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⁻: $Co(NH_3)_5OH^{+2}$ derives 63% of its oxygen from the solvent while $CF_3CO_2^-$ derives 72%. Thus of the total of three oxygen atoms appearing in each $Co(NH_3)_5$-OH^{+2}-$CF_3CO_2^-$ 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 $CF_3CO_2^-$ 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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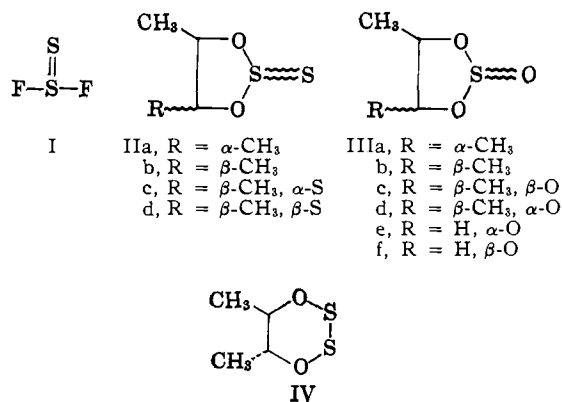## Thionosulfites. A New Class of Cyclic Esters Containing Branch-Bonded Sulfur

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 $1\alpha,2\beta$-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 $C_4H_8O_2S_2$: 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   IIIa, R = α-CH₃
        b, R = β-CH₃   b, R = β-CH₃
        c, R = β-CH₃, α-S   c, R = β-CH₃, β-O
        d, R = β-CH₃, β-S   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 C_4-$H_8O_2S_2$: 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 $C_{14}H_{12}$-O_2S_2 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.

(aromatic protons, complex multiplet entered at 7.05 p.p.m., methenyl protons, sharp singlet at 6.32 p.p.m.), and a minor isomer, Vb,[9] m.p. 89–90° (aromatic protons, single peak at 7.11 p.p.m., and methenyl protons, singlet at 5.76 p.p.m.). Each isomer gave the correct analysis and molecular weight, and each yielded *meso*-hydrobenzoin on desulfurization. Conversion of *meso*-hydrobenzoin to the cyclic sulfite with thionyl chloride

Va, β-Ph, β-Ph, α-S
b, β-Ph, β-Ph, β-S
c, α-Ph β-Ph, β-S

VIa, β-Ph, β-Ph, αO
b, β-Ph, β-Ph, β-O
c, α-Ph, β-Ph, β-O
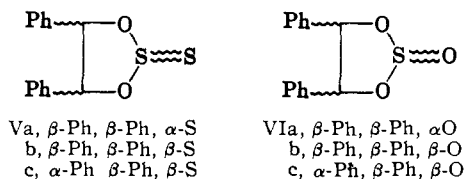
and pyridine gave a sulfite mixture VIa,b consisting of approximately nine parts of a major isomer, VIa, m.p. 130–131°,[10] and one part of a minor isomer, VIb, m.p. 129–131°. P.m.r. spectra of the major and minor sulfite isomers were identical in character (major isomer, complex aromatic protons at ~7.04 p.p.m., methenyl protons, singlet at 6.14 p.p.m.; minor isomer, sharp aromatic signal at 7.13 p.p.m. with methenyl singlet at 5.84 p.p.m.) with Va and Vb, respectively.

dl-Hydrobenzoin was converted to the thionosulfite Vc, m.p. 78–80° (correct analysis for $C_{14}H_{12}O_2S_2$), and the sulfite VIc, m.p. 85–86°.[10a,c] Single compounds were obtained in each case. Their p.m.r. spectra were essentially equivalent with each showing the expected nonequivalence of methenyl protons.

The isolation of individual sulfite and thionosulfite isomers and the striking similarities between the two classes constitutes compelling evidence for the existence of branch-bonded thiono analogs of cyclic sulfites.

(10) (a) C. C. Price and G. Berti, *J. Am. Chem. Soc.*, **76**, 1211 (1954); (b) Z. Kitasato and C. Sone, *Ber.*, **64**, 1142 (1931); (c) D. Reulos and S. LeTellier, *Compt. rend.*, **217**, 698 (1943).
(11) Inorganic Chemicals Division.

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Formation of Phenyl Radical by Heterolysis of N-Phenyl-N'-benzoyldiimide[1]
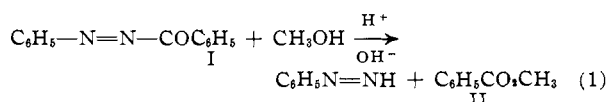
Sir:

We wish to report that treatment of solutions of N-phenyl-N'-benzoyldiimide, C_6H_5—N=N—COC_6H_5 (I), with acid or base leads to free phenyl radical, presumably *via* phenyldiimide, C_6H_5N=NH (II). Compound I is thermally stable[2] at 135° and may be crystallized from ethanol.[3] We have found that the presence of 0.01 N hydrogen chloride led to rapid decomposition of 0.006 M I in methanol, 90% yield of nitrogen, 85% yield of methyl benzoate, and *ca.* 55% yield of benzene; 0.01 N NaOH also led to rapid heterolysis. At higher initial concentration (1.6 M) of I, the yields of

(2) H. Wieland, H. vom Hove, and K. Borner, *Ann.*, **446**, 31 (1926).
(3) G. Ponzio and G. Charrier, *Gazz. chim. ital.* **39**, I, 596 (1909).

methyl benzoate and benzene fell to 43 and 12%, respectively, as a considerable part of the phenyldiimide and/or phenyl radical added to I, preventing its heterolysis, and led to a combined 26% yield of N,N-diphenyl-N'-benzoylhydrazine,[4] $(C_6H_5)_2NNHCOC_6H_5$ (III), m.p. 189–191°, and N,N'-diphenyl-N-benzoylhydrazine,[5] $C_6H_5NHN(C_6H_5)COC_6H_5$ (IV), m.p. 136–138°.

At intermediate initial concentration (0.2 M) of I, acid-catalyzed methanolysis also led to lower yields of methyl benzoate (45%) and benzene (*ca.* 15%). However, addition of 2 M fumaric acid led again to a high yield of methyl benzoate (75%), but to a still lower yield of benzene (4%). The fumaric acid competed with I for phenyldiimide and phenyl radical, allowing extensive methanolysis of I and formation of methyl benzoate, diverted phenyldiimide and phenyl radical from formation of benzene, and led to phenylsuccinic acid, m.p. 165–167°, 46% yield.

Acid-catalyzed heterolysis of 0.2 M I in 2-propanol led to a 32% yield of 2-propyl benzoate, 35% nitrogen, 26% benzene, 16% acetone, and to compounds III and IV. In 3:1 carbon tetrachloride–methanol, 0.16 M I led to a 58% yield of methyl benzoate, 40% chlorobenzene, 19% chloroform, and a low yield of benzene. In benzene containing 3% of methanolic hydrogen chloride, 0.17 M I led to a 41% yield of methyl benzoate and to a 38% yield of biphenyl. In 3:1 nitrobenzene–methanol, 0.18 M I led to a 59% yield of methyl benzoate, 10% of benzene, and to a 33% combined yield of nitrobiphenyls, of which the 2-, 3-, and 4- isomers were obtained in the ratio 31:8:61. Finally, acid methanolysis of 0.075 M I in acrylonitrile led to exothermic polymerization, 65% conversion to polyacrylonitrile.

Methanolysis probably occurs *via*

$$C_6H_5\text{—N=N—}COC_6H_5 + CH_3OH \xrightarrow[OH^-]{H^+}$$
$$C_6H_5N\text{=NH} + C_6H_5CO_2CH_3 \quad (1)$$

with I labeled under the first term and II under the second.

Phenyldiimide may add to unreacted I, leading to III and IV, or to fumaric acid, or it may decompose within a solvent cage to form benzene. It may also lead to phenyl radical, the course of which reaction will be discussed in a later publication. The phenyl radical may then (i) add to I leading to III and IV; (ii) add to fumaric acid and lead to phenylsuccinic acid; (iii) abstract hydrogen from alcohol, forming benzene and leading 2-propanol to acetone; (iv) abstract chlorine from carbon tetrachloride; (v) arylate benzene and nitrobenzene, leading in the latter case to a predominance of *o*- and *p*-nitrobiphenyls; and (v) initiate polymerization.

Aryl radicals may thus be produced in satisfactory yield from thermally stable N-acyl-N'-aryldiimides by simple treatment with dilute acid or base at room temperature in homogeneous medium, conditions which may make them more desirable than other sources of free radicals, diazonium salts,[6] diazohydroxides,[7] and diazoacetates,[7] acylarylnitrosoamines,[8]

(4) E. Fischer, *Ann.*, **190**, 178 (1878).
(5) J. Biehringer and A. Busch, *Ber.*, **36**, 139 (1902).
(6) H. A. H. Pray, *J. Phys. Chem.*, **30**, 1417, 1477 (1926); W. A. Waters, *J. Chem. Soc.*, 864 (1939).
(7) M. Gomberg and W. E. Bachmann, *J. Am. Chem. Soc.*, **46**, 2339 (1924).
(8) W. S. M. Grieve and D. H. Hey, *J. Chem. Soc.*, 1797 (1934).