($CDCl_3$) δ 126.0, 126.2 (2 C), 130.9 (tertiary C), 131.2, 132.0, 142.2 (lower intensity, quaternary C); UV (C_6H_{12}) λ_{max} 254 nm (log ε 4.94), 273 sh (4.66), 294 sh (4.40), 304 sh (4.32), 317 sh (4.14), 346 sh (3.02), and 361 sh (2.96). Anal. Calcd for $C_{28}H_{16}$: C, 95.42, H, 4.58. Found: C, 94.84, H, 4.74.

(h) 2,17-Dithia[3.3](3,3′)biphenylophane *S,S,S′,S′*-Tetroxide (12). The dithiacyclophane **10** (100 mg; 0.23 mmol) was dissolved in toluene (100 mL) and acetic acid (20 mL) and brought to reflux. Hydrogen peroxide (30%, 5 mL, excess) was added dropwise and the mixture was heated under reflux for 18 h. The precipitate was filtered, washed with sodium bicarbonate (5% aqueous) and water, and dried to yield 2,17-dithia[3.3](3,3′)biphenylophane *S,S,S′,S′*-tetroxide (**12**) (90 mg, 84%) as white prisms: mp >300 °C; mass spectrum $M^+ + 2$ at *m/e* 490 (6% rel intensity), $M^+ + 1$ 489 (10), M^+ 488.1116 (24) [$C_{28}H_{24}S_2O_4$ requires 488.1116], and fragmentation ions at 360 (74), 194 (86), 181 (69), 180 (82), 179 (71), 178 (98), 167 (100), and 165 (94); IR (Nujol mull) ν_{max} 1120, 1320 cm^{-1} (strong, sharp, $-SO_2-$). Anal. Calcd for $C_{28}H_{24}S_2O_4$: C, 68.85; H, 4.92; S, 13.12. Found: C, 68.48; H, 4.89; S, 13.0.

(i) [2.2](3,3′)Biphenylophane (16). (A) Freshly prepared W-2 Raney Nickel[17] (0.5 g) was added to a solution of the disulfoxide **15** (100 mg; 0.21 mmol) in ethanol (50 mL) and the mixture was heated under reflux for 3 h. The solution was filtered and concentrated; the residue was chromatographed on alumina to yield [2.2](3,3′)biphenylophane (**16**) (50 mg, 67%) as white needles (C_6H_{12}): mp 174–176 °C; mass spectrum $M^+ + 2$ at *m/e* 362 (14% rel intensity), $M^+ + 1$ 361 (32), M^+ 360.1878 (100) [$C_{28}H_{24}$ requires 360.1878], and fragmentation peaks at 178 (23), 177 (36), 176 (23), 175 (27), 166 (27), and 164 (32); ^1H NMR ($CDCl_3$) δ 2.86 (s, 2 H), 5.95 (dt, J = 1.7 and 0.7 Hz, H_i), 6.97 (dt, J = 7 and 1.7 Hz, $H_{b/d}$), 7.13 (dt, J = 7 and 1.7 Hz, $H_{d/b}$), 7.15 (t, J = 7 Hz, H_c); ^{13}C NMR ($CDCl_3$) δ 38.6 (benzylic C), 124.6, 127.0, 128.5, 131.2 (tertiary C), 140.4, 141.3 (lower intensity, quaternary C). Anal. Calcd for $C_{28}H_{24}$: C, 93.33; H, 6.66. Found: C, 93.23; H, 6.59.

(B) The disulfone **12** (80 mg; 0.16 mmol) was heated at 500 °C (100 mm) in a silica tube using a tube-furnace and a slow stream of nitrogen. The product which sublimed was collected and chromatographed on alumina with cyclohexane to yield the cyclophane **16** (40 mg, 68%) identical in all respects to the sample described in (A).

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Registry No.—**9**, 66018-33-5; **10**, 66018-32-4; **11**, 66018-31-3; **12**, 66018-34-6; **13**, 63838-46-0; **14**, 66008-63-7; **15**, 66008-62-6; **16**, 24656-54-0; 3,3′-bis(mercaptamethyl)biphenyl, 66018-35-7; 3,3′-bis(bromomethyl)biphenyl, 24656-53-9; dimethoxycarbonium tetrafluoroborate, 18346-68-4.

References and Notes

(1) Part VIII: P. J. Jessup and J. A. Reiss, *Aust. J. Chem.*, **30**, 851 (1977). This work was presented in part at an Organic Synthesis Symposium of the Royal Australian Chemical Institute, Melbourne, in December 1976.
(2) J. H. Dopper and H. Wynberg, *Tetrahedron Lett.*, 763 (1972).
(3) (a) E. Clar and M. Zander, *J. Chem. Soc.*, 4616 (1957); (b) W. Baker, F. Glocking, and J. F. W. McOmie, *ibid.*, 118 (1951); (c) J. T. Craig, B. Halton, and S. F. Lo, *Aust. J. Chem.*, **28**, 913, (1975); (d) J. R. Davy and J. A. Reiss, *J. Chem. Soc., Chem. Commun.*, 806 (1973).
(4) H. Erdtmann and H. E. Hogberg, *Tetrahedron Lett.*, 3389 (1970).
(5) D. Hellwinkel and G. Reiff, *Angew. Chem., Int. Ed. Engl.*, **9**, 527 (1970).
(6) J. H. Dopper and H. Wynberg, *J. Org. Chem.*, **40**, 1957 (1975).
(7) W. E. Barth and R. G. Lawton, *J. Am. Chem. Soc.*, **93**, 1730 (1971).
(8) J. C. Hanson and C. E. Nordman, Abstracts of the American Crystallography Association, August 1967, p 69 (N8). See also ref 7.
(9) B. Thulin and O. Wennerstrom, *Acta Chem. Scand., Ser. B*, **30**, 369 (1976).
(10) P. J. Jessup and J. A. Reiss, *Aust. J. Chem.*, **29**, 173 (1976).
(11) B. Thulin and O. Wennerstrom, *Tetrahedron Lett.*, 929 (1977).
(12) (a) The nomenclature that we have used for the biphenylcyclophanes is based on that of Staab[12b] for a related series of (4,4′)biphenylophanes; (b) H. A. Staab and M. Haenel, *Chem. Ber.*, **106**, 2190 (1973).
(13) D. F. Balaam, J. Chippindall, J. R. Davy, and J. A. Reiss, *Chem. Ind. (London)*, 354 (1975).
(14) W. Wenner, *J. Org. Chem.*, **17**, 523 (1952).
(15) R. F. Borch, *J. Org. Chem.*, **34**, 627 (1969).
(16) R. H. Mitchell, T. Otsubo, and V. Boekelheide, *Tetrahedron Lett.*, 219 (1975).
(17) R. Mozingo, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1955, p 181.

Gas-Phase Photolysis of 1,2,3-Thiadiazoles: Evidence for Thiirene Intermediates

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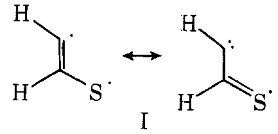
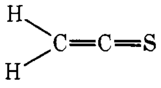
The gas-phase photolyses of 1,2,3-thiadiazole (VIa), 4-methyl-1,2,3-thiadiazole (VIb), and 5-methyl-1,2,3-thiadiazole (VIc) have been studied. Evidence for the formation of thiirene intermediates has been obtained by trapping experiments with hexafluoro-2-butyne. While VIa yields 2,3-bis(trifluoromethyl)thiophene, both isomers VIb and VIc yield only one and the same product, 5-methyl-2,3-bis(trifluoromethyl)thiophene, suggesting a common precursor, namely, methylthiirene.

The question of the existence of thiirenes, the family of unsaturated thiiranes, has only recently been considered. Thiirenes were first postulated as short-lived transients in the addition of $^1D_2$ sulfur atoms to alkynes[1] and in the case of acetylene the following isomeric C_2H_2S structures can be considered:



I

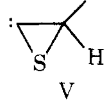
II



III

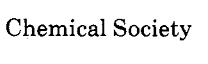
HC≡CSH

IV



V

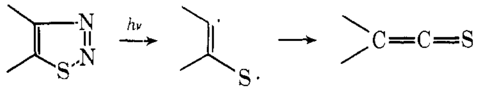
Flash photolysis experiments with kinetic mass spectrometry[2] have shown the presence of adducts having lifetimes from a tenth to several seconds, depending on the nature of the alkyne. Conventional photolysis of COS, a source of $S(^1D_2)$ atoms, in the presence of alkynes has been shown to yield thiophene, carbon disulfide, benzene, and a solid polymer as end products. The thiophene yield is highest from the $S(^1D_2)$ + $CF_3C{\equiv}CCF_3$ reaction, which makes III, IV, and V unlikely precursors since forth and back migration of CF_3 would be required here and the migrational aptitude of CF_3 is lower than that of H or CH_3 in C_2H_2, $CH{\equiv}CCH_3$, or $CH_3C{\equiv}CCH_3$. Preference for thiirene II as the precursor, compared with thioformyl methylene I, was stated on the basis of preliminary semiempirical MO computations which indicated that the least motion reaction path



is spin and orbital symmetry allowed and energetically feasible.

1,2,3-Thiadiazoles VI appeared to be the most promising source of compounds for the generation of C_2H_2S isomers. The formation of thioketene in the thermal decomposition of 1,2,3-thiadiazoles has been detected in flash thermolysis,[3] by chemical scavenging experiments, e.g., the thermolysis of VI in ethylene glycol produces thiono esters,[4] and by means of photoelectron spectroscopy.[5] Attempts to trap thiirene II intermediates via complexation with diiron carbonyl catalyst have been unsuccessful,[6,7] but on the other hand two isomeric thioketocarbene I-$Fe_2(CO)_6$ complexes have been isolated[7] from 4,5-substituted VI, indicating the possibility of a common precursor, most probably thiirene II.

The first reported study of the photolysis of 1,2,3-thiadiazoles is that of Kirmse and Hörner in 1958[8] who described the formation of thiofulvenes upon irradiation of 1,2,3-thiadiazole and several of its derivatives via the reaction of diradical I with thioketene III, presumably formed from the rearrangement of II:



VI I III

Subsequently Huisgen[9] characterized diradical I as a 1,3-dipolarophile which adds preferentially across the C=S bond as compared to C=C or C=N bonds. Since then the photolysis of 1,2,3-thiadiazoles in benzene solution has been extensively studied by Zeller *et al.*[10] Thiofulvenes, thioanthrenes, thiophenes, and 1,2,5-trithiepins were identified as reaction products, formed via self- and cross-combination reactions of I and III (Scheme I). On the other hand, photolysis of VI using unfiltered (λ >290 nm) radiation in an argon matrix at 8 K generates ethynyl mercaptan as well as thioketene.[11] In addition, a photolabile intermediate, which was claimed[12] to be thiirene, is observed upon irradiation with (λ 300 nm) filtered light. Photolysis of matrix-isolated substituted thiadiazoles, however, does not generate ethynyl mercaptans, and when the exciting radiation is filtered (λ 265 nm) new IR spectra are observed which are consistent with the carriers being the corresponding thiirenes II.[13] It was also shown that thiirenes undergo secondary photolysis to yield thioketenes III.

Scheme I

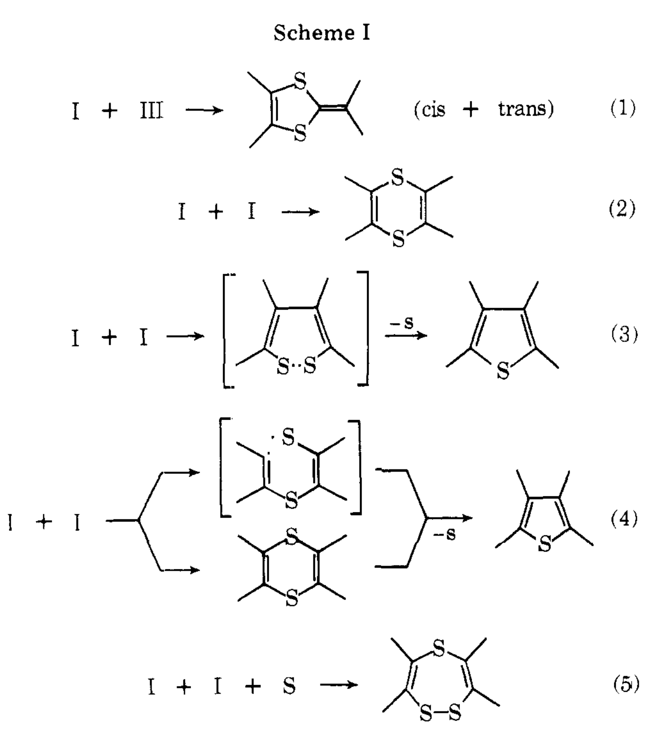


Table I. Gas-Phase Photolysis of VIa, VIb, and VIc[a]

Thiadiazole	Alkyne, %	Methane, %	CS_2, %
VIa	12.6		1.8
VIb	14.4	5.0	3.6
VIc	16.1	4.8	4.8

[a] Percentages are given in terms of N_2.

The present study of the gas-phase photolysis of 1,2,3-thiadiazole (VIa), 4-methyl-1,2,3-thiadiazole (VIb), and 5-methyl-1,2,3-thiadiazole (VIc) was therefore undertaken under conditions similar to those used in the COS + acetylene studies in order to examine the effects of radical scavengers and to obtain further chemical evidence for the transient existence of thiirene.

Experimental Section

Apparatus. Standard high-vacuum techniques and apparatus were employed throughout the investigation. The light source was a medium-pressure, mercury arc, Hanovia Model 30620, equipped with a 7910 vycor filter. Photolyses were carried out in a 10 × 4.5 cm quartz cell.

A Varian Aerograph (90P) GC was used for preparation purposes. UV spectra were obtained on a Perkin-Elmer Model 137 spectrophotometer and the NMR spectra were recorded on a Varian Associates Model HR-100 spectrometer using Me_4Si as internal standard. Values are given in τ units. Mass spectra were determined on a Metropolitan Vickers Model MS-2 at an ionization potential of 70 eV.

Materials. 1,2,3-Thiadiazole (VIa) was prepared according to Hurd and Mori[14] as a clear liquid: bp 50–52 °C (14 Torr); ^1H NMR (CCl_4) AB system centered at 1.2; UV $\lambda_{max}^{cyclohexane}$ (ϵ) 211 (4380), 249 (1460), 294 (195); mass spectrum, *m/e* 86 (11), 58 (100), 57 (19), 45 (6), 44 (6), 32 (9).

4-Methyl-1,2,3-thiadiazole (VIb) was similarly obtained from acetone: bp 57–58 °C (15 Torr); ^1H NMR (CCl_4) 1.8 (q, 1 H), 7.2 (d, 3 H); UV $\lambda_{max}^{cyclohexane}$ (ϵ) 213 (4820), 258 (1850), 290 (220); mass spectrum, *m/e* 100 (2), 72 (84), 71 (100), 57 (3), 45 (42).

5-Methyl-1,2,3-thiadiazole (VIc) was prepared according to the method of Schmidt *et al.*:[15] bp 65 °C (18 Torr); ^1H NMR (CCl_4) 1.65 (q, 1 H), 7.31 (d, 3 H); UV $\lambda_{max}^{cyclohexane}$ (ϵ) 217 (5300), 253 (2100), 293 (245); mass spectrum, *m/e* 100 (3), 72 (64), 71 (100), 69 (20), 57 (7), 45 (62).

Hexafluoro-2-butyne (Columbia) was purified by low-pressure vacuum distillation at −130 °C.

Procedure. 1,2,3-Thiadiazoles VIa, VIb, and VIc were introduced in excess into the quartz cell with or without known amounts of hexafluoro-2-butyne. The cell was then immersed in a water bath and kept at 60–65 °C throughout the photolysis (at this temperature the vapor pressures are approximately 21 Torr for VIa and 3 Torr for VIb and VIc) which was carried out for 2 h.

Non-condensable gases were measured in a gas buret and analyzed on a 10-ft medium-activity silica gel column. The alkyne products and CS_2 were recovered in separate distillations and also analyzed on the silica gel column. The remaining fraction condensable at −78 °C was found (10 ft 10% tricresyl phosphate on diatoport, 110 °C) to consist only of unreacted substrate.

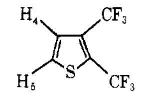
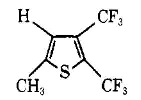
In experiments with added hexafluoro-2-butyne the butyne was distilled out of the reaction mixture and the remainder was analyzed on the tricresyl phosphate column.

Results

Photolysis of 1,2,3-thiadiazoles VIa, VIb, and VIc at λ >220 nm afforded, in addition to N_2, the corresponding alkyne[16] and CS_2; small amounts of methane were also formed from VIb and VIc. The results are summarized in Table I.

Photolysis of VIa in the presence of 200 Torr of hexafluoro-2-butyne afforded 2,3-bis(trifluoromethyl)thiophene (VIIa), identified by its mass ($M^{+\cdot}$ 220) and NMR spectra, Table II. The positions of protons H_4 and H_5 have been assigned by comparison with those of similarly disubstituted thiophenes.[17,18] Photolysis of either VIb or VIc under the same conditions afforded only 5-methyl-2,3-bis(trifluoromethyl)-

Table II. Photolysis of VIa, VIb, and VIc in the Presence of Hexafluoro-2-butyne

Thiadiazole	Registry no.	Thiophene	Registry no.	Yield,[a] %	NMR[b]	Mass spectrum
VIa	288-48-2		773-61-5	6.7	AB system with fine structure due to long-range coupling with CF_3: H_4 2.72, H_5 2.54 ($J_{4,5}$5.4 Hz)	220 (100), 201 (94), 151 (73), 69 (21), 57 (13), 45 (21)
VIb	18212-62-9		55162-36-2	12.3	3.07 (s, 1 H, with fine structure); 7.49 (s, 3 H)	234 (57), 233 (27), 215 (30), 165 (100), 69 (19), 45 (14)
VIc	50406-54-7			12.5		

[a] At 270 Torr pressure of $CF_3C{\equiv}CCF_3$. [b] In CCl_4 solution with Me_4Si as internal standard. Values are given in τ units.

Table III. Yield of 5-Methyl-2,3-bis(trifluoromethyl)thiophene as a Function of the Pressure of Hexafluoro-2-butyne

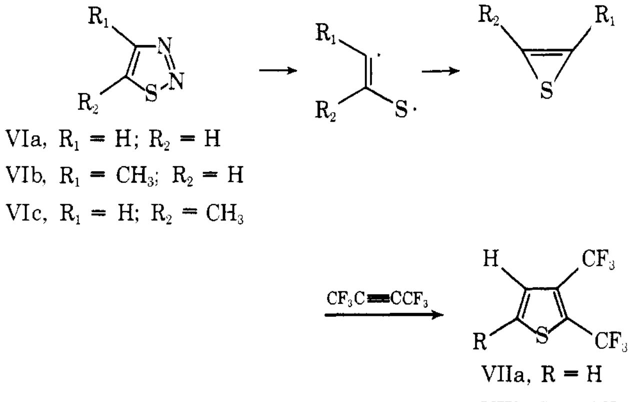
	Yield of VIIb[a]	
Pressure of C_4F_6, Torr	From VIb	From VIc
270	12.3	12.5
600	20.8	30.5
900	23.1	34.0
1200	33.3	37.5

[a] In terms of N_2 produced.

thiophene (VIIb). It was identified as the 5-methyl isomer from its mass spectrum ($M^{+\cdot}$ 234) and the NMR chemical shifts, Table II, by using the additivity rule and the available data for 2- and 3-methyl-substituted thiophenes.[17,18] Considering as basic values the chemical shift for H_4 and H_5 in VIIa, a methyl group in the 4 position would be expected to shift H_5 to τ 2.99 whereas a methyl group in the 5 position should shift H_4 to τ 3.09. The actual value of 3.07 clearly favors the latter. Similarly, the assignment of the methyl group in VIIb at τ 7.49 to the 5 position is reasonable compared to τ 7.59 for 2-methylthiophene and τ 7.80 for 3-methylthiophene. Moreover, decoupling experiments with VIIb, irradiating it in the methyl position, simplified the H multiplet into a quartet with a J value of 1.35 Hz, which is comparable to the one obtained for the long-range coupling between H_4 and fluorine in VIIa (J = 1.40 Hz). The results are summarized in Scheme II.

The yield of 5-methyl-2,3-bis(trifluoromethyl)thiophene is dependent on the pressure of hexafluoro-2-butyne and increases with increasing pressure as seen from the data in Table III. The highest yield obtained, 37.5% at 1200 Torr of pressure and still exhibiting a rising tendency, is comparable to the 50% yield of perfluorotetramethylthiophene obtained in the conventional photolysis of COS in the presence of hexafluorobutyne.[1]

Scheme II



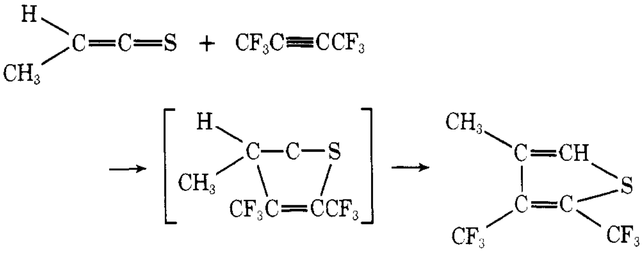
VIa, $R_1 = H$; $R_2 = H$
VIb, $R_1 = CH_3$; $R_2 = H$
VIc, $R_1 = H$; $R_2 = CH_3$

VIIa, R = H
VIIb, $R = CH_3$

Discussion

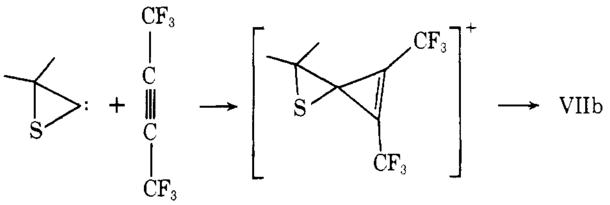
The completely analogous behavior of VIb and VIc suggests the intervention of a common intermediate which makes methyl substitution in either isomer indistinguishable. Diradical or carbene structure I can therefore definitely be ruled out. Acetylenethiol IV can also be ruled out on the ground that it has been shown[13] not to be formed in the matrix isolation photolysis of VIb and VIc.

Thioketenes would not be expected to react with acetylenes via 1,3 addition,

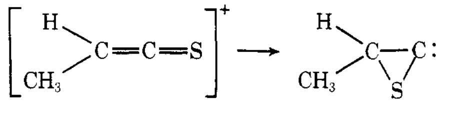


and if they did the 4-methyl-2,3-bis(trifluoromethyl)thiophene rather than the 5-methyl-2,3-bis(trifluoromethyl)thiophene should be the predominant product on account of the greater migrational aptitude of the hydrogen atom compared with the methyl radical. Therefore thioketene can also be eliminated as the precursor of thiophene.

The cyclic carbene V may undergo a cycloaddition reaction with perfluorobutyne-2 to yield a chemically activated thiaspiropentene which may collapse to 5-methyl-2,3-bis(trifluoromethyl)thiophene.

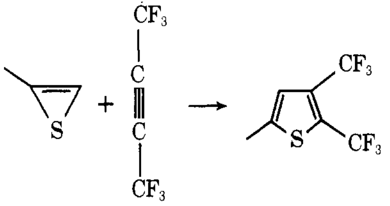


The intervention of the cyclic carbene formed presumably via the rearrangement of an excited thioketene,

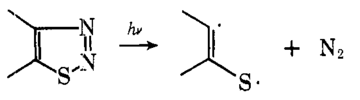


however, is not likely since the yield of thiophene from either the 4-methyl- or 5-methylthiadiazole is higher than from thiadiazole. Also, the yield of thiophene from the addition of singlet excited sulfur atom to the alkynes C_2H_2, C_3H_4, C_4H_6-2, and C_4F_6-2 is highest from the latter whereas the migrational aptitude varies in the order $CF_3 < CH_3 < H$. It can also be pointed out that the IR spectra of the matrix isolated photolyzate of 1,2,3-thiadiazole and its 4-methyl, 5-methyl, 4-*tert*-butyl, 5-*tert*-butyl, 4-methyl-5-carboethoxy, 5-methyl-4-carboethoxy, and 4-trifluoromethyl derivatives did not indicate the presence of the cyclic carbene, V.[13]

Thus, the most likely precursor left for thiophene formation is the thiirene structure, and the formation of only the 5-methyl isomer appears to be a consequence of the combined electronic and steric effects of the methyl substituent and can be rationalized by addition of the alkyne to thiirene across the less hindered C-S side:



The enthalpy change of the reaction



VI I

can be estimated to be about 50–60 kcal/mol; photolysis at $\lambda > 220$ nm would therefore provide sufficient excess energy to form the singlet excited state of thioketocarbene which, according to recent MO calculations,[19] lies only 8.8 kcal/mol above its ground triplet state and also to form singlet thiirene which lies 15.5 kcal above the singlet state thioketocarbene. Thiirene would thus be formed on a singlet surface by analogy with the oxirene–ketocarbene rearrangement[20] which in the case of the sulfur system lies above the ground state triplet surface.

These results are in line with those obtained from the photolysis of matrix-isolated 1,2,3-thiadiazoles.[11-13] They provide chemical evidence for thiirene formation and do not contradict previous results on the solution photolysis of 1,2,3-thiadiazoles. On the contrary, matrix isolation photolysis studies have shown that thiirene rearranges to thioketene on photolysis.[13]

Acknowledgments. The authors thank the National Research Council of Canada for financial support and Dr. E. M. Lown for helpful assistance.

Registry No.—II ($R_1 = R_2$ H), 157-20-0; II ($R_1 = CH_3$; $R_2 = H$), 45345-86-6; hexafluoro-2-butyne, 692-50-2.

References and Notes

(1) E. L. Dedio, Ph.D. Thesis, The University of Alberta, 1967.
(2) O. P. Strausz, J. Font, E. L. Dedio, P. Kebarle, and H. E. Gunning, *J. Am. Chem. Soc.*, **89**, 4805 (1967).
(3) G. Seybold and C. Heibl, *Angew. Chem., Int. Ed. Engl.*, **14**, 248 (1975); *Chem. Ber.*, **110**, 1225 (1977).
(4) H. Bühl, B. Seitz, and H. Meier, *Tetrahedron*, **33**, 449 (1977).
(5) H. Bock, B. Solouki, G. Bert, and P. Rosmus, *J. Am. Chem. Soc.*, **99**, 1663 (1977).
(6) G. N. Schrauzer and H. Kisch, *J. Am. Chem. Soc.*, **95**, 2501 (1973).
(7) T. L. Gilchrist, P. G. Mente, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 2165 (1972); P. G. Mente and C. W. Rees, *J. Chem. Soc., Chem. Commun.*, 418 (1972).
(8) W. Kirmse and L. Hörner, *Justus Liebigs Ann. Chem.*, **614**, 4 (1958).
(9) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 565 (1963).
(10) K. P. Zeller, H. Meier, and E. Müller, *Tetrahedron Lett.*, 537 (1971); K. P. Zeller, H. Meier, and E. Müller, *Justus Liebigs Ann. Chem.*, **766**, 32 (1972).
(11) A. Krantz and J. Laureni, *J. Am. Chem. Soc.*, **96**, 6768 (1974).
(12) J. Laureni, A. Krantz, and R. A. Hajdu, *J. Am. Chem. Soc.*, **98**, 7872 (1976).
(13) M. Torres, J. Font, A. Clement, J. E. Bertie, and O. P. Strausz, *J. Org. Chem.*, following paper in this issue.
(14) Ch. D. Hurd and R. I. Mori, *J. Am. Chem. Soc.*, **77**, 5359 (1955).
(15) U. Schmidt, E. Heymann, and K. Kabitzke, *Chem. Ber.*, **96**, 1478 (1963).
(16) Zeller *et al.*[10] reported the failure to detect any acetylene or propyne in the gas-phase photolysis of VIa and VIb respectively but did not use a high vacuum system in their experiments.
(17) J. W. Emsley, J. Fecucy, and L. H. Sutcliffe, "High Resolution NMR Spectroscopy", Vol. II, Pergamon Press, Elmsford, N.Y., 1966, pp 802–5; J. W. Robinson, "Handbook of Spectroscopy", Vol. VII, Chemical Rubber Publishing Co., Cleveland, Ohio 1974, pp 358–359.
(18) T. J. Botterham, "NMR Spectra of Simple Heterocycles", Wiley, New York, N.Y., 1973, pp 429–41.
(19) O. P. Strausz, R. K. Gosavi, F. Bernardi, P. G. Mezey, J. D. Goddard, and I. G. Csizmadia; *Chem. Phys. Lett.*, **53**, 211 (1978).
(20) J. Fenwick, G. Frater, K. Ogi, and O. P. Strausz, *J. Am. Chem. Soc.*, **95**, 124 (1973).

Low-Temperature Matrix Isolation of Thiirenes

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Several thiirene molecules have been prepared by the argon matrix photolysis of 1,2,3-thiadiazoles at 8 K and identified by IR spectroscopy. Of the expected eight IR absorption bands of the parent thiirene molecule, seven have been located and a tentative assignment of them made. Thiirene, trifluoromethylthiirene, and benzothiirene are highly unstable, but electron-withdrawing substituents exert a marked stabilizing effect on the 4π-electron ring system: carboethoxymethylthiirene is stable up to at least 73 K.

The synthesis of thiirene, like that of the analogous three-membered heterocycles, oxirene and 2-azirene, presents a formidable challenge to the synthetic chemist since they belong to the $4n$ π-electron ring systems which defy Hückel's aromaticity rule. According to Breslow's postulate[1] these systems possess an antiaromatic character as manifested by their low thermodynamic stability. Indeed, detailed molecular orbital computations confirm this prediction and oxirene,[2] 2-azirene,[3] and thiirene[4] are all computed to be thermodynamically less stable than their acyclic isomers, the ketocarbenes, or 1-azirene. Coupled with their thermodynamic instability is the apparent kinetic instability of the ring system since the ab initio MO computed activation energy of the ring-opening reaction of oxirene is only 7 kcal/mol.[2] Although none of these species could be isolated until quite recently, there are several reports in the literature[5] providing indirect although compelling evidence for their transient existence as short-lived intermediates. The possibility of chemical trapping of thiirenes, from the gas-phase photolysis of 1,2,3-thiadiazoles, with hexafluoro-2-butyne to give the corresponding thiophene has also been demonstrated.[6] Photolysis of 1,2,3-thiadiazole in the presence of hexafluoro-2-butyne yields

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