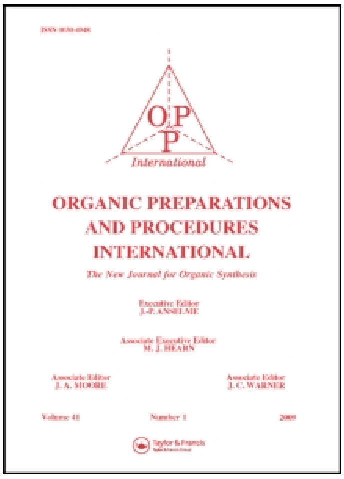

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# STUDIES OF BENZOYLSULFENE. VI. THE CYCLOADDITION REACTION OF BENZOYLSULFENE WITH KETENIMINES

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# STUDIES OF BENZOYLSULFENE. VI.[1]

# THE CYCLOADDITION REACTION OF BENZOYLSULFENE WITH KETENIMINES

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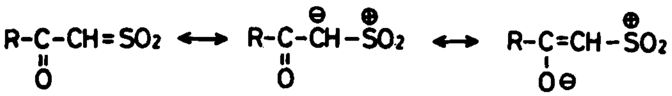
Recently, we found that benzoylsulfene ($PhCOCH=SO_2$), generated in situ from benzoylmethanesulfonyl chloride (I) and triethylamine, reacts with the C=N bonds of anils[3] and carbodiimides[4] to give the (2+2) and/or (4+2) cycloadducts, while simple sulfenes ($RCH=SO_2$) do not react with the C=N bond.[5] This might indicate that the electron-attracting benzoyl group makes benzoylsulfene more reactive than the sulfenes ($RCH=SO_2$), and that benzoylsulfene behaves as a 1,2- and/or 1,4-dipole.

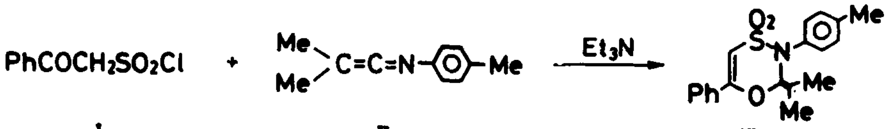


$$\mathrm{R{-}\underset{\underset{O}{\|}}{C}{-}CH{=}SO_2} \longleftrightarrow \mathrm{R{-}\underset{\underset{O}{\|}}{C}{-}\overset{\ominus}{C}H{-}\overset{\oplus}{S}O_2} \longleftrightarrow \mathrm{R{-}\underset{\underset{O^{\ominus}}{|}}{C}{=}CH{-}\overset{\oplus}{S}O_2}$$

It was also found that the reaction of I with cinnamylideneamines in the presence of triethylamine gives the Diels-Alder adducts of benzoylsulfene as a dienophile to the α,β-unsaturated anils.[6] On the other hand, it is known that, in the cycloaddition to ketenimines, the addition generally does not take place to the C=N bond, but to the C=C bond in the ketenimine. For example, when o-quinones react with diphenylketene-N-arylimine, the 1,4-dioxane compound is formed.[7] It is of interest to investigate which type of cycloadditions might take place in the reaction of benzoylsulfene with ketenimines.

The reaction of I with dimethylketene-N-p-tolylimine (II) in the presence of triethylamine gave a crystalline compound III, mp. 165°C (dec.), in a good yield. The elemental analysis and the molecular weight ($M^+$ m/e 341) of III were consistent with those of the expected 1:1 adduct of benzoylsulfene and II.

The (2+2) and (4+2) cycloadducts of benzoylsulfene to the C=C or C=N bond in the ketenimine II are possible for the structure of III. However, adduct III was identified as 2-isopropylidene-6-phenyl-3-p-tolyl-1,4,3-oxathiazine-4,4-dioxide, whose structure corresponds to the (4+2) cycloadduct of benzoylsulfene to the C=N bond in the ketenimine II.

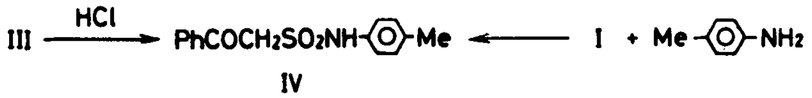


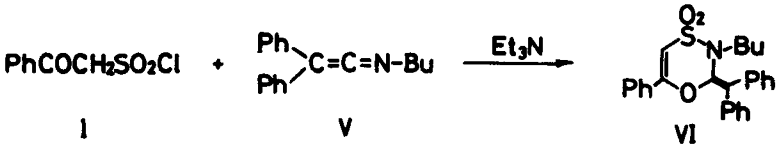
I II III

The IR spectrum of III showed characteristic bands at 1698 (νC=C, weak), 1570 (νC=C), 1340 and 1152 $cm^{-1}$ ($\nu SO_2$), and the NMR spectrum in $CDCl_3$ exhibited signals at τ 8.02, 8.12 (each 3H, $C\underline{H}_3$-C=, singlet), 7.70 (3H, -$C\underline{H}_3$, siglet), 3.58 (1H, -C$\underline{H}$=, siglet), 2.1-2.9 (9H, aromatic protons, multiplet).

4-Benzoyl-3-phenyl-2-n-propyl-1,2-thiazetidine which is the (2+2) cycloadduct of benzoylsulfene to benzylidene-n-propylamine, is easily reduced with sodium borohydride,[3] while the reduction of III under the same conditions did not take place.

The following experiment provided additional evidence for the proposed structure for III. The hydrolysis of III with hydrochloric acid in methanol gave benzoylmethanesulfonyl-p-toluidine (IV), which was identical with the authentic sample prepared from benzoylmethanesulfonyl chloride (I) and p-toluidine.





Similar reaction of the chloride I with diphenylketene-n-butylimine (V) in the presence of triethylamine gave the corresponding 1,4,3-oxathiazine (VI).

## EXPERIMENTAL

All the melting points are uncorrected. 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 at 70 eV. The IR spectra were measured in a KBr disc. The elemental analyses were done by Miss M. Akita at our laboratory.

2-isoPropylidene-6-phenyl-3-p-tolyl-1,4,3-oxathiazine-4,4-dioxide (III). To a vigorously-stirred solution of 1.6 g. (0.01 mole) of dimethylketene-p-tolylimine (II)$^8$ and 1.0 g. (0.01 mole) of triethylamine in 10 ml. of dioxane at room temperature, a solution of 2.2 g. (0.01 mole) of benzoylmethanesulfonyl chloride (I) in 40 ml. of dioxane was added dropwise over a period of 30 minutes. After the addition, the reaction mixture was stirred at the same temperature for 1.5 hours, then the precipitated triethylamine hydrochloride was removed by filtration. The filtrate was evaporated under reduced pressure, leaving an oily residue, which was triturated with 10 ml. of methanol to give 2.5 g. (74%) of colorless crystals. Recrystallization from petroleum ether (bp. 42-60°C) gave the 1,4,3-oxathiazine (III), mp. 165°C (dec.), as colorless prisms.

Anal. Calcd. for $C_{19}H_{19}O_3NS$: C, 66.85; H, 5.61; N, 4.10.
Found: C, 66.69; H, 5.61: N, 4.14.

Mass spectrum: m/e 341 ($M^+$), 340, 277 ($M^+$-$SO_2$), 276, 262 ($277^+$-Me), 235, 207, 175, 172, 159, 144, 132, 118, 117, 105, 102, 91 and 77.

Hydrolysis of the 1,4,3-oxathiazine (III). A solution of 300 mg. of III and 5 ml. of concentrated hydrochloric acid in 10 ml. of methanol was refluxed for 9 hours. The reaction mixture was concentrated under reduced pressure to leave a residue, which on trituration with 2 ml. of methanol gave 101 mg. of unreacted III. Water was added to the filtrate and the precipitated crystals (98 mg., 39%) were filtered. Recrystallization from petroleum ether afforded benzoylmethanesulfonyl-p-toluidine (IV), mp. 166-167°C, as colorless needles.

Anal. Calcd. for $C_{15}H_{15}O_3NS$: C, 62.28; H, 5.23; N, 4.84.
Found: C, 62.35; H, 5.20; N, 4.95.

Mass spectrum: m/e 289 ($M^+$), 225 ($M^+$-$SO_2$).

This compound was obtained in quantitative yield from the reaction of I with p-toluidine in dioxane at room temperature for 10 minutes.

3-n-Butyl-2-diphenylmethylidene-6-phenyl-1,4,3-oxathiazine-4,4-dioxide (VI). The reaction of 2.2 g. of I with 2.5 g. of diphenylketene-n-butylimine (V)[8] in the presence of triethylamine afforded 1.8 g. (48%) of the 1,4,3-oxathiazine (VI), mp. 137°C (dec.), as colorless prisms (petroleum ether).

Anal. Calcd. for $C_{26}H_{25}O_3NS$: C, 72.37; H, 5.84; N, 3.25.
Found: C, 72.63; H, 5.73; N, 3.24.

IR spectrum: $cm^{-1}$ 1660 ($\nu$C=C, weak), 1570 ($\nu$C=C), 1340 and 1150 ($\nu SO_2$).

NMR spectrum: $\tau$ 3.53 (1H, -CH=, singlet), n-butyl and aromatic protons.

Mass spectrum: m/e 431 ($M^+$), 430, 367 ($M^+-SO_2$), 366, 249, 194, 166, 165, 105 and 77.

## REFERENCES

1. Part V: O. Tsuge, S. Iwanami and S. Hagio, Bull. Chem. Soc. Japan, 45, No. 2 (1972).
2. To whom inquiries should be sent.
3. O. Tsuge and S. Iwanami, Bull. Chem. Soc. Japan, 43, 3543 (1970).
4. O. Tsuge and S. Iwanami, Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sec.), 92, 448 (1971).
5. H. Ulrich, "Cycloaddition Reactions of Heterocumulenes", p. 286, Academic Press, New York, N.Y., 1967.
6. O. Tsuge and S. Iwanami, Bull. Chem. Soc. Japan, 44, 2750

(1971).

7. W. Ried and W. Radt, Ann. Chem., 688, 174 (1965).

8. C. L. Stevens and J. C. French, J. Am. Chem. Soc., 76, 4393 (1954).

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