from methylene chloride–ether. Pure epidihydroeburnamenine was thus obtained in two crops of colorless crystals (1.75 g, 62%) with mp 183–184°: ir (Nujol) 1625 cm^{-1}; nmr ($CDCl_3$) 0.76 (unsym t, 3 H),[29] 0.9–3.3 (m, 15 H), 3.5–4.3 (m, 2 H), and 7.0–7.6 (m, 4 H); mass spectrum *m/e* 279 (100%) and 280 (82%, M^+).

Anal. Calcd for $C_{19}H_{24}N_2$: C, 81.38; H, 8.63; N, 9.99. Found: C, 81.21; H, 8.37; N, 9.89.

(29) Unlike the case with **34**, the ethyl group of **35** does not appear to be a simple A_3B_2 system, probably as a consequence of its more hindered environment.

4-Alkyl-5-sulfonylimino-1,2,3,4-thiatriazolines. Interesting Starting Materials for the Synthesis of Sulfonylcarbodiimides and Novel Heterocycles

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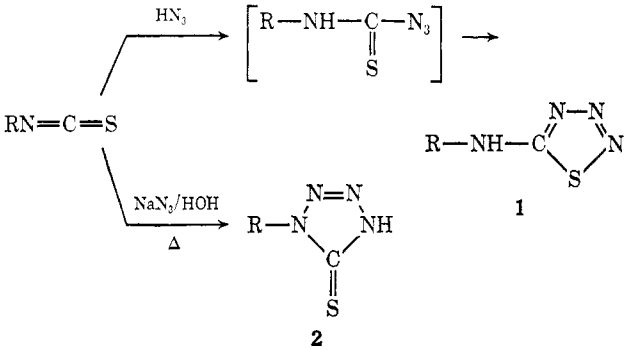
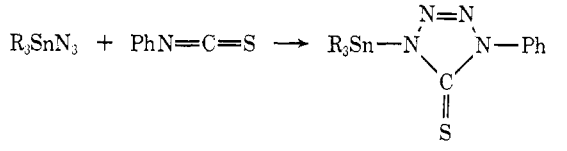
Abstract: Alkyl azides react with sulfonyl isothiocyanates at room temperature to give 4-alkyl-5-sulfonylimino-1,2,3,4-thiatriazolines (**4**) in reasonable good yields (49–76%). These heterocyclic compounds are smoothly thermolyzed at 45–80° to sulfonylcarbodiimides **5**. When heated in the presence of enamines, 4-aminothiazolidines (*e.g.*, **11–13**) and/or thiazolines (*e.g.*, **17** and **18**) are obtained, the latter resulting from the 4-aminothiazolidines by loss of amine. Ynamines and keto-stabilized phosphorus ylides also react with the thiatriazolines to give thiazolines (*e.g.*, **20**, **22–24**), whereas vinyl ethers, vinyl acetates, and electron-poor olefins and acetylenes are unable to give addition products. Structure assignment of the new products was based on chemical evidence and spectroscopic study including ^{13}C nmr analysis. The mechanism of thiazolidine formation is discussed.

The behavior of isothiocyanates toward inorganic azides is well known.[1] Thus, the reaction of hydrazoic acid with isothiocyanates furnishes 5-(substituted) amino 1,2,3,4-thiatriazoles (**1**) probably *via* unstable thiocarbamoyl azides. Sodium azide, on the contrary, reacts with isothiocyanates to give 1-substituted-Δ^2-tetrazoline-5-thiones (**2**) which are also obtained in part by the base-catalyzed isomerization of **1** when R = aryl.



2

Recently, Dunn and Oldfield[2] reported the reaction of tri-*n*-butyltin azide and triphenyltin azide with phenyl isothiocyanate to give the C=N adducts **3**. These were converted to **2** (R = Ph) upon treatment with cold dilute HCl. Other organometallic azides also produced C=N adducts.[3]



3, R = *n*-Bu or Ph

No reactions of isothiocyanates with organic azides have thus far been reported, although reactions with other 1,3-dipoles are known:[4] diazoalkanes, nitrile ylides, and azomethine ylides yield C=S adducts, azomethine imines and nitrones give C=N adducts and nitrile imines are capable to add onto the C=N and/or C=S bonds of isothiocyanates. In view of these results, addition of azides across the C=N and/or C=S bonds of isothiocyanates may formally be considered. We have now found that alkyl azides react readily with sulfonyl isothiocyanates to give 4-alkyl-5-sulfonylimino-1,2,3,4-thiatriazolines (**4**) exclusively.[5] Despite the large number of investigations carried out with the aromatic 1,2,3,4-thiatriazoles,[6] 1,2,3,4-thiatriazolines have only been mentioned in a few reports.[3,7]

Results and Discussion

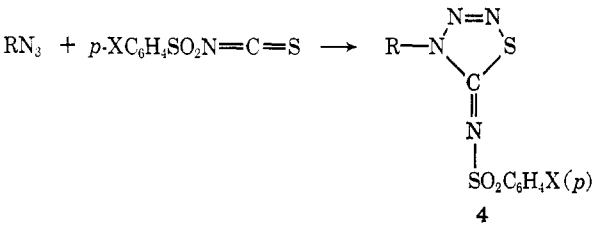
The reaction of *n*-butyl azide and benzyl azide with equimolar amounts of sulfonyl isothiocyanates at room temperature readily afforded 4-alkyl-5-sulfonylimino-

(1) See, for instance, E. Lieber, C. N. Pillai, and R. D. Hites, *Can. J. Chem.*, **35**, 832 (1957); E. Lieber and J. Ramachandran, *ibid.*, **37**, 101 (1959), and references cited therein.
(2) P. Dunn and D. Oldfield, *Aust. J. Chem.*, **24**, 645 (1971).
(3) P. Kreutzer, C. Weis, H. Boehme, T. Kemmerich, W. Beck, C. Spencer, and R. Mason, *Z. Naturforsch. B*, **27**, 745 (1972).
(4) Review: E. Van Loock, *Ind. Chim. Belg.*, in press.
(5) For a preliminary report on this topic, see E. Van Loock, J. M. Vandensavel, G. L'abbé, and G. Smets, *J. Org. Chem.*, **38**, 2916 (1973).
(6) Review: K. A. Jensen and C. Pedersen, *Advan. Heterocycl. Chem.*, **3**, 263 (1964).
(7) E. Lieber, E. Oftedahl, and C. N. R. Rao, *J. Org. Chem.*, **28**, 194 (1963); R. Neidlein and J. Tauber, *Arch. Pharm. (Weinheim)*, **304**, 687 (1971).

Table I. Synthesis of 4-Alkyl-5-sulfonylimino-1,2,3,4-thiatriazolines (**4**)

Compd	R	X	Reaction time, hr[a]	Yield, %	Mp (recryst solvent), °C	Ir, cm^{-1} C=N	Ir, cm^{-1} SO_2
4a	*n*-Bu	H	24	49	60–61 dec (ether)	1530	1310, 1145
4b	*n*-Bu	Me	10	59	74–75 dec (ether)	1530	1285, 1140
4c	*n*-Bu	Cl	48	76	102–104 dec (CCl_4–$CHCl_3$)	1510	1320, 1140
4d	$PhCH_2$	H	24	*b*	Oil	1525	1320, 1145
4e	$PhCH_2$	Me	20	70	101–103 dec (acetone)	1535	1305, 1140
4f	$PhCH_2$	Cl	7	62	116–118 dec (acetone)	1515	1320, 1140

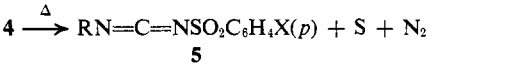
[a] All experiments were carried out at room temperature with equimolar amounts of each reagent in CCl_4 (except for **4c** which was prepared in the absence of solvent). [b] This compound decomposed slowly at room temperature.



4

1,2,3,4-thiatriazolines (**4**) (see Table I). Structure assignment was based on spectral analyses and thermal decomposition. In particular, the ir spectra showed broad and strong absorptions at 1510–1535 cm^{-1} which are assigned to the C=N bonds.[8] The mass spectra exhibited fragments corresponding to $M\cdot^+ - N_2$ and $M\cdot^+ - N_2 - S$ in addition to very small molecular ion peaks.

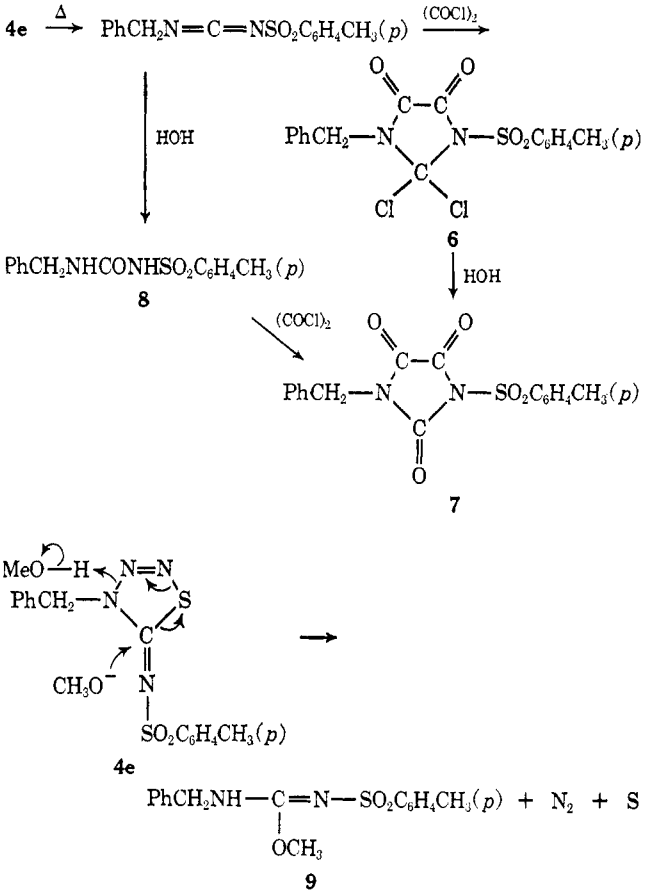
Solutions of **4a–f** in inert solvents (dry toluene, CCl_4, acetone, etc.) at 45–80° evolve nitrogen with formation of sulfur and sulfonylcarbodiimides (**5**). The pres-



5

ence of the latter was inferred from their ir absorption bands[9] at 2160 cm^{-1} and from trapping experiments.[10] Thus, when **4e** was first decomposed in CCl_4 at 80° and then treated with oxalyl chloride at room temperature, 1-benzyl-2,2-dichloro-3-tolylsulfonylimidazolidine-4,5-dione (**6**) was obtained in 57% yield. Further hydrolysis of **6** with water yielded the parabanic acid derivative **7** in 90% yield. This product was characterized by spectral analysis (see Experimental Section) and by comparison with an authentic sample prepared from *N*-benzyl-*N'*-tolylsulfonylurea (**8**) and oxalyl chloride. Compound **8** was obtained when **4e** was thermolyzed in a mixture of acetone–water at 65°.

4-Alkyl-5-sulfonylimino-1,2,3,4-thiatriazolines (**4**) also decompose under the influence of bases at room temperature. Thus, *O*-methyl-*N*-benzyl-*N'*-tolylsulfonylisourea (**9**) was obtained in 79% yield when **4e** was treated with sodium methoxide in methanol solution. Its structure was ascertained by ir (NH at 3340, C=N at 1610 cm^{-1}), nmr (benzyl protons at τ 5.6, coupled with NH), and mass spectrum ($M\cdot^+$ at *m/e* 318). Similar treatment of **4a** with sodium hydroxide in a mixture of methanol–water at room temperature



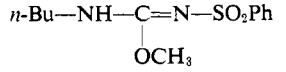
6

7

4e

9

furnished the corresponding *O*-methylisourea **10** in



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61% yield (for structure analysis, see Experimental Section). From the reactions outlined above, it is evident that 4-substituted-5-sulfonylimino-1,2,3,4-thiatriazolines (**4**) constitute excellent precursors for the synthesis of sulfonylcarbodiimides. The utility of this new synthetic method is based on the ready availability of **4** (which in most cases can be stored for indefinite time at room temperature), their facile and clean thermal decomposition in anhydrous solvents, and the fact that no protic substances are involved in the synthetic method—a feature not shared by other syntheses of sulfonylcarbodiimides.[9,11] Thus, for most synthetic purposes, a thermolyzed solution of **4** in

(8) J. Goerdeler and U. Krone, *Chem. Ber.*, **102**, 2273 (1969).

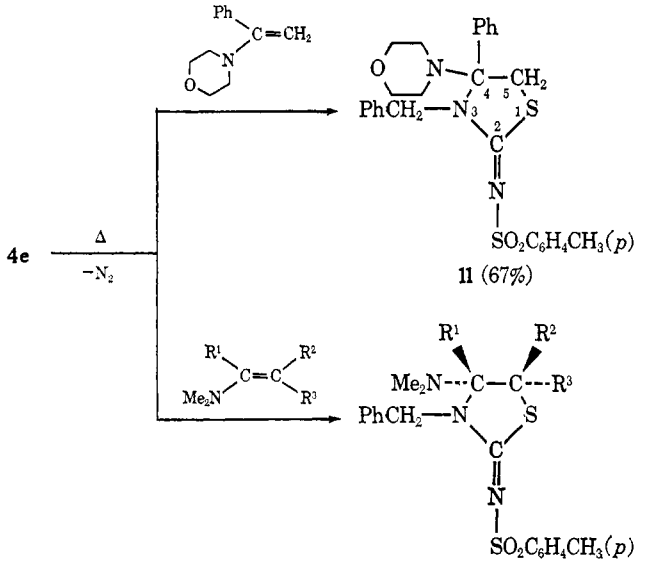
(9) R. Neidlein, W. Haussmann, and E. Heukelbach, *Chem. Ber.*, **99**, 1252 (1966); R. Neidlein and E. Heukelbach, *Arch. Pharm. (Weinheim)*, **299**, 944 (1966); H. Ulrich, B. Tucker, and A. A. R. Sayigh, *Tetrahedron*, **22**, 1565 (1966).

(10) For reviews on carbodiimides, see H. G. Khorana, *Chem. Rev.*, **53**, 145 (1953); F. Kurzer and K. D. Zadeh, *ibid.*, **67**, 107 (1967).

(11) B. Anders and E. Kühle, *Angew. Chem.*, **77**, 430 (1965); *Angew. Chem., Int. Ed. Engl.*, **4**, 430 (1965).

acetone may be filtered (to remove sulfur) and then conveniently used without further purification.

4-Alkyl-5-sulfonylimino-1,2,3,4-thiatriazolines (**4**) are not only of interest as precursors for the synthesis of sulfonylcarbodiimides (**5**), but also as starting materials for the synthesis of other heterocyclic compounds such as thiazolidines and thiazolines. Thus, when 4-benzyl-5-tosylimino-1,2,3,4-thiatriazoline (**4e**) was decomposed in the presence of **enamines**, adducts **11–13**

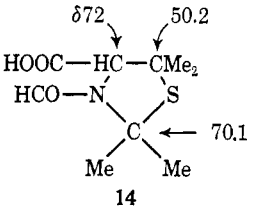


were obtained and characterized by spectral analyses. In particular, the ir absorption patterns in the region 1600–1400 cm^{-1} were similar to that of the precursor **4e** with typical broad and strong C=N bands at 1515–1530 cm^{-1}. The indicated stereochemistry of **12** was established by the small C-4–C-5 hydrogen coupling constant (J = 2.5 Hz) in the nmr spectrum. This means that the addition occurred in a stereospecific syn fashion. A point of particular importance is the regiochemistry of the adducts, since two modes of addition are in principle feasible. That the amine function occupies the 4 position in all the adducts was proven beyond doubt by ^{13}C nmr analysis (see Table II). For compound **11**, the ring methylene carbon

Table II. ^{13}C Chemical Shifts in ppm with Respect to TMS

Compd	C_2	C_4	C_5	Other shift values
11	167.6	88.1 (s)	30.5 (t)	Benzyl CH_2 at 48.1
12	167.8	87.9 (d)	43.8 (d)	$N(CH_3)_2$ at 38.2
13	168	87.7 (d)	51.7 (s)	$N(CH_3)_2$ at 36–46 (broad) $C(CH_3)_2$ at 21.9 and 32.4

atom absorbed at δ 30.5 comparable with the reported chemical shift of the α-methylene carbon atom in tetrahydrothiophene at δ 32.5.[12] The regioisomer of **11**, with the CH_2 located next to the more electronegative N atom, would be expected to absorb around δ 47.1 which is the chemical shift of the α-carbon atom in tetrahydropyrrole.[12] Table II also shows that the absorption values for the C-5 atoms of **12** and **13** have shifted to lower field with respect to **11** by the introduction of the methyl and phenyl substituents. In compound **13**, for instance, the C-5 atom is substituted with two methyl groups and absorbed at δ 51.7. This shift value is completely comparable with the C-5 carbon absorption of thiazolidine **14** which has been prepared by a different method[13] (the absorption values of **14**



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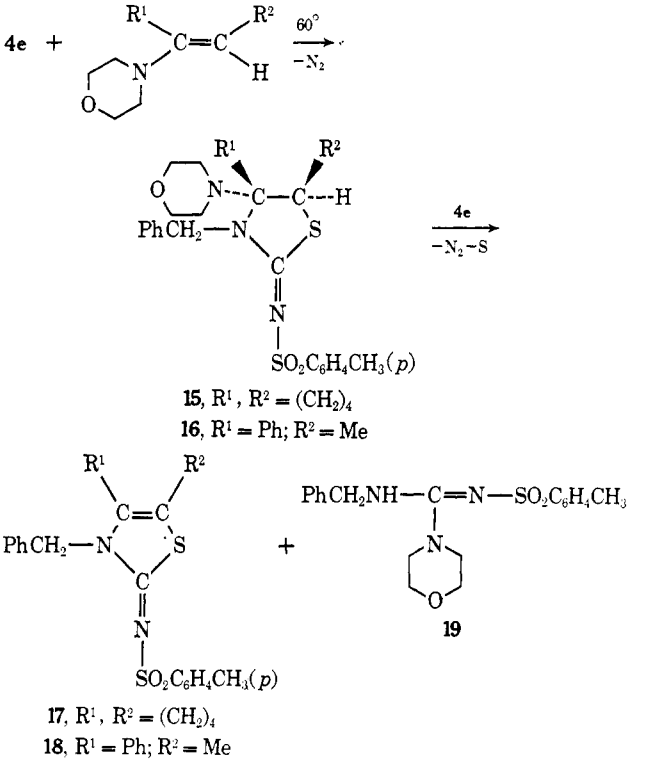
are indicated on the structure). Note also that the C-4 carbon atom absorptions of **11–13** are situated at low field (δ 87–88) due to the attachment of two electronegative N atoms.

In a few cases, the thiazolidines (*e.g.*, **15** and **16**) obtained from **4e** and morpholinoenamines underwent partially loss of morpholine under the reaction conditions to yield the corresponding thiazolines (*e.g.*, **17** and **18**) in addition to guanidine **19**. The latter com-



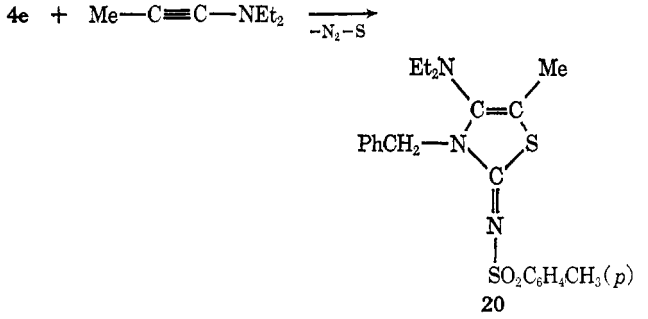
pound is believed to result from reaction of morpholine with the species **4e** and **5** (formed as side product). For synthetic purposes, the reaction mixture is best treated with HCl at room temperature in order to convert the remaining thiazolidine (**15** and **16**) into thiazoline (**17** and **18**).

Ynamines as electron-rich olefins are also suitable reagents for **4e**, giving access to 2-tosylimino-4-aminothiazolines such as **20**.

Keto-stabilized phosphorus ylides constitute another class of electron-rich olefins. Indeed, they are known to exist essentially in the enolate structure (C=O at *ca.*

(12) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley-Interscience, New York, N. Y., 1972, pp 52–53.

(13) S. Toppet, P. Claes, and J. Hoogmartens, *Org. Magn. Resonance*, **6**, 48 (1974).



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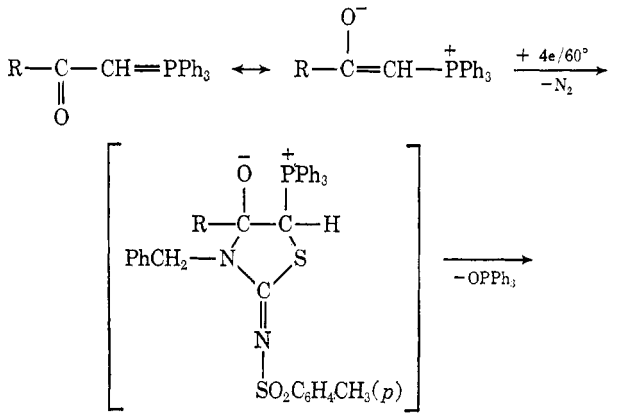
1530 cm^{-1}) and have been shown to manifest a pronounced dipolarophilic activity.[14] We have now found that they also react with **4e** to give thiazolines (*e.g.*, **22–24**). The reaction is assumed to give first a



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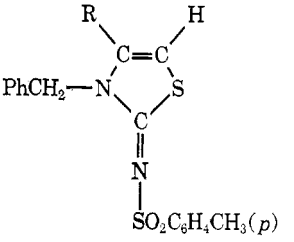
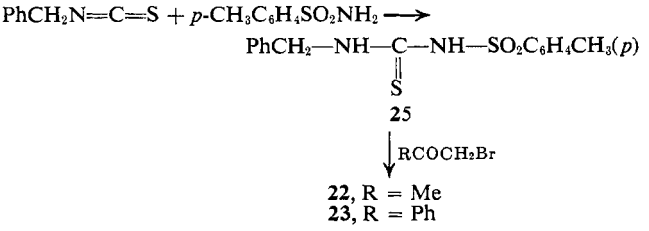


22, R = Me (60%)
23, R = Ph (95%)
24, R = $C_6H_4NO_2$(p) (65%)

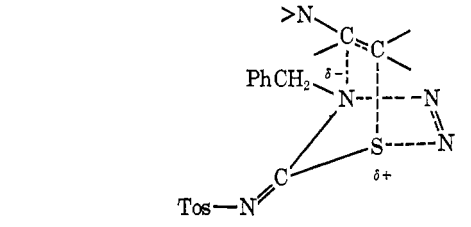
cyclic betaine intermediate **21**, followed by a Wittig-type elimination of $OPPh_3$. The structures of **22–24** were elucidated by spectral analysis (see Experimental Section) and further proven beyond any doubt by an independent synthesis starting from benzyl isothiocyanate and tosylamide. The thiourea **25** formed in this reaction was treated with bromoacetone and phenacyl bromide to give the cyclic products **22** and **23**, re-



spectively. Since compound **11** could also be transformed into **23** (90%) under the influence of hydrochloric acid, the independent synthesis of **23** once more confirms the assigned structure of the enamine adducts.

In contrast to the electron-rich olefins discussed above, vinyl ethers, vinyl acetates, and electron-poor olefins (methyl acrylate, dimethyl acetylenedicarboxylate, etc.) refused to give cycloadducts. The carbodiimide formed from **4e** in these reactions was converted to **9** in *ca.* 60% yield upon addition of methanol.

Two mechanisms can be considered for the formation of the cycloadducts discussed above: (i) attack of the olefin onto **4e** with simultaneous loss of nitrogen *via* transition state **26**, and (ii) the generation *in situ* of a 3-sulfonyliminothiaziridine **27** or its ring-opened dipolar form **28**. Kinetic experiments showed that the



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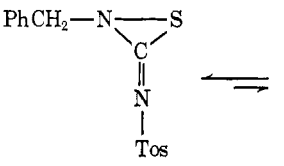

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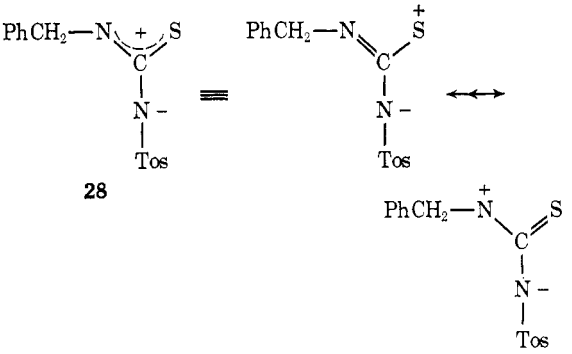

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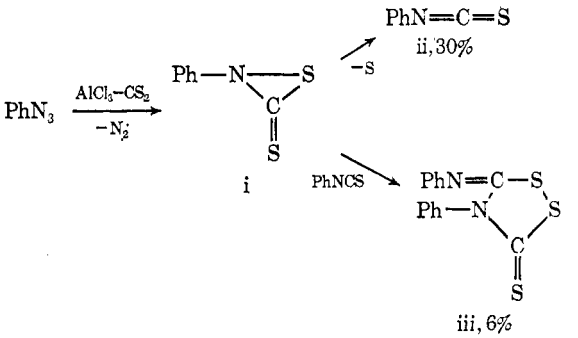
rate of decomposition of **4e** is not influenced by the presence of enamines in various concentrations (the first-order rate constant being $k_1 = 42 \times 10^{-5}$ sec^{-1} in CCl_4 at 60°. This result clearly indicates that path (i) is not operating, but that a discrete intermediate is formed by an unimolecular process. The most obvious structure of the intermediate is **27** and/or **28**.[15]

(14) P. Ykman, G. L'abbé, and G. Smets, *Tetrahedron Lett.*, 5225 (1970); *Tetrahedron*, **27**, 845, 5623 (1971); *J. Indian Chem. Soc.*, **49**, 1245 (1972); P. Ykman, G. Mathys, G. L'abbé, and G. Smets, *J. Org. Chem.*, **37**, 3213 (1972); G. L'abbé, J.-M. Borsus, and G. Smets, *Chem. Ind. (London)*, 1491 (1971).

(15) To our knowledge, thiaziridines have never been isolated, and reports on their occurrence as intermediates are rare. W. Borsche (*Ber.*, **75**, 1312 (1942)) reported the formation of thiaziridinethione (i) as an intermediate in the $AlCl_3$ catalyzed decomposition of phenyl azide in CS_2 to give phenyl isothiocyanate (ii) and 4-phenyl-5-phenylimino-1,2,4-dithiazolidine-3-thione (iii).

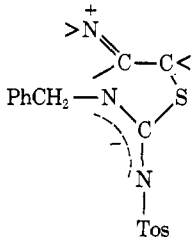


i

ii, 30%

iii, 6%

Loss of sulfur from these species would give the carbodiimide, whereas addition of olefins would yield the cycloadducts. However, this intermediate cannot add concertedly to olefins by the most general supra–supra fashion because it would involve a four-electron transition state.[16] Since, on the other hand, a stepwise addition *via* **29** would hardly rationalize the stereospecificity observed during the formation of **12**, we are left with a symmetry-allowed [$_\pi 2_s + {}_\sigma 2_a$] path for **27** or a [$_\pi 2_s + {}_\pi 2_a$] path for **28**. This means that the thiaziridine **27** (or the 1,3-dipole **28**) would participate in an antarafacial way as shown in **30**. This unexpected, but very



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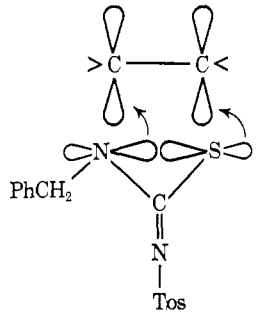

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interesting conclusion needs further substantiation. Experiments directed to gain more insight into the behavior of this new small ring system are in progress.

Experimental Section

All melting points were obtained on a Leitz apparatus and are uncorrected. Ir spectra were taken on a Perkin-Elmer 521 spectrometer. ^{1}H nmr spectra were recorded with a Varian A-60 or XL-100 spectrometer using TMS as an internal reference. For ^{13}C nmr spectra, the XL-100 apparatus was equipped with a device for pulsed Fourier transform operation. Mass spectra were obtained with an AEI MS-12 instrument operating at an ionizing potential of 70 eV. The sulfonyl isothiocyanates used in this work were prepared by the method of Hartke[17] as follows.

$$p\text{-}XC_6H_4SO_2NH_2 + CS_2 + 2KOH \xrightarrow[DMF]{} p\text{-}XC_6H_4SO_2N{=}C(SK)_2 \xrightarrow[ether]{COCl_2} p\text{-}XC_6H_4SO_2N{=}C{=}S + COS + 2KCl$$

General Procedure for the Synthesis of 4-Alkyl-5-sulfonylimino-1,2,3,4-thiatriazolines, Exemplified for 4e. Equimolar amounts (0.06 mol) of benzyl azide and tosyl isothiocyanate were allowed to react in CCl_4 (30 ml) at room temperature. After complete reaction (20 hr), the precipitate was collected (70%) and crystallized from acetone: mp 101–103° dec; ir (KBr) 1535 (C=N), 1305, and 1140 cm^{-1} (SO_2); nmr (CD_3COCD_3) τ 2.28 (d, 2 H, ortho aromatic protons), 2.62 (d, 2 H, ortho aromatic protons), 2.64 (s, 5 H, phenyl), 4.34 (s, 2 H, CH_2), and 7.57 (s, 3 H, CH_3); mass spectrum *m/e* (%) 346 (0.2, M·$^+$), 318 (0.15, M·$^+$ − N_2), 286 (6, M·$^+$ − N_2 − S), 270 (4), 254 (1), 155 (32), 139 (18), 131 (26), 124 (3), 91 (100).

Anal. Calcd for $C_{15}H_{14}N_4O_2S_2$ (346): C, 52.02; H, 4.04; N, 16.18; O, 9.24; S, 18.49. Found: C, 51.85; H, 4.00; N, 16.20; O, 9.25; S, 18.35.

The other thiatriazolines were prepared in a similar manner. In some cases (*e.g.*, for **4a**), the adduct did not precipitate directly from the reaction mixture. The solvent was then removed under reduced pressure and the residue was crystallized from the appropriate solvent (see Table I). The adducts were characterized by spectral and elemental analysis.

Thermolysis of 4e and Reaction with Oxalyl Chloride. Compound **4e** (0.01 mol) was allowed to decompose in dry CCl_4 (50 ml) at 80°. After 3 hr, gas evolution ceased and the ir spectrum showed a strong carbodiimide band at 2160 cm^{-1}. Oxalyl chloride (0.01 mol) was then added and the reaction mixture was stirred at room temperature for 48 hr. Compound **6** precipitated in 57% yield: mp 147–149°; ir (KBr) 1790 and 1755 (with shoulder at 1770, C=O), 1400 and 1200 cm^{-1} (SO_2); nmr ($CDCl_3$–DMSO-d_6 4:1 ratio) τ 2.02 (d, 2 H, ortho aromatic protons), 2.40–2.90 (m, 7 H, aromatic protons), 5.35 (s, 2 H, CH_2), and 7.55 (s, 3 H, CH_3). This compound (1.05 g) was dissolved in a mixture of acetone (25 ml) and water (5 ml) and then stirred at room temperature for 4 days. Evaporation of the solvent afforded a crude product (90%) which, on crystallization from toluene–CCl_4, gave pure **7** in 54% yield: mp 187–189°; ir (KBr) 1805, 1790 and 1760 (C=O), 1410 and 1200 cm^{-1} (SO_2); nmr ($CDCl_3$) τ 1.97 (d, 2 H, ortho aromatic protons), 2.50–2.80 (m, 7 H, aromatic protons), 5.27 (s, 2 H, CH_2), and 7.56 (s, 3 H, CH_3); mass spectrum *m/e* (%) 358 (1.6, M·$^+$), 294 (0.7, M·$^+$ − SO_2), 266 (0.7, M·$^+$ − SO_2 − CO), 203 (37, M·$^+$ − $CH_3C_6H_4SO_2$), 175 (9), 155 (15, $CH_3C_6H_4SO_2^+$), 132 (7), 91 (100, $CH_3C_6H_4^+$). Alternately, when **4e** (1.73 g) was decomposed in a mixture of acetone (50 ml) and water (5 ml) at 65° and the solvent removed after complete reaction, a residue was obtained which was treated with methanol (15 ml) to give compound **8** in 60% yield, mp 172–173° (MeOH). To 1.52 g of this compound in 15 ml of CH_2Cl_2 was added dropwise with stirring and cooling 0.96 g of oxalyl chloride. The mixture was stirred at room temperature for 1 hr and then refluxed for 2 hr. Evaporation of the solvent furnished a crude product which was crystallized from toluene–CCl_4 (3:1 ratio) to give pure **7** in 51% yield.

Decomposition of 4 under Influence of Bases. Treatment of **4e** (0.5 g) with a 1.5 *M* solution of MeONa in MeOH (5 ml) caused decomposition within 2 hr. The solvent was removed and the residue was treated with water (25 ml) to give pure **9** in 79% yield: mp 130° (MeOH); ir (KBr) 3340 (N–H), 1610 (C=N), 1280, and 1130 cm^{-1} (SO_2); nmr ($CDCl_3$) τ 2.22 (d, 2 H, ortho aromatic protons), 2.6–2.9 (m, 7 H, aromatic protons), 5.6 (d, 2 H, CH_2), 6.19 (s, 3 H, CH_3O), and 7.59 (s, 3 H, CH_3); mass spectrum *m/e* (%) 318 (14, M·$^+$), 253 (4, M·$^+$ − SO_2H, m* at 201.6), 196 (1.4, $CH_3C_6H_4SO_2NCNH^+$), 163 (68, M·$^+$ − $CH_3C_6H_4SO_2$, m* at 83.5), 155 (4, $CH_3C_6H_4SO_2^+$), 139 (2, $CH_3C_6H_4SO^+$), 131 (5, $PhCH_2NCN^+$), 106 (8, $PhCH_2NH^+$), 91 (100, $CH_3C_6H_4^+$ and $C_6H_5CH_2^+$).

Anal. Calcd for $C_{16}H_{18}N_2O_3S$ (318): C, 60.38; H, 5.66; N, 8.80; S, 10.06. Found: C, 60.50; H, 5.70; N, 8.75; S, 10.10.

Similarly, when a methanol solution (15 ml) of **4a** (1.49 g) was treated with a 5 *M* solution of NaOH (5 ml), decomposition occurred at room temperature within 15 min. After addition of water (100 ml) *O*-methyl-*N*-butyl-*N'*-benzenesulfonylisourea (**10**) was isolated in 61% yield: mp 71–72° (MeOH); ir (KBr) 3340 (N–H), 1615 (C=N), 1280 and 1130 cm^{-1} (SO_2); nmr ($CDCl_3$) τ 2.0–2.7 (m, 5 H, Ph), 6.18 (s, 3 H, CH_3O), 6.77 (q, 2 H, CH_2), and 8.3–9.2 (m, 7 H, Bu); mass spectrum *m/e* (%) 270 (4, M·$^+$), 255 (8, M·$^+$ − CH_3), 241 (5, M·$^+$ − C_2H_5), 239 (4, M·$^+$ − CH_3O, m* at 211.5), 227 (11, M·$^+$ − C_3H_7), 215 (11), 198 (8), 149 (17), 141 (73, $PhSO_2^+$), 125 (2, $PhSO^+$), 77 (100, Ph^+).

Anal. Calcd for $C_{12}H_{18}N_2O_3S$ (270): C, 53.33; H, 6.66; N, 10.37; S, 11.85. Found: C, 53.40; H, 6.90; N, 10.35; S, 11.80.

Decomposition of 4e in the Presence of Enamines. Compound **4e** (0.01 mol) was allowed to decompose at 60° in the presence of an equimolar amount of enamine in dry CCl_4 (50–75 ml). After complete reaction (2–3 hr), the mixture was worked up as specified below.

2-Tosylimino-3-benzyl-4-phenyl-4-morpholinothiazolidine (11) was obtained in 67% by cooling of the reaction mixture after complete reaction (2 hr): mp 178–180° (MeOH); ir (KBr) 1515 (C=N), 1155, and 1320 cm^{-1} (SO_2); nmr ($CDCl_3$) τ 2.24–3.58 (m, 14 H, aromatic protons), 5.52 (s, 2 H, benzyl CH_2), 6.16–6.46 (m, 4 H, morpholino), 6.32 (s, 2 H, ring CH_2), 7.33–7.80 (m, 4 H, morpholino), and 7.62 (s, 3 H, CH_3); mass spectrum *m/e* (%) 507 (very small, M·$^+$), 420 (1, M·$^+$ − morpholine), 265 (3, *m/e* 420 − Tos), 221 (2, morpholino-C(Ph)CH_2S^+), 189 (100).

Anal. Calcd for $C_{27}H_{29}N_3O_3S_2$ (507): C, 63.90; H, 5.72; N, 8.28; S, 12.62. Found: C, 63.80; H, 5.70; N, 8.15; S, 12.55.

***trans*-2-Tosylimino-3-benzyl-4-dimethylamino-5-phenylthiazolidine (12)** was obtained in 73% by partial evaporation and cooling of the reaction mixture: mp 161–162° (CCl_4); ir (KBr) 1530 (C=N), 1300, and 1150 cm^{-1} (SO_2); nmr ($CDCl_3$) τ 2.13 (d, 2 H, ortho aromatic protons), 2.6–3.2 (m, 12 H, aromatic protons), 4.72 (d,

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1 H, benzyl proton, J = 14.5 Hz), 5.55 (d, 1 H, ring proton, J = 2.5 Hz), 5.68 (d, 1 H, ring proton, J = 2.5 Hz), 5.81 (d, 1 H, benzyl proton, J = 14.5 Hz), 7.56 (s, 3 H, CH_3), and 7.69 (s, 6 H, NMe_2); mass spectrum m/e (%) 465 (3, $M\cdot^+$), 421 (8, $M\cdot^+ - NMe_2$, m* at 381.2), 420 (34, $M\cdot^+ - HNMe_2$, m* at 379.3), 179 (6, $PhCHCH(NMe_2)S\cdot^+$), 91 (100).

Anal. Calcd for $C_{25}H_{27}N_3O_2S_2$ (465): C, 64.51; H, 5.80; N, 9.03; O, 6.88; S, 13.76. Found: C, 64.40; H, 5.80; N, 8.90; O, 6.75; S, 13.50.

2-Tosylimino-3-benzyl-4-dimethylamino-5,5-dimethylthiazolidine (13) was obtained in 55% by evaporation of the solvent and treatment of the residual oil with ether (20 ml), followed by cooling: mp 132–133° (MeOH); ir (KBr) 1530 (C=N), 1295, 1285, 1150, and 1140 cm^{-1} (SO_2); nmr ($CDCl_3$) τ 2.18 (d, 2 H, ortho aromatic protons), 2.60–3.00 (m, 7 H, aromatic protons), 4.55 (d, 1 H, benzyl proton, J = 14.5 Hz), 6.08 (d, 1 H, benzyl proton, J = 14.5 Hz), 6.12 (s, 1 H, ring proton), 7.48 (s, 6 H, NMe_2), 7.60 (s, 3 H, aromatic CH_3), 8.66 (s, 3 H, ring CH_3), and 8.77 (s, 3 H, ring CH_3); mass spectrum m/e (%) 417 (3, $M\cdot^+$), 373 (64, $M\cdot^+ - NMe_2$, m* at 333.6), 131 (2.5, $Me_2NCHCMe_2S\cdot^+$), 91 (100).

Anal. Calcd for $C_{21}H_{27}N_3O_2S_2$ (417): C, 60.43; H, 6.47; N, 10.07; S, 15.35. Found: C, 60.35; H, 6.60; N, 9.90; S, 15.30.

Thiazoline 17 was formed together with **15** and **19** in the reaction of **4e** with morpholinocyclohexene. After complete reaction (2 hr), the solvent was cooled and **19** was isolated by filtration in 16% yield: mp 193–194° (CCl_4–$CHCl_3$); ir (KBr) 3340 (N–H), 1530 (C=N), 1265, and 1135 cm^{-1} (SO_2); nmr ($CDCl_3$) τ 2.37 (d, 2 H, ortho aromatic protons), 2.58–3.00 (m, 7 H, aromatic protons), 2.90 (br, 1 H, NH), 5.75 (d, 2 H, benzyl CH_2), 6.2–6.8 (m, 8 H, morpholino), and 7.62 (s, 3 H, CH_3); mass spectrum m/e (%) 373 (1, $M\cdot^+$), 218 (40, $M\cdot^+ - Tos$), 106 (100, $PhCH_2NH^+$), 91 (100, $C_7H_7^+$).

Anal. Calcd for $C_{19}H_{24}N_3O_3S$ (373): C, 61.12; H, 6.16; N, 11.26; S, 8.58. Found: C, 61.40; H, 6.30; N, 11.15; S, 8.50.

The mother liquor was evaporated to dryness and the residual oil was dissolved in DMF (100 ml) and treated with a 2 *N* HCl solution (20 ml) at room temperature for 4 hr. The reaction mixture was poored into ice–water; the precipitate (**17**) was collected, washed with water, and dried, yield 79%: mp 180–182° (MeOH); ir (KBr) 1500 (C=N), 1300, and 1145 cm^{-1} (SO_2); nmr ($CDCl_3$) τ 2.23 (d, 2 H, ortho aromatic protons), 2.67–3.15 (m, 7 H, aromatic protons), 4.89 (s, 2 H, benzyl CH_2), 7.40–7.85 and 8.08–8.45 (two m, 8 H, cyclohexene protons), and 7.64 (s, 3 H, CH_3); mass spectrum m/e (%) 398 (10, $M\cdot^+$), 243 (49, $M\cdot^+ - Tos$), 91 (100, $C_7H_7^+$).

Anal. Calcd for $C_{21}H_{22}N_2O_2S_2$ (398): C, 63.32; H, 5.53; N, 7.03; S, 16.08. Found: C, 63.20; H, 5.60; N, 6.90; S, 15.80.

2-Tosylimino-3-benzyl-4-phenyl-5-methylthiazoline (18) was formed together with **16** and **19** in the reaction of **4e** with α-morpholino-β-methylstyrene. After complete reaction (2 hr), the insoluble guanidine **19** was isolated (21%). The solvent was removed from the mother liquor and the residue was dissolved in DMF (50 ml) and treated with a 2 *N* HCl solution (20 ml) at room temperature for 1 hr. The mixture was then poored into ice–water and the precipitate (**13**) was collected and washed with water and ether, yield 48%: mp 167–168° (MeOH); ir (KBr) 1500 (C=N), 1285, and 1155 cm^{-1} (SO_2); nmr ($CDCl_3$) τ 2.21 (d, 2 H, ortho aromatic protons), 2.50–3.50 (m, 12 H, aromatic protons) 5.03 (s, 2 H, CH_2), 7.61 (s, 3 H, tosyl CH_3), and 8.00 (s, 3 H, ring CH_3); mass spectrum m/e (%) 434 (28, $M\cdot^+$), 279 (68, $M\cdot^+ - Tos$), 91 (100, $C_7H_7^+$).

Anal. Calcd for $C_{24}H_{22}N_2O_2S_2$ (434): C, 66.36; H, 5.07; N, 6.45; S, 14.75. Found: C, 66.50; H, 5.10; N, 6.30; S, 14.90.

Decomposition of 4e in the Presence of Ynamines. Equimolar amounts (0.01 mol) of **4e** and *N,N*-diethylaminopropyne were heated at 60° in benzene (35 ml) for 4 hr. Nmr analysis of the reaction mixture showed the presence of thiazoline **20** in 50–60% yield. Removal of the solvent and crystallization of the residue from ether furnished pure **20** in 19%: mp 118–119° (MeOH); ir (KBr) 1500 (C=N), 1300, and 1150 cm^{-1} (SO_2); nmr ($CDCl_3$) τ 2.29 (d, 2 H, ortho aromatic protons), 2.67–3.20 (m, 7 H, aromatic protons), 4.90 (s, 2 H, benzyl CH_2), 7.13 (q, 4 H, CH_2CH_3), 7.63 (s, 3 H, tosyl CH_3), 7.85 (s, 3 H, ring CH_3), and 9.14 (t, 6 H, CH_2CH_3); mass spectrum m/e (%) 429 (8, $M\cdot^+$), 338 (4, $M\cdot^+ - C_7H_7$), 274 (23, $M\cdot^+ - Tos$), 91 (100, $C_7H_7^+$). *Anal.* Calcd for $C_{22}H_{27}N_3O_2S_2$ (429): C, 61.54; H, 6.29; N, 9.79; S, 14.92. Found: C, 61.60; H, 6.45; N, 9.60; S, 15.15.

Decomposition of 4e in the Presence of Acylphosphoranes. Compound **4e** (0.01 mol) was allowed to decompose at 60° in the presence of an equimolar amount of acylphosphorane in dry CCl_4 (25 ml) until N_2 evolution ceased. The reaction mixture was then cooled to room temperature or below in order to crystallize the cycloadducts **22–24**. A second crop of cycloadduct may eventually be obtained by evaporating the mother liquor, dissolving the residue in methanol, and cooling.

2-Tosylimino-3-benzyl-4-methylthiazoline (22) was obtained in 60% yield after crystallization from MeOH: mp 119–121°; ir (KBr) 3100 (=CH), 1485 (C=N), 1285, and 1145 cm^{-1} (SO_2); nmr (DMSO-d_6, 50°, HMDS as standard) τ 2.45 (d, 2 H, aromatic protons), 2.7–3.2 (m, 7 H, aromatic protons), 3.55 (1 H, ring CH), 4.9 (s, 2 H, CH_2), 7.75 (s, 3 H, tosyl CH_3), and 7.95 (d, 3 H, ring CH_3); mass spectrum m/e (%) 358 (24, $M\cdot^+$), 203 (100, $M\cdot^+ - Tos$).

2-Tosylimino-3-benzyl-4-phenylthiazoline (23) was obtained in 95% yield: mp 167.5–169.5° (MeOH); ir (KBr) 3100 (=CH), 1490 (C=N), and 1140 cm^{-1} (SO_2); nmr ($CDCl_3$) τ 2.25 (d, 2 H, ortho aromatic protons), 2.5–3.7 (m, 12 H, aromatic protons), 3.70 (s, 1 H, ring CH), 4.91 (s, 2 H, CH_2), and 7.62 (s, 3 H, tosyl CH_3); mass spectrum m/e (%) 420 (27, $M\cdot^+$), 265 (62, $M\cdot^+ - Tos$), 91 (100).

Anal. Calcd for $C_{23}H_{20}N_2O_2S_2$ (420): C, 65.71; H, 4.76; N, 6.67; O, 7.62; S, 15.24. Found: C, 65.85; H, 4.80; N, 6.65; O, 7.70; S, 15.15.

Compound **23** was also obtained when **11** (1 g) was dissolved in DMF (30 ml) and treated with a 2 *N* HCl solution (10 ml) for 15 min. The mixture was collected, washed with water, and dried; yield 90%.

2-Tosylimino-3-benzyl-4-(*p*-nitrophenyl)thiazoline (24) was obtained in 65% yield after crystallization from MeOH: mp 196–198°; ir (KBr) 1500–1530 (C=N, NO_2), 1350 and 1150 cm^{-1} (NO_2 and SO_2); nmr ($CDCl_3$) τ 1.7–3.4 (m, 13 H, aromatic protons), 3.5 (s, 1 H, ring CH), 4.86 (s, 2 H, CH_2), and 7.6 (s, 3 H, tosyl CH_3); mass spectrum m/e (%) 465 (8, $M\cdot^+$), 310 (14, $M\cdot^+ - Tos$), 91 (100, $C_7H_7^+$).

Anal. Calcd for $C_{23}H_{19}N_3O_4S_2$ (465): C, 59.35; H, 4.09; N, 9.09; S, 13.76. Found: C, 59.40; H, 4.10; N, 9.15; S, 13.75.

Independent Synthesis of 22 and 23. An acetone–water solution (50:50 ml) of benzyl isothiocyanate (0.1 mol), tosylamide (0.1 mol), and NaOH (4.5 g) was refluxed for 1 hr and then stirred at room temperature for another 3 days. The reaction mixture was diluted with water (100 ml) and acidified with a 5 *N* solution of HCl. The precipitate was filtered, washed several times with water, dried, and crystallized from MeOH–ether to give **25** in 53% yield: mp 163–165° (lit.[18] 164–165°); ir (KBr) 3330 (NH), 3200–2600 (br), 1545, 1390, 1345, 1175, and 1135 cm^{-1}; nmr (100 MHz, DMSO-d_6, HMDS as standard) τ −1.55 (br, 1 H, $NHSO_2$), 1.12 (t, 1 H, $NHCH_2$), 2.17 (d, 2 H, ortho aromatic protons), 2.58 (d, 2 H, ortho aromatic protons), 2.6–2.9 (m, 5 H, aromatic protons), 5.28 (d, 2 H, CH_2), and 7.59 (s, 3 H, CH_3); mass spectrum m/e (%) 320 (2.5, $M\cdot^+$). Compound **25** (0.01 mol) was treated with an equimolar amount of bromoacetone or phenacyl bromide in EtOH (50 ml) at reflux temperature for 1.5 hr. Upon cooling the mixture to room temperature, the cycloadducts **22** and **23** crystallized out in quantitative yield. They were identical in all respects with the products obtained from **4e** and the phosphorus ylides.

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