Fig. 1.—Bond parameters for the cubane molecule; the back CH group was omitted for clarity.

The structure was refined by least-squares techniques using the Hughes weighting scheme.[4] The refinement was carried out varying all independent parameters; anisotropic temperature factors were used for the carbon atoms and isotropic for the hydrogens. The final disagreement factor, R, was 7.3%. As seen from Table II the carbon atoms are vibrating almost isotropically.

TABLE I

FRACTIONAL COORDINATES AND STANDARD DEVIATIONS OF CUBANE ATOMS[a]

Atom	x	y	z
C_{gen}	-0.18711	0.19519	0.10706
σ	0.00060	0.00061	0.00062
C_{spec}	0.11546	0.11546	0.11546
σ	0.00040	0.00040	0.00040
H_{gen}	-0.3246	0.3468	0.1848
σ	0.0085	0.0081	0.0080
H_{spec}	0.2100	0.2100	0.2100
σ	0.0060	0.0060	0.0060

[a] σ is the standard deviation as given by the least-squares program.

TABLE II

TEMPERATURE FACTORS FOR CUBANE

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C_{gen}	0.0410^a	0.0425	0.0450	-0.0042	-0.0051	-0.0142
C_{spec}	0.0468	0.0468	0.0468	-0.0143	-0.0143	-0.0143
C^b	0.0415	0.0415	0.0415	-0.0097	-0.0097	-0.0097
H_{gen}	4.0^c					
H_{spec}	3.6^c					

[a] $\sigma_{av} = 0.002$. [b] Carbon with isotropic vibration for comparison. [c] Isotropic temperature factor.

The independent bond distances and angles for the cubane molecule are shown in Fig. 1. The molecule has cubic symmetry to within the errors of the determination. The carbon–carbon bond distances in cubane are similar to those obtained by microwave and electron diffraction for cyclobutane derivatives (1.548 ± 0.003 Å. in cyclobutane[5] and 1.548 ± 0.003 Å. in bromocyclobutane[6]).

(4) M. J. Beurger, "Crystal-structure Analysis," John Wiley and Sons, Inc., New York, N. Y., 1960, Chapter 22.

(5) A. Almenningen, O. Bastiansen, and P. N. Skancke, Acta Chem. Scand., 15, 711 (1961).

(6) W. G. Rothschild and B. P. Dailey, J. Chem. Phys., 36, 2931 (1962).

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Kinetic and Tracer Studies[1] on the Alkaline Hydrolysis of $Co(NH_3)_5O_2CCF_3^{+2}$

Sir:

The experiments we have been doing on the alkaline hydrolysis of $Co(NH_3)_5O_2CCF_3^{+2}$ reveal some unusual effects which are not anticipated by earlier work in this subject area.[2]

The rate law for the hydrolysis has the form

$$\frac{-d \ln (\text{complex})}{dt} = k_1(OH^-) + k_2(OH^-)^2$$

At 25.0° and $\mu = 1.0$ (NaCl), $k_1{}^3 = 1.6 \times 10^{-2}$ M^{-1} sec.$^{-1}$ and $k_2 = 0.50$ M^{-2} sec.$^{-1}$; $\Delta H_1{}^*$ and $\Delta S_1{}^*$ are 27 kcal. mole^{-1} and 24 cal. mole^{-1} deg.$^{-1}$; $\Delta H_2{}^*$ and $\Delta S_2{}^*$ are 7.5 kcal. mole^{-1} and -35 cal. mole^{-1} deg.$^{-1}$. The term second order in (OH^-) is novel for ammine complexes; our observations suggest that it appears when the carboxyl group is strongly activated by an electronegative group. Thus, it is featured also by $Co(NH_3)_5C_2O_4{}^+$ but not by $Co(NH_3)_5O_2CH^{+2}$.

Oxygen isotopic experiments show that on complete hydrolysis at 0° and 1.00 M NaOH, the product $Co(NH_3)_5OH^{+2}$ derives only 1.3% of its oxygen from the solvent, while the product $CF_3CO_2^-$ derives 49.3%. Thus it is clear that under these conditions bond breaking is entirely ($>98\%$) at the C–O position, and there is little exchange of oxygen between the reacting complex and the solvent (exchange would lead to the incorporation of more than one solvent oxygen into the products for each act of hydrolysis). It should be noted that under the conditions specified, $>99\%$ of the reaction takes place by the k_2 path.

Oxygen exchange between the complex and solvent does become significant when the temperature is raised, especially when the concentration of alkali is reduced. That exchange takes place has been shown by examining the oxygen isotopic composition of the residual complex after partial hydrolysis. The reaction mixture was quenched by acidifying, and the trifluoroacetate complex was separated from the product aquo using $Cr^{+2}(aq)$ which, under selected conditions, reacts more rapidly with the aquo than with the trifluoroacetate complex. Isotopic analysis of the trifluoroacetate complex was accomplished taking advantage of the clean isotopic course of the hydrolytic reaction at 0° and 1 M NaOH. The experiments show that Co–O–C oxygen at 25° and 0.10 M OH$^-$ exchanges with solvent at a half-life of 60 $\pm$ 10 sec. and that the half-life varies inversely with (OH$^-$).

The isotopic composition of the hydroxo product on complete hydrolysis as a function of (OH$^-$) can be accounted for by allowing for exchange as described above, and by assuming that by the k_1 path only Co–O bond scission takes place while by the k_2 path there is only C–O bond scission. The results are, however, not very sensitive to the assumption about bond breaking by the k_1 path, because over the range of (OH$^-$) covered, the k_2 path is dominant and as much

(2) C. A. Bunton and D. R. Llewellyn, J. Chem. Soc., 1692 (1953).

(3) In the kinetic work of F. Basolo, J. G. Bergmann, and R. G. Pearson, J. Phys. Chem., 56, 22 (1952), the concentration of OH⁻ was so low (0.004 M) that only the k_1 path contributed to the rate they measured. Our value of k_1 is consistent with theirs (0.73 × 10⁻² M⁻¹ sec.⁻¹) at lower ionic strength.

as 10 or 15% of C–O bond breaking by the k_1 path would still be consistent with the data. To illustrate the magnitude of the exchange effect, we report the results of determining the isotopic compositions of the products on complete hydrolysis at 25° and 0.1 M OH⁻: Co(NH₃)₅OH⁺² derives 63% of its oxygen from the solvent while CF₃CO₂⁻ derives 72%. Thus of the total of three oxygen atoms appearing in each Co(NH₃)₅-OH⁺²–CF₃CO₂⁻ pair, in addition to the one solvent atom necessarily appearing as a· result of the act of hydrolysis, 1.07 appear as a result of exchange.

At elevated temperatures and low (OH⁻), the k_1 path can be isolated. At 0.01 M NaOH and 90°, >99% of the reaction proceeds by the k_1 path. Under these conditions, the hydroxo product is found to derive 85% of its oxygen from the solvent, and the product CF₃CO₂⁻ approximately 16%. Exchange is seen to account for the incorporation of only 0.17 atom of solvent oxygen; the results show rather unambiguously that the k_1 path at 90° leads largely to Co–O bond breaking.

The results summarized answer some important questions concerning the mechanism of the reactions, but obviously raise others which will be considered in a more complete paper on this subject.

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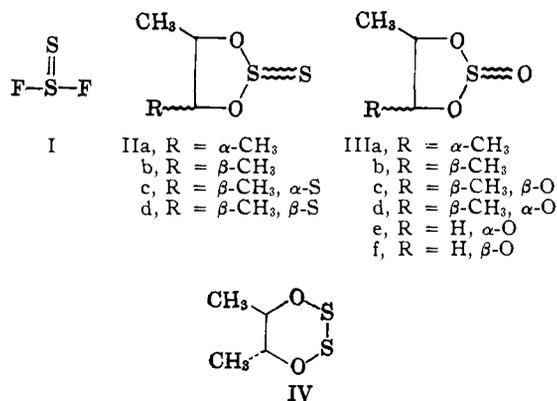## Thionosulfites. A New Class of Cyclic Esters Containing Branch-Bonded Sulfur

Sir:

The existence of branch bonding, >S=S, in organosulfur compounds has never been clearly established. Foss[1,2] has summarized evidence contraindicating such bonding in systems heretofore examined.

Recent studies of sulfur monofluoride,[3,4] however, suggest that it exists predominantly as I. While investigating the reaction between sulfur monochloride and 1,2-diols, cyclic disulfur esters were obtained to which only the branch-bonded structure II can be ascribed.

A mixture of dl-2,3-butanediol (1 mole) and triethylamine (2 moles) was allowed to react with sulfur monochloride (1 mole) at 10° under high dilution conditions in methylene chloride. Cyclic 1α,2β-dimethylethylene sulfite[5] (IIIa) and a second neutral ester (43%), b.p. 32° (0.45 mm.), n^{25}D 1.5148, $\lambda_{max}^{Isooctane}$ 257 mμ (ϵ 2446), were distilled from the polymeric residue. *Anal.* Calcd. for C₄H₈O₂S₂: C, 31.56; H, 5.30; S, 42.13; mol. wt., 152. Found: C, 31.37; H, 5.29; S, 42.27; mol. wt., 160.[6] The p.m.r. spectrum of the new sulfur ester closely resembled that of the cyclic sulfite in that it exhibited nonequivalent methyl groups,

(1) O. Foss, *Acta Chem. Scand.*, **4**, 404 (1950).

(2) O. Foss, "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press, New York, N. Y., 1961, pp. 75–77.

(3) R. L. Kuczkowski and E. B. Wilson, *J. Am. Chem. Soc.*, **85**, 2028 (1963); R. L. Kuczkowski, *ibid.*, **85**, 3047 (1963).

(4) F. Seel, R. Budenz, and D. Werner, *Ber.*, **97**, 1369 (1964).

(5) The α (down) and β (up) notations denote steric relationships of ring substituents.

(6) Mechrolab Model 301 vapor pressure osmometer.

I

IIa, R = α-CH₃
b, R = β-CH₃
c, R = β-CH₃, α-S
d, R = β-CH₃, β-S

IIIa, R = α-CH₃
b, R = β-CH₃
c, R = β-CH₃, β-O
d, R = β-CH₃, α-O
e, R = H, α-O
f, R = H, β-O

IV

two doublets, centered at 1.5 and 1.6 p.p.m.,[7] and nonequivalent methenyl protons, two doubled quartets, at 4.0 and 5.1 p.p.m. No significant change in the p.m.r. spectrum was observed between −40 and 158°. Desulfurization reconverted the compound to sterically pure dl-2,3-butanediol. The rigidity of the ring system and similarity of the p.m.r. spectrum to that of IIIa strongly favored a thionosulfite structure (IIa) over the expected 1,4,2,3-dioxadithiane (IV). The corresponding cis-dimethyl analog (IIb), b.p. 36° (0.13 mm.), n^{25}D 1.5232, $\lambda_{max}^{Isooctane}$ 255 mμ (ϵ 2549), was prepared (21%) in the same manner from meso-2,3-butanediol, along with comparable amounts of the cyclic sulfite isomers[8] IIIc,d. *Anal.* Calcd. for C₄H₈O₂S₂: C, 31.56; H, 5.30, S, 42.13; mol. wt., 152. Found: C, 31.50; H, 5.55; S, 41.88, mol. wt., 162. Desulfurization reconverted IIb to sterically pure meso-2,3-butanediol. Despite extensive purification and correct analytical data, the p.m.r. spectrum of IIb indicated the presence of 5–10% of a structurally related "impurity," a fact which suggested that both of the structural isomers IIc and IId expected from IIb were present. The p.m.r. spectrum of IIb was again similar to that of the cyclic sulfite isomers IIIc,d except that in the latter case the minor isomer was present in larger amount. Methyl protons were equivalent and methenyl protons appeared as complex multiplets in both the sulfite and thionosulfite cases. P.m.r. spectra of IIb were essentially unchanged between −40 and 158°.

Powerful evidence in support of the thionosulfite structure was obtained when meso-hydrobenzoin was converted to a mixture which was separable into the pure crystalline α- and β-thiono components, Va,b. One mole of meso-hydrobenzoin in dry tetrahydrofuran was converted to its dimagnesium alkoxide with 2.1 moles of methylmagnesium bromide. The alkoxide was caused to react with 1 mole of sulfur monochloride at 15° in ether under high dilution conditions. A mixture of monomers (Va,b) and hydroxyl-containing polymeric material was obtained. The two C₁₄H₁₂-O₂S₂ isomers could be separated by fractional crystallization giving a major isomer, Va,[9] m.p. 80–81°

(7) P.m.r. spectra were determined with a Varian A-60 spectrometer equipped with a variable temperature probe or with a Varian HR-60 spectrometer. Chemical shifts (δ) are in p.p.m. downfield from tetramethylsilane as zero.

(8) Isomerism in substituted cyclic sulfites (IIIb,e,f) arising from the tetrahedral (>S=O) sulfur atom has been demonstrated by J. G. Pritchard and P. C. Lauterbur [*J. Am. Chem. Soc.*, **83**, 2105 (1961); see also P. C. Lauterbur, J. G. Pritchard, and R. L. Vollmer, *J. Chem. Soc.*, 5307 (1963)].

(9) Tentative assignment based on chemical shift of methenyl protons. *Cf.* ref. 8a.