On the Behavior of Sulfonyl Imide as a Reactive Intermediate. The Reaction with Enamines

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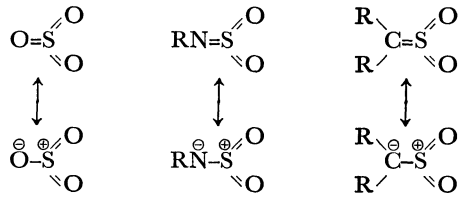
The reactions of *N*-alkylsulfamoyl chloride with enamines in the presence of triethylamine showed the presence of *N*-alkylsulfonyl imide ($RN{=}SO_2$) as a reaction intermediate to give either acyclic (sulfonamides) or cyclic products (1,2-thiazetidine 1,1-dioxides), depending upon the enamines used. The enamines leading to the acyclic products possess either a methylene group on the α-carbon or a hydrogen on the β-carbon of the enamine; the enamine leading to the cyclic product has no such available hydrogen atom. It is thought that the products are formed *via* a zwitter ionic intermediate provided by the electrophilic attack of the sulfonyl imide sulfur atom on the β-carbon atom of the enamine.

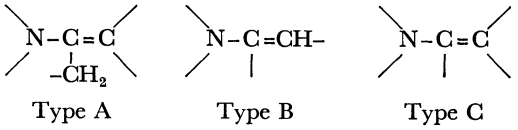
Sulfonyl imides,[1] $RN{=}SO_2$, are isoelectronic with sulfur trioxide and sulfenes, and are located between sulfenes and sulfur trioxide in regard to the electronegativities of the elements adjacent to the reaction centers. An attractive sulfonyl imide synthesis was



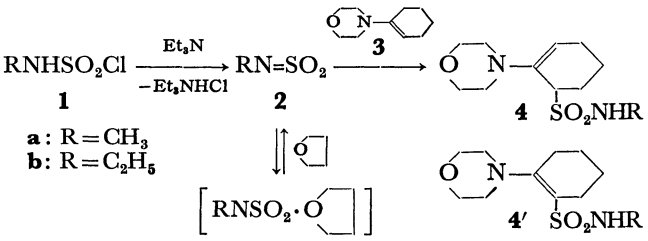
achieved by Burgess[2] in 1967, though the imide had been proposed as an intermediate in the photolysis of benzenesulfonyl azide.[3] Dehydrohalogenation of ethylsulfamoyl chloride by triethylamine at −78 °C led to the generation of *N*-ethylsulfonyl imide, whose interception was accomplished by the addition of aniline to give the sulfamide. *N*-Ethylsulfonyl imide, furthermore, was found to react with strongly nucleophilic olefins such as 2-(dichloromethylene)-1,3-dioxolane[2] and the pyrrolidine enamine of isobutyraldehyde[4] to afford cycloadducts. In this study on sulfonyl imides, the reaction of alkylsulfonyl imides with enamines give acyclic or cyclic adducts depending on the type of the enamine used, and the sulfonyl imides undergo oligomerization in the presence of less nucleophilic olefins or in the absence of the substrates.

Results and Discussion

The reactions of *N*-alkylsulfonyl imide (**2**) with three types of enamines (Types A, B, and C) were conducted.

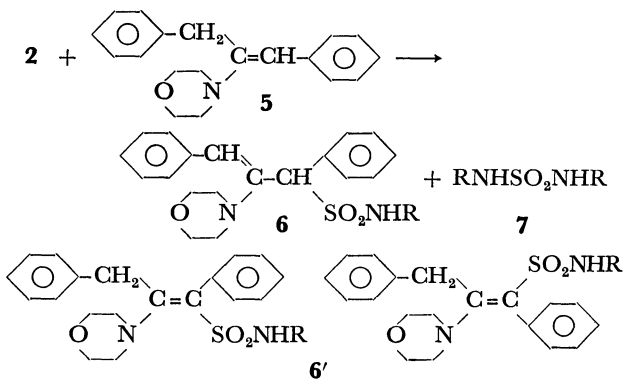


Reaction of 2 with Type A Enamine. A solution of an alkylsulfamoyl chloride (**1**) in tetrahydrofuran (THF) was added dropwise with stirring to a solution of 1-morpholinocyclohexene (**3**) and triethylamine in THF at −78 °C. Triethylamine hydrochloride was formed nearly quantitatively and removed by filtration. Treatment of the filtrate afforded a colorless crystalline compound characterized not as 1-alkylsulfamoyl-2-morpholinocyclohexene (**4'**) but as the 3-alkylsulfamoyl isomer (**4**) in about 60% yield.



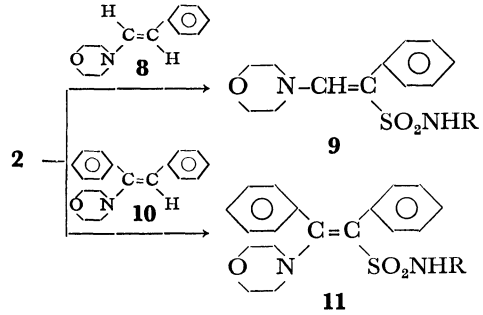
The structure of **4** was established by IR, NMR, and mass spectra analyses (experimental section). Subsequently, a THF solution of triethylamine was added dropwise to a stirred THF solution of **1** at −78 °C. After the removal of the amine hydrochloride at −78 °C, the addition of **3** to the filtrate (maintained at the same temperature) led to **4**, the yield of which varied with the age of the filtrate. These results suggest the intermediacy of *N*-alkylsulfonyl imide (**2**), which may be stabilized in a mode similar in the THF complex of *N*-methoxycarbonyl imide.[5]

The addition of 2-morpholino-1,3-diphenylpropene (**5**) to a THF solution of **2a** at −78 °C produced 3-methylsulfamoyl-2-morpholino-1,3-diphenylpropene (**6a**) rather than the isomeric sulfonamide **6'**, **6a** was isolated in a 26% yield together with *N,N'*-dimethylsulfamide (**7a**) in a 65% yield. When **1a** was added to a mixture of **5** and triethylamine in THF at an elevated temperature, 20 °C, the yield of **6a** increased to 67% and that of **7a** decreased to 7%. In the same manner,

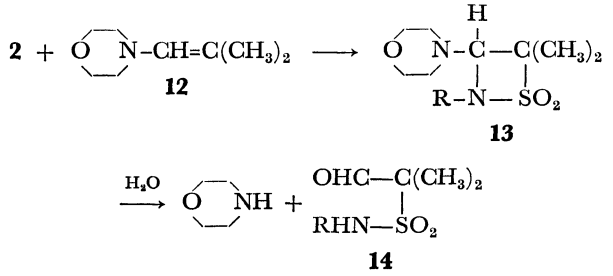


6b was given in a 68% yield from **1b** at 20 °C. That **5** is less reactive than **3** is interpreted in terms of a smaller nucleophilic character due to the phenyl ring on the enamine double bond.

Reaction of 2 with Type B Enamine. The reaction of **2** with either (*E*)-*β*-morpholinostyrene (**8**) or (*E*)-morpholinostilbene (**10**) provided the 1-alkylsulfamoyl-2-morpholinoethylene derivative (**9** or **11**) in a moderate yield (**9a**: 46%, **9b**: 58%, **11a**: 47%, **11b**: 56%), at 20 °C. The reaction did not take place at −78 °C. In a similar mode as the reaction with the enamines **3** and **5**, the hydrogen atom *β* to the morpholino moiety served in the formation of the acyclic products:

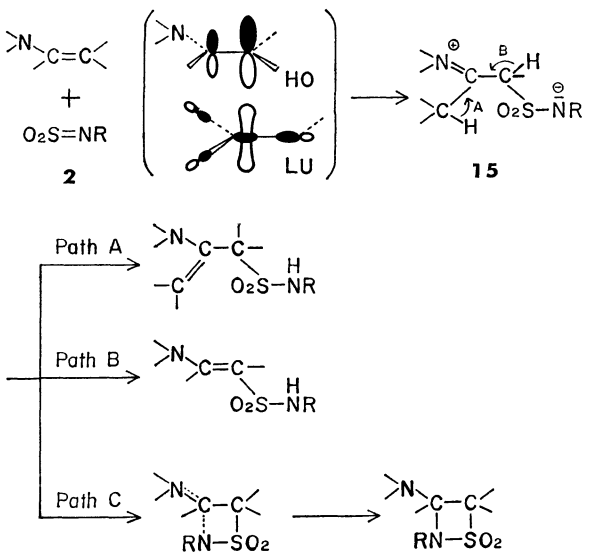


Reaction of 2 with Type C Enamine. From the above results, the cycloadduct formation in reaction of **2** appears to require an enamine having no available hydrogen atom. When **2** was generated at −78 °C in the presence of 2-methyl-1-morpholinopropene (**12**), the expected cycloadduct, 2-alkyl-4,4-dimethyl-3-morpholino-1,2-thiazetidine 1,1-dioxide (**13**) was obtained. Since **13a** and **13b** were very sensitive to moisture,[6] attempts at purification were unsuccessful. The structures of **13** were established on the basis of the IR and NMR spectra and by their subsequent hydrolyses. The IR spectra of **13** showed no ν_{NH} and exhibited ν_{SO_2}



at 1320 and 1125 cm^{-1}. The NMR spectrum ($CDCl_3$, 60 MHz) of **13b** was very similar to that of 4,4-dimethyl-2-ethyl-3-(1-pyrrolidinyl)-1,2-thiazetidine 1,1-dioxide.[4] Chromatographs of **13a** and **13b** over silica gel led to the hydrolyses, giving **14a** and **14b** in 55 and 62% yields respectively.

Reaction Pathway. The reactions of the *N*-alkylsulfonyl imides (**2**) with the enamines provided three kinds of the products, the 3-sulfamoylpropene derivative, the sulfamoylethylene derivative, and the cycloadduct, depending upon the enamine used. The formation of these products can be explained by a mechanism *via* a zwitter ionic intermediate (**15**) shown in Scheme 1.



Scheme 1.

The reaction is initiated by an electrophilic attack of the sulfur atom of the sulfonyl imide on the *β*-carbon of the enamines, leading to **15**. In the cases of Type A and B enamines, prototropy followed by the formation of a new olefinic linkage (Path A) or prototropy followed by the reformation of the olefinic linkage (Path B) takes place to give the corresponding acyclic products. In the reaction with Type A enamine, the exclusive formation of the sulfonamide **4** or **6** which arises from the proton transfer of the methylene, instead of the isomeric sulfonamide **4′** or **6′** ascribable to the transfer of the olefinic proton, may be considered as follows: Both the sulfonamides **4′** and **6′** are destabilized by the steric inhibition of the resonance involving the nitrogen lone pair and the double bond.[9] On the other hand, the zwitter ionic intermediate resulting from the Type C enamine affords the cyclic adduct since there is no mobile proton (Path C).

As an alternative mechanism, the formation of the cycloadduct may be envisaged as resulting from a concerted thermal [$_\pi 2_s + _\pi 2_a$] process.[10] However, in the cycloaddition of *N*-methoxycarbonylsulfonyl imide with variously substituted alkenes to afford the corresponding 1,2-thiazetidines and 2,3-dihydro-1,4,5-oxathiazines, the one-step multi-center cycloaddition has not been accepted on the basis of the adduct distribution with solvent change.[5] Moreover, the addition of sulfene, which closely resembles sulfonyl imide, to enamines has been explained not by a concerted mechanism but by a nonconcerted process on the basis of the stereoselectivity of the cycloaddition and of the product distribution between the cyclic and acyclic adducts.[9]

Oligomerization of 2. The reaction of **2** with the enamine (**5**) possessing a phenyl ring on the double bond gave dimethylsulfamide (**7**) in a significant yield, especially at low temperatures. A dimer of sulfonyl imide which had failed to react with the enamine present might be subjected to hydrolysis to afford **7** with the loss of sulfuric acid. When **1a** was added dropwise to triethylamine in either benzene or ether in the absence

$$2CH_3NSO_2 \longrightarrow (CH_3NSO_2)_2 \xrightarrow[-H_2SO_4]{2H_2O} CH_3NHSO_2NHCH_3$$
2a **7a**

of enamine followed by chromatography, **7a** was isolated in a 90% yield respectively. Furthermore, the reactions of **2a** with less nucleophilic olefins, *e.g. trans*-stilbene and dimethyl fumarate, in THF gave no adduct, affording the amine hydrochloride in the theoretical amount and an unidentified solid which appears to be a polymerization product of **2a**. In addition, the olefins were recovered nearly quantitatively.

The explanation for the favored oligomerization, as well as the preferred tendency of prototropy to form the acyclic compound with enamine, of sulfonyl imide, compared with sulfene, is based on the following consideration: owing to the larger electronegativity of the nitrogen atom than that of the carbon atom, sulfonyl imide and the zwitter ionic intermediate (**15**) are more stabilized and have a longer lifetime than sulfene and the resulting intermediate[9] (like **15**).

Experimental

The IR spectra were recorded on Hitachi EP-S and Hitachi 215 spectrophotometers, and the NMR spectra on a Varian EM-360 (60 MHz) instrument, using tetramethylsilane as an internal standard. The NMR spectra of the products, except for dimethylsulfamide, were measured in chloroform-*d* and all the chemical shifts were given in δ values. The melting points are uncorrected.

Materials. Alkylsulfamoyl chlorides (**1**) were prepared according to the reported method:[13] **1a**; 67 °C/0.03 mmHg, **1b**: 70 °C/0.03 mmHg (lit,[14] 52 °C/0.05 mmHg). All of the enamines, **3**,[15] **5**,[16] **8**,[17] **10**,[18] and **12**[19] were prepared by the respective methods in the literature. *trans*-Stilbene and dimethyl fumarate were commercial materials and used after recrystallizations from 95% ethanol and from methanol respectively. Triethylamine and the solvents were obtained commercially and used after purification by the published direction.[20]

Reactions of 1 with Enamines. Method A: A sulfamoyl chloride (10 mmol) in THF (30 ml) was added dropwise over a period of 1 h to a stirred solution containing an enamine (10 mmol) and triethylamine (10 mmol) in THF (70 ml) at the desired temperature. After the addition, the mixture was stirred for 1 h at that temperature. The precipitates of triethylamine hydrochloride (quantitative amount) were removed by filtration, and the solvent was evaporated under reduced pressure leaving an oily substance tinged with yellow. The addition of methanol to the residue gave the sulfamoyl imide-enamine adduct as a precipitate. The reaction temperatures were maintained at −78 °C in the reactions with enamines **3** and **12**, and at 20 °C for enamines **5**, **8**, and **10**. Method B: A solution of triethylamine (10 mmol) in THF (20 ml) was added dropwise over 15 min to a stirred solution of **1** (10 mmol) in THF (60 ml) at −78 °C. After further stirring for 15 min, to the stirred solution kept at −78 °C was added a solution of the enamine (10 mmol) in THF (20 ml) dropwise over a period of 30 min. After the resulting mixture was stirred for an additional 15 min, the mixture was allowed to attain room temperature. The precipitates of the amine hydrochloride (quantitative amount) were removed by filtration and the solvent evaporated from the filtrate under reduced pressure. Methanol was added to the residual oily substance and the sulfamoyl imide-enamine adduct was obtained as a precipitate.

Reaction with 1-Morpholinocyclohexene (3): By Method A, 3-methylsulfamoyl- and 3-ethylsulfamoyl-2-morpholinocyclohexenes (**4a** and **4b**) were isolated in 1.5 g (58%) and 1.5 g (55%) yields respectively. By Method B, **4a** and **4b** were isolated in 1.3 g (50%) and 1.4 g (51%) yields respectively. As a modification of Method B, when the amine hydrochloride was removed at −78 °C prior to the addition of enamine **3**–THF solution, **4a** and **4b** were obtained in 1.2 g (46%) and 1.1 g (40%) yields respectively. **4a**: mp 120—122 °C. IR (Nujol, cm^{-1}); 3280 (NH), 1645 (C=C), 1315 and 1160 (SO_2). NMR; 1.6—3.2 (m, 10H, NCH_2 and CH_2), 3.65—3.95 (m, 5H, OCH_2 and SO_2CH), 5.05 (bs, 1H, NH), 5.38 (t, 1H, J=4 Hz, vinyl H). MS (70 eV); *m/e* 260 (M^+). Found: C, 50.31; H, 7.72; N, 10.57%. Calcd for $C_{11}H_{20}N_2O_3S$: C, 50.75; H, 7.74; N, 10.76%. **4b**: white crystal, mp 89—90 °C. IR (Nujol, cm^{-1}); 3260 (NH), 1645 (C=C), 1315 and 1160 (SO_2). NMR; 1.22 (t, 3H, J=7 Hz, CH_3), 1.5—3.4 (m, 12H, NCH_2 and CH_2), 3.73 (m, 5H, OCH_2 and SO_2CH), 5.10 (bt, 1H, NH), 5.35 (t, 1H, J=4 Hz, vinyl H). Found: C, 52.84; H, 8.10; N, 10.20%. Calcd for $C_{12}H_{22}N_2O_3S$: C, 52.54; H, 8.08; N, 10.21%.

Reactions with 2-Morpholino-1,3-diphenylpropene (5): The reaction of **1a** was run as in Methods A and B. By Method A, 2.5 g (67%) of 3-methylsulfamoyl-2-morpholino-1,3-diphenylpropene (**6a**) was yielded as the precipitate. The filtrate was evaporated under reduced pressure to give a brownish, oily substance. The residue was chromatographed on silica gel, and 0.04 g (7%) of *N,N'*-dimethylsulfamide (**7a**) was eluted with chloroform. The recrystallization of **6a** from methanol gave colorless needles; mp 153—154 °C. IR (KBr, cm^{-1}): 3200 (NH), 1320 and 1140 (SO_2). NMR: 2.70 (d, 3H, J=5 Hz, CH_3), 2.65—2.90 (m, 4H, NCH_2), 3.55—3.75 (m, 4H, OCH_2), 4.29 (bs, 1H, NH), 5.10 (s, 1H, vinyl H), 6.81 (s, 1H, SO_2CH), 7.2—7.8 (m, 10H, benzene ring). MS (70 eV): *m/e* 372 (M^+). Found: C, 64.23; H, 6.61; N, 7.54%. Calcd for $C_{20}H_{24}N_2O_3S$: C, 64.49; H, 6.49; N, 7.52%. The recrystallization of **7a** from benzene gave colorless leaflets; mp 78—79 °C.[13] IR (KBr, cm^{-1}): 3320 (NH), 1325 and 1160 (SO_2). NMR (DMSO-d_6): 2.47 (d, 6H, J=5 Hz, CH_3), 6.70 (bs, 2H, NH). MS (70 eV): *m/e* 124 (M^+). Found: C, 19.21; H, 6.37; N, 22.97%. Calcd for $C_2H_8N_2O_2S$: C, 19.35; H, 6.49; N, 22.56%. Method B gave **6a** and **7a** in 1.0 g (26%) and 0.4 g (65%) yields respectively. When the reaction of **1b** was run as in Method A, 3-ethylsulfamoyl-2-morpholino-1,3-diphenylpropene (**6b**) was isolated in 2.6 g (68%) yield. The recrystallization from methanol gave colorless needles; mp 133—134 °C. IR (KBr, cm^{-1}): 3250 (NH), 1310 and 1140 (SO_2). NMR: 1.10 (t, 3H, J=7 Hz, CH_3), 2.65—3.30 (m, 6H, NCH_2), 3.60—3.75 (m, 4H, OCH_2), 4.36 (bt, 1H, NH), 5.00 (s, 1H, vinyl H), 6.85 (s, 1H, SO_2CH), 7.3—7.9 (m, 10H, benzene ring). MS (70 eV): *m/e* 386 (M^+). Found: C, 65.15; H, 6.85; N, 7.26%. Calcd for $C_{21}H_{26}N_2O_3S$: C, 65.27; H, 6.78; N, 7.25%.

Reactions with (E)-β-Morpholinostyrene (8): The reactions of **1a** and **1b** gave α-methylsulfamoyl- and α-ethylsulfamoyl-β-morpholinostyrenes (**9a** and **9b**) in 1.3 g (46%) and 1.7 g (58%) yields, respectively, Method A. The recrystallization of **9a** from methanol gave colorless prisms; mp 144—145 °C. IR (KBr, cm^{-1}): 3240 (NH), 1622 (C=C), 1300 and 1130 (SO_2). NMR: 2.62 (d, 3H, J=5 Hz, CH_3), 2.9—3.1 (m, 4H, NCH_2), 3.45—3.65 (m, 4H, OCH_2), 3.65—4.0 (bs, 1H, NH), 7.26 (s, 1H, vinyl H), 7.35 (s, 5H, benzene ring). MS (70 eV): *m/e* 282 (M^+). Found: C, 55.04; H, 6.41; N, 9.90%. Calcd for $C_{13}H_{18}N_2O_3S$: C, 55.31; H, 6.43; N, 9.92%. The recrystallization of **9b** from methanol gave

colorless prisms; mp 117—118 °C. IR (KBr, cm^{-1}): 3260 (NH), 1622 (C=C), 1300 and 1130 (SO_2). NMR: 1.10 (t, 3H, J=7 Hz, CH_3), 2.8—3.1 (m, 6H, NCH_2), 3.45—3.65 (m, 4H, OCH_2), 3.65—3.9 (bs, 1H, NH), 7.22 (s, 1H, vinyl H,) 7.33 (s, 5H, benzene ring). Found: C, 56.45; H, 6.76; N, 9.37%. Calcd for $C_{14}H_{20}N_2O_3S$: C, 56.74; H, 6.80; N, 9.45%.

Reactions with (E)-Morpholinostilbene (10): The reactions of **1a** and **1b** were run as in Method A. Methylsulfamoyl- and ethylsulfamoyl-morpholinostilbenes (**11a** and **11b**) were isolated in yields of 2.6 g (47%) and 2.1 g (56%) respectively. The recrystallization of **11a** gave pale yellow prisms: mp 153—154 °C. IR (KBr, cm^{-1}): 3275 (NH), 1539 (C=C), 1309 and 1140 (SO_2). NMR: 2.46 (d, 3H, J=5 Hz, CH_3), 2.5—2.7 (m, 4H, NCH_2), 3.3—3.5 (m, 4H, OCH_2), 3.7 (bs, 1H, NH), 7.2—7.5 (m, 10H, benzene ring). MS (70 eV): *m/e* 358 (M^+). Found: C, 63.48; H, 6.18; N, 7.74%. Calcd for $C_{19}H_{22}N_2O_3S$: C, 63.67; H, 6.19; N, 7.82%. **11b**: colorless prisms (from methanol), mp 140—142 °C. IR (KBr, cm^{-1}); 3250 (NH), 1545 (C=C), 1297 and 1138 (SO_2). NMR; 0.93 (t, 3H, J=7 Hz, CH_3), 2.5—2.7 (m, 4H, morpholino ring NCH_2), 2.92 (q, 2H, J=7 Hz, NCH_2), 3.33—3.53 (m, 4H, OCH_2), 3.70 (bs, 1H, NH), 7.3—7.5 (m, 10H, benzene ring). MS (70 eV); *m/e* 372 (M^+). Found: C, 64.38; H, 6.50; N, 7.65%. Calcd for $C_{20}H_{24}N_2O_3S$: C, 64.50; H, 6.50; N, 7.52%.

Reactions with 2-Methyl-1-morpholinopropene (12): The reactions of **1a** and **1b** were run as in Method A. The precipitates of triethylamine hydrochloride were removed from the reaction mixture by filtration and the solvent evaporated under reduced pressure, the last traces of solvent being removed at a pressure of 0.1 mmHg. The residual oily, impure 2,4,4-trimethyl-3-morpholino-1,2-thiazetidine 1,1-dioxide (**13a**) displayed the following NMR spectrum: 1.56 (s, 6H, C-CH_3), 2.50—3.13 (m, 4H, NCH_2), 2.76 (s, 3H, NCH_3), 3.31 (s, 1H, CH), 3.60—3.83 (m, 4H, OCH_2). Since attempts to crystallize **13a** were unsuccessful, the oil was chromatographed over silica gel. Elution with benzene gave α-(methylsulfamoyl)isobutyraldehyde (**14a**) as a colorless oil in a yield of 0.9 g (55%). IR (neat, cm^{-1}): 3340 (NH), 1730 (C=O), 1318 and 1130 (SO_2). NMR: 1.53 (s, 6H, CH_3), 2.76 (d, 3H, J=5 Hz, NCH_3), 4.63 (bs, 1H, NH), 9.63 (s, 1H, CHO). From the reaction of **1b**, 2-ethyl-4,4-dimethyl-3-morpholino-1,2-thiazetidine 1,1-dioxide (**13b**) was obtained as an oily residue. IR (neat, cm^{-1}): 1320 and 1122 (SO_2). NMR: 1.26 (t, 3H, J=7 Hz, CH_3), 1.56 (s, 6H, CH_3), 2.50—3.13 (m, 4H, NCH_2), 3.46 (s, 1H, CH), 3.60—3.83 (m, 4H, OCH_2), 3.25 (q, 2H, J=7 Hz, CH_2). The impure **13b** was chromatographed over silica gel to give colorless, oily α-(ethylsulfamoyl)isobutyraldehyde (**14b**): yield 1.1 g (62%). IR (neat, cm^{-1}): 3280 (NH), 1725 (C=O), 1315 and 1130 (SO_2). NMR; 1.17 (t, 3H, J=7 Hz, CH_3), 1.50 (s, 6H, CH_3), 3.18 (q, 2H, J=7 Hz, CH_2), 5.07 (bs, 1H, NH), 9.68 (s, 1H, CHO).

Reaction of 1a in Benzene and in Ether. A benzene (0.5 mol, 39 g) solution of **1a** (20 mmol, 2.6 g) was added dropwise over a period of 1 h to a stirred benzene (0.5 mol) solution of triethylamine (20 mmol, 2.1 g) at 20 °C. The reaction mixture was stirred for a further hour at the temperature and the precipitates of triethylamine hydrochloride were collected by filtration (weighed 2.7 g, 98%). Evaporation of the solvent under reduced pressure gave a yellow oil, which was chromatographed over silica gel. The fraction eluted by chloroform gave 1.05 g (85%) of **7a**, which was recrystallized from benzene. The reaction in ether gave 1.12 g (91%) of **7a**.

Attempted Reactions with trans-*Stilbene and with Dimethyl Fumarate.* The reactions of **1a** were run as in Method A at 20 °C using double the molar quantities of the reactants and the solvent. The reaction with *trans*-stilbene gave 2.64 g (96%) of the amine hydrochloride, and the evaporation of the solvent under reduced pressure gave a yellow solid, which was extracted with benzene. Removal of benzene gave 5.3 g (95%) of the recovered stilbene. Chromatography of the benzene insoluble part on silica gel using chloroform as an eluent gave one gram of a white solid, the NMR of which showed no absorption for protons resulting from the incorporation of stilbene. The reaction with dimethyl fumarate gave 2.5 g (91%) of the amine hydrochloride. Evaporation of the solvent followed by trituration with methanol gave 2.6 g (91%) of the recovered ester. From the methanol solution, the solvent was removed under reduced pressure to give a pale yellow solid, the chromatography of which over silica gel gave 0.8 g of a white product similar to that obtained in the reaction with stilbene.

References

1) According to Chemical Abstracts, $HN{=}SO_2$ is called "sulfimide," but the term is used for $HN{=}SH_2$ in the IUPAC names. The term "sulfonyl imide" will be used in the present paper: J. H. Fletcher, O. C. Dermer, and R. B. Fox, "Nomenclature of Organic Compounds," in "Advances in Chemistry Series," ed by R. F. Gould, American Chemical Society, Washington, D. C. (1974), pp. 304, 308, and 310.

2) G. M. Atkins, Jr. and E. M. Burgess, *J. Am. Chem. Soc.*, **89**, 2502 (1967).

3) W. Lwowski and E. Scheiffele, *J. Am. Chem. Soc.*, **87**, 4359 (1965). Thermolysis of 2,3,5,6-tetramethylbenzenesulfonyl azide also gives a sulfonyl imide intermediate: R. A. Abramovitch, T. Chellathurai, W. D. Holcomb, I. McMaster, and D. P. Vanderpool, *J. Org. Chem.*, **42**, 2920 (1977).

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5) E. M. Burgess and W. M. Williams, *J. Am. Chem. Soc.*, **94**, 4386 (1972).

6) The hydrolysis of **13b** in chloroform-*d* in the open system was followed by monitoring the NMR spectrum over 72 h. The lapse of time permitted the disappearance of the peak due to the methylidyne proton (δ 3.46) with the appearances of the two peaks due to the amide proton (δ 5.07)[7] and the aldehyde proton (δ 9.68).

7) Although the amino proton of morpholine is observed at δ 1.92 as a singlet,[8] the NMR spectrum of a mixture of equimolar amounts of **14b** and morpholine has given a broad singlet at δ 5.07 which corresponds to two protons.

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