hydroxide ion initiated 1,3 elimination of HBr in 40% aqueous dioxane from isopropyl α-bromobenzyl sulfone (**1**) in the Ramberg-Bäcklund reaction is 560 times faster than deuterium exchange of the tertiary α hydrogen of the analogous isopropyl benzyl sulfone (**2**) under these conditions. (Exchange of the benzylic hydrogen atoms in **2** precedes, of course, the exchange of the tertiary hydrogen atom.)

$$(CH_3)_2CHSO_2CHBrC_6H_5 + 3HO^- \xrightarrow[H_2O]{\text{dioxane}} (CH_3)_2C{=}CHC_6H_5 + SO_3^{2-} + Br^- + 2H_2O$$

1

$$(CH_3)_2CHSO_2CH_2C_6H_5 + DO^- \xrightarrow[D_2O]{\text{dioxane}} (CH_3)_2CDSO_2CD_2C_6H_5$$

2

We estimate that only *ca.* fivefold of the 560-fold increase in rate for **1**, relative to **2**, can be accounted for by the inductive effect of the bromine atom.[7] Furthermore, there is good reason to believe that the additional acceleration is not caused by concerted breaking of the HC and CBr bonds of **1** in the Ramberg-Bäcklund reaction.[10] Additional information as to the cause of the rate difference was derived from the observation that the rate of exchange was affected dramatically by alkyl substitution, whereas the rate of Ramberg-Bäcklund reaction was not. In the series $C_6H_5CH_2SO_2CHMe_2$ (**2**), $C_6H_5CH_2SO_2CH_2Me$ (**3**), $C_6H_5CH_2SO_2CH_3$ (**4**), the rate of exchange at the nonbenzylic α position was in the order $1.0:10^2:10^4$.[11] In contrast, the rates of the Ramberg-Bäcklund reaction, under comparable conditions, for $Me_2CHSO_2CHBrC_6H_4$ (**1**), $MeCH_2SO_2CHBrC_6H_5$ (**5**), and $CH_3SO_2CHBrC_6H_5$ (**6**) were in the order 1.0:1.7:0.62.

The rates of internal return (k_{-1}), solvent exchange (k_2), and ring closure in the Ramberg-Bäcklund reaction (k_3) will all be affected somewhat by methyl substitution. Methyl groups should be effective in excluding solvent molecules from the vicinity of the carbanion, suggesting that the rate of solvent exchange could be decreased markedly with methyl substitution. This would account for at least part of the 10^4 decrease in k_{obsd} for deuterium exchange of **2** relative to **4**.[12] On the other hand, methyl substitution may have relatively little effect on the rate of internal return or the rate of ring closure in the Ramberg-Bäcklund reaction. This would explain why k_{obsd} for the Ramberg-Bäcklund reaction of **1** is much *faster* than deuterium exchange of the methinyl proton (as judged by comparison with **2**) whereas k_{obsd} for the Ramberg-Bäcklund reaction of **6** is much *slower* than deuterium exchange of the methyl protons (recovered **6** showed complete exchange of methyl protons).

$$C_6H_5CH(Br)SO_2CHR_1R_2 + DO^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$

1, $R_1 = R_2 = Me$
5, $R_1 = Me$; $R_2 = H$
6, $R_1 = R_2 = H$

$$C_6H_5CH(Br)SO_2\overset{R_1}{\underset{R_2}{C}}\cdots HOD]^-$$

$$\xrightarrow[DOD]{k_2} C_6H_5CH(Br)SO_2\overset{R_1}{\underset{R_2}{C}}\cdots DOD]$$

$$\xrightarrow{k_3} C_6H_5CH\!\!-\!\!\overset{CR_1R_2}{\underset{O_2}{S}}$$

One would expect elimination of bromide ion, or the like, from a carbon atom adjacent to a carbanion center (carbanoid 1,2 elimination) to be much more successful than carbanoid 1,3 elimination in competing with solvent exchange. The fact that syn and anti 1,2 eliminations from 2-*p*-tolylsulfonylcyclohexyl and 2-*p*-tolylsulfonylcyclopentyl tosylates are *ca.* 10^5–10^7 times faster than deuterium exchange in the corresponding sulfones,[15] can be interpreted as support for this view. (Here, we estimate that the inductive effect of the OTs group might cause *ca.* 10^3 acceleration.[7,15,16]) It is possible that the faster rates for the elimination reactions are due to their concerted nature,[15] but it now appears more likely that the difference in rates, after correction for inductive effects, is a measure of the relative ability of (intramolecular) elimination *vs.* (intermolecular) solvent exchange to compete with internal return from a carbanion intermediate.[16]

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(7) This assumes a ρ^* value of *ca.* 2 for the deprotonation reaction (by analogy with $\rho^* = 1.59$ for the acetate ion catalyzed bromination of ketones[8] and $\rho^* = 1.78$ for the methoxide ion catalyzed deuterium exchange of the α hydrogen atoms in esters[9]) and a transmission coefficient of 2.8.[5]

(8) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. Newman, Ed., Wiley, New York, N. Y., 1956, p 608.

(9) J. Hine, L. G. Mahone, and C. L. Liotta, *J. Amer. Chem. Soc.*, **89**, 5911 (1967).

(10) F. G. Bordwell, *Accounts Chem. Res.*, **3**, 281 (1970).

(11) Comparable differences in rates of tritium exchange in NaOMe–MeOH have been observed by J. R. Jones (private communication) in the series p-$ClC_6H_4SO_2CHMe_2$, p-$ClC_6H_4SO_2CH_2Me$, p-$ClC_6H_4SO_2CH_3$.

(12) Judging from hydroxide deprotonation rates for CH_3NO_2 *vs.* Me_2CHNO_2 ($89:1.0^{13}$), where internal return is not a factor, and for $(CH_3)_2C{=}O$ *vs.* $(Me_2CH)_2C{=}O$ ($119:1.0^{14}$), where internal return is probably minimal, substitution of two methyl groups α to the sulfone group should cause a *ca.* 10^2 decrease in k_1. On this basis as much as 10^2 of the 10^4 decrease in k_{obsd} could have its origin in a decrease in k_2.

(13) R. P. Bell and D. M. Goodall, *Proc. Roy. Soc., Ser. A*, **294**, 273 (1966).

(14) R. P. Bell and H. C. Longuet-Higgens, *J. Chem. Soc.*, 636 (1946).

(15) J. Weinstock, J. L. Bernardi, and R. G. Pearson, *J. Amer. Chem. Soc.*, **80**, 4961 (1958).

(16) A more complete discussion is given by F. G. Bordwell, J. Weinstock, and T. F. Sullivan, *ibid.*, **93**, 4728 (1971).

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Flash Thermolysis. The Reactivity and Infrared Spectrum of Sulfene[1]

Sir:

We have recently reported[2] that flash thermolysis of chlorosulfonylacetic acid ($ClSO_2CH_2COOH$) at 650° gives at least a small amount of sulfene ($CH_2{=}SO_2$) as a volatile intermediate. The transient, formed in the hot zone, reacts with methanol on the cold finger to give methyl methanesulfonate. We now report further

(1) Flash Thermolysis. VII. Organic Sulfur Mechanisms. XI.

(2) J. F. King, P. de Mayo, and D. L. Verdun, *Can. J. Chem.*, **47**, 4509 (1969).

experiments which have allowed us to obtain sulfene at −196°, to observe its infrared spectrum at that temperature, and to follow certain of its reactions. Though the existence of sulfenes as short-lived intermediates has been demonstrated previously,[2,3] this is the first time that evidence has been obtained for a direct observation of any kind on any sulfene.

In the previous experiments[2] a "sandwich" technique was used. Modification of the apparatus has now been made to allow "homogeneous" trapping,[4] by which means, using methanol as the sulfene trap, the yield of methyl methanesulfonate was increased from 2.6 to 40%; at the same time the yield of methanesulfonyl chloride dropped from about 55% to a mere trace.[5] These experiments indicated that, as had been previously suspected,[2] the methanesulfonyl chloride formed in the "sandwich" experiments probably derived from trapping of the sulfene by hydrogen chloride, itself formed in the thermolysis. When hydrogen chloride was bled into the apparatus, a 58–59% yield of methanesulfonyl chloride was obtained. That this material was derived largely (and perhaps entirely) from sulfene was shown by using DCl instead of HCl as the sulfene trap and obtaining CH_2DSO_2Cl as the principal product.[6]

These experiments show that at least 50% of the chlorosulfonylacetic acid is converted to sulfene under these conditions. It therefore appeared worthwhile to examine the infrared spectrum of the thermolysate when trapped on a sodium chloride plate in a cryostat at −196°. The spectrum[7] (Figure 1a) shows bands ascribed to sulfene at 3170, 3040, 1330, 1230, and 950 cm^{-1}; the first two bands are assigned to the $CH_2{=}$ group[8] and the second two appear not unreasonable for the ${=}SO_2$ function. On warming, these bands disappear and are simultaneously replaced by the spectrum of methanesulfonyl chloride (Figures 1b and 1c). This change, which begins around −140° and is complete by −80°, is clearly in full accord with the experiments with DCl described above.

When methanol is deposited (by the "homogeneous" technique[4]) along with the thermolysate, the infrared spectrum shows the characteristic bands at 1330 and 1230 cm^{-1}, the remainder being obscured by the methanol. On warming above −155° these bands begin to disappear and are replaced by the spectrum of methyl methanesulfonate, again, exactly as expected from the earlier experiments.

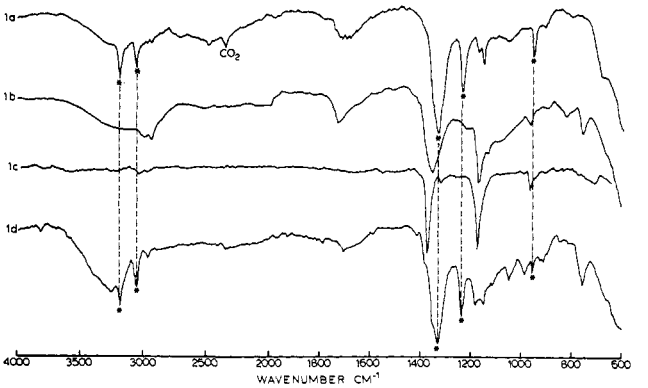

Figure 1. Infrared spectra of (a) the thermolysate from $ClSO_2CH_2COOH$ at −196°, (b) the same material as in (a) after warming to −70°, (c) authentic CH_3SO_2Cl, (d) the thermolysate from $CH_3SO_2OSO_2CH_3$ at −196°. The spectrum of authentic CH_3SO_2Cl was taken at room temperature in $CHCl_3$ solution (with a $CHCl_3$-filled NaCl cell in the reference beam); the other spectra are of the materials as collected on the NaCl plate (no solvent) with only air in the reference beam.

Final evidence that the unstable intermediate being observed in these reactions was indeed sulfene was obtained by thermolysis at 650° (<4 μ) of methanesulfonic anhydride.[9] The infrared spectrum of the thermolysate at −196° (Figure 1d) shows the same characteristic bands as those obtained by the other route.

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(3) (a) For a summary of the earlier evidence see G. Opitz, *Angew. Chem., Int. Ed. Engl.*, **6**, 107 (1967); (b) J. F. King and T. W. S. Lee, *J. Amer. Chem. Soc.*, **91**, 6524 (1969).

(4) In the "homogeneous" technique the trapping reagent is bled into the apparatus at a point between the oven and the cold finger during the thermolysis, thereby giving an intimate mixture of trap and thermolysate on the cold finger.

(5) Yields were determined by distilling the material on the cold finger through a trap at −45° while allowing the cold finger to warm to room temperature. The excess methanol passed through the −45° trap while the methanesulfonyl chloride and methyl methanesulfonate were retained. Control experiments showed that methanesulfonyl chloride and methanol gave no methyl ester under these conditions.

(6) In two runs using DCl (isotopic purity 95%) the methanesulfonyl chloride showed the following composition as estimated by mass spectrometry: CH_3SO_2Cl, 12.6 and 19.9; CH_2DSO_2Cl, 87.4 and 80.1%. No detectable amount (<0.5%) of CHD_2SO_2Cl was present. Presumably at least some of the CH_3SO_2Cl arose from HCl produced in the thermolysis.

(7) In all spectra there was a variable background due to adventitious water and a few peaks presumably deriving from sulfene coupling products; in the previous work the formation of a small amount of presumed sulfene polymer was noted.[2]

(8) *Cf.* diazomethane, 3182 and 3069 cm^{-1} (N_2 matrix at 20°K) (C. B. Moore and G. C. Pimentel, *J. Chem. Phys.*, **38**, 2816 (1963)), and ketene, 3155 and 3062 cm^{-1} (Ar matrix, 20°K) (C. B. Moore and G. C. Pimentel, *ibid.*, **40**, 342 (1964)).

(9) M. H. Karger and Y. Mazur, *J. Org. Chem.*, **36**, 528 (1971). We thank Mr. D. R. K. Harding for calling this paper to our attention and Dr. E. G. Lewars for the specimen of methanesulfonic anhydride.

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Negamycin, a Novel Hydrazide Antibiotic

Sir:

Negamycin is a new antibiotic isolated from the culture filtrate of three strains related to *Streptomyces purpeofuscus*, possessing a strong inhibitory activity against resistant Gram-negative bacteria including *Pseudomonas*.[1] We report herein the structural elucidation and partial synthesis of negamycin, and an interesting novel acid-catalyzed rearrangement of 1-methylhydrazinoacetic acid discovered during the structural study.

Negamycin (**1**) has the formula $C_9H_{20}N_4O_4$ (derived from the high-resolution mass spectrum of di-*N*-acetylnegamycin methyl ester (**2**), mp 157–158°; M^+ = 346.188, calcd for $C_{14}H_{26}O_6N_4$, M^+ = 346.185) and shows: mp 110–120° dec; $[\alpha]^{29}D$ +2.5° (*c* 2, H_2O); pK_a' = 3.55, 8.10, and 9.75; uv end absorption; ir (KBr) 3430, 3200, 3050, 2950, 1660, 1590, 1405, 1320,

(1) M. Hamada, T. Takeuchi, S. Kondo, Y. Ikeda, H. Naganawa, K. Maeda, Y. Okami, and H. Umezawa, *J. Antibiot.*, **23**, 170 (1970).