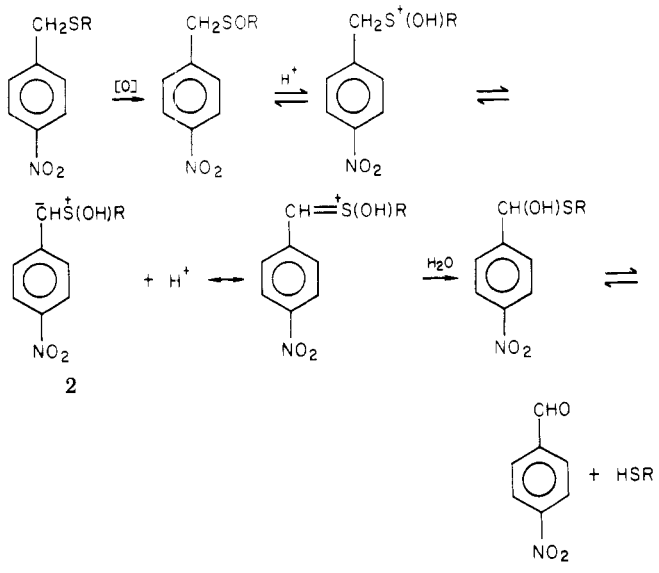
Scheme I



of the intermediate sulfoxide from **1e** (or the corresponding *p*-nitrobenzyl methyl sulfide), resulting in a 90% yield of *p*-nitrobenzaldehyde. The *p*-nitro group must facilitate the Pummerer reaction by stabilizing the zwitterionic intermediate **2** (Scheme I). *p*-Nitro-α,α-dimethylbenzyl phenyl sulfide could be oxidized to the sulfone in high yield by treatment with 30% hydrogen peroxide in glacial acetic acid but was stable to refluxing aqueous acetic acid solutions of hydrogen peroxide.

The *p*-nitrobenzyl phenyl or methyl sulfoxides can be formed by oxidation of the sulfides with 1 equiv of *m*-chloroperbenzoic acid in chloroform at −10 °C. Treatment of these sulfoxides with aqueous mineral acid readily brings about the Pummerer reaction, whereas *p*-nitrocumyl phenyl sulfoxide is stable to aqueous acid. Under similar conditions (24-h reflux, 3 M H_2SO_4 in aqueous acetic acid) *p*-methoxybenzyl phenyl sulfoxide gave but a trace of benzaldehyde, *p*-chlorobenzyl phenyl sulfoxide gave 30% of *p*-chlorobenzaldehyde, and *p*-cyanobenzyl phenyl sulfoxide gave 85% of *p*-cyanobenzaldehyde. The ability of acid-strengthening para substituents in benzyl sulfoxides to promote the Pummerer reaction is analogous to the β-carbonyl group in β-keto sulfoxides, wherein the Pummerer reaction occurs readily.[3]

Experimental Section

Substituted benzyl chlorides were reacted with a 200% excess of sodium benzenethiolate[4] or methyl mercaptide[5] in ethanol to yield the sulfides shown in Table I in yields of 63–96%. The benzylic hydrogen atoms in ^{1}H NMR were a singlet at δ 3.60–4.15 (Me_2SO-d_6), depending upon the structure. *p*-Nitro-α,α-dimethylbenzyl phenyl sulfide was formed in a similar fashion in 86% yield: ^{1}H NMR δ 1.75 (s, 6), 7.3 (m, 7), 8.11 (d, 2).

Oxidation of the appropriate sulfides in chloroform at −10 °C for 24 h by 1 equiv of *m*-chloroperbenzoic acid (83% assay) gave the corresponding sulfoxides in 90–95% yield.[6,7] The sulfoxides all had IR absorption at 1030–1055 cm^{-1} except for phenyl *p*-methoxybenzyl sulfoxide which absorbed at 1125 cm^{-1}. The sulfoxides possess diastereotopic benzylic hydrogen atoms which give rise to an AB ^{1}H NMR quartet centered at $(\delta_A + \delta_B)/2$ = 3.95–4.3 (J = 12.7–12.9 Hz) (Me_2SO-d_6), depending on structure.[8]

Oxidation of the sulfides in glacial acetic acid containing an excess of aqueous hydrogen peroxide (30% assay) gave after 45 min of reflux an essentially quantitative yield of the sulfones. The sulfones possessed a benzylic ^{1}H NMR singlet (Me_2SO-d_6) at δ 4.3–4.65 and IR absorptions at 1100 and 1350 cm^{-1}. In a similar fashion *p*-nitro-α,α-dimethylbenzyl phenyl sulfone, mp 82–84 °C, was prepared in 80% yield: ^{1}H NMR (Me_2SO-d_6) δ 1.9 (s, 6), 7.6 (m, 7), 8.1 (d, 2); mass spectrum (70 eV) m/e 305 (M^+).

An alternate procedure applicable to benzyl, *p*-chlorobenzyl, *p*-cyanobenzyl, or *p*-methoxybenzyl phenyl or methyl sulfides involved treatment of the sulfide in a mixture of acetic acid (60%)–water (40%) acidified to 3 M with sulfuric acid. An excess of 30% hydrogen peroxide was added dropwise and the mixture refluxed for 24 h before dilution with water and extraction with chloroform to yield the sulfone.

Pummerer rearrangement of the performed sulfoxides involved refluxing the sulfoxides in acetic acid (60%)–water (40%) acidified to 3 M with sulfuric acid for a period of 24 h followed by GC analysis of the ether-soluble products.

Table I. Para-Substituted Benzyl Sulfides, Sulfoxides, and Sulfones (p-$XC_6H_4CH_2S(O)_nR$)

		mp, °C		
R	X	n = 0	n = 1	n = 2 (lit. mp)
CH_3	H	liq	53-55	125-127 (125-127)[a]
C_6H_5	H	40-41	124-126	144-145 (147-148)[b]
CH_3	NO_2	69-71	101-102	162-166 (167-168)[c]
C_6H_5	NO_2	74-75	153-155	205-206 (209.5-210.5)[b]
CH_3	Cl	liq	*d*	120-122 (120-122)[a]
C_6H_5	Cl	79-80	162-164	190-193 (189-191)[b]
C_6H_5	CN	74-75	73-76	205-209 (208-210)[b]
C_6H_5	CH_3O	83-85	*d*	139-140 (140-141)[e]

[a] T. R. Lewis and S. Archer, *J. Am. Chem. Soc.*, **73**, 2109 (1951). [b] B. B. Jarvis and J. C. Saukautis, *ibid.*, **95**, 7708 (1973). [c] C. K. Ingold, E. H. Ingold, and F. R. Shaw, *J. Chem. Soc.*, 813 (1928). [d] Obtained as oils. [e] B. R. Brown and M. R. Shaw, *J. Chem. Soc., Perkin Trans. 1*, 2036 (1974).

Registry No. **1a**, 5023-67-6; **1b**, 831-91-4; **1c**, 7693-30-3; **1d**, 51229-54-0; **1e**, 7703-38-0; benzyl methyl sulfide, 766-92-7; *p*-nitrobenzyl methyl sulfide, 51392-53-1; *p*-chlorobenzyl methyl sulfide, 5925-82-6; benzyl methyl sulfoxide, 824-86-2; benzyl phenyl sulfoxide, 833-82-9; *p*-nitrobenzyl methyl sulfoxide, 15733-10-5; *p*-nitrobenzyl phenyl sulfoxide, 17530-84-6; *p*-chlorobenzyl methyl sulfoxide, 24176-68-9; *p*-chlorobenzyl phenyl sulfoxide, 17530-80-2; *p*-cyanobenzyl phenyl sulfoxide, 71426-19-2; *p*-methoxybenzyl phenyl sulfoxide, 71426-20-5; benzyl methyl sulfone, 3112-90-1; benzyl phenyl sulfone, 3112-88-7; *p*-nitrobenzyl methyl sulfone, 61081-34-3; *p*-nitrobenzyl phenyl sulfone, 34063-53-1; *p*-chlorobenzyl methyl sulfone, 5925-80-4; *p*-chlorobenzyl phenyl sulfone, 51229-56-2; *p*-cyanobenzyl phenyl sulfone, 51229-59-5; *p*-methoxybenzyl phenyl sulfone, 55539-39-4; sodium benzenethiolate, 930-69-8; sodium methyl mercaptide, 5188-07-8; benzyl chloride, 100-44-7; *p*-nitrobenzyl chloride, 100-14-1; *p*-chlorobenzyl chloride, 104-83-6; *p*-cyanobenzyl chloride, 874-86-2; *p*-methoxybenzyl chloride, 824-94-2; *p*-nitro-α,α-dimethylbenzyl phenyl sulfide, 15013-24-8; *p*-nitro-α,α-dimethylbenzyl phenyl sulfone, 70951-74-5; *p*-nitrobenzaldehyde, 555-16-8; *p*-methoxybenzaldehyde, 123-11-5; *p*-chlorobenzaldehyde, 104-88-1; *p*-cyanobenzaldehyde, 105-07-7.

(3) G. A. Russell and G. J. Mikol, *Mech. Mol. Migr.*, **1**, 157–207 (1968).
(4) W. R. Waldrin and E. E. Reid, *J. Am. Chem. Soc.*, **45**, 2399 (1923).
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(8) M. Nishio, *Chem. Pharm. Bull. Jpn.*, **15**, 1609 (1967); *ibid.*, **17**, 262 (1969).

4-Imino-4,5-dihydro-1,2λ^6-3-oxathiazol-2-ones. Ring-Opening Cycloaddition Reactions with Maintenance of the Ring Size

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Many cycloaddition reactions where heterocycles are transformed into other heterocycles of the same size but with a different skeleton involve elimination of a good leaving group. Examples of this are the mesoionic

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compounds[1] and the masked 1,3-dipoles.[2] We now report on cycloaddition reactions where a five-membered ring is transformed into another five-membered ring without the extrusion of a leaving group. Although this type of reaction is well documented for sulfur-containing heterocycles involving a thiapentalene ring structure as intermediate or final product,[3] examples in the nonsulfur field are rare. A typcial case, studied by Steglich et al.,[4] is the conversion of oxazolin-5-ones into pyrrolin-3-ones with ynamines as reagent.

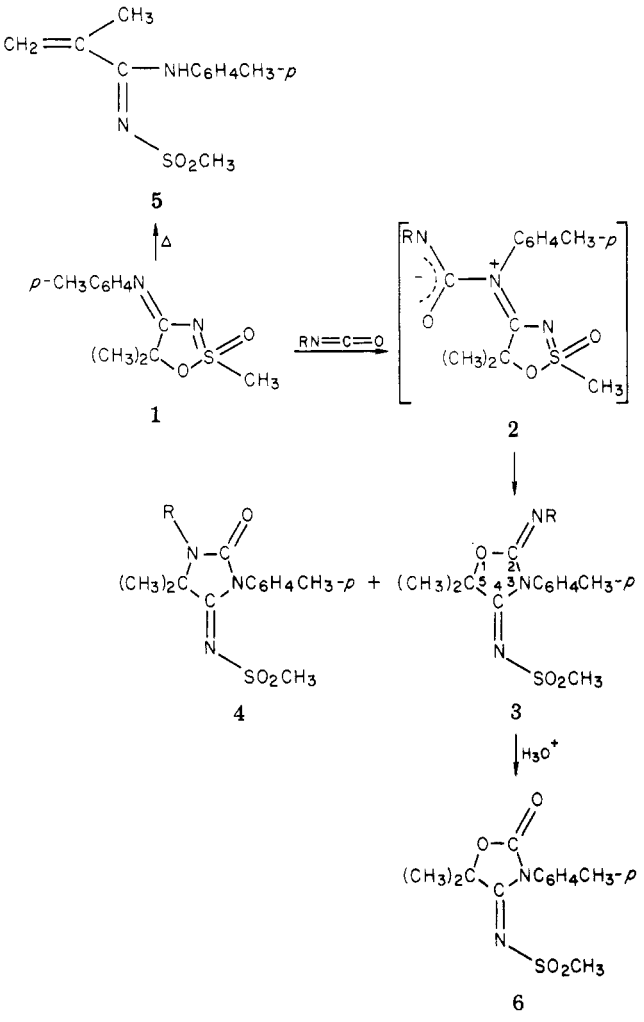
Recently, we reported two methods for the synthesis of a new class of heterocycles, namely, 4-imino-4,5-dihydro-1,2λ⁶,3-oxathiazol-2-ones (e.g., **1**).[5] These compounds have proved to be suitable candidates to further illustrate the title concept. The results are discussed below.[6]

Treatment of **1** with a tenfold excess of phenyl isocyanate at room temperature led to the isolation of **3a** as the major product in addition to **4a**. The product ratio was found to depend on the reaction conditions. For instance, when the reaction was carried out in chloroform solution, **3a** and **4a** were obtained in a ratio of 2:1; in the absence of solvent **4a** only resulted in trace amounts.

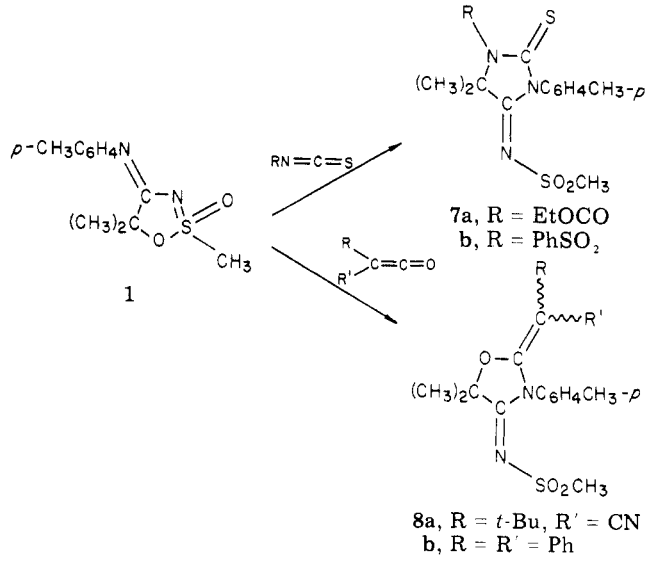
Benzoyl isocyanate also reacted with an equimolar amount of **1** at room temperature to yield **3b** as the sole cycloadduct in addition to the methacrylic amidine **5** (decomposition product of **1**).[5] The adducts **3a,b** were readily hydrolyzed to **6** under acidic conditions or, in the case of **3b**, simply upon treatment on a silica gel column.

With phenylsulfonyl isocyanate, the two cycloadducts **3c** and **4c** were formed again, and the product ratio was determined under various conditions (see Table I). The relative amounts of products were estimated from the crude ^{1}H NMR spectra by integration of the ring methyl proton signals. In all cases studied, **3c** was the main product, but the amount of **4c** increased when the polarity of the reaction mixture decreased. We have also verified that **3c** and **4c** remained unchanged in the presence of an excess of starting materials.

An examination by ^{1}H NMR of the reaction conditions disclosed that polar solvents and electron-withdrawing substituents on the isocyanate increased the rate of cycloaddition ($PhSO_2NCO$ > PhCONCO > PhNCO). This is interpreted in terms of stabilization of the intermediate **2**, formed by nucleophilic attack of **1** onto the isocyanate. This intermediate then undergoes ring closure to the cycloadducts. The preferential formation of **3** is probably dictated by steric interactions during ring closure.[7]



Whereas phenyl isothiocyanate and *tert*-butyl isothiocyanate were unreactive toward **1**, carbethoxy isothiocyanate and phenylsulfonyl isothiocyanate reacted readily at room temperature to give **7a,b** in high yields.



The reactions of **1** with *tert*-butylcyanoketene and diphenylketene yielded cycloadducts **8a,b**. Here again, the formation of the C=O instead of the C=C adduct is explained by invoking steric arguments.

We have found that **1** was unreactive toward dicyclohexylcarbodiimide, dimethyl acetylenedicarboxylate,

(1) H. C. Van der Plas, "Ring Transformations of Heterocycles", Vol. I, Academic Press, London and New York, 1973, pp 258, 286, 365.

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(7) Cycloadditions across the C=O bond of isocyanates are uncommon; see, for instance, H. Ulrich, "Cycloaddition Reactions of Heterocumulenes", Academic Press, New York, 1967, pp 122–219.

Table I. Product Distribution in the Reaction of 1 with $PhSO_2NCO$ at 20 °C

solvent	% yield 3c	% yield 4c
C_6D_6[a]	75	25
$CDCl_3$[a]	80	20
CD_3CN[a]	92	8
$PhSO_2NCO$[b]	100	0

[a] Equimolar amounts of 1 and $PhSO_2NCO$ were used. [b] Tenfold excess without solvent.

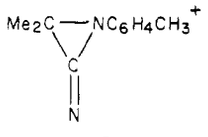
methyl acrylate, acrylonitrile, methyl vinyl ketone, nitriles, ketones, thioketones, enamines, and isonitriles.

The structures of the reaction products were established on the basis of IR, ^1H NMR, ^{13}C NMR and mass spectroscopy (see Table II, and Experimental Section). In particular, the IR spectra exhibited C_2=N absorptions at 1670–1705 cm^{-1} for **3**, C_2=O absorptions at 1760–1800 cm^{-1} for **4** and **6**, and a C=C stretching frequency at 1660 cm^{-1} for **8a**. In the ^{13}C NMR spectra, the C_5 carbon resonances of **3**, **6**, and **8** are situated at δ 86–91, indicating an oxygen atom in the α-position. Those of **4** and **7** are found at higher field (δ 65–73) as would be expected for a nitrogen atom in the α-position.

Experimental Section

Reaction of 1 with Phenyl Isocyanate. A solution of 1 (0.002 mol) and phenyl isocyanate (0.03 mol) in 5 mL of dry chloroform was stirred at room temperature for 5 days. The excess of isocyanate was then removed in vacuo, and the residue was chromatographed on silica gel with ether–hexane as the eluent.

Compound **3a** was obtained in 54% yield: mp 199–201 °C (*n*-hexane–chloroform); ^1H NMR ($CDCl_3$) δ 1.96 (s, 6 H, 2 CH_3), 2.4 (s, 3 H, CH_3), 2.96 (s, 3 H, CH_3SO_2), 7.0–7.4 (m, 9 aromatic H); mass spectrum, *m/e* (rel intensity) 371 (45, M^+·), 252 (46, M^+· – PhNCO), 173 (100, I). Anal. Calcd for $C_{19}H_{21}N_3O_3S$ (mol wt 371): C, 61.46; H, 5.66; N, 11.32. Found: C, 61.39; H, 5.78; N, 11.66.



I

Compound **4a** was obtained in 28% yield: mp 189–190 °C (chloroform–ether); ^1H NMR (Me_2SO-d_6, HMDS) δ 1.72 (s, 6 H, 2 CH_3), 2.3 (s, 3 H, CH_3), 2.92 (s, 3 H, CH_3SO_2), 7.0–7.6 (m, 9 aromatic H); mass spectrum, *m/e* (rel intensity) 371 (100, M^+·), 356 (67, M^+· – CH_3), 292 (27, M^+· – CH_3SO_2), 173 (19). Anal. Calcd for $C_{19}H_{21}N_3O_3S$ (mol wt 371): C, 61.46; H, 5.66; N, 11.32. Found: C, 61.50; H, 5.77; N, 11.34.

When the reaction was carried out with a tenfold excess of phenyl isocyanate in the absence of solvent, compound **3a** was obtained in 70% yield. The ^1H NMR spectrum of the crude reaction mixture indicated that **4a** was formed in trace amounts.

Reaction of 1 with Benzoyl Isocyanate. Equimolar amounts (0.002 mol) of **1** and benzoyl isocyanate were allowed to react in 5 mL of dry chloroform with stirring under a nitrogen atmosphere for 5 h. The solvent was removed, and the ^1H NMR spectrum of the residue indicated the presence of **3b** and **5** in a ratio of 3:1. The residue was triturated with ether to give **3b** in 47% yield: mp 164–165 °C (ether–chloroform); ^1H NMR ($CDCl_3$) δ 1.96 (s, 6 H, 2 CH_3), 2.40 (s, 3 H, CH_3), 2.96 (s, 3 H, CH_3SO_2), 7.0–7.9 (2 m, 5 aromatic H), 7.24 (s, 4 aromatic H); mass spectrum, *m/e* (rel intensity) 399 (100, M^+·), 322 (70, M^+· – Ph), 320 (9, M^+· – CH_3SO_2), 294 (6, M^+· – PhCO), 252 (6, M^+· – PhCONCO), 173 (64), 133 (11, $CH_3C_6H_4NCO^+$·, 105 (88, $PhCO^+$). Anal. Calcd for $C_{20}H_{21}N_3O_4S$ (mol wt 399): C, 60.15; H, 5.26; N, 10.53. Found: C, 60.08; H, 5.35; N, 10.53.

In another experiment, **1** (0.002 mol) was treated with 10 equiv of benzoyl isocyanate in 5 mL of dry chloroform under a nitrogen atmosphere for 20 min. After removal of the solvent and the excess of benzoyl isocyanate, the residue was subjected to column chromatography on silica gel with *n*-hexane–ether as the eluent. This furnished benzamide (560 mg, mp 122–123 °C) and **6** in 71% yield: mp 191–192 °C; ^1H NMR ($CDCl_3$) δ 1.95 (s, 6 H, 2 CH_3), 2.40 (s, 3 H, CH_3), 3.0 (s, 3 H, CH_3SO_2), 7.1–7.4 (m, 4 aromatic H); mass spectrum, *m/e* (rel intensity) 296 (55, M^+·), 252 (3, M^+· – CO_2), 173 (100), 133 (13, $CH_3C_6H_4NCO^+$·), 131 (12, $CH_3C_6H_4NCN^+$). Anal. Calcd for $C_{13}H_{16}N_2O_4S$ (mol wt 296): C, 52.70; H, 5.41; N, 9.46. Found: C, 52.77; H, 5.41; N, 9.57.

Compound **6** was also obtained when **3a** (0.74 g) was stirred in 20 mL of ethanol containing 20 mL of HCl (6 N) at room temmperature for 1 day. The white precipitate was filtered off, washed with water, and dried to give 0.45 g of **6**. The combined filtrate and washings were evaporated, and the solid residue was treated with water (20 mL) and then filtered, dried, and purified by column chromatography on silica gel with benzene–hexane as the eluent. This furnished another 30 mg of **6** (total yield 82%). From the filtrate, aniline hydrochloride (0.25 g, 96%) was isolated and identified by comparison with an authentic sample.

Reaction of 1 with Phenylsulfonyl Isocyanate. Equimolar amounts (0.002 mol) of **1** and phenylsulfonyl isocyanate were stirred in 8 mL of chloroform under nitrogen atmosphere at room temperature for 10 min. The solvent was removed in vacuo, and the reaction residue was crystallized from hexane–chloroform to give **3c**. The filtrate was evaporated, and the residue was subjected to column chromatography on silica gel with ether–hexane as the eluent, yielding **4c**.

Compound **3c** was obtained in 44% yield: mp 204–205 °C (carbon tetrachloride–chloroform); ^1H NMR ($CDCl_3$) δ 1.94 (s, 6 H, 2 CH_3), 2.38 (s, 3 H, CH_3), 2.94 (s, 3 H, CH_3SO_2), 7.0–8.0 (3 m, 9 aromatic H); mass spectrum, *m/e* (rel intensity) 435 (31, M^+·), 356 (8 M^+· – CH_3SO_2), 294 (10, M^+· – $PhSO_2$), 252 (11, M^+· – $PhSO_2NCO$), 173 (100). Anal. Calcd for $C_{19}H_{21}N_3O_5S_2$ (mol wt 435): C, 52.41; H, 4.83; N, 9.66. Found: C, 52.26; H, 4.82; N, 9.76.

Table II. Spectral Characterization of the Reaction Products[a]

compd	IR (KBr), cm^{-1}	^{13}C NMR[b] C_2	C_4	C_5
3a	1705 (s, C_2=N), 1590-1615 (s br, C_4=N)	147.1	167.9	87.5
3b	1745 (m, C=O), 1670 (m, C_2=N), 1620 (s, br, C_4=N)	150.2	167.7	89
3c	1680 (m, C_2=N), 1600-1620 (s br, C_4=N)	155.2	166.9	91.1
4a	1760 (s, C=O), 1590 with shoulder at 1620 (s br, C=N)	152.3	167.7	65
4c	1775 (s, C=O), 1620 (s br, C=N)	150.7	165.1	69.1
6	1800 (s, C=O), 1630 (s br, C=N)	153	168.5	86.4
7a	1735 (s, C=O), 1640 (s, C=N)	177.7	167.7	69.5
7b	1630 (s br, C=N)	178	166.5	73
8a	2190 (m, CN), 1660 (m, C=C), 1610 (s, C=N)	158.1	167.5	87.9
8b	1580-1620 (br, C=N)	146.2	168.2	85.6

[a] The atoms comprising the five-membered ring are all numbered as shown in structure 3. [b] All the spectra (δ values in parts per million from $(CH_3)_4Si$) were recorded in $CDCl_3$ except those of **4a** and **7b** (Me_2SO-d_6). Other resonances are (in ppm) CH_3Ar at 21, $(CH_3)_2$ at 23-25, CH_3SO_2 at 43-44, tolyl carbon absorptions at 127-128 (C_o), 129-132 (C_i), 130 (C_m) and 138-140 (C_p), C=O of **3b** at 175.2, C=O of **7a** at 150.8, $(CH_3)_3C$-C-CN of **8a** at 29.7, 32.6, 78, and 115.7, and Ph_2C=C of **8b** at 99.8.

Compound **4c** was obtained in 18% yield: mp 229–230 °C (ether–chloroform); ^{1}H NMR ($CDCl_3$) δ 2.20 (s, 6 H, 2 CH_3), 2.36 (s, 3 H, CH_3), 2.94 (s, 3 H, CH_3SO_2), 7.0–8.2 (3 m, 9 aromatic H); mass spectrum, *m/e* (rel intensity) 435 (62, $M^{+\cdot}$), 371 (11, $M^{+\cdot} - SO_2$), 356 (7, $M^{+\cdot} - CH_3SO_2$), 294 (4, $M^{+\cdot} - PhSO_2$), 292 (100, $M^{+\cdot} - CH_3SO_2 - SO_2$), 173 (57), 133 (8.5, $CH_3C_6H_4NCO^{+\cdot}$). Anal. Calcd for $C_{19}H_{21}N_3O_5S_2$ (mol wt 435): C, 52.41; H, 4.83; N, 9.66. Found: C, 52.37; H, 4.85; N, 9.62.

In order to determine the product distribution under various conditions (Table I), we used the same procedure, and the reaction mixture was analyzed by ^{1}H NMR.

Reaction of 1 with Carbethoxy Isothiocyanate. A solution of **1** (0.002 mol) and a tenfold excess of carbethoxy isothiocyanate in 5 mL of dry chloroform was stirred at room temperature for 16 h. After removal of the solvent and the excess of isothiocyanate in vacuo, the residue was triturated with 20 mL of ether–hexane to give **7a** in 78% yield: mp 122–123 °C (ether–hexane); ^{1}H NMR ($CDCl_3$) δ 1.42 (t, 3 H, CH_3), 2.12 (s, 6 H, 2 CH_3), 2.42 (s, 3 H, CH_3), 2.92 (s, 3 H, CH_3SO_2), 4.44 (q, 2 H, CH_2), 7.04 and 7.28 (2 d, 4 aromatic H); mass spectrum, *m/e* (rel intensity) 383 (100, $M^{+\cdot}$), 310 (4, $M^{+\cdot} - EtCO_2$), 234 (2, $M^{+\cdot} - CH_3C_6H_4NCS$), 173 (5), 149 (5, $CH_3C_6H_4NCS^{+\cdot}$). Anal. Calcd for $C_{16}H_{21}N_3O_4S_2$ (mol wt 383): C, 50.13; H, 5.48; N, 10.97. Found: C, 50.02; H, 5.48; N, 10.95.

Reaction of 1 with Phenylsulfonyl Isothiocyanate. Equimolar amounts (0.002 mol) of **1** and phenylsulfonyl isothiocyanate were stirred in 5 mL of chloroform at room temperature for 1 day. The solvent was then removed under reduced pressure, and the white residue was crystallized from carbon tetrachloride–chloroform to give **7b** in 94% yield: mp 262–263 °C; ^{1}H NMR (Me_2SO-d_6, HMDS) δ 2.28 (s, 9 H, 3 CH_3), 2.88 (s, 3 H, CH_3SO_2), 7.0–8.2 (3 m, 9 aromatic H); mass spectrum, *m/e* (rel intensity) 451 (0.2, $M^{+\cdot}$), 387 (52, $M^{+\cdot} - SO_2$), 372 (6, $M^{+\cdot} - CH_3SO_2$), 310 (6, $M^{+\cdot} - PhSO_2$), 308 (100, $M^{+\cdot} - SO_2 - CH_3SO_2$), 173 (55), 149 (8, $CH_3C_6H_4NCS^{+\cdot}$), 131 (14, $CH_3C_6H_4NCN^{+}$). Anal. Calcd for $C_{19}H_{21}N_3O_4S_3$ (mol wt 451): C, 50.55; H, 4.66; N, 9.31. Found: C, 50.48; H, 4.59; N, 9.30.

Reaction of 1 with *tert*-Butylcyanoketene. *tert*-Butylcyanoketene was generated by thermolysis of 2,5-di-*tert*-butyl-3,6-diazidobenzoquinone (0.75 mmol) in 10 mL of dry benzene for 1 h.[8] After the mixture was cooled to room temperature, **1** (1.5 mmol) was added, and the solution was stirred at room temperature for 1 day. The ^{1}H NMR spectrum of the reaction mixture showed the presence of **8a** and **5** in a ratio of 3:1. Purification of the reaction residue by column chromatography on silica gel with ether–hexane as the eluent furnished pure **8a** in 70% yield: mp 215.5–216.5 °C (chloroform–ether); ^{1}H NMR ($CDCl_3$) δ 1.26 (s, 9 H, *t*-Bu), 1.98 (s, 6 H, 2 CH_3), 2.44 (s, 3 H, CH_3), 2.88 (s, 3 H, CH_3SO_2), 7.0–7.4 (2 d, 4 aromatic H); mass spectrum, *m/e* (rel intensity) 375 (37, $M^{+\cdot}$), 360 (100, $M^{+\cdot} - CH_3$), 252 (13, $M^{+\cdot}$ – *t*-Bu(CN)C=C=O), 173 (11), 107 (20, *t*-Bu(CN)C=$C^{+\cdot}$). Anal. Calcd for $C_{19}H_{25}N_3O_3S$ (mol wt 375): C, 60.80; H, 6.67; N, 11.20. Found: C, 60.69; H, 6.73; N, 11.20.

Reaction of 1 with Diphenylketene. A solution of **1** (0.002 mol) and a threefold excess of diphenylketene in 5 mL of dry chloroform was stirred at room temperature for 7 h. After removal of the solvent the residue was chromatographed on silica gel with ether–hexane as the eluent to give **8b** in 98% yield: mp 151–152 °C (ether–hexane); ^{1}H NMR ($CDCl_3$) δ 2.00 (s, 6 H, 2 CH_3), 2.18 (s, 3 H, CH_3), 2.84 (s, 3 H, CH_3SO_2), 6.6–7.4 (2 m, 14 aromatic H); mass spectrum, *m/e* (rel intensity) 446 (98, $M^{+\cdot}$), 252 (100, $M^{+\cdot} - Ph_2CCO$), 194 (14, $Ph_2CCO^{+\cdot}$), 173 (55), 166 (17, $Ph_2C^{+\cdot}$). Anal. Calcd for $C_{26}H_{26}N_2O_3S$ (mol wt 446): C, 69.96; H, 5.83; N, 6.28. Found: C, 70.01; H, 5.89; N, 6.20.

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Registry No. 1, 66255-50-3; **3a**, 62962-34-9; **3b**, 71436-55-0; **3c**, 71436-56-1; **4a**, 71436-57-2; **4c**, 71436-58-3; **5**, 62962-31-6; **6**, 62962-36-1; **7a**, 71436-59-4; **7b**, 71436-60-7; **8a**, 71436-61-8; **8b**, 71436-62-9; phenylsulfonyl isocyanate, 2845-62-7; phenyl isocyanate, 103-71-9; benzoyl isocyanate, 4461-33-0; benzamide, 55-21-0; carbethoxy isothiocyanate, 16182-04-0; phenylsulfonyl isothiocyanate, 1424-53-9; *tert*-butylcyanoketene, 29342-22-1; 2,5-di-*tert*-butyl-3,6-diazidobenzoquinone, 29342-21-0; diphenylketene, 525-06-4.

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Facile Entry into the Thiazolo[3,2-*a*]indol-3(2*H*)-one System via an Unusual Reaction with Thionyl Chloride[1a]

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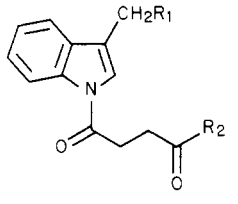
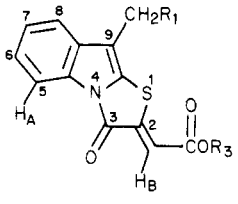
During the course of our synthetic investigations into the canthin-6-one series[2] we treated γ-oxo-3-[(methoxycarbonyl)methyl]-1*H*-indole-1-butanoic acid (**1a**) with oxalyl chloride to give the acid chloride **1b** which was used without isolation in a Friedel–Crafts intramolecular cyclization. However, similar reaction of **1a** with refluxing thionyl chloride followed by methanol treatment did not give the expected methyl ester **1c** but instead gave orange fibrous needles of **2a** in 20% yield. This represents only



1a, $R_1 = CO_2CH_3$; $R_2 = OH$
b, $R_1 = CO_2CH_3$; $R_2 = Cl$
c, $R_1 = CO_2CH_3$; $R_2 = OCH_3$
d, $R_1 = H$; $R_2 = OH$



2a, $R_1 = CO_2CH_3$; $R_3 = CH_3$
b, $R_1 = H$; $R_3 = CH_3$
c, $R_1 = H$; $R_3 = CH_2C(CH_3)_3$

the second documented entry into this class of tricyclic heterocycles and serves as a convenient synthetic alternative to the procedure of Ficken and Kendall[3] into this relatively inaccessible ring system. The corresponding reaction of γ-oxo-3-methyl-1*H*-indole-1-butanoic acid (**1d**) with thionyl chloride followed by quenchings with methanol or neopentyl alcohol led respectively to **2b** (62%) and **2c** (63%).

The unequivocal structural proof of **2** rests on its ^{1}H and ^{13}C NMR data along with comparison to **3** whose

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