Partie experimentale. – 1. *Produits de départ:* La diamine A (n = 2), $TiCl_4$ ainsi que les solvants utilisés sont des produits du commerce (*Fluka*). Ils ont été séchés suivant les méthodes habituelles et distillés avant l'emploi.

Les autres amines ont été préparées d'après [13] (diamine A, n = 1), [14] (diamine A, n = 3), et [15] (diamine A, n = 4, triamines B, n = 2 et n = 3).

2. *Préparation des complexes:* A une quantité connue de $TiCl_4$, dissous dans 20 ml de solvant anhydre (benzène pour les diamines et heptane pour les triamines), on ajoute goutte à goutte en 40 à 60 min. à 5–10° la quantité, indiquée dans le tableau, d'amine dissoute dans le même solvant. Un précipité se forme immédiatement. Après 10 minutes d'agitation, on laisse reposer une nuit à 5° La filtration, le lavage par le même solvant et le séchage sous vide sont effectués dans une boîte à gants sous azote et à l'abri de l'humidité.

3. *Méthodes analytiques:* Titane et chlore: voir [16]. Amines: dosage par acidimétrie après hydrolyse alcaline et extraction à l'éther.

4. *Spectres IR.:* enregistrés à l'aide d'un spectrophotomètre *Perkin-Elmer*, modèle 521.

Les spectres des ligands ont été déterminés sur des films capillaires ou de 0,025 mm d'épaisseur (fenêtre de KBr ou CsBr); les spectres des complexes, en pastille de KBr (concentration: 0,5–1%).

BIBLIOGRAPHIE

[1] VIII[e] communication: *A. Jacot-Guillarmod, R. Tabacchi & J. Porret*, Helv. *53*, 1491 (1970)
[2] *R. Tabacchi & A. Jacot-Guillarmod*, Chimia *24*, 271 (1970).
[3] *K. Boustany, K. Bernauer & A. Jacot-Guillarmod*, Helv. *50*, 1120 (1967).
[4] *G. S. Rao*, Z. anorg. all. Chem. *304*, 176 (1960).
[5] *G. W. H. Fowles & R. A. Hoodless*, J. chem. Soc. *1963*, 33.
[6] *J. H. Clark*, J. chem. Soc. *1963*, 1377.
[7] *R. D. Hill & J. H. Meakins*, J. chem. Soc. *1958*, 760.
[8] *M. Antler & A. W. Laubengayer*, J. Amer. chem. Soc. *77*, 5250 (1955).
[9] *K. Nakamoto*, «Infrared Spectra of Inorganic and Coordination Compounds», Wiley & Sons, New-York 1963.
[10] *S. C. Jain & R. Rivest*, J. inorg. nucl. Chemistry *29*, 2792 (1967).
[11] *F. J. Ashley & E. G. Torrible*, Canad. J. Chemistry *47*, 167 (1969).
[12] *R. J. H. Clark, J. Lewis, R. S. Nyholm, P. J. Pauling & G. B. Roberson*, Nature *192*, 222 (1961).
[13] *L. Henri*, Bull. Acad. Roy. Belg. *26*, 203 (1893).
[14] *J. Clarke*, J. chem. Soc. *103*, 16, 99 (1913).
[15] *A. Marxer & K. Miescher*, Helv. *34*, 927 (1951).
[16] *K. S. Boustany, K. Bernauer & A. Jacot-Guillarmod*, Helv. *50*, 1080 (1967).

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179. Pyramidal Inversion in Cyclic Sulfonium Salts [1])

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Summary. 5- and 6-membered cyclic sulfonium salts carrying methyl substituents on the ring have been synthetized and partially resolved. These salts undergo thermal stereomutation at rates which are 10^3 times lower than that of non-cyclic sulfonium cations. Very stringent evidence is presented that racemisation or, where the case may be, epimerisation takes place by pyramidal inversion of the sulfur atom.

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Unsymmetrically substituted sulfonium ions, $R^1R^2R^3S^+$, may undergo stereomutation by a variety of mechanisms, including: (*i*) reversible direct displacement on one of the alpha carbons by nucleophiles [1], (*ii*) pyramidal inversion [2] [3], and (*iii*) ionization of one of the carbon-sulfur bonds followed by return from the ion-molecule pair [4]. The factors which may affect mechanisms *i* and *iii* are clearly understandable since they are the same as those which govern S_N2 and S_N1 reactivity; however, knowledge concerning the inversion mechanism is slight. Although the evidence available is scanty, it appears that electronic factors exert only a minor influence on the inversion mechanism [2] [4] which on the other hand would be expected to be more susceptible to steric factors. This expectation has been predicted [5] and indeed receives some experimental support. For example, methyl-ethyl-*t*-butyl-sulfonium [2] and methyl-ethyl-adamantyl-sulfonium [3] invert about one hundred times faster than methyl-ethyl-benzyl-sulfonium ion [4]. It appears probable that substitution of *t*-butyl or adamantyl for the less bulky benzyl increases the inversion rate because of the relief of steric compression in going from the pyramidal initial state to the presumably trigonal transition state.

The opening of the C–S–C angle, which is the most obvious requirement of the inversion mechanism, suggests other interesting steric possibilities which may operate when the sulfur pyramid is constrained, as is the case in heterocyclic sulfur systems. At least for small and common rings it may be expected that the rigidity of such systems and the angle strain which would result in the motion through a planar state produce rate retardation. This expectation seems in fact so obvious that any considerable decrease in stereomutation rate which might be observed in going from a non-cyclic system to a cyclic system of the above mentioned type would *per se* constitute strong evidence of the inversion mechanism.

On this basis we have prepared and partially resolved a number of unsymmetrically substituted cyclic sulfonium salts (5- and 6-membered), and have measured their rate of stereomutation. All compounds used comprised a S-methyl group. They were prepared by methylation of the corresponding cyclic sulfides. These had been prepared by conventional synthetic procedures. Partial resolution of the sulfonium salts has been obtained by crystallization of the corresponding (−)-di-*o*-toluylhydrogentartrates. Their optical purity is unknown. The salient physical characteristics of the compounds are given below[3]).

1,2-dimethylthiolanium perchlorate (*I*), $[\alpha]_{436}^{25} = -31°$ ($c = 0.8$; methanol); m.p. 216–228° (dec.). The NMR. spectrum indicated that it is a mixture of two diastereoisomers: the 2-methyl group gives rise at high field to two doublets ($J = 7$ Hz) separated by about 0.03 ppm. Similarly the S-methyl group gives rise at lower field to two singlets, separated by 0.24 ppm. Integration of the appropriate signals puts the isomer ratio at 1.9:1. No attempt was made to assign resonance to the *cis* and *trans* isomers.

$C_6H_{13}ClO_4S$ Calc. C 33.3 H 6.04 S 14.8% Fd. C 33.5 H 6.13 S 14.7%

1,3,3-trimethylthiolanium perchlorate (*II*), $[\alpha]_{436}^{25} = +6.6°$ ($c = 1.0$; methanol); m.p. 183–186°. The 3-methyl groups in the NMR. spectrum show at high field two singlets of equal intensities (separation 0.24 ppm). Clearly the two methyls are non-equivalent, corresponding to their *cis* or *trans* relation with respect to the S-methyl group.

$C_7H_{15}ClO_4S$ Calc. C 36.4 H 6.55 S 13.9% Fd. C 36.14 H 6.37 S 13.6%

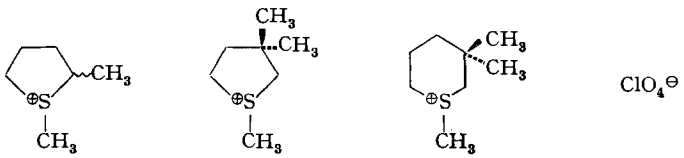
[3]) 60-MHz NMR. spectra were taken in D_2O at 35°.

1,3,3-trimethylthianium perchlorate (III), $[\alpha]_{436}^{25} = +20°$ ($c = 0.87$; methanol); m.p. 129° to 131°. At high field the NMR. spectrum displays a sharp signal of intensity 6H. Evidently the chemical shifts of the two methyls do not differ significantly.

$C_8H_{17}ClO_4S$ Calc. C 39.3 H 7.00 S 13.1% Fd. C 39.3 H 7.14 S 13.0%

Compounds II and III possess only one chiral center, the sulfur atom. Therefore the loss of optical activity can only occur by stereomutation at that center. Compound I contains two chiral centers, and alteration of optical activity may occur by stereomutation of either center.

The rate of change of optical activity, k_α, was measured for the three compounds in acetic acid as solvent at 100°. In every case a first-order rate law was rigorously obeyed. The following values of the rate constant were obtained ($10^4\, k_\alpha$, s^{-1}): I, 1.25;



I II III

II, 1.04; III, 0.81. The change of optical activity was not accompanied by any appreciable solvolysis or other side reactions. In the case of II and III the product isolated after ten half-lives had zero optical activity, and the melting point and the NMR. spectrum were unchanged with respect to the starting material. On the other hand, for I the optical activity changed from an initial, negative rotation $[\alpha]_{436}^{25} = -12°$ ($c = 1.0$; acetic acid) to a final (ten half-lives) positive rotation $[\alpha]_{436}^{25} = +1°$ ($c = 1.0$; acetic acid) which, however, did not undergo further change during twenty additional half-lives. The product isolated after 30 half-lives had m.p. 206–220° (dec.). The NMR. spectrum was about the same as that of the starting material; however, the relative intensities of the signals of the two diastereoisomers had changed, the equilibrium ratio being very nearly 1:1, compared to 1.9:1 at the start. The residual optical activity can hardly be due to an impurity. The maximum amount of acid used in the resolution that may have remained in the sample, was estimated by UV. analysis to be less than 0.04%, which would have given a negligible contribution to the total optical activity. None the less, in order to confirm that the residual optical activity is a property intrinsic to this partially resolved sulfonium salt, other fractions of optically active 1,2-dimethylthiolanium perchlorate were subjected to thermal stereomutation. While in each case the same rate of change of optical activity was obtained within experimental error, different residual activities were obtained. Thus a sample having an initial $[\alpha]_{436}^{25} = -1.5°$ ($c = 3.2$; methanol) gave a final value $[\alpha]_{436}^{25} = -3.5°$ ($c = 3.2$; methanol); another sample, $[\alpha]_{436}^{25} = +8.0°$ ($c = 1.58$; methanol), gave a residual value $[\alpha]_{436}^{25} = -5.0°$ ($c = 1.58$; methanol).

The presently determined values of k_α are several orders of magnitude smaller than those which are characteristic of non-cyclic sulfonium salts. From the only published values of the activation parameters, those for methyl-ethyl-adamantyl-sulfonium ion, it can be calculated that the latter would racemize at 100° in CH_3COOH some 2500 times faster than our cyclic sulfonium ions. This is in itself an evidence in favor of the pyramidal inversion mechanism. However, our results provide stronger

evidence. Since the counter ion was ClO_4^-, an extremely poor nucleophile, mechanism *i* needs not being considered. On the other hand mechanism *iii* can be excluded on the following grounds: (*a*) If ionization of the C–S bond followed by ion-molecule pair return were responsible for the change of optical activity, then a completely racemic product should be finally obtained in every case, *including compound I*. On the contrary in the case of I the final product maintains some optical activity. The only reasonable explanation is that I epimerizes by stereomutation at sulfur while retaining configuration at carbon. (*b*) Compounds I and II react at very nearly the same rate. If ionization of the C–S bond were implicated, I would be expected to undergo stereomutation much faster since it would yield a secondary rather than a primary carbonium ion.

The relative rate of stereomutation for the 5- and 6-membered compounds deserves some discussion. In reactions of carbocyclic compounds which involve rehybridization of the reaction center from sp^3 to sp^2 or *vice versa*, the 5-membered compounds react faster than the 6-membered ones for a sp^3 to sp^2 change [6], and slower for a sp^2 to sp^3 change [7]. Thus ring strain is the leading factor, high strain corresponding to fast reaction [8]. The same trend has been found for sulfur heterocycles undergoing S_N2 substitution at the heteroatom [9][4]). On the contrary in the pyramidal inversion these two heterocycles appear to react at very nearly the same rate. This different behaviour indicates that the transition states for S_N2 substitution and for inversion cannot have the same geometry. A possible explanation is that in the transition state for substitution the reaction center has not yet achieved complete rehybridization to sp^2, or at least not to the same extent it does in pyramidal inversion.

BIBLIOGRAPHY

[1] *M.P.Balfe, J.Kenyon & H.Phillips,* J. chem. Soc. *1930,* 2554.
[2] *D.Darwish & G.Tourigny,* J. Amer. chem. Soc. *88,* 4303 (1966).
[3] *R.Scartazzini & K.Mislow,* Tetrahedron Letters, *1967,* 2719.
[4] *D.Darwish, S.H.Hui & R.Tomilson,* J. Amer. chem. Soc., *90,* 5631 (1968).
[5] *J.F.Kincaid & F.C.Henriquez,* J. Amer. chem. Soc., *62,* 1474 (1940).
[6] *R.Heck & V.Prelog,* Helv., *38,* 1341 (1955); *L.Schotsman, P.J.C.Fierens & T.Verlie,* Bull. Soc. chim. belg., *68,* 580 (1959).
[7] *H.C.Brown & K.Ichicava,* Tetrahedron *7,* 221 (1957).
[8] *J.Sicher,* 'Progress in Stereochemistry', p.225, *P.D.B.de la Mare & W.Klyne,* Editors, Butterworths, London 1962.
[9] *L.Sagramora, A.Garbesi & A.Fava,* unpublished.
[10] *K.Mislow,* Record chem. Progr., *28,* 217 (1967); *E.Ciuffarin & A.Fava,* 'Progress in Physical Organic Chemistry', Vol.6, p.95, *A.Streitwieser, Jr. & R.W.Taft,* Editors, Interscience, New-York 1968.

[4]) These authors found that the HCl-catalysed stereomutation of 5- and 6-membered sulfoxides (2-methylthiolane-1-oxide and 2-methyl-thiane-1-oxide), a reaction which appears to be a S_N2 displacement at sulfur [10], the former compound reacts about 3×10^2 times faster than the latter.