

500-ml., 3-necked flask and heated at 120° for 4 hr. with vigorous stirring. The gray mass was then poured into 300 ml. of ice water and allowed to stand for 1 hr. so as to hydrolyze the unreacted phosphorus oxychloride. The two layers were separated and the aqueous layer was extracted with chloroform (2 × 50 ml.). After drying over Na₂SO₄, removal of chloroform left a brown oil which was distilled at 74–75° (15 mm.), *n*_D²⁰ 1.4750, to give 17.1 g. (55%) of the colorless 2-propenesulfonyl chloride.

General Procedure for Preparation of the Thietane 1,1-Dioxides.—In order to avoid repetition, the method for obtaining the title compounds is generalized. Detailed procedures, however, are given for the reactions of 1-propene and 2-propenesulfonyl chlorides with ketene diethylacetal as the separation of isomers necessitated different methods of work-up. The experiments in which no adduct was obtained are similar to that described for the reaction between ethanesulfonyl chloride and ketene diethylacetal.

The sulfonyl chloride (0.03–0.05 mole) was dissolved in anhydrous diethyl ether (50–75 ml.) or an equivalent amount of tetrahydrofuran. This solution was added dropwise (1–2 hr.), under a nitrogen atmosphere, to a stirred equimolar solution of triethylamine (0.03–0.05 mole) and ketene diethylacetal (0.03–0.05 mole) in diethyl ether (150 ml.) at room temperature (25°) contained in a 300-ml. 3-necked flask. A white precipitate formed immediately, and the solution was allowed to stir 2–12 hr. after the addition was complete. The precipitated triethylamine hydrochloride was filtered and washed with small portions of anhydrous ether to give the dried salt in 80–100% yields, m.p. 253–256° dec. The filtrate was evaporated to a yellow oil or solid on a Rinco rotatory evaporator, and the residue recrystallized from *n*-pentane, *n*-hexane, or ethanol (see Table I). An analytical sample usually required two additional recrystallizations and was dried *in vacuo* over phosphorus pentoxide.

Reaction of 2-Propenesulfonyl Chloride with Ketene Diethylacetal.—To a stirred solution of 3.22 g. (0.028 mole) of ketene diethylacetal and 2.80 g. (0.028 mole) of triethylamine in 100 ml. of anhydrous ether was added a solution of 3.89 g. (0.028 mole) of 2-propenesulfonyl chloride in 50 ml. of anhydrous ether. The solution turned cloudy with the first drop and a heavy white precipitate formed. After stirring overnight the triethylamine hydrochloride (3.55 g., 100%, m.p. 242–252°) was filtered from the solution. Removal of the ether on a Rinco rotatory evaporator left a yellow semicrystalline solid. This solid was dissolved in 300 ml. of hot *n*-hexane, and on cooling 0.40 g. (6.5%) of light yellow crystals precipitated. These could be purified by suspending them in 30 ml. of hot *n*-hexane and adding ethanol dropwise until dissolution was complete. After three recrystallizations, white platelets, identified as compound VIII (see Table I), were obtained, m.p. 118–120°.

The initial 300 ml. of *n*-hexane was evaporated to dryness giving 2.79 g. (46%) of light yellow crystals (m.p. 46–49°). After three recrystallizations from *n*-pentane, the soft white crystals melted at 46–48°, and were identified as compound VII (see Table I).

Reaction of 1-Propenesulfonyl Chloride with Ketene Diethylacetal.—In a manner similar to the preceding experiment, 7.03 g. (0.05 mole) of 1-propenesulfonyl chloride in ether was allowed to react with a solution of 5.80 g. (0.05 mole) of ketene diethylacetal and 5.05 g. (0.05 mole) of triethylamine to give triethylamine hydrochloride in 81% yield. Evaporation of the ether left a yellow oil which was boiled in 400 ml. of *n*-hexane, and, when cooled, there was obtained a yellow solid. Recrystallization from ethanol and water gave 0.76 g. (7.6%) of light yellow crystals, m.p. 114–118°. Two additional recrystallizations gave white platelets, m.p. 118–120°. A mixture melting point with the high melting isomer from 2-propenesulfonyl chloride gave no depression (m.p. 118–120°) and their infrared spectra were superimposable.

The initial 400 ml. of *n*-hexane was evaporated to a yellow oil, which, when recrystallized from *n*-pentane (tendency to oil), gave 5.14 g. (51%) of crystals which melted at 42–46°. A second recrystallization from *n*-pentane raised the melting point to 49–50°. A mixture melting point with the low-melting isomer from 2-propenesulfonyl chloride showed no depression (48–50°) and the infrared spectra were identical.

Reaction of Ethanesulfonyl Chloride with Ketene Diethylacetal.—Ethanesulfonyl chloride (7.72 g., 0.06 mole) was dissolved in 60 ml. of anhydrous ether and added dropwise to a solution of ketene diethylacetal (6.96 g., 0.06 mole) and triethylamine (6.06 g., 0.06 mole), dissolved in 150 ml. of anhydrous ether. After about 5 ml. of the sulfonyl chloride solution had been added, a white finely-divided precipitate formed which turned yellow and finally coagulated to a brown gummy resin. After stirring overnight the resin was filtered from the solution and suspended in acetone. The acetone dissolved the resin leaving 5.40 g. (65%) of triethylamine hydrochloride, m.p. 256–257° dec. Removal of the initial ether solution gave a dark oil which possessed the strong odor of ethanesulfonyl chloride. Attempts to recrystallize this oil from common organic solvents failed. It was then distilled, but could not be efficiently fractionated, and gave 4.63 g. of distillate boiling over a wide range; b.p. 45–102° (1.0 mm.). On a preparative vapor phase chromatograph⁵⁰ twelve peaks were observed. The major peak (ca. 55–70%) was collected with a retention time of 7 min. on the column described and was identified as ethyl ethanesulfonate by comparing its retention time and physical properties with an authentically prepared sample.⁵¹ The sulfonate was obtained in approximately 35% yield based on ethanesulfonyl chloride.

Acknowledgments.—The authors are very grateful to the Phillips Petroleum Company, Gulf Research and Development Corporation, and the National Institutes of Health under Grant CY-4536 for support of this work.

(50) An Aerograph Autoprep Model A-700, by Wilkens Instrument and Research, Inc., Walnut Creek, Calif., with a 20 ft. × 3/8 in. aluminum column packed with 20% GE-SF-96 on 60/80 firebrick at 200° and a helium flow rate of 200 ml./min. was used.

(51) L. Carius, *J. prakt. Chem.*, [2] **2**, 267 (1870).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, IND.]

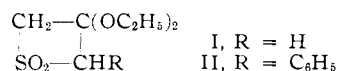
Reactions of 3,3-Diethoxythietane 1,1-Dioxide and 2-Phenyl-3,3-diethoxythietane 1,1-Dioxide¹

BY WILLIAM E. TRUCE AND JOHN R. NORELL

RECEIVED JUNE 3, 1963

The compounds referred to in the title were studied with regard to their acidic and basic hydrolyses, pyrolyses, and reactions with reducing agents.

In a previous paper² the synthesis and physical properties of nine new substituted thietane sulfones³ were discussed. The present communication is concerned with some of the chemistry of these compounds, in particular when R is hydrogen (I) or phenyl (II).



(1) Abstracted from the Ph.D. Thesis of John R. Norell, Purdue University, 1963.

(2) W. E. Truce and J. R. Norell, *J. Am. Chem. Soc.*, **85**, 3231 (1963).

(3) D. C. Dittmer and M. E. Christy, *ibid.*, **84**, 399 (1962), have discussed their findings on the reactions of thiete sulfone, but other than this recent article, there appear to be no reports concerning the reactions of these compounds.

Acid Hydrolysis.—Two independent methods^{4,5} have recently been used for the preparation of 3-thietanone; however, the corresponding sulfone, 3-thietanone 1,1-dioxide (III), has remained unknown.⁶ When I is dissolved in concentrated hydrochloric acid at 25°, a white solid precipitates after about 15 min., which can be recrystallized from dioxane or sublimed at 100° (1.0 mm.) to give the ketosulfone III. The structural assignment is supported by elemental analysis, molecular weight determination, n.m.r., and infrared spectroscopy. In the n.m.r. spectrum there exists a

(4) R. Mayer and K. F. Funk, *Angew. Chem.*, **73**, 578 (1961).

(5) H. Prinzbach and G. Voh, *Z. Naturforsch.*, **16b**, 763 (1961).

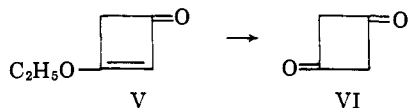
(6) See W. E. Truce and J. R. Norell, *Tetrahedron Letters*, in press, for a brief communication concerning this compound.



single unsplit peak at 4.22 δ in DMSO or at 4.92 δ in dioxane. The infrared spectrum (Nujol) exhibits a strong carbonyl absorbance at 5.62 μ with a weak side band at 5.45 μ and strong sulfone absorbances at 7.61 and 8.36 μ . Two other strong bands are prevalent at 8.86 and 13.84 μ . Compound III readily forms a bright yellow 2,4-dinitrophenylhydrazone. Hydrogenation attempts with Adams catalyst at 65° for 48 hr. at three atmospheres pressure yielded none of the known 3-hydroxythietane 1,1-dioxide (IV)⁷; 90% of the ketosulfone was recovered. However, reduction with diborane,⁸ by external generation, gave the desired hydroxysulfone in 56% yield, thus confirming the assigned structure for 3-thietanone 1,1-dioxide.

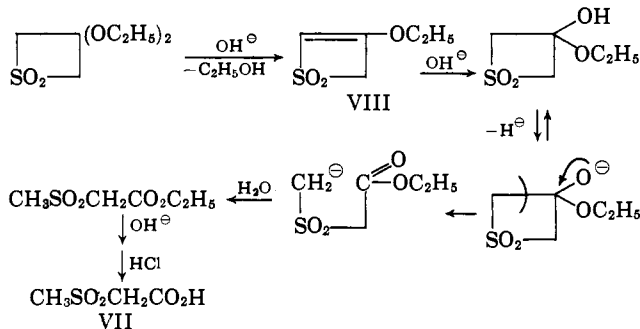
Compound III exhibits acidic properties in that a vigorous effervescence is observed with a sodium bicarbonate solution. It is difficultly soluble in most organic solvents. This compound can also be formed in cold 90% sulfuric acid in low yield or in 85% phosphoric acid in moderate amounts. Further studies on the chemistry of 3-thietanone 1,1-dioxide (III) are currently being investigated and will be presented at a later date.

Dilute acids, such as 5% hydrochloric or 10% sulfuric, have little effect on I or II. Neither acid dissolves these adducts at 25° and after several days the starting compounds are recovered unchanged. However, on boiling, dissolution occurs; on evaporating to dryness none of the starting material is obtained nor any of the expected ketone. Possibly a ring opening process occurs followed by decomposition to smaller fragments, which are lost during evaporation of the aqueous solution. Ring fragmentation has been reported⁹ when dilute acid acts on V, whereas with cold 90% sulfuric acid, 1,3-cyclobutanedione (VI) is obtained. Also, when 3-hydroxythietane is oxidized to the sulfone in hot acetic acid, ring cleavage occurs⁷



to form dimethylsulfone, whereas the desired sulfone is obtained at 0° with hydrogen peroxide in acetic acid.

Attempts to hydrolyze II in cold 90% sulfuric acid leads to excessive tar formation, probably due to sulfonation of the phenyl ring. Reaction of II in concentrated hydrochloric acid at 25° gives a polymeric substance and recovery of starting material. When II is heated in concentrated hydrochloric acid, excessive decomposition occurs, yielding intractable resins.

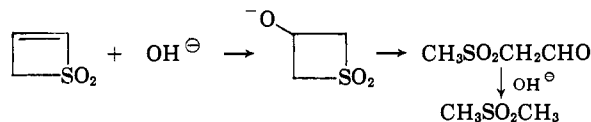


(7) D. C. Dittmer and M. E. Christy, *J. Org. Chem.*, **26**, 1324 (1961).

(8) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **82**, 681 (1960).

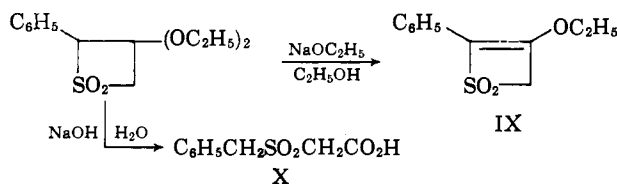
(9) H. H. Wasserman and E. V. Dehmlow, *ibid.*, **84**, 3786 (1962).

Basic Hydrolysis.—A 5% sodium hydroxide solution reacts with I to open the ring and on acidification yields methylsulfonylacetic acid (VII). A rationalization for the formation of VII is through 3-ethoxythiete sulfone (VIII), followed by a Michael addition of water, ring opening, and saponification to the observed product. An analogy exists³ in that when thiete sulfone is treated with sodium hydroxide a ring cleavage occurs to yield dimethyl sulfone.



Attempts were made to isolate VIII by employing other bases, *e.g.*, potassium *t*-butoxide in *t*-butyl alcohol or *n*-butyllithium in ether. However, with these, I yields viscous oils, which contain carbonyl and olefinic bands in the infrared. Attempts to identify these substances have failed. Reaction with sodium ethoxide in ethanol yields 93% of recovered starting material.

However, when II is treated with sodium ethoxide in ethanol, the thiete sulfone derivative IX, is obtained in 40% yield, but if II is treated with sodium hydroxide in either water or ethanol, a ring opening occurs and benzylsulfonylacetic acid (X) is formed. These

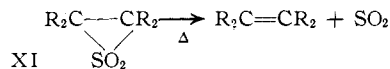


results support the assumption that the thiete sulfone derivative VIII may be an intermediate during the basic hydrolysis of I.

Identification of IX is based on elemental analysis, molecular weight determination, and n.m.r. and infrared spectroscopy. The n.m.r. spectrum, which is in excellent agreement with the structure, shows the following chemical shifts (δ units), multiplicities, relative areas, and interpretations of the signals produced in CDCl_3 : 7.38, singlet, 5, phenyl protons; 4.55, singlet, 2, ring methylene protons; 4.13, quartet, 2, methylene protons in the ethoxyl group; 1.38, triplet, 3, methyl protons in the ethoxyl group. The infrared spectrum exhibits a strong band at 6.05 μ , indicative of a phenyl-conjugated double bond and sulfone bands at 7.46 and 8.45 μ . In addition to the physical data, compound IX rapidly decolorizes a 1% potassium permanganate solution, whereas benzylsulfonylacetic acid (X) or II does not.

The identity of benzylsulfonylacetic acid (X) was confirmed by comparison with an independently prepared sample.¹⁰ A mixed melting gave no depression and their infrared spectra were superimposable. Interestingly, the n.m.r. spectrum of the sodium salt of benzylsulfonylacetic acid contains only two singlets in D_2O . The phenyl protons appear at 7.58 δ , whereas the other four hydrogens appear as one peak at 4.78 δ . The ratio is the expected 5:4. The benzylic hydrogens and those α to the carboxyl group seem to be nearly equivalent with regard to their proton spectra.

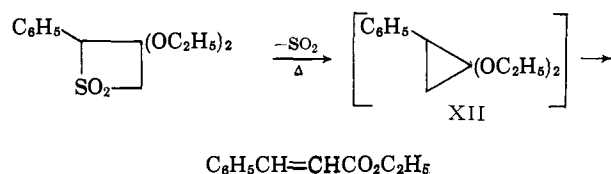
Pyrolysis.—Since ethylenic sulfones (XI) are known to decompose readily yielding olefins and sulfur di-



(10) G. G. Stoner, *ibid.*, **63**, 1481 (1941).

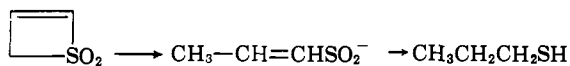
oxide,¹¹ thietane sulfones might be expected to pyrolyze under more strenuous conditions to sulfur dioxide and cyclopropane derivatives. These sulfones, however, show some thermal stability. For example, compound I can be distilled at 94–95° (0.5 mm.) or passed through a gas chromatograph at 200° unchanged. In an attempt to pyrolyze I at 300°, according to the method of Bailey and Hewitt,¹² total recovery of the sulfone is obtained. However, at pyrolysis conditions of 500°, excessive tar formation occurs and only ethanol, acetic acid, and sulfur dioxide are isolated.

Pyrolysis of II occurs when attempts are made to distil it under reduced pressure. In addition to ethanol, sulfur dioxide, and excessive tar formation, there is obtained a low yield of ethyl cinnamate. A possible explanation is that phenylcyclopropanone diethylketal (XII) may be initially formed but decomposes to ethyl cinnamate under the reaction conditions. A

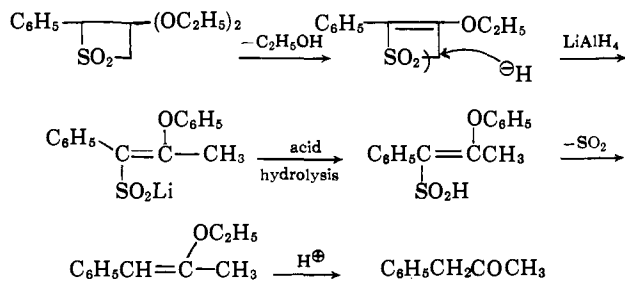


similar decomposition has been shown by McElvain and Weyna¹³ to take place when attempts were made to purify phenylcyclopropanone diethylketal obtained from the reaction of phenylchlorocarbene on ketene diethylacetal. Attempted distillation gave ethyl cinnamate and ethyl atropate in 19 and 44% yields, respectively.

Effect of Reducing Agents.—Neither I nor II is changed by treatment with sodium borohydride in methanol. However, treatment with lithium aluminum hydride is subject to several complications. It is known that both sulfones and ketals react in the presence of this reagent. Small ring sulfones yield sulfides,¹⁴ and ketal groups are converted to ethers, especially when aluminum chloride is present.¹⁵ Moreover, the methylene protons are acidic and loss of ethanol may occur, thus yielding a thiete sulfone derivative. Thiete sulfone, itself, undergoes ring opening to yield propanethiol when treated with lithium aluminum hydride.³ When I is treated with an ethereal



solution of LAH, there is obtained only a small quantity of an unidentified foul-smelling oil. When II was treated likewise, phenylacetone was obtained in low yield on acid work-up. This was the only compound identified; however, mercaptan-like odors were noticed.



(11) (a) H. Staudinger and F. Pfenninger, *Ber.*, **49**, 1941 (1916); (b) C. V. Vargha and E. Kovacs, *ibid.*, **75**, 794 (1942); (c) N. P. Neurieter and F. G. Bordwell, *J. Am. Chem. Soc.*, **85**, 1209 (1963).

(12) W. J. Bailey and J. J. Hewitt, *J. Org. Chem.*, **21**, 543 (1956).

(13) S. M. McElvain and P. L. Weyna, *J. Am. Chem. Soc.*, **81**, 2579 (1959).

(14) F. G. Bordwell and W. H. McKellin, *ibid.*, **73**, 2251 (1951).

(15) M. N. Rerick and E. L. Eliel, *ibid.*, **84**, 2356 (1962).

The preceding mechanism, one of the possible reaction paths for this result, is analogous to that proposed by Dittmer and Christy³ for reduction of thiete sulfone.

Experimental¹⁶

3,3-Diethoxythietane 1,1-dioxide and 2-phenyl-3,3-diethoxythietane 1,1-dioxide were prepared as previously described.²

3-Thietanone 1,1-Dioxide (II).—3,3-Diethoxythietane 1,1-dioxide (5.00 g., 0.026 mole) was suspended in 40 ml. of concentrated hydrochloric acid which was contained in a 100-ml. beaker. Stirring with a glass rod effected dissolution in a few minutes at 25° and after 15 min. a white crystalline solid appeared. The mixture was allowed to stand overnight and was then filtered through a sintered glass funnel. The crystals were washed on the filter successively with small amounts of water, ethanol, and ether, and after drying in air yielded 1.64 g. of product, m.p. 216–219° dec. Evaporation of the filtrate and the washings using a Rinco rotatory evaporator on a steam bath yielded, after a similar washing, an additional 0.56 g., m.p. 215–217° dec., giving a combined yield of 2.20 g. (70%). Three recrystallizations from purified dioxane or sublimation at 100° (1.0 mm.) produced hard white crystals, m.p. 219–221° dec.

Anal. Calcd. for C₈H₈O₆S: C, 29.99; H, 3.36; S, 26.69; mol. wt., 120.1. Found: C, 29.79; H, 3.30; S, 26.42; mol. wt., 121.2 (in dioxane).

Dissolution of II in dioxane and addition of a standard 2,4-dinitrophenylhydrazine solution¹⁷ afforded a bright yellow 2,4-dinitrophenylhydrazone, which could be recrystallized from dioxane; m.p. 241° dec.

Anal. Calcd. for C₉H₈N₄O₆S: C, 36.00; H, 2.69; N, 18.66; S, 10.68. Found: C, 36.31; H, 2.91; N, 18.49; S, 10.81.

Diborane Reduction of 3-Thietanone 1,1-Dioxide.—The basic apparatus has been described by Brown and Subba Rao.⁸ In the reaction flask was placed 1.44 g. (12 mmoles) of the 3-thietanone 1,1-dioxide dissolved in 70 ml. of purified dioxane. Diborane was generated externally from 50 ml. of a saturated NaBH₄ solution in diglyme and 5 ml. of boron trifluoride etherate. After the diborane addition was complete (20 min.) the solution was stirred an additional 20 min. and hydrolyzed with 15 ml. of water. Removal of the dioxane left a colorless oil. Crystallization could be achieved from *n*-hexane and ethanol yielding 0.80 g. (56%) of white crystals, m.p. 99–100.5°; reported for 3-hydroxythietane 1,1-dioxide,⁷ m.p. 99.5–102°. The infrared spectrum showed no carbonyl band but a strong hydroxyl band was present at 2.90 μ.

Catalytic Hydrogenation of 3-Thietanone 1,1-Dioxide.—Into a Parr hydrogenation bottle were placed 1.00 g. of 3-thietanone 1,1-dioxide, a small amount of platinum oxide, 20 ml. of purified dioxane, and 2 drops of concentrated hydrochloric acid. The bottle was shaken for 48 hr. at 65° under a hydrogen pressure of three atmospheres. The solution was then filtered and evaporated to dryness. A yellow-brown solid (0.96 g.) remained which melted at 185–200°. Recrystallization of a small portion from ethyl acetate melted at 215–218° and the infrared spectrum was superimposable with that of the starting material.

Reaction of 3,3-Diethoxythietane 1,1-Dioxide with Aqueous Sodium Hydroxide.—The title compound (3.00 g., 0.016 mole) was suspended in 20 ml. of 5% sodium hydroxide solution and heated at gentle reflux for 1 hr., after which time dissolution was complete. The light yellow solution was extracted with ether and the aqueous layer was acidified with dilute hydrochloric acid and again extracted with ether. Evaporation of both ether layers left only trace amounts of unidentifiable oils. The acidified aqueous layer was evaporated to dryness, boiled in ethanol, and filtered. Evaporation of the ethanol left a viscous yellow oil (0.71 g.) which solidified on cooling in ice (m.p. 80–105°). Two recrystallizations from ethyl acetate and *n*-hexane yielded white crystals of methylsulfonylacetic acid; m.p. 115–117° (lit.¹⁸ m.p. 115°). The n.m.r. spectrum in pyridine gave two unsplit peaks,¹⁹ at 3.48 and at 4.67 δ in the expected ratio of 3:2.

Anal. Calcd. for C₈H₈SO₄: C, 26.08; H, 4.38; S, 23.22. Found: C, 26.57; H, 4.50; S, 22.90.

Reaction of 2-Phenyl-3,3-diethoxythietane 1,1-Dioxide with Aqueous Sodium Hydroxide.—To 60 ml. of a 5% sodium hydroxide solution was added 3.00 g. (0.011 mole) of 2-phenyl-3,3-

(16) (a) All melting points are uncorrected. Microanalyses were determined by C. S. Yeh, M. Hudgens, and T. Eikeri. (b) The molecular weights were obtained on a Mechrolab vapor pressure osmometer.

(17) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 111.

(18) A. Mellander, *Svensk Kem. Tidkr.*, **46**, 99 (1934) [*Chem. Abstr.*, **28**, 5408 (1934)].

(19) At a sweep width of 100 c.p.s. these peaks show splitting into a triplet and a quartet, respectively, indicating interactions through the sulfonyl group.

diethoxythietane 1,1-dioxide which after heating at reflux for 2 hr. gave a homogeneous solution. Acidification with 10% hydrochloric acid precipitated 1.60 g. (58%) of benzylsulfonylacetic acid, which after recrystallization from water and ethanol melted at 136–138°. A mixture melting point with an authentic sample²⁰ showed no depression (m.p. 136–138°) and their infrared spectra were superimposable.

If the basic hydrolysis is carried out with sodium hydroxide in ethanol the sodium salt of the acid precipitates (52%) from the solution and on recrystallization from ethanol and water melts at 210–211°.

Anal. Calcd. for C₉H₉NaSO₄: C, 45.76; H, 3.84; Na, 9.74; S, 13.58. Found: C, 45.40; H, 3.74; Na, 9.75; S, 13.50.

2-Phenyl-3-ethoxythiete 1,1-Dioxide.—2-Phenyl-3,3-diethoxythietane 1,1-dioxide (9.00 g., 0.03 mole) was dissolved in a solution of sodium ethoxide prepared from 0.69 g. (0.03 g.-atom) of sodium in 150 ml. of absolute ethanol under a nitrogen atmosphere. The solution was heated at 70° for 5 hr. after which time the solution had taken on a yellow color, but no formation of a precipitate was observed as with sodium hydroxide in ethanol. The solution was cooled and 150 ml. of water was added forming a yellow precipitate. Acidification with dilute sulfuric acid removed most of the yellow color. The solid was recrystallized from absolute ethanol, giving 2.71 g. (m.p. 128–132°) of product. An analytical sample was prepared by suspending 1.0 g. of the solid in boiling *n*-hexane (30 ml.) and adding ethanol dropwise until dissolution was complete. Cooling slowly gave long white needles, m.p. 132–134°.

Anal. Calcd. for C₁₁H₁₂SO₃: C, 58.93; H, 5.40; S, 14.31; mol. wt., 224. Found: C, 59.00; H, 5.32; S, 14.29; mol. wt., 228 (CHCl₃).

Pyrolysis of 3,3-Diethoxythietane 1,1-Dioxide.—Over a period of 25 min., 10.0 g. of the adduct was dropped through a pyrolysis tube packed with 4-mm. glass beads and externally heated at 500° under a slow nitrogen flow. Excessive decomposition occurred and tar formed throughout the tube. However, 2.0 g. of a black oil with a very acrid odor was collected in an ice-cooled container, and distilled over a large range (80–115°) to a colorless acidic liquid. Vapor phase chromatographic analysis

indicated the presence of about 76% ethanol and 20% acetic acid with several other peaks. The Dry Ice trap was found to contain 2.0 g. of a yellow liquid which was mostly sulfur dioxide.

Pyrolysis of 2-Phenyl-3,3-diethoxythietane 1,1-Dioxide.—Pyrolysis was achieved by distilling 5.5 g. (0.02 mole) of the adduct at a 200° pot temp. through a 6-in. Vigreux column at 12 mm. pressure. A yellow liquid, 0.67 g., distilled between 130–140° (12 mm.). A portion of this oil when boiled in a 10% sodium hydroxide solution yielded cinnamic acid on acidification. The infrared spectrum of the oil was identical with that of a known sample of ethyl cinnamate. Vapor phase chromatographic analysis indicated 85% purity and the retention times of the above oil and ethyl cinnamate were identical.

Lithium Aluminum Hydride Reduction of 2-Phenyl-3,3-diethoxythietane 1,1-Dioxide.—Finely ground lithium aluminum hydride (7.6 g., 0.20 mole) was suspended in 150 ml. of anhydrous ether. A solution of 5.40 g. (0.02 mole) of 2-phenyl-3,3-diethoxythietane 1,1-dioxide, dissolved in 50 ml. of anhydrous tetrahydrofuran, was added dropwise to the hydride mixture over a period of 30 min. After stirring at 25° for 6 hr. the gray mixture was cautiously poured over 300 ml. of ice-water. The hydrolysate was then made strongly acidic with 200 ml. of 6 *N* hydrochloric acid. The solution was steam distilled until 400 ml. of distillate had been collected, the aqueous layer was extracted with ether, and the combined extracts were dried over Na₂SO₄. The ether was then removed by distillation at 35–37° and the yellow residue which remained was distilled at 73° (4.5 mm.), giving 0.50 g. (17%) of phenylacetone. The infrared spectrum showed a strong carbonyl absorbance at 5.8 μ.

Anal. Calcd. for C₉H₁₀O: C, 80.56; H, 7.51; mol. wt., 134. Found: C, 80.34; H, 7.79; mol. wt., 139 (CHCl₃).

A yellow 2,4-dinitrophenylhydrazone was obtained; m.p. 150–151° from 95% ethanol (lit.²¹ m.p. 153°).

Acknowledgment.—The authors gratefully acknowledge the support of this work by the Gulf Research and Development Corporation and by the National Institutes of Health under grant No. CY-4536.

(21) C. D. Hodgman, Ed., "Tables for Identification of Organic Compounds," Chemical Rubber Publishing Co., Cleveland, O., 1960, p. 95.

(20) G. G. Stoner, *J. Am. Chem. Soc.*, **63**, 1481 (1941)

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY, ATLANTA 13, GA.]

Polar Effects on Rates and Equilibria. VIII. Double Bond-No Bond Resonance¹

BY JACK HINE

RECEIVED JANUARY 15, 1963

Thermochemical data on the polyfluorides of methane show that these compounds are stabilized (relative to the stability that would be expected from carbon-hydrogen bonds like those in methane and a carbon-fluorine bond like that in methyl fluoride) by about 3.2 kcal./mole for each double bond-no bond resonance structure

(*e.g.*, $\overset{\oplus}{\text{F}}=\overset{\ominus}{\text{C}}\text{F}_2$) that may be written. Much less stabilization of this type would be expected for the chlorides and bromides of methane and much less (if any) is found. It is pointed out that the data may be explained by a strong attraction between geminate fluorine atoms or by the relative exemption of pairs of fluorine atoms from a strong repulsion operating between most pairs of geminate atoms. However, from the ordinary methods of estimating the magnitudes of London forces, van der Waals repulsions, and polar interactions between substituents, it appears that these factors do not explain the data at hand. From the heats of formation of trioxane, 1,3-dioxane, 1,4-dioxane, tetrahydropyran, and related compounds it appears that two oxygen atoms attached to the same saturated carbon atom give about as strong a double bond-no bond resonance interaction as two fluorine atoms do. Such resonance involving oxygen-oxygen interaction also explains the isomerization of glycol ethers to acetals and the following hydrolysis rate sequence: CH₃OEt < CH₂(OEt)₂ < CH(OEt)₃ > C(OEt)₄. There is also evidence for a number of examples of double bond-no bond resonance involving two different atoms attached to the same saturated carbon atom.

Introduction

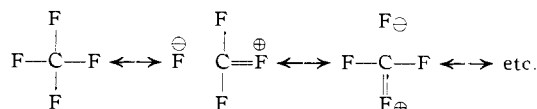
In 1937, Brockway reported that carbon-fluorine bond distances in the fluoromethanes and the fluorochloromethanes are significantly shorter in compounds with several fluorine atoms attached to the same carbon atom than in monofluorides.^{2,3a} The shortened bond distances were explained in terms of the following type

(1) Much of this material was presented at the 18th National Organic Symposium of the American Chemical Society, Columbus, Ohio, June 20, 1963. For paper VII in this series see J. Hine and H. E. Harris, *J. Am. Chem. Soc.*, **85**, 1476 (1963).

(2) L. O. Brockway, *J. Phys. Chem.*, **41**, 185, 747 (1937).

(3) L. Pauling, "The Nature of the Chemical Bond," 3rd. Ed., Cornell University Press, Ithaca, N. Y., 1960: (a) pp. 314–315; (b) p. 264; (c) p. 260.

of resonance



which will be referred to as *double bond-no bond resonance*.⁴ This resonance should stabilize the molecule

(4) The present paper shall discuss only double bond-no bond resonance in which an atom attached to carbon is no-bonded *with* the bonding electron pair. Hyperconjugation involving the no-bonding of hydrogen, one type of double bond-no bond resonance in which an atom is no-bonded *without* the bonding electron pair, has been discussed in detail by other investigators.