Photocyclization Reactions of Phenylthioethenes

S. H. Groen, Richard M. Kellogg, J. Buter, and Hans Wynberg

Department of Organic Chemistry, The University, Groningen, The Netherlands

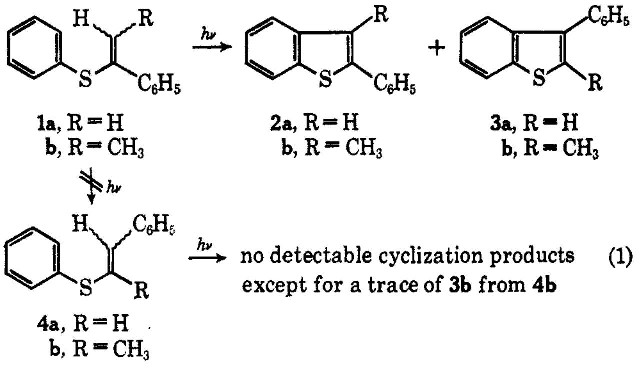
Received December 19, 1967

Upon irradiation, a number of phenylthioethenes undergo a low-yield cyclization reaction (up to 11.5% yield) in addition to the formation of high molecular weight products. Photolysis of 1-phenyl-1-phenylthioethene (**1a**) leads to cyclization to form "normal" 2-phenylbenzo[*b*]thiophene (**2a**) and "abnormal" 3-phenylbenzo[*b*]thiophene (**3a**) in low yields. Similar results were obtained with 1-phenyl-1-phenylthiopropene-1 (**1b**) which gave 3-methyl-2-phenylbenzo[*b*]thiophene (**2b**) and 2-methyl-3-phenylbenzo[*b*]thiophene (**3b**). The yields of the "normal" cyclization products **2a** and **2b** were raised in the presence of iodine. Photolysis of **1a** and **1b** did not yield detectable amounts of the isomeric 1-phenyl-2-phenylthioethene (**4a**) or 1-phenyl-2-phenylthiopropene-1 (**4b**), respectively, nor did these isomers upon independent photolysis yield more than a trace of cyclization products. The benzo[*b*]thiophenes were not interconverted upon photolysis. Some other phenylthioethenes as well as phenyl sulfide formed "normal" benzo[*b*]thiophenes in low yields but no detectable amounts of "abnormal" cyclization products.

The currently favored interpretation of the photochemically induced valence bond isomerizations found in arylthiophenes involves an intermediate with an expanded valence shell for sulfur.[1] A study of some thioethenes was undertaken in order to gain information about the photochemical behavior of other unsaturated sulfur-containing systems. Phenylthioethenes proved to be particularly interesting and were investigated in some detail.

Results

Photolysis of 1-phenyl-1-phenylthioethene (**1a**) under N_2 in ether solution gave 2-phenylbenzo[*b*]thiophene (**2a**) and 3-phenylbenzo[*b*]thiophene (**3a**) (eq 1).

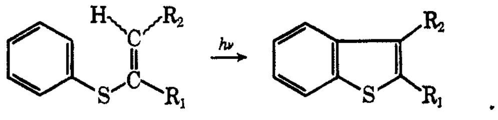


no detectable cyclization products except for a trace of **3b** from **4b** (1)

The yield of **2a** was raised from a trace (<1%) to 5% in the absence and the presence of iodine, respectively, while the yield of **3a** was about 4% either with or without iodine. No photochemically induced interconversion of **2a** and **3a** occurred. No 1-phenyl-2-phenylthioethene (**4a**) could be detected in the photolysis mixtures nor did this sulfide give any observable amounts of cyclization products **2a** or **3a** (eq 1) thereby eliminating the possibility that sulfide isomerization precedes ring closure.

In a similar manner photolysis of 1-phenyl-1-phenylthiopropene-1 (**1b**) gave 3-methyl-2-phenylbenzo[*b*]thiophene (**2b**) and 2-methyl-3-phenylbenzo[*b*]thiophene (**3b**) in yields of 2 and 4%, respectively. In the presence of iodine the yield of **2b** was raised to 8% while that of **3b** was 3.5%. No detectable isomerization of **1b** to 1-phenyl-2-phenylthiopropene-1 (**4b**) took place nor did **4b** upon photolysis yield any identifiable product other than a trace of **3b**. Interconversion of **2b** and **3b** did not occur upon photolysis. The cyclization reaction proceeded in nearly the same yield at 300 as at 254 mμ (see Experimental Section). Attempts to raise the yield by using different oxidizing agents failed. Benzophenone did not have any effect on the cyclization reaction.

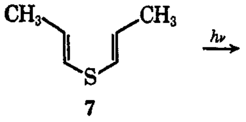
The photochemical reactions of some other phenylthioethenes (**5a–h**) were examined and the results of these experiments are shown in eq 2. In the cases where cyclization occurred only the "normal" products (**6**) could be found (eq 2). In the case of 1-phenylthioethene (**5a**) it was shown that the yield of benzo[*b*]thiophene was enhanced in the presence of iodine. 1,2-Di(phenylthio)ethene (**5g**) and 1-(1-propenylthio)propene-1 (**7**) (eq 3) gave no detectable amounts of cyclization products.



(2)

5 **6**

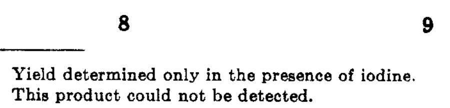
	Yield, %	
	Without I_2	With I_2
a, $R_1 = R_2 = H$	6.5	9.5
b, $R_1 = CH_3$; $R_2 = H$	...	9.0[2]
c, $R_1 = H$; $R_2 = CH_3$	...	2.5[2]
d, $R_1 = CH_3$; $R_2 = CH_3$	...	5.0[2]
e, $R_1 = R_2 = -(CH_2)_4-$	...	6.0[2]
f, $R_1 = R_2 = C_6H_5$	...	0.0[2-4]
g, $R_1 = H$; $R_2 = C_6H_5S$	...	0.0[2,3]
h, $R_1 = R_2 = -(CH{=}CH)_2-$	0[3,4]	2.5[4]



7

no cyclization products (3)

The photochemical cyclization of *p*-tolylthioethene (**8**) proceeded in the presence of iodine to give 5-methylbenzo[*b*]thiophene (**9**) in 9% yield (eq 4). No other



(4)

8 **9**

---

[1] For a summary of results, see H. Wynberg, R. M. Kellogg, H. van Driel, and G. E. Beekhuis, *J. Amer. Chem. Soc.*, **89**, 3501 (1967).

[2] Yield determined only in the presence of iodine.

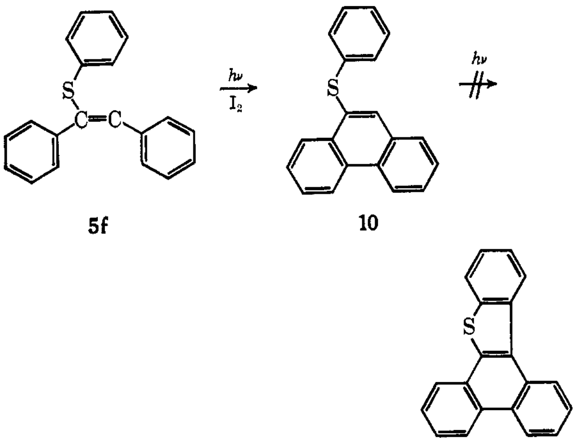
[3] This product could not be detected.

[4] Other product(s) were also identified.

cyclization products were detected. The rate of cyclization of **8** was much slower than that of phenylthioethene (**5a**) (see Experimental Section).

Phenyl sulfide (**5h**), upon photolysis in the presence of iodine, gave, in addition to the reported[5] phenyl disulfide (5% yield) and biphenyl (7.5% yield), bibenzothiophene (**6h**) in 2.5% yield. In the absence of iodine only biphenyl and phenyl disulfide were found, as previously reported.[5]

Photolysis of 1,2-diphenyl-1-phenylthioethene (**5f**) in the presence of iodine gave a 78% yield of 9-phenylthiophenanthrene (**10**) (eq 5) and no observable amounts of **6f** or **11**. The product **10** was identified by comparison with material prepared by an unambiguous synthesis. None of the cyclization product **11** was observed when **10** was photolyzed independently.



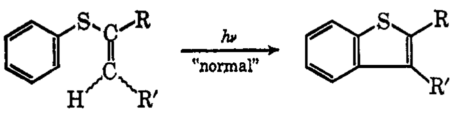
(5)

A number of attempts were made to characterize the other materials formed from photolyses of the phenylthioethenes. In the cases of **5b** and **5c** considerable amounts of phenyl disulfide were formed; this product was, however, found in no more than trace amounts in the photolyses of **5a** and **5d–h**. The crude photolysis mixtures consisted of a benzene- or ether-soluble oil as well as an undefined black or brown deposit. The soluble oil contained the benzo[*b*]thiophene plus undistillable material which resisted characterization.

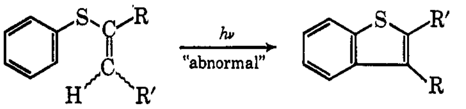
No reactions were observed with any of the phenylthioethenes in solution in the dark. Addition of a trace of acid or iodine also failed to induce any dark reactions. The possibility that the cyclization products arise from ground-state free-radical reactions was examined with **1b**; reaction at 80° in cyclohexane with azobisisobutyronitrile (AIBN) as initiator led only to formation of high molecular weight products and no benzo[*b*]thiophenes. The possibility that free phenylthiyl radicals might play a role in the photolyses was examined with **1b**; photolysis in the presence of phenyl disulfide and iodine led to products **2b** and **3b** in decreased rather than increased yield.

Discussion

In the photochemically induced cyclization of phenylthioethenes substituted in the α position with hydrogen or methyl, only the "normal" products are observed (eq 6). Iodine seems to enhance the yields in these reactions. When the α position is substituted with phenyl an "abnormal" benzo[*b*]thiophene is formed (eq 7) in addition to the "normal" product (eq 6). The yields of the "abnormal" products appear to be insensitive to the presence of iodine. These "abnormal" benzo[*b*]thiophenes must be primary photoproducts derived from a photoreaction of the α-phenyl-substituted phenylthioethenes.



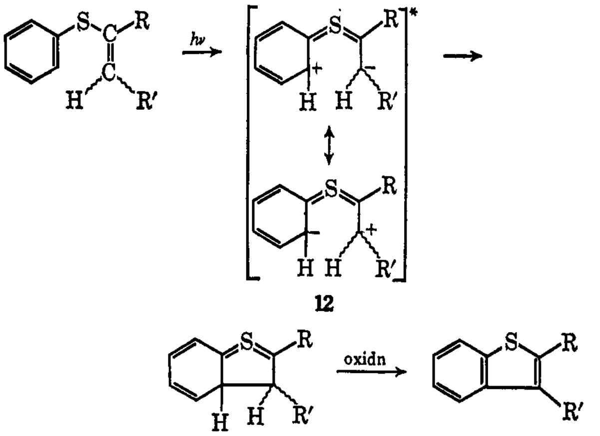
(6)



(7)

The photolysis of *p*-tolylthioethene (**8**) was carried out in order to determine if "normal" cyclization involves bond formation between the terminal carbon atom of the vinyl group and an *ortho* carbon in the phenyl ring. The formation of 5-methylbenzo[*b*]thiophene (**9**) as the exclusive product from this reaction supports this conclusion and argues against any unusual rearrangements in the phenyl ring. More involved labeling experiments with other systems are planned in order to check this possibility further.

A possible mechanistic rationalization for the formation of normal product is shown in eq 8.[6] The effectiveness of iodine in oxidizing the proposed dihydro intermediate has ample precedent in other systems.[7]



(8)

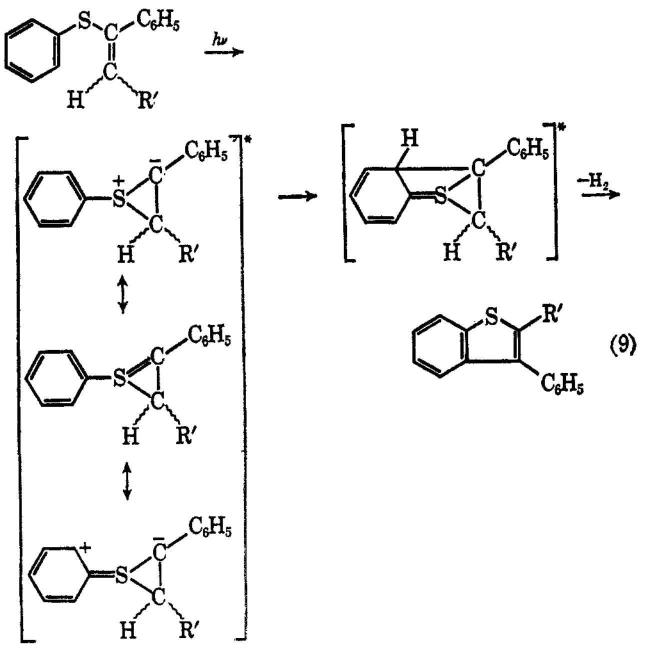
The presence of a phenyl group in the α position of the phenylthioethene appears to be essential to "abnormal" cyclization. This effect might arise from stabilization of structures such as **13** derived from interaction of the sulfur atom with the vinylic double bond (eq 9). Subsequent ring expansion followed by loss of hydrogen provides a rationalization for the formation of "abnormal" product. The failure to obtain "abnormal" cyclization products when the α position is substituted by hydrogen or methyl could be attributed to the

---

(5) W. Carruthers, *Nature*, **209**, 908 (1966); N. Kharasch and A. I. A. Khodair, *Chem. Commun.*, 98 (1967).

(6) One may, of course, imagine other valence bond structures for the proposed (excited?) intermediate **12**. Some precedent exists for sulfur valence shell expansion in photochemical reactions.[1]

(7) See, for example, F. B. Mallory, C. S. Wood, J. T. Gordon, L. C. Lindquist, and M. L. Savitz, *J. Amer. Chem. Soc.*, **84**, 4361 (1962).



13

(9)

inability of these substituents to stabilize effectively an adjacent partially charged center. The apparent ineffectiveness of iodine in the formation of the "abnormal" product suggests a spontaneous elimination of hydrogen in the formation of the thiophene ring.

Experimental Section

All melting points are corrected. Ultraviolet spectra were taken on a Zeiss PMQ II spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer Model 257 grating infrared spectrophotometer. Nuclear magnetic resonance (nmr) spectra were taken on a Varian A-60 instrument with tetramethylsilane (TMS) as internal reference. For mass spectra an Associated Electronic Industries MS 9 mass spectrophotometer was used. Microanalyses were carried out in the analytical section of this department under the direction of Mr. W. Hazenberg.

The small-scale photolyses were performed with a Hanau S 81 high pressure mercury lamp. Larger scale reactions were done using a Hanau Q 700 high pressure mercury lamp. The equipment has been described previously.[8] A few reactions were carried out in a Rayonet photochemical reactor using the light sources described elsewhere in this section. All irradiations were performed under nitrogen either with or without a trace of iodine as noted. The irradiations were continued until the starting material had disappeared. The irradiated solutions were concentrated by means of a rotatory evaporator, checked by glpc, and then chromatographed over aluminium oxide (Merck active neutral, activity I). The oily residue thus obtained contained higher molecular weight products in addition to the cyclization products. Preliminary identification and yield calculations were done by glpc using a F & M Model 810 gas chromatograph equipped with hydrogen flame detectors. Preparative glpc was done either with an F & M Model 775 Prepmaster or with a F & M Model 700 gas chromatograph, both equipped with thermal conductivity detectors.

1-Phenyl-2-phenylthioethene (4a)[9] had uv maxima (96% C_2H_5OH) at 304 mμ (ϵ 18,000); **1-phenyl-1-phenylthiopropene-1 (1b)**[10] had uv maxima (96% C_2H_5OH) at 250 mμ (ϵ 17,100); **phenylthioethene (5a)**[11] had uv maxima (96% C_2H_5OH) at 247 mμ (ϵ 8300) and 265 (8000); **1-phenylthiopropene-1 (5c)**[12] had uv maxima (96% C_2H_5OH) at 248 mμ (ϵ 10,200) and 264 (10,800); **1-phenylthiocyclohexene (5e)**[13] had uv maxima (96% C_2H_5OH) at 247 mμ (ϵ 8400) and 260 (7000); **1,2-diphenyl-1-phenylthioethene (5f)**[10] had uv maxima (96% C_2H_5OH) at 263 mμ (ϵ 15,100) and 308 (12,300); **1,2-di(phenylthio)ethene (5g)**[14] had uv maxima (96% C_2H_5OH) at 280 mμ (ϵ 16,300); **1-(1-propenylthio)propene-1 (7)**[15] had uv maxima (96% C_2H_5OH) at 240 mμ (ϵ 8400); and **5-methylbenzo[*b*]thiophene (9)**[16] had uv maxima (96% C_2H_5OH) at 230 mμ (ϵ 28,700), 258 (6300), 286 (1800), 291 (2400), 296 (2200), and 303 (3200).

These compounds were prepared as described in the literature.

1-Phenyl-2-phenylthiopropene-1 (**4b**)[17] was prepared in an analogous manner to **4a**[9] from the addition of thiophenol to methyl phenyl acetylene: bp 138–140° (1.1 mm); n^{20}_{D} 1.6457; uv, $\lambda_{\max}$ (96% C_2H_5OH) 260 mμ (ϵ 12,500), 285 (12,300); nmr (CCl_4), τ 8.0 (m, 3, CH_3, *cis–trans* isomers present), 3.4 (m, 1, $=CH$), and 2.8 [m, 10, $(C_6H_5)_2$].

1-Phenyl-1-phenylthioethene (**1a**) **and 2-phenylthiopropene-1** (**5b**) were prepared in low yield as described for 1-phenyl-1-phenylthiopropene-1 (**1b**)[10] by using acetophenone and acetone, respectively, in place of propiophenone. Campaigne and coworkers[10] did not obtain **1a** in a reaction carried out under similar conditions. **1-Phenyl-1-phenylthioethene** (**1a**)[18] had the following properties: bp 90–91.5° (0.12 mm); n^{21}_{D} 1.6323; uv, shoulder (96% C_2H_5OH) 244 mμ (ϵ 11,000); nmr (CCl_4), τ 4.48 (s, 1, $=CHH$), 4.82 (s, 1, $=CHH$), 2.8 [m, 10, $(C_6H_5)_2$]. **2-Phenylthiopropene-1** (**5b**) had the following properties: bp 91° (14 mm), n^{20}_{D} 1.5642 [lit.[19] bp 68–69° (8 mm), n^{20}_{D} 1.5690]; uv $\lambda_{\max}$ (96% C_2H_5OH) 244 mμ (ϵ 5100) and 264 (4000); nmr (CCl_4), τ 8.05 (q, 3, J = 1.2 and 0.7 Hz, CH_3), 5.15 (m, 1, $=CHH$), 4.90 (m, 1, $=CHH$), 2.75 (m, 5, C_6H_5).

2-Phenylthiobutene-2 (**5d**) was prepared by isomerization of 3-phenylthiobutene-1[20] with potassium *t*-butoxide in dimethoxyethane:[15] bp 85–86° (1 mm); n^{21}_{D} 1.5707; uv $\lambda_{\max}$ (96% C_2H_5OH) 247 mμ (ϵ 8900) and 261 (7000); nmr (CCl_4), τ 8.10 (m, 6, $(CH_3)_2$), 4.10 (m, 1, $=CH$), 2.80 (m, 5, C_6H_5).

***p*-Tolylthioethene** (**8**) was prepared by a multistep synthesis beginning from the reaction of *p*-tolylthiol with 1-chloro-2-hydroxyethane.[21] The 1-*p*-tolylthio-2-hydroxyethane obtained was converted into 1-*p*-tolylthio-2-chloroethane by treatment with thionyl chloride.[22] Reaction[11] with aqueous KOH gave **8**: bp 95–97° (15 mm); n^{20}_{D} 1.5770 [lit.[9] bp 78.0° (4.0 mm); n^{20}_{D} 1.5727]; uv $\lambda_{\max}$ (C_6H_{12}) 250 mμ (ϵ 7300) and 267 (7000).

Photolysis of 1-phenyl-1-phenylthioethene (**1a**) (190 mg in 125 ml of ether) in the presence of a trace of iodine gave two products detectable by glpc (6-ft DEGS, 190°). These were isolated from the exit port of the F & M 700 (6-ft DEGS, 170°). The ir spectra of these compounds were identical in all respects with those of 3-phenylbenzo[*b*]thiophene (**3a**) and 2-phenylbenzo[*b*]thiophene (**2a**), respectively. Further confirmation of the identity of **2a** was obtained from its isolation, in very low yield, as a precipitate from another reaction mixture; ir and uv spectra were identical with those of authentic material and a mixture melting point determination with the latter showed no depression. No isomeric 1-phenyl-2-phenylthioethene (**4a**) could be detected in gas chromatograms of samples taken during the course of photolysis. Product yields from irradiations carried out in the presence of iodine, calculated by glpc (4-ft DEGS, 190°), were about 5% **2a** and 4% **3a**. Without iodine the yield of **3a** remained approximately the same while only a trace of **2a** was formed.

2-Phenylbenzo[*b*]thiophene (**2a**)[23] had mp 170–172°; uv maxima (CH_2Cl_2) were at 232 mμ (ϵ 17,400), 256 (9800), 299

---

[8] H. Wynberg, H. van Driel, R. M. Kellogg, and J. Buter, *J. Amer. Chem. Soc.*, **89**, 3487 (1967).

[9] W. E. Truce, H. E. Hill, and M. M. Boudakian, *ibid.*, **78**, 2760 (1956).

[10] E. Campaigne and J. R. Leal, *ibid.*, **76**, 1272 (1954).

[11] F. Montanari, *Boll. Sci. Fac. Chim. Ind. Bologna*, **14**, 55 (1956); *Chem. Abstr.*, **51**, 5723 (1957).

[12] D. S. Tarbell and M. A. McCall, *J. Amer. Chem. Soc.*, **74**, 48 (1952).

[13] We are indebted to Professor W. E. Parham for this procedure taken from the M.S. Thesis of N. Gill, University of Minnesota, Minneapolis, Minn., 1964.

[14] W. E. Parham and J. Heberling, *J. Amer. Chem. Soc.*, **77**, 1175 (1955).

[15] C. C. Price and W. H. Snyder, *J. Org. Chem.*, **27**, 4639 (1962).

[16] D. S. Tarbell, D. K. Fukushima, and H. Dam, *J. Amer. Chem. Soc.*, **67**, 1643 (1945).

[17] Y.-C. Liu and T.-I. Chang, *Hua Hsueh Hsueh Pao*, **30**, 197 (1964); *Chem. Abstr.*, **61**, 8217 (1964).

[18] H. J. Schneider, U. S. Patent 3,050,563 (Aug 21, 1962); *Chem. Abstr.*, **58**, 1350 (1963).

[19] N. K. Kul'bovskaya, E. P. Gracheva, M. F. Shostakovskii, *Zh. Obshch. Khim.*, **30**, 81 (1960); *Chem. Abstr.*, **54**, 20949*g* (1960).

[20] A. C. Cope, D. E. Morrison, and L. Field, *J. Amer. Chem. Soc.*, **72**, 59 (1950).

[21] W. Steinkopf, J. Herold, and J. Stöhr, *Ber.*, **53**, 1007 (1920).

[22] W. R. Kirner and W. Windus, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 136.

[23] S. Middelton, *Aust. J. Chem.*, **12**, 218 (1959).

(18,700). Irradiation of this material (125 mg in 125 ml of ether) either with or without iodine failed to give any 3-phenylbenzo[*b*]thiophene (**3a**). On one occasion irradiation without iodine led to the formation of a small amount of an extremely insoluble white solid which detonated upon an attempt to determine its melting point.[24] This material is likely peroxidic in nature.

3-Phenylbenzo[*b*]thiophene (**3a**) was prepared by the described method:[25] bp 117–118° (0.25 mm); $n^{20}\text{D}$ 1.6823 [lit.[25] bp 100–120° (0.1 mm); $n^{20.5}\text{D}$ 1.6792]; uv, $\lambda_{\max}$ (CH_2Cl_2) 235 mμ (ϵ 29,500), 264 (8300), 294 (6000), 303 (6200). Irradiation (320 mg in 115 ml of ether) with or without iodine failed to produce 2-phenylbenzo[*b*]thiophene (**2a**) or any other identifiable products other than recovered starting material.

Irradiation of 1-phenyl-2-phenylthioethene (**4a**) (isomer with J_{vinyl} = 15 Hz, mp 33.5–34°; 201 mg in 120 ml of ether) for 2 hr with or without iodine gave an oil in which no 2- or 3-phenylbenzo[*b*]thiophene (**2a** and **3a**) could be detected by glpc (6-ft DEGS, 190°) or ir spectroscopy. Only the presence of starting material and its geometrical isomer (J_{vinyl} = 10 Hz) could be demonstrated.

Photolysis of 1-phenyl-1-phenylthiopropene-1 (**1b**) was always done with one pure isomer (mp 42.5–43°). Irradiation (500 mg in 150 ml ether) with an S-81 lamp for 20 min led to a mixture of geometrical isomers as shown by the nmr spectrum which gave an additional doublet for the methyl protons and new vinyl splittings. Very small amounts of two longer retention time products could also be seen in the gas chromatograms. Irradiation for 5 hr led to disappearance of the starting material and its geometric isomer and an increase in the amount of the two longer retention time products. These latter products, prepared on larger scale by photolysis with a Q-700 lamp, were isolated by preparative gas chromatography (F & M 775, 8-ft 25% DEGS, 195°). Infrared, uv, and nmr spectra and glpc retention times of these two photoproducts were identical with those of authentic 2-methyl-3-phenylbenzo[*b*]thiophene (**3b**) and 3-methyl-2-phenylbenzo[*b*]thiophene (**2b**). The molecular weights determined by mass spectrometry agreed with those calculated for the above mentioned products. The yields calculated by glpc (4-ft DEGS, 190°) were 2% **2b** and 4% **3b**. When the reactions were carried out in the presence of traces of iodine the yields were 8% **2b** and 3.5% **3b**.

Examination of crude irradiation mixtures by nmr spectroscopy showed no peaks assignable to the isomers of the starting sulfide, 1-phenyl-2-phenylthiopropene-1 (**4b**) or 2-phenyl-1-phenylthiopropene-1; this was also substantiated by gas chromatographic separations.

The same reaction was observed, although in lower yields, in methanol solution. Photolyses in ethanol with cupric chloride and iodine as oxidant or in benzene with selenium as oxidant failed to give any cyclization products. Reactions in ether solution with iodine as oxidant carried out in Rayonet reactor using 3000-Å lamps gave similar yields with those carried out with the S-81 lamps. Further reactions in the same reactor showed that equimolar amounts of benzophenone had no observable effect on the photolysis (although *cis–trans* equilibrium was very rapidly established in the presence of benzophenone upon brief exposure to room light). Starting material disappeared but no cyclization products were formed when benzene was used as solvent with iodine as oxidant. Irradiation with 3500-Å lamps in benzene solution with added benzophenone likewise caused disappearance of starting material but no benzo[*b*]thiophenes were formed.

3-Methyl-2-phenylbenzo[*b*]thiophene (**2b**) was prepared in 45% yield by cyclization of 1-phenyl-1-phenylthiopropan-2-one with polyphosphoric acid as described for 3-phenylbenzo[*b*]thiophene (**3a**):[25] mp 77–78°; uv, $\lambda_{\max}$ (CH_2Cl_2) 236 mμ (ϵ 20,800), 251 (18,600), 293 (15,900); nmr (CCl_4), τ 7.60 (s, 3, CH_3) and 2.75 (m, 9, aromatic H). Irradiation of **2b** (125 mg in 125 ml of ether) with or without iodine failed to yield any 2-methyl-3-phenylbenzo[*b*]thiophene (**3b**) or any other identifiable products other than recovered starting material.

Anal. Calcd for $C_{15}H_{12}S$: C, 80.31; H, 5.40; S, 14.29. Found: C, 80.0; H, 5.5; S, 14.1.

2-Methyl-3-phenylbenzo[*b*]thiophene (**3b**)[26] was prepared in 70% yield by cyclization of α-(phenylthio)propiophenone with polyphosphoric acid: bp 112–114° (0.15 mm) [lit.[23] bp 145–150 (3 mm)]; $n^{20}\text{D}$ 1.6630; mp 37.5–39°; uv, $\lambda_{\max}$ (CH_2Cl_2) 236 mμ (ϵ 31,700), 266 (9300), 293 (4800), 302 (4600); nmr (CCl_4), τ 7.57 (s, 3, CH_3) and 2.7 (m, 9, aromatic H). Irradiation of this material (300 mg in 150 ml of ether) with or without iodine failed to produce any 3-methyl-2-phenylbenzo[*b*]thiophene (**2b**).

Irradiation of 1-phenyl-2-phenylthiopropene-1 (**4b**) (225 mg in 125 ml of ether) in the presence of a trace of iodine gave an oil after chromatography over aluminium oxide. By glpc (4-ft DEGS, 190°) a trace of a compound (<1%) was observed which had a retention time the same as that of 2-methyl-3-phenylbenzo[*b*]thiophene (**3b**).

Irradiation of phenylthioethene (**5a**) (220 mg in 150 ml of ether) in the presence of iodine for 1 hr gave in 9.5% yield as determined by glpc (6-ft DEGS, 140°) benzo[*b*]thiophene (**6a**). The uv spectrum of material isolated by means of glpc (4-ft SE-30, 150°) was identical with that of authentic benzo[*b*]thiophene. In the absence of iodine the yield was 6.5%.

Irradiation of 2-phenylthiopropene-1 (**5b**) (400 mg in 115 ml of ether) in the presence of iodine gave 2-methylbenzo[*b*]thiophene (**6b**) in 9% yield as determined by glpc (4-ft SE-30, 180°). This product was identified by its glpc retention time and by the characteristic peak in the nmr spectrum for the methyl protons: τ 7.50 (d, J = *ca.* 1 Hz). No 3-methylbenzo[*b*]thiophene (**6c**) could be detected either by nmr spectroscopy or glpc. A large amount of phenyl disulfide was formed which was isolated by preparative glpc and identified by comparison with authentic material.

2-Methylbenzo[*b*]thiophene (**6b**) was prepared following the described procedure:[27] uv, $\lambda_{\max}$ (C_2H_5OH) 229 mμ (ϵ 29,100), 260 (7900), 287 (1900), 298 (2200); nmr (CCl_4), τ 7.50 (d, 3, J = *ca.* 1 Hz, CH_3) and 2.7 (m, 5, aromatic H).

3-Methylbenzo[*b*]thiophene (**6c**) was obtained as reported in the literature:[28] uv $\lambda_{\max}$ (C_2H_5OH) 230 mμ (ϵ 29,300), 262 (4500), 290 (2800), 299 (3300); nmr (CCl_4), τ 7.70 (d, 3, J = *ca.* 1.5 Hz, CH_3) and 2.7 (m, 5, aromatic H).

Irradiation of 1-phenylthiopropene-1 (**5c**) (*cis–trans* mixture, 400 mg in 115 ml of ether) in the presence of iodine for 1.5 hr gave 3-methylbenzo[*b*]thiophene (**6c**) in 2.5% yield as determined by glpc (4-ft SE-30, 180°). The product was identified by its glpc retention time and the characteristic peak in the nmr spectrum for the methyl protons: τ 7.70 (d, J = *ca.* 1.5 Hz). No 2-methylbenzo[*b*]thiophene (**6b**) could be detected by nmr spectroscopy or glpc. A large amount of phenyl disulfide was formed which was isolated by preparative glpc.

Photolysis of 2-phenylthiobutene-2 (**5d**) (300 mg in 115 ml of ether) in the presence of iodine for 2.25 hr led to the formation of 2,3-dimethylbenzo[*b*]thiophene (**6d**) in 5% yield as determined by glpc (4-ft SE-30, 165°). A small amount of this product was trapped from the exit port of the F & M 700 and its ir spectrum was shown to be identical with that of authentic **6d** prepared as described in the literature.[28]

Photolysis of 1-phenylthiocyclohexene (**5e**) (1.0 g in 550 ml of ether) in a Q-700 lamp for 3 hr with a trace of iodine gave 1,2,3,4-tetrahydrodibenzo[*b*]thiophene (**6e**) in 6% yield as determined by glpc (4-ft SE-30, 260°). This product was isolated from the exit port of the F & M 700 and its ir spectrum was shown to be identical with that of authentic **6e** prepared as described in the literature.[29]

Photolysis of *p*-tolylthioethene (**8**) (365 mg in 125 ml of ether) for 50 hr in the presence of iodine gave, after work-up, 202 mg of an oil. The ir spectrum of this oil showed mainly peaks corresponding to 5-methylbenzo[*b*]thiophene (**9**) plus a few peaks in the aromatic region. The 5-methylbenzo[*b*]thiophene was isolated by glpc separation (4-ft SE-30, 170°) and its ir and nmr spectra were shown to be completely identical with those of authentic material. The yield calculated by glpc was 9%. The balance of the oil was undistillable and we were unable to characterize any product from it. Upon standing in the dark in ether solution containing hydrogen iodide no cyclization occurred eliminating the possibility of a "dark" acid-catalyzed reaction.

Photolysis of 1,2-diphenyl-1-phenylthioethene (**5f**) (200 mg in 115 ml of ether) for 3.75 hr in the presence of iodine gave,

---

[24] Observation by Mr. G. E. Beekhuis of these laboratories.

[25] O. Dann and M. Kokorudz, *Ber.*, **91**, 172 (1958).

[26] T. Srinivasa Murthy and B. D. Tilak, *J. Sci. Ind. Res.*, **19B**, 395 (1960); *Chem. Abstr.*, **55**, 11388 (1961).

[27] C. Hansch and W. A. Blondon, *J. Amer. Chem. Soc.*, **70**, 1561 (1948).

[28] E. E. G. Werner, *Rec. Trav. Chim. Pays-Bas*, **68**, 509 (1949).

[29] K. Rabindran and B. D. Tilak, *Curr. Sci.*, **20**, 207 (1951); *Chem. Abstr.*, **47**, 3294 (1953).

after work-up, 180 mg of crude solid, mp 110–130°. This material, after recrystallization from *n*-hexane, gave 156 mg (78% yield) of white crystals, mp 141–143°, shown by glpc (4-ft SE-30, 250°) and ir, nmr, and uv spectra to be 9-phenylthiophenanthrene (**10**). No other reaction products could be detected.

9-Phenylthiophenanthrene (**10**) was prepared by reaction of the Grignard reagent of 9-bromophenanthrene[29] in benzene–ether with phenyl disulfide.[30] After repeated sublimations, chromatography over aluminium oxide, and recrystallization from methanol, a 40% yield of **10** was obtained, mp 134–136°. The material appeared to contain a trace of phenyl disulfide but ir, uv, and nmr spectra agreed with those of photolysis product **10**. Irradiation of **10** for 6.5 hr in ether solution in the presence of iodine led only to slow decomposition.

Anal. Calcd for $C_{20}H_{14}S$: C, 83.87; H, 4.93; S, 11.20. Found: C, 84.2; H, 4.8; S, 10.8.

Irradiation of phenyl sulfide (**5h**) (1.5 g in 550 ml of ether) in the Q-700 lamp for 3 hr in the presence of iodine led to formation of biphenyl (7.5% yield), dibenzothiophene (**6h**) (2.5% yield), and phenyl disulfide (5% yield) as determined by glpc (4-ft SE-30, 185°). These products were collected from the exit port of the gas chromatograph and either their uv or ir spectra shown to be identical with those of the authentic materials. When phenyl sulfide (500 mg in 115 ml ether) was irradiated for 5.3 hr in the absence of I_2 only biphenyl and phenyl disulfide could be identified.

Photolysis of 1,2-diphenylthioethene (**5g**) **and 1-(1-propenylthio)propene-1** (**7**) on a small scale in the presence of iodine failed to yield any cyclization products.

Dark reactions were not observed with the phenylthioethenes in ether solution. Addition of iodine likewise failed to promote a dark reaction. The reaction of **1b** at 80° in the dark in cyclohexane solution with AIBN initiator was examined; the material was consumed under these conditions but no benzo[*b*]thiophenes were formed. A photochemical reaction of **1b** carried out with an equimolar amount of phenyl disulfide gave a somewhat lower yield of **2b** and **3b** than a comparison reaction run without phenyl disulfide.

Registry No.—**1a**, 16336-45-1; **1b**, 16336-46-2; **2b**, 10371-50-3; **5a**, 1822-73-7; **5b**, 7594-43-6; **5c** (*cis*), 16336-50-8; **5c** (*trans*), 15436-04-1; **5d**, 16336-52-0; **5e**, 4922-47-8; **5f**, 6052-46-6; **5h**, 139-66-2; **8**, 16336-54-2; **10**, 16336-55-3.

---

[30] A. Burton and W. A. Davy, *J. Chem. Soc.*, 528 (1948).

Chemistry of Enolates. V. Solvent Effects on the Activity of Carbanions[1]

H. D. Zook, T. J. Russo, E. F. Ferrand, and D. S. Stotz

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania

Received December 6, 1967

The kinetics and orientation in the alkylation of ketone enolates are extremely sensitive to solvent media. Alkylation rates and O/C product ratios are markedly increased by polyether solvents capable of chelating the accompanying metallic cation and by certain polar additives which exhibit first-order participation in the reaction kinetics. Increased electrical conductance of the enolate solutions parallels these chemical effects. In a specific solvent system, O/C product ratios are dependent on the steric requirements of both enolate and alkylating agent.

Much recent research has uncovered several factors affecting the reactivity and orientation of ambident[2] anions in nucleophilic reactions.[2–11] The factor producing the most significant effects is the reaction medium. Anions derived from phenols,[3–5] pyrroles,[8] ketones,[9] fluorene,[7] and malonic ester[6] exhibit similar behavior to changes in media. Two distinct effects are recognized: anion solvation by hydrogen bonding in protic solvents[3] and solvation of the accompanying cation by the bulk media,[7] the reaction product,[10] or an additive.[6]

Although ketone enolates are among the simpler ambident ions and are widely found in synthetic reactions, very little concerning their properties in solution or their orientation in the alkylation reaction has been reported. In this study ten dialkyl and alkyl aryl ketones are converted into the corresponding alkali metal enolates in a variety of solvent systems. Information on the nature of the enolates in solution is obtained from measurements of electrical conductivity, infrared and nmr spectra, boiling point elevation, orientation, and kinetics of alkylation.

Results and Discussion

Table I contains a summary of kinetic data for the alkylation of sodiodiphenylacetophenone in diglyme and mixed solvent systems. The alkylation of this ketone in these solvents occurs exclusively on oxygen to give enol ethers which, unlike ketonic products, do not compete in the solvation of the cation. Thus, excellent first-order dependence on enolate can be observed through the second and third half-lives of the reaction. A comparison of the alkylation of this ketone with that of butyrophenone in monoglyme is shown in Figure 1. Autocatalysis in the latter reaction causes the downward curvature of the line as the concentration of ketonic product increases.[10]

Most of the alkylations were carried out by a large excess of halide under pseudo-first-order conditions, although two runs made under second-order conditions gave linear plots (Figure 2) and rate constants in good agreement with those calculated from pseudo-first-order constants. These results are consistent with

---

[1] We gratefully acknowledge grants from the National Science Foundation in support of this work; the Department of Chemistry for an A-60 nmr spectrometer; an Eastman Kodak Co. Fellowship (T. J. R.); and an NSF Science Faculty Fellowship (E. F. F.).

[2] Anions which may undergo covalent bond formation at one or the other of two available positions: N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *J. Amer. Chem. Soc.*, **77**, 6269 (1955).

[3] N. Kornblum, P. J. Berrigan, and W. J. LeNoble, *ibid.*, **85**, 1141 (1963); N. Kornblum, R. Seltzer, and P. Haberfield; *ibid.*, **85**, 1148 (1963).

[4] V. A. Zagorevsky, *J. Gen. Chem. USSR*, **27**, 3055 (1957); **28**, 488 (1958); *Chem. Abstr.*, **52**, 8108, 14572 (1958).

[5] D. Y. Curtin, R. J. Crawford, and M. Wilhelm, *J. Amer. Chem. Soc.*, **80**, 1391 (1958); D. Y. Curtin and R. R. Fraser, *ibid.*, **80**, 6016 (1958).

[6] H. E. Zaugg, B. W. Horrom, and S. Borgwardt, *ibid.*, **82**, 2895 (1960). H. E. Zaugg, *ibid.*, **82**, 2903 (1960); **83**, 837 (1961).

[7] G. W. H. Scherf and R. K. Brown, *Can. J. Chem.*, **38**, 2450 (1960).

[8] C. F. Hobbs, C. K. McMillin, E. P. Papadopoulos, and C. A. VanderWerf, *J. Amer. Chem. Soc.*, **84**, 43 (1962).

[9] H. D. Zook and T. J. Russo, *ibid.*, **82**, 1258 (1960).

[10] H. D. Zook and W. L. Gumby, *ibid.*, **82**, 1386 (1960).

[11] J. F. Garst, D. Walmsley, C. Hewitt, W. R. Richards, and E. R. Zabolotny, *ibid.*, **86**, 412 (1964).