SYNTHESIS AND PROPERTIES OF SULFOALKENYL AMIDES

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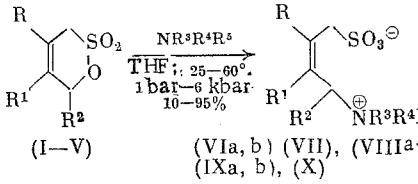
Amines are known to undergo sulfoalkylation on treatment with sultones, to give sulfobetaines [1]. Some of these have found applications as surfactants [2] and buffers [3] for biological studies, and some sultams obtained from these salts have displayed interesting pharmacological properties [4]. We here describe for the first time the sulfoalkenylation of a number of amines at normal and elevated pressure, using the β,γ-unsaturated δ-sultones (I)-(V) previously obtained by us [5], and discuss some properties of the betaines (VI)-(X) thus obtained.

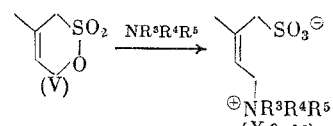
The cyclic allyl sulfonates (I)-(V) were generally reactive in Menshutkin-type reactions, being readily converted in THF at 25-60°C on treatment with ammonia, primary, secondary, and tertiary aliphatic, alicyclic, araliphatic, (hetero)aromatic, heterocyclic and other functionally substituted amines into the corresponding δ-aminosulfonic acids (VI)-(X).



(I—V) (VIa, b) (VII), (VIIIa-e), (IXa, b), (X)

R = R¹ = R² = H (I), (VI); R = R¹ = H, R² = Me (II), (VII); R² = H, R = R¹ = Me (III), (VIII); R¹ = R² = H, R = $Me_2C=CHCH_2CH_2$ (IV), (IX); R¹ = R² = H, R = Me (V), (X). $NR^3R^4R^5 = H_2NC_6H_{11}$ (VIa), (VIIIa); H_2NCH_2Ph (VII), (VIIIб), (IXa); $HN(CH_2)_4$ (VIIIc); $HN(CH_2)_5$ (VIIId); $HN(CH_2)_4O$ (VIIIe); $N(CH_2CH_2OH)_3$ (IXb); NC_5H_5 (VIb).

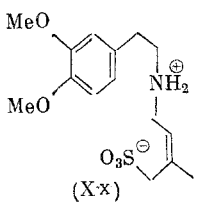
Thus, treatment of butadiene (I), piperylene (II), 2, 3-dimethylbutadiene (III) and myrcene sultones (IV) with cyclohexyl- or benzylamine at 50-60°C and atmospheric pressure for 40-50 h gave the internal salts (IVa), (VII), (VIIIa and b), and (IXa) in 30-90% yields. Noteworthy also is the extremely smooth sulfobutenylation of pyridine (25°C, 1 h, 55%) with butadiene cyclosulfonate (I) to give the betaine (VIb)



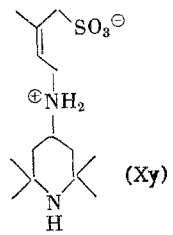
(V) (X a-w)

$NR^3R^4R^5 = NH_3$ (a); $H_2NC_{18}H_{37}$-*n* (b); H_2NCH_2Ad (c); $H_2NCHMeAd$ (d); $H_2NCHEtAd$ (e); H_2NAd (f); $H_2NC_6H_{11}$ (g); $H_2NCH_2CH=CMe_2$ (h); E — $H_2NCH_2CH=CMe(CH_2)_2CH=CMe_2$ (i); $H_2NC(CH_2OH)_3$ (j); $H_2NCH_2CHMePh$ (k); H_2NCH_2Ph (*l*); H_2NPh (m); $HNMe_2$ (n); $HN(CH_2)_4$ (o); $HN(CH_2)_5$ (p); $HN(CH_2)_4O$ (q); $HN(CH_2)_4NH$ (r) *; $HN(CH_2)_4N(CH_2)_2OH$ (s) †; imidazole (t); NEt_3 (u); $N(CH_2CH_2OH)_3$ (v); NC_5H_5 (w).
Ad = 1-adamantyl

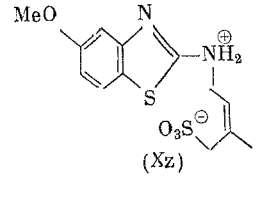
The data for 23 compounds of different types (Xa-w) given in Table 1, together with those for salts (Xx-aa) obtained from the sultone (V), show that virtually any amines can be sulfopyrenylated. The results show that when two nitrogen atoms are present in the molecule, the less substituted one is preferentially alkylated by sultone (V) (cf. Xs, y), indicating that the reaction is sensitive to steric factors. In agreement with this, the high resolution PMR spectra of (Xy) and 4-amino-2,2,6,6-tetramethylpiperidine under the same conditions of measurement (CF_3COOH) do not show any significant changes in the shape of the signals for the Me_2CNCMe_2 moiety, and no relative distortion for the CH_2CHCH_2 group is observed. As to the



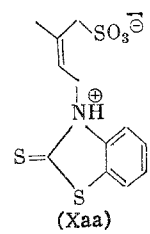
(Xx)



(Xy)



(Xz)



(Xaa)

*Only the monosulfoprenyl derivative was formed.
†Sulfoprenylation occurred only at the secondary nitrogen.

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TABLE 1. Conditions of Preparation of Internal Salts of 4-Amino-2-methylbut-2Z-ene-1-sulfonic Acid (Xa-t), 5-Ammonio-2-methylbut-2Z-ene-1-sulfonates (Xu-w) from Sultone (V) in THF at 1 bar, and Some of Their Properties

(X)	Reaction conditions		Yield, %	mp, °C (decomp), MeOH–ether	Empirical formula	Found/Calculated, %			
	T., °C	time, h				C	H	N	S
a	25	240	15	275–280	$C_5H_{11}NO_3S$	36,30 36,35	6,80 6,71	8,56 8,48	19,60 19,41
b	55	60	65	212–217	$C_{23}H_{47}NO_3S$	66,47 66,14	11,27 11,34	3,35 3,35	7,60 7,67
c	55	45	55	321–324	$C_{16}H_{27}NO_3S$	61,40 61,31	8,97 8,68	4,43 4,47	10,08 10,22
d	55	20	75	309–314	$C_{17}H_{29}NO_3S$	62,18 62,35	8,99 8,92	4,23 4,27	9,54 9,79
e	55	20	80	296–297	$C_{18}H_{31}NO_3S$	63,28 63,30	9,02 9,15	4,15 4,10	9,35 9,39
f	60	60	80	318–320	$C_{15}H_{25}NO_3S$	59,87 60,17	8,58 8,42	4,68 4,68	10,62 10,70
g	40	10	80	290–294	$C_{11}H_{21}NO_3S$	53,41 53,41	8,61 8,56	5,79 5,66	12,78 12,96
h	60	45	40	237–239	$C_{10}H_{19}NO_3S$	51,51 51,47	8,19 8,21	6,02 6,00	13,71 13,74
i	60	90	20	218–220	$C_{15}H_{27}NO_3S$	59,81 59,76	9,00 9,03	4,69 4,65	10,68 10,64
j *	50	100	10	235–238	$C_9H_{19}NO_6S$	40,32 40,16	6,98 7,10	5,01 5,20	11,98 11,90
k	55	50	65	241–244	$C_{14}H_{21}NO_3S$	59,25 59,33	7,40 7,47	5,00 4 97	11,13 11,31
l	60	50	85	288–291	$C_{12}H_{17}NO_3S$	56,50 56,45	6,90 6,71	5,50 5,49	12,29 12,56
m	25	50	75	233–237	$C_{11}H_{15}NO_3S$	55,10 54,75	6,25 6,26	6,15 5,80	13,46 13,29
n	25	240	55	241–242	$C_7H_{15}NO_3S$	43,41 43,50	7,79 7,82	6,90 7,25	16,59 16,59
o	40	20	70	211–213	$C_9H_{17}NO_3S$	49,26 49,29	7,88 7,81	6,38 6,39	14,57 14,62
p	55	20	90	278–280	$C_{10}H_{19}NO_3S$	51,51 51,47	8,19 8,21	6,35 6,00	13,66 13,74
q	55	10	92	285–287	$C_9H_{17}NO_4S$	45,62 45,94	7,09 7,28	5,59 5,95	13,73 13,63
r	55	20	80	224–227	$C_9H_{18}N_2O_3S$	45,74 46,13	7,75 7,74	11,90 11,96	13,69 13,68
s	55	30	80	228–230	$C_{11}H_{22}N_2O_4S$	47,41 47,46	7,86 7,96	10,16 10,06	11,55 11,52
t	40	10	92	267–270	$C_8H_{12}N_2O_3S$	44,38 44,43	5,49 5,59	12,97 12,95	15,04 14,83
u	55	50	35	210–213	$C_{11}H_{23}NO_3S$	53,07 52,98	9,55 9,30	5,63 5,62	13,10 12,86
v	25	170	7	200–205	$C_{11}H_{23}NO_6S$	44,60 44,43	7,92 7,80	4,55 4,71	10,84 10,78
w	25	80	3	198–200	$C_{10}H_{13}NO_3S$	53,01 52,85	5,64 5,76	6,21 6,16	13,91 14,10

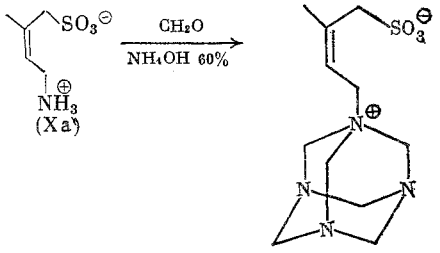
*Im DmF.

possibility of this reaction occurring at other centers, such as the sulfur atom in the precursors of salts (Xz) and (Xaa), this is excluded by the IR spectra of these salts, which contain strong absorption for C=N (1645 cm^{-1}, which is also present in the original amine) and C=S (1145 cm^{-1}) respectively.

It is noteworthy that the method of preparation of betaines (VI)-(X) described in [6] failed only in the sulfoalkylation of urotropin, as a result of its low solubility in aprotic solvents, in which the cyclic sulfonates (I)-(V) are stable [5]. In this connection, one of the salts (Xab) was obtained from the aminosulfonate (Xa) by a method described perviously [7] for other primary ammonium salts.

The structures of (VI)-(X) were confirmed by their elemental and spectral analyses. The Z-geometry of their sulfonatoalkenyl chains, present in the original sultones (I)-(V), is not affected, as shown by the constancy of the chemical shifts for CH_2S (δ 3.6-3.8 and 3.8-4.0 ppm) and CH_2N (δ 3.7-5.3 and 3.9-4.8 ppm) in the substituted Z-butenyl moeity, in the PMR spectra of (VI), (VIII)-(X), measured in solution in CD_3OD and CF_3COOH respectively. Z-Stereochemistry was assigned to the piperylene derivative (VII) by analogy.

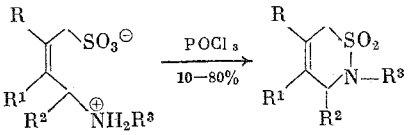
The sensitivity of this Menshutkin-type reaction to steric factors has been mentioned above in the case of (Xy), and this is consistent with the low yields (2-5%) of (VIIId) and (VIIIe) in the alkylation of piperidine or morpholine respectively with 2,3-dimethylbutadiene sultone (III) (1 bar, 20-60°C, 50-170 h), in contrast to the almost quantitative yields from the same sultone of the cyclohexyl (VIIIa) and benzylammonium (VIIIb) salts (1 bar, 60°C,



(Xab)

40-50 h). In addition the data presented in the table very clearly indicate the reduction in the efficiency of sulfoprenylation of amines as their nucleophilicity decreases. For example, under comparable conditions the yields of the triethanolammonium (Xv) and pyridinium (Xw) salts at atmospheric pressure are only 3-7%, as compared with 35% for the triethylammonium derivative (Xu). In order to increase the yields of these betaines, the pressure was raised. These reactions evidently occur by an S_N2 mechanism via a polar transition state, and must therefore possess a high negative $\Delta V^{\neq}$ value, with the result that reactions of this type are greatly accelerated by pressure [8]. It was in fact found that the sulfoalkenylation of such widely varied amines as piperidine, morpholine, triethanolamine, and pyridine proceeds at a pressure of 6 kbar, giving after 6 h at 60°C the corresponding sulfobetaines (VIIId, e), (IXb), and (Xv, w) in 75-97% yields.

All the salts mentioned here (VI-X) are high-melting, crystalline solids which are readily soluble in water and somewhat less so in the lower alcohols. As far as their chemical properties are concerned, their greatest interest appears to reside in the possibility of converting the primary compounds into the corresponding saltams by treatment with $POCl_3$ [1]. This method was used to obtain nine cyclic sulfonamides (XI), (XII), (XIIIa,b), (XIVa-e) from the corresponding salts (VIa), (VII), (VIIIa, b), (Xc, g, h, *l*, x) in 10-80% yields. The



(VIa), (VII), (VIIIa, b), (Xc, g, h, *l*, x) — (XI), (XII), (XIII a, b), (XIV(a-e)

R = R^1 = R^2 = H, R^3 = C_6H_{11} (XI); R = R^1 = H, R^2 = Me, R^3 = CH_2Ph (XII); R^2 = H, R = R^1 = Me, R^3 = C_6H_{11} (XIIIa); R^2 = H, R = R^1 = Me, R^3 = CH_2Ph (XIIIb); R^1 = = R^2 = H, R = Me, R^3 = CH_2Ad (XIVa); R^1 = R^2 = H, R = Me, R^3 = C_6H_{11} (XIVb); R^1 = R^2 = H, R = Me, R^3 = CH_2CH = CMe_2 (XIVc); R^1 = R^2 = H, R = Me, R^3 = CH_2Ph (XIVd); R^1 = R^2 = H, R = Me, R^3 = $(CH_2)_2C_6H_3(OMe)_2$-*m*, *p* (XIVe), Ad = 1-adamantyl

structures of sultams (XI)-(XIV) were confirmed by their elemental and spectral analyses. In particular, their PMR spectra contained signals for the protons of all the structural fragments of their molecules in the expected regions, including the HC=C signals for (XIVa-e) at δ 5.4 ppm. This reaction also supports the Z-geometry of the internal salts, demonstrating simultaneously the possibility of using the sultones (I)-(V) to synthesize a variety of functionally substituted organic compounds.

EXPERIMENTAL

Melting points were determined on a Kofler block. IR spectra were obtained on a UR-20 apparatus in KBr (for VI-X) and $CHCl_3$ (for XI-XIV). PMR spectra were measured relative to TMS on a Varian DA-60-IL or Tesla BS-497 (100 MHz) spectrometer, sultams (XI)-(XIV) being

dissolved in $CDCl_3$. Mass spectra were obtained at an ionizing voltage of 70 eV on a Varian MAT-CH-6 spectrometer. R_f values are given for bound layers of Silufol SiO_2 or Woelm alumina.

The prenylamine starting material for (Xh) was obtained as described in [9]. Geranylamine [10] for the synthesis of (Xi) was obtained in 30% yield by the reduction of geranial oxime [11] with $LiAlH_4$.

Internal Salt of 4-Cyclohexylaminobut-2Z-en-1-sulfonic Acid (VIa). A solution of 1 g (7.5 mmole) of (I) and 0.9 ml (740 mg, 7.5 mmole) of cyclohexylamine in 20 ml of THF was heated for 50 h at 50°C. The solid which separated was filtered off, washed with ether, and crytallized from methanol–ether to give 520 mg (30%) of (VIa) as colorless prisms, mp 227.5-228°C (decomp.). IR spectrum (ν, cm^{-1}): 728, 1035, 1142, 1163, 1190, 1218, 1255, 1457, 1480, 1610, 2800-3450. PMR spectrum (CD_3OD, δ, ppm): 1.4-2.3 m (10H, CH_2), 3.05m (1H, CHN), 3.65 m (2H, CH_2S), 3.71 m (2H, CH_3N), 5.93 m (2H, HC=CH). Found: C 51.13; H 8.13; N 6.33; S 13.66%. $C_{10}H_{19}NO_3S$. Calculated: C 51.47; H 8.21; N 6.00; S 13.74%.

4-Pyridinio-2Z-ene-1-sulfonate (VIb). Similarly, from 1 g (7.5 mmole) of (I) and 0.6 ml (7.5 mmole) of pyridine in 20 ml of THF at 25°C for 1 h there was obtained 790 mg (55%) of (VIb), mp 240-245°C (decomp.) (MeOH–ether). IR spectrum (ν, cm^{-1}): 620, 690, 1045, 1165, 1190, 1220, 1490, 1630, 3060, 3450. PMR spectrum (CD_3OD, δ, ppm): 3.60 d (J = 6 Hz, 2H, CH_2S), 5.32 d (J = 5.5 Hz, 2H, CH_2N), 6.0-6.3 m (2H, HC=CH), and 8.0-9.2 m (5H, C_5H_5N). Found: C 50.63; H 5.22; N 6.38; S 14.84%. $C_9H_{11}NO_3S$. Calculated: C 50.69; H 5.20; N 6.57; S 15.03%.

Internal Salt of 4-Benzylaminopent-2Z-ene-1-sulfonic Acid (VII). A solution of 2.6 g (17.5 mmole) of (II) and 2.1 ml (2.06 g, 19.2 mmole) of benzylamine in 30 ml of THF was heated for 50 h at 50°C, the solid filtered off, washed with ether, and crystallized from methanol–ether to give 2.2 g (50%) of (VII) as colorless needles, mp 312-314°C (decomp.). IR spectrum (ν, cm^{-1}): 730, 1043, 1160, 1170, 1197, 1215, 1255, 1450, 1455, 1600, 2800-3450. PMR spectrum (CF_3COOH, δ, ppm): 1.46 d (J = 6.5 Hz, 3H, CH_3), 3.6-4.6 m (5H, CH_2Ph, CHN, CH_2S), 5.80 m (2H, CH=CH), 7.26 m (5H, C_6H_5). Found: C 56.66; H 6.79; N 5.63; S 12.69%. $C_{12}H_{17}NO_3S$. Calculated: C 56.45; H 6.71; N 5.49; S 12.56%.

Internal Salt of 4-Cyclohexylamino-2,3-dimethylbut-2Z-ene-1-sulfonic Acid. (VIIIa). A solution of 0.5 g (3.1 mmole) of (III) and 0.4 ml (330 mg, 3.3 mmole) of cyclohexylamine in 20 ml of THF was heated for 50 h at 60°C, the solid filtered off, washed with ether, and crytallized from methanol–ether to give 770 mg (92%) of (VIIIa) as colorless needles, mp 300-305°C (decomp.) (methanol–ether). IR spectrum (ν, cm^{-1}): 765, 1030, 1130, 1220, 1455, 1620, 2455, 2600, 2770-3100. PMR spectrum (CD_3OD, δ, ppm): 1.0-2.2 m (10H, CH_2), 1.93 br.s (6H, CH_3), 3.05 m (1H, CHN), 3.69 m (4H, CH_2N, CH_2S). Found: C 55.10; H 8.88; N 5.28; S 12.15%. $C_{12}H_{23}NO_3S$. Calculated: C 55.14; H 8.87; N 5.36; S 12.27%.

Internal Salt of 4-Benzylamino-2,3-dimethylbut-2Z-ene-1-sulfonic Acid (VIIIb). Similarly, from 1 g (6.2 mmole) of (III) and 0.75 ml (740 g, 6.9 mmole) of benzylamine in 10 ml of THF at 60°C for 40 h there was obtained 1.5 g (90%) of (VIIIb) as colorless needles, mp 305-306°C (decomp.) (methanol–ether). IR spectrum (ν, cm^{-1}): 773, 1040, 1150, 1168, 1195, 1226, 1455, 1480, 1610, 2800-3450. PMR spectrum (CF_3COOH, δ, ppm): 1.86 s, 1.91 s (6H, CH_3), 3.75m (4H, CH_2S, CH_2N), 4.23 (2H, CH_2Ph), 7.43 s (5H, C_6H_5). Found: C 58.18; H 7.26; N 5.32; S 11.86%. $C_{12}H_{19}NO_3S$. Calculated: C 57.97; H 7.11; N 5.20; S 11.90%.

Internal Salt of 4-Pyrrolidino-2,3-dimethylbut-2Z-ene-1-sulfonic Acid (VIIIc). Similarly, from 440 mg (2.7 mmole) of (III) and 0.27 ml (230 mg, 2.8 mmole) of pyrrolidine in 20 ml of THF at 60°C for 15 h, there was obtained 420 mg (73%) of (VIIIc) as colorless needles, mp 290-293°C (decomp.) (methanol–ether). IR spectrum (ν, cm^{-1}): 775, 950, 1030, 1140, 1170, 1210, 1250, 1450, 1500, 2590, 2690, 2865, 2930, 2955, 3000, 3420-3490. PMR spectrum (CF_3COOH, δ, ppm): 2.01 br.s. (6H, CH_3), 2.2 m (8H, CH_2), 4.0 m (4H, CH_2N, CH_2S). Found: C 51.44; H 8.27; N 6.27; S 13.53%. $C_{10}H_{19}NO_3S$. Calculated: C 51.47; H 8.21; N 6.00; S 13.74%.

Internal Salt of 4-Piperidino-2,3-dimethylbut-2Z-ene-1-sulfonic Acid (VIIId). Similarly, from 1.62 g (10 mmole) of (III) and 1.2 ml (1.0 g, 12 mmole) of piperidine in 15 ml of THF at 25°C for 150 h there was obtained 40 mg (~2%) of (VIIId) as colorless prisms, mp 311-314°C (decomp.) (methanol–ether). IR spectrum (ν, cm^{-1}): 770, 950, 1030, 1140, 1180, 1210, 1440, 1500, 2590, 2695, 2830, 2855, 3420-3480. PMR spectrum (CD_3OD, δ, ppm): 1.90 m and 3.40 m (10H, CH_2), 2.06 br.s. (6H, CH_3), 3.90 m (4H, CH_2N, CH_2S). Found: C 53.44; H 8.70; N 5.49; S 12.85% $C_{11}H_{21}NO_3S$. Calculated: C 53.41; H 8.56; N 5.66; S 12.96%.

Internal Salt of 4-Morpholino-2,3-dimethylbut-2Z-ene-1-sulfonic Acid (VIIIe). Similarly, from 1 g (6.2 mmole) of (III) and 0.6 ml (679 mg, 7.7 mmole) of morpholine in 40 ml of

THF at 60°C for 50 h there was obtained 50 mg (~5%) of (VIIIe) as colorless prisms, mp 293-295°C (decomp.) (methanol—ether). IR spectrum (ν, cm^{-1}): 770, 865, 930, 1120-1220, 1460, 2480-2700, 2880, 2990, 3400. PMR spectrum (CD_3OD, δ, ppm): 1.68 br.s. (6H, CH_3), 3.1-3.9 m (12H, CH_2). Found: C 47.97; H 7.90; N 5.33; S 12.69%. $C_{10}H_{19}NO_4S$. Calculated: C 48.17; H 7.69; N 5.62; S 12.86%.

Internal Salt of 4-Benzylamino-2-(4'-methylpent-3'-en)ylbut-2Z-ene-1-sulfonic Acid (IXa). Similarly, from 680 mg (3.14 mmole) of (IV) and 0.35 ml (340 mg, 3.14 mmole) of benzylamine in 15 ml of THF at 55°C for 45 h there was obtained 610 mg (60%) of (IXa) as colorless plates, mp 271-274°C (decomp.) (methanol—ether). IR spectrum (ν, cm^{-1}): 690, 750, 1040, 1165, 1220, 1480, 1620, 2770-3040. PMR spectrum (CD_3OD, δ, ppm): 1.60 s and 1.65 s (6H, CH_3), 2.0-2.5 m (4H, $CH_2C{=}C$), 3.70 m (4H, CH_2N), 4.14 br.s. (2H, CH_2S), 5.09 br.t. (J = 7.5 Hz, 1H, $HC^{3'}$), 5.60 t (J = 7 Hz, 1H, HC^3), 7.42 m (5H, C_6H_5). Found: C 63.06; H 7.89; N 4.51; S 9.81%. $C_{17}H_{25}NO_3S$. Calculated: C 63.12; H 7.79; N 4.33; S 9.91%.

4-(Tri-β-hydroxyethyl)ammonio-2-(4'-methylpent-3'-en)ylbut-2Z-ene-1-sulfonate (IXb). Similarly, from 0.7 g (3.24 mmole) of (IV) and 480 mg (3.2 mmole) of triethanolamine in 15 ml of THF at 25°C for 180 h there was obtained 30 mg (~2%) of (IXb) as colorless needles, mp 116-119°C (decomp.) (methanol—ether). IR spectrum (ν, cm^{-1}): 940, 1040, 1185, 1450, 2850-2980, 3390. PMR spectrum (CD_3OD, δ, ppm): 1.60 s and 1.65 s (6H, CH_3), 2.0-2.5 m (4H, $CH_2C{=}C$), 3.60 br.s. (2H, CH_2S), 3.64 m (6H, CH_2N), 3.94 m (6H, CH_2O, 4.32 br.d. (J = 7.5 Hz, 2H, HC^4), 5.04 br.t. (J = 7.5 Hz, 1H, $HC^{3'}$), 5.67 br.t. (J = 7.5 Hz, 1H, HC_3). Found: C 52.57; H 8.60; N 3.58; S 8.98%. $C_{18}H_{31}NO_6S$. Calculated: C 52.58; H 8.55; N 3.63; S 8.77%.

Internal Salt of 4-Amino-2-methylbut-2Z-ene-1-sulfonic Acid (Xa). A solution of 0.2 g (12 mmole) of NH_3 and 1.5 g (10 mmole) of (V) in 30 ml THF was kept at 25°C for 10 days, the solid filtered off, washed with THF and ether, and crystallized from methanol—ether to give 230 ml (15%) of (Xa) as colorless needles, mp 275-280°C (decomp.), (methanol—ether). IR spectrum (ν, cm^{-1}): 675, 760, 865, 880, 925, 1000, 1040, 1120, 1200, 1490, 1625, 2990, 3080-3170. PMR spectrum (CD_3OD, δ, ppm): 2.02 br.s. (3H, CH_3), 3.72 br.d., (J = 7 Hz, 2H, CH_2N), 3.82 br.s. (2H, CH_2S), 5.71 br.t. (J = 7 Hz, 1H, HC^3). Found: C 36.30; H 6.80; N 8.56; S 19.60%. $C_5H_{11}NO_3S$. Calculated: C 36.35; H 6.71; N 8.48; S 19.41%.

Internal Salt of 4-Octadecylamino-2-methylbut-2Z-ene-1-sulfonic Acid (Xb). A solution of 1.28 g (8.65 mmole) of (V) and 2.32 g (8.65 mmole) of octadecylamine in 30 ml of THF was heated at 55°C for 60 h, the solid filtered off, washed with ether, and crystallized from methanol—ether to give 2.4 g (65%) of (Xb) as colorless needles, mp 212-217°C (decomp.) (methanol—ether). IR spectrum (ν, cm^{-1}): 765, 1040, 1160, 1215, 1470, 2855, 2930. PMR spectrum (CF_3COOH, δ, ppm): 0.8 t (J = 6 Hz, 3H, CH_3), 1.35 m (32H, CH_2), 1.98 br.s. (3H, CH_3—C^2), 3.10 m (2H, CH_2N), 3.95 m (4H, HC^1, HC^4), 5.76 br.t. (J = 7.5 Hz, 1H, HC^3). Found: C 66.47; H 11.27; N 3.35; S 7.60%. $C_{22}H_{47}NO_3S$. Calculated: C 66.14; H 11.34; N 3.35; S 7.67%.

The remaining salts (Xc-w) listed in the Table 1 were obtained exactly as described above. using approximately equimolar amounts of the sultone (V) (0.5-1.0 g) and the appropriate amines in 20-30 ml of THF under the conditions given.

Internal Salt of 4-[β-(3',4'-Dimethoxyphenyl)ethyl]amino-2-methylbut-2Z-ene-1-sulfonic Acid (Xx). Similarly, from 1 g (6.75 mmole of (V) and 1.2 g (6.64 mmole) of 3,4-dimethoxy-β-phenylethylamine [12] in 20 ml of THF at 55°C for 20 h there was obtained 3.25 g (50%) of (XIII) as a colorless powder, mp 222-223°C (decomp.) (methanol—ether). IR spectrum (ν, cm^{-1}) 550, 685, 768, 1040, 1145-1270, 1480, 1520, 1600, 2835-3010. PMR spectrum (CF_3COOH, δ, ppm): 2.02 br.s. (3H, CH_3), 2.98 m (2H, CH_2N), 3.42 m (2H, CH_2Ar), 3.80 m (10H, HC^1, HC^4, CH_3O,) 5.77 br.t. (J = 7 Hz, 1H, HC^3), 6.80 m (3H, C_6H_3). Found: C 54.65; H 7.07; N 4.27; S 9.76%. $C_{15}H_{23}NO_5S$. Calculated: C 54.69; H 7.04; N 4.25; S 9.73%.

Internal Salt of 4-(2',2',6',6'-Tetramethylpiperid-4'-yl)amino-2-methylbut-2Z-ene-1-sulfonic Acid (Xy). Similarly, from 590 mg (4.0 mmole) of (V) and 620 mg (3.8 mmole) of 2,2,6,6-tetramethylpiperidine [13] in 15 ml of THF at 55°C for 10 h there was obtained 0.9 g (75%) of (Xy) as a colorless powder, mp 262-267°C (decomp.) (methanol—ether). IR spectrum (ν, cm^{-1}): 765, 1030, 1165, 1245, 1380, 1480, 1615, 2840, 2975, 3420-3515. PMR spectrum (CF_3COOH, δ, ppm): 1.65 br.s. and 1.70 br.s. (12H, CH_3), 2.14 br.s (3H, CH_3—C^2), 2.43 m (4H, CH_2CHCH_2), 4.05 m (5H° HCN, HC^1, HC^4), 5.88 br.t. (J = 7.5 Hz, 1H, HC^3). Found: C 55.34; H 9.22; N 9.08; S 10.68%. $C_{14}H_{28}H_2O_3S$. Calculated: C 55.23; H 9.27; N 9.20; S 10.53%.

Internal Salt of 4-(5'-Methoxybenzothiazol-2'-yl)amino-2-methylbut-2Z-ene-1-sulfonic Acid (Xz). Similarly, from 430 mg (3 mmole) of (V) and 540 mg (3 mmole) of 2-amino-5-methoxybenzo-

thiazole in 15 ml of THF at 55°C for 160 h there was obtained 0.5 g (50%) of (Xz) as a bright yellow powder, mp 268-273°C (decomp.) (methanol—ether). IR spectrum (ν, cm^{-1}): 650, 755, 1030, 1140, 1170, 1230, 1320, 1445, 1495, 1590, 1645, 2950-3245. PMR spectrum (CF_3COOH, δ, ppm): 1.71 br.s. (3H, CH_3), 3.57 s (3H, CH_3O), 3.80 br.s. (2H, CH_2S), 4.80 br.d. (J = 7 Hz, 2H, CH_2N), 5.11 br.t. (J = 7 Hz, 1H, CH^3), 7.00 m (3H, C_6H_3). Found: C 47.12; H 5.00; N 8.58; S 19.28%. $C_{13}H_{16}N_2O_4S_2$. Calculated: C 47.54; H 4.9; N 8.53; S 19.52%.

Internal Salt of 4-(2'-Thiono-2',3'-dihydrobenzothiazol-3'-yl)-2-methylbut-2Z-ene-1-sulfonic Acid (Xaa). Similarly, from 0.4 g (2.7 mmole) of (V) and 450 mg (2.7 mmole) of 2-mercaptobenzothiazole in 15 ml of THF at 55°C for 120 h there was obtained 380 mg (45%) of (Xaa) as bright yellow prisms, mp 165-167°C (decomp.) (methanol—ether). IR spectrum (ν, cm^{-1}): 650, 765, 1030, 1155, 1228, 1445, 1530, 1670, 2860-2980, 3440-3520. PMR spectrum (CF_3COOH, δ, ppm): 1.98 br.s. (3H, CH_3), 4.06 br.s. (2H, CH_2S), 4.34 br.s. (J = 7 Hz, 2H, CH_2N), 6.52 br.t. (J = 7 Hz, 1H, HC^3), 7.6-8.0 m (4H, C_6H_4). Found: C 45.78; H 4.07; N 4.50; S 30.51%. $C_{12}H_{13}NO_3S_3$. Calculated: C 45.69; H 4.15; N 4.44; S 30.49%.

Synthesis of Salts (VIIId, e), (IXb), and (Xv, w) at a Pressure of 6 kbar (60°C, 6 h). A solution of 1.62 g (10 mmole) of (III) and 1.2 ml (1.0 g, 12 mmole) of piperidine in 15 ml of THF was kept under the above conditions in a Teflon ampul placed in a thermostatted-pressure vessel. The resulting product was filtered off, washed with ether, and crystallized from methanol—ether to give 2.35 g (95%) of (VIIId), mp 311-314°C (decomp.), identical (IR, PMR, mixed melting point) with the sample of (VIIId) described above.

Similarly, 1 g (6.2 mmole) of (III) and 0.6 ml (670 mg, 7.7 mmole) of morpholine afforded 1.3 g (85%) of (VIIIe), mp 293-295°C, identical with the sample of (VIIIe) described above.

Similarly, 0.7 g (3.24 mmole) of (IV) and 480 mg (3.2 mmole) of triethanolamine afforded 660 mg (75%) of (IXb), mp 116-119°C (decomp.), identical with the sample of (IXb) described above.

4-(Tri-β-hydroxyethyl)ammonio-2-methylbut-2Z-ene-1-sulfonate (Xv) was obtained (3.7 g, 92%) similarly from 2 g (13.5 mmole) of (V) and 2.2 ml (2.5 g, 16.5 mmole) of triethanolamine, as colorless needles, mp 200-205°C (decomp.) (methanol—ether). IR spectrum (ν, cm^{-1}): 670, 935, 1040, 1195, 1450, 3350. PMR spectrum (CD_3OD), δ, ppm): 2.00 br.s. (3H, CH_3), 3.2-4.3 m (16H, CH_2), 5.72 t (J = 7 Hz, 1H, HC^3). The elemental analysis is given in Table 1.

4-Pyridinio-2-methylbut-2Z-ene-1-sulfonate (Xw) was obtained (0.9 g, 97%) similarly from 0.6 g (4.0 mmole) of (V) and 350 mg (4.5 mmole) of pyridine, as colorless needles, mp 198-200°C (decomp.) (methanol—ether). IR spectrum (ν, cm^{-1}): 660, 780, 865, 1030, 1120, 1180, 1210, 1265, 1460, 2480, 2590, 2610, 2870, 2990, 3480. PMR spectrum (CD_3OD, δ, ppm): 1.94 br.s. (3H, CH_3), 3.77 s (2H, CH_2S), 5.19 d (J = 7 Hz, 2H, CH_2N), 5.65 t (J = 7 Hz, 1H, HC^3), 7.9-8.7 m (5H, C_6H_5N). The elemental analysis is given in Table 1.

1-(1'-Sulfonato-2'-methylbut-2'Z-en-4'yl)-3,5,7-thiaza-1-azoniatricyclo[3.3.1.$1^{3,7}$]decane (Xbb). To a stirred solution of 4.4 g of (Xa) in 40 ml of methanol at 25°C were added simultaneously 20 ml of 30% formalin and 20 ml of 25% NH_4OH. The solid which separated was filtered off, washed with THF, and crystallized from methanol—ether to give 4.4 g (60%) of (Xbb) as colorless prisms, mp 210-212°C (decomp.). IR spectrum (ν, cm^{-1}): 765, 1040, 1165, 1225, 1265, 1370, 1485, 1620, 2845, 2900, 3030. PMR spectrum (CF_3COOH, δ, ppm): 2.14 br.s. (3H, CH_3), 3.8-4.2 (4H, HC^1, $HC^{4'}$), 4.9-5.6 (12H, CH_2), 6.94 t (J = 6 Hz, 1H, $HC^{3'}$). Found: C 44.84; H 6.97; N 19.48; S 11.06%. $C_{11}H_{20}N_4O_3S$. Calculated: C 44.90; H 6.95; N 19.45; S 11.02%.

2-Cyclohexyl-3,6-dihydro-2H-1,2-thiazine 1,1-Dioxide (XI). A suspension of 720 mg of (VIa) in 5 ml of $POCl_3$ was stirred at 0°C for 40 min, and the resulting solution was evaporated in vacuo at 25°C. The residue was treated with ether, the ether solution neutralized with $NaHCO_3$, washed with water, and dried over $MgSO_4$. The residue (170 mg) after removal of the solvent was chromatographed on a plate (13 × 18 cm) with an unbound layer (2 mm) of silica in the system ether—hexane (1:1). From the zone with R_f 0.6-0.7 there was isolated 60 mg (10%) of (XI) as a colorless, viscous oil, R_f 0.65 (solufol, ether—hexane, 1:1). IR spectrum (ν, cm^{-1}): 1080, 1113, 1172, 1290, 1370, 1455. PMR spectrum (δ, ppm): 1.3-2.3 m (10H, CH_2), 3.7-3.9 m (5H, CH_2NCH, CH_2S), 5.83 m (2H, CH=CH). Found: M^+ 215. $C_{10}H_{17}NO_2S$. Calculated: mol. wt. 215.3.

3-Methyl-2-benzyl-3,6-dihydro-2H-1,2-thiazine 1,1-Dioxide (XII). Similarly, from 1.1 g of (VII) and 10 ml of $POCl_3$ at 60°C for 45 min there was obtained 0.9 g of product which was chromatographed on 50 g of alumina (200-250 mesh, activity grade I-II) under nitrogen.

Gradient elution from hexane to ether (up to 80% of the latter) gave 150 mg (15%) of (XII) as a colorless, viscous oil, R_f 0.39 (Woeln, ether–hexane, 3:2). IR spectrum (ν, cm^{-1}): 1067, 1140, 1165, 1330, 1358, 1450. PMR spectrum (δ, ppm): 1.30 d (J = 7.5 Hz, 3H, CH_3), 3.59 m (2H, CH_2S), 4.35 s (2H, CH_2N), 5.05 m (1H, CHN), 5.66 m (2H, HC=CH), 7.28 m (5H, C_6H_5). Found: M^+ 237. $C_{12}H_{15}NO_2S$. Calculated: mol. wt. 237.3.

4,5-Dimethyl-2-cyclohexyl-3,6-dihydro-2H-1,2-thiazine 1,1-Dioxide (XIIIa). Similarly, from 1.05 g of (VIIIa) in 10 ml of $POCl_3$ at 60°C for 30 min there was obtained 1 g of product which was chromatographed on 50 g of alumina (200–250 mesh, activity grade I–II) under nitrogen. Gradient elution from hexane to ether (up to 70% of the latter) gave 780 mg (80%) of (XIIIa) as colorless needles, mp 102–103°C (ether–hexane). IR spectrum (ν, cm^{-1}): 830, 870, 1010, 1130, 1170, 1285, 1330, 1350, 1450, 2865, 2940. PMR spectrum (δ, ppm): 1.68 br.s (6 H, CH_3), 1.1–2.1 m(10H, CH_2), 3.37 br.s (2H, CH_2S), 3.61 br.s (2H, CH_2N), 3.80 m (1H, HCN). Found: C 59.41; H 8.75; N 5.76; S 13.28%. $C_{12}H_{21}NO_2S$. Calculated: C 59.22; H 8.70; N 5.76; S 13.18%.

4,5-Dimethyl-2-benzyl-3,6-dihydro-2H-1,2-thiazine 1,1-Dioxide (XIIIb). Similarly, from 1.48 g of (VIIIb) in 15 ml of $POCl_3$ there was obtained 1.1 g of product which was chormatographed on 70 g of alumina (200–250 mesh, grade I–II activity) under nitrogen. Gradient elution from hexane to ether (up to 80% of the latter) gave 580 mg (40%) of (XIIIb) as colorless needles, mp 25–27°C (ether–isopentane). IR spectrum (ν, cm^{-1}): 1065, 1130, 1154, 1166, 1319, 1342, 1455. PMR spectrum (δ, ppm): 1.54 and 1.67 br.s. (6H, CH_3), 3.50 m (4H, CH_2N, CH_2S), 4.20 s (2H, CH_2Ph), 7.3 m (5H, C_6H_5). Found: C 62.44; H 7.01; N 5.30; S 12.66%. $C_{12}H_{17}NO_2S$. Calculated: C 62.12; H 6.82; N 5.57; S 12.76%.

5-Methyl-2-(1'-adamantyl)methyl-3,6,5-dihydro-2H-1,2-thiazine 1,1-Dioxide (XIVa). Similarly, for 1.7 g of (Xc) at 60°C for 40 h there was obtained 950 mg of product which was chromatographed on 50 g of alumina (200–250 mesh, activity grade I–II) under nitrogen. Gradient elution from hexane to ether gave 0.6 g (40%) of (XIVa) as colorless prisms, mp 120–123°C (ether–hexane). IR spectrum (ν, cm^{-1}): 855, 1135, 1165, 1340, 1455, 2855, 2910. PMR spectrum (δ, ppm): 1.4–1.9 m (15H, $C_{10}H_{15}$), 1.96 br.s. (3H, CH_3), 2.67 br.s. (2H, CH_2S), 3.46 s (2H, CH_2NAd), 3.90 m (2H, CH_2N), 5.47 m (1H, HC^4). Found: C 65.46; H 8.80; N 4.62; S 10.92%. $C_{16}H_{25}NO_2S$. Calculated: C 65.05; H 8.53; N 4.53; S 10.83%.

5-Methyl-2-cyclohexyl-3,6-dihydro-2H-1,2-thiazine 1,1-Dioxide (XIVb). Similarly, from 0.5 g of (Xg) at 25°C for 30 min without further chromatographic purification there was obtained 230 mg (50%) of (XIVb) as colorless prisms, mp 105–107°C (ether–hexane). IR spectrum (ν, cm^{-1}): 1055, 1107, 1163, 1175, 1290, 1374, 1455, 1470, 1612. PMR spectrum (δ, ppm): 1.2–2.3 m (10H, CH_2), 2.10 br.s. (3H, CH_3), 3.67 m (5H, CH_2NCH, CH_2S), 4.66 (1H, HC^4). Found: C 57.79; H 8.30; N 6.00; S 14.11%. $C_{11}H_{19}NO_2S$. Calculated: C 57.61; H 8.35; N 6.11; S 13.98%

5-Methyl-2-(3'-methylbut-2'-enyl)-3,6-dihydro-2H-1,2-thiazine 1,1-Dioxide (XIVc). Similarly, from 1.5 g of (Xh) at 25°C for 2 h there was obtained 820 mg of product which was chromatographed on 50 g of alumina (200–250 mesh, activity grade I–II) under nitrogen. Gradient elution from hexane to ether gave 0.4 g (30%) of (XIVc) as a colorless, viscous oil, R_f 0.66 (Solufol, ether). IR spectrum (ν, cm^{-1}): 1030, 1140, 1195, 1235, 1330, 1383, 1450. PMR spectrum (δ, ppm): 1.65 br.s (3H, CH_3), 1.77 br.s. (6H, CH_3), 3.4–3.9 m (6H, CH_2S, CH_2N), 5.17 br.t (J = 7 Hz, 1H, $HC^{2'}$), 5.46 m (1H, HC^4). Found: M^+ 215. $C_{10}H_{17}NO_2S$. Calculated: mol.wt. 215.3.

5-Methyl-2-benzyl-3,6-dihydro-2H-1,2-thiazine 1,1-Dioxide (XIVd). Similarly, from 3.5 g of (Xl) at 25°C for 1 h without further chromatographic purification, there was obtained 2.42 g (75%) of (XIVd) as colorless prisms, mp 52.5–53.5°C (ether–hexane). IR spectrum (ν, cm^{-1}): 1068, 1143, 1169, 1330, 1360, 1445. PMR spectrum (δ, ppm): 1.77 br.s. (3H, CH_3), 3.45 m (2H, CH_2S), 3.58 m (2H, CH_2N), 4.13 s (2H, CH_2Ph), 5.36 m (1H, HC^4), 7.26 m (5H, C_6H_5). Found: C 61.03; H 6.52; N 6.01; S 13.50%. $C_{12}H_{15}NO_2S$. Calculated: C 60.73; H 6.37; N 5.90; S 13.51%.

5-Methyl-2-[β-(3',4'-dimethoxyphenyl)ethyl]-3,6-dihydro-2H-1,2-thiazine 1,1-Dioxide (XIVe). Similarly, from 2 g of (Xx) at 50°C for 2 h there was obtained 1.0 g of product which was chromatographed on 80 g of alumina (200–250 mesh, activity grade I–II) under nitrogen. Gradient elution from hexane to ether (up to 80% of the latter) gave 0.6 g (35%) of (XIVe) as a colorless, viscous oil, R_f 0.55 (Woelm, ether–hexane, 2:1). IR spectrum (ν, cm^{-1}): 820, 910, 1030, 1145, 1165, 1270, 1340, 1520, 2840, 2935, 3030. PMR spectrum (δ, ppm): 1.72 br.s. (3H, CH_3), 2.81 m (2H, CH_2Ar), 3.34 m (4H, CH_2N), 3.82 m (8H, CH_3O, CH_2S), 5.44 m (1H, HC^4), 6.74 m (3H, C_6H_3). Found: M^+ 311. $C_{15}H_{21}NO_4S$. Calculated: mol. wt. 311.4.

CONCLUSIONS

1. Sulfoalkenylation of a variety of amines with β,γ-unsaturated δ-sultones at normal and elevated pressures gives the corresponding internal salts of δ-amino-sulfonic acids.

2. Z-Sulfoalkenyl derivatives of primary amines can be cyclized to β,γ-unsaturated δ-sultams.

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FLUORINE-CONTAINING IMINES.

COMMUNICATION 3*. OXIDATION OF DIMETHYLBENZYLAMINE INTO AMINOCARBENE BY HEXAFLUOROACETONE BENZOYLIMINE

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Several hydride transfer reactions with strong electrophiles are now known for tertiary amines [1-7]. When they react with hydride ion acceptors, amines containing β-H atoms form enamines, which then enter the cycloaddition reaction [1] or give products of the substitution of vinyl H atoms [1, 3-7]. If an enamine cannot be formed in the oxidation of the amine, as, for example, in the case of dimethylbenzylamine and methyldiisopropylamine†, the reaction may stop at the stage of the immonium salt formation [2, 8].

It has already been shown that hexafluoroacetone (HFA) benzoylimine splits a hydride ion from triethylamine [1]. One molecule of HFA benzoylimine is thus reduced, and the second enters into a 1,4-cycloaddition reaction with the intermediately formed enamine.‡

*For Communication 2, see [1].

†The isopropyl groups are not affected by the action of hydride ion acceptors [3, 5], probably because of steric factors. For the same reason, dimethylbenzymamine donates the hydride ion from the methyl group and not fromthe methylene group [2].

‡Besides the cyclic product, a product of the substitution of the enamine vinyl H atom is also formed.

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