tonide **6** was hydrolyzed to the α-glycol (quantitative) **11**, but the two antipodal glycols could not be distinguished by nmr (^1H and ^{13}C) after addition of the chiral shift reagents tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium(III)[11a] and tris-[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium(III).[11b] The DL-glycol **11** was therefore allowed to react with (+)-α-methoxy-α-trifluoromethylphenylacetyl (MTPA) chloride[12] to give a (1:1) mixture of the two diastereomers **12** which were distinguishable by the following sets of nmr proton peaks (but not by ^{19}F): diastereomer I, H_A δ 4.30 (d of d, J = 12.5 and 5.0 Hz), H_B 4.60 (d of d, J = 12.5 and 3.0 Hz), H_β 6.07 (d of t, J = 16 and 6.5 Hz), H_α 6.37 (d, J = 16 Hz); diastereomer II, H_A δ 4.28 (d of d, J = 12 and 5.0 Hz), H_B 4.68 (d of d, J = 12 and 3.0 Hz), H_β 6.02 (d of t, J = 16 and 6.5 Hz), H_α 6.31 (d, J = 16 Hz).

The optically active specimen **6** from (*S*)-(−)-malic acid was similarly hydrolyzed and converted to the di-MTPA ester corresponding to **12**. The ester showed only one set of nmr peaks corresponding to those of diastereomer I. As it is inconceivable that partial racemization should occur in steps leading from **6** to **9** (Scheme I), the final product **9** can be regarded as being optically pure.

The small amount of natural base isolated previously[1] exhibited a positive Cotton effect at 264 nm as in the case of synthetic (+)-**9**, and the physical properties of natural and synthetic specimens were identical. The full structure of the natural base is thus established. The side-chain C-4′ configuration is opposite to that at C-4′ of D-ribose, and therefore the unique side chain is presumably not derived from D-ribose but from glutamic acid.

Acknowledgment. Support from National Institutes of Health Grant No. CA 11572 and the Hoffman-La Roche Foundation is acknowledged.

(11) (a) H. L. Goering, J. N. Eikenberry, and G. S. Koermer, *J. Amer. Chem. Soc.*, **93**, 5913 (1971); (b) R. R. Fraser, M. A. Petit, and J. K. Saunders *Chem. Commun.*, 1450 (1971).

(12) J. A. Dale, D. L. Dull, and H. S.Mosher, *J. Org. Chem.*, **34**, 2543 (1969).

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Received March 13, 1973

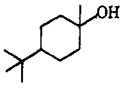
Thermal Decomposition of *N*-Chlorosulfonylurethanes. The Conversion of Alcohols to Amines

Sir:

There is a series of thermal reactions, ROCOZ → RZ + CO_2,[1-5] which serve in effect to convert alcohols to other functionalities. Such a reaction with Z = N< should be of considerable synthetic importance but has not been realized heretofore. We have found that the *N*-chlorosulfonylurethans of tertiary alcohols and of other alcohols, ROH, in which R^+ is a moderately stable carbonium ion, decompose smoothly slightly above room temperature to yield monoalkyl sulfamyl chlorides, $RNHSO_2Cl$.[6] The reaction is simply effected in practice by dissolving the alcohol (ROH) in hexane,[7] adding equimolar chlorosulfonyl isocyanate ($ClSO_2NCO$), and warming until gas evolution subsides. Taken with the removal of the chlorosulfonyl group the sequence offers a facile synthetic conversion of alcohol to amines.

The scope of the reaction is explored in Table I,[8] along with the order of reactivity of the substrates chosen. The several alcohol derivatives which did not undergo the reaction yielded carbonyl-containing sulfamic polymers when heated to higher temperatures. The stereochemistry of the reaction was investigated with (*S*)(−)-α-phenethyl alcohol and with the 4-*tert*-butyl-1-methylcyclohexanols (cis and trans). In the former case the optical rotation of the product was essentially zero.[9] In the latter case both of the tertiary alcohols yielded an approximately 1:1 mixture of the sulfamyl chloride diastereomers (C-1 epimers). Decomposition of the two related allylic chlorosulfonylurethanes from crotyl and 1-methylallyl alcohols yielded in each case essentially the same ratio of the crotyl and 1-methylallyl products (67:33 from crotyl; 68:34 from 1-methylallyl), analyzed by nmr spectra of the sulfanilide derivative mixture (*cf.* Table I).

Table I. Conversion of Alcohols to Amines

ROH	$RNHSO_2Z$,[8] Z =	% yield (mp, °C)	RNH_2 yield[a]
$(C_6H_5)_2CHOH$	NHNHCOO-*t*-Bu	88 (183)	51
$(C_2H_5)_3COH$	NHC_6H_5	12 (154)	
α-Tetralol	NHC_6H_5	44 (175)	
	NHNHCOO-*t*-Bu	28 (166)	13
$C_6H_5CHOHCH_3$	NH-*t*-Bu(*dl*-)	71 (94)	
	NHNHCOO-*t*-Bu	74 (108)	71
1-Methylcyclohexanol	NHNHCOO-*t*-Bu	78 (110)	80
	*cis*-NHNHCOO-*t*-Bu	55[c]	48
	cis-NHC_6H_5	42[c]	
	trans-NHC_6H_5	43[c]	
$(CH_3)_3COH$	*R*(+)-NHCH(CH_3)-C_6H_5	85 (96)	
$CH_2{=}CHCH(CH_3)OH$	NHC_6H_5	42[c]	
$CH_3CH{=}CHCH_2OH$	NHC_6H_5	12[c]	
Cyclohexanol	*b*		
Benzyl alcohol	*b*		
1-Adamantanol	*b*		

[a] Yield from isolated $RNHSO_2NHNHCOO$-*t*-Bu. [b] No decarboxylation of initial chlorosulfonylurethane. [c] Mixture of isomers, see text.

The restriction of substrates ROH to those of moderately good carbonium ions, R^+, and the qualitative order of rates (Table I) parallel the chlorocarbonate decomposition[2] and imply a carbonium ion mechanism.

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(1) These reactions include Z = Cl,[2] SR,[3] OCOR,[4] and OAr[5] previously studied.

(2) K. L. Olivier and W. G. Young, *J. Amer. Chem. Soc.*, **81**, 5811 (1959).

(3) J. L, Kice, R. L, Scriven, E. Koubek, and M. Barnes, *ibid.*, **92**, 5608 (1970).

(4) R. C. L. Chow and D. S. Tarbell, *J. Org. Chem.*, **32**, 2188 (1967).

(5) L. M. McDonough, *Chem. Ind. (London)*, 1501 (1965).

(6) The comparable decarboxylative decomposition of carboxylic acid derivatives from chlorosulfonyl isocyanate has already been established (RCOOH + $ClSO_2NCO$ → $RCOOCONHSO_2Cl$ → $RCONHSO_2Cl$ − CO_2); R. Graf, German patent 931,255 (1956); *Chem. Abstr.*, **50**, 7861*a* (1956).

(7) Other solvents gave higher proportions of elimination products.

(8) Satisfactory ir, nmr, and mass spectra as well as elemental analyses were obtained for these derivatives.

(9) Established on the *tert*-butyl sulfamide derivative; authentic optically pure derivative for comparison was prepared from *t*-$BuNHSO_2Cl$ and (*R*)(+)-α-phenethylamine.

The inactivity of adamantyl and the production of identical products from both allylic cases also tend to rule out any internal or pericyclic thermal bond reordering alternative. The mechanism involves initial dissociation (k_1) of the urethane into the carbonium ion R^+ and the counterion $ClSO_2NHCOO^-$, which may recombine (k_{-1}) or decarboxylate (k_2) and recombine (k_3) to form $RNHSO_2Cl$ (eq 1).

$$\mathrm{ROCONHSO_2Cl} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{R^+\ {}^-OCONHSO_2Cl} \xrightarrow{k_2} \mathrm{R^+\ {}^-NHSO_2Cl} \xrightarrow{k_3} \mathrm{RNHSO_2Cl} \quad (1)$$

In the analogous decomposition of the chlorocarbonates this mechanism was invoked[2] but complete retention of configuration was observed for α-phenethyl chlorocarbonate.[10] This implies faster decarboxylation of the ion $ClCOO^-$ to stable chloride, or $k_2 \gg k_{-1}$. With the ion $ClSO_2NHCOO^-$, however, the rate of decarboxylation should be slower than recombination ($k_2 \ll k_{-1}$), so that the observed racemization, before decarboxylation, is expected. This was substantiated by lithium aluminum hydride reduction after only partial decomposition of the *N*-chlorosulfonylurethane of *trans*-4-*tert*-butyl-1-methylcyclohexanol, which afforded in 93% yield a nearly 1:1 mixture of *cis*- and *trans*-4-*tert*-butyl-1-methylcyclohexanols.

The longer lifetime of $ClSO_2NHCOO^-$ and the greater basicity of $ClSO_2NH^-$ make E1 elimination a significant side reaction. After a solution of $(C_2H_5)_3COCONHSO_2Cl$ in CCl_4 was decomposed, the nmr spectrum of the solution was virtually identical with that of 3-ethyl-2-pentene, and styrene was identified as the major by-product from α-phenethyl alcohol. Acidic catalysts lowered the yields of sulfamyl chloride product.

In order to achieve a synthetically useful and simple overall conversion of these alcohols to amines, we required a facile transformation of $RNHSO_2Cl$ to RNH_2. This proved unexpectedly difficult with many normal reducing agents (*cf.*, heating with triethyl phosphite afforded amines in only 30% yield). Furthermore, while lithium aluminum hydride afforded RNHSSNHR (presumably as salts while still in the reductive medium), sodium aluminum hydride or aluminum amalgam yielded major amounts of the sulfamide, $RNHSO_2NHR$. This finding points up a problem with direct, one-step reduction, *viz.*, that reductively liberated amine reacts faster with sulfamyl chloride than the reducing agent. Hence a two-step conversion was preferred and that outlined in eq 2 ultimately proved simple and satisfactory.

$$\begin{aligned}&\mathrm{RNHSO_2Cl + H_2NNHCOO\text{-}}t\mathrm{\text{-}Bu} \longrightarrow \\ &\quad \mathrm{RNHSO_2NHNHCOO\text{-}}t\mathrm{\text{-}Bu} \xrightarrow{\mathrm{Pb(OAc)_4}} \\ &\quad [\mathrm{RNHSO_2N{=}NCOO\text{-}}t\mathrm{\text{-}Bu}] \xrightarrow{\mathrm{H^+}} \\ &\qquad \mathrm{RNH_3^+ + SO_2 + N_2 + CH_2{=}C(CH_3)_2} \quad (2)\end{aligned}$$

The *tert*-butoxycarbonyl hydrazides are crystalline derivatives formed in high yield from authentic sulfamyl chlorides. Oxidation with lead tetraacetate in methylene chloride is rapid and followed by filtration and treatment of the unisolated azo compound with trifluoracetic acid or dry hydrogen chloride to obtain the amine salts in reasonable overall yields (Table I).

The reaction sequence reported converts tertiary alcohols to *tert*-carbinyl amines, a transformation hitherto available only under the concentrated acid conditions of the Ritter reaction;[11] the present procedure should significantly extend the range of viable polyfunctional substrates for this conversion as a synthetic tool.

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(10) K. B. Wiberg and T. M. Shryne, *J. Amer. Chem. Soc.*, 77, 2774 (1955).

(11) L. I. Krimen and D. J. Cotta, *Org. React.*, 17, 213 (1969).

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Received December 27, 1972

Thione Photochemistry. Chemical Evidence for Intersystem Crossing from a Second Excited Singlet State[1,2]

Sir:

Recently we have reported that adamantanethione (**1**) undergoes cycloaddition reactions upon excitation to the $^1(n,\pi^*)$ state followed by intersystem crossing to the $^3(n,\pi^*)$ state.[3] We have also reported (a conclusion based on flash photolysis experiments) that the triplet thione molecules undergo self-quenching by ground-state molecules at a diffusion-controlled rate.[4] We now present evidence that suggests that the lowest singlet state of **1** is also quenched at approximately such a rate, *that excitation to the second excited state* $^1(\pi,\pi^*)$ *leads to significant intersystem crossing from that state,*[5] and that, in fact, the products obtained by excitation into that state essentially derive from triplets formed by such crossing.

Irradiation[6] of a solution (6.46×10^{-3} *M*) of **1** in *n*-hexane at 250 nm., $^1(\pi,\pi^*)$, gives the dimer[3] ($\Phi = 0.028$). The dimer formation can be quenched with 1,1′-azoisobutane[7] giving a linear Stern–Volmer plot. The reaction at 250 nm passes, therefore, through the triplet as is the case following irradiation at 500 nm.[3] In the latter case, however, with 0.2 *M* thione[8] in ben-

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(1) Photochemical Synthesis. LIV. This is the 12th in a series on thione photochemistry.

(2) Publication Number 75 from the Photochemistry Unit, Department of Chemistry, The University of Western Ontario.

(3) C. C. Liao and P. de Mayo, *Chem. Commun.*, 1525 (1971).

(4) A. H. Lawrence, P. de Mayo, R. Bonneau, and J. Joussot-Dubien, *Mol. Photochem.*, in press. Experiments are there reported concerning excitation at 265 and 530 nm (quadrupled and doubled neodymium laser emissions) of degassed *n*-hexane solutions (0.9–5.05×10^{-3} *M*) of 1. These give rise to the *same* short-lived transient as determined by quenching experiments. From the effect of concentration on the lifetime both self-quenching rate constant ($(9.98 \pm 0.52 \times 10^9)$ M^{-1} sec^{-1}) and unimolecular rate constant for decay ($(6.83 \pm 0.28) \times 10^5$ sec^{-1}) were extracted.

(5) Y. H. Li and E. C. Lim (*J. Chem. Phys.*, **56**, 1004 (1972)) have shown from emission studies that intersystem crossing from the second and third excited singlet states of phthalazine is significant. See, however, V. L. Alvarez and S. G. Hadley, *J. Phys. Chem.*, 76, 3937 (1972).

(6) The light source was a JASCO Model CRM-FA Spectroirradiator equipped with a 2-kW xenon source. Quantum yields at 250 nm were determined by reference to the ferrioxalate actinometer. Relative light intensities 500–250 nm were measured with a thermopile.

(7) The ratio of triplet lifetimes[4] with and without quencher τ/τ_Q (excitation being conducted at 530 nm) agreed within the limits of error with the ratio of photodimerization rates, Φ_0/Φ_Q (excitation at 250 nm) for Q equal to 1,1′-azoisobutane. We conclude from this that the same, lowest, triplet is involved in reaction at both wavelengths. Further[4] the same transient was detected by flash experiments at both wavelengths. We make here the explicit assumption that the azo compound is acting as a triplet quencher as in the case of ketones.

(8) The difference in extinction coefficient of over three orders of magnitude at the two wavelengths precluded the use of the same concentrations of thione.