Reactions of α-Ketosulfenes with *C,N*-Diarylnitrones[1]

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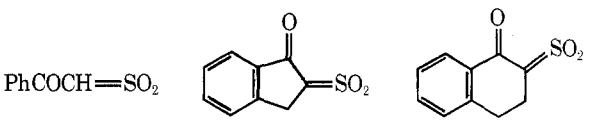
Benzoylsulfene **1** and two cyclic α-ketosulfenes **2** and **3**, generated in situ from the corresponding sulfonyl chlorides and triethylamine, react with nitrones [ArCH=N(O)Ph] to produce the corresponding rearranged adducts, seven-membered cyclic azasultones **5**, **11**, and **13**, accompanied by the formation of by-products, **6**, **12** and **14**, which arise from the rearranged adducts with the elimination of the benzaldehyde (ArCHO), respectively. An interconversion between **5** and **6** is described, and the stereochemistry of rearranged adduct **5** is also discussed.

In previous papers, it has been reported that benzoylsulfene **1**, generated in situ from benzoylmethanesulfonyl chloride and triethylamine, reacts with the C=N bonds of anils,[2] carbodiimides,[3] and ketene imines[4] to give the [2 + 2] and/or [4 + 2] cycloadducts, while simple sulfenes ($RCH{=}SO_2$) do not react with the C=N bond.[5] In addition, new cyclic α-ketosulfenes **2** and **3**, generated in situ from 2-chlorosulfonylindanone and -1-tetralone, and triethylamine, respectively, added to the C=N bonds of anils to yield the corresponding cycloadducts.[6] These results indicate that the electron-attracting acyl group makes the α-ketosulfene more reactive than simple sulfenes, and the α-ketosulfenes behave as 1,4 and/or 1,2 dipoles.



1 **2** **3**

Recently, Truce and Allison[7] reported that benzoylsulfene **1** and also simple sulfenes reacted with azomethine imines to form a [3 + 2] cycloadduct. The reaction of simple sulfenes with *C,N*-diarylnitrones proceeds via 1,3 cycloaddition followed by rearrangement to yield seven-membered cyclic azasultones.[8] We now report the reactions of α-ketosulfenes **1–3** with *C,N*-diarylnitrones.

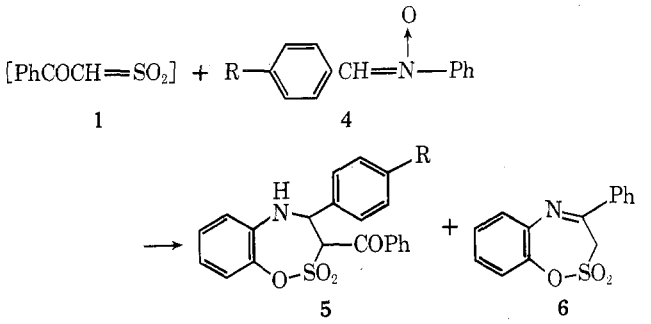
Results and Discussion

Reaction of Benzoylsulfene 1. When equimolar quantities of *C,N*-diphenylnitrone **4a** and triethylamine were stirred at room temperature in dry dioxane, and a solution of benzoylmethanesulfonyl chloride in dry dioxane was added dropwise in an atmosphere of nitrogen, there was an immediate precipitation of triethylammonium chloride. After the mixture was stirred at the same conditions for 2 h, two crystalline products, **5a** and **6**, were obtained from the solution. On the basis of its spectral data (Table I) and chemical conversion, 1:1 adduct **5a** was assigned to be 4,5-dihydro-3-benzoyl-4-phenyl-3*H*-1,2,5-benz[*f*]oxathiazepine 2,2-dioxide, whose ring system is the same as that of the product from simple sulfene and **4a**. The stereochemistry of **5a** will be described later.

On the other hand, the molecular formula of **6** agreed with that of the compound derived from **5a** with the elimination of benzaldehyde. The ir spectrum exhibited strong absorption bands at 1370 and 1165 cm^{-1} (SO_2), while no bands ascribable to NH and CO absorptions appeared. The NMR spectrum displayed a singlet (2 H) at δ 4.49 in addition to a complicated signal of aromatic protons (9 H). On the basis of the above facts, **6** was assigned to be 4-phenyl-3*H*-1,2,5-benz[*f*]oxathiazepine 2,2-dioxide. Further support for this assignment was obtained through chemical conversions. Reduction of **6** with sodium borohydride in ethanol afforded 4,5-dihydro-4-phenyl-3*H*-1,2,5-benz[*f*]oxathiazepine 2,2-dioxide (**7**),[8] which was identical with an authentic sample prepared from sulfene ($CH_2{=}SO_2$) and nitrone **4a**. On treatment with hydrochloric acid in boiling ethanol for a long while **6** was converted into *o*-aminophenol, whereas hydrolyisis of **6** under rather mild conditions afforded *o*-aminophenyl benzoylmethanesulfonate (**8**), which on reduction with sodium borohydride gave *o*-aminophenyl 2-hydroxy-2-phenylethanesulfonate (**9**). By dehydration **8** easily reverted to **6**.

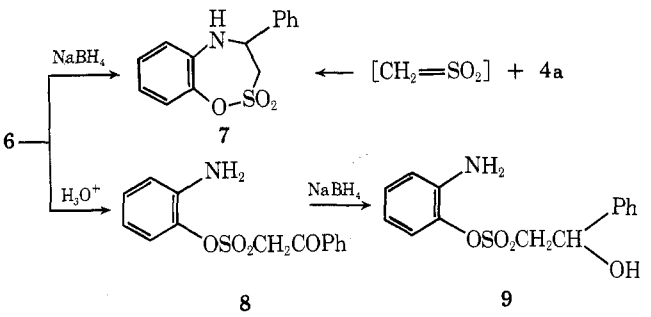
Similarly, the reaction of ketosulfene **1** with *C*-(*p*-anisyl)-*N*-phenyl- (**4b**), *C*-(*p*-chlorophenyl)-*N*-phenyl- (**4c**), and *C*-(*p*-nitrophenyl)-*N*-phenylnitrone (**4d**) gave the corresponding seven-membered cyclic azasultones, **5b–d**, and **6** (Scheme I). The yields of **5** and **6** and physical and spectral data of **5** are given in Table I.

Scheme I



1 **4** **5** **6**

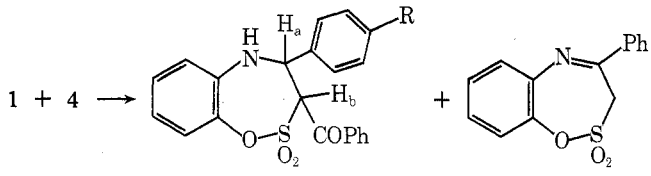
a, R = H; b, R = OMe; c, R = Cl; d, R = NO_2



7 **8** **9**

When treated with hydrochloric acid in methanol at room temperature, or chromatographed on acidic alumina, **5a** and **5c** were converted into **6** along with benzaldehyde and *p*-chlorobenzaldehyde, respectively. This fact indicates that the formation of **6** in the reaction of **1** with nitrones **4** was derived from the corresponding rearranged adduct **5**, and that on conversion of **5** into **6** the benzoyl group at the 3 position in **5** was not involved in the elimination of the benzaldehyde. On treatment with hydorochloric acid under similar conditions, the rearranged adduct **10** which was prepared from phenylsulfene and nitrone **4a** was unchanged. It appears that the electron-attracting benzoyl group at the 3 position in **5** enhances the reactivity of the oxathiazepine ring toward hydrolysis.

Table I



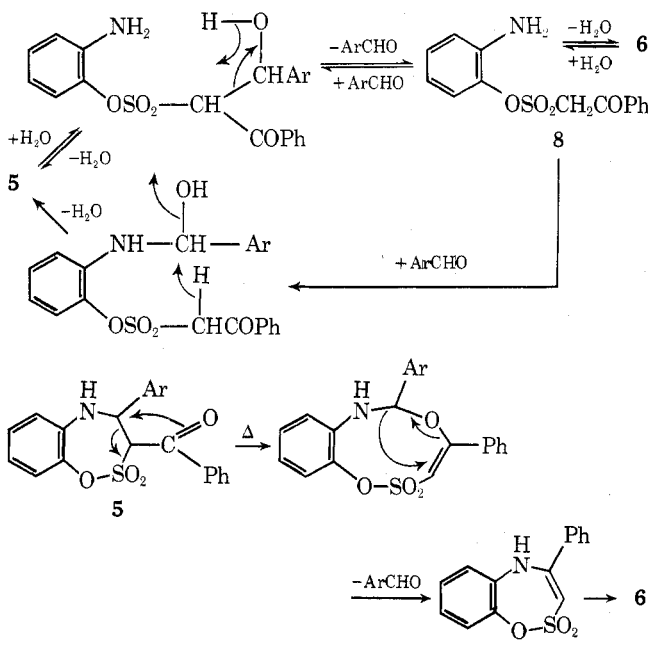
5 6

				Cyclic azasultones 5[a]					
		Yield, %					Found (calcd), %			M+
	R	5[c]	6	Mp, °C	Ir (KBr), cm⁻¹	NMR ($CDCl_3$), δ (J, Hz)	C	H	N	m/e
a	H	28	8[d]	155–156	3380 (NH), 1680 (CO), 1370, 1155 (SO_2)	3.7 (1 H, br, NH, exchanged with D_2O), 5.27 (1 H, d, H_a, J = 9.8), 5.81 (1 H, d, H_b, J = 9.8), 6.8–7.8 (14 H, m, aromatic protons)	66.64 (66.48)	4.24 (4.52)	3.71 (3.69)	379
b	OMe	10	5	154–155.5	3340 (NH), 1690 (CO), 1370, 1165 (SO_2)	3.69 (3 H, s, OCH_3), 3.8 (1 H, br, NH, exchanged with D_2O), 5.21 (1 H, d, H_a, J = 10), 5.79 (1 H, d, H_b, J = 10), 6.7–7.9 (13 H, m, aromatic protons)	64.71 (64.54)	4.67 (4.68)	3.52 (3.42)	409
c	Cl	36	6	178–180	3400 (NH), 1675 (CO), 1370, 1155 (SO_2)	3.8 (1 H, br, NH, exchanged with D_2O), 5.26 (1 H, d, H_a, J = 9.8), 5.79 (1 H, d, H_b, J = 9.8), 6.5–7.9 (13 H, m, aromatic protons)	60.94 (60.90)	3.68 (3.87)	3.04 (3.05)	415 413
d	NO_2	35	6	200–202 dec	3400 (NH), 1670 (CO), 1370, 1160 (SO_2)	5.36 (1 H, d, H_a, J = 10), 6.3 (1 H, br, NH, exchanged with D_2O), 6.75 (1 H, d, H_b, J = 10), 6.8–8.3 (13 H, m, aromatic protons)[b]	59.60 (59.43)	3.74 (3.80)	6.48 (6.60)	424

[a] 5a, 5b, and 5c, pale yellow needles; 5d, yellow needles. [b] Measured in Me_2SO-d_6. [c] Registry no. are, respectively, 59043-88-8, 59043-89-9, 59043-90-2, 59043-91-3. [d] Registry no., 16261-68-0.

As mentioned above, sulfonate 8 was easily converted into 6 by dehydration. The conversion of 5 into 6 might be interpreted as an initial formation of 8 and the benzaldehyde, followed by dehydration of 8 into 6. Thus it was expected that the reaction of 8 with the benzaldehyde would result in the formation of the corresponding rearranged adduct 5. In fact 8 reacted with *p*-chlorobenzaldehyde in ethanol to give 5c. Interconversion between 5 and 6 is illustrated in Scheme II.

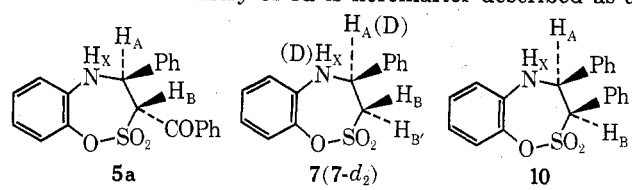
Scheme II



Further, thermolysis of 5a or 5c under reduced pressure afforded 6 and the benzaldehyde. Since the thermolysis was performed under anhydrous conditions, water was not involved in the formation of 6 from 5. The exact pathway is not clear, but we tentatively propose a potential pathway as depicted in Scheme II. Ring expansion of the oxathiazepine ring to the nine-membered cyclic 1,5,2,7-dioxathiazonine ring, followed by elimination of the benzaldehyde, gives 5*H*-1,2,5-oxathiazepine. Subsequent hydrogen shift affords the final product 6.

Although the reaction of methyl-, phenyl-, and bromosulfenes with nitrones 4 which resulted in the formation of seven-membered cyclic azasultones has been reported,[8] no stereochemical aspects are known. The NMR spectra of all 5, as well as azasultone 10, showed a typical ABX pattern for the protons of the oxathiazepine ring. However, the values of vicinal coupling constants J_{AB} in azasultones 5 and 10 are ca. 10 (see Table I) and 3.1 Hz, respectively.

The stereochemistry of 5a is hereinafter described as a

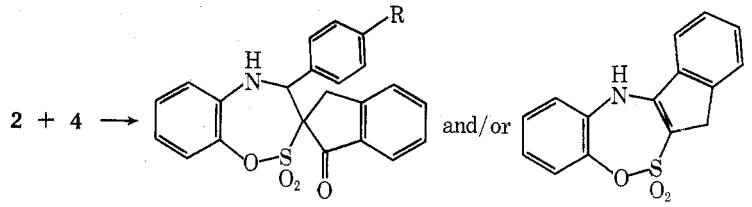


5a 7(7-d_2) 10

representative example. The measurement of NMR spectra in dioxane indicated that the values of J_{AB} in both 5a and 10 were not changed in the range of 35–90 °C. Thus it seems reasonable to conclude that 5a is the trans azasultone, while 10 is cis. The validity of these trans and cis assignments is also supported by inspection of the NMR spectra of azasultones 7 and 7-d_2 which was prepared by reduction of 6 with sodium borohydride-d_4; the values of coupling constants J_{AB}, $J_{AB'}$, and $J_{BB'}$ in 7 were found to be 10.5, 2.7, and 14.5 Hz, respectively.

It is known that the reaction of sulfenes with diarylnitrones proceeds via 1,3 cycloaddition, followed by rearrangement through a four-membered cyclic transition state to yield an azasultone.[8] Thus the stereochemistry of the azasultone seems to be determined by the stereochemical course of initial 1,3 cycloaddition. Although a concerted $[_\pi 4_s + _\pi 2_s]$ process could

Table II



11 12

	R	Yield, % 11[c]	12	Mp, °C	Ir (KBr), cm^{-1}	NMR ($CDCl_3$), δ (J, Hz)	Found (calcd), % C	H	N	M$^+$ m/e
		Cyclic azasultones 11[a]								
a	H	28	4[d]	178–179.5	3370 (NH), 1730 (CO), 1380, 1170 (SO_2)	3.94 (1 H, br, NH, exchanged with D_2O), 4.14 (2 H, pseudo s, CH_2), 5.47 (1 H, s, >CH), 6.6–7.6 (13 H, m, aromatic protons)	67.45 (67.51)	4.39 (4.38)	3.54 (3.58)	391
b	OMe	0	30							
c	Cl	31	5	167.5–169	3360 (NH), 1715 (CO), 1370, 1160 (SO_2)	3.87 (1 H, br, NH, exchanged with D_2O), 4.07 (2 H, pseudo s, CH_2), 5.4 (1 H, s, >CH), 6.7–7.7 (12 H, m, aromatic protons)	62.20 (62.04)	3.90 (3.79)	3.38 (3.29)	427 425
d	NO_2	52	3	181.5–183	3350 (NH), 1720 (CO) 1370, 1170 (SO_2)	3.9, 4.34 (each 1 H, d, CH_2, J = 20), 5.42 (1 H, s, >CH), 6.25 (1 H, br, NH, exchanged with D_2O), 6.9–8.2 (12 H, m, aromatic protons)[b]	60.75 (60.55)	3.71 (3.70)	6.42 (6.42)	436

[a] 11a and 11c, colorless prisms; 11d, yellow prisms. [b] Measured in Me_2SO-d_6. [c] Registry no. are, respectively, 59043-92-4, 59043-93-5, 59043-94-6, 59043-95-7. [d] Registry no., 59043-96-8.

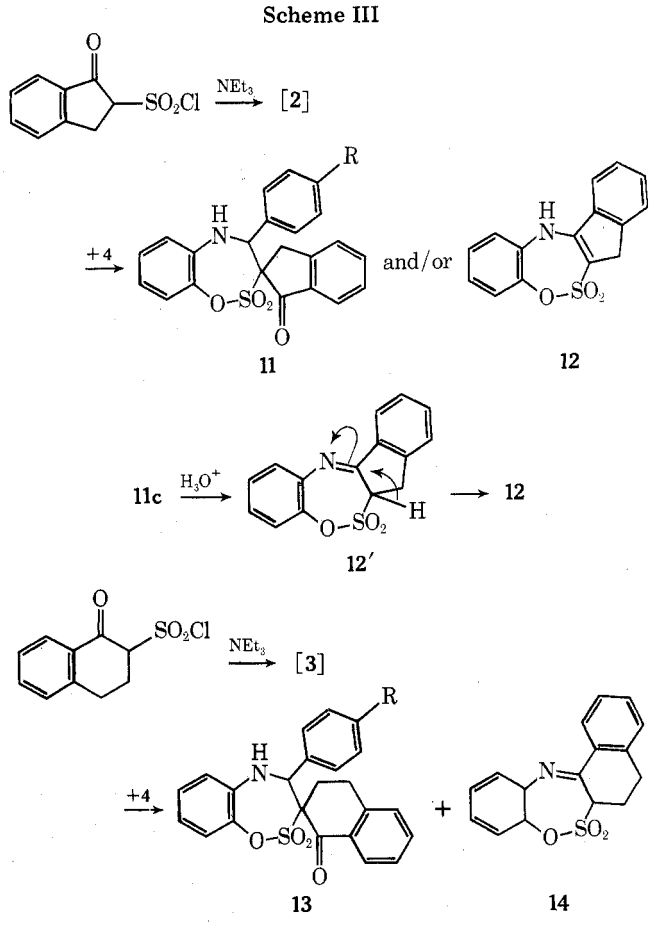
conceivably account for cis preference in the geometry of **10**, the formation of trans azasultone **5a** would be explained by a stepwise process. However, an alternative explanation for the formation of trans azasultone **5a** should not be overlooked. Truce and Rach[9] demonstrated the postisomerization of cis cycloadducts obtained from the reaction of benzoyl- and cyanosulfenes with enamines. Several attempts to isolate cis azasultones from the reaction mixtures were unsuccessful. However, since the acidity of the hydrogen atom at the 3 position in the initial cis azasultone is enhanced by the electron-attracting benzoyl group, a base should be capable of catalyzing epimerization to thermodynamically stable trans arrangement via carbanion formation at the 3 position. During the early stages of the reaction triethylamine is in excess, and the postepimerization of initial cis azasultone could be caused by the amine.

Whether the hydrogen atom H_B in **5a** is exchanged with deuterium oxide or not was determined by NMR analysis. When a dioxane solution of **5a** was treated with deuterium oxide in the presence of excess triethylamine (5.6 molar ratio to **5a**) at room temperature for 1 and 2 h, the exchange percentages of the hydrogen atom H_B were found to be about 30 and 50%, respectively. In addition, when a solution of **5a** in Me_2SO-d_6 was treated with deuterium oxide at room temperature, the complete exchange occurred in a period of from 3 to 5 h even if the amine was absent.

Reaction of Cyclic α-Ketosulfenes. Next our attention was directed toward the reaction of cyclic α-ketosulfenes **2** and **3** with diarylnitrones **4**. The reaction of 2-chlorosulfonylindanone with *C,N*-diphenylnitrone **4a** in the presence of triethylamine in tetrahydrofuran afforded a rearranged 1:1 adduct, 4,5-dihydro-2,2-dioxo-4-phenyl-3*H*-1,2,5-benz[*f*]-oxathiazepine-3-spiro-2′-indanone (**11a**) and 12*H*-indeno-[2,3-*c*]benz[*f*]-1,2,5-oxathiazepine 6,6-dioxide (**12**), mp 236–237 °C dec. Similarly, ketosulfene **2** reacted with nitrones **4c** and **4d** to yield rearranged 1:1 adducts **11c** and **11d**, together with small amounts of **12**. In the reaction with nitrone **4b**, however, **2** gave only **12**. Attempts to obtain **11b** were not successful. The yields of **11** and **12** and physical and spectral data of **11** are given in Table II.

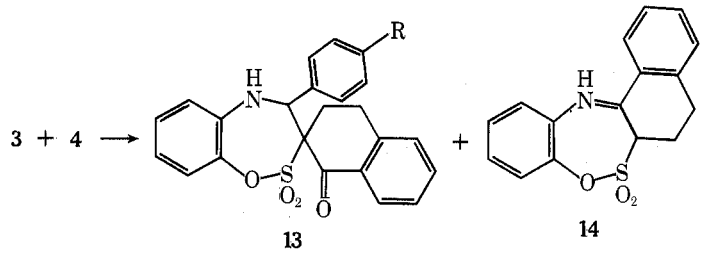
Hydrolysis of **11c** under mild conditions gave **12** and *p*-chlorobenzaldehyde. The structure of **12** was confirmed by the following evidence. The molecular formula of **12** agreed with that of the compound derived from the rearranged cyclic azasultone **11** with the elimination of the benzaldehyde. The

Scheme III



a, R = H; b, R = OMe; c, R = Cl; d, R = NO_2

Table III



13 14

		Yield, %		Cyclic azasultones 13[a]						
							Found (calcd), %			M+
	R	13[d]	14	Mp, °C	Ir (KBr), cm^{-1}	NMR ($CDCl_3$), δ (*J*, Hz)	C	H	N	*m/e*
a	H	23	6[e]	178.5–179.5	3400 (NH), 1680, 1670 (CO), 1365, 1150 (SO_2)	2.1–3.7 (4 H, m, CH_2CH_2), 4.1 (1 H, br, NH, exchanged with D_2O), 5.97 (1 H, s, >CH), 6.6–8.2 (13 H, m, aromatic protons)	68.41 (68.14)	4.73 (4.72)	3.22 (3.46)	405
b	OMe	13.5	5	146–147	3360 (NH), 1655 (CO), 1365, 1155 (SO_2)	2.1–3.9 (4 H, m, CH_2CH_2), 3.72 (3 H, s, OCH_3), 4.0 (1 H, br, NH, exchanged with D_2O), 5.91 (1 H, s, >CH), 6.5–8.2 (12 H, m, aromatic protons)	66.07 (66.20)	4.84 (4.86)	3.25 (3.20)	435
c	Cl	30	5	167.5–169	3360 (NH), 1655 (CO), 1365, 1155 (SO_2)	1.8–3.6 (4 H, m, CH_2CH_2), 3.9 (1 H, br, NH, exchanged with D_2O), 5.95 (1 H, s, >CH), 6.6–8.2 (12 H, m, aromatic protons)	62.84 (62.82)	4.15 (4.01)	3.15 (3.19)	441 439
d	NO_2	26	5	154.5–156	3380 (NH), 1670 (CO), 1350, 1150 (SO_2)	2.8–3.3 (4 H, m, CH_2CH_2), 5.98 (1 H, br, >CH),[b] 6.4 (1 H, br, NH, exchanged with D_2O), 6.5–8.4 (12 H, m, aromatic protons)[c]	61.37 (61.33)	4.05 (4.03)	6.19 (6.22)	450

[a] **13a** and **13c**, colorless prisms; **13b**, yellow needles; **13d**, pale yellow prisms. [b] Changed to a singlet when treated with D_2O. [c] Measured in Me_2SO-d_6. [d] Registry no. are, respectively, 59043-97-9, 59043-98-0, 59043-99-1, 59044-00-7. [e] Registry no., 59044-01-8.

ir and NMR spectra showed the presence of an NH group. Conversion of **11** into **12** by hydrolysis can be understood by a similar pathway to that of hydrolysis of **5** to yield **12′**, followed by hydrogen shift (Scheme III).

Similarly, cyclic ketosulfene **3**, generated in situ from 2-chlorosulfonyl-1-tetralone and triethylamine, reacted with nitrones **4** to yield the corresponding cyclic azasultones, 4,5-dihydro-2,2-dioxo-4-aryl-3*H*-1,2,5-benz[*f*]oxathiazepine-3-spiro-2′-(1′-tetralones) (**13**), and 5,6-dihydro-7*H*-naphtho[2,1-*c*]benz[*f*]-1,2,5-oxathiazepine 7,7-dioxide (**14**), mp 195–196 °C. The results and physical and spectral data of **13** are given in Table III.

The molecular formula of **14** agreed with that of the compound derived from the rearranged cyclic azasultone **13** with the elimination of the benzaldehyde, and the ir spectrum did not show NH and CO absorption bands. The NMR spectrum of **14** displayed a double doublet (1 H, J = 6.3 and 3.8 Hz) at δ 4.22, besides methylene (4 H) and aromatic protons (8 H). The above facts support the assigned structure. However, in deuteriochloroform **14** (colorless needles) was partially converted into an isomer **14′**, mp 194–195 °C, yellow prisms. In addition, the interconversion between **14** and **14′** was observed in deuteriopyridine by NMR analysis. Thus **14′** can be deduced to be an epimer of **14**, but the stereochemistry of **14** and **14′** is not clear.

Experimental Section[10]

Materials. Benzoylmethanesulfonyl chloride, mp 88 °C (lit.[11] mp 87.5–88.2 °C), was prepared according to the method of Truce and Vriesen.[11] 2-Chlorosulfonylindanone, mp 95–98 °C, and 2-chlorosulfonyl-1-tetralone, mp 87–88.5 °C, were prepared from the sulfonation of 1-indanone and 1-tetralone with SO_3–dioxane complex, followed by reaction with PCl_5.[6]

General Procedure for the Reaction of Benzoylmethanesulfonyl Chloride and Diarylnitrones. The reaction was performed in a nitrogen atmosphere. To a vigorously stirred solution of nitrone **4** (5 mmol) and 0.7 ml (5 mmol) of triethylamine in 30 ml of dry dioxane, a solution of 1.09 g (5 mmol) of benzoylmethanesulfonyl chloride in 30 ml of dry dioxane was added, drop by drop, at room temperature over a period of 1 h. After the addition was complete, the reaction mixture was stirred at the same temperature for 2 h. At this time, the reaction mixture was filtered, resulting in 90–95% yields of triethylammonium chloride. The filtrate was evaporated in vacuo, yielding colored oils which were induced to crystallize by adding 20 ml of methanol. Filtration gave rearranged cyclic azasultone **5**. The mother liquor was chromatographed on silica gel using a mixture of benzene and chloroform (3:1) as the eluent to give 4-phenyl-3*H*-1,2,5-benz[*f*]oxathiazepine 2,2-dioxide (**6**), mp 166 °C, as yellow needles.

The yields of products and physical and analytical data of **5** are given in Table I.

6: ir (KBr) 1575 (C=N), 1370, 1165 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 4.49 (2 H, s, CH_2), 7.4–8.1 (9 H, m, aromatic protons); mass *m/e* 273 (M^+), 209 ($M^+ - SO_2$), 196 ($M^+ - Ph$), 104, 103 ($PhCN^+$, base peak), 77.

Anal. Calcd for $C_{14}H_{11}NO_3S$: C, 61.54; H, 4.06; N, 5.13. Found: C, 61.63; H, 4.06; N, 5.07.

Hydrolysis of Azasultone 5a. A suspension of 0.3 g of **5a** in 40 ml of methanol was stirred with 3 ml of concentrated hydrochloric acid at room temperature for 2 h. After the reaction mixture was concentrated in vacuo, a small amount of water was added to the residue, and then the mixture was extracted with benzene. The benzene extract was dried over sodium sulfate, and then evaporated in vacuo. The residue was triturated with 10 ml of methanol to afford 113 mg (53%) of yellow crystals, whose ir spectrum was compatible with that of **6**. A solution of 2,4-dinitrophenylhydrazine in ethanol was added to the

mother liquor, yielding 48 mg (21%) of benzaldehyde 2,4-dinitrophenylhydrazone.

Similarly, hydrolysis of 0.15 g of **5c** with 2 ml of concentrated hydrochloric acid in 20 ml of methanol for 6 h afforded 36 mg (36%) of **6** and 16 mg (14%) of *p*-chlorobenzaldehyde 2,4-dinitrophenylhydrazone.

Thermolysis of Azasultone 5c. In a 20-ml flask equipped with a condenser 0.85 g of **5c** was placed. The flask was heated at 170–180 °C (bath temperature) under reduced pressure (2 mmHg) for 2 h; during the thermolysis 90 mg (31%) of *p*-chlorobenzaldehyde adhered to the glass surface. The dark brown residue was triturated with 10 ml of methanol to give yellow crystals, and filtration afforded 0.51 g (91%) of **6.** The methanol filtrate was treated with an ethanol solution of 2,4-dinitrophenylhydrazine to give 0.14 g (21%) of *p*-chlorobenzaldehyde 2,4-dinitrophenylhydrazone.

Similarly, 2.0 g of **5a** was pyrolyzed at 165–170 °C (bath temperature) under reduced pressure (3 mmHg) for 20 min; 0.73 g (51%) of **6** and 0.4 g (27%) of benzaldehyde 2,4-dinitrophenylhydrazone were obtained.

Reduction of 6 with Sodium Borohydride. A. A mixture of 0.15 g of **6** and 0.2 g of sodium borohydride in 40 ml of ethanol was stirred at room temperature for 16 h. The reaction mixture was concentrated in vacuo, and then 50 ml of water was added to the residue, giving 64 mg (42.5%) of 4,5-dihydro-4-phenyl-3*H*-1,2,5-benz[*f*]oxathiazepine 2,2-dioxide (**7**), mp 158–159 °C (lit.[8] mp 160 °C), which was identical with an authentic sample prepared according to the method of Truce et al.[8] NMR ($CDCl_3$) δ 3.3–4.1 (3 H, complicated signal, CH_2 and NH), 4.75 (1 H, dd, J = 2.7 and 10.5 Hz), 6.6–7.6 (10 H, m, aromatic protons).

B. A mixture of 50 mg of **6** and 80 mg of sodium borohydride-d_4 in 15 ml of ethanol was stirred at room temperature for 18 h. To the mixture was added 30 ml of water, giving 27 mg (53%) of colorless crystals. Recrystallization from benzene afforded **7**-*d*, mp 160 °C, as colorless prisms: NMR ($CDCl_3$ + D_2O) δ 3.43, 3.92 (each 1 H, d, J = 14.5 Hz), 6.7–7.6 (10 H, m, aromatic protons).

On the basis of the NMR spectra of **7** and **7**-d_2, the assignments of protons were as follows: δ 3.43 ($H_{B'}$, dd), 3.92 (H_B, dd), 4.75 (H_A, dd), J_{AB} = 10.5, $J_{AB'}$ = 2.7, $J_{BB'}$ = 14.5 Hz.

Hydrolysis of 6. A. A suspension of 0.1 g of **6** in 20 ml of methanol was refluxed with 4 ml of concentrated hydrochloric acid for 4 h. The reaction mixture was evaporated in vacuo to leave yellow crystals. The crystals were treated with aqueous sodium hydrogen carbonate, and then extracted with benzene. The benzene extract was dried over calcium chloride, and evaporated in vacuo at room temperature to give 60 mg (56%) of yellow crystals. Recrystallization from a benzene–petroleum ether (bp 60–80 °C) mixture afforded *o*-aminophenyl benzoylmethanesulfonate (**8**), mp 114 °C, as pale yellow needles: ir (KBr) 3460, 3360 (NH), 1680 (CO), 1355, 1160 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 4.3 (2 H, br, NH_2, exchanged with D_2O), 4.89 (2 H, s, CH_2, exchanged with D_2O), 6.5–8.2 (9 H, m, aromatic protons); mass *m/e* 291 (M^+), 273, 209, 180, 108 (M^+ − $PhCOCH_2SO_2$, base peak), 105, 103, 91, 77.

Anal. Calcd for $C_{14}H_{13}NO_4S$: C, 57.73; H, 4.50; N, 4.82. Found: C, 57.63; H, 4.28; N, 4.78.

B. A suspension of 0.1 g of **6** in 30 ml of ethanol was refluxed with 3 ml of concentrated hydrochloric acid for 18 h. The reaction mixture was evaporated in vacuo, and the residue was treated with aqueous sodium hydrogen carbonate and then extracted with diethyl ether. The ether extract was evaporated in vacuo to give yellow crystals, which on recrystallization from a benzene–petroleum ether (bp 60–80 °C) mixture afforded 22 mg (55%) of *o*-aminophenol, mp 173–175 °C.

Reduction of Benzoylmethanesulfonate 8. A solution of 0.62 g of **8** in 40 ml of methanol was stirred with 0.2 g of sodium borohydride at room temperature for 2 h. The reaction mixture was evaporated in vacuo to leave a residue, which was triturated with petroleum ether to give 0.18 g (78%) of *o*-aminophenol. The filtrate was chromatographed on silica gel using a benzene–chloroform mixture as the eluent, giving small amounts of oil (M^+ *m/e* 293). A solution of the oil in diethyl ether was treated with hydrogen chloride to give the hydrochloride of *o*-aminophenyl 2-hydroxy-2-phenylethanesulfonate (**9**): mp 196–198 °C dec; ir (KBr) 3360 (OH), 3000, 2880, 2620 (NH_3^+), 1370, 1190, 1150 cm^{-1} (SO_2).

Dehydration of 8. A solution of 0.1 g of **8** in 12 ml of acetic acid was stirred with 0.5 ml of acetic anhydride at room temperature for 10 h. The mixture was poured into water and filtration gave yellow crystals, which on recrystallization from benzene afforded 80 mg (86%) of **6.**

Reaction of 8 with *p*-Chlorobenzaldehyde. A suspension of 275 mg (0.945 mmol) of **8** in 30 ml of ethanol was stirred with 135 mg (0.96 mmol) of *p*-chlorobenzaldehyde at room temperature for 14.5 h; the reaction mixture changed to a clear solution. The solution was cooled in an ice bath to give yellow crystals. Recrystallization from a benzene–petroleum ether (bp 60–80 °C) mixture gave 215 mg (55%) of cyclic azasultone **5c** as pale yellow needles.

4,5-Dihydro-3,4-diphenyl-3*H*-1,2,5-benz[*f*]oxathiazepine 2,2-Dioxide (10). To a stirred solution of 1.03 g (5.25 mmol) of nitrone **4a** and 0.53 g (5 mmol) of triethylamine in 25 ml of dry dioxane, a solution of 1.0 g (5.25 mmol) of benzylsulfonyl chloride in 25 ml of dry dioxane was added, drop by drop, at room temperature over a period of 1 h. After the addition was complete, the reaction mixture was stirred at the same temperature for 30 h. Filtration gave 0.67 g (93%) of triethylammonium chloride, and the filtrate was evaporated in vacuo to leave brown oil, which was triturated with 10 ml of ethanol to give crystals. Recrystallization from ethanol afforded 1.13 g (61%) of **10,** mp 220–221 °C, as colorless plates: ir (KBr) 3340 (NH), 1360, 1150 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 3.7 (1 H, br, NH, exchanged with D_2O), 4.42, 5.36 (each 1 H, d, CH, J = 3.1 Hz), 6.6–7.7 (14 H, m, aromatic protons); mass *m/e* 391 (M^+), 287 (M^+ − SO_2), 198, 197 (base peak), 196, 120, 104, 93, 91, 77.

Anal. Calcd for $C_{20}H_{17}NO_3S$: C, 68.37; H, 4.88; N, 3.99. Found: C, 68.24; H, 4.90; N, 4.11.

General Procedure for the Reaction of 2-Chlorosulfonylindanone with Diarylnitrones. The reaction was performed in a nitrogen atmosphere. To a stirred solution of nitrone **4** (5 mmol) and 0.7 ml (5 mmol) of triethylamine in 30 ml of dry tetrahydrofuran, a solution of 1.15 g (5 mmol) of 2-chlorosulfonylindanone in 30 ml of dry tetrahydrofuran was slowly added, drop by drop, under cooling in an ice bath over a period of 1 h. After the addition was complete, the reaction mixture was stirred at room temperature for 5 h. The mixture was filtered, resulting in ca. 80% yield of triethylammonium chloride. The filtrate was evaporated in vacuo, and the residue was chromatographed on silica gel using a benzene–chloroform mixture as the eluent, giving rearranged cyclic azasultone **11** and/or 12*H*-indeno[2,3-*c*]benz[*f*]-1,2,5-oxathiazepine 6,6-dioxide (**12**), mp 236–237 °C dec, as pale yellow needles.

The yields of products and physical and analytical data of **11** are given in Table II.

12: ir (KBr) 3370 (NH), 1340, 1170 cm^{-1} (SO_2); NMR (Me_2SO-d_6) δ 3.92 (2 H, s, CH_2), 6.9–8.4 (8 H, m, aromatic protons), 9.77 (1 H, br, NH); mass *m/e* 285 (M^+), 221 (M^+ − SO_2), 220 (base peak), 193, 192, 191.

Anal. Calcd for $C_{15}H_{11}NO_3S$: C, 63.13; H, 3.89; N, 4.91. Found: C, 62.93; H, 3.82; N, 4.75.

Hydrolysis of Cyclic Azasultone 11c. A suspension of 150 mg of **11c** in 20 ml of methanol was stirred with 1 ml of concentrated hydrochloric acid at room temperature for 20 h. The reaction mixture was concentrated in vacuo to one-third of its original volume, and then cooled to give yellow crystals. Recrystallization from acetic acid afforded 38 mg (38%) of **12.** The filtrate was treated with a solution of 2,4-dinitrophenylhydrazine in ethanol, giving 22 mg (20%) of *p*-chlorobenzaldehyde 2,4-dinitrophenylhydrazone.

General Procedure for the Reaction of 2-Chlorosulfonyl-1-tetralone with Diarylnitrones According to the above general procedure for 2-chlorosulfonylindanone, the reaction of 1.22 g (5 mmol) of 2-chlorosulfonyl-1-tetralone with nitrone **4** (5 mmol) in the presence of 0.7 ml (5 mmol) of triethylamine in dry tetrahydrofuran was carried out under a nitrogen atmosphere for 5 h. The products were chromatographed on silica gel using a benzene–chloroform mixture as the eluent, giving cyclic azasultone **13** and 5,6-dihydro-7*H*-naphtho[2,1-*c*]benz[*f*]-1,2,5-oxathiazepine 7,7-dioxide (**14**), mp 195–196 °C, as colorless needles.

The yields of the products and physical and analytical data of **13** are given in Table III.

14: ir (KBr) 1595 (C=N), 1370, 1170 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 2.3–4.0 (4 H, m, CH_2CH_2), 4.22 (1 H, dd, CH, J = 6.3 and 3.8 Hz), 7.2–8.5 (8 H, m, aromatic protons); mass *m/e* 299 (M^+), 235 (M^+ − SO_2, base peak), 234, 221, 220, 218, 206, 191, 179, 178, 127, 120, 117, 116, 115, 64.

Anal. Calcd for $C_{16}H_{13}NO_3S$: C, 64.21; H, 4.38; N, 4.68. Found: C, 64.01; H, 4.38; N, 4.65.

In chloroform solution the compound **14** was partially converted into an epimer **14′**, mp 194–195 °C, as yellow prisms: ir (KBr) 1600 (C=N), 1370, 1180 cm^{-1} (SO_2); mass *m/e* 299 (M^+), 235 (M^+ − SO_2, base peak), 234, 221, 220, 218, 207, 206, 129, 128, 127, 120, 118, 117, 116, 104, 103, 102, 77.

Anal. Calcd for $C_{16}H_{13}NO_3S$: C, 64.21; H, 4.38; N, 4.68. Found: C, 64.30; H, 4.39; N, 4.69.

Registry No.—**1,** 32116-82-8; **2,** 59069-51-1; **3,** 59069-52-2; **4a,** 1137-96-8; **4b,** 3585-93-1; **4c,** 5909-74-0; **4d,** 3585-90-8; **7,** 5172-50-9; **8,** 59044-02-9; **9,** 59044-03-0; **10,** 59044-04-1; 2-chlorosulfonylindanone,

51834-39-0; 2-chlorosulfonyl-1-tetralone, 51834-37-8; o-aminophenol, 95-55-6; benzylsulfonyl chloride, 1939-99-7.

References and Notes

(1) Studies of α-Ketosulfenes. 8. Part 7 of this series: O. Tsuge and M. Noguchi, *Chem. Lett.*, 113 (1974).
(2) O. Tsuge and S. Iwanami, *Bull. Chem. Soc. Jpn.*, **43**, 3543 (1970).
(3) O. Tsuge and S. Iwanami, *Nippon Kagaku Zasshi*, **92**, 448 (1971).
(4) O. Tsuge and S. Iwanami, *Org. Prep. Proced. Int.*, **3**, 283 (1971).
(5) H. Ulrich, "Cycloaddition Reactions of Heterocumulenes", Academic Press, New York, N.Y., 1967, p 286. However, it has been recently reported that phenylsulfene reacted with benzylidenemethylamines to give 1,2-thiazetidine 1,1-dioxides: T. Hiraoka and T. Kobayashi, *Bull. Chem. Soc. Jpn.*, **48**, 480 (1975).
(6) O. Tsuge and M. Noguchi, *Chem. Lett.*, 113 (1974).
(7) W. E. Truce and J. R. Allison, *J. Org. Chem.*, **40**, 2260 (1975).
(8) W. E. Truce, J. W. Fieldhouse, D. J. Vrencur, J. R. Norell, R. W. Campbell, and D. G. Brady, *J. Org. Chem.*, **34**, 3097 (1969).
(9) W. E. Truce and J. F. Rach, *J. Org. Chem.*, **39**, 1109 (1974).
(10) All melting points are uncorrected. NMR spectra were recorded on a Hitachi R-20 NMR spectrometer with tetramethylsilane as internal standard. Mass spectra were obtained on a Hitachi RMS-4 mass spectrometer, using a direct inlet and an ionization energy of 70 eV.
(11) W. E. Truce and C. W. Vriesen, *J. Am. Chem. Soc.*, **75**, 2526 (1953).

Concurrent Nitration and Oxygenation of o-Xylene and Hemimellitene with Aroyl Nitrates

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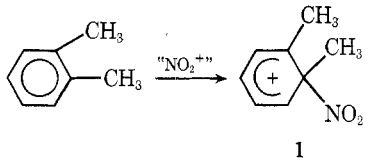
Upon reaction with a series of aroyl nitrates, o-xylene underwent not only nitration but also aroyloxylation to yield dimethylphenyl benzoates comprised primarily of the 3,4 isomer. Nitration ratios were little affected by the nature of the aroyl nitrate substituent suggesting a common nitrating species. The aryl ester product patterns were quite different than those resulting from reaction of o-xylene with aroyl peroxide and either cupric chloride or nitric acid where aroyloxy radical substitution is known to occur. The analogous product situation was observed for hemimellitene. This and other evidence was indicative of a mechanism involving nitronium ion attack at an ipso ring position followed by benzoate trapping of the resultant carbonium ion. The addition product so formed then rearomatized to an aryl benzoate by elimination of nitrous acid analogous to the addition–elimination scheme proposed earlier for acetyl nitrate.

The observation by Fischer and co-workers that o-xylene undergoes not only nitration but also acetoxylation when treated with nitric acid–acetic anhydride[1] has spurred a considerable amount of further investigation into this dual substitution process.[2] The acetate esters have been accounted for by an electrophilic addition–elimination process involving initial nitronium ion attack at the 1 position (ipso attack) to give a phenonium ion (1). This species, which is reluctant to lose either a nitro or methyl group, instead adds a nucleophilic acetate to form a cis–trans pair of 1,4-cyclohexadienes (2 and 3, eq 1), which have been isolated upon careful quenching of the reaction.[3] Upon workup 2 and 3 rearomatize to produce primarily 3,4-dimethylphenyl acetate (eq 2).[3,4]



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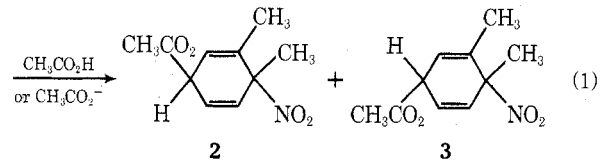
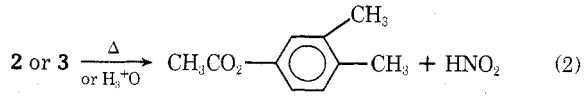


(1)

2 3



(2)

Analogous cyclohexadiene intermediates and the subsequent aryl acetates have been observed in the reactions of acetyl nitrate with hemimellitene,[5] p-xylene,[5] pseudocumene,[2a] toluene,[6] and others.[7] The demonstration of the occurrence of ipso attack has led to critical reinvestigations of previously reported substitution patterns in the nitration of polyalkylbenzenes.[4,8]

Previous work in this laboratory had demonstrated that dimethylphenyl benzoates are produced in yields ranging from 3 to 14% upon treating o-xylene with benzoyl nitrate under a variety of conditions.[9] However, radical breakdown of benzoyl nitrate to the benzoyloxy and ultimately phenyl radicals (eq 3) had been reported[10] and the former radical is known to substitute on aromatic rings to form aryl benzoates (eq 4) in the presence of suitable oxidants.[11]

$$C_6H_5CO_2NO_2 \longrightarrow NO_2 + C_6H_5CO_2\cdot \longrightarrow C_6H_5\cdot + CO_2 \quad (3)$$

$$C_6H_5CO_2\cdot + ArH \xrightarrow[-H^+]{\text{oxidant}} C_6H_5CO_2Ar \quad (4)$$

Since either a scheme involving benzoyloxy radicals (eq 3 and 4) or an electrophilic ipso nitration process as proposed for acetyl nitrate (eq 1 and 2) seemed to be feasible, we set out to determine which mechanism of benzoate ester formation was applicable in the interaction of a series of para-substituted benzoyl nitrates with o-xylene. The reaction of benzoyl nitrate with hemimellitene was also examined.

Results and Discussion

All of the para-substituted benzoyl nitrates were prepared and used in situ both to ensure a known concentration of the nitrate ester and to reduce the possibility of their hydrolysis. They were prepared from the reaction of silver nitrate and the appropriate para-substituted benzoyl chloride in accordance with the following stoichiometry (eq 5).

$$XC_6H_4COCl + AgNO_3 \xrightarrow[25\ ^\circ C]{CH_3CN} XC_6H_4CO_2NO_2 + AgCl \quad (5)$$

The organic products from the reaction of benzoyl nitrate with o-xylene at room temperature are listed in Table I. Nitration and benzoyloxylation products (nitro-o-xylenes and