period (Table I); the acidification led to *ca.* 35 g of a syrup that was insoluble in both H_2O and benzene and presumably represented secondary reaction products.

C. Effect of Light. A mixture of **1** (8.33 g, 40.4 mmol) and **2** (1.98 g, 20.2 mmol) was irradiated with occasional swirling in a quartz flask at *ca.* 50–75° using a 6-in. distant 250-W Hg lamp [General Electric Co. UA-2 Uviarc; rated per cents of wattage (Å range) were 4.6 (<2800), 4.3 (2800–3200), and 3.4 (3200–3800)]. A brown oil began to separate after *ca.* 1 hr. Considerable carbonization seemed to occur. After 8 hr, a brown solid and pale yellow supernatant layer resulted. Addition of H_2O (5 ml) and warming effected dissolution of the solid. An iced solution of KOH (2.29 g, 40.9 mmol) in H_2O (25 ml) was added, and the mixture was extracted well with Et_2O. Acidification (pH 7) and benzene extraction gave 0.07 g of material, a *maximum* yield of only 2% of **5**.

Authentic 2-(*n*-Pentylthio)succinic Acid (5). Sodium hydroxide (5.3 g, 133 mmol) and purified *n*-pentyl iodide (27.8 g, 140 mmol) were added to a solution of mercaptosuccinic acid (19.4 g, 129 mmol)[19] and Na_2CO_3 (13.7 g, 129 mmol) in H_2O (58 ml). The mixture was stirred at high speed under N_2 for 6 hr.[20] Heat was applied briefly at the outset to raise the temperature to 70°, after which the temperature remained at *ca.* 70–83°, mainly apparently because of the heat of stirring. The homogeneous mixture was washed with Et_2O, acidified, and extracted with benzene (300 ml) and Et_2O (200 ml) in several portions (**5** is sparingly soluble). The combined extracts were washed (H_2O), dried ($MgSO_4$), and evaporated, yield, 20.0 g (70%), mp 105.5–107°. Recrystallization [H_2O, $Cl(CH_2)_2Cl$] gave **5** of constant mp 108.5–109°, undepressed by the analytically pure **5** described in B (lit. mp 99.5°,[11] 107°,[21] 107.7–108°[22]). *Anal.* Calcd for $C_9H_{16}O_4S$: C, 49.07; H, 7.32. Found: C, 49.26; H, 7.21.

When essentially the same mixture merely was shaken vigorously at ~25° for 28 hr, the yield of greasy **5** (mp 93–102°) was quite small.

Thermal Stability of 1. In a simulation of expt 1, **1** (7.45 g) was heated alone at 153–158° for 19 hr. In contrast to the dark color typically seen in less than 1 hr with **1** and **2** (*e.g.*, in expt 1 and 8), **1** became only very pale yellow; no odor of a thiol or of H_2S was perceptible. Even the first fraction on distillation was pure **1** [0.46 g (6%), n^{25}D 1.4872 (lit.[15] n^{25}D 1.4868, 1.4875)], and remaining fractions were quite pure as well [6.42 g (86%), bp 140–145° (19 mm), n^{25}D 1.4873, n^{25}D for 1-pentanethiol, 1.4439[23]].

Substitution of Diphenyl Disulfide for 1. In a simulation of expt 1, recrystallized $(PhS)_2$ (7.68 g, 35.2 mmol) and **2** (3.00 g, 30.6 mmol) were heated at 160–170° for 23 hr. The $(PhS)_2$, isolated as in A, amounted to 7.62 g (99% recovery), mp and mmp 57–59°. Acidification of the aqueous layers and continuous Et_2O extraction gave 2.92 g (82%) of maleic acid, mp and mmp 126.5–129°.

Registry No.—**1**, 112-51-6; **2**, 108-31-6; **5**, 5413-66-1; diphenyl disulfide, 882-33-7.

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(13) Melting points are corrected, and boiling points are uncorrected.

(14) *Good commercial grades of* **1** *and* **2** *usually were used; as a check,* however, for expt 5 the disulfide **1** was fractionally distilled (also used in expt 8), n^{25}D 1.4869 (lit.[15] n^{25}D 1.4868, 1.4875), and the anhydride **2** was recrystallized from $Cl(CH_2)_2Cl$, mp 52.5–54° (lit.[16] mp 52.8°).

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(17) Benzene proved best for extracting crude **5**, while leaving maleic and fumaric acids mainly in the aqueous phase. However, it is a rather poor solvent and in some experiments (when the extract was dried) Et_2O had to be added to preclude crystallization of **5**.

(18) Typically, after the first recrystallization, products were washed with a little ice water and then pressed on a vacuum filter with a rubber dam. The water expressed carried more or less of the "black oil" that appeared in the filtrate in each such instance except in expt 11. Decolorizing carbon was used frequently in the recrystallizations.

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Hydrolytic Reactions of Carbyl Sulfate

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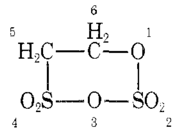
Carbyl sulfate (2,2,4,4-tetraoxo-1,3,2,4-dioxadithiane, **1**) is a colorless, crystalline solid, mp 107–108°, commonly prepared by the direct reaction of ethylene with SO_3.[1b,2] Crude "carbyl sulfate" of mp 80°[1b] has been shown to be complexed with excess SO_3.[2] The pure compound reacts vigorously with alcohols,[3] amines,[4] and other compounds possessing active hydrogens. The reaction of carbyl sulfate with water has been reported to produce ethionic acid ($HOSO_2OCH_2CH_2SO_3H$),[2,5] isethionic acid ($HOCH_2CH_2SO_3H$),[5,6] and/or vinylsulfonic acid or its sodium salt.[2,3,5-7] We have sought to elucidate the reactions of carbyl sulfate with water.



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When 0.01 mol of purified carbyl sulfate is added to 200–400 ml of water at 0–80° a fast exothermic reaction goes to completion within seconds. Titration shows formation of 2 equiv of strong acid. Similar results are obtained when carbyl sulfate is predissolved in 1,2-dichloroethane or dioxane, and when water is replaced by dilute mineral acid. The reaction product is ethionic acid.

$$\overline{\mathrm{SO_2OCH_2CH_2SO_2O}} + \mathrm{H_2O} \longrightarrow \mathrm{HOSO_2OCH_2CH_2SO_3H} \qquad (1)$$

Dilute acidic aqueous solutions of ethionic acid are stable for days at room temperature. At about 60° and above, the ratio (equivalents of acid formed):(moles of carbyl sulfate reacted) slowly increases from 2.0 to 3.0, following pseudo-first-order kinetics. At 70° $k \cong 1 \times 10^{-6}$ sec^{-1}. The activation energy (70–90°) is approximately 33 kcal mol^{-1}. A solution of ethionic acid in water was held at 80° for 24 hr, then cooled and titrated with $BaCl_2$ to remove sulfate. The filtrate was neutralized with dilute NaOH and water was removed to yield sodium isethionate. The only reaction evident in hot acidic aqueous solutions is simple ester hydrolysis. Under these conditions no vinylsulfonic acid is formed.

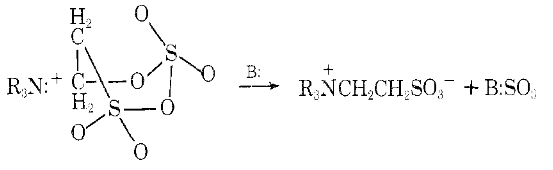
$$HOSO_2OCH_2CH_2SO_3H + H_2O \longrightarrow H_2SO_4 + HOCH_2CH_2SO_3H \quad (2)$$

Addition of carbyl sulfate to aqueous alkaline solutions at 25-90° (pH 12.0-13.3) resulted in rapid reactions yielding in all cases *mixtures* of ethionate and vinylsulfonate salts. No isethionate was detected and no secondary hydrolysis of ethionate was observed. The ratios (equivalents of acid formed):(moles of carbyl sulfate reacted) were in the range 2.5-2.8. These ratios were difficult to reproduce from one run to another, but ratios found in individual runs were reproducible and invariant with time. No systematic temperature dependency was evident. These observations are consistent with a competition between two fast irreversible processes, one forming ethionate and the other forming vinylsulfonate *directly from carbyl sulfate*.

$$\overline{SO_2OCH_2CH_2SO_2O} + OH^- \longrightarrow CH_2{=}CHSO_3^- + H_2SO_4 \quad (3)$$

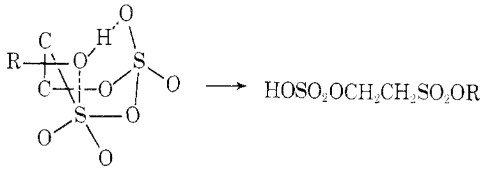
In titrating alkaline ethionate solutions to neutrality it was observed that at about pH 9 and below additional acid was formed spontaneously. Similarly, titrations of acidic solutions of ethionic acid were characterized by fading end points. An acidic solution of ethionic acid was brought to pH 7.8-8.0 with a measured excess of $NaHCO_3$, allowed to stand for 15 min at 23°, then acidified and assayed for acid functions by a quick-titration method; the ratio (equivalents of acid formed):(moles of carbyl sulfate reacted) was found to have increased from 2.0 to 3.0. The organic product of this reaction is sodium vinylsulfonate. These observations indicate that ethionic acid in aqueous solutions is stable at pH's below about 5, and its anion is stable at pH's above about 10, but in the intermediate range (pH 6-9) a facile elimination occurs.

The foregoing, taken together with literature reports,[2-7] suggests that carbyl sulfate can undergo three distinct ring-opening attacks by Lewis bases. Soft bases which do not possess active hydrogens (for example, tertiary amines[4]) make a SN2 attack upon C-6 (eq 4), where B: is excess amine or any other available base. In aqueous solutions this reaction is preempted by either or both of the following reactions.



(4)

Soft bases possessing active hydrogens (alcohols, primary and secondary amines, water) have available to them another very facile ring-opening mechanism. We suggest that this may be an attack upon S-4 facilitated by interaction with the flagpole oxygen of S-2 (eq 5). With water (R = H) the product is ethionic acid, with alcohols the corresponding sulfonate esters.[3]



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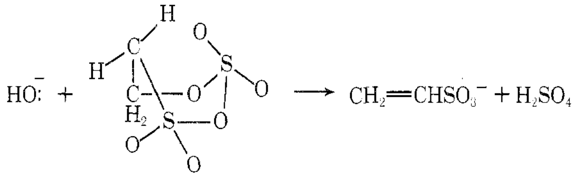
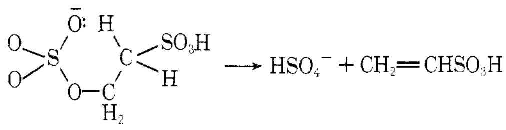
Hard bases such as hydroxide ion not only may attack sulfur to form ethionate ion, but also may attack the most acidic hydrogen at C-5, to produce vinylsulfonate (eq 6).



(6)

Another feature of the aqueous system is the fast elimination which ethionic acid undergoes in neutral solutions. The intramolecular elimination of the monoanion looks reasonable (eq 7). However, a rate optimum at pH 7-8 requires that $K_1K_2 \cong 10^{-15}$, a smaller product than expected for a molecule containing a hydrogen sulfate and an alkylsulfonic acid function.[8] Furthermore, Geiger[9] has shown that the methyl half-ester of ethionic acid fails to undergo the corresponding elimination reaction under these conditions. A possible explanation lies in the conformations available to ethionic acid. This may assume a strainless conformation with two intramolecular hydrogen bonds (2). In conformation 2 one of the hydrogens adjacent to the sulfonic acid function is also anti to the sulfate function, that is, in favored position for elimination. Although the concentration of undissociated ethionic acid is very low in neutral solutions, the high susceptibility of 2 to E2 attack by OH^- may compensate and thereby explain this fast elimination.



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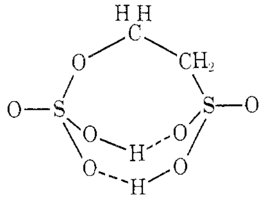

2

Experimental Section

Commercial carbyl sulfate (brown crystals) was recrystallized three times from 1,2-dichloroethane under nitrogen, dried for 90 min under vacuum to remove all traces of solvent and occluded SO_3, then stored in sealed bottles at −20°. Carbyl sulfate purified in this manner is in the form of colorless crystals, mp 107-108°, nmr spectrum in dichloroethane consisting of two triplets (60 MHz), δ 2.48 and 5.09 ppm, and stable in dry storage for at least 1 year. With less rigorous purification or in the presence of moisture the compound deteriorates within a few weeks.

Ethionic acid, formed by the reaction of carbyl sulfate with water, decomposes upon isolation. Its aqueous solution was identified by its infrared spectrum (AgCl cell) with major $-SO_2-$ peaks at 1200, 1160, 1040, and 1020 cm^{-1}, its nmr spectrum, characterized by triplets at δ 3.35 and 4.42 ppm, the 2:1 stoichiometry of acid function per carbyl sulfate reacted, and its subsequent reactions noted below.

Isethionic acid was isolated from the reaction of 2.5 g of carbyl sulfate with 400 ml of 0.01 *M* sulfuric acid, after hydrolysis of the intermediate ethionic acid by refluxing for 12 hr and removal of sulfate by $BaCl_2$ precipitation. The aqueous filtrate was neutralized with NaOH. One portion was concentrated by evaporation at reduced pressure; its nmr spectrum showed two triplets at δ 3.29 and 4.09 ppm. A second portion was dried; the white, crystalline salt yielded (KBr pellet) infrared absorption peaks at 3300, 1180, 1040, and 740 cm^{-1}, in good agreement with published values.[10] Nmr and infrared spectra of a commercial sample of sodium isethionate were essentially identical with the above.

Vinylsulfonic acid was prepared and identified as follows. To 250 ml of 0.02 *M* sulfuric acid at 22° was added 0.020 mol of carbyl sulfate, to form ethionic acid. To this solution was added an excess (0.080 mol) of $NaHCO_3$ and the buffered solution was stirred for 15 min. Analysis of an aliquot showed 3.0 equiv of acid per mole of carbyl sulfate. (This was confirmed with poor precision by a bisulfite additon assay.) The neutralized solution was dried at 50° and reduced pressure and the resulting salt mixture was subjected to a 12-hr Soxhlet extraction with methanol. The extract, containing the organic salt, was divided into aliquots. One portion, treated with *S*-benzylthiuronium chloride, formed the corresponding vinylsulfonate salt, mp 145–146° from ethanol, in good agreement with the reported value.[11] Another portion was dried; the white salt yielded (KBr pellet) major infrared maxima at 1190, 1045, 1620, and 755 cm^{-1}, in the expected regions for $-SO_2-$ asymmetric and symmetric stretch, vinyl, and S–O stretch, respectively. The remaining portion was examined in aqueous solution by nmr, yielding a seven-peak spectrum characteristic of vinyl splitting with $J_{gem} \cong 0$.[12] The three vinylic protons appeared at δ 6.00, 6.04, and 6.86 ppm, similar to those found for methyl vinyl sulfone (5.95, 6.13, and 6.70 ppm)[13] and reasonably close to the values predicted by the Pascual equation[14] for $CH_2{=}CH{-}SO_2-$ (6.23, 6.43, and 6.86 ppm).

Acid–base titrations were carried out using standard 0.10 *N* Na_2CO_3 or NaOH. Since ethionic acid undergoes an acid-generating elimination in near-neutral solutions, it was found useful to make one or two preliminary range-finding titrations, prior to carrying out rapid analytical titrations to first end points.

Reactions in dilute aqueous base were examined by addition of 2–3 mmol of pure carbyl sulfate to 100-ml portions of 0.10 *N* KOH, followed by titration with standard acid. At 25, 50, and 90° the average values of the ratio (equivalents of acid formed):(moles of carbyl sulfate reacted) were found to be 2.7, 2.6, and 2.7. (When carbyl sulfate is predissolved in 10 ml of dry dioxane and this solution is added to the aqueous base, this observed ratio falls to 2.0.) Identification of vinylsulfonate in the product mixture was made by infrared examination and by reaction with measured amounts of bisulfite ion to form potassium ethanedisulfonate.[15]

Quantitative information on the elimination of sulfate by ethionate in near-neutral solutions was sought by combining solutions of ethionic acid and phosphate buffers, then assaying these for vinylsulfonate by the semiquantitative bisulfite method.[15] Vinylsulfonate yields of 80–90% were obtained at pH 7.70, 70–78% at pH 7.01 and 8.90, 45–55% at pH 5.5 and 10.2, and 80–95% with authentic sodium vinylsulfonate. While these data suggest a maximum elimination in nearly neutral solutions, we were unable to obtain acceptably reproducible assays by this procedure.

Acknowledgment. We acknowledge with thanks support of this work by an Air Products and Chemicals Corp. fellowship.

Registry No.—Carbyl sulfate, 503-41-3.

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Ester Enolates. A New Preparation of Malonates, Phosphonoacetates, and α-Selenyl and Sulfinyl Esters

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The formation of α carbanions of carboxylic acids and esters by means of nonnucleophilic bases such as disubstituted lithium amides has recently been widely investigated owing to their great synthetic utility.

At the present time, the reactions of these anions with electrophilic substrates are restricted to alkyl halides,[1-6] halogens,[7] epoxides,[1] alkyl nitrates,[8] substituted ammonias,[9] alkyl silyl chlorides,[10] and carbonyl compounds such as CO_2,[11] esters,[8,12] acyl chlorides,[13] aldehydes,[14,15] and ketones.[15]

In this paper we wish to report the extension of this range of substrates to ethyl chloroformate, chlorophosphates, diphenyl disulfide, and benzeneselenenyl bromide. Also included are certain substrates that did not react satisfactorily. Esters of α-branched and straight-chain acids (isobutyric, hexanoic, and acetic acid) were employed to test the general applicability of the investigated reactions in relation with self-condensation reactions. The α anions were prepared with the readily available base lithium diisopropylamide (LDA) using published procedures.[5,6]

The reaction of ethyl chloroformate with these α anions was explored, leading to the expected substituted malonates in yields as high as 70% at −15° and 90% at −78°.

$$R_2CHCO_2R' \xrightarrow[2.\ ClCO_2Et]{1.\ LDA} R_2C(CO_2Et)CO_2R'$$

Of special interest is the facile preparation of ethyl *tert*-butyl malonate,[16] useful in β-keto ester synthesis.[17] This reagent can be obtained in a yield of 70–75%, whereas the normal three-step procedure[16] has an overall yield of 40–45%. This reaction can presumably be extended to the synthesis of other useful mixed malonates.

The synthetic utility of β-carboalkoxy phosphates (phosphonoacetates) and phosphinoxides as starting materials for olefination reactions suggested their preparation by treating the α anions with chlorophosphates and chlorophosphinoxides. Isobutyrates, on reaction with chlorophosphates, gave high yields of the expected products.

$$(CH_3)_2CHCO_2R \xrightarrow[2.\ (R'O)_2POCl]{1.\ LDA} (CH_3)_2C(CO_2R)P(O)(OR')_2$$

$$\textbf{a},\ R = Et;\ R' = Et,\ CH_3$$
$$\textbf{b},\ R = CH_3;\ R' = CH_3$$

The same reaction attempted with methyl hexanoate and ethyl acetate failed to give the expected products, thus detracting from synthetic use in olefination reactions. As self-condensation products were indicated by nmr spectra, we looked at the analogous *tert*-butyl esters, whose anions are known to be more stable.[5,6,18] The anion of *tert*-butyl acetate gave 65% of the desired reaction with $(EtO)_2P(O)Cl$, indicating the advantages of using hindered esters.

It was observed that $Ph_2P(O)Cl$ was unreactive with isobutyrate and acetate α anions, probably owing to steric crowding, $Ph_2P(O)OH$ being recovered after quenching of the reaction mixture with water. However, the obvious possibility of reaction on oxygen[19] by both sets of phosphorus chloride reagents must be considered, the intermediate phosphates being hydrolized during work-up. The relative success of esters sterically hindered on the α car-