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The Cycloaddition Reactions of Benzoylsulfene with Anils

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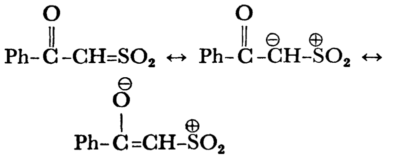
The reactions of benzoylmethanesulfonyl chloride with various anils (Ar–CH=N–R) in the presence of triethylamine have been studied. It has been found that the corresponding (4+2) and/or (2+2) cycloadducts of benzoylsulfene and the anil were obtained, depending on the nature of the substituents, R, in the anils. The reaction of the chloride with benzylidene-*n*-propylamine in the absence of triethylamine gave only the (2+2) cycloadduct, while the (4+2) cycloadduct was exclusively obtained in the presence of triethylamine. The chloride reacted with dibenzylidenethylenediamine in the presence of triethylamine to give the corresponding bis(4+2) cycloadduct.

Recently, Fusco and his co-workers[1] found that the treatment of benzoylmethanesulfonyl chloride (I) with triethylamine (NEt_3) afforded the 1,2,4-oxadithin tetroxide. Later, it has been shown in a review[2] that, in the presence of NEt_3, I reacted with isobutenyl ether to give the 1,4-oxathin dioxide, while it reacted with 2-methyl-1-pyrrolidino-1-propene to give the thiethane dioxide (Scheme 1). These reactions can be formulated as below, assuming a benzoylsulfene ($PhCOCH=SO_2$) intermediate.

The above observations indicate that, in the cycloaddition reaction with unsaturated substances benzoylsulfene behaves as a 1,2- and/or 1,4-dipole, depending on the nature of the unsaturated substances.

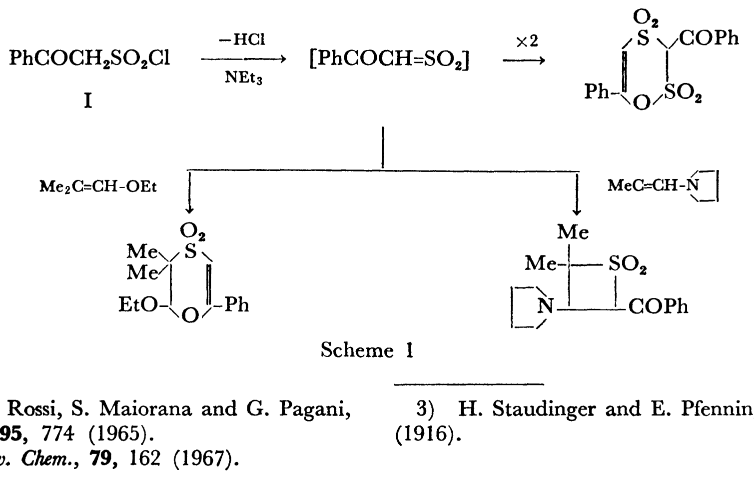


$$Ph\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH=SO_2 \leftrightarrow Ph\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}\overset{\ominus}{C}H\text{-}\overset{\oplus}{S}O_2 \leftrightarrow Ph\text{-}\overset{\overset{\ominus}{O}}{\overset{|}{C}}=CH\text{-}\overset{\oplus}{S}O_2$$

The reactions of sulfenes ($RCH=SO_2$), generated *in situ* from alkanesulfonyl chlorides and NEt_3, with electron-rich olefins, such as enamines or ketene acetals, have been extensively investigated. However, the study of the cycloaddition of sulfene to the C=N bond has not been extended beyond of Staudinger and Pfenninger,[3] who reported that the reaction of diphenylsulfene, generated from diphenyldiazomethane and sulfur dioxide, with benzylidenaniline gave the four-membered cyclic compound.

New heterocyclic compounds may be formed by the cycloaddition of benzoylsulfene to the C=N bond, because the electron-attracting benzoyl group will make benzoylsulfene more reactive than sulfenes ($RCH=SO_2$).

In the present paper we wish to report on the formation of (2+2) and (4+2) cycloadducts *via* the reactions of benzoylsulfene with various benzylidenamines. In this cycloaddition reaction, for the first time, a sulfene, generated from sulfonyl chloride and a base, reacted with a C=N bond



Scheme 1

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[1] R. Fusco, S. Rossi, S. Maiorana and G. Pagani, *Gazz. Chim. Ital.*, **95**, 774 (1965).

[2] Opitz, *Angew. Chem.*, **79**, 162 (1967).

[3] H. Staudinger and E. Pfenninger, *Ber.*, **49**, 1941 (1916).

to give a cycloadduct.

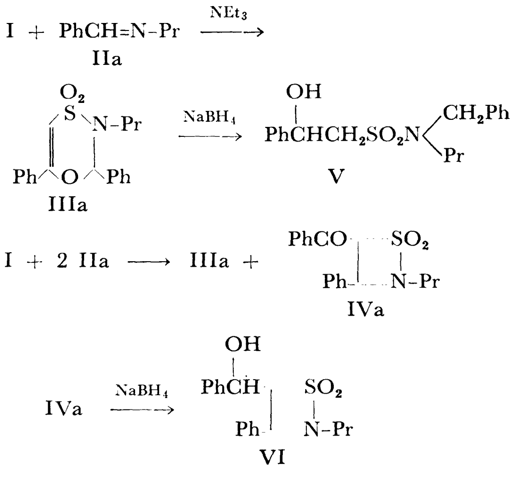
Results and Discussion

The reaction of I with equimolar benzylidene-*n*-propylamine (IIa) and NEt_3 in dioxane at room temperature for 15 hr gave a crystalline compound IIIa, mp 123°C (decomp.), in a 57% yield, besides triethylammonium chloride in a quantitative yield. The results of elemental analysis and the molecular weight (M^+ m/e 329) of IIIa were consistent with those of the expected 1 : 1 adduct of benzoylsulfene and IIa.

On the other hand, I reacted with two molar quantities of IIa in the absence of NEt_3 at room temperature for 3 hr, thus affording IIIa and its isomeric 1 : 1 adduct, IVa, mp 148°C, in 57 and 13% yields respectively, together with benzylidene-*n*-propylamine hydrochloride.

The infrared spectrum of IIIa showed characteristic bands at 1575 ($\nu_{C=C}$), 1150, and 1335 cm^{-1} (ν_{SO_2}), while the NMR spectrum in deuteriochloroform ($CDCl_3$) exhibited singlets at τ 3.56 (1H, methine proton) and 3.00 (1H, olefinic proton), besides signals of *n*-propyl and aromatic protons. These observations indicate that IIIa is the (4+2) cycloadduct of benzoylsulfene, and IIa, 2,6-diphenyl-3-*n*-propyl-1,4,3-oxathiazine 4,4-dioxide. The mass spectrum was also in harmony with the proposed structure: peaks appeared at m/e 329 (M^+), 300 (M^+-29[Et]), 288 (M^+-41[CH_2=CH-CH_2]), and 265 (M^+-64[SO_2]) in the spectrum. Furthermore, IIIa was reduced with sodium borohydride in methanol at 30°C for 20 min to *N*-benzyl-*N*-*n*-propyl-2-hydroxy-2-phenylethane-1-sulfonamide (V) in a 73% yield (Scheme 2). The structure for IIIa is also supported by this fact.

On the other hand, IVa was confirmed to be the (2+2) cycloadduct, 4-benzoyl-3-phenyl-2-*n*-propyl-1,2-thiazetidine 1,1-dioxide, by the spectral studies as well as by the chemical transformation. The infrared spectrum showed strong bands at 1690 ($\nu_{C=O}$), 1165, and 1315 cm^{-1} (ν_{SO_2}), and the NMR spectrum in deuterionitromethane (CD_3NO_2) revealed two pairs of doublets, at τ 5.07 and 4.42 (each 1H, J=6 Hz), besides the peaks of the *n*-propyl and aromatic protons. Although the molecular ion peak was not observed, the peak of m/e 265 (M^+-64[SO_2]) appeared in the mass spectrum of IVa.



Scheme 2

When IVa was treated with sodium borohydride under the same conditions as were used for IIIa, a ring cleavage did not take place, but IVa was reduced to the 4-(α-hydroxybenzyl)thiazetidine VI in an 84% yield (Scheme 2).

In order to make it clear whether or not IVa is virtually formed in the reaction under the influence of NEt_3, the amounts of products and reactants in the reaction system were estimated by NMR spectroscopy. As is shown in Table 1, in the presence of NEt_3 only IIIa was formed.

The effect of the amount of IIa on the yields of IIIa and IVa was investigated in the absence of NEt_3; the results are also shown in Table 1. It is shown that IIIa and IVa were formed even when I was caused to react with an equimolar amount of IIa. As the adduct IIIa proved rather unstable and decomposed during purification, however, the yield isolated was lower than that estimated by NMR spectroscopy.

The interconversion of IIIa and IVa was not observed under these reaction conditions. The reason why benzoylsulfene behaves differently depending on the nature of the dehydrochlorinating agents is not clear.

In the reaction of I with benzylidenaniline (IIb) under the influence of NEt_3 for 1 hr, the (4+2) cycloadduct, 2,3,6-triphenyl-1,4,3-oxathiazine 4,4-dioxide (IIIb), was exclusively formed, but it

TABLE 1. REACTION OF I WITH IIa IN THE PRESENCE OR ABSENCE OF NEt_3 IN DIOXANE AT ROOM TEMPERATURE FOR 3 HR

I	IIa	NEt_3	Products (%)		Unreacted reactants (%)	
(molar ratio)			IIIa	IVa	I	IIa
1	1	1	82	0	0	9
1	1	0	36	6	40	0
1	2	0	82	13	0	0
1	3	0	84	14	0	33

could not be isolated in a pure form because of its instability. On the other hand, a similar reaction for 24 hr gave the (2+2) cycloadduct, 4-benzoyl-2,3-diphenyl-1,2-thiazetidine 1,1-dioxide (IVb), in a 22% yield, but here the formation of IIIb was not observed.

The structures for IIIb and IVb were confirmed by the spectral studies as well as by the chemical transformations. The infrared spectrum of a relatively pure IIIb showed bands at 1570 ($\nu_{C=C}$), 1150, and 1335 cm^{-1} (ν_{SO_2}), while the NMR spectrum in dioxane revealed a singlet at τ 3.05 (1H, methine proton) and a vinyl proton signal in a region of aromatic protons. When IIIb was refluxed in methanol for several minutes, a ring cleavage took place to give the sulfonamide VII in a 64% yield (Scheme 3).

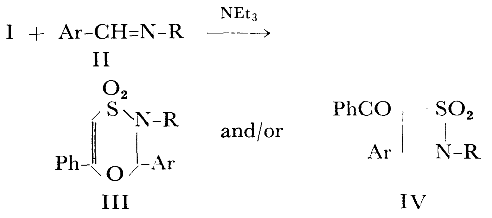
On the other hand, the infrared spectrum of IVb showed strong bands at 1685 ($\nu_{C=O}$), 1151, and 1324 cm^{-1} (ν_{SO_2}), while the NMR spectrum in CD_3NO_2 revealed two pairs of doublets, at τ 3.85 and 4.19 (each 1H, J=6 Hz). The structure for IVb was also supported by the mass spectrum: peaks of *m/e* 363 (M^+) and 299 (M^+-64[SO_2]) appeared in the spectrum.

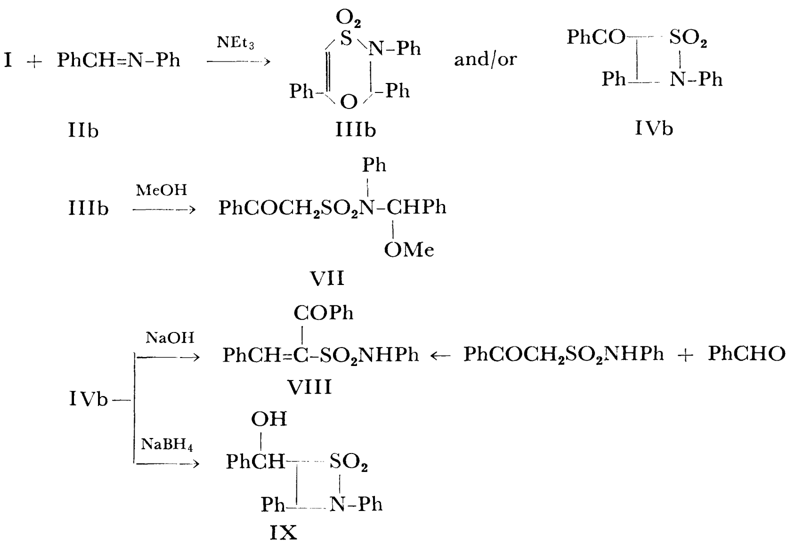
The treatment of IVb with methanolic sodium hydroxide gave β-benzoyl-β-phenylsulfamoylstyrene (VIII), which was identical with the authentic sample prepared from benzoyl methanesulfonanilide and benzaldehyde. Furthermore, IVb was reduced with sodium borohydride to give the 4-(α-hydroxybenzyl)thiazetidine compound, IX (Scheme 3).

The effect of the reaction time on the yields of IIIb and IVb was investigated by the quantitative estimation of IIIb and IVb, using NMR spectroscopy. The results are shown in Table 2.

The data in Table 2 indicate that, when the reaction is carried out under the same conditions, the quantity of unreacted IIb is essentially independent of the reaction time, and that the quantity of IIIb decreases, and that of IVb increases with an increase in the reaction time.

The reactions of I with various benzylidenamines (II) were investigated in the presence of NEt_3; the results are summarized in Table 3.





Scheme 3

Table 2. Reaction of I with IIb in the presence of NEt_3 in dioxane at room temperature

I	IIb	NEt_3	Time (hr)	Products (%)		Unreacted IIb (%)
(molar ratio)				IIIb	IVb	
1	1	1	1	38	0	59
1	1	1	12	ca. 14	20	56
1	1	1	24	0	30	56
2	1	2	1	66	0	34
2	1	2	24	0	44	30

Table 3. Reaction of I with II in the presence of NEt_3 in dioxane at room temperature

II	Ar	R	Reaction time (hr)	Products (%)	
				III	IV
a	Ph	*n*-Pr	15	57	0
b	Ph	Ph	25	0	22
c	Ph	*p*-MeC_6H_4	100	0	24
d	Ph	*p*-$MeOC_6H_4$	50	0	10*
e	*p*-$NO_2C_6H_4$	Ph	15	0	0*
f	Ph	$PhCH_2$	100	32	5
g	Ph	Cyclohexyl	15	27	0

* Unreacted IId and IIe were recovered in 25 and 10% yields respectively.

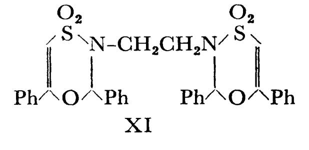
The structures of the products were established by the spectral studies as well as by the elemental analyses (Table 4).

When the substituent, R, in II is aliphatic, such as *n*-propyl and cyclohexyl, only the (4+2) cycloadduct III was obtained in the presence of NEt_3. On the other hand, the reaction with II when R is aromatic, such as phenyl and *p*-tolyl, for a long time gave the (2+2) cycloadduct IV exclusively; this can presumably be attributed to the fact that the 3-aryl-1,4,3-oxathiazine compound is unstable compared with the corresponding 3-alkyl compound. On the other hand, benzylidenebenzylamine (IIf) exhibited an intermediate character to give both the (4+2) and (2+2) cycloadducts. A similar reaction of I with diphenylmethylenaniline for 25 hr did not give the expected cycloadduct of benzoylsulfene and the anil, but rather the dimer of benzoylsulfene, 3-benzoyl-6-phenyl-1,2,4-oxadithin tetroxide,[1] in a 55% yield.

It may be assumed that benzoylsulfene reacts with a compound with two C=N bonds, thus leading to the formation of a mono-, bis(2+2), bis(4+2), or mixed biscycloadduct.

When dibenzylidenethylenediamine (X) was caused to react with two molar quantities of I in the presence of NEt_3, the expected 2 : 1 adduct of benzoylsulfene and X was obtained in a 52% yield, together with a small amount of an unidentified substance. Although the NMR spectrum of XI could not be measured because of its poor solubility, the infrared spectrum was very similar to that of IIIa and did not show any carbonyl bands except the band ascribed to the C=C bond at 1572 cm^{-1}. This fact indicates that XI is a bis-oxathiazine.

$$\text{I} + PhCH{=}N\text{-}CH_2CH_2\text{-}N{=}CHPh \xrightarrow{NEt_3}$$



XI

The mass spectrum was in harmony with the proposed structure: the molecular ion peak was not observed, but peaks of *m/e* 418 (M^+-182[$PhCOCH{=}SO_2$]), 354 (418^+-64[SO_2]), and 250 (354^+-104[PhCNH]) appeared in the spectrum.

Experimental

All the melting and boiling points are uncorrected. The infrared spectra were measured in KBr disks, and the NMR spectra were determined at 60 MHz with a Hitachi R-20 NMR spectrometer, using TMS as an internal reference. The mass spectra were obtained on a Hitachi RMS-4 mass spectrometer, using a direct inlet and an ionization energy of 70 eV.

Materials. Benzoylmethanesulfonyl chloride (I), mp 88°C (lit,[4] mp 87.5—88.2°C), was prepared according to the method of Truce and Vriesen.[4] Benzylidenamines (II) and dibenzylidenethylenediamine (X) were prepared from the corresponding aldehyde and amine. Benzylidene-*n*-propylamine (IIa), bp 101—102°C/15 mmHg (lit,[5] bp 208—210°C/744 mmHg); -aniline (IIb) mp 54°C (lit,[6] mp 53.5°C); -*p*-toluidine (IIc), bp 176—177°C/10 mmHg (lit,[7] bp 178°C/10 mmHg); -*p*-anisidine (IId), mp 73—74°C (lit,[8] mp 72°C); -benzylamine (IIf), bp 200—201°C/18 mmHg (lit,[9] bp 205°C/20 mmHg); -cyclohexylamine (IIg), bp 154°C/18 mmHg (lit,[10] bp 136°C/16 mmHg); *p*-nitrobenzylidenaniline (IIe), mp 93°C (lit,[11] mp 93°C); dibenzylidenethylenediamine (X), mp 54°C (lit,[12] mp 53—54°C). Diphenylmethylenaniline was prepared from benzophenone dichloride and aniline; mp 116—117°C (lit,[13] mp 116°C).

General Procedure for the Reaction of I with II in the Presence of NEt_3. To a vigorously stirred solution of 0.01 mol of II and 1.0 g (0.01 mol) of NEt_3 in 10 m*l* of dioxane, a solution of 2.2 g (0.01 mol) of I in 40 m*l* of dioxane was added, drop by drop, at room

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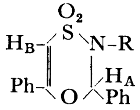
4) W. E. Truce and C. W. Vriesen, *J. Amer. Chem. Soc.*, **75**, 2525 (1953).
5) H. Zaunschirm, *Ann. Chem.*, **245**, 282 (1888).
6) G. Pyl, *Ber.*, **60**, 288 (1927).
7) A. Pictet, *ibid.*, **19**, 1063 (1886).
8) F. G. Pope and R. Fleming, *J. Chem. Soc.*, **93**, 1915 (1908).
9) A. T. Mason and G. R. Winder, *ibid.*, **65**, 191 (1894).
10) A. Skita and C. Wulff, *Ber.*, **59**, 2691 (1926).
11) O. Fischer, *ibid.*, **14**, 2525 (1881).
12) A. T. Mason, *ibid.*, **20**, 270 (1887).
13) M. Pauly, *Ann. Chem.*, **187**, 198 (1877).

Table 4. Physical properties and elemental analyses of III and IV

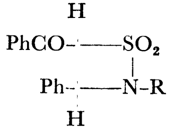
3-Substituted 2,6-diphenyl-1,4,3-oxathiazine 4,4-dioxide



III

III	R	Mp (°C)	Appearance	IR (cm⁻¹) $\nu_{C=C}$	IR (cm⁻¹) ν_{SO_2}		NMR $H_A(\tau)$	NMR $H_B(\tau)$	NMR Solvent	Analysis (%) Found (Calcd) C	H	N	M⁺ (m/e)
a	n-Pr	123 (decomp.)	colorless prisms	1575	1335	1150	3.26 3.56	2.93 3.00	dioxane $CDCl_3$	65.86 (65.64)	5.67 (5.82)	4.07 (4.25)	329
f	$PhCH_2$	158 (decomp.)	colorless prisms	1573	1340	1160	3.24	*	$CDCl_3$	70.30 (70.02)	5.23 (5.07)	3.53 (3.71)	377
g	Cyclohexyl	153 (decomp.)	colorless prisms	1570	1318	1145	3.47	2.90	$CDCl_3$	68.34 (68.28)	6.30 (6.28)	3.79 (3.79)	369

2-Substituted 4-benzoyl-3-phenyl-1,2-thiazetidine 1,1-dioxide



IV

IV	R	Mp (°C)	Appearance	IR (cm⁻¹) $\nu_{C=O}$	IR (cm⁻¹) ν_{SO_2}		NMR $>CH(\tau)$		NMR J(Hz)	NMR Solvent	Analysis (%) Found (Calcd) C	H	N	M⁺ (m/e)
b	Ph	164—165	colorless needles	1685	1324	1151	3.85 3.88	4.19 4.23	6 6	CD_3NO_2 dioxane	69.63 (69.41)	4.56 (4.72)	3.82 (3.82)	363
c	p-MeC_6H_4	163	colorless prisms	1690	1339	1160	3.85	4.23	6	CD_3NO_2	70.25 (70.02)	4.95 (5.07)	3.69 (3.71)	377
d	p-$MeOC_6H_4$	138	colorless needles	1698	1337	1165	3.90	4.32	6	dioxane	67.20 (67.17)	4.78 (4.87)	3.52 (3.71)	393
f	$PhCH_2$	143	colorless needles	1680	1335	1165	4.05 4.43	4.98 5.03	7 6	dioxane $CDCl_3$	69.70 (70.02)	5.17 (5.07)	3.75 (3.71)	**

* The H_B signal appeared in a region of phenyl protons.

** A molecular ion peak was not observed but [M^+-SO_2] peak appeared at m/e 313 in the mass spectrum.

temperature over a period of 30 min. After the reaction mixture had been stirred at the same temperature for a long while, triethylammonium chloride was removed by filtration. The filtrate was evaporated *in vacuo* to leave an oily substance, which was then crystallized on trituration with methanol or petroleum benzine (bp 45—60°C).

The reaction conditions, yields, physical properties, and elemental analyses of adducts are summarized in Tables 3 and 4.

Reaction of I with IIa in the Absence of NEt_3. To a solution of 3.0 g (0.02 mol) of IIa in 10 m*l* of dioxane, was added, drop by drop, a solution of 2.2 g (0.01 mol) of I in 40 m*l* of dioxane. After the mixture had then been stirred at room temperature for 2.5 hr, the precipitated benzylidene-*n*-propylamine hydrochloride was removed by filtration. The filtrate was evaporated *in vacuo* to give 3.4 g of a viscous oily substance, found to be a mixture of IIIa (85%) and IVa (15%) by NMR spectroscopy. Although IIIa could not be isolated in a pure state because of its instability, the recrystallization of the mixture from methanol gave IVa, mp 148°C, as colorless prisms.

Found: C, 65.85; H, 6.22; N, 4.24%. Calcd for $C_{18}H_{19}O_3NS$: C, 65.64; H, 5.82; N, 4.25%.

Reduction of IIIa with Sodium Borohydride. A mixture of 0.45 g of IIIa and 0.5 g of sodium borohydride in 20 m*l* of methanol was stirred at 30°C for 20 min. To the mixture was added 50 m*l* of water, and then the mixture was extracted with benzene. The benzene-extract was washed twice with water, dried over sodium sulfate, and then evaporated *in vacuo* to give a colorless, viscous oil (0.3 g, 73%), which crystallized on standing for a long while. Recrystallization from petroleum benzine (bp 45—60°C) gave *N*-benzyl-*N*-*n*-propyl-2-hydroxy-2-phenylethane-1-sulfonamide (V), mp 48—49°C, as colorless needles.

Found: C, 64.68; H, 6.82; N, 4.25%. Calcd for $C_{18}H_{23}O_3NS$: C, 64.85; H, 6.95; N, 4.20%.

IR: 3520 (ν_{OH}), 1325, 1137 cm^{-1} (ν_{SO_2}). NMR ($CDCl_3$): τ 2.67 (10H, singlet, aromatic protons), 4.76 (1H, quartet, $\geqslant$CH), 5.63 (2H, singlet, $-C\underline{H}_2Ph$), 6.17 (1H, broad signal, OH, exchanged with D_2O), 6.5—7.1 (4H, multiplet, $-CH_2SO_2-$ and $-\overset{|}{N}-C\underline{H}_2-$), 8.3—8.9 (2H, quintet, $-CH_2-C\underline{H}_2-Me$), 9.13 (3H, triplet, CH_3).

The mass spectrum gave a parent peak at *m/e* 333 (M^+) and other peaks at *m/e* 316 (M^+–OH), 304 (M^+–Et), and 242 ($M^+-C_7H_7$).

Reduction of IVa with Sodium Borohydride. A mixture of 0.12 g of IVa and 0.15 g of sodium borohydride in 10 m*l* of methanol was stirred at 30°C for 20 min. Fifty m*l* of water were then added to the mixture, affording 0.1 g (84%) of colorless crystals. Recrystallization from a mixture of benzene-petroleum benzine gave 4-(α-hydroxybenzyl)-3-phenyl-2-*n*-propylthiazetidine 1,1-dioxide (VI), mp 103—104°C, as colorless needles.

Found: C, 65.46; H, 6.47; N, 4.22%. Calcd for $C_{18}H_{21}O_3NS$: C, 65.24; H, 6.39; N, 4.23%.

IR: 3480 (ν_{OH}), 1300, 1147 cm^{-1} (ν_{SO_2}). NMR ($CDCl_3$): τ 2.6—3.1 (10H, multiplet, aromatic protons), 4.76 (1H, doublet, $Ph\overset{|}{C}\underline{H}-N\langle$), 5.58 (1H, quartet, $\rangle CH-SO_2-$), 6.14 (1H, doublet, OH, exchanged with D_2O), 6.6—7.5 (3H, multiplet, $-CH_2-\overset{|}{N}-$ and $PhC\underline{H}$(OH)–), 8.2—8.8 (2H, quintet, $-CH_2-CH_2-Me$), 9.10 (3H, triplet, CH_3).

The mass spectrum showed a parent peak at *m/e* 331 (M^+) and other peaks at *m/e* 313 (M^+-H_2O), 301 ($M^+-C_2H_4$), and 267 (M^+-SO_2).

A similar reduction of IVb with sodium borohydride gave the corresponding 4-(α-hydroxybenzyl)thiazetidine IX, mp 195°C (decomp.), as colorless prisms (from acetonitrile). Yield, 83%.

Found: C, 68.76; H, 5.45: N, 3.58%. Calcd for $C_{21}H_{19}O_3NS$: C, 69.03; H, 5.24; N, 3.83%.

IR: 3550 (ν_{OH}), 1315, 1170 cm^{-1} (ν_{SO_2}). NMR (CD_3CN): τ 2.4—3.3 (15H, multiplet, aromatic protons), 4.65 (1H, quartet, $ph\overset{|}{C}H(OH)-$), 5.2—5.5 (2H, multiplet, $-\overset{|}{C}\underline{H}-SO_2-$ and $Ph\overset{|}{C}H-\overset{|}{N}-$), 5.86 (1H, doublet, OH, exchanged with D_2O).

Methanolysis of IIIb. A solution of 0.5 g of IIIb in 50 m*l* of methanol was refluxed for several minutes and then cooled to give the sulfonamide VII, mp 120—121°C, as colorless needles. Yield, 0.35 g (64%).

Found: C, 66.60; H, 5.28; N, 3.40%. Calcd for $C_{22}H_{21}O_4NS$: C, 66.82; H, 5.35; N, 3.54%.

IR: 1680 (ν_{CO}), 1250, 1150 cm^{-1} (ν_{SO_2}). NMR ($CDCl_3$): τ 1.9—3.0 (15H, multiplet, aromatic protons), 3.6 (1H, singlet, $\geqslant$CH), 5.25 (2H, double doublet, J=14 Hz, $-CH_2-$), 6.36 (3H, singlet, OCH_3).

The mass spectrum showed peaks at *m/e* 395 (M^+), 364 (M^+–OMe), 275 (364^+–PhC), 182 (275^+-PhNH_2), and 105 ($PhCO^+$).

β-Benznyl-β-phenylsulfamoylstyrene (VIII). *i*) After a solution of 0.4 g of IVb and 0.1 g of sodium hydroxide in aqueous methanol (methanol 20 m*l* and water 5 m*l*) had been refluxed for 20 min, the mixture was extracted with benzene. The benzene-extract was evaporated *in vacuo*, affording 52 mg (13%) of colorless crystals. Recrystallization from petroleum benzine (bp 45—60°C) gave VIII, mp 188—189°C, as colorless needles.

Found: C, 69.54; H, 4.68; N, 3.77%. Calcd for $C_{21}H_{17}O_3NS$: C, 69.41; H, 4.72; N, 3.86%.

IR: 3230 (ν_{NH}), 1635 (ν_{CO}), 1615 ($\nu_{C=C}$), 1340, 1150 cm^{-1} (ν_{SO_2}). The mass spectrum showed peaks at *m/e* 363 (M^+), 299 (M^+-SO_2), 271 (M^+–PhNH), and 105 ($PhCO^+$).

ii) A solution of 1.0 g of benzoylmethanesulfonanilide, 0.5 g of benzaldehyde, and 2 m of 1 N sodium hydroxide aqueous solution in 50 m*l* of ethanol was fluxed for 2 hr and then evaporated *in vacuo* to give an oily substance. A benzene solution of it was chromatographed over alumina, affording colorless crystals which were proved, by a study of their infrared spectrum, to be identical with VIII. Yield, 0.1 g (8%). The other products were not examined.

Spectroscopic Determination. After the reac-

TABLE 5. KEY SIGNALS FOR I, II AND III

Compound	Key signal
I	4.31 (singlet, $-CH_2-$)
IIa	1.82 (singlet, -CH=N-)
IIb	1.50 (singlet, -CH=N-)
IIIa	3.26 (singlet, $\geqslant$CH)
IIIb	3.05 (singlet, $\geqslant$CH)
IVa	4.43 (doublet, $\geqslant$CH)
IVb	3.88 (doublet, $\geqslant$CH)

tion of I with IIa or IIb in the presence or absence of NEt_3 had been carried out in dioxane for a definite time, 1-m*l* aliquots of the mixture were withdrawn by means of a pipet and triethylammonium chloride or benzylidene-*n*-propylamine hydrochloride was removed by filtration. The quantitative estimation of the reactants and products in the filtrate was done by means of NMR spectroscopy. The key signals for the reactants and products are shown in Table 5, while the results are summarized in Tables 1 and 2.

Reaction of I with X. To a stirred solution of 1.6 g (6.8 mmol) of X and 1.4 g (13.8 mmol) of NEt_3 in 10 m*l* of dioxane, a solution of 3.0 g (13.8 mmol) of I in 40 m*l* of dioxane was added, drop by drop, at room temperature over a period of 30 min. After the reaction mixture had then been stirred at room temperature for 14.5 hr, colorless crystals were collected by filtration and washed three times with 10 m*l* of methanol to leave 2.1 g (52%) of the bis(4+2) cycloadduct XI, mp 153°C (decomp.).

Found: C, 63.83; H, 4.88; N, 4.74%. Calcd for $C_{32}H_{28}O_6N_2S_2$: C, 63.99; H, 4.70; N, 4.66%.

Triethylammonium chloride was obtained from the methanol washings; yield, 1.9 g (quantitative). On the other hand, the dioxane filtrate was after the reaction, evaporated *in vacuo* to give an oily substance which solidified on treatment with methanol. Recrystallization from methanol gave colorless prisms, mp 139°C. Yield, 0.4 g. This compound could not be identified (Found: C, 60.97; H, 5.58; N, 4.27%).