C, 26.16; H, 1.54. (Another sample, Found: C, 24.24; H, 1.50.) Extraction of this material with acetone followed by filtration to remove mercuric oxide and evaporation of the solvent afforded the normal salt, $(PhCO_2)_2Hg$, mp 118–122°. *Anal.* Calcd for $C_{14}H_{10}O_4Hg$: C, 38.0; H, 2.26. Found: C, 39.07; H, 2.50. Another sample had mp 120–129°. Found: C, 38.38; H, 2.39. When aqueous acetone was used as the extraction agent, the product was mainly mercuric benzoate monohydrate, mp 140–149°. *Anal.* Calcd for $C_{14}H_{12}O_5Hg$: C, 36.4; H, 2.60. Found: C, 36.26; H, 2.21.

Mercuric benzoate monohydrate was formed by interaction of aqueous mercuric nitrate and sodium benzoate solutions, mp 161–163° (lit.[31] 165°). *Anal.* Calcd for $C_{14}H_{12}O_5Hg$: C, 36.4; H, 2.60. Found: C, 36.52; H, 2.21. An attempt to obtain the anhydrous salt by azeotropic distillation of the water with CCl_4 was unsuccessful.

Hydrolysis of Hydrated Mercuric Benzoate.—Suspension of hydrated mercuric benzoate (3.0 g) in boiling water (100 ml) for 1 hr gave an off-white solid (2.1 g, mp >360°) which analyzed for a basic mercuric salt $(PhCO_2)_2Hg\cdot 2HgO$. *Anal.* Calcd for $C_{14}H_{10}O_6Hg_3$: C, 19.2; H, 1.14. Found: C, 18.87; H, 1.07.

Hydrolysis of Basic Mercuric Benzoate.—Suspension of $(PhCO_2)_2Hg\cdot HgO$ (1.0 g) in boiling water caused hydrolysis to occur. The orange product (0.7 g) analyzed for $(PhCO_2)_2Hg\cdot 3HgO$ (*Anal.* Calcd for $C_{14}H_{10}O_7Hg_4$: C, 15.34; H, 0.91. Found: C, 14.60; H, 0.89.) but was apparently a mixture of starting material and mercuric oxide, mp 170–172°, undepressed by admixture with starting material. On cooling the filtered reaction mixture a small quantity (0.08 g) of hydrated mercuric benzoate was obtained, mp 161–165°. (Found: C, 36.18; H, 2.27.)

Basic (?) Mercuric *o*-Nitrobenzoate.—Interaction of *o*-nitrobenzoic acid and mercuric oxide in either CCl_4 or $CHCl_3$ gave, in addition to unreacted *o*-nitrobenzoic acid in solution and mercury oxide at the bottom of the flask, a yellow powder in suspension. The solution was decanted and the yellow powder was removed by filtration, mp 195–197° dec. Analysis indicated the composition $3(ArCO_2)_2Hg\cdot HgO$, but it is unclear whether the substance is a compound of this composition or is the normal salt, contaminated with mercuric oxide. (*Anal.* Calcd for $C_{42}H_{24}N_6O_{25}Hg_4$: C, 27.8; H, 1.32; N, 4.62. Found: C, 28.24; H, 1.26; N, 4.61.)

Registry No.—Mercuric oxide, 21908-53-2; 2-iodocyclohexyl acetate, 32865-61-5; mercuric valerate, 26719-05-1; mercuric isobutyrate, 19348-33-5; mercuric pivalate, 32276-77-0; mercuric heptanoate, 26719-06-2; mercuric 2-ethylhexanoate, 13170-76-8; mercuric nonanoate, 28043-55-2; mercuric benzilate, 32865-67-1; mercuric benzilate basic salt, 32839-01-3; $(PhCH_2CO_2)_2Hg\cdot HgO$, 32839-02-4; $(PhCH_2CO_2)_2Hg$, 14085-69-9; $(PhCO_2)_2Hg\cdot HgO$, 32839-03-5; $(PhCO_2)_2Hg$, 583-15-3; mercuric benzoate monohydrate, 32839-04-6; $(PhCO_2)_2Hg\cdot 2HgO$, 32839-05-7; $3(ArCO_2)_2Hg\cdot HgO$ ($Ar = o\text{-}NO_2C_6H_4$), 32839-06-8.

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Notes

Reaction Pathway in the Modified Hunsdiecker Reaction

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During the period since Cristol and Firth[1] published a simplified modification of the Hunsdiecker reaction for synthesis of bromides from carboxylic acid silver salts, the modified procedure, which utilizes a free carboxylic acid and mercuric oxide, has been used to advantage in several published investigations. The specific conditions employed in the published procedures have been rather diverse, as have the yields. In the initial report,[1] among the reactions carried out in boiling carbon tetrachloride solution was synthesis of heptadecyl bromide in 90% yield (crude) from stearic acid. In contrast, the "Organic Syntheses" procedure,[2] appearing subsequently, reported about 50% yield of cyclopropyl bromide, with tetrachloroethane as solvent at a temperature of 30–35°. In a procedure similar to that originally reported,[1] except that the acid and bromine were added concurrently to a boiling slurry of mercuric oxide in carbon tetrachloride, about 50% yield was again realized for a small-ring bromide;[3] however, this same procedure applied to the half-ester of an open-chain dicarboxylic acid has given 90% yield of bromo ester.[4]

Since the literature provides little evidence concerning the mechanism of the modified Hunsdiecker reaction, or the best way in which to carry out the synthesis, we have investigated its application to myristic acid. Our considerable and varied experience[5] with the classical Hunsdiecker reaction suggested that most of the difficulties are likely to be encountered with a moderately high molecular weight aliphatic structure. To this end, there was examined a procedure for tridecyl bromide which was based on the original successful method,[1] with some modification in recognition of the "Organic Syntheses" procedure.[2] Subsequent investigations revealed that the most important modification was operation at 25–30° rather than in boiling carbon tetrachloride. In 15 runs by different people,[6] the highest yield was about 5% (*cf.* Table I, run 4).

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(1) S. J. Cristol and W. C. Firth, Jr., *J. Org. Chem.*, **26**, 280 (1961).

(2) J. S. Meek and D. T. Osuga, *Org. Syn.*, **43**, 9 (1963).

(3) K. B. Wiberg and G. M. Lampmann, *J. Amer. Chem. Soc.*, **88**, 4432 (1966).

(4) John I. Crowley, Ph.D. Dissertation, University of California, Berkeley, 1971.

(5) See, *inter alia*, J. Cason and R. L. Way, *J. Org. Chem.*, **14**, 31 (1949); J. Cason and R. H. Mills, *J. Amer. Chem. Soc.*, **73**, 1354 (1951); J. Cason, M. J. Kalm, and R. H. Mills, *J. Org. Chem.*, **18**, 1670 (1953); J. Cason and M. J. Kalm *ibid.*, **19**, 1836 (1954).

(6) For several specific procedures, multiple runs were carried out by students in the advanced organic laboratory course at Berkeley. Of particular value was the work of Richard P. Fisher, Howard B. Gamper, Maria del Carmen Kutas, Ronald M. Rodehorst, and Thomas M. Yarnell.

TABLE I

TRIDECYL BROMIDE FORMED IN VARIOUS PROCEDURES FOR THE MODIFIED HUNSDIECKER REACTION

Run no.	Procedure[a]	Total time, hr:min	Temp, °C[b]	Yield, %
1	A	1:35	BP	89
2	A[c]	1:45	BP	88
3	A[d]	2	BP	68
4	A	4	25–35	3–5
5	A	24	25	30
6	P	2	BP	90
7	C	2	BP	89
8	C[e]	1:30	BP	70
9	C	24	25	39
10	B	2	<30	0
11	B	2	30–70	18–35
12	B[f]	2	30–70	71–75

[a] Procedures are those described in the Experimental Section. [b] BP = boiling temperature of CCl_4. [c] Procedure altered by adding solution of bromine and myristic acid to slurry of HgO in boiling CCl_4. [d] Procedure same in same equipment except double size of run. [e] Half of bromine added at room temperature, with no evidence of reaction; heated cautiously until onset of exothermic reaction, which was controlled by an ice bath. Final half of bromine added as in run 7. [f] Molar ratio of myristic acid doubled.

More recently, Jennings and Ziebarth[7] have proposed that the initial step in the modified Hunsdiecker reaction is generation of Br_2O which reacts with the carboxylic acid to give the acyl hypobromite, an intermediate in the classical Hunsdiecker reaction. The following stoichiometry was proposed.

$$HgO + 2Br_2 \longrightarrow HgBr_2 + [Br_2O]$$

$$[Br_2O] + RCO_2H \longrightarrow [RCO_2Br] + HOBr$$

$$[RCO_2Br] \longrightarrow RBr + CO_2$$

It may be noted that the ratio required by these equations is $HgO:2Br_2:RCO_2H$, which contrasts with other published procedures that have used approximately equimolar amounts of bromine and carboxylic acid,[1-4] with somewhat more than 0.5 molar equiv of mercuric oxide. This divergence in ratio might be inferred to suggest something about 50% yields that have been reported; however, this interpretation is quite inconsistent with the 90% yield of Cristol and Firth.[1] A procedure for tridecyl bromide based on the stoichiometry and conditions required by the Br_2O intermediate has been examined.[6] When the reaction was run at temperatures below 30° (Table I, run 10), in recognition of the statement[7] that "Br_2O decomposes slowly at temperatures above $-50°$," no yield of tridecyl bromide could be detected. When the reaction mixture from mercuric oxide and bromine was heated after, or during, addition of the carboxylic acid, modest yields could be secured (run 11). When the higher temperature was used and the ratio of carboxylic acid was *doubled, yields were much higher (run 12), even though based on carboxylic acid as limiting reagent.*

Since the above cited observations appear to eliminate significant participation of the mechanism involving Br_2O as an intermediate, we have investigated the possibility that the modified Hunsdiecker reaction is what the name implies—a Hunsdiecker reaction on the mercury salt rather than the silver salt of a carboxylic acid. This proves to be the case and we have established conditions which give excellent yields. Intermediacy of the mercury salt was originally rejected[1] on the grounds that (a) water formed in generation of the mercury salt from mercuric oxide would destroy the intermediate acyl hypobromite; (b) the Hunsdieckers[8] originally reported that the mercury salt is quite inferior to the silver salt for higher molecular weight bromides. Nevertheless, the present investigation shows that, if the reaction is carried out in boiling carbon tetrachloride, the yield is the same (about 90%), whether the preformed mercury salt or carboxylic acid and mercuric oxide are used (*cf.* Table I, runs 1, 7).

Examination of the Hunsdieckers' paper reveals that no experimental evidence is included in support of the statement that the mercury salt is inferior in their reaction, in the case of higher molecular weight bromides; however, it is probable (judging from experimental procedures which were described[8]) that the reactions were run without stirring and at temperatures below the boiling point of carbon tetrachloride. This type of procedure would give poor results for higher molecular weight mercury salts, on account of low solubility in the solvent. At room temperature, with mercuric myristate, there is no evolution of either carbon dioxide or heat when bromine is added, and only partial reaction occurs after 24 hr (Table I, runs 5, 9). Results were similar whether or not the mercury salt was preformed. This contrasts sharply with the violent reaction, difficult to control, when the preformed mercury salt is used in boiling carbon tetrachloride.

Failure of water to interfere significantly with the modified Hunsdiecker reaction is most reasonably ascribed to a faster reaction of the acyl hypobromite with radicals such as bromine atoms, in preference to water present in a maximum of stoichiometric amounts.[9] Water is indeed formed in the reaction; it is evident on the coils of the condenser. Furthermore, in boiling carbon tetrachloride, with no provision for removing water, about one-third of the runs gave yields of 75–80%, and, when the size of run was doubled, a yield of about 70% resulted (Table I, run 3). These observations suggest that retention of water in the two-phase condensate in the reflux condenser is of some importance in reducing the concentration of water in the reaction mixture. Consistently high yields result when water is removed by azeotropic distillation as the reaction is carried out in boiling carbon tetrachloride (Experimental Section, procedure P; Table I, run 6). There is some evidence (*e.g.*, run 8) that yields are lower if the first part of the reaction is carried out at temperatures below the boiling point of carbon tetrachloride; however, at room temperature

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(7) P. W. Jennings and T. D. Ziebarth, *J. Org. Chem.*, **34**, 3216 (1969).

(8) H. Hunsdiecker and C. Hunsdiecker, *Ber.*, **75**, 291 (1942).

(9) An investigation of the modified Hunsdiecker reaction, carried out by Dr. N. J. Bunce, *J. Org. Chem.*, **36**, 664 (1972), came to our attention as a result of his presentation of this material at the Washington meeting of the American Chemical Society, Sept 1971. Communication between Dr. Bunce and us has revealed that our investigations are along quite different lines, but we have arrived at the same conclusions regarding the reaction pathway. His explanation of the failure of water to seriously interfere with the modified Hunsdiecker reaction is somewhat different from ours, but reasonably so, since his investigations concentrated on mercury salts which are relatively soluble in CCl_4, whereas we are concerned with the rather insoluble mercuric myristate.

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.

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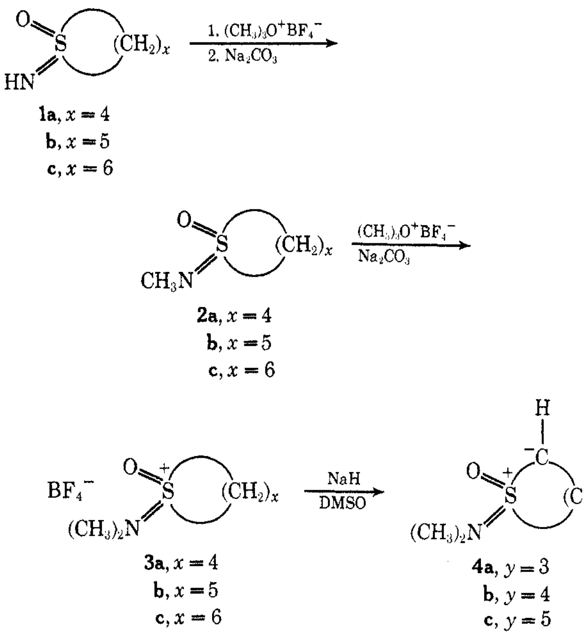
Several articles[2] from this laboratory have described some of the properties and uses of oxosulfonium ylides derived from salts of sulfoximines. The previous reports commented on the ease of handling, stability, ability to transfer alkyl groups larger than methyl, and the synthesis of optically active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

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(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).