corrected. The IR spectra were recorded on a Perkin-Elmer Infracord spectrophotometer; the NMR spectra were obtained on a Varian Associates Model T-60 spectrometer.

(9) M. S. Newman and F. W. Hetzel, *Org. Synth.*, **51**, 139 (1971).
(10) T. Noguchi et al., *Yakugaku Zasshi*, **88**, 227 (1968).
(11) The disappearance of the two *N*-methyl singlets in the NMR spectrum of the *O*-arylcarbamates and the appearance of an *N*-methyl singlet for the *S*-arylcarbamates were observed to determine the progress of reaction.
(12) W. H. Hunter and A. H. Kohlhase, *J. Am. Chem. Soc.*, **54**, 2425 (1932).
(13) We are indebted to Mira Smolarek for the mass spectra determinations.

Mechanism of Thiophene Formation upon Photolysis of Enethiol Esters

John R. Grunwell,* Denis L. Foerst, and Michael J. Sanders

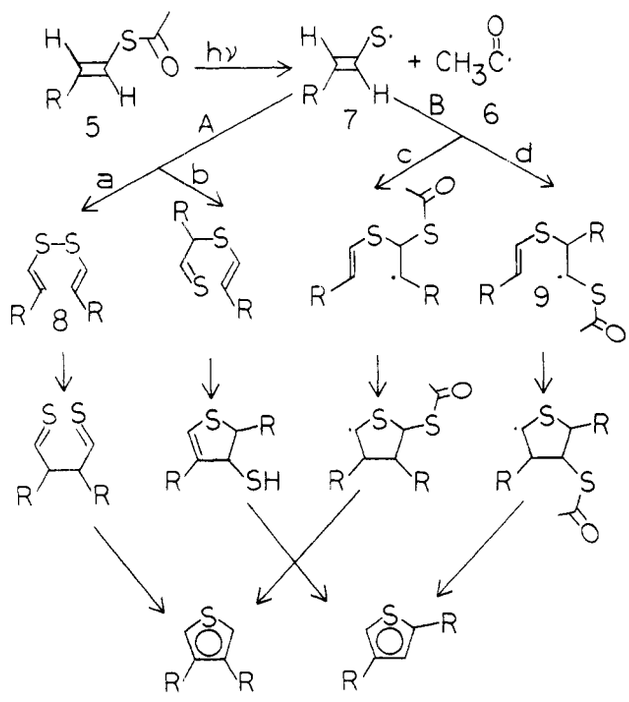
Department of Chemistry, Miami University, Oxford, Ohio 45056

Received June 2, 1976

Evidence for the mechanism of thiophene formation from the photolysis of enethiol esters was obtained by studying β-monosubstituted vinylthiol acetates. Styrylthiol acetate gave exclusively 3,4-diphenylthiophene while β-*tert*-butylvinylthiol acetate yielded β-*tert*-butylvinyl disulfide and no thiophenes. These results suggest that the photolysis involves homolytic cleavage of the *S*-acyl bond followed by dimerization of the enethiyl radical at sulfur to form a vinyl disulfide which undergoes a Cope rearrangement and subsequent loss of hydrogen sulfide to give the thiophenes.

The photolysis of 1-cyclohexene thiolacetate (**1a**) to octahydrodibenzothiophene (**2a**) and *cis*- and *trans*-2-acetylcyclohexane thiolacetate (**3**) was reported in a previous communication.[1] The object of this research was to provide evidence for the mechanism of thiophene production. As shown in Scheme I, there are two basic routes leading to the formation of thiophenes from the photolysis of enethiol esters **5** assuming that following absorption of light by **5** the sulfur–carbonyl carbon bond cleaves homolytically to form an acyl radical **6** and an enethiyl radical **7** in analogy with arylthiol esters.[2] In the first mechanism, **7** can dimerize either by head to head coupling (path Aa) or by head to tail coupling (path Ab) with path Aa being greatly preferred since the spin density is highest at sulfur for **7**.[3] The resultant divinyl disulfides **8** are known to rearrange, ring close, and lose hydrogen sulfide to form thiophenes,[4] which would be 3,4-disubstituted if **5** were β-monosubstituted. In the second mechanism, **7** reacts with starting **5** at either the α position (path Bc) or the β position (path Bd). β-Addition is favored in most cases to form the radical **9**[5] which ring closes and loses thiolacetic acid and hydrogen to give the thiophene, which would be 2,4-disubstituted if **5** were β-monosubstituted.

Scheme I

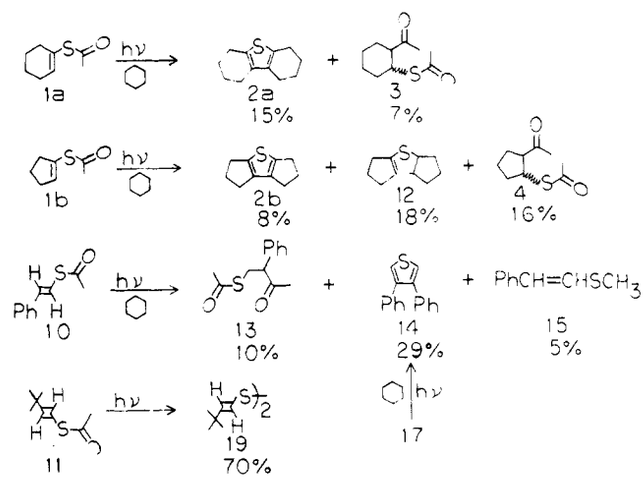


Therefore, to distinguish between pathways Aa and Bd, we wish to report the photolysis of two β-monosubstituted enethiol esters, styryl thioacetate (**10**) and *tert*-butylvinylthiol acetate (**11**), and additionally to report the experimental details for the photolysis of 1-cyclohexene thiolacetate (**1a**) and 1-cyclopentene thiolacetate (**1b**).

Results and Discussion

Irradiation at 254 nm of **1a** dissolved in cyclohexane gave the thiophene **2a** and the *cis*- and *trans*-2-acetylcyclohexane thiolacetates **3**. Similarly, **1b** photolyzed to the homologous products **2b** and **4**, and in addition formed a substantial amount of the dihydrothiophene **12**. The identities of **2a** and **2b** were established by independent synthesis and comparison of spectral properties. Reduction of **2b** with lithium dissolved in liquid ammonia and *tert*-butyl alcohol gave **12**. Despite a report that thiophene is reduced by sodium dissolved in liquid ammonia and methanol to a 2:1 mixture of 2,5- and 2,3-dihydrothiophene,[6a,b] we have assigned the reduction product structure **12** in which sulfur is conjugated with the double

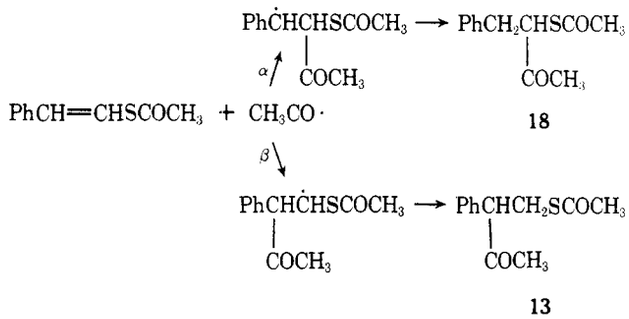
Scheme II



bond because the maximum UV absorbance occurs at 234 nm with a large molar absorptivity, ϵ_{max} 5800. These numbers are in reasonable agreement with those reported for 2-(2-propyl)-5-methyl-2,3-dihydrothiophene, λ_{max} 240 nm (ϵ_{max} 2800).[7] The stereochemistry of **12** was not rigorously established but is most likely cis. The identities of the esters **3** and **4** were established by synthesizing a mixture of each pair by the addition of thiolacetic acid to the 1-acetylcycloalkene.

Irradiation of a 4:1 cis:trans mixture of styryl thiolacetate (**10**) in cyclohexane for 6 h gave 3-phenyl-4-mercaptoacetyl-2-butanone (**13**), 3,4-diphenylthiophene (**14**), and methyl styryl sulfide (**15**). The cis:trans ratio for **10** changed to 1:1 after 0.5 h and 1:9 after 6 h. No 2,4-diphenylthiophene (**16**) was formed. The thiophene **16** has been photolyzed to **14** under similar conditions, but even after 23 h the ratio of **16**:**14** was 1:1.[9] In our hands, irradiation of **16** for 6 h in cyclohexane gave a minor amount (less than 2%) of **14**. The photolysis[19] of styryl disulfide **17** for 6 h in cyclohexane resulted in the complete disappearance of **17** and the formation of **14** but no **16**. Therefore, in the photolysis of **10**, the formation of **14** occurs via **17** and not **16**.

Products of the type **3**, **4**, and **13** are probably formed by addition of an acetyl radical to the starting enethiol esters **1**



and **10** followed by hydrogen atom transfer. With **10**, addition may occur at either the α or β carbon to form either **18** or **13**.

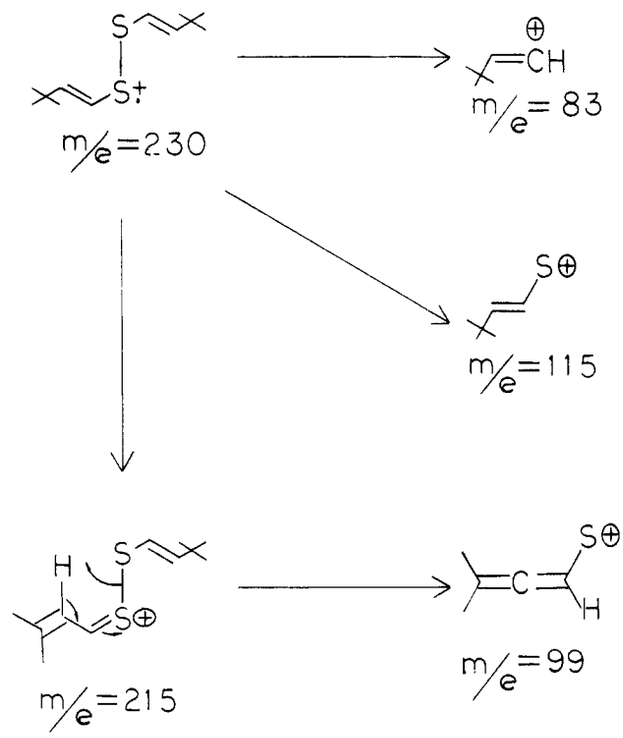
The thiol ester **18** was synthesized from 3-chloro-4-phenyl-2-butanone and sodium thiolacetate and was ruled out as the photoproduct of **10** because **18** had a different GLC retention time and mass spectrum than the true photoproduct **13**, prepared from 2-phenyl-3-buten-2-one and thiolacetic acid.

Irradiation of *trans-tert*-butylvinyl thiolacetate (**11**) in pentane for 6 h led to a mixture of *trans,trans*- and *cis,-trans*-β-*tert*-butylvinyl disulfide (**19**). The NMR spectrum of **19** showed a multiplet at δ 5.9 and singlets at δ 1.0 and 1.4 in a 2:9 ratio. In the mass spectrum, a parent ion was observed at *m/e* 230 (49) in addition to fragment ions at *m/e* 215 (15), 115 (15), 99 (89), and 83 (100) (Scheme III).

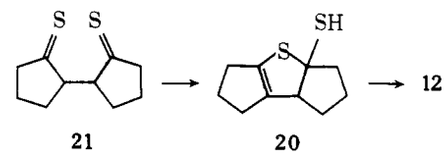
The formation of 3,4-di-*tert*-butylthiophene appears to be blocked. The repulsive effects of the bulky *tert*-butyl groups are probably responsible first by increasing the energy of activation for the Cope rearrangement of **19** and second by reducing the aromatic stabilization of the 3,4-di-*tert*-butylthiophene.[10a,b] However, 2,4-di-*tert*-butylthiophene is a known compound which does not suffer the repulsive destabilization of the 3,4 isomer. The absence of the 2,4 isomer and the isolation of **19** in the photolysis of **11** support the earlier argument that head to tail dimerization (path Ab, Scheme I) of **7** is not important.

The exclusive formation of **13**, **14**, and **19** and the formation of **14** from **17** demonstrates that the mechanism of thiophene production involves head to head dimerization of **7** at sulfur (path Aa). The addition of **7** to the α position of **5** which also leads to the 3,4 isomer (path Bc) is ruled out since the acetyl radical added to the β position of **10** to form **13**. The absence

Scheme III



of 2,4-disubstituted thiophenes eliminates head to tail dimerization of **7** (path Ab) and the addition of **7** to the β position of **5** (path Bd) as possible mechanisms. The formation of the dihydrothiophene **12** may be accounted for within the framework of path Aa by assuming the loss of sulfur from the intermediate **20** which arises from ring closure of **21**.



Our results and mechanistic conclusions are in striking contrast to the data presented by Nishimura et al.,[3] who found that the photolysis of *S*-(*cis*-1-propenyl)-L-cysteine in water gave 1-propenethiol, alanine, and a mixture of 2,4- and 3,4-dimethylthiophene in which the 2,4-dimethylthiophene predominated over the 3,4 isomer. The 2,4 isomer probably arose by a path similar to Bd rather than the head to tail dimerization of path Ab proposed by Nishimura.

In our systems, we found no enethiols, products derived from enethiols, or 2,4-disubstituted thiophenes. The photolysis of the propenylcysteine was conducted in water while our work was done in cyclohexane or *n*-pentane. It is not clear, however, how this difference in solvent polarity accounts for the disparity of products.

Experimental Section

All boiling and melting points are uncorrected. IR spectra were obtained on a Perkin-Elmer Model 237 or Model 81 infrared spectrophotometer. UV spectra were recorded on a Cary 14 spectrophotometer. NMR spectra were taken on a Varian A-60, EM-300, or JEOL-C-60H spectrometer with Me_4Si as internal standard. Mass spectra were obtained on an Hitachi Perkin-Elmer RMU-6 spectrometer. Gas chromatography was performed on a Hewlett-Packard Model 700 or 810 gas chromatograph equipped with a thermal conductivity detector and either on OV-225 (20 ft), SE-30 (6 ft), SE-52 (5 ft), or Carbowax 20M (6 ft) column. Photolyses were conducted with a Rayonet photochemical reactor equipped with 2537-A mercury arc lamps. Cyclohexane (Baker reagent) was washed with 18 N sulfuric acid until the acid remained colorless, washed with distilled water three times, and then distilled from barium oxide or lithium alumi-

num hydride directly into the photolysis vessel. *n*-Pentane was distilled from lithium aluminum hydride directly into the photolysis vessel. Solutions were purged with prepurified nitrogen. Microanalyses were done by Scandinavian Microanalytical Laboratory and Galbraith Laboratories, Inc.

1-Cycloalkene Thiolacetate (1a and 1b). These esters were synthesized according to a method previously reported.[5]

***cis*-2-Styrene Thiolacetate (10).** The ester **10** was prepared by the addition of thiolacetic acid to phenylacetylene:[11] mp 43–44.5 °C (lit[11] 43–45 °C); IR (Model 81, KBr) 3390 (m), 3074 (s), 1720 (s), 1665 (m), 1491 (s), 1100 (s), 971 (s), and 959 cm^{-1} (s); NMR ($CDCl_3$) δ 2.35 (3, s), 6.55 (1, d, J_{AB} = 10.5 Hz), 6.85 (1, d, J_{AB} = 10.5 Hz), and 7.23 (5, m); mass spectrum *m/e* (rel intensity) 178 (14.8), 137 (9.2), 136 (78), 135 (45), 134 (15), 102 (6), 92 (4), 91 (34), 89 (7), 77 (9), 65 (11), 63 (9), 51 (15), 50 (5), 45 (7), 43 (100), and 39 (11).

***trans*-β-*tert*-Butylvinyl Thiolacetate (11).** The ester **11** was prepared by addition of thiolacetic acid to *tert*-butylacetylene:[12] bp 85–92 °C (24 mm) [lit.[12] 77 °C (12 mm)]; IR (81, film) 3370 (w), 3040 (m), 1697 (s), 1610 (w), 1460 (s), 1105 (s), and 953 cm^{-1} (s); NMR (neat) δ 1.05 (9, s), 2.25 (3, s), 5.73 (1, d, J_{AB} = 16.5 Hz), and 6.30 (1, d, J_{AB} = 16.5 Hz); mass spectrum *m/e* (rel intensity) 158 (11), 116 (16), 102 (3), 101 (42), 99 (43), 83 (50), 55 (13), 43 (100), and 41 (22).

Photolysis of 1a. A solution of 3.0 g (1.9 mmol) of **1a** dissolved in 600 mL of cyclohexane was irradiated for 9 h. According to GLC 80% of **1a** had reacted. The solution was evaporated and the residue analyzed with GLC (Carbowax 20M) using *n*-eicosane as internal standard. The components of the mixture were collected and identified by comparison of retention time and spectral data with that of authentic samples. The products in order of increasing retention time were 2-acetylcyclohexanethiolacetate (**3**, 7%) and 1,2,3,4,6,7,8,9-octahydrodibenzothiophene (**2a**, 15%).

***trans*- and *cis*-2-Acetylcyclohexane Thiolacetate (3).** Freshly distilled thiolacetic acid (38.0 g, 0.5 mol) was added to 10 g (0.08 mol) of 1-acetylcyclohexene in a flask cooled to 0 °C with an ice bath. After addition was complete the solution was allowed to stand at room temperature for 15 h and then the thiolacetic acid was removed under vacuum to give 15.0 g of a 30/70 mixture of **3** isomers. An analytical sample and spectral data samples were prepared by collection of the peaks from GLC. The analytical sample was a mixture of the two esters. For **3a:** IR (CCl_4) 3420 (w), 2940 (w), 2860 (m), 1710 (s), 1695 (s), 1450 (m), 1350 (m), 1240 (w), 1155 (m), 1130 (m), 1110 (m), and 950 cm^{-1} (m); UV (95% EtOH) 232 nm (ϵ 4650). For **3b:** IR (CCl_4) 3420 (w), 3360 (w), 2940 (s), 2860 (m), 1710 (s), 1690 (s), 1445 (m), 1350 (m), 1240 (w), 1200 (w), 1155 (m), 1120 (m), and 950 cm^{-1} (m); UV (95% EtOH) 232 nm (ϵ 5200).

Anal. Calcd for $C_{10}H_{16}O_2S$: C, 59.96; H, 8.05; S, 16.01. Found: C, 59.84; H, 8.09; S, 16.21.

1,2,3,4,6,7,8,9-Octahydrodibenzothiophene (2a). The thiophene **2a** was prepared according to a literature procedure:[13] bp 89–90 °C (0.1 mm) [lit. bp 119–120 °C (1.0 mm)]; IR (neat) 2940 (s), 2860 (m), 2845 (m), 1450 (m), 1345 (w), 1300 (w), 1270 (w), 1245 (w), 1140 (w), 1120 (w), 1075 (w), 1030 (w), 955 (w), 850 (w), and 820 cm^{-1} (w); UV (95% EtOH) 239 nm (ϵ 6350); NMR δ (CCl_4) 1.80 (m, 8), 2.40 (m, 4), and 2.70 (m, 4); mass spectrum (80 eV) *m/e* (rel intensity) 192 (91), 191 (20), 164 (100), 163 (20), 160 (12), 136 (15), 81 (16), 55 (16), and 41 (17).

Photolysis of 1b. A solution of 3.0 g (2.1 mmol) of **1b** dissolved in 600 mL of cyclohexane was irradiated for 10 h. The solution was treated the same as in the photolysis of **1a.** The products were analyzed by GLC (Carbowax 20M) with *n*-nonadecane as internal standard. The products in increasing retention time are 1,2,3,5,6,7,8,9-octahydrodicyclopenta[*b,d*]thiophene (**12,** 18%); 1,2,3,5,6,7-hexahydrodicyclopenta[*b,d*]thiophene (**2b,** 8%); and 2-acetylcyclopentane thiolacetate (**4,** 16%).

1,2,3,5,6,7-Hexahydrodicyclopenta[*b,d*]thiophene (2b). The thiophene **2b** was synthesized according to the literature procedure:[14] bp 60–61 °C (0.3 mm); IR (CCl_4) 2950 (s), 2860 (s), 1440 (w), 1310 (w), and 1140 cm^{-1}; UV (95% EtOH) 241 nm (ϵ 6650); mass spectrum (80 eV) *m/e* (rel intensity) 164 (100), 163 (72), 149 (23), 137 (29), 136 (21), 135 (26), 131 (22), 115 (12), 91 (15), and 39 (14).

1,2,3,5,6,7,8,9-Octahydrodicyclopenta[*b,d*]thiophene (12). Into a flask were placed 3.0 g (0.018 mol) of **2b,** 10 mL of *tert*-butyl alcohol, 10 mL of tetrahydrofuran, and 20 mL of liquid ammonia. Lithium metal (0.3 g, 0.043 g-atom) was added. After the lithium had reacted and the ammonia evaporated, the residue was partitioned between ether and water. The ether was separated, dried ($MgSO_4$), filtered, and evaporated to give 1.8 g of oil which was a mixture of 25% **12** and 75% **2b.** The dihydrothiophene was separated from **2b** by GLC (Carbowax 20M, then SE-30): IR (CCl_4) 2950 (s), 2895 (m), 2870 (s), 1450 (m), 1350 (w), 1320 (w), 1130 (w), and 940 cm^{-1} (w); UV (95% EtOH) 234 nm (ϵ 5800); mass spectrum (80 eV) *m/e* (rel intensity) 166 (47), 165 (6), 138 (15), 137 (100), 133 (16), 91 (14), 67 (9), and 39 (8).

Anal. Calcd for $C_{10}H_{14}S$: C, 72.23; H, 8.48; S, 19.29. Found: C, 72.25; H, 8.43; S, 19.43

***trans*- and *cis*-2-Acetylcyclopentane Thiolacetate (4).** A 95/5 mixture of **4** was prepared by the same method as for **3** by adding thiolacetic acid to 1-acetylcyclopentene.[15] spectral data for **4a:** IR (CCl_4) 3400 (w), 3360 (w), 2960 (s), 2870 (m), 1710 (s), 1690 (s), 1450 (m), 1360 (m), 1300 (w), 1225 (w), 1115 (s), and 950 cm^{-1} (m); UV (95% EtOH) 234 nm (ϵ 4800). Data for **4b:** IR (CCl_4) 3400 (w), 3360 (w), 2960 (s), 2860 (m), 1710 (s), 1690 (s), 1450 (m), 1360 (m), 1300 (w), 1275 (w), 1225 (w), 1160 (m), 1120 (m), and 950 cm^{-1} (m). An analytical sample was prepared by collection of the mixture of **4** isomers from GLC.

Anal. Calcd for $C_9H_{14}O_2S$: C, 58.03; H, 7.57; S, 17.22. Found: C, 57.84; H, 7.41; S, 17.46.

Photolysis of 10. Two 10-mL aliquots of a solution obtained by dissolving 1.94 g of **10** in 250 mL of cyclohexane were irradiated for 0.5 and 6 h respectively. The photomixture was analyzed by GLC (OV-225) using *trans*-stilbene as internal standard. The products were after 0.5 h methylstyryl sulfide (**15,** 7%), 3,4-diphenylthiophene (**14,** 14%), and 3-phenyl-4-acetylmercapto-2-butanone (**13,** 6%) and after 6 h **15** (5%), **14** (29%), and **13** (10%).

Methyl Styryl Sulfide (15). The sulfide was prepared according to the literature procedure:[16] mass spectrum *m/e* (rel intensity) 150 (90), 135 (83), 134 (33), 104 (14), 103 (14), 102 (12), 101 (17), 91 (100), 77 (31), 76 (12), 65 (14), 63 (14), 51 (36), 50 (21), 45 (17), and 39 (21).

3,4-Diphenylthiophene (14). The thiophene **14** was synthesized according to the literature procedure:[17] mp 112–113 °C (lit.[17] 113–114 °C); IR (KBr) 1460 (w), 850 (m), 795 (s), 770 (m), 750 (s), 730 (m), 720 (m), and 680 cm^{-1} (s); UV (95% EtOH) 260 nm (sh, ϵ 11 527), 234 (22 558); NMR ($CDCl_3$) δ 7.15 and 7.25; mass spectrum *m/e* (rel intensity) 236 (100), 235 (6), 234 (28), 221 (16), 202 (14), 189 (12), 117 (12), 104 (11), 89 (10), 77 (6), 63 (12), 51 (14), and 39 (11).

3-Phenyl-4-acetylmercapto-2-butanone (13). Freshly distilled thiolacetic acid (14.4 g, 0.19 mol) was added to 10.1 g (0.07 mol) of 3-phenyl-3-buten-2-one.[18] The solution was stirred for 6 h and distilled to give 2.5 g (16%) of **13:** bp 97–105 °C (0.5 mm); IR (film) 3300 (w), 2980 (m), 2910 (m), 1710 (s), 1690 (s), 1590 (w), 1465 (m), 1440 (m), 1400 (m), 1340 (s), 1120 (s), 950 (s), 770 (s), 725 (s), and 690 cm^{-1} (s); NMR ($CDCl_3$) δ 2.00 (3, s), 2.20 (3, s), 3.25 (2, complex multiplet), 3.80 (1, d of d, J_{AX} = 13.5, J_{BX} = 7.5 Hz), 7.15 (5, m); mass spectrum *m/e* (rel intensity) 222 (<1), 147 (5), 146 (9), 137 (5), 131 (4), 118 (5), 105 (5), 104 (54), 103 (30), 91 (4), 78 (3), 77 (12), 76 (2), 51 (9), 44 (6), and 43 (100). Attempts to obtain a satisfactory analysis were frustrated by elimination of thiolacetic acid.

4-Phenyl-3-acetylmercapto-2-butanone (18). A solution of 1.1 g (11.0 mmol) of sodium thiolacetate and 2.0 g (11.0 mmol) of 3-chloro-4-phenyl-2-butanone dissolved in 50 mL of ethanol was refluxed for 6 h under stirring, cooled, and filtered. The solvent was removed with the aspirator, and the residue partitioned between benzene and 4% aqueous NaOH, then washed with water, dried ($MgSO_4$), and distilled to give 1.15 g (47%) of a light yellow oil: bp 85–89 °C (0.05 mm); IR (neat) 3060 (m), 3020 (m), 2918 (m), 2848 (m), 1680 (s), 1600 (m), 1492 (s), 1450 (s), 1425 (s), 1351 (s), 1220 (w), 1195 (s), 1120 (s), 1075 (m), 1025 (m), 1000 (w), 950 (s), 478 (m), 720 (m), and 695 cm^{-1} (s); NMR ($CDCl_3$) δ 2.05 (3, s), 2.20 (3, s), 2.75 (1, d of d, J_{AX} = 7.5, J_{AB} = 15 Hz), 3.20 (1, d of d, J_{BX} = 7.5, J_{AB} = 15 Hz), 4.45 (1, d of d, J_{AX} = J_{BX} = 7.5 Hz), 7.1 (5, s); mass spectrum *m/e* (rel intensity) 148 (7.5), 147 (45), 137 (12), 105 (3), 104 (8), 103 (6), 91 (18), 77 (6), 51 (6), 44 (8), and 43 (100).

Anal. Calcd for $C_{12}H_{14}O_2S$: C, 64,83; H, 6.34; S, 14.42. Found: C, 64.63; H, 6.19; S, 14.65.

***cis*-Styryl Disulfide (17).** To a solution of 6.5 g (0.036 mol) of **10** dissolved in 150 mL of anhydrous ether was added 0.08 mol of methyllithium as a 1.5 *m* solution in ether at 0 °C. The resulting yellow solution was treated with 50 mL of water and then with enough of a concentrated aqueous solution of a 1:1 molar ratio of potassium iodide and iodine until an orange color persisted in the ether layer. The ether was separated, extracted with aqueous sodium thiosulfate and then twice with water, and dried (Na_2SO_4). The ether was evaporated and the oily residue remaining was chromatographed on silica gel and eluted with petroleum ether to give 0.7 g (14%) of yellow, crystalline **17:** mp 58–59 °C; NMR (CCl_4) δ 6.42 (2 H, collapsed AB quartet), and 7.38 (5 H, m); mass spectrum *m/e* (rel intensity) 270 (12), 236 (94), 136 (83), 135 (100), 134 (39), 91 (78), 77 (27), 51 (30).

Anal. Calcd for $C_{16}H_{14}S_2$: C, 71.06; H, 5.22; S, 23.72. Found: C, 70.94; H, 5.30; S, 23.54.

Photolysis of 17. A 1% solution of **17** in cyclohexane was irradiated

for 6 h and analyzed by GLC (SE-52). The major product was the thiophene **14**. No **16** was found.[19]

Photolysis of 11. A solution of 3.75 g of **11** dissolved in 600 mL of *n*-pentane was irradiated for 4 h. Solvent was removed with the aspirator and the reaction was analyzed by GLC (OV-225) with tetralin as internal standard. About 20% of the ester **11** had disappeared. The only product was *β-tert*-butylvinyl disulfide (**19**, 70%). Samples of **19** for analysis and spectral data were collected from gas chromatography: IR (film) 3018 (w), 2980 (s), 1706 (w), 1608 (w), 1465 (m), 1453 (m), 1383 (m), 1355 (m), 1293 (w), 1255 (m), 1230 (m), 1028 (w), 948 (m), 914 (w), 822 (w), 802 (w), 778 (w), and 620 cm^{-1} (w); UV (cyclohexane) 214 nm (ε 675); NMR (neat) δ 1.0 (s), 1.4 (9, s), and 5.9 (2, m); mass spectrum *m/e* (rel intensity) 230 (49), 215 (15), 174 (8), 116 (11), 115 (15), 113 (10), 103 (11), 101 (32), 100 (8), 99 (89), 85 (13), 83 (100), 81 (30), 79 (10), 73 (12), 67 (22), 65 (12), 61 (11), 59 (52), 57 (47), 55 (63), 53 (18), 47 (10), 45 (50), 44 (71), 43 (40), 41 (93), and 39 (37).

Anal. Calcd for $C_{12}H_{22}S$: C, 62.54; H, 9.62; S, 27.82. Found: C, 62.27; H, 9.63; S, 27.61.

Registry No.—**1a**, 15786-82-0; **1b**, 16214-69-0; **2a**, 15869-74-6; **2b**, 4427-74-1; *trans*-**3**, 61363-79-9; *cis*-**3**, 61363-80-2; *trans*-**4**, 61363-81-3; *cis*-**4**, 61363-82-4; *cis*-**10**, 27675-80-5; *trans*-**10**, 61363-83-5; **11**, 61363-84-6; **12**, 61363-85-7; **13**, 61363-86-8; **14**, 16939-13-2; **15**, 7715-02-8; **17**, 61363-87-9; **18**, 61363-88-0; *trans,trans*-**19**, 61363-89-1; *cis,trans*-**19**, 61363-90-4; thiolacetic acid, 507-09-5; phenylacetylene, 536-74-3; *tert*-butylacetylene, 917-92-0; 1-acetylcyclohexene, 932-66-1; 1-acetylcyclopentene, 16112-10-0; 3-phenyl-3-buten-2-one, 32123-84-5; sodium thiolacetate, 34832-35-4; 3-chloro-4-phenyl-2-butanone, 20849-77-8.

References and Notes

(1) J. R. Grunwell, *Chem. Commun.*, 1437 (1969).
(2) J. R. Grunwell, N. A. Marron, and S. I. Hanhan, *J. Org. Chem.*, **38**, 1559 (1973).
(3) H. Nishimura and J. Mizutani, *J. Org. Chem.*, **40**, 1567 (1975).
(4) H. Boelens and L. Brandsma, *Recl. Trav. Chim. Pays-Bas*, **91**, 141 (1972).
(5) J. D. Willett, J. R. Grunwell, and G. A. Berchtold, *J. Org. Chem.*, **33**, 2297 (1968).
(6) (a) S. F. Birch and D. T. McAllan, *Nature (London)*, **165**, 899 (1950); (b) *J. Chem. Soc.*, 2556 (1951).
(7) L. Bateman and R. W. Glazebrook, *J. Chem. Soc.*, 2834 (1958).
(8) K. von Auwers, *Justus Liebigs Ann. Chem.*, **420**, 84 (1920).
(9) H. Wynberg, H. van Driel, R. M. Kellogg, and J. Buter, *J. Am. Chem. Soc.*, **89**, 3487 (1967).
(10) (a) E. H. Wiebenga and E. Bouwhuis, *Tetrahedron*, **25**, 453 (1969); (b) R. M. Kellogg, J. K. Dik, H. van Driel, and H. Wynberg, *J. Org. Chem.*, **35**, 2737 (1970).
(11) A. A. Oswald, K. Griesbaum, B. E. Hudson, and J. M. Bregman, *J. Am. Chem. Soc.*, **86**, 2877 (1964).
(12) H. Behringer, *Justus Liebigs Ann. Chem.*, **564**, 219 (1949).
(13) W. Cooper, *J. Chem. Soc.*, 1386 (1955).
(14) H. Paul, *Chem. Ber.*, **93**, 2395 (1960).
(15) P. F. Casals, *Bull. Soc. Chim. Fr.*, 253 (1963).
(16) M. C. Caserio, R. E. Pratt, and R. J. Holland, *J. Am. Chem. Soc.*, **88**, 5747 (1966).
(17) H. J. Backer and W. Stevens, *Recl. Trav. Chim. Pays-Bas*, **59**, 423 (1940).
(18) W. Wilson and Z. Kyi, *J. Chem. Soc.*, 1321 (1952).
(19) We wish to thank the referees for challenging us to photolyze **17**.

Ionic Reactions in Bicyclic Systems. 10. The Effect of 6,7-Dimethoxy Substituents on Rates of Solvolysis in Secondary and Tertiary 2-Benzonorbornenyl Systems

Harlan L. Goering,* David C. K. Chang, and Wei-Shing Chang

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Received August 2, 1976

The effect of 6,7-dimethoxy substituents in *exo*- and *endo*-2-benzonorbornenyl *p*-bromobenzenesulfonate (**5a**-OBs) and 2-methyl-*exo*-2-benzonorbornenyl *p*-nitrobenzoate (*exo*-**5b**-OPNB) on rates of solvolysis has been determined. The effect of the two substituents is essentially the same as that reported for a single methoxyl group at C-6 (homo-para position). At 25 °C the rate of acetolysis of *exo*-**5a**-OBs is 204 times larger than that of unsubstituted *exo*-2-benzonorbornyl *p*-bromobenzenesulfonate (*exo*-**2a**-OBs). The rate of solvolysis of *exo*-**5b**-OPNB in 90% aqueous acetone at 100 °C is 17 times larger than that for the unsubstituted tertiary system, *exo*-**2b**-OPNB. Moreover, ion-pair return (determined by the rate of carboxyl oxygen equilibration) is more important for *exo*-**5b**-OPNB than for *exo*-**2b**-OPNB, which means that ionization rates differ by a larger factor (~40) than solvolysis rates (16.6). Acetolysis rates for *endo*-2-norbornyl *p*-bromobenzenesulfonate (*endo*-**1a**-OBs), *endo*-**5a**-OBs, and *endo*-**2a**-OBs span a range of >260 at 100 °C. However, the stereochemistry for solvolysis of the optically active endo brosylates is very similar. In each case pure exo acetate is formed with from 96% (*endo*-**5a**-OBs) to 94% (*endo*-**1a**-OBs) loss of optical activity

It is clear from the effect of substituents in the aromatic ring that solvolytic reactions of *exo*-2-benzonorbornenyl derivatives (*exo*-**2a**) involve assisted ionization.[1a] A 6-methoxy substituent (homo-para) has a large rate-accelerating effect and a 7-methoxy substituent (homo-meta) a negligible effect.[1-3] In connection with other work[4] it was necessary to determine if the effect of 6,7-dimethoxy substituents in secondary (**5a**) and tertiary (**5b**) 2-benzonorbornenyl systems is comparable to that of a single 6-methoxyl substituent. That work involved optically active systems, and active 6,7-dimethoxy-2-benzonorbornenyl compounds (**5**) can be readily prepared by asymmetric hydroboration of the symmetrical 6,7-dimethoxybenzonorbornadiene.[5] On the other hand, preparation of optically active 6-methoxy derivatives (**3**) appears to be much more complicated.

This paper reports a comparison of 6,7-dimethoxy (**5**), 6-methoxy (**3**), and 7-methoxy (**4**) substituent effects on rates of solvolysis of secondary and tertiary (2-methyl) 2-benzonorbornenyl derivatives. We also have examined the effect of 6,7-dimethoxy substituents on (a) the stereochemistry of acetolysis of the optically active secondary *endo*-*p*-bromobenzenesulfonates (*endo*-**2a**-OBs and *endo*-**5a**-OBs) and (b) the magnitude of ion-pair return associated with solvolysis of the tertiary *exo*-*p*-nitrobenzoates (*exo*-**2b**-OPNB and *exo*-**5b**-OPNB).

Rates and relative rates of acetolysis of *exo*-2-norbornyl (*exo*-**1a**-OBs), *exo*-2-benzonorbornenyl (*exo*-**2a**-OBs), and methoxy substituted *exo*-2-benzonorbornenyl *p*-bromobenzenesulfonates are presented in Table I. This reaction was chosen because data were available for *exo*-**1a**-OBs,[6] *exo*-