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Pyrolysis of *S*-[2-(Phenylthio-, Phenylsulfinyl-, and Phenylsulfonyl)-ethyl]-*N*-*p*-tosylsulfilimine[1)]

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Synopsis. The β-substituent effect on the rate of Ei reaction was investigated by using *S*-[2-(phenylthio-, phenylsulfinyl-, and phenylsulfonyl)ethyl]-*N*-*p*-tosylsulfilimines. The reactivity lies in the order of β-substituents: $PhSO_2 > PhSO > PhS > Ph$. From this and the kinetic isotope effect, the rate determining step is the intramolecular β-hydrogen abstraction by the *N*-*p*-tosyl group.

In previous studies,[2)] we found that *S*-alkyl-*N*-*p*-tosylsulfilimines having a β-hydrogen atom can readily undergo pyrolysis to afford the corresponding olefins and the sulfenamide in high yields. The kinetic study revealed that the rate of the pyrolysis of *S*-1-phenyl-substitdted-*N*-*p*-tosylsulfilimine is 10^3 times faster than that of the unsubstitdted derivative. Meanwhile, the *S*-2-phenyl-substituted-derivative was found to be pyrolyzed only 2.5 times faster than the unsubstituted one. Thus, although the rates of the pyrolysis vary widely upon changing the structure of the sulfilimine, the reaction has been suggested to proceed *via* nearly an ideal concerted *cis*-elimination mechanism. In order to collect further evidence to clarify the Ei reaction and especially to examine the effect of the electron withdrawing β-substituent, *S*-[2-(phenylthio-, phenylsulfinyl-, and phenylsulfonyl)ethyl]-*N*-*p*-tosylsulfilimines were subjected to the usual pyrolysis. This paper describes the results of the kinetic study of the pyrolysis.

Results and Discussion

S-(Phenyl)ethyl-*S*-phenyl-(I), *S*-[2-(phenylthio)-ethyl]-*S*-phenyl-(II), *S*-[2-(phenylsulfinyl)ethyl]-*S*-phenyl-(III), and *S*-[2-(phenylsulfonyl)ethyl]-*S*-phenyl-(IV)-*N*-*p*-tosyl-sulfilimines were prepared in the usual manner from the corresponding sulfides with chloramine-T in methanol and subjected to the pyrolysis. The pyrolysis was carried out by heating the solution of each of these sulfilimines in chloroform. The product analyses performed by NMR spectroscopy *in situ* in $CDCl_3$, showed a mixture of the olefins and the sulfenamide.

$$\text{Ph-S-CH}_2\text{CH}_2\text{X} \longrightarrow \text{Ph-S-NHTs} + \text{CH}_2\text{=CHX}$$
$$\downarrow$$
$$\text{NTs}$$

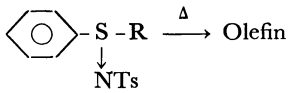
(X=Ph, PhS, PhSO, $PhSO_2$)

The kinetic data were obtained by following the IR absorption of the NH band of *N*-phenylthio-*p*-toluenesulfonamide which appears at 3310 cm^{-1}. The rates of the pyrolysis were correlated well by the first order rate equation; the data are summarized in the Table together with the relative rates of other sulfilimines obtained previously.

The data in the Table indicate that the effects of the β-substituent for the pyrolysis on the reactivity lie in the following sequence: $PhSO_2 > PhSO > PhS >$ Ph. This trend corresponds to that found in the E_2 elimination reaction which we studied previously[3)] and also to that in the base-catalyzed H-D exchange.[4)]

In order to study the nature of the transition state for the Ei reaction of the sulfilimine having a strong electron withdrawing β-substituent, *S*-phenyl-*S*-[2-(phenylsulfonyl)ethyl-2,2-d_2]-*N*-*p*-tosylsulfilimine was prepared and subjected to the pyrolysis. The kinetic study indicated the isotope effect in the pyrolysis reaction, calculated as k_H/k_D, to be 4.2. This clearly indicates that the reaction is also a concerted process that involves the rate-determining intramolecular β-hydrogen abstraction by the *N*-*p*-tosyl group. This rather large value of the kinetic isotope effect, as compared to the previous values obtained for *S*-ethyl-*S*-phenyl (3.0) and *S*-(α-methylbenzyl)-*S*-phenyl-*N*-*p*-tosylsulfilimine (2.9), and the small rate-enhancement by the β-phenyl group in the pyrolysis of *S*-2-(substituted)ethyl-*N*-*p*-tosylsulfilimine, as compared to the re-

TABLE 1. THE KINETIC RESULTS OF THE PYROLYSIS OF SULFILIMINE



Sulfilimine R	Temp °C	k $s^{-1}\times10^5$	Rel.[b)] rate	$\Delta H^{\neq}$ kcal/mol	$\Delta S^{\neq}$ e.u.
CH_2CH_3	80.3	1.08	1.0	26.5	−5.8
$CH_2CH_2C_6H_5$	95.2	6.28	1.5		
$CH(C_6H_5)CH_3$	31.0	16.0	10^3	20.8	−7.2
$CH_2CH_2S(O)_2C_6H_5$	60.0	34.5	4.8×10^2	20.4	−12.6
$CH_2CH_2S(O)C_6H_5$[a)]	60.0	1.12	15	26.6	−1.7
$CH_2CH_2SC_6H_5$	60.0	0.48	7	26.8	−2.4

a) In order to obtain the trend of the β-substituent, one isomer having a mp 124—127 °C was subjected to the pyrolysis. b) The relative rates are all calculated by correcting the number of available β-hydrogen atoms at 60.6 °C.

latively large acceleration by the phenyl group in the pyrolysis of *N*-ethyl-*N*-methyl-*N*-phenethylamine oxide,[5] may indicate that the transition state for the Ei reaction of *S*-(α-methylbenzyl)-*N*-*p*-tosylsulfilimine takes nearly the E_1 like process, namely S(III)–N bond cleavage is the rate-determining step, while that for the 2-phenylsulfonyl derivative corresponds to the ideal concerted Ei process, though shifting slightly to a carbanion-like state. In view of these observations in the pyrolysis of the 2-phenyl-sulfonyl derivative, the hydrogen abstraction is believed to be more important step than in the pyrolysis of the above mentioned sulfilimines. The large negative value of the activation entropy found for the 2-phenylsulfonyl compound is also in keeping with the ideal type transition state in which the large negative charge in the vicinal bulky sulfonyl group approaches the negatively charged *N*-*p*-tosyl group, thus making the transition state substantially more rigid.

Experimental

S-[*2-(Phenylthio)ethyl*]-S-*phenyl*-N-p-*tosylsulfilimine (II)*. The sulfilimine was prepared in the usual manner[6] by treating 1,2-bis(phenylthio)ethane with chloramine-T in ethanol. The yield was 84%, mp 133 °C, IR 1150, 1290 (ν_{SO_2}), 990 (ν_{SN}), NMR (δ ppm), $-CH_2CH_2-$ (s, 3.20, 4H), *p*-CH_3 (s, 2.50, 3H), Phenyl-H (m, 7.0—8.0, 14H). Found: C, 60.64; H, 4.97; N, 3.42%. Calcd for $C_{21}H_{21}S_3O_2N$: C, 60.69; H, 5.09; N, 3.37%.

S-[*2-(Phenylsulfinyl)ethyl*]-S-*phenyl*-N-p-*tosylsulfilimine (III)*. 2-(Phenylsulfinyl)ethyl phenyl sulfide (1.0 g) which was prepared from 1,2-bis(phenylthio)ethane and perbenzoic acid was dissolved in chloroform. The chloroform solution of the sulfide was treated at room temperature with chloramine-T as described above. After 30 min the solution was quenched with aqueous sodium hydroxide solution to remove *p*-toluenesulfonamide. The chloroform solution was washed with water and dried over anhyd. sodium sulfate. After the evaporation of chloroform, a solid crystalline residue was obtained in 0.7 g (70%) yield. The NMR spectra of the crude crystals indicated a broad peak at δ 2.5 ppm, suggesting that the compound (III) is a composite of two stereoisomers. The crude crystals, therefore, were separated by fractional crystallization from ethanol several times to give two different crystals; one has mp 119—120 °C, the other mp 124—127 °C. Found: C, 58.08; H, 4.79; N, 3.27%. Calcd for $C_{21}H_{21}S_3O_3N$: C, 58.44; H, 4.90; N, 3.25% (mixture).

S-[*2-(Phenylsulfonyl)ethyl*]-S-*phenyl*-N-p-*tosylsulfilimine (IV)*. A mixture of 2-(phenylthio)ethyl phenyl sulfone (2.0 g) and chloramine-T was heated in methanol solution for a few minutes in the presence of a drop of acetic acid. After the work-up, the crystalline product was isolated and recrystallized from ethanol. The yield was 1.75 g (55%) mp 87 °C. Found: C, 56.52; H, 4.74; N, 3.22%. Calcd for $C_{21}H_{21}S_3O_4N$: C, 56.35; H, 4.73; N, 3.13%.

S-[*2-(Phenylsulfonyl)ethyl*]-*2,2*-d_2-S-*phenyl*-N-p-*tosylsulfilimine*. The sulfilimine was prepared by the usual method mentinoned above from 2-(phenylthio)ethyl-2,2-d_2 phenyl sulfone, which was prepared in advance by treating the sulfone and D_2O in dioxane in the presence of sodium carbonate.

Kinetics. The kinetic study was carried out by the method reported elsewhere following the increase of the IR NH stretching band which appeared at 3310 cm^{-1}. The reaction was found to obey a good first-order kinetic equation.

Product Analysis. The olefins formed were not isolated except in the case of the phenethyl derivative. When the pyrolysis was carried out in the NMR tube until the alkyl protons of the starting sulfilimine disappeared, the NMR peaks were found to be a 1 : 1 mixture of the corresponding olefin and the sulfenamide, which corresponds to the authentic samples prepared separately.

References

1) Part V of Ei reaction.

2) S. Oae, K. Tsujihara, and N. Furukawa, *Tetrahedron Lett.*, **1970**, 2663; K. Tsujihara, N. Furukawa, and S. Oae, *Tetrahedron*, **27**, 4911 (1971); K. Tsujihara, K. Harada, N. Furukawa, and S. Oae, *ibid.*, **27**, 6101 (1971); S. Oae, K. Harada, K. Tsujihara, and N. Furukawa, *Bull. Chem. Soc. Jpn.*, **46**, 3482 (1973).

3) T. Yoshida, Y. Yano, and S. Oae, *Tetrahedron*, **27**, 5343 (1971).

4) S. Oae, W. Tagaki, and A. Ohno, *Tetrahedron*, **20**, 417 (1964).

5) A. C. Cope, M. A. Lebel, H. H. Lee, and W. E. Moore, *J. Am. Chem. Soc.*, **79**, 4720 (1957).

6) K. Tsujihara, N. Furukawa, K. Oae, and S. Oae, *Bull. Chem. Soc. Jpn.*, **42**, 2631 (1969).