194-195 °C (lit.[12] mp 193-194 °C); ^{1}H NMR (DMSO-d_6) δ 7.55 (vinyl).

Next, 6.0 g (25 mmol) of the iodo acid was dissolved in 6 mL of acetic anhydride, cooled to 0 °C, and treated with 17.6 g 30% peracetic acid (67 mmol) at such a rate that the reaction temperature remained between 0 and 5 °C. After the addition was complete, the reaction was stirred and kept at 0 °C for 5 h. It was then allowed to warm to 25 °C overnight. A white precipitate formed and was filtered, washed with cold water, and dried under vacuum. We thus obtained 3.9 g (15 mmol, 60%) of the crude, white 5-carboxylic acid derivative of **10**-OH; mp 130-132 °C.

Decarboxylation was carried out by adding 3 g (11.6 mmol) of this material to 15 mL of water and by refluxing the mixture. Carbon dioxide was evolved, and after 15 min the solution clarified. The solution was refluxed for an additional 45 min and then cooled to afford a white precipitate. This was filtered and recrystallized twice from hot water to give 1.8 g (8.4 mmol, 72%) of shiny white needles of **10**-OH: mp 156-157 °C; IR (Fluorolube) 2400 (OH), 1630 (C=O), 1580 (C=C) cm^{-1}; ^{1}H NMR (DMSO-d_6) AB quartet centered at δ 7.4, J = 8 Hz (2 vinyl H). This material is unstable after ~5 min in DMSO. It showed >99% iodoso activity on titration.[11]

Anal. Calcd for $C_3H_3O_3I$: C, 16.8; H, 1.41; I, 59.3. Found: C, 16.8; H, 1.30; I, 59.3.

Kinetic Studies. The straightforward equipment and methods have previously been described.[8] Conditions for the determination of pH-rate profiles are described in the text (above), and the profiles for **8**-OH and **7**-OH appear in Figures 1 and 2, respectively. Conditions for the determination of rate constant-[surfactant] profiles are also described above, with the results summarized in Table I and illlustrated in Figures 3 and 4. Reactions of excess PNPDPP with **8**-OH are summarized in Table **II**. Micellar reactions were generally followed to >90% completion and showed good first-order kinetics (r > 0.999).

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Formation of Benzoxathiete under Mild Conditions and Its Valence Tautomerism in Solution to Monothio-*o*-benzoquinone: An Experimental and Quantum Chemical Study

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Abstract: Aprotic diazotization of 2-[(2-acetoxyethyl)sulfinyl]aniline in dimethoxyethane affords products that include biphenylene and dibenzo-1,4-oxathiane. Detection of these products is consistent with the formation of benzoxathiete and the valence tautomerism to monothio-*o*-benzoquinone with concomitant formation of dehydrobenzene by a competing pathway. The latter was independently trapped with 1,3-diphenylisobenzofuran and with 9,10-dimethylanthracene. The requirement for SO group participation in the formation of benzoxathiete is established by comparison with the behavior of the analogous thioether and sulfone compounds. EPR and spin-trapping experiments confirm the intermediacy of both oxygen- and nitrogen-centered free radicals which is consistent with the homolytic pathways proposed for the diazotization process. Parallel aqueous diazotization of 2-[(2-acetoxyethyl)sulfinyl]aniline affords vinyl acetate, phenol, and halobenzene consistent with the generation of dehydrobenzene but not benzoxathiete under these conditions. Spin-trapping/EPR studies gave no evidence for free-radical components in the protic diazotization reaction. Ab initio calculations using the 3-21G* and 6-31G* basis sets within the Hartree-Fock approximation, as well as the MP2/3-21G* method, predict an energetically feasible tautomerism of benzoxathiete to monothio-*o*-benzoquinone. The 3-21G* calculations reveal the presence of a biradical intermediate for this reaction which, as a singlet, features an energy higher than the benzoxathiete by 33 kcal/mol, while as the corresponding triplet it proves to be lower in energy than the benzoxathiete by 2.5 kcal/mol. This process, however, might be symmetry forbidden. By contrast, the symmetry-allowed [8s + 2s] cycloreversion pathway of benzoxathiete to dehydrobenzene and SO is energetically much less favorable.

1,2-Oxathietanes are novel hetereocycles[1-3] which, while they are of practical and theoretical interest by analogy with the more extensively studied 1,2-dioxetanes,[4] also exhibit unique chemical properties.[1-3] Thus 1,2-oxathietanes, which are isolable at moderate temperatures in organic solvents, undergo characteristic formal [σ2s + σ2a] cycloreversion[5] via a biradical species[6] to thiocarbonyl and carbonyl compounds, as well as the alternative cycloreversion to olefin and SO and, in certain cases, rearrangement via intramolecular oxygen transfer to ring-opened thioether aldehydes.[1-3] The characteristic reactions were found to be sensitive to the nature and extent of substitution. For example, aryl-substituted 2-chloroethyl sulfoxide precursors give rise to competing cyclizations to alternative 1,2-oxathietanes with concomitant vinylogous 1,4-halogen participation.[3]

1,2-Oxathietanes were originally recognized as principal intermediates in the decomposition of anticancer (2-chloroethyl)-sulfinyl nitrosoureas under physiological conditions.[1,2] (2-Halo-

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Table I. Products from Aqueous Diazotization of Substituted Aryl Alkyl Sulfoxides, Sulfones, and Thioethers at 0 °C

source		GC retn time, min			
			authentic sample	theor yield, %	*m/z* (rel intens, fragments)
3d 2-[(2-acetoxyethyl)-sulfinyl]aniline	vinyl acetate	4.7	4.7	4–9	86 (M^+, 52.3), 44 (25.7), 43 (100), 42 (30.4), 27 (18.1)
	chlorobenzene	18.6	18.6	4–6	114 ($M^+ + 2$, 32.8), 112 (M^+, 100), 77 (53.5), 51 (20.5)
	phenol	61.3	61.0	7–12	94 (M^+, 100), 66 (21.3), 65 (19.41), 51 (14.3), 40 (10.8), 39 (19.6)
3b 2-[(2-bromoethyl)-sulfinyl]aniline·HBr	vinyl bromide	1.8	1.7	2–4	108 ($M^+ + 2$, 88.3), 106 (M^+, 90.1), 81 (70.6), 79 (71.2), 28 (21.0), 27 ($M^+ - Br$, 100)
	bromobenzene	20.9	20.8	6–10	158 ($M^+ + 2$, 72.6), 156 (M^+, 75.2), 77 ($M^+ - Br$, 100), 51 (72.7)
	phenol	62.5	62.4	8–10	94 (M^+, 100), 66 (55.8), 65 (37.01), 63 (12.7), 51 (10.9), 40 (28.0), 39 (56.0), 38 (20)
3c 2-[(2-methoxyethyl)-sulfinyl]aniline	methyl vinyl ether	2.58	2.60	trace	59 (6.41), 58 (M^+, 81.9), 57 (4.1), 43 (100), 42 (20.7), 31 (1.5), 29 (4.8), 27 (14.6)
	chlorobenzene	18.5	18.6	3–6	114 ($M^+ + 2$, 32.7), 112 (M^+, 100), 77 (86.4), 51 (55.8)
	phenol	61.3	61.3	2–4	94 (100), 66 (56.7), 65 (38.1), 63 (12.7), 51 (11.4), 40 (32.1), 39 (59.2)
4d 2-[(2-acetoxyethyl)-sulfonyl]aniline	vinyl acetate	4.6	4.6	3–6	86 (M^+, 2.9), 44 (4.9), 43 (100), 42 (7.4), 27 (16.0)
	chlorobenzene	18.8	18.8	5–7	114 ($M^+ + 2$, 35.9), 112 (100), 77 (59.4), 51 (20.6)
	phenol	64.0	64.1	3–6	94 (100), 66 (23.0), 65 (18.3), 51 (4.3), 40 (9.3), 39 (18.2), 38 (6.2)
4c 2-[(2-methoxyethyl)-sulfonyl]aniline	methyl vinyl ether	2.57	2.59	trace	59 (1.1), 58 (M^+, 33.9), 57 (0.8), 43 (100), 42 (6.7), 27 (5.6)
	chlorobenzene	18.8	18.8	2–4	114 ($M^+ + 2$, 32.2), 112 (M^+, 100), 77 (49.0), 51 (16.8)
	phenol	64.0	64.0	1–2	94 (100), 66 (23.1), 65 (18.2), 63 (4.9), 51 (3.9), 40 (9.5), 39 (17.7)
4b 2-[(2-bromoethyl)-sulfonyl]aniline·HBr	vinyl bromide	1.93	1.95	1–2	108 ($M^+ + 2$, 37.5), 106 (M^+, 40.6), 81 (11.6), 79 (12.0), 28 (36.4), 27 ($M^+ - Br$, 100)
	bromobenzene	21.49	21.51	4–6	158 ($M^+ + 2$, 43.6), 156 (M^+, 45.2), 77 ($M^+ - Br$, 100), 51 (38.9)
	phenol	66.20	66.24	5–6	94 (100), 66 (34.2), 65 (24.7), 51 (5.9), 40 (12.4), 39 (28.2), 38 (9.5)
2b 2-[(2-bromoethyl)-thio]aniline·HBr	2[(2-bromoethyl)thio]-bromobenzene	22.95	23.0	5–7	298 ($M^+ + 4$, 29.9), 296 ($M^+ + 2$, 61.1), 294 (M^+, 29.9), 217 (62.5), 215 (62.7), 189 (24.6), 187 (24.2), 122 (32.1), 108 (100), 76 (5.6), 51 (5.6)
2c 2-[(2-methoxyethyl)-thio]aniline	2-[(2-methoxyethyl)thio]-chlorobenzene	23.54	23.56	4–6	204 ($M^+ + 2$, 36.0), 202 (M^+, 100), 170 (1.8), 158 (7.4), 157 (86.0), 108 (27.2), 59 (22.9), 51 (4.5)
	2-[(2-methoxyethyl)thio]-bromobenzene	23.64	23.68	4–7	248 ($M^+ + 2$, 90.3), 246 (M^+, 89.3), 216 ($M^+ + 2 - CH_3OH$, 1.6), 214 ($M^+ - CH_3OH$, 1.2), 203 (45.1), 201 (44.3), 190 (34.2), 188 (34.0), 122 (100), 108 (52.5), 59 (31.7), 51 (6.2)
2c 2-[(2-acetoxyethyl)-thio]aniline	2-[(2-acetoxyethyl)thio]-chlorobenzene	28.52	28.50	6–8	232 ($M^+ + 2$, 8.7), 230 (M^+, 23.6), 172 (36.7), 170 (100), 135 (92.8), 108 (23.8), 87 (19.1), 51 (4.0)
	2-[(2-acetoxyethyl)thio]-bromobenzene	28.57	28.55	5–7	276 ($M^+ + 2$, 35.3), 274 (M^+, 34.4), 216 ($M^+ + 2 - CH_3COOH$, 60.0), 214 ($M^+ - CH_3COOH$, 56.4), 135 (100), 123 (3.4), 122 (27.9), 108 (31.8), 51 (3.5)

ethyl)nitrosoureas (HENUs) have been shown to exert their cytotoxic effects by reacting directly with cellular DNA causing interstrand cross-links and alkylation of bases.[7] The active sulfinyl (2-chloroethyl)nitrosoureas[8] have, in addition, the capability of generating, via the intermediate 1,2-oxathietanes, reactive thiocarbonyls and reactive carbonyl compounds. We demonstrated previously, for 1,2-oxathietane and 3,4-dimethyl-1,2-oxathietane,[6] that energetically excited thiocarbonyl and carbonyl are not formed. However, the ground-state thiocarbonyls may be sufficiently reactive toward sensitive cellular targets to account for alternative cytotoxic pathways.[9] For these reasons further examination of the chemical properties of these novel and reactive heterocycles was warranted.

We next wished to examine the effects of benzene ring fusion on the reactivity of the heterocycle. Therefore we report the generation of benzoxathiete under mild conditions,[10] as well as an exploration of the chemical reactivity including valence tautomerism. Additionally, EPR and spin-trapping techniques were employed to verify the presence and identify free-radical intermediates during the aprotic diazotization reactions. Ab initio computations of energies and geometries afforded an insight into the structure and reactivity of the parent 1,2-oxathietanes.[5] Therefore we also include quantum chemical treatment of ben-

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Table II. Products from Aprotic Diazotization of Substituted Aryl Alkyl Sulfoxides and Sulfones

source	products	yield, %	mp, °C	m/z (rel intens, fragments)
3c 2-[(2-acetoxyethyl)-sulfinyl]aniline	biphenylene	trace	110	153 (12.96), 152 (100), 151 (18.58), 150 (9.68), 126 (4.71), 125 (1.06), 76 (13.25), 51 (1.40)
	dibenzo-1,4-thioxine	trace	59	200 (M^+, 100), 199 (4.70), 172 (M^+ - 28, 6.40), 168 (M^+ - 32, 24.51), 76 (0.8)
	9,10-epoxy-9,10-diphenyl-9,10-dihydroanthracene	40	189	346 (M^+, 100), 328 (23.66), 269 (33.07), 268 (35.31), 267 (4.46), 241 (38.90), 240 (13.22), 239 (42.18), 105 (95.34)
	9,10-dimethyltriptycene	36	>300	282 (M^+, 59.43), 267 ($M^+ - CH_3$, 100), 252 ($M^+ - 2CH_3$, 70.18), 126 (28.43)
3c 2-[(2-methoxyethyl)-sulfinyl]aniline	biphenylene	trace	110	153 (12.72), 152 (100), 151 (20.58), 150 (10.13), 126 (4.53), 125 (1.04), 76 (15.64), 51 (1.40)
	dibenzo-1,4-thioxine	trace	58	200 (M^+, 100), 199 (2.96), 172 (M^+ - 28, 7.77), 168 (M^+ - 32, 26.96), 51 (2.07)
	9,10-epoxy-9,10-diphenyl-9,10-dihydroanthracene	32	189	346 (M^+, 100), 328 (16.85), 269 (26.57), 268 (27.05), 267 (3.86), 241 (29.11), 240 (11.06), 239 (28.14), 105 (78.79)
	9,10-dimethyltriptycene	30	>300	282 (M^+, 63.69), 267 ($M^+ - CH_3$, 100), 252 ($M^+ - 2CH_3$, 65.01), 126 (32.47)
4d 2-[(2-acetoxyethyl)-sulfonyl]aniline	biphenylene	trace	110	153 (15.44), 152 (100), 151 (18.46), 150 (12.24), 126 (5.08), 125 (6.59), 76 (22.98), 51 (6.97)
	9,10-epoxy-9,10-diphenyl-9,10-dihydroanthracene	30	188	346 (M^+, 94.76), 328 (19.55), 269 (31.30), 268 (31.50), 267 (4.24), 241 (35.94), 240 (11.95), 239 (37.79), 238 (2.58), 105 (100), 51 (2.51)
	9,10-dimethyltripytcene	34	>300	282 (M^+, 56.43), 267 ($M^+ - CH_3$, 100), 252 ($M^+ - 2CH_3$, 72.74), 126 (23.64), 77 (1.62)
4c 2-[(2-methoxyethyl)-sulfonyl]aniline	biphenylene	trace	110	153 (12.79), 152 (100), 151 (14.45), 150 (8.55), 126 (5.39), 125 (1.08), 76 (14.17), 51 (2.02)
	9,10-epoxy-9,10-diphenyl-9,10-dihydroanthracene	25	189	346 (M^+, 76.37), 328 (14.48), 269 (24.63), 268 (25.93), 267 (5.15), 242 (7.03), 241 (32.42), 240 (9.53), 239 (31.69), 237 (5.22), 105 (100), 77 (29.77), 51 (5.65)
	9,10-dimethyltrypticene	20	>300	282 (M^+, 58.69), 267 ($M^+ - CH_3$, 100), 252 ($M^+ - 2CH_3$, 66.51), 126 (12.15), 125 (1.90)

zoxathiete and related structures to interpret their reactivity.

Synthesis of Benzoxathiete Precursors. It was considered possible that participation by an ortho sulfinyl group to an aryl diazonium center or related speices followed by elimination of a substituted vinyl fragment would generate benzoxathiete by analogy with the methods of generation of 1,2-oxathietanes.[1-3] The synthesis of 2-[(2-acetoxyethyl)thio]aniline as well as the corresponding 2-[(2-methoxyethyl)thio]- and 2-[(2-bromoethyl)thio]anilines is outlined in Scheme I. Subsequent studies indicated the need to examine the properties under diazotization of the corresponding 2-[(2-acetoxyethyl)sulfonyl]anilines so that these and related structures were prepared. Treatment of the thioethers with *m*-chloroperbenzoic acid afforded mixtures of sulfoxides and sulfones (**3**, **4**) which were separated chromatographically, or the sulfoxides were prepared from the thioethers by selective oxidation with singlet oxygen.[11]

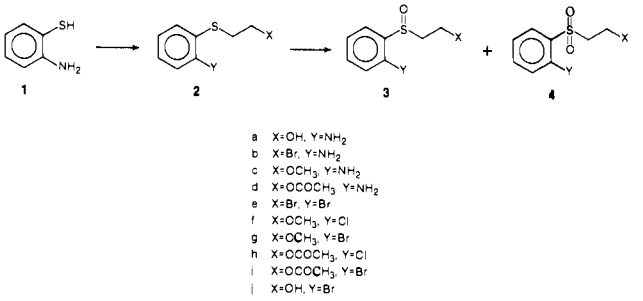
Results

Aprotic Diazotization of 2-[(X-ethyl)sulfinyl- and Sulfonyl]-anilines. Diazotization of 2-[(2-acetoxyethyl)sulfinyl]aniline (**3d**) was effected with isoamyl nitrite[12a] in dry 1,2-dimethoxyethane.[12b] The products were separated and quantified by GC and HPLC and identified by GC-MS, and by isolation, followed by comparison with authentic samples. The products are summarized in Table II and Scheme IIA. The products included biphenylene (**11**)[13b] and the dibenzo-1,4-thioxine (**10**). Addition of the reagents 1,3-diphenylisobenzofuran and 9,10-dimethylanthracene to the reaction mixture afforded the adducts of dehydrobenzene, 9,10-epoxy-9,10-diphenyl-9,10-dihydroanthracene (**12**) and the dimethyltriptycene **13**, respectively.[14a] No products corresponding to the nucleophilic attack of isoamyl alcohol at the sulfinyl group (e.g., isoamyl 2-acetoxyethanesulfinate) were detected.[14b]

Aprotic diazotization of 2-[(2-methoxyethyl)sulfinyl]aniline (**3c**) under similar conditions afforded a similar array of products and adducts. Refluxing the 2-[(2-acetoxyethyl)sulfinyl]aniline in dry DME resulted in quantitative recovery of this substance.

Treatment of 2-[(2-acetoxyethyl)sulfonyl]aniline (**4d**) under similar conditions of aprotic diazotization also afforded biphenylene (**11**).[13b] Addition of appropriate trapping agents resulted in formation of the dehydrobenzene-trapped adducts **12** and **13** (Scheme IIIA). No products corresponding to nucleophilic attack of isoamyl alcohol at the sulfone group in the intermediate arenediazo hydroxide (e.g., isoamyl 2-acetoxyethanesulfonate)

Scheme I[a]



[a] Reaction conditions: first step, $BrCH_2CH_2OCOCH_3$, or appropriate 2-bromoethyl derivative, $NaHCO_3$, H_2O–dioxane for compounds **a–d**; the preparation of compounds **e–i** used similar conditions except the *o*-halothiophenol replaced **1**; second step, *m*-CPBA, CH_2Cl_2, 0 °C, 1 h; or uv irradiation in MeOH with rose bengal and O_2 to produce **3** selectively.

(11) Oxidation of the thioether group may be effected with *m*-chloroperbenzoic acid of hydrogen peroxide, while selective photosensitized S-oxidation to the sulfinyl group with molecular oxygen in the presence of rose bengal or methylene blue is convenient for ^{18}O labeling.[1-3]

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(14) (a) Previous examples of the trapping of dehydrobenzene with anthracenes include: (a) Wittig, G.; Neithammer, K. *Chem. Ber.* **1960**, *93*, 944. (b) Wittig, G.; Harle, H.; Knauss, E.; Niethammer, K. *Chem. Ber.* **1960**, *93*, 951. (c) Side-chain nucleophilic participation in the decomposition of arenediazonium ions has been observed previously: Stiles, M.; Sisti, A. J. *J. Org. Chem.* **1961**, *26*, 3639. See also: Gilchrist, T. L.; Rees, C. W. *Carbenes, Nitrenes and Arynes*; Appleton: New York, 1969; p 48.

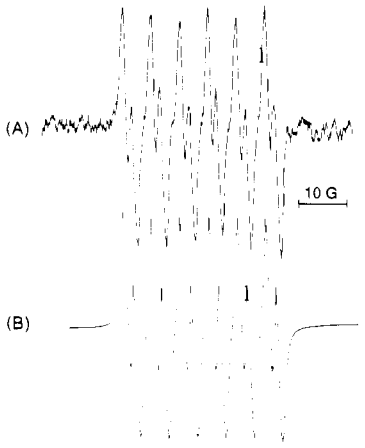


Figure 1. (A) EPR spectrum from system containing *i*-AmONO (1.3 mmol L^{-1}) and DMPO (17 mmol L^{-1}) in deaerated benzene. Experimental settings: microwave power 20 mW, modulation amplitude 1.0 G, time constant 55.5 s, scan rate 500 s, gain 10×10^5. (B) Simulated spectrum (coupling constants in Table III).

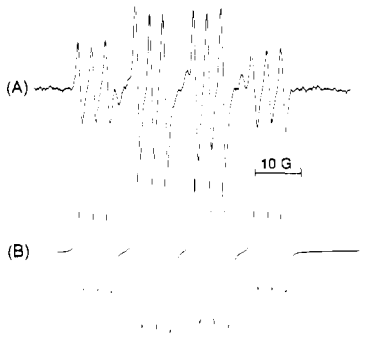


Figure 2. (A) EPR spectrum from system containing *i*-AmONO (1.3 mmol L^{-1}), **3d** (130 mmol L^{-1}), and DMPO (17 mmol L^{-1}) in deaerated benzene. [**3d**]/[*i*-AmONO] ratio = 100. Experimental settings: modulation amplitude 0.67 G, gain 3.2×10^5, others as in Figure 1A. (B) Simulated spectrum (coupling constants in Table III).

were detected.[14b] Similar aprotic diazotization of 2-[(2-methoxyethyl)sulfonyl]aniline (**4c**) afforded a similar array of products. The 2-[(2-acetoxyethyl)sulfonyl]aniline was recovered unchanged after refluxing in dry DME.

Diazotization of 2-[X-ethyl)sulfinyl- and Sulfonyl]anilines in Aqueous Media. Diazotization of the hydrohalides of **3d** with sodium nitrite in aqueous solution gives vinyl acetate, phenol (**15**), and the corresponding halobenzene **16** (either chlorobenzene or bromobenzene). Under these conditions there was no evidence for formation of **10** or **11** (Scheme IIB).[15] Aqueous diazotization of **3b** and **3c** afforded identical products except for vinyl bromide or methyl vinyl ether respectively in place of vinyl acetate. Fragmentation requires the participation of the S=O group, since diazotization of the hydrobromide of **2d** affords only **2i**. Similarly, the hydrobromides of **2b** and **2c** afford only **2e** and **2g**, respectively. Aqueous diazotization of the hydrochloride of the sulfone derivative **4d** affords vinyl acetate, phenol (**15**), and chlorobenzene **16** (Scheme IIIB). The products of these reactions are summarized in Table I.

EPR/Spin-Trapping Detection of Free-Radical Species. Possible involvement of free-radical mechanism in the diazotization reaction of the aryl alkyl sulfoxides (**3a–3d**) by the isoamyl nitrite (*i*-AmONO) was examined by employing the EPR/spin-trapping technique. Compound **3d** was selected for those experiments, and the EPR measurements were conducted in DME and benzene as solvents. Various concentrations of reactants were used, ranging from 10 to 130 mmol L^{-1} for **3d** and from 1.3 to 20 mmol L^{-1} for *i*-AmONO. It was found that the nature of radicals trapped by DMPO depended upon the concentration of the spin trap and the ratio [**3d**]/[*i*-AmONO]. This is illustrated in Figures 1A, 2A, and 3A for the samples measured in benzene and for the ratios 0 ([DMPO] = 17 mmol L^{-1}), 100 ([DMPO] = 17 mmol L^{-1}), and 0.48 ([DMPO] = 170 mmol L^{-1}, respectively.

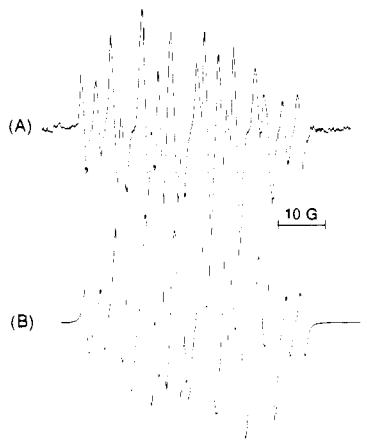


Figure 3. (A) EPR spectrum from system containing *i*-AmONO (21 mmol L^{-1}), **3d** (10 mmol L^{-1}), and DMPO (170 mmol L^{-1}) in deaerated benzene. Experimental settings: modulation amplitude 0.27 G, gain 4×10^5, others as in Figure 1A. (B) Simulated spectrum (coupling constants in Table III).

Table III. Coupling Constants for the EPR Spectra of DMPO Adducts[a]

radical trapped	a_N, G	a_H^β, G	a_H^γ, G	ΔH, G	modulatn amp, G
Ȯ—Am (benzene)	12.6	6.2	1.8	1.0	1.2
Ṅ=N—Ar (benzene)	13.75 3.3	13.8		0.8	0.2
Ṅ=N—Ar (DME)	14.05 3.0	14.25		1.0	0.5
DMPOX (H_2O)	7.1		4.1 (2×)	1.25	0.5

[a] These parameters were used to simulate the EPR spectra shown in Figures 1–3.

A control experiment (Figure 1A) shows the presence of an alkoxyl–DMPO adduct originating, most plausibly, from a thermal decomposition of the *i*-AmONO. The spectrum in Figure 2A, obtained in the presence of a large excess of **3d** over *i*-AmONO, contains almost exclusively components from a DMPO adduct of a nitrogen-centered radical showing coupling to the two nitrogens and one hydrogen atom. Identification of this and other spin-trapped radicals was achieved by a computer simulation, and the best fits were obtained by using the values of the hyperfine coupling constants given in Table III. Formation of such a radical is consistent with the mechanism outlined in Scheme IIA and it can be ascribed to Ṅ=N—Ar radical, formed by the scission of the ···N—OAm bond (**5** → **6**). The EPR spectrum of the radical could be observed for at least several hours. Figure 3A (ratio = 0.48) demonstrates the simultaneous presence of the two kinds of radicals mentioned above and is formed by a superimposition of the spectra shown in Figures 1A and 2A. Analogous experiments performed in DME as a solvent show generation of the same types of radicals as were found in benzene.[15b]

Chloride and bromide salts of **3d** and $NaNO_2$ were used to determine whether the diazotization process in aqueous solutions involves free-radical intermediates. The reactions were run in the presence of DMPO at low temperature (−5 to 0 °C). Small aliquots of the samples were taken for the EPR experiments, and the spectra were recorded at room temperature. The EPR spectrum of an oxidation product of the spin trap (DMPOX)[15c]

(15) (a) One factor that may influence the observation of different types of products from aqueous and aprotic diazotization is temperature. The former employed temperatures close to 0 °C, whereas the latter required temperatures closer to 60 °C. The latter conditions may have just sufficiently promoted the formally disallowed valence tautomerism of the high-energy **7** to permit generation and trapping of **8** to form **10**. (b) An important difference is, however, that in DME there is a significantly higher contribution of the DMPO spin adducts of oxygen-centered radicals to the EPR spectrum in comparison to the system studied in benzene. (c) Rosen, G. M.; Rauckman, E. J. *Mol. Pharmacol.* **1980**, *17*, 233.

Table IV. Energies of Benzoxathiete and Its Alternative Decomposition Products (au)[a]

species	3-21G*	6-31G*	MP2/3-21G*
benzoxathiete (7)	−698.2911	−701.8202	−699.0417
dehydrobenzene (9)	−228.0808	−229.3600	−228.6228
7a (singlet)	−698.2381		
7a (triplet)	−698.3391		
monothio-*o* benzoquinone 8	−698.2947		
^{3}SO	−470.0747	−472.3278	−470.2933
^{1}SO	−470.0094	−472.2619	

[a] Optimized geometries of these species are available upon request.

Table V. Energy Differences (kcal/mol)

	3-21G*	6-31G*	MP2/3-21G*
(a) $E_7 - [E_9 + E_{^3SO}]$ (for SO triplet)	−85.1	−83.1	−75.0
(b) $E_7 - [E_9 + E_{^1SO}]$ (for SO singlet)	−126.1	−124.4	−103
(c) $E_{7a} - E_7$	−33.3		

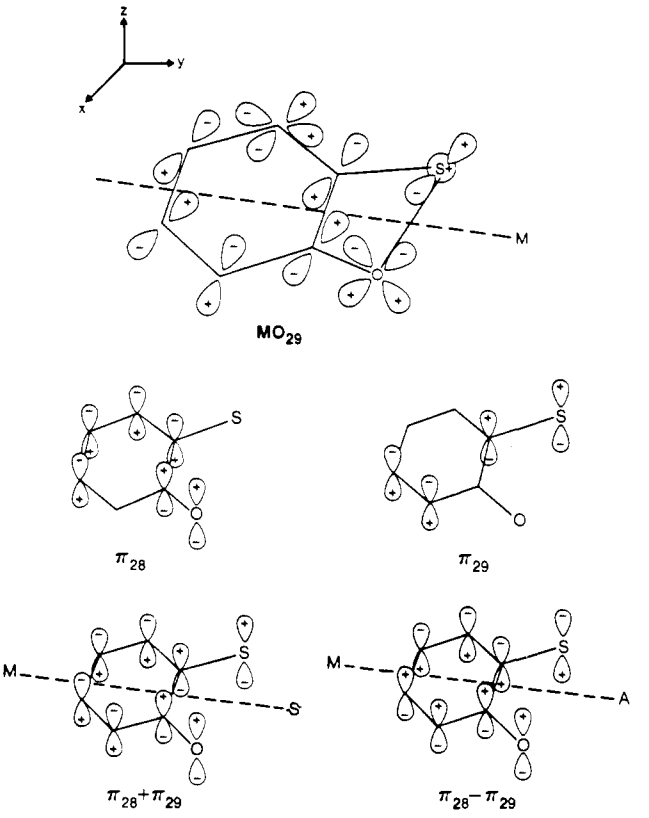
was recorded in the presence of the bromide salt of **3d** and $NaNO_2$.

Ab Initio Calculations of Optimized Geometries and Energies of Benzoxathiete and Fragmentation Products. Self-consistent field (SCF) ab initio calculations were made with full geometry optimization of the energies of benzoxathiete and its reaction products. The ab initio calculations at the Hartree–Fock level were performed on the heterocycles and subsystems with the 3-21G* Gaussian basis set, as implemented in the GAUSSIAN-82 program.[16] Calculations were also performed with the 6-31G* basis set.[17] The geometry optimization was performed by using the Berny optimization techniques.[18]

Since the heterocycle contains sulfur, the inclusion of d orbitals is particularly necessary for a good theoretical description.[19a] The optimized geometries have been used to perform the single-point MP2/3-21G* calculations in order to estimate the correlation energies of the systems and to assess their influence on the stability of the heterocycle. The Hartree–Fock energies and the MP2/3-21G* energies are shown in Table IV. The differences between the energies of benzoxathiete and its fragmentation products are shown in Table V.[19b]

It may be seen that benzoxathiete and its tautomer are very close in energy, with a difference of only 2 kcal/mol. However, structure **7a**, which is seen in Scheme IV is the transition state in the reaction **7** → **8**, is higher in energy than **7** by 33 kcal/mol. Species **7a** is the singlet biradical; so if the reaction takes place via a singlet biradical, it features an activation energy of ca. 33 kcal/mol. As seen from Table IV, the 3-21G* calculations revealed the existence of a triplet biradical form of **7a**, with a lower energy than either **7** or **8** (by ~2.5 kcal/mol). This additional stabilization of the **7a** triplet is exaggerated by the neglect of correlation energy and by the fact that there was some spin contaminant.[20] However, it can be inferred that the reaction **7** to **8** might have a low activation energy. In contrast, the combined energies of the alternative products dehydrobenzene (**9**)[21] and

Chart I[a]



[a] Orbitals of benzoxathiete relevant to a discussion of the formally disallowed thermal electrocyclic opening of the SO bond in the valence tautomerism to monothio-*o*-benzoquinone.

sulfur monoxide are much higher in energy at all levels of calculation. Experimentally, although both products **8** and **9** are formed, and may be trapped, the reaction course is almost entirely in favor of generation of dehydrobenzene. However, the above considerations of the energetics suggest that the direct cycloreversion **7** → **7b** does not contribute and that other mechanisms must be considered (q.v.).

Orbital symmetry was also considered[5] since it may influence the selection of preferred pathways. The molecular orbital containing the SO σ bond in **7** is designated MO_{29} (Chart I). It is symmetric with respect to the plane of the molecule, and it is almost symmetric with respect to the plane perpendicular to the SO bond axis. If there is a conrotatory motion (for a $k = 4q$ π electron system[5]) of the σ orbital of the SO bond to form C=S and C=O π bonds in **8**, it should correlate with the orbitals of **8** which contains these bonds. These are designated π_{28} and π_{29}, respectively (Chart I). To obtain the symmetries one takes ($\pi_{28} + \pi_{29}$) and ($\pi_{28} - \pi_{29}$) (Chart I). The first orbital is symmetric with respect to the plane M but antisymmeric with respect to the plane of the molecule. The second orbital is antisymmetric with respect to both planes. The relevant orbital transformations are

orbitals (29) of **7** → MO_{29} of **7**

orbitals of **8** → ($\pi_{28} + \pi_{29}$) and ($\pi_{28} - \pi_{29}$)

The orbital symmetry relations may be summarized as follows:

orbital	M plane	molecular plane
MO_{29} of **7**	S	S
$\pi_{28} + \pi_{29}$	S	A
$\pi_{28} - \pi_{29}$	A	A

(16) Binkley, J. S.; Frisch, M. J.; Defrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluter, E. M.; Pople, J. A. *Gaussian 82*; Carnegie Mellon University: Pittsburgh, PA, 1982; 15213.

(17) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(18) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214. SCF calculations with split valence or larger basis sets are known usually to predict accurate geometries:[18] Hehne, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *81*, 2657.

(19) (a) Goddard has compared the results of the 3-21G* basis set with those of larger basis sets and has found that the 3-21G* basis set provides a good description: Goddard, J. D. *Can. J. Chem.* **1985**, *63*, 1910. (b) Similarities also exist in the benzothiete system, which has been the subject of experimental studies (Jacob, D.; Peter-Niedermann, H.; Meier, H. *Tetrahedron Lett.* **1986**, *27*, 5703. Kanakarajan, K.; Meier, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 244. Kanakarajan, K.; Meier, H. *J. Org. Chem.* **1983**, *48*, 881. Schultz, R.; Schweig, A. *Tetrahedron Lett.* **1980**, *21*, 343) and quantum chemical treatment (Kolshorn, H.; Meier, H. *Z. Naturforsch.* **1986**, *27*, 5703. Schultz, R.; Schweig, A. *Tetrahedron Lett.* **1980**, *21*, 343).

(20) That this may be due to a spin contaminant is indicated because instead of $s^2 = 2$, $s^2 = 2.27$, which implies that quintuplet structures are contributing.

(21) The enthalpy of formation of dehydrobenzene has been calculated to be 118 ± 5 kcal/mol; Gruetzmacher, H. F.; Lohmann, J. *Justus Leibigs Ann. Chem.* **1967**, *705*, 81. CNDO/2 calculations show dehydrobenzene exists as a singlet in the ground state: Gheorghiu, M. D.; Hoffmann, R. W. *Rev. Roum. Chim.* **1969**, *14*, 947.

Attempted orbital correlation leads to the following result

benzoxathiete **7**	monothio-*o*-benzoquinone **8**
MO(S)/**7**—SS	AA—$\pi_{28} - \pi_{29}$ SA—$\pi_{28} + \pi_{29}$

No correlation exists, and therefore this transformation is predicted to be symmetry forbidden. While the valence tautomerism **7** → **8** is formally disallowed under thermal conditions, nevertheless the evidence suggests that it does contribute driven, in part, by the relief of ring strain in **7** and the high energy characteristic of **7**.

By contrast the [8s + 2s] cycloreversion **7** → **9** + SO, which is precluded on energetic grounds, is symmetry allowed.[22] It may be seen from Scheme V that the σ orbitals of the C–S and C–O bonds in benzoxathiete **7** have the same symmetry as the σ orbitals in dehydrobenzene (**9**) and SO.

Intermediate structures **7b** in the hypothetical and energetically unfavorable cycloreversion pathway **7** → **9** were also examined theoretically. The C–S and C–O bonds were progressively elongated and the resulting energies calculated:

CS = 2.0Å, CO = 1.6Å, → E = −698.2555 au

CS = 2.2Å, CO = 1.8Å, → E = −698.1865 au

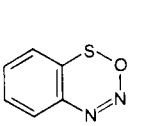
These data indicate that as the bonds in the benzoxathiete are elongated, the energy would increase progressively to that of the products without an intervening transition state.

Discussion

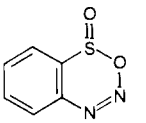
The array of products from aprotic diazotization of the sulfinylaniline **3d** indicates some deep-seated molecular rearrangements have occurred. The isolation of the dibenzo-1,4-oxathiane (**10**) require generation of the monothio-*o*-benzoquinone **8** and implies breakage of the S–O bond, followed by trapping of **8** by dehydrobenzene. Compound **8** arises from valence tautomerism of the intermediate benzoxathiete (**7**)[23,24] (vide infra), and this process provides a logical explanation for the breakage of the original S–O bond and the disposition of the S and O atoms in **10**.

The reaction of arylamines with amyl nitrite in organic solvents has been conclusively demonstrated to proceed by a free-radical mechanism.[25] Therefore the formation of **7** may be envisioned in terms of formation of species **6**. Ring closure of **6** to **6a** is conceivable,[26a] since radicals are known to add to the S=O bond[26b] and ring closure might be favored as an exo–trig process.[26c] However, the successful spin trapping of the aryldiazo radical **6** (vide supra) suggests that ring closure to **6a** would be slow, and moreover, loss of nitrogen from aryldiazo radicals has been shown to be fast.[26d]

Hydrogen atom abstraction from the side chain in the solvent cage and loss of vinyl acetate, for which there is precedent,[1-3] could lead via **6b** to **6c**. Species **6c** is a plausible precursor of dehydrobenzene (**9**) (by analogy with the reaction of benzothiadiazole 1,1-dioxide[27]) and, via species **6f**, of benzothiete (**7**). The question of the intermediacy of the benzothiirene *S*-oxide (**6g**) is moot. While there is precedent for thiirene formation from a 1,2,3-thiadiazole,[28] specific ^{2}H labeling discounted the intermediacy of the monocyclic thiirene *S*-oxide in formation of 1,2-oxathietanes.[1,2] Moreover, entropic and ring strain considerations favor the formation of **7** rather than **6g** from **6f**, and the precedent of addition of a S=O bond in DMSO[29] (or C=O bond)[24] to dehydrobenzene leads to four-membered-ring species such as a 2,2-dimethylbenzoxathiete intermediate[29] rather than the strained species analogous to **6g**. A simpler interpretation of the experimental results is formation of **6**, rapid loss of nitrogen to species **6d**, and preferred ring closure to **6e** with subsequent loss of the vinyl acetate[30] outside the solvent cage giving rise to **7**.



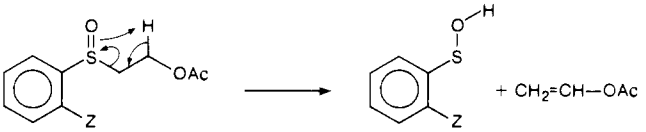
6b



18a

The requirement for participation of a sulfinyl group in the generation of the benzoxathiete is demonstrated by the rection of the thioether **2d** under aprotic diazotization conditions. The only product in that case is that of hydroxydediazoniation. Participation of the oxygen of an S=O bond to an incipient unsaturated arene center and subsequent cleavage of the S—O bond in connection with dehydrobenzene precursors has a precedent in the reaction of *o*-benzenediazonium carboxylate with dimethyl sulfoxide.[29a] An *S,S*-dimethylbenzoxathiete intermediate is implicated leading to *o*-dimethylsulfonium phenoxide ion by S–O bond clevage rather than elimination to form dehydrobenzene.

It was conceivable that the vinyl acetate and analogous vinyl derivatives could arise from **3** via a sigmatropic rearrangement[5] in the side chain. This reaction may be discounted because the



sulfinylaniline **3c** may be recovered unchanged after refluxing in dimethoxyethane. It was also conceivable but unlikely that the corresponding sulfenic acid (which would be very unstable[31]) generated by sigmatropic rearrangement in intermediates **5** or **6** might ring close to the benzoxathiete. However, it is unlikely that this would occur in the light of the result with **3c**.

The sulfone oxygens show nucleophilicity only under unusual conditions,[32] and therefore the corresponding sulfonylanilines were used as an additional test for the requirement of sulfinyl group

(22) This corresponds to the case of 8π(dehydrobenzene) + 2π(SO) = 4 q + 2, predicted to obey an $m_s + n_s$ selection rule in the ground state for (m + n) cycloadditions and cycloreversions.[5]

(23) This type of valence tautomerism has the following analogies. (a) Thiete to thioacrolein: Dittmer, D. C.; Takahashi, D.; Iwanami, M.; Tsai, A. I.; Chang, P. L.; Blidner, B. B.; Stamos, I. K. *J. Am. Chem. Soc.* **1976**, *98*, 2795. (b) Oxete to acrolein: Martino, P. C.; Shevlin, P. B. *J. Am. Chem. Soc.* **1980**, *102*, 5430. Figuera, J. M.; Shevlin, P. B.; Warley, S. D. *J. Am. Chem. Soc.* **1976**, *98*, 3820. Friedrich, L. E.; Bower, J. D. *J. Am. Chem. Soc.* **1973**, *95*, 6869. Friedrich, L. E.; Schuster, G. B. *J. Am. Chem. Soc.* **1971**, *93*, 4602. (c) 1,2-Dithiete to α-dithione: Kusters, W.; de Mayo, P.; Weedon, A. C. *Nouv. J. Chim.* **1978**, *2*, 331. (d) 1-Azetine to 2-azabutadiene: Guillemin, J. C.; Denis, J. M.; Lablache-Combier, A. *J. Am. Chem. Soc.* **1981**, *103*, 468. (e) Dimethyl Δ^3-1,2-diazetine-1,2-dicarboxylate: Nunn, E. E.; Warrener, R. N. *J. Chem. Soc., Chem. Commun.* **1972**, 818.

(24) Another analogy for the proposed ring closure to **7**, followed by valence tautomerism, is afforded by the decomposition of benzenediazonium carboxylate. In that case, participation to the incipient arenium center gives benzoxetone which is in tautomeric equilibrium with *o*-quinone methide ketene: Hoffmann, R. W.; Sieber, W.; Guhn, G. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 704. Gompper, R.; Seybold, G.; Schmolke, B. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 389.

(25) (a) Friedmann, L.; Chlebowski, J. F. *J. Org. Chem.* **1968**, *33*, 1633. (b) Bunnett, J. F.; Takayama, H. *J. Org. Chem.* **1968**, *33*, 1924. (c) Broxton, T. J.; Mcleish, M. J. *Aust. J. Chem.* **1983**, *36*, 1031. Broxton, T. J.; Mcleish, M. J. *J. Org. Chem.* **1983**, *48*, 191. (d) Fukunishi, K.; Hira, J.; Yamanaka, H.; Nomura, M.; Kojo, S. *J. Chem. Soc., Perkin Trans. 1* **1985**, 991.

(26) (a) This mechanism was suggested by one of the reviewers: (b) Taniguchi, H.; Takagi, H.; Hatano, H. *J. Phys. Chem.* **1972**, *76*, 135. (c) Beckwith, A. L. J.; Easton, C. J.; Serelis, A. K. *J. Chem. Soc., Chem. Commun.* **1980**, 482. (d) Brede, O.; Mehnert, R.; Naumann, N.; Becker, H. G. O. *Ber. Bunsenges. Phys. Chem.* **1980**, *84*, 666. The rate of decomposition of an alkoxy-substituted arenediazo radical is 34 × 10^5 s^{-1} at 20 °C. The decomposition of **3** was carried out at 60–70 °C.

(27) Wittig, G.; Hoffmann, R. W. *Org. Synth.* **1967**, *47*, 4.

(28) Torres, M.; Strausz, O. P. *Nouv. J. Chim.* **1980**, *4*, 703.

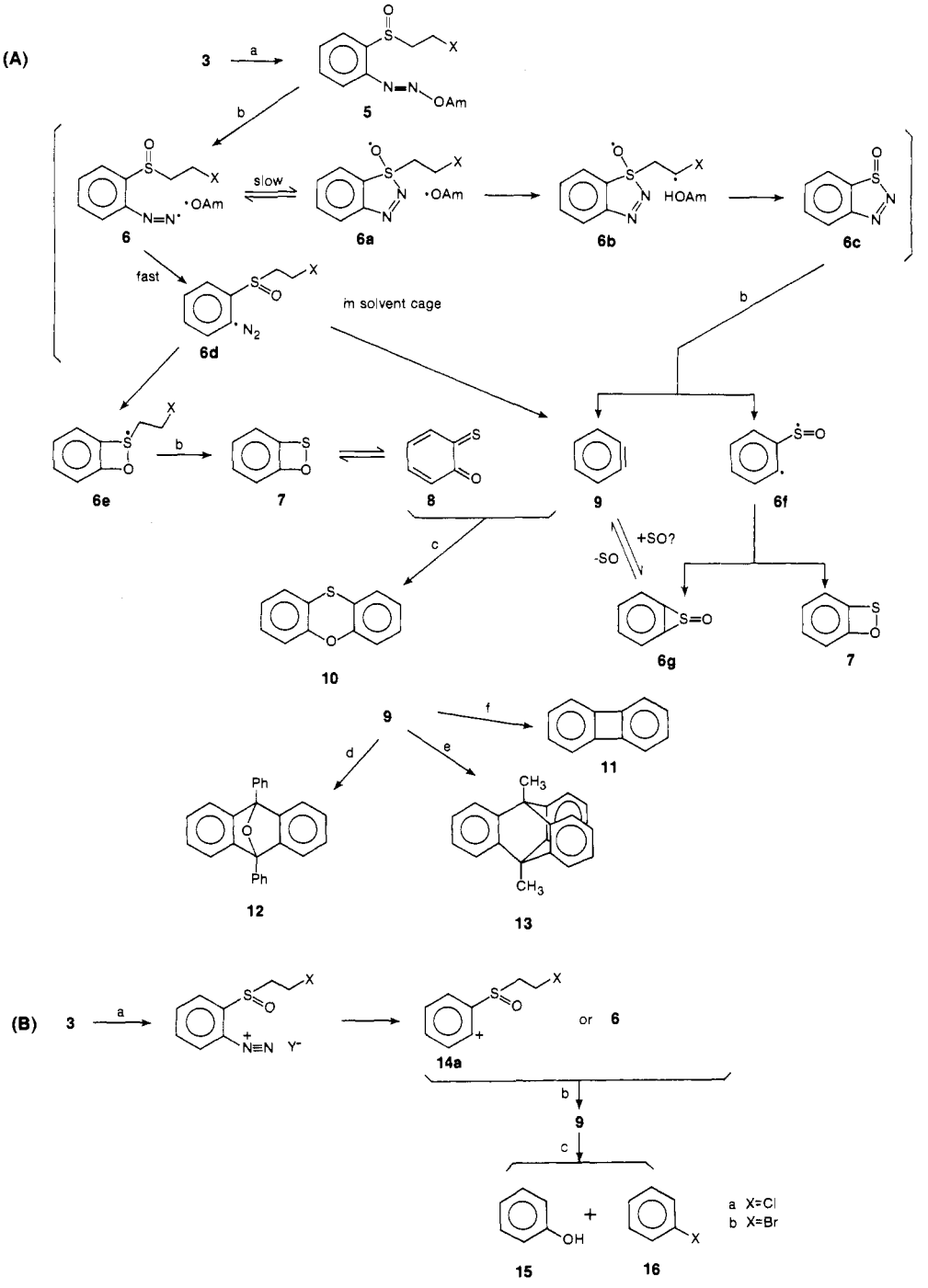
(29) Szmant, H. H.; Vazquez, S. *Chem. Ind. (London)* **1967**, *276*, 1000. Gompper, R.; Kutter, E.; Seybold, G. *Chem. Ber.* **1968**, *101*, 2340.

(30) The fact that vinyl acetate is observed only under the ionic conditions prevailing in aqueous conditions is in accord with its polymerization under the free-radical conditions demonstrated to exist during aprotic diazotization.[25]

(31) Allinger, N. L.; Cava, M. P.; de Jongh, D. C.; Johnson, D. R.; Lebel, N. A.; Stevens, C. L. *Organic Chemistry*, 2nd ed.; Worth: New York, 1976; p 801.

(32) (a) Cometero, J. C.; Garcia Ruano, J. L.; Martinez, M. C.; Rodriguez, J. H. *Tetrahedron Lett.* **1987**, *43*, 4417. (b) Chalkley, G. R.; Snodin, D. J.; Stevens, G.; Whiting, M. C. *J. Chem. Soc. C* **1970**, 682.

Scheme II[a]

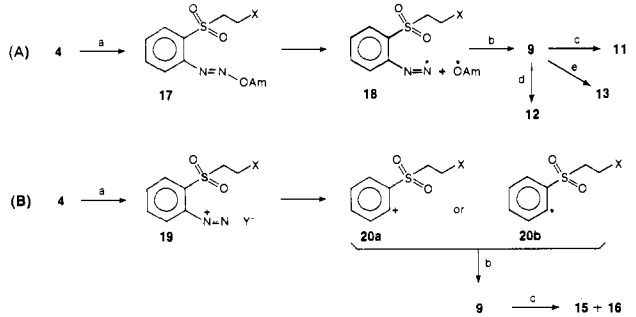


[a] Products and alternative pathways of diazothization of 2-[(2-acetoxyethyl)sulfinyl]- and related anilines under (A) aprotic conditions (B) aqueous conditions. Reaction conditions: A (a) isoamyl nitrite, DME, 60–70 °C; (b) spontaneous; (c) spontaneous dimerization; (d) 1,3-diphenylisobenzofuran, DME; (e) 9,10-dimethylanthracene, DME; (f) spontaneous dimerization. B (a) $NaNO_2$, HCl or HBr, H_2O, CH_2Cl_2, −5 to 0 °C; (b) spontaneous; (c) H_2O or HX.

participation in the generation of the benzoxathiete (**7**). In the event aprotic diazotization of **4d** gave vinyl acetate and biphenylene (**11**) as well as adducts **12** and **13**, confirming the intermediacy of dehydrobenzene. However, there was no evidence of products corresponding to either benzoxathiete *S*-oxide (by analogy with benzoxetone[24]) or its putative valence tautomer in accord with the reduced nucleophilicity of the SO_2 compared with SO.[32] The fact that **4d** may be recovered unchanged from refluxing DME suggests that, as in the case of **3d**, a sigmatropic rearrangement involving the sulfonyl group does not account for the elimination of vinyl acetate. These results with the thioethers **2** and the sulfones **4** strongly imply direct participation of the sulfinyl group in **6** or a related species in the generation of benzoxathiete (**7**).

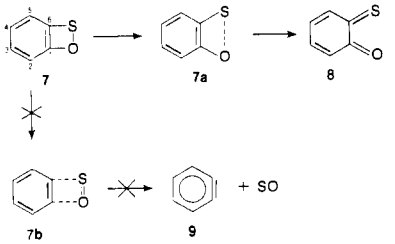
Although the benzoxathiete (**7**) is an obligatory intermediate in the formation of **8** and **10**, it seemed an unlikely precursor for the generation of the major product dehydrobenzene (**9**). The fact that no products corresponding to the existence of the valence tautomers of benzoxathiete *S*-oxide were identified from the sulfonyl precursors **4** strongly suggests that the generation of dehydrobenzene, at least from **4**, is independent of any ring closure to the benzoxathiete. This is because, although the formal [8s + 2s] cycloreversion[5] with elimination of SO is formally allowed from orbital symmetry considerations, it is most unfavorable energetically (vide supra). This result was not unexpected on other grounds. Thus there is no evidence from mass spectrometry for loss of SO from the daughter ions assigned to benzoxathiete in

Scheme III[a]



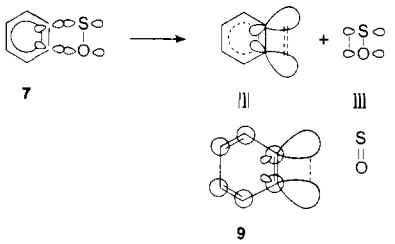
[a] Pathways and products of diazotization of 2-[(2-acetoxyethyl)-sulfonyl]- and related anilines under (A) aprotic conditions or (B) aqueous conditions. Reaction conditions: A (a) isoamyl nitrite, DME, 60–70 °C; (b) spontaneous; (c) spontaneous dimerization; (d) 1,3-diphenylisobenzofuran, DME; (e) 9,10-dimethylanthracene, DME. B (a) $NaNO_2$, HCl or HBr, H_2O, CH_2Cl_2, 5–0 °C; (b) spontaneous; (c) H_2O or HX.

Scheme IV[a]



[a] Alternative pathways of reaction of benzoxathiete: valence tautomerism and cycloreversion.

Scheme V[a]



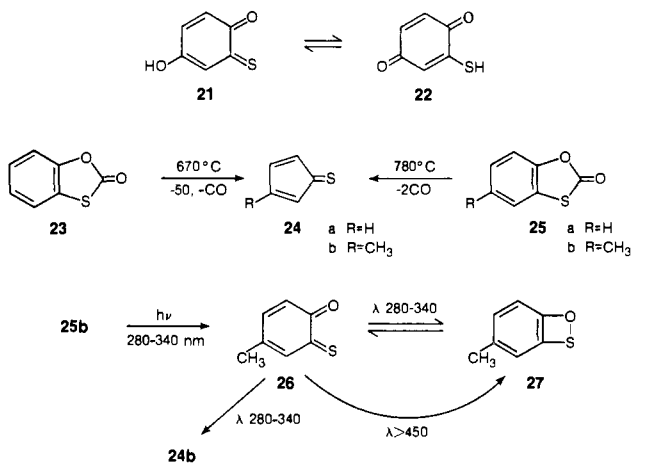
[a] Depiction of the thermally allowed cycloreversion of benzoxathiete to dehydrobenzene and sulfur monoxide.

the valence tautomer **8**.[10d] A more likely precursor of **9** is species **6d**.

A possible alternative pathway involving attack of a nucleophile (i.e., isoamyl alcohol released during the aprotic diazotization) at the sulfur atom in the intermediate arenediazo hydroxides **5** or **17** may be discounted since neither of the anticipated products, isoamyl 2-acetoxyethanesulfinate[33] nor isoamyl 2-acetoxyethanesulfonate, respectively, were isolated. Instead, the side-chain moiety appears only as a vinyl derivative (acetate, methyl ether, or bromide).

The fact that equally facile elimination to a vinyl derivative occurs when X = $OCOCH_3$, OCH_3, or Br implies that the intermediate involved is not cationic.[34a] The understanding of the dediazoniation process is complicated by the fact that its mechanism is not unique but quite dependent on the reaction conditions.[25,35a-e] Dediazoniation can occur by both ionic and free-radical pathways.[25,34a-e] However, amyl arenediazoates **5** (the initial species generated by aprotic diazotization), are known to be prone to free-radical cleavage.[25a]

Scheme VI[a]



[a] Schematic depiction of previous approaches to the generation of benzoxathiete or its valence tautomer under pyrolytic or photolytic conditions.

The results of the EPR/spin trapping experiments confirm the susceptibility of aprotic diazotization by alkyl nitrites to give rise to free-radical species.[25] Spin-trapping experiments conducted with **3d** and *i*-AmONO in the presence of DMPO in DME and benzene at room temperature give rise to adducts of both nitrogen- and oxygen-centered radicals consistent with the reactions outlined of Scheme IIA. The nitrogen-centered radical, Ar—N=Ṅ, detected in this work corresponds to a transient intermediate,[26d] preceding formation of an aryl radical, and was invoked in the dediazoniation schemes proposed in the past by other authors.[25,26d] It is likely that analogous radicals are generated upon diazotization of aryl thioethers **2** and aryl sulfones **4** in organic solvents.

The situation with diazotization in protic media is perhaps less clear since arenediazonium halides may apparently give rise to ionic species as well as aryl radicals by electron-transfer processes.[25,28] For example, simple halide counterions (Cl^- and Br^-) seem to favor a decomposition of the diazonium compound via a radical mechanism,[34a] whereas dediazoniation of diazonium tetrahalogenoborates favor cationic intermediates.[34c] The factors that might cause the different reactivity of the halogen ions are the electronegativity and strength of the hydration shell as well as the increasing polarizability and nucleophilicity.[34d] In the present cases, EPR/spin-trapping experiments provided no evidence for the intermediacy of free radicals associated with the reactions of the aryl sulfinyl amines upon aqueous diazotization. But again the mechanism of the dediazoniation in protic media depends on the substituent on the aromatic ring, the atmosphere (N_2 or O_2), and pH. Recently it has been demonstrated that the dediazoniation of substituted benzenediazonium ions is accelerated by β-cyclodextrin and proceeds via a radical pathway irrespective of the nature of the substituent or the atmosphere in aqueous solution.[25d]

Interest has been shown previously in the chemistry of oxathietes and benzoxathiete.[10] α-Keto thiones, on spectroscopic evidence, exist as such, and attempts to demonstrate the generation from them, and existence, of oxathietes have been unsuccessful.[10a,b] Photolysis of the benzoxathiolone **25c** (R = OH) eliminates carbon monoxide to give a mixture of tautomers **21** and **22** (Scheme VI).[10c] Presumably the presence of the hydroxyl substituent biases the equilibrium in favor of **22** and perhaps precludes formation of the benzoxathiete. Photolysis of the benzoxathiolone **25b** in ethyl vinyl ether afforded an adduct.[10d] One possible interpretation of this result was formation of the monothio-*o*-benzoquinone **26** and trapping of the latter via a Diels–Alder reaction with the solvent, although the authors state that alternative pathways are possible.[10d] For example, formation of the adduct could involve addition of vinyl ether to a photoexcited form of **25b** or via the biradical species. Attempts to distinguish these mechanisms by

(33) Although sulfenic acids are generally unstable, their esters are sufficiently stable to permit isolation.[31]

(34) (a) Meyer, G.-J.; Rossler, K.; Stocklin, G. *J. Am. Chem. Soc.* **1979**, *101*, 3121. (b) Hey, D. H.; Jones, G. H.; Perkins, M. J. *J. Chem. Soc., Chem. Commun.* **1970**, 1438. (c) Olah, G. A.; Tolgyesi, W. S. *J. Org. Chem.* **1961**, *26*, 2053. (d) Cohen, T.; Dietz, A. G.; Miser, J. R. *J. Org. Chem.* **1977**, *42*, 2053. (e) Zollinger, H. *Azo and Diazo Chemistry*; Interscience: New York, 1961. Zollinger, H. *Acc. Chem. Res.* **1973**, *6*, 335.

photochemical generation of **26** or **27** in an inert matrix at 77 K and subsequent dark addition of vinyl ether were unsuccessful.[10d] However, irradiation of **25b** in an alcohol glass at 77 K gave spectroscopic evidence for the existence and photoinduced valence tautomerism of species **26** and **27**. This work suggested that there was no dark cycloreversion of the benzoxathiete to the monothio-*o*-benzoquinone under low-temperature conditions. This is in accord with the conclusions reached in the present study that this process is symmetry forbidden and could only be observed at higher temperatures. The conditions employed (i.e., concentrations of $\sim 10^{-4}$ M in glasses at 77 K) precluded the isolation of adducts.

The only other reported attempt to generate these species employed extremes of temperature in the other direction. Thus, pyrolysis of 1,2,3-benzoxadithiol 2-oxide (**23a**) or benzoxathiolone **25a** affords cyclopentadienethione which was assumed to proceed via the monothiobenzoquinone **8**.[10e]

The extremes of temperature employed hitherto (77–780 K) perhaps explain why the benzoxathiete has proven so elusive. Thus, the high-temperature conditions[10e] would preclude the detection of the higher energy benzoxathiete valence tautomer **7**. On the other hand, the photolytic conditions employed in the glasses at low temperature[10d] favor the photochemically allowed valence tautomerism between the monothio-*o*-benzoquinone **8** and the benzoxathiete (**7**). In fact the authors assumed no dark cycloreversion **7** → **8**. Thus, the present method of generation of benzoxathiete under relatively mild conditions complements the conditions employed hitherto and serves to extend the known chemistry of this novel heterocycle.

Experimental Section

Melting points were determined on a Fisher-Johns apparatus and are uncorrected. The IR spectra were recorded on a Nicolet 7199 FT spectrophotometer, and only the principal sharply defined peaks are reported. The NMR spectra were recorded on a Varian HA-100 or Bruker WH-200 or WH-400 spectrometer. The spectra were recorded on approximately 5–15% (w/v) solutions, depending upon the spectrometers, in appropriate deuteriated solvents with tetramethylsilane as internal standard. EI mass spectra were determined on an Associated Electrical Industries (AEI) MS-9 double-focusing high-resolution mass spectrometer with ionization energies at 70 eV. Peak measurements were made by comparison with perfluorotributylamine at a resolving power of 15000 on an AEI-MS-50 mass spectrometer. GC analyses were performed on a Hewlett-Packard 5840A analytical gas chromatograph equipped with a flame-ionization detector. GC/MS analyses were performed on an AEI-MS-12 spectrometer. Samples were injected onto a 6-ft, 10% Carbowax 20M 80-100 WAW-DMCS 5830 column with helium flow rate of 20 mL/min. The column was heated at 60 °C for 20 min and was heated further at a rate of 10 °C/min up to 150 °C for 1 h.

2-[(2-Acetoxyethyl)thio]aniline (2d). To a stirred solution of 2-aminothiophenol (**1**; 6.25 g, 50 mmol) in 1:1 water–dioxane (200 mL) was added sodium bicarbonate (12.65 g, 150 mmol). The reaction mixture was stirred for 1 h, to this was then added 2-bromoethyl acetate (16.79 g, 100 mmol), and the mixture was stirred for 48 h. The mixture was diluted with dichloromethane (200 mL) and filtered through Celite. The solvents were removed in vacuo, and the evaporation was repeated following addition of dichloromethane (3 × 100 mL) affording 2-[(2-acetoxyethyl)thio]aniline (**2d**) as a pale yellow oil. The residual heavy yellow oil was distilled [140 °C (0.5 mmHg)] to obtain the pure product: 9.5 g (90% yield); ^{1}H NMR ($CDCl_3$) δ 2.00 (s, 3 H, $OC(O)CH_3$), 2.9–3.0 (t, 2 H, SCH_2, J = 6 Hz), 4.1–4.2 (t, 2 H, $CH_2OC(O)$, J = 6 Hz), 4.4 (br s, 2 H, exch NH_2), 6.7–7.4 (m, 4 H, Ph); IR (Nujol) ν_{max} 3360 (NH_2), 1757 cm^{-1} ($OC(O)CH_3$); MS, m/z (rel intens) 211 (M^+, 58.55), 151 ($M^+ - CH_3COOH$, 18.48), 136 (46.38), 124 (46.30), 92 (3.37), 87 (100), 80 (29.61).

2-[(2-Acetoxy)sulfinyl]aniline (3d) and 2-[(2-Acetoxyethyl)sulfonyl]aniline (4d). To a stirred solution of (4.22 g, 20 mmol) of 2-[(2-acetoxyethyl)thio]aniline (**2d**) in dry dichloromethane (50 mL) at 0 °C was added dropwise over a period of 25–30 min a solution of *m*-chloroperbenzoic acid (4.66 g, 27 mmol) in dry of dichloromethane (50 mL). The resulting solution was stirred at 0 °C for 2 h. The mixture was washed successively with 10% solution of KI, 10% solution of sodium thiosulfate, saturated solution of sodium bicarbonate, and sodium chloride solution. Drying of the methylene chloride solution (Na_2SO_4) followed by solvent removal under vacuum gave the crude product which was purified by column chromatography [silica gel, ethyl acetate–hexane (2:1)] to afford first 2-[(2-acetoxyethyl)sulfone]aniline (**4d**): 1 g (20% yield); mp 69–71 °C; ^{1}H NMR ($CDCl_3$) δ 1.85 (s, 3 H, $OC(O)CH_3$), 3.45–3.55 (t, 2 H, $S(O)_2CH_2$, J = 6 Hz), 4.3–4.4 (t, 2 H, $CH_2OC(O)$, J = 6 Hz), 5.0 (br s, 2 H, exch NH_2), 6.7–7.7 (m, 4 H, Ph); MS, m/z (rel intens) 243 (M^+, 22.47), 201 (2.51), 183 ($M^+ - CH_3COOH$, 5.80), 156 (3.33), 140 (3.21), 93 (100), 92 (33.6), 65 (26.40).

Further elution with ethyl acetate–hexane (3:1) afforded 2-[(2-acetoxyethyl)sulfinyl]aniline (**3d**): 3.0 g (66% yield) as a heavy brown oil; ^{1}H NMR ($CDCl_3$) δ 2.0 (s, 3 H, $OC(O)CH_3$), 3.2–3.65 (m, 2 H, $S(O)CH_2$), 4.2–4.5 (m, 2 H, CH_2,$OC(O)$), 5.1 (br s, 2 H, exch NH_2), 6.7–7.3 (m, 4 H, Ph); MS, m/z (rel intens) 227 (M^+, 10.58), 167 ($M^+ - CH_3COOH$, 2.33), 140 (100), 92 (6.82), 87 (70.86), 65 (1.37).

2-[(2-Methoxyethyl)thio]aniline (2c). Sodium bicarbonate (2.52 g, 30 mmol) was added to a stirred soltuion of 2-aminothiphenol (**1**; 1.25 g 10 mmol) in 1:1 water–dioxane (20 mL). The resulting solution was stirred for 2 h and then a solution of freshly distilled 2-chloroethyl methyl ether (1.88 g, 20 mmol) was added. The reaction mixture was stirred for 48 h. The solvent and the excess of reagent were removed under vacuum, the residue was taken up in dichloromethane (100 mL), and the solution was filtered under Celite. The solvent was removed in vacuo and the residue subjected to column chromatography (silica gel, hexane with 20% ethyl acetate) afforded 2-[(2-methoxyethyl)thio]aniline (**2c**: 1.6 g (87% yield) as an oil; ^{1}H NMR ($CDCl_3$) δ 2.8–2.9 (t, 2 H, SCH_2, J = 6 Hz), 3.3 (s, 3 H, OCH_3), 3.4–3.5 (t, 2 H, CH_2O, J = 6 Hz), 4.4 (br s, 2 H, exch NH_2), 6.7–7.4 (m, 4 H, Ph); IR (Nujol) ν_{max} 3440 and 3320 cm^{-1} (HH_2); MS, m/z (rel intens) 183 (M^+3, 82.48)8 151 (M^+ – MeOH, 18.3)8 136 (41.19), 125 (100), 124 (32.54), 92 (3.65), 80 (31.39), 59 (18.08), 58 (1.04), 51 (2.70).

2-[(2-Methoxyethyl)sulfinyl]aniline (3c) and 2-[(2-Methoxyethyl)-sulfonyl]aniline (4c). A solution of *m*-chloroperbenzoic acid (9.32 g, 54 mmol) in dry dichloromethane (100 mL) was added dropwise over a period of 30-40 min to a cold (0 °C) and stirred solution of 2-[(2-methoxyethyl)thio]aniline (**2c**; 7.32 g, 40 mmol) in dry dichloromethane (100 mL). The reaction mixture was stirred at 0 °C for 1 h and washed successively with 10% solution of KI, 10% solution of sodium thiosulfate, saturated solution of sodium bicarbonate, and sodium chloride solution. The solvent was removed under vacuum, and the residue upon column chromatography [silica gel, hexane–ethyl acetate (2:1)] afforded pure 2-[(2-methoxyethyl)sulfonyl]aniline (**4c**): 2.5 g (29% yield) as an oil; ^{1}H NMR ($CDCl_3$) δ 3.2 (s, 3 H, OCH_3), 3.3–3.4 (t, 2 H, $S(O)_2CH_2$, J = 6 Hz), 3.6–3.7 (t, 2 H, CH_2O, J = 6 Hz), 5.1 (br s, 2 H, exch NH_2), 6.7–7.6 (m, 4 H, Ph); IR (Nujol) ν_{max} 3480 and 3360 cm^{-1} (NH_2); MS, m/z (rel intens) 215 (M^+, 27.45), 157 (13.14), 93 (100), 92 (16.31), 80 (1.38) 65 (13.79), 59 (11.56).

Further elution with [ethyl acetate–hexane (2:1)] afforded pure 2-[2-methoxyethyl)sulfinyl]aniline (**3c**): 5.1 g (64% yield) as a heavy oil; ^{1}H NMR ($CDCl_3$) δ 3.05–3.25 (m, 1 H, O=SCH), 3.35 (s, 3 H, OCH_3), 3.55–3.65 (m, 2 H, CH_2O), 3.75–3.85 (m, 1 H, O=SCH), 5.15 (br s, 2 H, exch NH_2), 6.7(–)7.4 (m, 4 H, Ph); IR (Nujol) ν_{max} 3420 and 3320 cm^{-1} (NH_2), 1115 (S=O); MS, m/z (rel intens) 199 (M^+, 33.12), 183 (1.12), 182 (1.89), 167 ($M^+ - CH_3OH$, 1.80), 154 (2.70), 140 (100), 124 (6.09), 123 (7.67), 92 (4.74), 65 (12.85), 51 (1.45).

2-[(2-Hydroxyethyl)thio]aniline (2a). To a stirred solution of sodium bicarbonate (12.6 g, 150 mmol) in water (100 mL) was added a solution of 2-aminothiophenol (6.25 g, 50 mmol) in dioxane (100 mL). The reaction mixture was stirred for 1 h, then 2-chloroethanol (8 g, 100 mmol) was added, and stirring was continued for 48 h. The mixture was diluted with dichloromethane (100 mL), and the solution was filtered through Celite. The solvent and excess of the reagent were removed in vacuo, and the residual solid was purified by column chromatography [(silica gel, hexane with 30% ethyl acetate)] to afford 2-[(2-hydroxyethyl)thio]aniline (**2a**): 7.1 g (84% yield); mp 32–35 °C; ^{1}H NMR ($CDCl_3$) δ 2.75–2.85 (t, 2 H, SCH_2, J = 6 Hz), 3.0 (br s, 1 H, exch OH), 3.5–3.6 (t, 2 H, CH_2O, J = 6 Hz), 4.45 (br s, 2 H, exch NH_2), 6.7–7.5 (m, 4 H, Ph); MS, m/z (rel intens) 169 (M^+, 100), 151 ($M^+ - H_2O$, 13.99), 150 (5.53), 138 (12.20) 136 (47.03), 125 (75.21), 124 (53.69), 94 (44.87), 80 (39.46), 77 (6.09), 65 (16.84), 53 (9.05).

2-[(2-Hydroxyethyl)sulfinyl]aniline (3a) and 2-[(2-Hydroxyethyl)-sulfonyl]aniline (4a). To a stirred solution of (3.38 g, 20 mmol) of 2-[(2-hydroxyethyl)thio]aniline (**2a**) in dichloromethane (50 mL) at –5 to 0 °C was added over a period of 35–40 min a cold solution of *m*-chloroperbenzoic acid (4.66 g, 27 mmol) in dichloromethane (50 mL). The reaction mixture was stirred at 0 °C for 2 h and then washed successively with 15% aqueous KI, 10–15% aqueous sodium thiosulfate, saturated aqueous sodium bicarbonate, and sodium chloride solution. Drying of the dichloromethane solution ($MgSO_4$) followed by solvent removal under vacuum gave the product which was purified by column chromatography (silica gel, ethyl acetate) to afford first 2-[(2-hydroxyethyl)sulfonyl]aniline (**4a**): 1.1 g (27% yield) as a heavy, light yellow oil; ^{1}H NMR ($CDCl_3$) δ 3.4–3.5 (t, 2 H, $S(O)_2CH_2$, J = 6 Hz), 4.0–4.5

(t, 2 H, CH_2O, J = 6 Hz), 4.8 (br s, 3 H, exch OH and NH_2), 6.8–7.8 (m, 4 H, Ph); MS, m/z (rel intens) 201 (M^+, 7.18), 156 (100)8 93 (25.67), 92 (7.89), 88 (21.63), 77 (6.91), 76 (5.94), 75 (2.20).

Further elution (ethyl acetate with 5% methyl alcohol) afforded 2-[(2-hydroxyethyl)sulfinyl]aniline (**3a**): 2.5 g (67.5% yield); mp 88–90 °C; ^1H NMR (Me_2SO-d_6) δ 2.95–3.15 (m, 2 H, O=SCH_2), 3.6–3.8 (m, 2 H, CH_2O), 5.0 (br s, 1 H exch OH), 5.7 (br s, 2 H, exch NH_2), 6.7–7.3 (m, 4 H, Ph), MS, m/z (rel intens) 185 (M^+, 28.25), 141 (13.39), 140 (100), 124 (5.63), 92 (5.72), 91 (3.55), 80 (7.60), 65 (15.34).

2-[(2-Bromoethyl)sulfinyl]aniline Hydrobromide (3b). A solution of freshly distilled thionyl bromide (2.07 g, 10 mmol) in dry dichloromethane (10 mL) was added to a stirred solution of 2-[(2-hydroxyethyl)sulfinyl]aniline (**3a**; 0.925 g, 5 mmol) in dry dichloromethane (30 mL) at −5 to 0 °C. After a further 2 h at 0 °C, the mixture was stirred at ambient temperature for 12 h and then the reaction mixture was refluxed for 45 minutes. The solvent and excess of thionyl bromide were removed in vacuo. Dichloromethane (40 mL) was added, the resulting precipitate was collected and washed with dry dichloromethane to remove traces of thionyl bromide, and the crude material was recrystallized from a $CHCl_3$–MeOH mixture to provide pure bromo compound **3b** as a white crystalline solid: 1.2 g (73% yield); mp 173–175 °C; ^1H NMR (Me_2SO-d_6) δ 2.90–3.30 (m, 2 H, O=SCH_2), 3.4–3.8 (m, 2 H, CH_2Br), 6.9–7.7 (m, 4 H, Ph), 7.8 (br s, 3 H, exch $NH_3^+Br^-$); IR (Nujol) ν_{max} 2840 cm^{-1} ($NH_3^+Br^-$); CIMS (NH_3) m/z (rel intens) 250 [(M^+H + 2) − HBr, 2.8], 248 (M^+H − HBr, 2.8), 232 (18.2), 230 (19.0), 169 (1.5), 152 (100), 123 (1.5). Anal. Calcd for $C_8H_{11}NOSBr_2$: C, 29.3; H, 3.0; N, 4.2. Found: C, 28.9; H, 3.0; N, 3.9.

2-[(2-Bromoethyl)thio]aniline Hydrobromide (2b). A stirred solution of 2-[(2-hydroxyethyl)thio]aniline (**2a**; 0.84 g, 5 mmol) in dry dichloromethane (20 mL) was saturated with dry HBr gas with cooling. A solution of thionyl bromide (2.0 g, 10 mmol) in dry dichloromethane (10 mL) was added dropwise at −5 to 0 °C. After a further 1.5 h at 0 °C, the mixture was stirred at ambient temperature for 12 h. The resulting precipitate was collected, washed with dry dichloromethane, and then recrystallized from MeOH–$CHCl_3$ to give 2-[(2-bromoethyl)thio]aniline hydrobromide (**2b**) as a white crystalline solid: mp 188–190 °C, 1 g (66% yield); ^1H NMR (Me_2SO-d_6) δ 3.3 (m, 2 H, SCH_2), 3.55 (m, 2 H, CH_2,Br), 7.4 (m, 4 H, Ph), 8.85 (br s, 3 H, exc, $NH_3^+Br^-$); CIMS (NH_3) m/z (rel intens) 234 [(M^+H + 2) − HBr, 100], 232 (M^+H − HBr, 98.0), 152 (38.5), 124 (12.2), 80 (7.1). Anal. Calcd for $C_8H_{11}NSBr_2$: C, 30.8; H, 3.2; N, 4.5. Found: C, 30.4; H, 3.1; N, 4.4.

2-[(2-Bromoethyl)sulfonyl]aniline Hydrobromide (4b). A solution of thionyl bromide (2907 g, 10 mmol) in dry dichloromethane (10 mL) was added to a stirred solution of 2-[(2-hydroxyethyl)sulfonyl]aniline (**4a**; 1.0 g, 5 mmol) in dichloromethane (30 mL) at −5 °C. After a further 3 h at −5 to 0 °C, the mixture was stirred at ambient temperature for 24 h, and then the reaction mixture was refluxed for 1 h. The solvent and excess of the reagent were removed in vacuo, and the residual solid was recrystallized from 1:4 MeOH–$CHCl_3$ (10 mL) to give 2-[(2-bromoethyl)sulfonyl]aniline hydrobromide (**4b**) as a white crystalline solid: mp 158–160 °C, 1.30 g (76% yield); ^1H NMR (Me_2SO-d_6) δ 3.35–3.45 (m, 2 H, $S(O)_2CH_2$), 3.6–3.7 (m, 2 H, CH_2Br), 6.7–7.5 (m, 4 H, Ph), 7.75 (br s, 3 H exch $NH_3^+Br^-$); IR (Nujol) 2845 cm^{-1} ($NH_3^+Br^-$); MS, m/z (rel intens) 265 (M^+ + 2) − HBr, 07), 263 (M^+ − HBr, 0.7), 201 (26.2), 170 (1.9), 157 (2.0), 93 (31.9), 92 (2.1), 82 (97.4), 80 (100)8 71 (2.1), 57 (2.8).

General Procedure for the Preparation of Thioethers. To a stirred solution of 2-bromo/chlorothiophenol (10 mmol) in 1:1 water–dioxane (40 mL) was added sodium bicarbonate (2.52 g, 30 mmol). The reaction mixture was stirred for 20–30 min, 2-bromoethyl acetate (3.34 g, 20 mmol) and 2-chloroethyl methyl ether (1.88 g, 20 mol) were added, and the mixture was stirred for 48 h. The mixture was diluted with dichloromethane (50 mL) and then filtered through Celite; the solvent and the excess of the reagent were removed in vacuo. The residue upon column chromatography (silica gel, 5% ethyl acetate in hexane) afforded the following thioethers from the appropriate reagents.

2-[(2-Acetoxyethyl)thio]chlorobenzene (2h): 2.0 g (87% yield) as an oil; ^1H NMR ($CDCl_3$) δ 191 (s, 3 H, $OC(O)CH_3$), 3.10 (t, 2 H, SCH_2, J = 6 Hz), 4.15 (t, 2 H, CH_2O, J = 6 Hz), 7.0–7.3 (m, 4 H, Ph); MS, m/z (rel intens) 232 (M^+ + 2, 7.92), 230 (M^+, 20.02), 135 (100), 108 (22.62), 87 (23.20).

2-[(2-Acetoxyethyl)thio]bromobenzene (2i): 2.2 g (80% yield) as an oil; ^1H NMR ($CDCl_3$) δ 2.05 (s, 3 H, $OC(O)CH_3$), 3.15 (t, 2 H, SCH_2, J = 6 Hz, 4.25 (t, 2 H, CH_2O, J = 6 Hz), 7.05–7.6 (m, 4 H, Ph); MS, m/z (rel intens) 276 (M^+ + 2, 15.07), 274 (M^+, 20.66), 216 (M^+ + 2 − CH_3COOH, 78.97), 214 (M^+ − CH_3COOH, 77.11), 135 (100), 123 (4.39), 122 (46.91), 121 (11.18), 108 (35.38).

2-[(2-Methoxyethyl)thio]chlorobenzene (2f): 1.80 g (81% yield) as an oil; ^1H NMr n$CDCl_3$) δ 3.15 (t, 2 H, SCH_2, J = 6 Hz), 3.35 (s, 3 H, OCH_3), 3.65 (t, 2 H, CH_2O, J = 6 Hz), 7.1–7.4 (m, 4 H, Ph); MS, m/z (rel intens) 204 (M^+ + 2, 36.83), 202 (M^+, 100), 158 (32.53), 156 (90.55), 108 (18.32), 59 (26.85).

2-[(2-Methoxyethyl)thio]bromobenzene (2g): 2.1 g (85% yield) as an oil; ^1H NMR ($CDCl_3$) δ 3.10 (t, 2 H, SCH_2, J = 6 Hz), 3.35 (s, 3 H, OCH_3), 3.60 (t, 2 H, CH_2O, J = 6 Hz), 7.07.55 (m, 4 H, Ph); MS, m/z (rel intens) 248 (M^+ + 2, 62.38), 246 (M^+, 60.01), 203 (40.54), 201 (39.84), 190 (41.20), 188 (41.0), 122 (100), 108 (37.92), 59 (36.95).

2-[(2-Hydroxyethyl)thio]bromobenzene (2j). Sodium bicarbonate (2.52 g, 30 mmol) was added to a stirred solution of 2-bromothiophenol (1.88 g, 10 mmol) in 1:1 water–dioxane (40 mL). The reaction mixture was stirred for 20–30 min, 2-chloroethanol was added (1.6 g, 20 mmol), and the mixture was stirred for 48 h. The solvent and the excess of the reagent were removed under vacuum, and the residue was taken up in dichloromethane (40 mL) and filtered through Celite. The solvent was removed in vacuo, and the residue upon column chromatography [silica gel, hexane–ethyl acetate (3:1)] afforded 2-[(2-hydroxyethyl)thio]-bromobenzene (**2j**): 1.75 g (75% yield) as an oil; ^1H NMR ($CDCl_3$) δ 2.35 (t, 1 H, exch OH, J = 5 Hz), 3.05 (t, 2 H, 5 CH_2, J = 6 Hz), 3.7 (q, 2 H, OCH_2, J_1 = 6 Hz, J_2 = 6 Hz), 7.0–7.5 (m, 4 H, Ph), after D_2O exchange 3.1 (t, 2 H, 5 CH_2, J = 6 Hz), 3.75 (t, 2 H, OCH_2, J = 6 Hz), 7.0–7.6 (m, 4 H, Ph); MS, m/z (rel intens) 234 (M^+ + 2, 81.19), 232 (M^+, 80.93), 203 (52.21), 201 (51.05), 190 (35.83), 188 (35.16), 122 (100), 109 (33.56), 108 (34.01), 77 (7.67), 51 (4.77).

2-[(2-Bromoethyl)thio]bromobenzene (2e). To a solution of 2-[(2-hydroxyethyl)thio]bromobenzene (**2j**; 2.32 g, 10 mmol) and triphenylphosphine (5.24 g, 20 mmol) in chloroform (12 mL) stirred at 40 °C was added a solution of carbon tetrachloride (4.96 g, 15 mmol) in chloroform (6 mL). After 3–4 h, the chloroform was removed in vacuo, and the residue upon column chromatography [silica gel, hexane–chloroform (1:1)] afforded 2-[(2-bromoethyl)thio]bromobenzene (**2e**): 2.15 g (72.6% yield) as an oil; ^1H NMR ($CDCl_3$) δ 3.35 (m, 2 H, SCH_2), 3.5 (m, 2 H, CH_2Br), 7.1–7.6 (m, 4 H, Ph); MS, m/z (rel intens) 298 (M^+ + 4, 27.4), 296 (M^+ + 2, 56.8), 294 (M^+, 27.6), 217 (64.3), 215 (64.6), 189 (27.4), 187 (26.8), 122 (34.4), 108 (100.0), 76 (5.7), 51 (5.5).

Generation of Benzoxathiete (7) and Trapping of Dehydrobenzene (9) with 1,3-Diphenylisobenzofuran and 9,10-Dimethylanthracene. Solutions of 2-[(2-acetoxyethyl)sulfinyl]aniline (**3d**; 0.568, 2.5 mmol) and isoamyl nitrate (1 mL, 7.5 mmol) each in glyme (3 mL) were added simultaneously in 1 h to a refluxing solution of 1,3-diphenylisobenzofuran (0.34 g, 1.25 mmol) in glyme (7 mL). After the addition was completed, the mixture was refluxed for 20–30 min and then allowed to cool. Dichloromethane (40 mL) was added, and the mixture was evaporated to dryness. The residual solid was purified by column chromatography (silica gel, pentane) to afford biphenylene (**11**) as a light yellow solid: mp 110 °C (lit.[35] mp 110 °C); trace; MS, m/z (rel intens) 153 (12.96), 152 (M^+, 100), 151 (18.58), 150 (9.68), 126 (4.71), 125 (1.06), 76 (13.25), 51 (1.40).

Further elution with [pentane–hexane (1:1)] afforded dibenzo-1,4-thioxine (**10**) as a white crystalline solid: mp 59 °C (lit.[36] mp 59 °C); trace; MS, m/z (rel intens) 200 (M^+, 100), 199 (4.70), 172 (M^+ − 28, 6.40), 168 (M^+ − 32, 24.51), 76 (0.8).

Further elution with chloforom afforded 9,10-epoxy-9,10-diphenyl-9,10-dihydroanthracene (**12**) as a white crystalline solid: mp 189 °C (lit.[37] mp 188–188.5 °C); 0.35 g (40% yield); ^1H NMR ($CDCl_3$) δ 7.0 (m, 4 H), 7.35 (m, 4 H), 7.45 (m, 2 H), 7.55 (m, 4 H), 7.95 (m, 4 H); MS, m/z (rel intens) 346 (M^+, 100), 328 (23.66), 269 (33.07), 268 (35.31), 267 (4.46), 241 (38.90), 240 (13.22), 239 (42.18), 105 (95.34).

When 9,10-dimethylanthracene (0.25 g, 1.25 mmol) was used, the residual solid was purified by column chromatography (silica gel, pentane) to afford biphenylene (**11**) as a light yellow solid: mp 109 °C (lit.[35] mp 110 °C); trace; MS, m/z (rel intens) 153 (12.15), 152 (M^+, 100), 151 (15.67), 150 (8.17), 126 (3.49), 76 (11.83).

Further elution with pentane–hexane (1:1) afforded dibenzo-1,4-thioxine (**10**) as a white crystalline solid: mp 58 °C (lit.[36] mp 59 °C); trace; MS, m/z (rel intens) 200 (M^+, 100), 199 (3.0), 172 (M^+ − 28, 5.29), 168 (M^+ − 32, 22.27), 51 (1.03). Further elution with hexane–$CHCl_3$ (2:1) afforded the dimethyltrypticene **13** as a white crystalline solid: mp >300 °C (lit.[38] mp 329–330 °C); 0.26 g (36% yield); ^1H NMR (pyridine-d_5) δ 2.45 (s, 6 H, methyl), 7.0–7.75 (m, 12 H, Ph); MS, m/z (rel intens) 282 (M^+, 59.43), 267 (M^+ − CH_3, 100), 252 (M^+ − $2CH_3$, 70.18), 126 (28.43).

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General Procedure for Analysis of the Products of Aprotic Diazotization of Substituted Aryl Alkyl Sulfoxides or Substituted Aryl Alkyl Sulfones. A solution of substituted aryl alkyl sulfoxide or corresponding sulfone (2.5 mmol) and isoamyl nitrite (1 mL, 7.5 mmol) each in glyme (3 mL) was added simultaneously in 1 h to a refluxing solution of trapping agent (1.25 mmol) in glyme (7 mL). After the addition was complete, the mixture was refluxed for 20-30 min and then allowed to cool. Dichloromethane (40 mL) was added, and the mixture was evaporated to dryness. The residual solid was purified by column chromatography as described previously to yield appropriate dihydroanthracene, **12** or **13**, and diphenylene (**11**) or dibenzo-1,4-thioxine (**10**).

General Procedure for Analysis of the Products of Aqueous Diazotization of Substituted Aryl Alkyl Sulfoxides, Substituted Aryl Alkyl Sulfones, or Substituted Aryl Alkyl Thioethers. A solution of substituted aryl alkyl sulfoxide, substituted aryl alkyl sulfone, or substituted aryl alkyl thioether (2 mmol) in dichloromethane (10 mL) and hydrochloric acid or hydrobromic acid (2 mL) was cooled to -10 °C, and solid sodium nitrite (4 mmol) was added slowly in portions. The temperature was maintained at -5 to 0 °C for 3 h. Samples were withdrawn with a microliter syringe and analyzed by GC HP-5840 and Hewlett-Packard GCMS with mass selective detector Model 5920 as described previously.[1-3]

EPR Spectroscopy. The spin trap 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) was from Aldrich Chemical Co. (Milwaukee, WI). It was distilled under low pressure before use. Samples were prepared in dry DME or benzene, and reactants were added in the following order: **3d**, spin trap, isoamyl nitrite. Total volumes of the samples were 500 μL. Subsequently the samples were transferred to EPR quartz tubes (internal diameter 5 mm) and gassed with argon for 15 min. Then the tubes were tightly sealed, and EPR spectra were recorded at intervals on the Bruker ER-400 EPR spectrometer operating at 9.5 GHz with 100-kHz field modulation. An aqueous solution of Fremy's salt (0.1 mM in 50 mM K_2CO_3) was used as a standard (separation between the first and second component of the EPR triplet equals 13.1 G). All EPR measurements were performed at room temperature.

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Absolute Rate Expressions for the Abstraction of Hydrogen by Primary, Secondary, and Tertiary Alkyl Radicals from Thiophenol[1]

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Abstract: Absolute rate expressions for the abstraction of hydrogen from thiophenol in nonane by *tert*-butyl, isopropyl, *n*-butyl, and *n*-octyl radicals were determined by kinetic absorption spectroscopy (KAS). Alkyl radicals were produced by photolysis of dialkyl disulfides or by photolysis of mixtures of di-*tert*-butyl peroxide and trialkylphosphine in the presence of thiophenol. Arrhenium expressions for alkyl radicals from the phosphine method from 255 to 355 K were as follows: *n*-butyl, $\log (k/M^{-1} s^{-1}) = (9.40 \pm 0.13) - (1.74 \pm 0.21)/\theta$, $\theta = 2.303RT$ kcal/mol; isopropyl, $\log (k/M^{-1} s^{-1}) = (9.26 \pm 0.19) - (1.70 \pm 0.21)/\theta$; *tert*-butyl, $\log (k/M^{-1} s^{-1}) = (9.26 \pm 0.26) - (1.50 \pm 0.20)/\theta$. Rate constants at 298 K vary from 0.8×10^8 to 1.5×10^8 $M^{-1} s^{-1}$ for the hydrogen-transfer reactions.

The knowledge of accurate rate expressions for the transfer of hydrogen from thiophenol to alkyl radicals would make available valuable rate standards for the competitive measurement of rapid intramolecular radical reactions. Convenient determination of rate constants of unimolecular radical "clock"[2] reactions such as the cyclopropylmethyl ring opening reaction (eq 1), or the trapping

$$c\text{-}C_3H_5CH_2^{\bullet} \rightarrow CH_2{=}CHCH_2CH_2^{\bullet} \quad (1)$$

$$c\text{-}C_3H_5CH_2^{\bullet} + DH \rightarrow c\text{-}C_3H_5CH_3 + D^{\bullet} \quad (2)$$

$$c\text{-}C_3H_5CH_2^{\bullet} + T \rightarrow c\text{-}C_3H_5CH_2T \quad (3)$$

of kinetic products of readily reversible rearrangements, requires a fast competing hydrogen-transfer (eq 2) or spin-trapping reaction (eq 3). In part because of the lack of accurate rate expressions for fast hydrogen-transfer reactions, rate expressions for spin-trapping reactions were recently measured by optical spectroscopy[3] and radical clock methods[4] for use as fast competitive rate standards. In nonpolar solvents, spin-trapping reactions exhibit bimolecular rate constants (k_3) about an order of magnitude slower than diffusion control.[3,4] Beckwith, Bowry, and Moad[4] have applied new trapping rate expressions to determine the most accurate rate expression to date for the cyclopropylmethyl ring opening reaction, $\log (k_1/s^{-1}) = 13.3 - 7.4/\theta$, over the range 40-130 °C. Mathew and Warkentin[5] reported a rate expression based on estimated competing trapping rates, combined with data from early ESR rate measurements of cyclopropylmethyl rearrangement by Ingold.[6a] While spin-trapping rections are valuable alternatives to hydrogen atom abstraction reactions, the products of trapping reactions usually cannot be analyzed by gas chromatography and are thus somewhat more difficult to quantitate.[4] A need clearly exists for the more simply utilized hydrogen ab-

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