1,3-Dipolar Cycloaddition Reactions of Benzonitrile *N*-Sulfide

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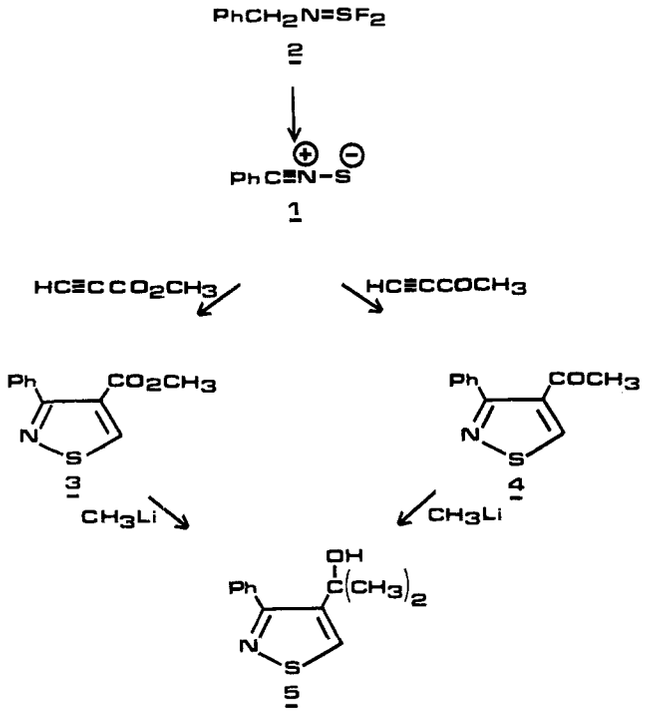
The reaction between benzonitrile *N*-sulfide, generated from the fluoride ion catalyzed elimination of two molecules of hydrogen fluoride from (benzylimino)sulfur difluoride, and either methyl propiolate or 3-butyn-2-one gave predominantly the 4-substituted isothiazole isomer. Comparison of the isothiazole isomer ratios found for the *N*-sulfide generated from iminosulfur difluoride and phenyloxathiazolone leads to the conclusion that hydrogen fluoride causes an increased amount of 4-substituted isothiazole. Molecular orbital calculations (CNDO/2) show that the interaction of the HOMO of the *N*-sulfide and the LUMO of the acetylenes gives the 4-substituted isothiazole. The observation that the 5-carbon absorbs significantly downfield from the 4-carbon in the ^{13}C NMR spectra of isothiazoles allows the unambiguous assignment of regiochemistry of the isothiazoles.

Benzonitrile *N*-sulfide (**1**) has been generated by several routes.[1-7] While **1** cannot be isolated, it reacted with acetylenes[1,8] and nitriles[9-11] to give isothiazoles and 1,2,4-thiadiazoles, respectively. We have reported the generation of **1** by the elimination of two molecules of hydrogen fluoride from *N*-(benzylimino)sulfur difluoride (**2**) and the 1,3-dipolar cycloaddition of **1** to maleic anhydride to form the first example of 2-isothiazoline.[12,13] The purpose of this research was to determine the regiospecificity of the cycloaddition reaction between **1** and unsymmetrical acetylenes and to understand this regiospecificity and the stability of **1** by the use of CNDO/2 molecular orbital calculations.



Results and Discussion

We found that benzonitrile *N*-sulfide, generated from *N*-(benzylimino)sulfur difluoride, reacted with methyl and ethyl propiolate to form 1.9:1 and 1.5:1 ratios of 4- and 5-(carbalkoxy)-1,2-thiazoles, respectively. The iminosulfur difluoride method gave a 2.3:1 ratio of 4- and 5-acetyl-3-phenyl-1,2-thiazole upon reaction with 3-butyn-2-one.

It was reported[1,8] that **1**, generated by the thermolysis of 5-phenyl-1,3,4-oxathiazol-2-one, reacted with ethyl propiolate to give a 1:1 mixture of 4- and 5-(carbethoxy)-3-phenyl-1,2-thiazole. In an effort to resolve the difference in isomer ratio found for the two methods of generating **1**, we repeated the reaction between methyl and ethyl propiolate and **1** generated from oxathiazolone, under the same conditions of time, temperature, and solvent as the iminosulfur difluoride method for generating **1**. We found 1.1:1 and 1.0:1 ratios of the 4- and 5-(carbalkoxy)isothiazoles from the methyl and ethyl esters, respectively. The reaction between 3-butyn-2-one and **1** generated from oxathiazolone gave a 0.6:1 ratio of 4- and 5-acetylisothiazoles. The isomer ratios are shown in Table I.

These results raise the question of how different isomer ratios are observed from distinct precursors which are postulated to form a common intermediate, **1**. The 5-acetyl- and 5-(carbomethoxy)-1,2-thiazoles were subjected to the reaction conditions used to generate **1** from iminosulfur difluoride in order to rule out the possibility that one isothiazole isomer is preferentially destroyed during the course of the cycloaddition reaction. No decomposition of either isothiazole was found. It seems unlikely that the two precursors are giving isothiazoles through distinct mechanisms. Thus, the only other possibility involves modification of the acetylenes. The oxathiazolone method gives no intermediate which would chemically alter an acetylene, but the iminosulfur difluoride forms hydrogen fluoride which may protonate the carbonyl oxygen of the acetylene. Thus, **1** may react with protonated acetylenes to give a larger ratio of 4-/5-substituted isothiazoles than the ratio found for **1** reacting with unprotonated acetylene. Examination of Table I shows that the iminosulfur difluoride method gave a higher ratio of 4-/5-isothiazoles than the oxathiazolone method. We tested this hypothesis by reacting 3-butyn-2-one with oxathiazolone in the presence of dry hydrogen fluoride and sodium fluoride and found a 1.2:1 ratio of 4-/5-acetylisothiazole isomers. While the ratio is not identical with the ratio found from the iminosulfur difluoride method, there is a significant increase in the ratio of 4-/5-isomer when hydrogen fluoride is present in the oxathiazolone method. The increased ratio supports the hypothesis that hydrogen fluoride is responsible for the higher ratio of the 4-/5-isothiazole isomers observed for the iminosulfur difluoride method as compared with the oxathiazolone method.

The structural assignment for the acetyl isomers was based on spectral data, and in the case of the 4-isomer the assignment was corroborated by a chemical correlation. The addition of methyllithium to **4** and **3**, whose structures have been unambiguously established,[14] gave the same alcohol, 4-(1-hydroxyl-1-methylethyl)-3-phenyl-1,2-thiazole (**5**).

In the ^1H NMR spectra of the isothiazoles, a proton on the 5 position absorbed between δ 8.4 and 9.2 and was downfield from a proton on the 4 position.[15] As shown in Table II, our structural assignments agree with this observation.

We found a similar chemical shift correlation in the ^{13}C NMR spectra. Using the off-resonance decoupled spectrum

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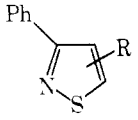
Table I. Ratios[a] of 4- and 5-Substituted Isothiazoles



R	oxathiazolone 4-/5-R	iminosulfur difluoride 4-/5-R
CH_3O_2C	1.1:1.0[c]	1.9:1.0
$CH_3CH_2O_2C$	1.0:1.0[d]	1.5:1.0
CH_3CO	0.6:1.0[e]	2.3:1.0
CH_3CO[b]	1.2:1.0	

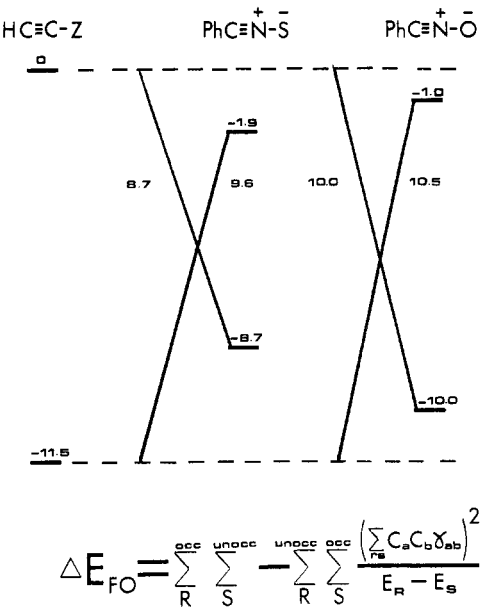
[a] Ratios were determined by gas chromatography using a 4 ft × ⅛ in. stainless steel column packed with 3% SE-30 absorbed on Chromosorb Q for the esters and a 6 ft × 0.25 in. stainless steel column packed with Apiezon L absorbed on Chromosorb W for the ketone. [b] With hydrogen fluoride added. [c] Registry no. 21905-48-6/68438-26-6. [d] Registry no. 67049-00-7/27545-57-9. [e] Registry no. 68438-27-7/68438-28-8.

to deduce the shift of the 4- and 5-carbon atoms in **3** and the 5-carbethoxy ester, we observed that the 5-carbon absorbs significantly downfield from the 4-carbon. For ketone **4**, as with **3**, the off-resonance doublet occurred with the downfield resonance. This confirmed our claim that the acetyl group in **4** must be substituted on the 4-carbon. (Table II).

Frontier molecular orbital theory may be used to understand the regiospecificity of the reaction between **1** and monosubstituted electron deficient acetylenes.[16,17] We performed CNDO/2 SCFMO calculations on **1** by geometry optimizing the N–S bond length and using standard geometry for the rest of the molecule. The results of the calculations are shown in Table III.

Examination of the term $(C_\gamma)^2/15$ for the HO and LU atoms of **1** shows that the larger term is associated with sulfur in the HO but with carbon in the LU. Thus, the 4-substituted isothiazole will predominate under HO dipole control while the 5-isomer will arise under LU dipole control. There is no experimental evidence concerning the energies of the HO and LU orbitals for nitrile *N*-sulfides. However, assuming that the calculated energy difference between the HO for the nitrile *N*-sulfide and the nitrile *N*-oxide would be the same as that derived from experiment and assuming Houk's estimated energies for benzonitrile *N*-oxide, a set of estimated values for the HO and LU energies may be derived for benzonitrile *N*-sulfide. These energies, as well as those for electron deficient acetylenes, are presented in Chart I. As can be seen, the energy of HO of the *N*-sulfide is raised to a greater extent than the LU is lowered. Thus, with respect to the nitrile *N*-oxide, the *N*-sulfide should show more HO dipole control. The reaction between benzonitrile *N*-oxide and methyl propiolate shows

Chart I



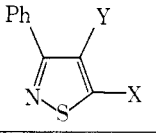
a small amount of HO dipole control (84% 5-isoxazole, 16% 4-isoxazole),[18] while the same acetylene reacted with **1** gives greater HO dipole control (50% 4-isothiazole, 50% 5-isothiazole) than the *N*-oxide. These facts tend to confirm the CNDO/2 prediction of increased HO dipole control for *N*-sulfide as compared with *N*-oxide.

The energy difference between the HO of **1** and the LU of electron deficient acetylenes is smaller by about 1 eV than the energy difference between the LU of **1** and the HO of the acetylene.

The $(C_\gamma)^2/15$ term for sulfur in the HO is much larger than the other $(C_\gamma)^2/15$ terms, even assuming a carbon–sulfur distance of 2.3 Å (the distance of 1.75 Å assumed by Houk for the transition states of 1,3-dipolar cycloaddition reactions is about 0.05 Å shorter than the average C–S single bond distance). The numerator of the term governing frontier orbital interactions in the equation shown in Chart I will be greater for the HO dipole, LU dipolarophile association than the corresponding term for the opposite interaction. Therefore, the smaller energy difference for HO dipole control and the larger $(C_\gamma)^2/15$ value for sulfur lead to the prediction that electron deficient acetylenes and **1** will react by HO dipole control to form 4-isothiazole predominantly.

The oxathiazolone method for generating **1** is better than the iminosulfur difluoride method for determining the success of the CNDO/2 predictions because the isomer ratios from the latter method are affected by the catalytic effect of the hy-

Table II. Selected NMR Data of Isothiazoles



X	Y	registry no.	4 position ^{13}C NMR (^1H NMR), δ	5 position ^{13}C NMR (^1H NMR), δ
CO_2CH_3	CO_2CH_3	27545-53-5	133	156
H	CO_2CH_3 (**3**)		139	156 (9.1)
H	$COCH_3$ (**4**)		135	154 (8.9)
H	$HOC(CH_3)_2$ (**5**)	68438-29-9		(8.4)
$CO_2CH_2CH_3$	H		125 (8.0)	158
$HOC(CH_3)_2$	H	68438-30-2	117 (7.2)	168
CO_2CH_3	H		125 (8.0)	157
CH_3CO	H		123 (7.8)	166

Table III. Summary of CNDO/2 Calculations[a]

	HO(π)							
	C_c	C_n	C_x	E, eV				
PhCNS	−0.229	−0.079	0.950	−9.748				
PhCNO	−0.438	−0.308	0.602	−11.028				
	LU(π)							
PhCNS	0.348	−0.408	0.130	1.265				
PhCNO	0.326	−0.477	0.253	2.193				
	π charges			total charges				
	q_c	q_n	q_x	q_c	q_n	q_x		
PhCNS	−0.12	−0.16	−0.96	+0.14	+0.07	−0.38		
PhCNO	−0.08	−0.12	−0.80	−0.07	+0.21	−0.41		
			$(C_x\gamma_{cx})^2/15$				$(C_c\gamma_{cc})^2/15$	
	$-\gamma_{cx}$	R_{cx}	HO	LU	$-\gamma_{cc}$	R_{cc}	HO	LU
PhCNS	4.17	2.30	1.046	0.020	6.22	1.75	0.135	0.312
PhCNO	5.38	1.75	0.699	0.124	6.22	1.75	0.495	0.274

[a] Registry no.: PhCNS, 873-67-6; PhCNO, 2362-05-2.

drogen fluoride formed during the course of the reaction. Thus, the iminosulfur difluoride method gives more HO dipole control than the oxathiazolone method because protonation of the acetylenic carbonyl will lower the energy of the acetylenic LU substantially and increase the difference in the value of the coefficients for the α and β carbons in favor of the latter.

The oxathiazolone method for generating **1** does not corroborate the CNDO/2 prediction of HO dipole control. While the acetylenic esters showed more HO dipole control than the ketone, none of the electron deficient acetylenes showed HO dipole control on an absolute basis (see Table I). The difference in isomer ratios for the ketone and esters is not without precedent, judging by the reactivity pattern of mesitonitrile *N*-oxide.[19]

The transient existence of **1** is significant in view of the fact that sulfur, while being less electronegative than nitrogen, is nevertheless at the negative end of the dipole of a coordinate covalent bond involving group V and VI elements. Benzonitrile *N*-sulfide is the first example of such bonding.[20,21] Examination of the charge densities calculated by the CNDO/2 method for **1** and the corresponding *N*-oxide shows there is +0.07 charge on nitrogen for the *N*-oxide. The sulfur of **1** and oxygen of the *N*-oxide are −0.38 and −0.41 charged, respectively. The minimized N–S distance is significantly longer than N–O distance. The coulombic stabilization for the N–S bond in **1** is very small and is much less than that for the *N*-oxide. However, while the N–S bond is weaker than the N–O bond, the transient existence of **1** may be accounted for by the π bonding between the $3p_y$ and $3p_z$ orbitals of sulfur and the $2p_y$ and $2p_z$ orbitals of nitrogen, respectively.

In summary, benzonitrile *N*-sulfide gave more HO dipole control than benzonitrile *N*-oxide in reaction with electron deficient acetylenes, and hydrogen fluoride caused an increased amount of HO dipole control.

Experimental Section

All melting and boiling points are uncorrected. Infrared spectra were recorded with a Perkin-Elmer IR-237. Mass spectra were taken on a single-focusing Hitachi RMU-6 spectrometer with an ionizing potential of 70 eV. Proton and fluorine-19 NMR spectra were run with a JEOL-C-60H spectrometer, and carbon-13 NMR spectra were taken on a Bruker WH-90 spectrometer, with Me_4Si as an internal standard for ^1H and ^{13}C NMR and dichlorodifluoromethane for ^{19}F NMR. Microanalyses were performed by Galbraith Laboratories, Inc. Phenylacetylene, ethyl phenylpropiolate, and ethyl propiolate were purchased from Aldrich Chemical Co., Inc., and methyl propiolate and 3-butyn-2-one were obtained from Farchan Chemical Co.

***N*-(Benzylimino)sulfur Difluoride (2).** Into a dried flask with a condenser maintained at −75 °C (dry ice–acetone) was placed 36 g (0.34 mol) of benzylamine, 28 g of sodium flouride and 100 g of trimethylamine. The flask was cooled to −45 °C (chlorobenzene slush). Sulfur tetrafluoride (30 mL) was added over a period of an hour. The solution became yellow and a precipitate formed. The reaction mixture was stirred at −45 °C for 2 h and then allowed to warm to room temperature to evaporate trimethylamine and any excess sulfur tetrafluoride.[22] All gases exited the experiment through a trap containing an aqueous solution of NaOH. The residue was distilled directly from the reaction vessel to give 30 g (52%) of **2**, bp 30–35 °C (10^{-5} mm); the iminosulfur difluoride is very air sensitive, precluding satisfactory analysis. The NMR spectra were run in sealed tubes: δ_{Me_4Si} (CCl_4) 7.07 (5 H, s) and 4.33 (2 H, deceptively simple triplet, J_{HF} = 10 Hz); δ (CCl_2F_2) 94.6 (J_{HF} = 10 Hz).

4,5-(Dicarbomethoxy)-3-phenyl-1,2-thiazole. A mixture of 3.5 g (0.025 mol) of dimethyl acetylenedicarboxylate, 40 mL of chlorobenzene, 1.2 g of NaF, and 0.3 g of 18-crown-6 polyether was refluxed for 20 min before 2.0 g (0.012 mol) of **2** was added. The resulting solution was refluxed under N_2 for 12 h and allowed to stand at room temperature for 12 h. Solvent and excess acetylene were removed under high vacuum, and the residue was treated with boiling heptane, from which crystallized 2.2 g (65%) of isothiazole, mp 70–71 °C (lit.[1] mp 70–71 °C). All spectral data were identical with those reported in the literature: ^{13}C NMR ($CDCl_3$) δ 52.0 (q), 53.2 (q), 127.8 (d), 128.8 (d), 129.9 (d), 133.0 (s), 134.1 (s), 155.8 (s), 159.4 (s), 165 (s), and 166 (s).

4- and 5-(Carbomethoxy)-3-phenyl-1,2-thiazole. A mixture of 13 g (0.15 mol) of methyl propiolate, 6 g of NaF, and 1.2 g of 18-crown-6 polyether dissolved in 80 mL of dry chlorobenzene was brought to reflux under prepurified N_2 at 130 °C before 8 g (0.05 mol) of **2** was added. The resulting solution was refluxed for 21 h. The NaF was filtered while the solution was hot, and the solvent was removed under high vacuum. The brown solid residue was analyzed by GLC to be a 1.9:1 mixture of 4- and 5-isomers and then was chromatographed over silica gel and eluted with 1:1 benzene–petroleum ether (60–90 °C) to give first 2.4 g of 5-substituted isothiazole and then 5.3 g of the 4-substituted isomer (78% overall yield). The 4-isomer was recrystallized from heptane: mp 95–96 °C (lit.[14] mp 85–87 °C); IR (KBr) 1695 cm^{-1} MS *m/e* (rel intensity) 219 (92), 204 (58), 188 (100), 160 (11), 85 (18), 77 (18), 57 (29), and 51 (18); ^1H NMR (CCl_4) δ 3.7 (3 H, s), 7.2 (5 H, m), and 9.1 (1 H, s); ^{13}C NMR ($CDCl_3$) δ 52 (q, 127.9 (d), 129 (s), 129.2 (d), 135.1 (s), 155.9 (d), 162.6 (s), and 168.9 (s). Anal. Calcd for $C_{11}H_9NO_2S$: C, 60.25; H, 4.14; N, 6.39; S, 14.62. Found: C, 60.41; H, 4.20; N, 6.33; S, 14.55.

The 5-isomer was recrystallized from hexane: mp 61–62 °C; IR (KBr) 1695 cm^{-1}; MS *m/e* (rel intensity) 219 (100), 188 (86), 160 (16), 103 (63), 77 (39), 76 (40), and 57 (47); ^1H NMR (CCl_4) δ 3.85 (3 H, s), 7.3 (3 H, m), 7.8 (2 H, m), and 8.0 (1 H, s); ^{13}C NMR ($CDCl_3$) δ 52.6 (q), 125.0 (d), 126.9 (d), 127.5 (d), 129 (d), 129.7 (d), 132.6 (s), 134.1 (s), 157.3 (s), 168.5 (s). Anal. Calcd for $C_{11}H_9NO_2S$: C, 60.25; H, 4.14; N, 6.39; S, 14.62. Found: C, 59.96; H, 4.06; N, 6.38; S, 14.53.

4- and 5-Acetyl-3-phenyl-1,2-thiazole. A mixture of 7.8 g (0.11 mol) of 3-butyn-2-one, 4.7 g of NaF, and 0.76 g of 18-crown-6 polyether dissolved in 40 mL of dry chlorobenzene was brought to reflux in an

oil bath at 130 °C under prepurified N_2 before 5 g (0.03 mol) of **2** was added. The mixture was refluxed for 2.5 h, when it began to darken. The NaF was filtered from the hot solution, and the solvent was removed under high vacuum. The residue was analyzed by GLC to be a 2.3:1 ratio of 4- and 5-isomers and then was chromatographed over silica gel and eluted with petroleum ether (60–90 °C), in which the concentration of benzene was gradually increased to give first 0.56 g of 5-substituted isothiazole and then 1.2 g of 4-substituted isothiazole (30% overall yield). The 4-isomer was recrystallized from heptane: mp 90–91 °C; IR (KBr) 1685 cm^{-1}; MS *m/e* (rel intensity) 203 (59), 188 (100), 160 (12), 135 (9), 103 (17), 85 (15), 77 (27), 57 (33), and 43 (47); ^1H NMR (CCl_4) δ 2.2 (3 H, s), 7.3 (5 H, m), and 8.9 (1 H, s); ^{13}C NMR ($CDCl_3$) δ 30.0 (q), 128.5 (d), 129.1 (d), 129.6 (d), 135.5 (s), 138.5 (s), 154.3 (d), 168.1 (s), and 193.4 (s). Anal. Calcd for $C_{11}H_9NOS$: C, 65.00; H, 4.46; N, 6.89; S, 15.74. Found: C, 65.31; H, 4.62; N, 6.74; S, 15.40.

The 5-isomer was recrystallized from pentane: mp 65–66 °C; IR (KBr) 1685 cm^{-1}; MS *m/e* (rel intensity) 203 (63), 188 (100), 160 (13), 135 (12), 85 (15), 77 (26), 57 (45), and 43 (56); ^1H NMR (CCl_4) δ 2.6 (3 H, s), 7.4 (3 H, s), 7.4 (3 H, m), 7.8 (2 H, m), and 7.9 (1 H, s); ^{13}C NMR ($CDCl_3$) δ 27.9 (q). 122.5 (d), 126.7 (d), 128.7 (d), 129.4 (d), 134.0 (s), 166.2 (s), 168.1 (s), and 187.8 (s). Anal. Calcd for $C_{11}H_9NOS$: C, 65.00; H, 4.46; N, 6.89; S, 15.74. Found: C, 65.14; H, 4.43; N, 7.02; S, 15.61.

4-(1-Hydroxy-1-methylethyl)-3-phenyl-1,2-thiazole (5). To a solution of 0.5 g (0.0023 mol) of **3** in 50 mL of anhydrous ether maintained at 0 °C was added 10 mL (2.05 M) of methyllithium dissolved in hexane through a rubber stopper. After 0.5 h, the reaction mixture was quenched with aqueous ammonium chloride. After separation, the ether was dried over Na_2SO_4 and evaporated to give 0.45 g (90%) of **5**, mp 99–100 °C. From 1.0 g (0.0049 mol) of **4** and 9.8 mL (2.05) of methyllithium, 0.87 g (81%) of **5** was obtained: mp 99–100 °C; ^1H NMR (CCl_4) δ 1.4 (6 H, s), 2.2 (1 H, s, disappears upon addition of D_2O), 7.3 (5 H, br s), and 8.4 (1 H, s). Anal. Calcd for $C_{12}H_{13}NOS$: C, 65.72; H, 5.97; S, 14.62. Found: C, 65.62; H, 5.88; S, 14.11.

4- and 5-(Carbethoxy)-3-phenyl-1,2-thiazole. A mixture of 5 g (0.051 mol) of ethyl propiolate, 4.7 g (0.11 mol) of NaF, 0.1 g of NaF, 0.1 g of 18-crown-6 polyether, and 60 mL of chlorobenzene was refluxed for 5 min under N_2 before 5 g (0.928 mol) of **2** was added. The mixture was refluxed for 20 h. After cooling, the solvent was removed under high vacuum and the residue was chromatographed over silica gel using a mixture of benzene and petroleum ether to give 0.8 g of the 5-isomer: mp 63.5–65 °C (lit.[1] mp 65–66 °C); ^1H NMR ($CDCl_3$) δ 1.4 (3 H, t), 4.3 (2 H, q), 7.5 (3 H, m), 7.9 (2 H, m), and 8.1 (1 H, s); ^{13}C NMR ($CDCl_3$) δ 14.2 (q), 61.9 (t), 124.8 (d), 127.0 (d), 128.9 (d), 129.6 (d), 134.2 (s), 157.9 (s), 160 (s), 168 (s). In addition, 1.5 g of the 4-isomer contaminated with the 5-isomer was isolated as an oil. Further attempts at purification were abandoned. Before subjecting the residue to elution column chromatography, the ratio of the 4- and 5-isomers was found by GLC to be 1.5:1 after treating the residue with water and ether to remove from the solution crown ether whose retention time is similar to that of the 5-isomer.

General Method For the Reaction Between Acetylenes and 5-Phenyl-1,3,4-oxathiazol-2-one. A solution of 5 g (0.03 mol) of 5-phenyl-1,3,4-oxathiazol-2-one and 0.06 mol of the appropriate acetylene dissolved in 50 mL of dry chlorobenzene was refluxed at 130 °C under prepurified N_2 for 21 h. In the case of 3-butyn-2-one, the reaction was conducted for 21 and 2.5 h with no change in the isomer ratio of the products. The solvent was removed under high vacuum, and the resulting residue was analyzed by GLC. The results are summarized in Table I.

Oxathiazolone and 3-Butyn-2-one in the Presence of Hydrogen Fluoride. Dry hydrogen fluoride was bubbled through a solution of 3.8 g (0.06 mol) of 3-butyn-2-one dissolved in 50 mL of dry chlorobenzene for 10 min. To the solution was added 5 g (0.03 mol) of 5-phenyl-1,3,4-oxathiazol-2-one, and the resulting solution was refluxed at 130 °C for 2.5 h. The solvent was removed under high vacuum, and the residue was analyzed by GLC to be a 1.2:1 mixture of 4-/5-acetyl-3-phenyl-1,2-thiazoles.

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Registry No.—**2**, 56973-71-8; 5-phenyl-1,3,4-oxathiazol-2-one, 5852-49-3; benzylamine, 100-46-9; sulfur tetrafluroride, 7783-60-0; dimethyl acetylenedicarboxylate, 762-42-5; methyl propiolate, 922-67-8; 3-butyn-2-one, 1423-60-5; methyllithium, 917-54-4; ethyl propiolate, 623-47-2; hydrogen fluoride, 7664-39-3.

References and Notes

(1) J. E. Franz and L. L. Black, *Tetrahedron Lett.*, 1381 (1970).
(2) R. K. Howe and J. E. Franz, *J. Chem. Soc., Chem. Commun.*, 524 (1973).
(3) H. Gotthardt, *Tetrahedron Lett.*, 1277 (1971).
(4) H. Gotthardt, *Chem, Ber.*, **105**, 188 (1972).
(5) A. Holm, N. Harrit, K. Bechgaard, O. Buchardt, and S. E. Harnung, *J. Chem. Soc., Chem. Commun.*, 1125 (1972).
(6) A. Holm, N. Harrit, and N. H. Toubro, *J. Am. Chem. Soc.*, **97**, 6197 (1975).
(7) H. Yoshida, H. Taketani, J. Ogata, and S. Inokawa, *Bull. Chem. Soc. Jpn.*, **49**, 3124 (1976).
(8) R. K. Howe, T. A. Gruner, L. G. Carter, L. L. Black, and J. E. Franz, *J. Org. Chem.*, **43**, 3736 (1978).
(9) R. K. Howe and J. E. Franz, *J. Org. Chem.*, **39**, 962 (1974).
(10) J. E. Franz, R. K. Howe, and H. K. Pearl, *J. Org. Chem.*, **41**, 620 (1976).
(11) R. K. Howe, T. A. Gruner, and J. E. Franz, *J. Org. Chem.*, **42**, 1813 (1977).
(12) J. R. Grunwell and S. L. Dye, *Tetrahedron Lett.*, 1739 (1975).
(13) R. K. Howe and J. E. Franz, *J. Org. Chem.*, **43**, 3742 (1978).
(14) T. Naito, *Tetrahedron*, **24**, 6237 (1968).
(15) T. Naito, S. Nakagawa, and K. Takahashi, *Chem. Pharm. Bull.*, **16**, 148 (1968).
(16) K. N. Houk, J. Sims, R. E. Duke, Jr., R. W. Strozier, and J. K. George, *J. Am. Chem. Soc.*, **95**, 7287 (1973).
(17) K. N. Houk, J. Sims, C. R. Watts, and T. J. Tuskees, *J. Am. Chem. Soc.*, **95**, 7301 (1973).
(18) C. Grundman, *Synthesis*, 344 (1970).
(19) K. N. Houk, Y-M. Chang, R. W. Strozier, and P Caramella, *Heterocycles*, **7**, 793 (1977).
(20) O. Foss, *Acta Chem. Scand.*, **4**, 404 (1950).
(21) R. Cramer, *J. Org. Chem.*, **26**, 3476 (1961).
(22) **Caution!** For no obvious reason the reaction mixture became violently exothermic on occasion.