and 1.7 V vs. a silver/0.1 M silver nitrate in acetonitrile reference electrode. However, it was hypothesized[3] that the ease of oxidation of aliphatic sulfides could be increased by suitably disposed neighboring groups. The studies reported in this paper substantiate this suggestion.

The hypothesis is that certain groups proximate to a sulfur atom but not bonded to it can assist oxidation at sulfur by either one or two electron donations and concomitant bond formation. To test this idea, compounds are required in which a sulfur atom of a sulfide and a potential neighboring group are held close together. Such compounds are the 2,6-di-*endo*-norbornyl derivatives **1**. In these compounds, the sulfur atom and X are held rigidly close to one another. A further advantage to this particular series is that a control system is readily accessible: *exo,endo*-norbornyl derivatives **2**. The number of bonds separating the sulfur atom and X in **1** and **2** is identical. Thus through-bond interactions should be the same in both series. However, owing to the rigidly different geometries in **1** and **2** through-space interactions should be very different.



1a, X = CO_2H
b, X = CO_2CH_3
c, X = CH_2OH
d, X = $NHCO_2CH_2CH_3$



2a, X = CO_2H
b, X = CO_2CH_3
c, X = CH_2OH
d, X = $NHCO_2CH_2CH_3$

The oxidation of these sulfides was studied by cyclic voltammetry in anhydrous acetonitrile. The oxidations of an endo acid salt **1e** and exo acid salt **2e** obtained by adding 2,6-di-*tert*-butylpyridine to endo acid **1a** and exo acid **2a**, respectively, were also studied. The peak potentials measured for these compounds are shown in Table I. All of the oxidations were irreversible even at scan rates up to 50 V/s. The peak potentials reported in Table I are all reproducible and all of the peaks are well defined. Furthermore, these results do not appear dependent on the nature of the electrode surface because similar results were obtained using a glassy carbon electrode in place of the platinum electrode. Perusal of the data in Table I shows that the peak potentials for all of the exo derivatives **2** and for the endo acid **1a** and endo ester **1b** are in the expected range for aliphatic sulfide oxidation. However, there is a dramatic shift in peak potentials toward more cathodic values for the endo acid salt **1e** and endo alcohol **1c**. For example, comparison of endo acid salt **1e** with exo acid salt **2e** reveals that the former has a peak potential 630 mV more cathodic than the latter. Compared with endo acid **1a**, the endo salt **1e** shows a peak potential 550 mW more cathodic, whereas in the exo series there is no difference in peak potential for the acid **2a** and its corresponding salt **2e**.

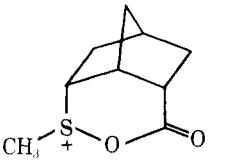
Table I. Anodic Oxidation of Norbornyl Derivatives using Cyclic Voltammetry

Compd	E_p[a]	Compd	E_p[a]
1a	1.20	**2a**	1.28
1b	1.21	**2b**	1.29
1c	0.56	**2c**	1.20
1d	0.98	**2d**	1.20
1e	0.65	**2e**	1.28

[a] Peak potentials of first oxidation peak determined at a Pt electrode (1 cm^2), 0.1-V/s scan rate, and measured in acetonitrile, 0.1 M *n*-Bu_4NClO_4 vs. Ag/0.1 M $AgNO_3$ in acetonitrile reference electrode.

To gain more insight into these anodic oxidations, the oxidation of endo acid salt **1e** was studied in more detail. Controlled potential electrolysis of endo salt **1e**, at a potential of 0.86 V, in the presence of a small amount of water and excess 2,6-di-*tert*-butylpyridine yielded the sulfoxide of endo acid **1a** as the principal product[4] and an apparent "*n*" value of 1.85. The isolated yield of the sulfoxide of endo acid **1a** was 78%. The fact that the carboxylic acid moiety is retained in the product demonstrates that a simple Kolbe reaction does not occur. Furthermore, the formation of a sulfoxide moiety on oxidation in the presence of water demonstrates that an oxidation mechanism analogous to that suggested by Cottrell and Mann[1] for the anodic oxidation of dimethyl sulfide also does not occur. Such a mechanism for the oxidation of endo acid salt **1e** would not lead to the sulfoxide of endo acid **1a**.

A possible intermediate in the two-electron oxidation of endo acid salt **1e** is acyloxysulfonium salt **3**.[5]



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Treatment of the tetra-*n*-butylammonium salt of endo acid **1a** in acetonitrile with 1 molar equiv of bromine and 2 formula weight equiv of silver tetrafluoroborate resulted in the precipitation of 2 formula weight equiv of silver bromide.[6] The bromine-free solution contained a material whose spectrum is consistent with **3** which was not stable at room temperature but was stable at −40 °C. If water was added to this material before it decomposed, the sulfoxide of endo acid **1a** was produced in good yield.

The mechanism for anodic oxidation of endo acid salt **1e** is unknown at present.[7] In any event, electron transfer is facilitated by the neighboring carboxylate group. If the mechanism involves two one-electron transfers, then the first electron-transfer step can be regarded as a sulfur oxidation with carboxylate participation or carboxylate oxidation with sulfur participation. The latter is reminiscent of a Kolbe reaction except that the carboxylate radical reacts with sulfur before loss of carbon dioxide (or charge transfer and participation are synchronous).[8,9] Because the oxidation potentials of sulfides are less anodic than those of carboxylates,[10] the former mechanism is preferred but, of course, the latter is not ruled

out. A similar mechanism is suggested for anodic oxidation of endo alcohol **1c**.

Acknowledgment. Support of this research by the National Institutes of Health is gratefully acknowledged.

References and Notes

(1) P. T. Cottrell and C. K. Mann, *J. Electrochem. Soc.*, **116**, 1499 (1969).
(2) Thiane (pentamethylene sulfide) was reported[1] to show a peak potential of 0.55 V. However, under our conditions a peak potential of 1.32 V is found.
(3) R. S. Glass, E. B. Williams, Jr., and G. S. Wilson, *Biochemistry*, **13**, 2800 (1974).
(4) One diastereomer was preferentially produced.
(5) (a) S. Allenmark and C.-E. Hagberg, *Acta Chem. Scand.*, **22**, 1694 (1968); (b) S. Allenmark and C.-E. Hagberg, *ibid.*, **24**, 2225 (1970); (c) W. A. Pryor and H. T. Bickley, *J. Org. Chem.*, **37**, 2285 (1972); (d) D. Landini, F. Rolla, and G. Torre, *Int. J. Sulfur Chem., Part A*, **2**, 43 (1972); (e) D. Landini and F. Rolla, *J. Chem. Soc., Perkin Trans. 2*, 1317 (1972); (f) O. Bohman and S. Allenmark, *Tetrahedron Lett.*, 405 (1973); (g) T. Varkey, G. F. Whitfield, and D. Swern, *J. Org. Chem.*, **39**, 3365 (1974); (h) T. Numata and S. Oae, *Tetrahedron*, **32**, 2699 (1976).
(6) J. B. Lambert, D. H. Johnson, R. G. Keske, and C. E. Mixan, *J. Am. Chem. Soc.*, **94**, 8172 (1972).
(7) The scan rate dependence of the cyclic voltammetric peak currents suggests an ECE mechanism. Rotating disk electrode data suggest faster chemical rates for **1a,c-e** than for the others. In these cases the currents approach those expected for an overall $2e^-$ process.
(8) Note that, even though the carboxylate group is the electron source in this mechanism, ultimately the sulfur atom is oxidized.
(9) For neighboring-group participation by sulfide in O–O bond homolysis, see W. G. Bentrude and J. C. Martin, *J. Am. Chem. Soc.*, **84**, 1561 (1962); P. Livant and J. C. Martin, *ibid.*, **98**, 7851 (1976).
(10) No oxidation peak with a peak potential of <1.6 V was observed for the 2,6-di-*tert*-butylpyridine salt of 5-norbornene-2-*endo*-carboxylic acid in acetontrile and using a Ag/0.1 M $AgNO_3$ in acetonitrile reference electrode.

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Trifluoromethylated "Dewar" Pyrroles: 5-Azabicyclo[2.1.0]pentene-2 Ring System[1]

Sir:

In previous papers,[2] we reported that 1,2,3,4-tetrakis(trifluoromethyl)-5-thiabicyclo[2.1.0]pentene-2, a "Dewar" thiophene (**1**), reacted as a dienophile with the conjugated dienes. In this report, we discuss the 1,3-dipolar cycloaddition of **1** and transformation of the adducts to "Dewar" pyrroles (Chart I).

Treatment of **1** with phenyl or cyclohexyl azide (**2a** or **2b**) in CH_2Cl_2 at room temperature gave the corresponding adduct (**3a** or **3b**).[3] **3a:** 28.1% yield, mp 62–64 °C; IR ($CHCl_3$) 3020, 1600, 1500, 1290, 1185 cm^{-1} (no absorption near 1700 cm^{-1} ascribable to the cyclobutenic double bond[2]); ^1H NMR ($CDCl_3$) δ 7.43; ^{19}F NMR ($CDCl_3$) −3.6 (3 F, m), −2.6 (3 F, m), −2.0 (3 F, m), 7.4 (3 F, m) ppm;[4] *m/e* 447 ($M - N_2$). **3b:** 81% yield, mp 59–60 °C; IR ($CHCl_3$) 2940, 2860, 1480, 1300, 1180, 1165 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.68 (1 H, m, N-CH), 1.2–2.36 [10 H, m, $(CH_2)_5$]; ^{19}F NMR ($CDCl_3$) −4.6 (3 F, m), −2.4 (3 F, m), 1.6 (3 F, m), 6.8 (3 F, m) ppm; *m/e* 453 ($M - N_2$).

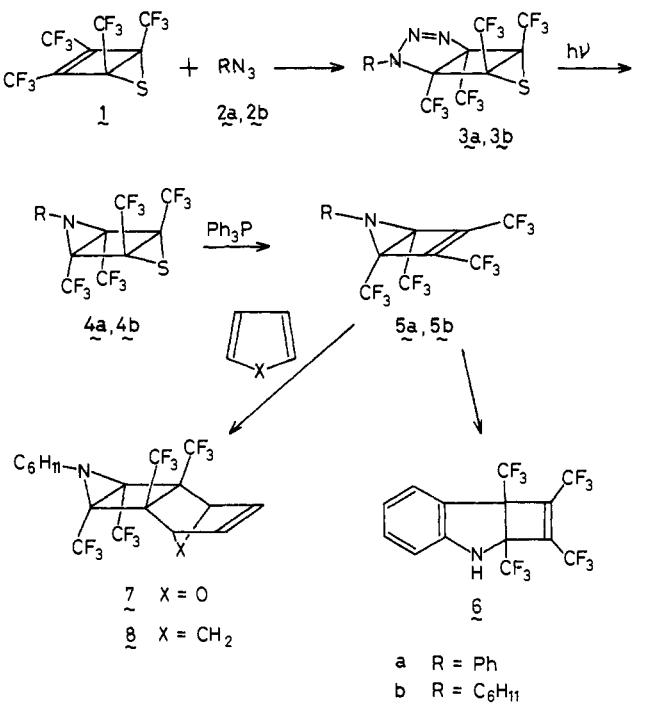
Irradiation of **3a** or **3b** in *n*-pentane with a low-pressure mercury lamp caused elimination of a nitrogen molecule to give the valence-bond isomers of 1,4-thiazine, compounds of a new ring system (**4a** or **4b**). **4a:** 55% yield, colorless oil; IR ($CHCl_3$) 3040, 1600, 1290, 1170 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.18; ^{19}F NMR ($CDCl_3$) −5.6 (6 F, s), 2.8 (6 F, s) ppm; *m/e* 447 (M^+); high resolution, *m/e* 446.997 (calcd 446.995). **4b:** quantitative yield, colorless oil; ^{19}F NMR spectrum is quite similar to that of **4a.**

Compounds **4a** and **4b** were desulfurized with triphenylphosphine in *n*-pentane at room temperature to yield the corresponding "Dewar" pyrrole (**5a** or **5b**). Compound **5a** was too unstable to be isolated, but its structure could be assumed by transient appearance of a pair of symmetrical peaks in the ^{19}F NMR spectrum [−0.4 (bridge head CF_3) and 2.8 (olefinic CF_3) ppm] and an absorption near 1715 cm^{-1} (C=C) in the IR spectrum. Compound **5a** rapidly isomerized to 1,2,2a,7b-tetrakis(trifluoromethyl)-2a,7b-dihydro-3*H*-cyclobuta[*b*]-indole (**6**): 35.6% yield, colorless oil; IR (*n*-pentane) 3430 (N-H), 1715 (C=C), 1210 (C-F) cm^{-1}; ^1H NMR (CCl_4) δ 7.2–7.5 (2 H, m), 6.75–7.04 (2 H, m), 4.72 (1 H, b); ^{19}F NMR ($CDCl_3$) −0.8 (3 F, m), 0.0 (3 F, m), 5.2 (3 F, m), 10.8 (3 F, m) ppm; *m/e* 415 (M^+); high resolution, *m/e* 415.024 (calcd 415.023). **5b:** 60% yield, colorless oil; IR (CCl_4) 2940, 2860, 1705, 1190, 1160 cm^{-1}; ^1H NMR (CCl_4) δ 2.6 (1 H, N-CH), 1.15–1.95 [10 H, m, $(CH_2)_5$]; ^{19}F NMR (CCl_4) 1.52 (6 F, s) (bridgehead CF_3), 2.72 (6 F, s) (olefinic CF_3) ppm; ^{13}C NMR ($CDCl_3$) 23.78 (3′ and 5′), 25.88 (4′), 31.97 (2′ and 6′), 49.95 (1 and 4), 55.11 (1′), 118.08, and 121.24 (CF_3 carbon), and 140.44 (2 and 3) ppm; *m/e* 421 (M^+); half-life at 100 °C in benzene, about 8.8 h.

Treatment of **5b** with furan and cyclopentadiene gave the Diels–Alder adducts (**7** and **8**).[3] **7:** 83% yield, mp 123–125 °C; IR (CCl_4) 2940, 2860, 1210, 1170 cm^{-1}; ^1H NMR (CCl_4) δ 6.6 (2 H, b, =CH-), 5.36 (2 H, s, O-CH<), 3.0 (1 H, b, N-CH<), 1.0–2.0 [10 H, m, $(CH_2)_5$]; ^{19}F NMR (CCl_4) −3.8 (6 F, s), −0.2 (6 F, s) ppm; *m/e* 421 (**5b**) and 68 (furan). **8:** 73% yield, mp 101–104 °C; IR (CCl_4) 2940, 2860, 1200, 1180 cm^{-1}; ^1H NMR (CCl_4) δ 6.40 (2 H, b, =CH-), 3.44 (2 H, b, >CH), 3.04 (1 H, b, N-CH<), 1.1–2.3 (12 H, m, methylenes); ^{19}F NMR (CCl_4) −3.5 (6 F, s), −1.8 (6 F, s); *m/e* 487 (M^+).

In this research, some quite novel compounds of new ring systems, too highly strained to be isolated without the trifluoromethyl groups, were obtained. The formation of these might be due to the stabilization of strained molecules by the perfluoroalkyl effect.

Chart I



References and Notes

(1) Dedicated to Professor R. B. Woodward on the occasion of his 60th birthday anniversary.
(2) Y. Kobayashi, I. Kumadaki, A. Ohsawa, and Y. Sekine, *Tetrahedron Lett.*,