The clear solution was evaporated and the solid produced recrystallized from n-heptane. The pure product weighed 2.2 g. (81%).

Acknowledgments.—This investigation was supported by the Materials Laboratory of Wright Air Development Command, Wright-Patterson Air Force Base, Ohio, under Contract AF-33(616)-5486. Reproduction of this communication in whole or in part is permitted for any purpose of the United States Government. The authors are particularly indebted to Messrs. C. F. Callis and M. M. Crutchfield of the Monsanto Chemical Company for their assistance with the nuclear magnetic resonance studies and to Professor T. L. Brown of the University of Illinois for his advice on the dipole moment studies.

CONTRIBUTION FROM NOYES CHEMICAL LABORATORY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

Some Characteristics of the Cyclic Trimeric Sulfanuric Chlorides

BY A. VANDI, T. MOELLER, AND T. L. BROWN

Received April 26, 1963

The dipole moments in benzene solution of cyclic trimeric α- and β-sulfanuric chlorides are 3.88 and 1.91 D., respectively. Correlations of the dipole moments and infrared spectra support assignment of a second chair-type configuration to the β isomer. The β compound is converted rapidly to the α isomer in polar solvents such as acetonitrile and diethyl ether but is more stable in nonpolar media and stable in the solid state. Cleavage of the sulfur–nitrogen bond rather than substitution on the ring appears to characterize reactions of the α compound with solvolytic reagents.

Among the cyclic inorganic systems, those represented by the sulfanuric chlorides, although of considerable potential interest, have been only incompletely investigated. Except for data on the synthesis of the trimers[1–3] and on the structure of the α isomer,[4] essentially no information is available. Yet even formal analogies with other related cyclic systems (*e.g.*, the phosphonitrilic systems) suggest the importance of extensive investigations of isomerism and chemical reactivity.

The trimeric sulfanuric chlorides are best prepared by the thermal cleavage of trichlorophosphazosulfonyl chloride.[1] This procedure yields a mixture of configurational isomers, of which only the α and β forms are sufficiently stable to permit ready isolation. The pyrolytic decomposition is best effected at 118–120° under a pressure of 2.5–5 mm. with a slow purge of dry nitrogen[5] to remove liberated phosphorus(V) oxytrichloride. Separation of the α and β forms is effected by extracting the pyrolysis residue with boiling n-heptane and either fractionally crystallizing the resulting solution or evaporating it and fractionally subliming *in vacuo*. At least one additional isomer has been detected in admixture with the β form recovered by vacuum sublimation, but the ease with which it decomposes to a red oil in most solvents has thus far prevented its recovery in a state of purity. In the light of subsequent discussions, it is reasonable to assume that other isomers may also be present in the pyrolysis product.

The α isomer melts at 144–145°; the β isomer at 46–47°. α-Sulfanuric chloride is much less soluble in general than its β isomer (Table I). Each gives a characteristic X-ray powder diffraction pattern (Table II). Recent X-ray studies[4] have shown crystals of the α compound to be orthorhombic and to contain four molecules to the unit cell. The distribution of bonds about each sulfur atom is roughly tetrahedral, and the chlorine atoms are arranged axially. The ring is in a chair configuration.

TABLE I
SOLUBILITY DATA FOR α-$[NS(O)Cl]_3$ AT 25°[a]

Solvent	Solubility, g./100 g. of solvent
Benzene	22.50
Acetonitrile	13.15
Carbon disulfide	4.10
Carbon tetrachloride	2.95
Petroleum ether (90–110°)	2.32
Cyclohexane	1.63
n-Heptane	1.56

[a] β-$[NS(O)Cl]_3$ much more soluble in each solvent. Solubility too large to permit accurate measurement.

The α compound is stable with respect to conversion to any other isomer either in the solid state or in solution in any solvent that does not effect its chemical decomposition. The β compound is stable in the solid state and in nonpolar media such as cyclohexane or benzene. However, isomerization to the α compound is rapid in more polar solvents such as acetonitrile or diethyl ether. That this conversion involves an equilibrium in solution between the two forms is suggested by the changes with time of the infrared absorption spectrum of the β compound in acetonitrile. The infrared spectra of freshly prepared equimolar acetonitrile solutions of both isomers have absorption bands at 665, 700, and 820 cm.$^{-1}$, but intensities vary between the two. On standing, the spectrum of the α compound

---

(1) A. V. Kirsanov, *J. Gen. Chem. USSR*, **22**, 93 (1952).

(2) M. Goehring, J. Heinke, H. Malz, and G. Roos, *Z. anorg. allgem. Chem.*, **273**, 200 (1953).

(3) M. Goehring and H. Malz, *Z. Naturforsch.*, **9b**, 567 (1954).

(4) (a) A. J. Banister and A. C. Hazell, *Proc. Chem. Soc.*, 282 (1962); (b) G. A. Wiegers and A. Vos, *ibid.*, 387 (1962).

(5) Kirsanov used dry air. Any dry, chemically inert gas may be used.

TABLE II

POWDER X-RAY DIFFRACTION DATA (2*d* IN CM.)

α-[NS(O)Cl]$_3$		β-[NS(O)Cl]$_3$
2.85 m[a]	10.45 vw	2.43 w
3.20 vw	10.66 m	3.23 m
3.62 s	11.12 w	4.31 s
3.75 m	11.66 m	5.04 w
4.02 m	12.10 m	5.36 vw
4.30 m	12.62 vw	6.02 w
4.65 vw	13.14 vw	6.54 s
5.22 s	13.52 w	7.36 w
5.49 w	13.86 m	7.82 vw
6.10 s	14.18 vw	8.16 vw
6.40 w	14.86 w	8.52 m
6.73 s	15.42 vw	8.88 m
7.12 w	15.58 vw	
7.46 s	15.84 vw	
7.70 w	16.21 vw	
8.38 w	16.98 vw	
8.70 m	17.73 vw	
8.92 w	18.50 vw	
9.16 m	19.48 w	
9.54 vw	19.76 w	
9.94 w	20.34 vw	
10.20 vw	21.08 w	

[a] vw, very weak; w, weak; m, medium; s, strong.

and the intensity of the 665 cm.$^{-1}$ band of the β compound remain unchanged. However, the intensities of the 700 and 820 cm.$^{-1}$ bands of the β isomer alter until after 1 hr. they are the same as those for the same bands of the α compound. On the other hand, the infrared spectrum of the β isomer in cyclohexane remains unchanged for at least 4 days.

The original proposal[1] that the α and β forms are *cis* and *trans* isomers of a planar ring compound is rendered untenable by proof[4] that the configuration of the sulfur–nitrogen ring in the α compound is chair-like rather than planar. In the absence of single-crystal X-ray data, infrared and dipole moment measurements may be used to give at least a reasonable indication of this configuration.

The infrared spectra of the α and β forms are closely similar (Table III and Fig. 1). The minor differences, which are more notable in the 600–300 cm.$^{-1}$ region, appear to be attributable to a stereochemical rather than a structural isomerism.

It seems reasonable to assume that the conversion of the β to the α form occurs without opening of the ring or cleavage of a sulfur–chlorine or sulfur–oxygen bond, since such a cleavage would in all probability lead to degradation of the compound. Granting this assumption, the β isomer must correspond to simply another conformation of the ring. There are then three possibilities for the β form: a chair configuration (I) and two boat forms, one of which is shown (II).

TABLE III

INFRARED SPECTRA OF CYCLOHEXANE SOLUTIONS OF SULFANURIC CHLORIDES

α-[NS(O)Cl]$_3$, cm.$^{-1}$	β-[NS(O)Cl]$_3$, cm.$^{-1}$
665 s[a]	665 s
700 vs	700 w
816 m	822 s
1110 vs[b]	1100 vs[b]
1344 vs	1340 vs[b]
1356 w	

[a] w, weak; m, medium; s, strong; vs, very strong. [b] Possibly a closely spaced doublet.

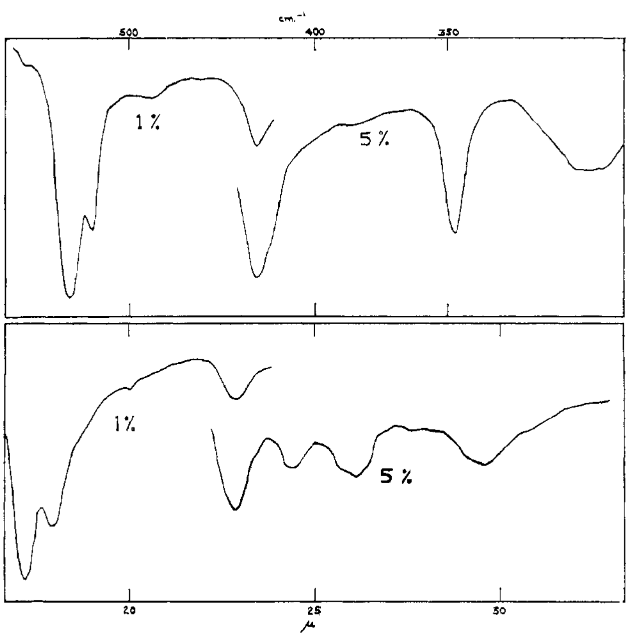
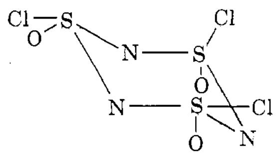
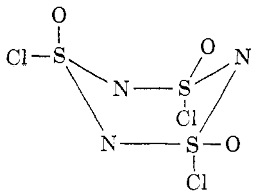


Fig. 1.—Infrared spectra of α (top) and β forms of $(SNOCl)_3$ in benzene solution.



I



II

Experimental data and dipole moments calculated by the method of Halverstadt and Kumler[6] are summarized in Table IV. No allowance has been made for atom polarization in the calculations: the uncertainties in the dipole moments are *ca.* ±0.01 D. for the α isomer and ±0.1 D. for the β. The larger moment is thus associated with the configuration having three axial chlorine atoms.

TABLE IV

DIPOLE MOMENT DATA FOR BENZENE SOLUTIONS AT 25°

Compound	α	β	γ	P_2, cm.^{3}	M.R., cm.^{3}	μ, D.
α-[NS(O)Cl]$_3$	5.7	−0.65	0.087	356	48	3.88
β-[NS(O)Cl]$_3$	1.44	−0.65	.087	123	48	1.91

The dipole moment results provide evidence for assignment of the β form to the chair conformation (I). From a vector analysis of the α form[7] based on the structural parameters reported, the dipole moment of the α form is given by

$$\mu = 1.29\mu_{SNS} + 0.87\mu_{SO} - 3\mu_{SCl} = 3.88 \text{ D.}$$

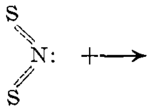
where μ_{SO} and μ_{SCl} represent the SO and SCl bond

---

[6] I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

[7] E. J. Corey and R. A. Sneen, *ibid.*, **77**, 2505 (1955).

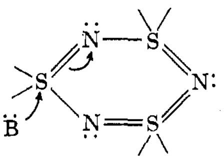
moments and μ_{SNS} represents the SNS group moment in the sense



and includes the lone-pair moment on nitrogen.

Similar equations can be set up for the other possible isomers, assuming the same bond angles as found in the α isomer. Since values for the group moments involved are not well established, the dipole moment results cannot be used to establish unambiguously the configuration of the β isomer. It is true, however, that a reasonable choice of group moments (μ_{SO} = 2.5 D., μ_{SCl} = 1 D., and μ_{SNS} = 3.6 D.) fits the chair conformation (I) and the α isomer to the data very well, whereas no choice of group moments which appears reasonable to us will fit either boat isomer to the data. The dipole moment results, therefore, lend some support to the contention that the β isomer is the chair conformation (I).

It is not surprising that the β form should not convert readily to the α form in nonpolar solvents. The reorientation of the bonds in the ring which is necessary to effect the conversion should have a high activation energy because of π-bonding between sulfur and nitrogen. In a basic solvent, on the other hand, a nucleophilic base interaction at sulfur is a possible mechanism by which the activation energy might be lowered.



Further studies of the role of the solvent and of solute bases in the isomerization are underway.

With regard to solvolysis reactions, the sulfanuric chlorides may be expected to resemble the somewhat analogous thiazyl chlorides, $(NSCl)_3$. The reported failure[8] to substitute other groups for chlorine atoms in the thiazyl series has its apparent parallel in the sulfanuric series. Thus water converts sulfanuric chloride to imidodisulfamide, sulfuric acid, and hydrochloric acid rather than to sulfanuric acid.[9] Ring cleavage rather than substitution appears to be characteristic of reactions with other nucleophiles. Thus reaction of α-sulfanuric chloride with morpholine in *n*-heptane gives N,N′-morpholinesulfamide as a major product. The possibility of the intermediate formation of an adduct between the donor substance and the sulfanuric chloride cannot be excluded. Studies designed to elucidate the nature of the aminolysis process will be reported in a subsequent communication.

Experimental

Materials.—All chemicals used were of reagent quality. Phosphorus(V) chloride was pulverized in a drybox prior to use. Sulfamic acid was dried over phosphorus(V) oxide and then ground in a drybox. The *n*-heptane used for fractional crystallization was dried over sodium wire. All solvents for solubility studies were fractionally distilled before being used.

Trichlorophosphazosulfonyl Chloride.—This compound was prepared by a slight modification of the Kirsanov procedure.[10] By use of a slight excess of sulfamic acid, the product was obtained directly in sufficient purity that recrystallization was unnecessary (m.p. 33–35°).

α- and β-Sulfanuric Chlorides.—Trichlorophosphazosulfonyl chloride (362 g., 1.40 moles) was placed in a 500-ml. pear-shaped distillation flask fitted with a 30-cm. Vigreux column and an inlet tube for dry air or nitrogen. A Liebig distillation head was mounted on top of the Vigreux column, a condenser was attached, and the entire system was attached to a vacuum pump through a receiving flask maintained at −70°. Either air or nitrogen previously dried with calcium chloride was passed through the contents of the flask at such a rate that the pressure in the system was maintained at 2.5–5 mm. The flask was slowly heated to 118–120°, at which temperature thermal decomposition with volatilization of phosphorus(V) oxytrichloride proceeded rapidly.

After 1 hr. at this temperature, the flask was warmed to 130° and maintained at that temperature for an additional hour. It was then raised to 140° for a short time to ensure complete removal of the oxychloride. A total of 197 g. of phosphorus(V) oxytrichloride, corresponding to conversion of 92% of the starting material, was recovered.

The brown residue in the flask was extracted ten times with 100–150 ml. quantities of hot *n*-heptane. When cooled to 0°, the solution obtained deposited large crystals of primarily α-sulfanuric chloride. These were removed. Removal of solvent from the filtrate *in vacuo* gave a second crop of crystals. The solids were combined, and the isomers were separated either by fractional crystallization from *n*-heptane or by vacuum sublimation. At 0.005 mm., the β form, together with small quantities of a third and less stable isomer, sublimes readily at room temperature, whereas the α form requires a temperature of 80° for sublimation. Pure β-sulfanuric chloride was obtained by extracting the sublimed mixture at room temperature with as little *n*-heptane as possible and then cooling to 0°. It separates as long needles. The α form crystallizes as rhombic prisms. The α isomer melts at 144–145° and the β isomer at 46–47°, both without decomposition; yields: α, 27.60 g. or 20% of theory; β, 20.0 g. or 14.3% of theory.

Anal. Calcd. for $\alpha[NS(O)Cl]_3$: N, 14.36; S, 32.87; Cl, 36.36; mol. wt., 292.57. Found: N, 14.47; S, 33.17; Cl, 36.36; mol. wt., 300. Calcd. for $\beta[NS(O)Cl]_3$: N, 14.36; S, 32.87; Cl, 36.36; mol. wt., 292.57. Found: N, 14.41; S, 32.86; Cl, 36.49; mol. wt., 294.

N,N′-Morpholinesulfamide.—α-Sulfanuric chloride (5.85 g., 0.02 mole) was suspended in 300 ml. of dry *n*-heptane in a 500-ml. three-necked flask equipped with a mechanical stirrer, a reflux condenser, and a dropping funnel. Morpholine (10.45 g., 0.12 mole) was dissolved in 150 ml. of dry *n*-heptane, and this solution was added dropwise at room temperature over a period of 2 hr. An insoluble, waxy substance separated at the bottom of the flask. The system was refluxed for 1 hr. after addition of the amine was completed. Evolution of sulfur(IV) oxide was noted. The hot heptane solution was then decanted from the waxy residue and cooled, whereupon white crystals separated. Upon recrystallization from ethanol, this product melted at 141–142°, gave no depression in melting point when mixed with an authentic sample of N,N′-morpholinesulfamide, and showed the same infrared spectrum as N,N′-morpholinesulfamide.

Anal. Calcd. for $C_8H_{16}N_2O_4S$: C, 40.65; H, 6.82; N, 11.86; mol. wt., 236. Found: C, 40.63; H, 6.87; N, 11.84; mol. wt., 223.

Solubility Determinations.—Saturated solutions of α-sulfanuric chloride were obtained by allowing the required solvent to equilibrate with excess solid for 24 hr. at 25 ± 0.1°. Aliquots were

---

[8] M. Becke-Goehring, *Advan. Inorg. Chem. Radiochem.*, **2**, 175 (1960).

[9] H. Malz, Doctoral Dissertation, Heidelberg, 1954.

[10] A. V. Kirsanov, *J. Gen. Chem. USSR*, **22**, 101 (1952).

removed, the solvent was evaporated, and the solid was weighed directly.

Infrared Measurements.—Spectra in the 4000–650 cm.$^{-1}$ region were obtained with a Beckman IR-7 instrument. Spectra in the 850–300 cm.$^{-1}$ region were obtained with a Beckman IR-5A instrument with cesium bromide optics.

X-Ray Diffraction Measurements.—All patterns were obtained with a Hayes unit using nickel-filtered Cu Kα radiation and a 7.0-cm. radius camera.

Dipole Moment Measurements.—Dielectric constants were measured with a heterodyne beat apparatus of conventional design. Specific volumes were obtained with a 4.5-ml. Lippincott pycnometer with calibrated side arms. Refractive indices were determined with a differential refractometer at the 436 mμ line of mercury according to the procedure of Brice and Halver.[11] The quantity $\nu = \partial n^2/\partial w^2$ was obtained graphically, and the molar refractivity was calculated as described by Halverstadt and Kumler.[6] Weight fractions were in the range 0.002 to 0.018. Dipole moments were then calculated by the Halverstadt–Kumler procedure.[6]

Acknowledgment.—The generous support provided by Picatinny Arsenal under Contract Ord. 2956 and by the Army Research Office under Contract DA-31-124-ARO(D)-35 is gratefully acknowledged.

[11] B. A. Brice and M. Halver, *J. Opt. Soc. Am.*, **41**, 1033 (1951).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
ISRAEL INSTITUTE OF TECHNOLOGY, HAIFA, ISRAEL

Organometallic Studies. VII. The Resolution of an Arenechromium Tricarbonyl Racemic Mixture[1,2]

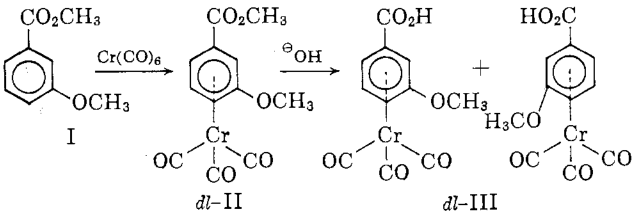
BY A. MANDELBAUM, Z. NEUWIRTH, AND MICHAEL CAIS

Received January 10, 1963

(*m*-Methoxybenzoic acid)-chromium tricarbonyl has been prepared and the resulting racemic mixture has been resolved to yield the pure enantiomers.

An inspection of the formulas of suitably disubstituted arenechromium tricarbonyl derivatives will show that the absence of any elements of symmetry in these compounds should allow them to exist as racemic mixtures and such mixtures should be resolvable into the respective enantiomeric pairs. The compound chosen to test this assumption was the chromium tricarbonyl derivative of *m*-methoxybenzoic acid.[3] Since the –COOH group is known[4] to promote decomposition of hexacarbonylchromium in the reaction with an arene, the methyl ester of *m*-methoxybenzoic acid was treated with hexacarbonylchromium and the resulting compound was hydrolyzed to give the required racemic mixture of III (see Reaction Scheme 1).

Reaction Scheme 1



The procedure for the separation of the enantiomers and the optical rotation data are given in the Experimental section. The optical rotation of the strongly colored solutions of III could not be measured in the polarimeter at the sodium D-line, owing to the limitations of the instrument and the light source. Consequently all rotations of III were measured in sodium hydroxide solutions, since the latter were colored a light yellow.

The optical rotations of the enantiomeric acids themselves were obtained by the use of an optical rotatory dispersion apparatus.[5]

As may be noted from Fig. 1, the optical rotation values for the acids at the sodium D-line exhibit the same sense (+) or (−) as the respective sodium salts of the enantiomeric acids.[6]

This appears to be the first optical resolution of a racemate of an arenechromium tricarbonyl derivative[7] and work is currently in progress to extend this procedure to metal carbonyl derivatives of naphthalene and similar systems in order to attempt studies of the kinetics of racemization of the resolved enantiomers. Such racemization could involve an intermolecular mechanism[8] in the case of benzene derivatives and/or an

---

[1] Part VI: R. T. Lundquist and M. Cais, *J. Org. Chem.*, **27**, 1167 (1962).

[2] (a) Communicated in part at the 30th Meeting of the Israel Chemical Society, Jerusalem, April, 1962; see A. Mandelbaum and M. Cais, *Bull. Res. Council Israel*, **11A**, 9 (1962); (b) Communicated at the Symposium on "The Theory and Structure of Complex Compounds," Wroclaw, Poland, June 15–19, 1962.

[3] For a recent review on arenemetal carbonyl complexes see H. Zeiss, "Organometallic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1960, pp. 380–425.

[4] B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959).

[5] We are greatly indebted to Prof. C. Djerassi, Stanford University, for carrying out the optical rotatory dispersion measurements for our compounds.

[6] Prof. Djerassi has commented in a private communication that whereas the over-all shape of the curves is significant, one cannot put too much value on the precise quantitative data because the measurements were carried out in very dilute solutions.

[7] While this work was in progress, R. Riemschneider and W. Hermann, *Ann.*, **648**, 68 (1961), reported the separation of enantiomers of (α-methyl-γ-carboxy)-cyclopentadienylmanganese tricarbonyl without proof of the respective structure, and more recently L. Westman and K. L. Rinehart, Jr., *Acta Chem. Scand.*, **16**, 1199 (1962), have reported a similar resolution of a trisubstituted ferrocene carboxylic acid derivative.

[8] W. Strohmeier and H. Mittnacht, *Z. Physik. Chem.*, **29**, 22 (1961).