of 1.0 g (7.70 mmol) of isoquinoline and 12 mL (240 mmol) of ethylene oxide in 50 mL of glacial HOAc was allowed to sit at room temperature overnight. The solution (clear and colorless) was then cooled to 0 °C, basified with 20% aqueous NaOH, and extracted with $CHCl_3$. Drying (Na_2SO_4), *filtration, and evaporation yielded* 1.39 g *of a yellow oil* **18** that gradually turned deep red: NMR ($CDCl_3$) δ 7.20 (m, 4), 6.15 (d, 1, J = 7 Hz), 5.65 (d, 1, J = 7 Hz), 5.60 (s, 1), 3.50 (s, 4); IR ($CHCl_3$) 3000, 2940, 2875, 1625, 1560, 1490, 1460, 1430 cm^{-1}. After sitting overnight, the now red viscous oil was purified by preparative TLC (silica gel eluted with $CHCl_3$–Et_2O–hexane, 1:1:1) to yield 465 mg (35%) of oxazolidine **19** (R_f 0.50) as a viscous yellow oil. With exposure to air the oil turned violet: for ^1H and ^{13}C NMR ($CDCl_3$), see Table I; IR ($CHCl_3$) 3050, 3000, 2910, 1620, 1600, 1560, 1480, 1175 (OCN),[11a] 1120 (OCN),[11a] 1060 (OCN),[11a] 830 (OCN)[11b] cm^{-1}; UV λ_{max} (EtOH) 208 nm (log ϵ 3.97), 231 (3.67), 246 (3.45); For high-resolution MS data, see Table II.

Acknowledgments. We thank Mrs. Nancita Lomax and Dr. Harry Wood for their help and encouragement, Drs. Paul Vouros (NU), James Evans (NU), and Catherine Costello (MIT) for mass spectra determinations and interpretation, and Dr. Homer Pearce (Harvard) for the ^{13}C NMR determination and interpretation for **19**. This investigation was supported by the National Cancer Institute, Contract 1-CM-53741.

Registry No.—**6**, 31309-65-6; **7**, 64345-81-9; **8**, 64345-80-8; **9**, 64345-79-5; **10a**, 64345-78-4; **10b**, 64345-76-2; **15a**, 64345-77-3; **15b**, 64345-75-1; **16**, 64345-74-0; **19**, 64345-73-0; ethylene oxide, 75-21-8; $CHCl_3$, 67-66-3; isoquinoline, 119-65-3.

References and Notes

(1) C. N. Filer, F. E. Granchelli, A. H. Soloway, and J. L. Neumeyer, *J. Med. Chem.*, **20,** 1504 (1977); presented in part at the 2nd joint CIC–ACS conference in Montreal, Canada, May 1977, Abstract no. 21 (MEDI).

(2) (a) J. L. Neumeyer, K. K. Weinhardt, R. A. Carrano, and D. H. McCurdy, *J. Med. Chem.*, **16,** 808 (1973); (b) J. I. G. Cadogan and G. A. Molina, *J. Chem. Soc., Perkins Trans. 1,* 541 (1973).

(3) (a) M. Giua, *Gazz. Chim. Ital.*, **52,** 349 (1922); (b) H. Lohmann *Angew. Chem.*, **52,** 407 (1939); (c) H. Lohmann, *J. Prakt. Chem.*, **153,** 57 (1939); (d) H. J. Roth and H. O. Schrimpf, *Arch. Pharm.* (*Weinheim, Ger.*), **293,** 22 (1960).

(4) H. J. Roth and R. Rohrbach, *Arch. Pharm.* (*Weinheim, Ger.*), **303,** 585 (1970).

(5) Previous workers (ref 4) have also noted the requirement for oxygen in this reaction.

(6) (a) S. Winstein and R. Boschan, *J. Am. Chem. Soc.*, **72,** 4669 (1950); (b) N. J. Leonard, K. Conrow, and R. R. Sauers, *ibid.*, **80,** 5185 (1958); (c) W. Schneider and B. Müller, *Ber.*, **93,** 1579 (1960).

(7) W. Schneider and B. Müller, *Arch. Pharm.* (*Weinheim, Ger.*), **294,** 360 (1961).

(8) Due to its air sensitivity, a satisfactory combustion analysis for oxazolidine **19** was not obtained; however, its empirical formula was confirmed by high-resolution mass spectral analysis.

(9) *(a) H. Ahlbrecht and F. Kröhnke, Tetrahedron Lett.*, 967 (1967); (b) *ibid.*, 3653 (1967).

(10) (a) W. Schneider and B. Müller, *Arch. Pharm.* (*Weinheim, Ger.*), 294, 645 (1961); (b) *ibid.*, **295,** 571 (1962); (c) W. Schneider and E. Kämmerer, *ibid.*, **299,** 817 (1966); (d) H. Möhrle, *ibid.*, **299,** 715 (1966); (e) *ibid.*, **300,** 308, (1967); (f) M. Sainsbury, S. F. Dyke, D. W. Brown, and W. G. D. Lugton, *Tetrahedon,* **24,** 427 (1968).

(11) (a) E. D. Bergmann, *Chem. Rev.*, **53,** 309 (1953); (b) G. Habermehl, *Ber.*, **96,** 2029 (1963).

Ozonation of Nucleophiles. 7.[1] Dibenzyl Sulfides

Philip S. Bailey* and Abdul-Ilah Y. Khashab

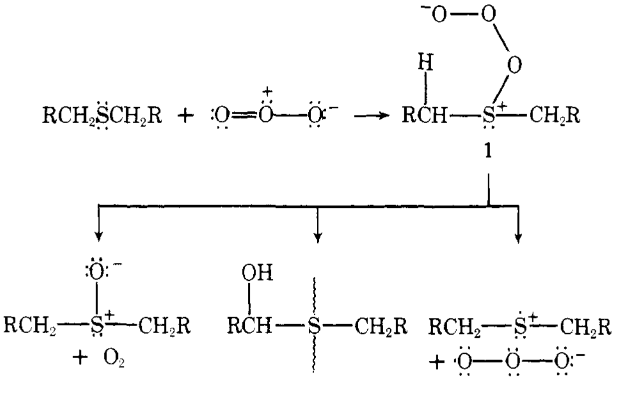
Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

Received July 25, 1977

Ozonation of dibenzyl sulfide and two unsymmetrical benzyl sulfides afforded both sulfur and alkyl side-chain oxidation products. Sulfur oxidation was predominant in protic solvents and side-chain oxidation in hydrocarbon solvents. Ozonation of thianthrene produced the monoxide as the major product and the cation radical as a minor product. Mechanistic pathways are discussed.

Earlier papers in this series[1–5] elucidated the mechanistic pathways involved in the reactions of ozone with various types of aliphatic amines. After the initial reaction between the electrophilic ozone and the nucleophilic amine, four fates of the resulting adduct were proposed. Reactions analogous to the initial attack and three of the adduct fates should also be possible with suitable organic sulfides, as illustrated in Scheme I. These include sulfoxide formation (the only reaction previously shown to occur),[6–12] intramolecular side-chain oxidation, and cation–radical formation. It was the purpose of the present research to test this premise.

Scheme I



The ozonation of organic sulfides has been studied previously by several workers.[6–12] In all cases the only products isolated were the corresponding sulfoxides and/or sulfones, usually in high yields, although Barnard[11] reported the odor of butyraldehyde and butyric acid on the crude sulfone obtained from dibutyl sulfide. Maggiolo and Blair[9] and Horner et al.[10] found 1:1 and 1:2 sulfide–ozone stoichiometry in the conversions to sulfoxide and sulfone, respectively. For this and other reasons they[9,10] proposed electrophilic ozone attack, followed by loss of molecular oxygen from the adduct, as shown in Scheme I, followed by a similar attack on the sulfoxide. On the other hand, Barnard,[11] Boer and Kooyman,[8] and Thompson[12] stated that less than 1 mol of ozone per mole of sulfide was required. Thompson[12] found that close to three oxygen atoms (of ozone) per atom of sulfur participated in the oxidation.

In the earlier work just outlined,[6–12] protic solvents such as chloroform or water were used. Our studies were conducted with four different sulfides in both protic and nonprotic solvents and at two different temperatures. Table I displays the results obtained from ozonations of dibenzyl sulfide and of

Table I. Ozonation of Dibenzyl Sulfides^a

Expt	R and R′ in RCH_2SCH_2R'	Solvent	Temp, °C	Sulfide recovered, %	O_3/ sulfide reacting	C_6H_5CHO, %^{b}	XC_6H_4CHO, %^{b}	Sulfoxide, %^{b}	Total product yield, %^{b}
1	R = R′ = $C_6H_5{}^h$	Pentane^c	0	34	1.42	76	~	21	97
2	R = R′ = $C_6H_5{}^h$	Isopentane^c	0	41	1.46	75	~	27	102
3	R = R′ = $C_6H_5{}^h$	$CH_2Cl_2{}^d$	0	15	0.97	32	~	72	104
4	R = R′ = $C_6H_5{}^h$	$CH_2Cl_2{}^e$	−75	13	1.12	18	~	77	95
5	R = R′ = $C_6H_5{}^h$	$CHCl_3{}^d$	0	14	0.97	30	~	69	99
6	R = R′ = $C_6H_5{}^h$	$CHCl_3{}^f$	−40	11	0.85	16	~	84	100
7	R = R′ = $C_6H_5{}^h$	CH_3OH^d	0	6	0.85	2	~	97	99
8	R = R′ = $C_6H_5{}^h$	CH_3OH^f	−40	21	0.90	0	~	100	100
9	R = C_6H_5; R′ = *p*-$ClC_6H_4{}^i$	Pentane^e	−40	24	1.3	24	29	50	103
10	R = C_6H_5; R′ = *p*-$ClC_6H_4{}^i$	$CHCl_3{}^e$	−40	17	1.1	18	22	66	106
11	R = C_6H_5; R′ = *p*-$ClC_6H_4{}^i$	CH_3OH^e	−40	0	0.94	0	0	97	97
12	R = C_6H_5; R′ = *p*-$CH_3OC_6H_4{}^j$	Pentane^f	0^g	0	1.0	16	12	48	76
13	R = C_6H_5; R′ = *p*-$CH_3OC_6H_4{}^j$	CH_3OH^f	0^g	0	0.87	7	5	86	98

[a] Sulfide (3–5 mmol) and a 1:1 ratio of ozone to sulfide was employed. Neither the sulfide nor the ozone reacted quantitatively. The percentage of recovered sulfide is shown in column 5 and the ratio of reacted ozone to reacted sulfide is shown in column 6. Excess ozone was avoided in order to prevent oxidation of sulfoxide to sulfone and to minimize oxidation of any mercaptan produced. [b] Percent yield based on sulfide actually reacting (unrecovered) and an expected 1 mol of each product per mole of sulfide reacting by the route yielding this product. In cases where the total yield was greater than 100%, the discrepancy is probably due to mercaptan (produced along with aldehyde) also reacting with ozone to give aldehyde. [c] Solvent (25 mL) per millimole of sulfide. [d] Solvent (10 mL) per millimole of sulfide. [e] Solvent (55–65 mL) per millimole of sulfide. [f] Solvent (16 mL) per millimole of sulfide. [g] A higher temperature was used in these experiments in order to increase the proportion of side-chain oxidation products to sulfoxide. [h] Registry no.: 538-74-9. [i] Registry no.: 7693-40-5. [j] Registry no.: 16133-88-3.

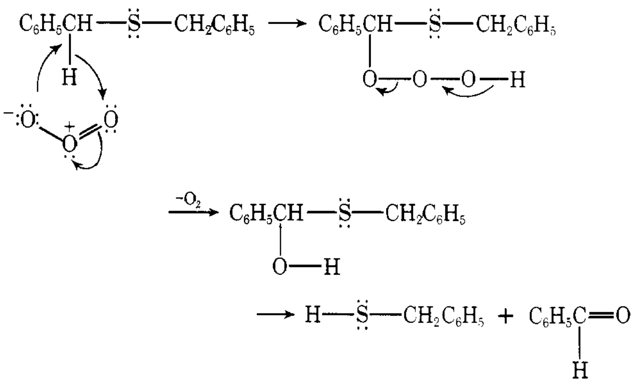
two unsymmetrically substituted dibenzyl sulfides, namely, the mono-*p*-chloro and -*p*-methoxy derivatives.

From a qualitative view of these data several facts are evident. First, both sulfur oxidation and alkyl group (side-chain) oxidation have occurred, in contrast to results of previous investigators. Second, side-chain oxidation is a major reaction only in hydrocarbon (nonprotic) solvents. Third, the more protic the solvent the lower the percentage of side-chain attack. Fourth, the lower the reaction temperature the lower the degree of side-chain attack.

These facts are reminiscent of the results obtained with *n*-butylamine[1] and tri-*n*-butylamine[2,3] and suggest that side-chain attack occurs by a mechanistic pathway involving the abstraction of a proton by the negative oxygen of adduct 1, as proposed earlier for amines with primary alkyl groups,[1–3] rather than by the 1,3-dipolar insertion mechanism[13] of Scheme II. Hydrogen bonding of the sulfide–ozone adduct 1 by the protic solvent would be expected[1–3] to slow down the proton abstraction, as required in the general equation of Scheme I. At low temperatures this abstraction would also be slow, and loss of oxygen to yield the sulfoxide should become increasingly favorable.

The results with the unsymmetrical dibenzyl sulfides also are qualitatively consistent with this mechanistic interpretation. With the *p*-chloro compound (experiments 9–11, Table I), the ratio of *p*-chlorobenzaldehyde to benzaldehyde was roughly 1.2, whereas the ratio of benzaldehyde to *p*-methoxybenzaldehyde from the *p*-methoxy sulfide (experiments 12 and 13) was 1.3–1.4. These results are more consistent with a carbanion-type transition state (Scheme I), which the *p*-chlorophenyl group should stabilize, than with a carbonium ion type transition state (Scheme II). However, the ratios are not as large as might be expected if the side-chain oxidation occurred entirely by the proton-abstraction mechanism. Therefore, it is quite possible that there is some competition from the mechanism of Scheme II. Both the *p*-chlorophenyl and the *p*-methoxyphenyl groups should stabilize the developing carbonium ion through resonance.

Scheme II



The proton-abstraction mechanism of Scheme I could proceed by at least three different pathways, as outlined in Scheme III. Pathways 1 and 2 are analogous to the pathways suggested for amines.[1–3] These would lead to benzaldehyde and benzyl mercaptan.

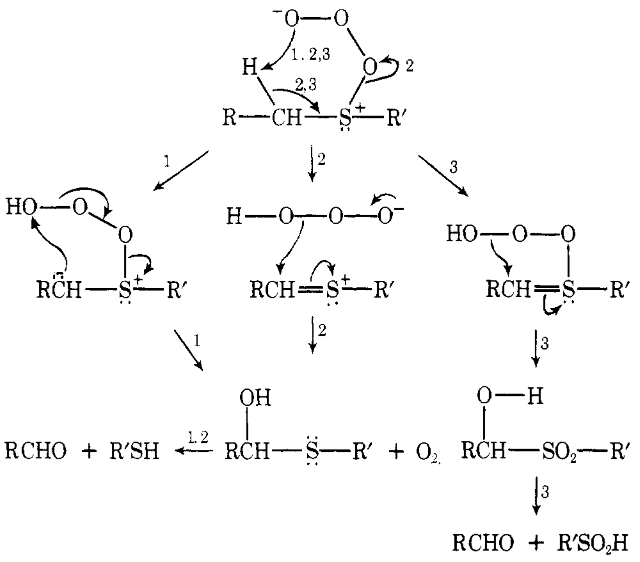
Pathway 3, which was not open to amines, would be available to sulfides because of the availability of the d orbitals of sulfur. It is analogous to the mechanism proposed by Corey and Ouannes[14] for oxidation of benzyl sulfides with singlet oxygen. It should lead to benzaldehyde and a sulfur acid (or oxygenated disulfides). We are unable to distinguish among these three pathways with the presently available data. The fact that benzyl mercaptan was not found among the products (even though it should have appeared on the column used to determine unreacted sulfide) would tend to favor pathway 3 of Scheme III. Further, the reaction mixture was acidic to litmus. On the other hand, the fact that the ratio of ozone reacting per mole of sulfide reacting was greater than 1 in the

Table II. Ozonation of Thianthrene[a]

Expt	Solvent	Temp, °C	O_3/thianthrene[a] reacting	Thianthrene recovered, %	Sulfoxide,[b] %	Cation radical
1	CH_2Cl_2[a] (40 mL)	−45	1.09	27	98	~
2	12 mL of CH_2Cl_2,[a] 50 mL of 0.5 N H_2SO_4 in HOAc	25	0.95	32	93	+[c,d]
3	20 mL of CH_2Cl_2,[a] 30 mL of CH_3OH, 15 mL of H_2SO_4	25	1.28	19	96	+[c,e]

[a] All experiments involved 2.5 mmol of thianthrene in the solvent shown, into which was passed 2.5 mmol of O_3 in a nitrogen stream. [b] The percent yield was based on thianthrene reacting (unrecovered). The total accounting was 95–99%. [c] The pink color of the cation-radical was observed as soon as ozone was passed into the solution but not before. At the end of the reaction the solution had turned yellow. [d] No EPR signal for the cation-radical before ozone was passed or after the solution turned yellow. The pink solution gave an EPR signal of five lines with $g = 2.0074$. [e] A slight EPR signal was observed before ozone was passed and after the solution turned yellow; also a strong signal while pink.

Scheme III

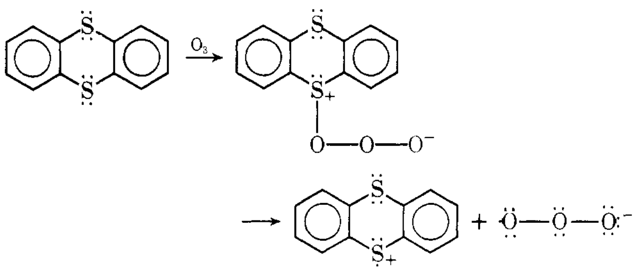


solvents which favored side-chain attack would appear to indicate that benzyl mercaptan was produced and then oxidized further by ozone. It was shown that ozonation of benzyl mercaptan does indeed give low yields of benzaldehyde. The slightly greater than 100% total for the sulfoxide and aldehyde yields found in some of these experiments also indicates this occurrence. At the present time we tend to believe that both pathway 3 and either 1 or 2 of Scheme III are occurring.

It also is of interest that with the experiments affording high sulfoxide yields, the ratio of ozone to sulfide reacting generally was less than one. A possible explanation is a competitive oxidation of the sulfide by either the ozone–sulfide adduct or the presumed singlet oxygen evolved from it (Schemes I and III). Thompson[12] showed that exposure of dimethyl sulfide to the triphenyl phosphate-ozone adduct caused oxidation of the sulfide to sulfoxide. It is not entirely certain whether the adduct itself or singlet oxygen was the oxidizing agent.[15] Singlet oxygen oxidation of dibenzyl sulfide produces benzaldehyde, along with other products.[14]

We also treated thianthrene (2) with excess ozone in a stream of nitrogen. The results are shown in Table II. The ozone to sulfide reacting ratios varied from 0.95 to 1.3. The only isolated product was the monosulfoxide in yields of 93–98%. However, when the ozonation was carried out in the presence of dilute sulfuric acid (Table II, experiment 2), the pink color of the thianthrene cation radical (EPR, five lines, $g = 2.0074$)[16] was observed. The color did not appear until ozone was passed into the solution; near the end of the ozonation the color changed to yellow. The EPR signal was observed only with the pink solution, showing that only ozone was responsible for the radical production.

Scheme IV



However, when a greater concentration of sulfuric acid was employed (experiment 3, Table II), a weak EPR signal was observed both before ozone was passed and after the solution became yellow. Strong sulfuric acid is known to produce the cation radical.[16] The ozonate anion-radical was not observed. It probably was protonated by the sulfuric acid and subsequently destroyed.

In summary, three of the reaction types observed earlier in the reactions of ozone with amines[1–4] have now been shown to occur during organic sulfide ozonations. These are sulfur oxidation, side-chain oxidation, and cation-radical formation. The latter is illustrated in Scheme IV.

Experimental Section

Materials. Dibenzyl sulfide, dibenzyl sulfoxide, and benzyl mercaptan were obtained from K and K Chemicals. **4-Methoxybenzyl chloride** was prepared by the method of Rorig et al.[17] Benzyl *p*-methoxybenzyl sulfide[18] and benzyl *p*-chlorobenzyl sulfide were synthesized by the general method of Tuleen and Marcum.[19] The corresponding sulfoxides were obtained through *N*-chlorosuccinimide oxidation of the sulfides.[20] Thianthrene monoxide was synthesized by the method of Hilditch.[21] All other materials were obtained from standard commercial sources.

General ozonation[22] and EPR[5] procedures were as described previously.

Ozonations were performed at the temperatures shown in Tables I and II with 1 mol equiv of ozone. With the benzyl sulfides the volume was reduced to 15 mL, and GLC determinations were performed. Unsymmetrical sulfoxides were determined by evaporation of the reaction mixture, purification of the crude sulfoxide by recrystallization, and comparison with known samples. The thianthrene reaction mixtures were poured into ice water and the resulting mixtures were extracted with ether. The ether extracts were dried (ca. 50 mL) and analyzed by GLC.

GLC Determinations. The aldehyde, the symmetrical sulfoxide, and the unreacted sulfide yields were determined with an Aerograph Model A-90-P_3 chromatograph using a 0.25 in. × 5 ft, 20% cyanosilicone fluid, F 1150, on a Chromosorb P, 60–80, column for the aldehyde determination (column temperature 140 °C) and a 0.25 in. × 10 ft column of 5% silicone oil on Haloport F at 190 °C for the sulfoxide and unreacted sulfide determinations. Diphenylmethane was used as an internal standard. The thianthrene and its monoxide determinations were made with a 0.25 in. × 10 ft column of diethylene glycol on adipate at 200 °C.

Acknowledgment. This work was supported by Grant F-042 from the Robert A. Welch Foundation, for which the authors are grateful. A.Y.K. was on sabbatical leave from the University of Mosul, Iraq, 1972–1973.

Registry No.—Thianthrene, 92-85-3.

References and Notes

(1) For the preceding paper in this series, see P. S. Bailey, T. P. Carter, Jr., and L. M. Southwick, *J. Org. Chem.*, **37**, 2997 (1972).
(2) P. S. Bailey, J. E. Keller, D. A. Mitchard, and H. M. White, *Adv. Chem. Ser.*, **77** (3), 58 (1968).
(3) P. S. Bailey, D. A. Mitchard, and A. Y. Khashab, *J. Org. Chem.*, **33,** 2675 (1968).
(4) P. S. Bailey and J. E. Keller, *J. Org. Chem.*, **33,** 2680 (1968).
(5) P. S. Bailey, J. E. Keller, and T. P. Carter, Jr., *J. Org. Chem.*, **35,** 2777 (1970).
(6) H. Bohme and H. Fischer, *Ber. Dtsch. Chem. Ges.*, **75,** 1310 (1942).
(7) C. C. Price and O. H. Bullitt, *J. Org. Chem.*, **12,** 238 (1947).
(8) H. Boer and F. C. Kooyman, *Anal. Chim. Acta*, **5,** 550 (1951).
(9) A. Maggiolo and E. A. Blair, *Adv. Chem. Ser.*, **21,** 200 (1959).
(10) L. Horner, H. Schaefer, and W. Ludwig, *Chem. Ber.*, **91,** 75 (1958).
(11) D. Barnard, *J. Chem. Soc.*, 4547 (1957).
(12) Q. E. Thompson, *J. Am. Chem. Soc.*, **83,** 845 (1961).
(13) J. E. Batterbee and P. S. Bailey, *J. Org. Chem.*, **32,** 3899 (1967).
(14) E. J. Corey and C. Ouannes, *Tetrahedron Lett.*, 4263 (1976).
(15) D. P. Higley and R. W. Murray, *J. Am. Chem. Soc.*, **96,** 3330 (1974).
(16) (a) G. Vincow in "Radical Ions", E. T. Kaiser and L. Kevan, Ed., Interscience, New York, N.Y., 1968, p 190; (b) H. J. Shine, C. F. Dais, and R. J. Small, *J. Org. Chem.*, **29,** 21 (1964).
(17) K. Rorig, J. D. Johnston, R. W. Hamilton, and T. J. Telinski, "Organic Syntheses", Collect. Vol. IV, Wiley, New York, N.Y., 1963, p 576.
(18) D. L. Tuleen, *J. Org. Chem.*, **32,** 4006 (1967).
(19) D. L. Tuleen and V. C. Marcum, *J. Org. Chem.*, **32,** 204 (1967).
(20) D. L. Tuleen and P. J. Smith, *J. Tenn. Acad. Sci.*, **46,** 17 (1971).
(21) T. P. Hilditch, *J. Chem. Soc.*, **97,** 2579 (1910).
(22) A. M. Reader, P. S. Bailey, and H. M. White, *J. Org. Chem.*, **30,** 784 (1965).

Synthesis of 4,5-Dicyano-2-methylthio-1,3-dithiolylium Salts: A Supposedly Impossible Alkylation

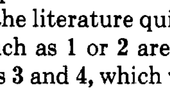
Neil F. Haley

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

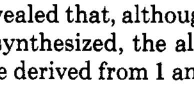
Received July 11, 1977

4,5-Dicyano-1,3-dithiol-2-thione and 4,5-dicarbomethoxy-1,3-dithiol-2-thione, two compounds that the literature states are impossible to alkylate, have been successfully alkylated with methyl fluorosulfonate in high yield. The alkylated salts undergo dye formation with both activated aromatic amines and methylene reagents.

Theoretical calculations and recent experimental data have shown quite conclusively that the C-2 carbon atom of a 1,3-dithiolylium cation is very electron deficient.[1,2] In our search for dye molecules that are easily reduced (reduction potential approaching zero), we prepared and measured the electrochemical reduction potentials of several 1,3-dithiolylium dyes. For this class of dyes (Table I) we found a range of reduction potentials of −0.9 to −0.5 V; however, a range of −0.5 to −0.2 V was desired. We therefore anticipated that placing electronegative groups such as cyano or carboxyl at the 4 and 5 positions of the dithiolylium ring would shift the reduction potentials of the corresponding dyes toward 0 V. A search of the literature quickly revealed that, although compounds such as 1 or 2 are easily synthesized, the alkylated derivatives 3 and 4, which would be derived from 1 and 2 and would be necessary for dye formation, were by normal methods "impossible to prepare by alkylation".[2] Our problem thus became the synthesis of dithiolylium salts 3 and 4.



1, R = $-CO_2CH_3$
2, R = CN-



3, R = $-CO_2CH_3$
4, R = CN-

We found that thiones 1 and 2 are alkylated rapidly and exothermally by methyl fluorosulfonate.[3] Thione 1 reacts readily in refluxing methylene chloride. However, thione 2 requires elevated temperatures for alkylation to proceed; in fact, alkylation occurs readily only in refluxing methyl fluorosulfonate (92 °C). The reaction becomes exothermic at about 90 °C and gives 4 in 96% yield within a few minutes.

4,5-Dicyano-2-methylthio-1,3-dithiolylium fluorosulfonate (4) and to a lesser extent the diester 3 react readily with nucleophilic reagents. The salts appear hygroscopic but are in fact reacting with atmosphere moisture. The 2-methylthio group is rapidly hydrolyzed, yielding 4,5-cyano- (or carbomethoxy) 1,3-dithiol-2-ones.[4] The hydrolysis of 4 can be monitored by either IR or NMR spectroscopy. The increase in absorption due to a carbonyl group at 1660 cm^{-1} in a sample of 4 in KBr is virtually complete in 30 min. Displacement of the $-SCH_3$ group in 4 by D_2O is complete within 5 min in acetonitrile/D_2O (followed by the disappearance of $^+SCH_3$ absorption and the appearance of CH_3SD in NMR).

Reactions of methylthio salts 3 and 4 with active methylene reagents yield the dithiolylium dyes shown in Table I. Dye formation proceeds readily in acetic anhydride (minimizes hydrolysis) without the necessity of added base. In fact, addition of external nitrogen bases results in either the formation of a charge-transfer complex between the dye and base (R_3N) or an addition compound (with RNH_2).[5] Apparently, the dyes (Table I) are extremely electron deficient (as indicated by their reduction potentials) and are active as electron acceptors with the nitrogen bases acting as the donors.

As expected, the dithiolylium dyes with electronegative groups in the 4 and 5 positions are more easily reduced electrochemically than the unsubstituted dyes. They exhibited reduction potentials in a range of −0.2 to −0.5 V. The increased (less negative) reduction potential was accompanied generally by a hyposochromic shift of the long-wavelength absorption maxima and a decrease in extinction coefficient.[6] It is unclear at this time whether this is a general phenomenon or a fortuitous correlation.

Experimental Section

All melting points are uncorrected. IR spectra were obtained with a Perkin-Elmer 137 spectrophotometer and NMR spectra with a Varian T-60 spectrometer using Me_4Si as an internal standard. UV

0022-3263/78/1943-0678$01.00/0