preformed mercury salt gave only slightly better yield than did carboxylic acid and mercuric oxide (runs 5, 9).

Experimental Section[10]

Tridecyl Bromide. Procedure A.—A dry flask equipped with a mechanical stirrer and a large inner spiral condenser (cooling water inside spiral) protected by a drying tube was charged with a solution of 17.2 g (0.075 mol) of myristic acid in 200 ml of dried CCl_4 and 10.2 g (0.047 mol) of red HgO. After the stirred mixture had been heated to boiling, heat was greatly reduced and a solution of 15 g (0.094 mol) of bromine in 10 ml of CCl_4 was added during about 35 min, during which time a small amount of heat was required to maintain reflux. After completion of addition, heating under reflux with stirring was continued for 1 hr. Mercury salts were removed from the cooled reaction mixture by filtration with suction through a Filter-Aid mat. The clear filtrate was extracted with 50 ml of 5% aqueous NaOH, and the coagulated precipitate which formed[11] was removed from the two-phase solution by suction filtration. After the CCl_4 phase had been washed with water, the tridecyl bromide was recovered by fractional distillation, or the solution was diluted to a measured volume, and yield was determined by glpc, using a response factor determined on distilled product. In three runs, yields were determined by both distillation and glpc; in one of these, yields were the same, in the other two yields by distillation were somewhat higher. Typical yields from this procedure, and modifications of it, are included in Table I.

Procedure B utilized a ratio of reagents and conditions consistent with the Jennings and Ziebarth[7] mechanism. In a closed system protected by a drying tube was stirred a slurry of 41 g (0.19 mol) of red HgO in 100 ml of CCl_4 as there was added at room temperature during about 10 min a solution of 60 g (0.37 mol) of bromine. There was insignificant evolution of heat. After this mixture had been stirred for an additional 5 min, there was added during about 15 min a solution of 34.3 g (0.15 mol) of myristic acid in 150 ml of CCl_4, at a temperature below 30°. Stirring was continued for 1 hr at room temperature or higher (*cf.* Table I). Work-up was similar to that described for procedure A.

Procedure C utilized preformed mercuric myristate. A mixture of 10.2 g of red HgO, 17.2 g of myristic acid, and 350 ml of CCl_4 was stirred and heated to reflux under a 50-cm Vigreux column so that the azeotrope of CCl_4 and water slowly distilled. After water evolution was no longer evident (about 2.5 hr), heating was continued for an additional 1 hr. Bromine (15 g) was then added to the stirred slurry of mercury salt as in Procedure A, except that, at reflux, about 1 hr was required for addition in order to keep the vigorous reaction under control by cooling in an ice bath. Work-up was as in procedure A.

Procedure P (Preferred).—A mixture of 20.4 g of red HgO, 34.3 g of myristic acid, and 250 ml of CCl_4 was heated under a 50-cm Vigreux column, with stirring, such that rate of distillation was about one drop/sec. After 15 min of distillation in this manner, addition was begun of a solution of 30 g of bromine in 100 ml of CCl_4. Addition was completed during 70 min; during the last few minutes, a majority of the bromine seemed to distil out as added; prior to this, only small amounts of bromine distilled. After bromine addition had been completed, an additional 100 ml of CCl_4 was added during 40 min, while distillation was continued as before. The cooled reaction mixture was worked up as described for procedure A (*cf.* Table I, run 6).

Registry No.—Tridecyl bromide, 765-09-3.

(10) Reagents used for the investigation were technical CCl_4, dried by azeotropic distillation of water (omission of drying had no significant effect); A.R. bromine; A.R. red HgO; reagent grade of myristic acid containing a total of <2% homologous fatty acids (glpc of resultant tridecylbromide). Microanalyses were by the Analytical Division, Department of Chemistry, University of California, Berkeley. Gas chromatographic analyses were on a 5-ft silicone column in an Aerograph A-90P, with reference to a response factor for tridecyl bromide determined on a pure sample.

(11) The salt precipitated by the NaOH wash, which was formed in larger amount in runs giving a lower yield of bromide, did not have the physical characteristics of a soap, and various elementary analyses were in major disagreement with the values for sodium myristate. Our investigations have not revealed the identity of this salt, and we have not determined whether its precursor is an intermediate in the reaction pathway to the bromide.

Synthetic Applications of Ylides Derived from 1-Dimethylamino-1-oxothioniacycloalkane Fluoroborates[1]

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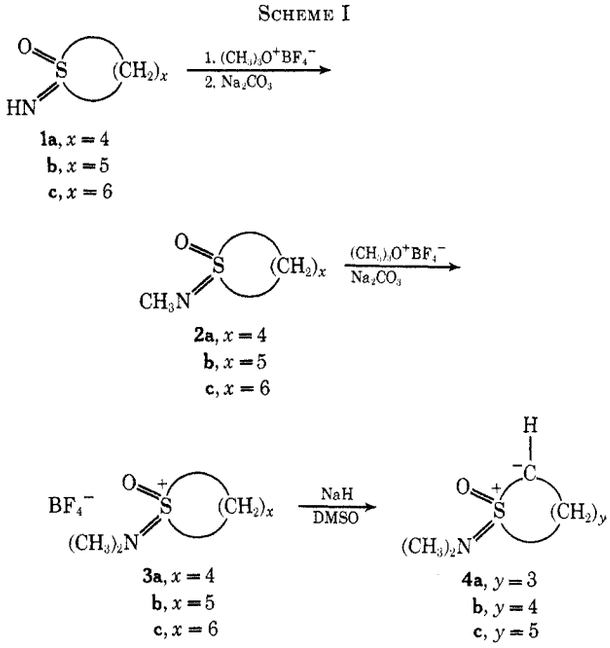
Received July 29, 1971

Several articles[2] from this laboratory have described some of the properties and uses of oxosulfonium ylides derived from salts of sulfoximines. The previous reports commented on the ease of handling, stability, ability to transfer alkyl groups larger than methyl, and the synthesis of optically active epoxides and cyclopropanes.

The present communication reports the transfer of alkyl groups functionalized with an ω-sulfinamide substituent. For this purpose the ylides **4a–c** were generated from a series of 1-dimethylamino-1-oxothioniacycloalkane fluoroborates (**3a–c**), Scheme I. The sulfoximines were prepared according to the earlier reports[2] from the sulfoxides and hydrazoic acid.[3] The sulfoximines were characterized by ir,[4] nmr, and elemental analysis of the hydrochloride salts.

SCHEME I



Reaction of the fluoroborates (**3a–c**) in dimethyl sulfoxide (DMSO) with sodium hydride at room temperature under nitrogen gave light yellow solutions of

(1) Part XXXVI in the series "Chemistry of Sulfoxides and Related Compounds." We gratefully acknowledge support by the National Science Foundation (GP 19623).

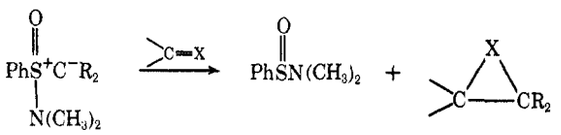
(2) (a) C. R. Johnson, E. R. Janiga, and M. Haake, *J. Amer. Chem. Soc.*, **90**, 3890 (1968); (b) C. R. Johnson and C. W. Schroeck, *ibid.*, **90**, 6852 (1968); (c) C. R. Johnson, R. F. Huxol, and E. R. Janiga, *ibid.*, **93**, 3771 (1971).

(3) (a) H. R. Bentley and J. K. Whitehead, *J. Chem. Soc.*, 2081 (1950); (b) J. K. Whitehead and H. R. Bentley, *ibid.*, 1572 (1952); (c) F. Misani, T. W. Fair, and L. Reimer, *J. Amer. Chem. Soc.*, **73**, 459 (1951).

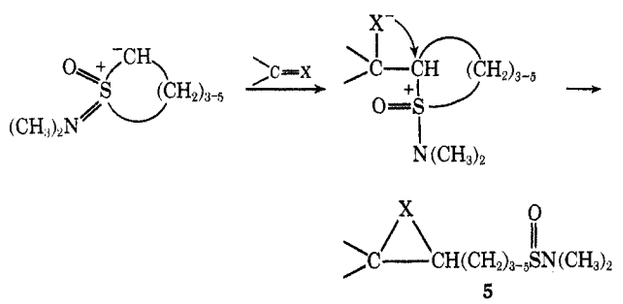
(4) The major absorption peaks agreed well with those found by N. Furukawa, K. Tsujihara, Y. Kawakatsu, and S. Oae, *Chem. Ind. (London)*, 266 (1969).

the ylides **4a–c**. Slow addition of a solution (DMSO) of an electrophilic reactant and stirring at ambient temperature for several hours completed the reaction.

In previous cases,[2] the reaction took the following course.



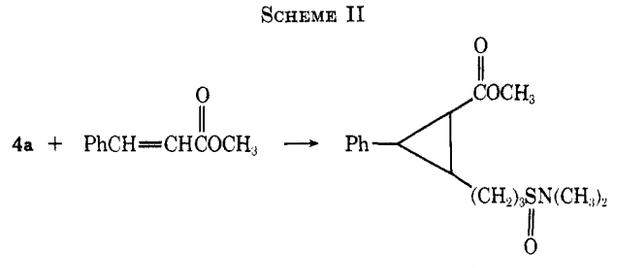
A cyclopropane or an epoxide was formed along with a sulfinamide. In the present case, both the small ring and the "by-product" are contained in the same molecule (**5**).



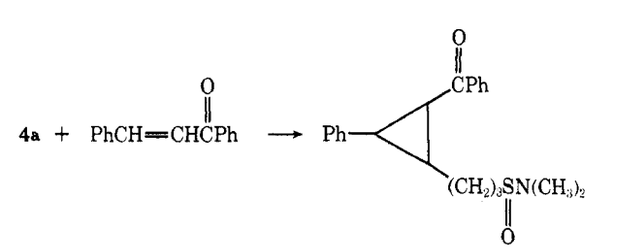
5

Thus, the reactions shown in Scheme II were completed (yield, per cent).

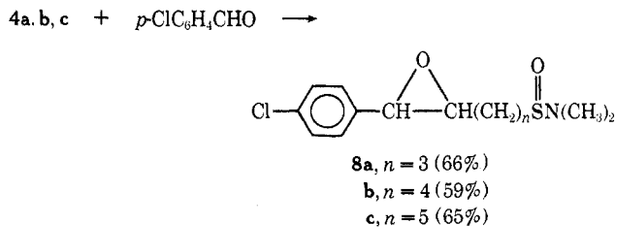
SCHEME II



6 (64%)



7 (50%)



8a, $n = 3$ (66%)
b, $n = 4$ (59%)
c, $n = 5$ (65%)

In all cases the crude reaction products were viscous oils which were purified by elution chromatography on silica gel. A curious feature of the reaction of the ylides with *p*-chlorobenzaldehyde is the stereochemistry[5] of the epoxides: **8a** (100% trans), **8b** (80% trans), **8c** (66% trans). An investigation of models shows that ylide **4a** (five-membered ring) would allow facile formation of an erythro betaine, which would collapse to the trans epoxide. As the size of the alicyclic portion increases, the dimethylamino group would encounter increasing steric interference with the aromatic ring in the erythro betaine.

Experimental Section

Melting points were determined with a Thomas–Hoover capillary tube melting point apparatus and are uncorrected. The infrared spectra were measured on a Perkin-Elmer 137B Infracord and were standardized with the polystyrene band at 1601 cm^{-1}. Nuclear magnetic resonance spectra were obtained on a Varian Associates A-60A spectrometer employing tetramethylsilane as internal standard. Microanalyses were performed by Midwest Microlab, Inc., Indianapolis, Ind.

The cyclic dimethylaminooxosulfonium salts were prepared by the procedures outlined for open-chain compounds[2b,3] and were purified by recrystallization from methanol–ether.

1-(*N*,*N*-Dimethylamino)-1-oxothioniacyclopentane fluoroborate (3a) was obtained in 76% yield: mp 78–79°; nmr (CD_3CN) δ 2.1–2.6 (m, 4), 3.15 (s, 6), 3.2–4.2 (m, 4).

Anal. Calcd for $C_6H_{14}BF_4NOS$: C, 30.66; H, 6.00. Found: C, 30.92; H, 5.93.

1-(*N*,*N*-Dimethylamino)-1-oxothioniacyclohexane fluoroborate (3b) was obtained in 37% yield: mp 129.5–130.5°; nmr (CD_3CN) δ 1.9–2.4 (m, 6), 3.1 (s, 6), 3.8–4.1 (m, 4).

Anal. Calcd for $C_7H_{16}BF_4NOS$: C, 33.76; H, 6.48. Found: C, 34.00; H, 6.63.

1-(*N*,*N*-Dimethylamino)-1-oxothioniacycloheptane fluoroborate (3c) was obtained in 61% yield: mp 102–103.5°; nmr (CD_3CN) δ 1.6–2.3 (m, 8), 3.1 (s, 6), 3.8–4.2 (m, 4).

Anal. Calcd for $C_8H_{18}BF_4NOS$: C, 36.52; H, 6.90. Found: C, 36.71; H, 7.09.

General Procedure.—Sodium hydride (1.25 equiv) dispersion in mineral oil in a round-bottomed side-armed flask was washed three times with dry pentane. The flask was immediately connected to a source of dry nitrogen and the fluoroborate salt (1 equiv) was added in one portion with stirring. Sufficient dry DMSO to prepare a 0.9–1.3 *M* solution of ylide was slowly introduced *via* syringe. After cessation of hydrogen evolution, the reaction was stirred for several more minutes. Then the substrate (1 equiv) was slowly introduced *via* syringe in DMSO or DMSO–THF solution and allowed to stir for 10–24 hr.

The work-up consisted of transferring the reaction mixture with water and ether to a separatory funnel and extraction of the aqueous phase with ether. The combined ether extracts were washed three times with water and once with saturated brine, and dried ($MgSO_4$). Filtration and concentration gave viscous oils, which were purified by chromatography on silica gel.

3-(2′-Carbomethoxy-3′-phenylcyclopropyl)-*N*,*N*-dimethylpropanesulfinimide (6) was obtained in 64% yield: nmr ($CDCl_3$) δ 1.3–2.7 (m, 9), 2.75 (s, 6), 3.75 (s, 3), 7.25 (m, 5), eluted with 4% methanol in methylene chloride.

Anal. Calcd for $C_{16}H_{23}NO_3S$: C, 62.11; H, 7.49. Found: C, 62.00; H, 7.65.

3-(2′-Benzoyl-3′-phenylcyclopropyl)-*N*,*N*-dimethylpropanesulfinimide (7) was obtained in 50% yield: nmr ($CDCl_3$) δ 1.3–2.2 (m, 6), 2.59 (s, 6), 2.65–3.2 (m, 3), 7.1–8.2 (m, 10), eluted with 2% methanol in ethyl acetate.

Anal. Calcd for $C_{21}H_{25}NO_2S$: C, 70.95; H, 7.09. Found: 70.57; H, 7.16. Molecular ion at *m/e* 355.

5-*p*-Chlorophenyl-4,5-epoxy-*N*,*N*-dimethylpentanesulfinamide (8a) was eluted with 5% methanol in ether: yield 66%; nmr ($CDCl_3$) δ 1.7–2.1 (m, 4), 2.6–3.1 (m, 3), 2.75 (s, 6), 3.61 (d, 1, J = 2 Hz), 7.2–7.5 (m, 4).

Anal. Calcd for $C_{13}H_{18}ClNOS$: C, 54.25; H, 6.30. Found: C, 54.43; H, 6.47.

6-*p*-Chlorophenyl-5,6-epoxy-*N*,*N*-dimethylhexanesulfinamide (8b) was obtained by elution with ethyl acetate and then with 1:1

(5) Calculated from the benzylic doublets in the nmr spectra. H. S. Gutowsky, M. Karplus, and R. M. Grant, *J. Chem. Phys.*, **31**, 1278 (1959); C. A. Reilly and J. D. Swalen, *ibid.*, **32**, 1378 (1960); C. A. Reilly and J. D. Swalen, *ibid.*, **34**, 980 (1961).

2-propanol–ethyl acetate: nmr ($CDCl_3$) δ 1.2–1.9 (m, 6), 2.74 (s, 6), 2.5–3.0 (m, 3), 3.6 (J = 2 Hz), 4.05 (d, 1, J = 4 Hz), 7.29 (m, 4).

Anal. Calcd for $C_{14}H_{20}ClNO_2S$: C, 55.71; H, 6.68. Found: C, 55.31; H, 6.83. Molecular ion at m/e 301.

7-*p*-Chlorophenyl-6,7-epoxy-*N*,*N*-dimethylheptanesulfinamide (8c).—The epoxide was prepared in 65% yield by the reaction of ylide **4c** and *p*-chlorobenzaldehyde. The oil was chromatographed on silica gel, developing with ethyl acetate. The infrared spectrum (neat) had peaks at 3050, 3920, 1490, 1450, 1175, 1065, 925, 828, and 778 cm^{-1}. The nmr ($CDCl_3$) had a multiplet at δ 7.28 (4 H, Ar **H**), a doublet at 4.03 (J = 4 Hz), and a doublet (J = 2 Hz) at 3.58 (combined area 1 H, Ar **CH** cis and trans), a three-proton multiplet at 3.1–2.6 (aliphatic –**CH** and CH_2S), a six-proton singlet at 2.73 [$N(CH_3)_2$], and at 1.8–1.1 [8 H, $-(CH_2)_4$] for the aliphatic chain.

Anal. Calcd for $C_{15}H_{22}ClNOS$: C, 57.04; H, 7.02. Found: C, 57.00; H, 7.24.

Registry No.—**3a**, 32846-71-2; **3b**, 32846-72-3; **3c**, 32846-73-4; **6**, 32846-69-8; **7**, 32846-70-1; **8a**, 32846-74-5; **8b**, 32846-75-6; *cis*-**8c**, 32846-76-7; *trans*-**8c**, 32958-92-2.

A New Synthesis of 3,4-(Difluoromethylenedioxy)benzaldehyde[1]

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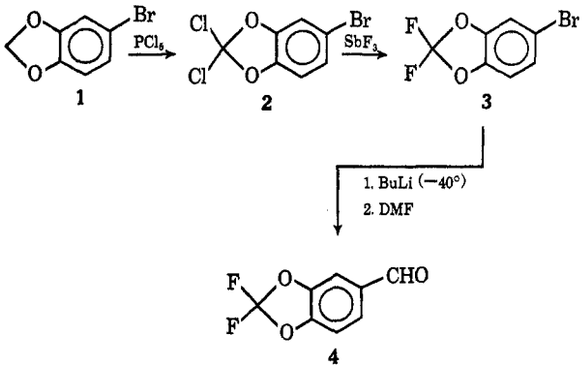
The methylenedioxyphenyl function is found in a broad spectrum of natural occurring materials[2] and appears to induce an enhancement or potentiation of biological activity.[3] The exchange of the methylene hydrogens for fluorine[4] represents an intriguing structural variation of biologically active substances containing this group. A particularly attractive intermediate for the introduction of this residue into organic molecules is 3,4-(difluoromethylenedioxy)benzaldehyde (**4**). Through a series of six synthetic steps Yagupol'skii[5] converted piperonylic acid into **4**, with an overall yield of approximately 30%. We wish to describe a much simpler three-step scheme to this valuable intermediate. The sequence of reactions is depicted below.

Chlorination of **1** with PCl_5 after the procedure of Barger[6] gave **2** in 83% yield. The exchange for fluorine was found to be very rapid and efficient if a solventless mixture of **2** and SbF_3 was heated under reduced pressure. In this manner, **3** distilled as it formed in a high state of purity. The chlorine–fluorine metathesis was considerably slower when the exchange was attempted in dioxane or hydrocarbon solvents.

Treatment of **3** with BuLi at −40° and subsequently adding freshly distilled dimethylformamide gave a 68% yield of **4**. An examination of the reaction products from this last step indicated that the halogen metal-interchange reaction occurred without loss of fluorine or rupture of the methylenedioxybenzene ring.[7]



In light of the ready formation of the aryllithium reagent from **3**, this reagent should also prove to be of value for the introduction of the 3,4-(difluoromethylenedioxy)phenyl functionality into organic substrates *via* the standard chemistry of organolithium reagents.

It is interesting to note that the alternative approach to **3**, *i.e.*, the exchange of methylene hydrogens for halogen prior to bromination, was ineffectual. Whereas the synthesis of (difluoromethylenedioxy)benzene was achieved without difficulty according to Yagupol'skii,[8] its bromination could not be realized without the destruction of the methylenedioxybenzene ring.

Experimental Section

3,4-(Dichloromethylenedioxy)bromobenzene (2).—Phosphorus pentachloride (400 g) and 112 g of 3,4-(methylenedioxy)-bromobenzene[9] were heated at 80° for 3 hr. Distillation gave an 83% yield of **3**, bp 107–109° (4 mm), $n^{20}D$ 1.5770.

Anal. Calcd for $C_7H_3Cl_2BrO_2$: C, 31.23; H, 1.12; O, 11.90. Found: C, 31.44; H, 1.10; O, 12.04.

3,4-(Difluoromethylenedioxy)bromobenzene (3).—Compound **2** (50 g) was heated with 50 g of SbF_3 at 20 mm. Redistillation of the collected liquid gave 35.3 g (80% yield) of **3**, bp 78–79° (20 mm), $n^{20}D$ 1.4722.

Anal. Calcd for $C_7H_3F_2BrO_2$: C, 35.47; H, 1.28; Br, 33.76. Found: C, 35.80; H, 1.30; Br, 33.69.

3,4-(Difluoromethylenedioxy)benzaldehyde (4).—To a solution of **3** (36.5 g) in 150 ml of Et_2O at −40° was added 100 ml of BuLi (1.6 *M*). After the addition was complete the reaction mixture was stirred for an additional hour at −40° and then treated with 33.6 g of DMF. The reaction was stirred for 1–2 hr at ambient temperature, treated with an exceess of NH_4Cl, and worked up in the usual manner. Vacuum distillation gave 19.6 g (68% yield) of **4**, bp 103–105° (20 mm).

Registry No.—**2**, 33070-31-4; **3**, 33070-32-5; **4**, 656-42-8.

(1) This work was supported by the U. S. Army Medicinal Research and Development Command under Contract No. DADA17-68-C-8103. This is Contribution No. 929 from the Army Research Program on Malaria.

(2) D. A. Archer, *et al.*, *Proc. Chem. Soc.*, 168 (1963); A. R. Battersby, *ibid.*, 188 (1963); M. Sribney and S. Kirkwood, *Nature (London)*, **71**, 931 (1953).

(3) C. F. Wilkinson, *J. Agr. Food Chem.*, **15**, 139 (1967); R. L. Metcalf, *Annu. Rev. Entomol.*, **12**, 299 (1967); J. E. Casida, J. L. Engel, E. G. Essac, F. X. Kamienski, and S. Kuwatsuka, *Science*, **153**, 1130 (1966).

(4) The rationale for exchanging hydrogen for fluorine in biologically active materials has been related to (a) altered electronic effects, (b) greater chemical stability, and (c) similarity in steric requirements. Discussions of these points are detailed by M. B. Chenweth and L. P. McCarty, *Pharmacol. Rev.*, **15**, 673 (1963); W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry," W. A. Benjamin, New York, N. Y., 1969, pp 454–463.

(5) L. M. Yagupol'skii and V. I. Troitskaya, *Zh. Obshch. Khim.*, **30**, 3129 (1960).

(6) G. Barger, *J. Chem. Soc.*, **93**, 566 (1908).

(7) Dichloromethylenedioxybenzene is reported to react with a variety of nucleophiles, including organometallics, to yield a product of displacement: H. Gross and J. Rusche, *Chem. Ber.*, **99** (8), 2625 (1966); H. Gross, *Chem. Abstr.*, **62**, 409a (1965).

(8) L. M. Yagupol'skii and V. I. Troitskaya, *Zh. Obshch. Khim.*, **34** (1), 307 (1964).

(9) Supplier: Frinton Laboratories, South Vineland, N. J.