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REACTION OF PHENYL(TRIHALOMETHYL)MERCURY COMPOUNDS WITH *N*-UNSUBSTITUTED SULFOXIMINES

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Summary

Reaction of phenyl(tribromomethyl)mercury and phenyl(bromodichloromethyl)mercury with sulfoximines gives the corresponding oxosulfonium ylide as the major product along with the respective sulfoxide and tetrahaloethylene as minor products.

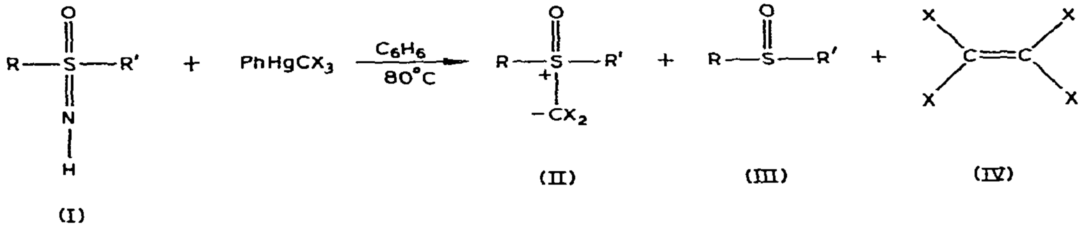
Introduction

For the past few years we have been trying to develop some reactions of carbenes with organic compounds having an S=N double bond [1]. The recent and initial studies by Furukawa et al. [2] on the previously unknown reaction [3] of carbenes with sulfoximines prompted us to explore this reaction using phenyl(trihalomethyl)mercury compounds, which have proved to be exceptionally versatile dihalocarbene precursors [4]. We chose three typical sulfoximines, *S,S*-diphenylsulfoximine, *S,S*-dimethylsulfoximine and *S*-methyl-*S*-phenylsulfoximine, as our model substrates and $PhHgCBr_3$ and $PhHgCBrCl_2$ as precursors of $:CBr_2$ and $:CCl_2$, respectively.

Results and discussion

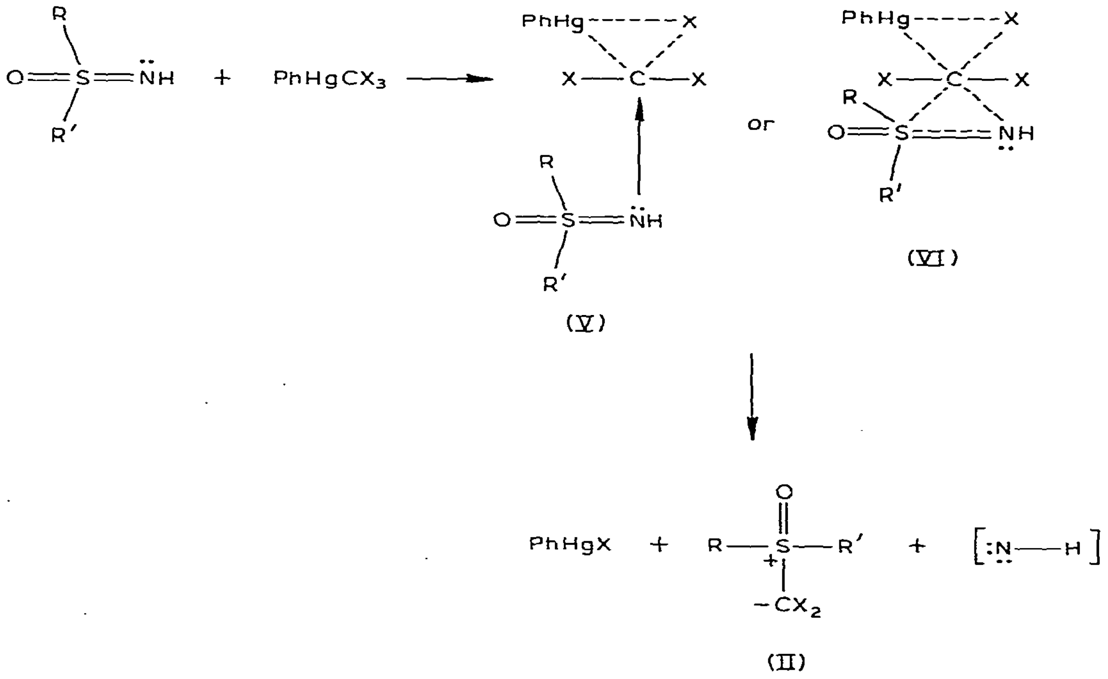
When equimolar amounts of sulfoximine(I) and the mercurial, in benzene, were heated to 80°C with stirring, under an atmosphere of prepurified nitrogen, immediate precipitation of PhHgBr took place and 2 to 3 h were required to effect decomposition of the mercurial (checked by thin-layer chromatography [5]). Precipitated PhHgBr was filtered off and the crude product obtained after rotary evaporation of the filtrate was resolved by column chromatography on silica gel. The reaction appears to be a general one, as in each case the oxosulfonium ylide(II) was obtained as major product. The corresponding sulfoxide(III) and tetrahaloethylene(IV) obtained as very minor products (Scheme 1) were authentic by m.p. and IR.

SCHEME 1



The oxosulfonium ylides(II) were characterized by chemical analysis and spectral studies. Their IR spectra showed the absence of characteristic N—H (3200—3250 cm^{-1}) and NSO (1200—1230 cm^{-1}) stretching frequency bands associated with the starting sulfoximines and the presence of the anticipated strong carbon—halogen frequency band in the 753—847 cm^{-1} region. The NMR spectra were consistent with the assigned oxosulfonium ylide structure. The mass spectra of the oxosulfonium ylide obtained contain the peaks expected for these compounds, showing the typical peak pattern for the chlorine- and bromine-containing ions due to the characteristic isotope pattern of these elements. (The *m/e* values reported correspond to the ^{35}Cl and ^{79}Br isotopes.) Abundant molecular ion peaks were present in all the spectra but the base peaks were, in the case of diphenyl- and methylphenyl-oxosulfonium ylide, the molecular ions of the corresponding sulfoxides, while in the case of dimethyloxosulfonium ylides the base peak was found at *m/e* 63 (CH_3—S^+=O). The *m/e* 82 (CCl_2^+) and *m/e* 170 (CBr_2^+) peaks evidently arise from dissociation of the correspond-

SCHEME 2



ing oxosulfonium ylide which might have occurred either thermally or on electron impact.

The mercurial—sulfoximine reaction appears to occur much more rapidly than does the cyclopropanation of olefins by phenyl(trihalomethyl)mercury compounds. The mechanisms of the reactions of phenyl(trihalomethyl)mercury compounds with substrate containing atoms with lone-pair electrons in most cases are unresolved [4,6]. We can, at present, only speculate concerning the mechanism of the mercurial—sulfoximine reaction. One possibility is that we are dealing with a two-step process, involving decomposition of the organomercury reagent to give a free dihalocarbene which subsequently reacts with the sulfoximine. Alternatively, a noncarbene process in which a direct interaction between the organomercurial and the sulfoximine at nitrogen is involved in the CX_2 transfer(V) is a possibility. (For evidence in favor of such a process in the case of reaction of $PhHgCBrCl_2$ with benzophenone, see ref. 7.) Seyferth et al. [6e] have suggested that stronger nucleophiles may react directly with the mercurial in a bimolecular reaction with a transition state resembling that suggested for the iodomethylzinc iodide—olefin reaction by Simmons et al [8]. Hence in the case of the very rapid mercurial—sulfoximine reaction an attractive mechanism for the formation of the oxosulfonium ylide is pictured in Scheme 2.

Experimental

General comments

The sulfoximines used in this study are known compounds and were prepared by standard literature procedure [9]. Mercurials were prepared by the method of Seyferth et al. [10]. All reactions were carried out under an atmosphere of prepurified nitrogen. Thiophene-free benzene was distilled from calcium hydride. All melting points are uncorrected. Infrared spectra were obtained with a Perkin—Elmer 621 spectrophotometer in Nujol. Nuclear magnetic resonance spectra were run in $CDCl_3$ on a Varian A60 D instrument with tetramethylsilane as the internal standard. Mass spectra were obtained with a JEOL-OSIG mass spectrometer at 70 eV.

Reaction of S,S-diphenylsulfoximine (I, R = R′ = Ph) with phenyl(tribromomethyl)mercury

In a three-necked, round-bottomed flask a mixture of 1.09 g (5 mmol) of *S,S*-diphenylsulfoximine and 2.65 g (5 mmol) of phenyl(tribromomethyl)mercury in 50 ml of dry benzene was stirred and heated at 80°C for 2 h under nitrogen. The resulting dark yellow-brown reaction mixture was filtered from 1.35 g (76%) of crude phenylmercuric bromide, m.p. 265—268°C. The filtrate on rotary evaporation gave 1.02 g of a crude dark yellow-brown semisolid material which was chromatographed on silica gel (30 g). Elution with petroleum ether/benzene (1/4) gave 0.05 g (5%) of diphenyl sulfoxide (III, R = R′ = Ph). Further elution with benzene gave 0.068 g (4%) of tetrabromoethylene (IV, X = Br). Elution with chloroform gave 0.804 g (43%) of pure, white, solid diphenyloxosulfonium ylide (II, R = R′ = Ph, X = Br), m.p. 93—94°C. Anal.: Found: C, 41.63; H, 2.64; Br, 42.69. Calcd. for $C_{13}H_{10}Br_2OS$: C, 41.73; H, 2.69; Br, 42.72%. NMR ($CDCl_3$): δ 7.75—7.90 ppm (10H, m, Ph—H). IR

(Nujol): 760s cm^{-1} (CBr_2). Mass spectrum (^{79}Br), *m/e* (rel. int.): 372 (70.8) M^+ ($C_{13}H_{10}Br_2OS$); 293 (30.0) $(M-Br)^+$; 202 (100.0) $C_{12}H_{10}OS^+$; 186 (24.0) $C_{12}H_{10}S^+$; 174 (12.1) $C_{11}H_{10}S^+$; 173 (17.2) $C_{11}H_9S^+$; 170 (4.9) CBr_2^+; 154 (64.0) $C_{12}H_{10}^+$; 109 (72.3) $C_6H_5S^+$; 93 (9.5) $C_6H_5O^+$; 91 (2.1) CBr^+; 79 (1.4) Br^+; 77 (46.0) $C_6H_5^+$; 65 (23.0) $C_5H_5^+$; 51 (45.0) $C_4H_3^+$; 48 (0.93) SO^+.

Reaction of S,S-diphenylsulfoximine (I, R = R' = Ph) with phenyl(bromodichloromethyl)mercury

The reaction, which was carried out in similar fashion with 1.09 g (5 mmol) of *S,S*-diphenylsulfoximine and 2.2 g (5 mmol) of phenyl(bromodichloromethyl)mercury in 45 ml of benzene, took about 3 h for complete decomposition of the mercurial. The work up procedure described previously afforded 1.47 g (82%) of crude PhHgBr, m.p. 279—281°C, and 0.93 g of crude semisolid material. Chromatographic resolution of this product, using the same sequence of eluents as described previously, gave 0.06 g (6%) of diphenyl sulfoxide (III, R = R' = Ph), 0.34 g (4%) of tetrachloroethylene (IV, X = Cl) and 0.456 g (32%) of pure, white, solid diphenyloxosulfonium ylide (II, R = R' = Ph, X = Cl), m.p. 90—92°C. Anal.: Found: C, 54.69; H, 3.49; Cl, 24.84. Calcd. for $C_{13}H_{10}Cl_2OS$: C, 54.75; H, 3.53; Cl, 24.86%. NMR ($CDCl_3$): δ 7.85—8.00 ppm (10H, m, Ph—H). IR (Nujol): 846s cm^{-1} (CCl_2). Mass spectrum (^{35}Cl), *m/e* (rel. int.): 284 (72.0) M^+ ($C_{13}H_{10}Cl_2OS$); 249 (31.2) $(M-Cl)^+$; 202 (100.0) $C_{12}H_{10}OS^+$; 186 (24.9) $C_{12}H_{10}S^+$; 174 (12.3) $C_{11}H_{10}S^+$; 173 (17.5) $C_{11}H_9S^+$; 154 (64.2) $C_{12}H_{10}^+$; 109 (72.1) $C_6H_5S^+$; 93 (9.8) $C_6H_5O^+$; 82 (3.1) CCl_2^+; 77 (46.1) $C_6H_5^+$; 65 (23.0) $C_5H_5^+$; 51 (45.7) $C_4H_3^+$; 48 (0.85) SO^+; 47 (1.9) CCl^+; 35 (1.3) Cl^+.

Reaction of S,S-dimethylsulfoximine (I, R = R' = CH_3) with phenyl(tribromomethyl)mercury

Reaction with 0.93 g (10 mmol) of *S,S*-dimethylsulfoximine and 5.29 g (10 mmol) of phenyl(tribromomethyl)mercury in 50 ml of benzene for 2 h in the above described manner afforded 2.61 g (73%) of PhHgBr, m.p. 265—267°C, and 0.91 g of a crude semisolid, from which on chromatographic separation was obtained 0.07 g (9%) of dimethyl sulfoxide (III, R = R' = CH_3), 0.138 g (7%) of tetrabromoethylene (IV, X = Br), and 0.675 g (27%) of dimethyloxosulfonium ylide (II, R = R' = CH_3, X = Br) as a white solid, m.p. 69—71°C. Anal.: Found: C, 14.32; H, 2.37, Br, 63.89. Calcd. for $C_3H_6Br_2OS$: C, 14.41; H, 2.41; Br, 63.93%. NMR ($CDCl_3$): δ 3.73 ppm (6H, s, SCH_3). IR (Nujol):753s cm^{-1} (CBr_2). Mass spectrum (^{79}Br), *m/e* (rel. int.): 248 (43.3) M^+($C_3H_6Br_2OS$); 170 (9.8) CBr_2^+; 169 (17.1) $(M-Br)^+$; 91 (8.6) CBr^+; 79 (8.1) Br^+; 78 (66.1) $C_2H_6OS^+$; 63 (100.0) CH_3OS^+; 61 (20.2) $C_2H_5S^+$; 48 (10.3) SO^+; 45 (62.0) CHS^+; 15 (18.1) CH_3^+.

Reaction of S,S-dimethylsulfoximine (I, R = R' = CH_3) with phenyl(bromodichloromethyl)mercury

The reaction was carried out similarly with 0.93 g (10 mmol) of *S,S*-dimethylsulfoximine and 4.40 g (10 mmol) of phenyl(bromodichloromethyl)mercury in 40 ml of benzene at 80°C for 2 h. The usual work-up gave 2.86 g (80%) of PhHgBr, m.p. 278—281°C, and 0.90 g of a crude semisolid product, from which on chromatographic separation was obtained 0.055 g (7%) of dimethyl sulfoxide (III, R = R' = CH_3), 0.10 g (6%) of tetrachloroethylene (IV, X = Cl), and 0.612 g (38%) of dimethyloxosulfonium ylide (II, R = R' = CH_3, X = Cl) as a white solid of m.p. 68—69°C. Anal.: Found: C, 22.29; H, 3.69, Cl, 44.01. Calcd. for $C_3H_6Cl_2OS$: C, 22.37; H, 3.75; Cl, 44.02%. NMR ($CDCl_3$): δ 3.75 ppm (6H, s, SCH_3). IR (Nujol): 842s cm^{-1} (CCl_2). Mass spectrum (^{35}Cl), *m/e* (rel. int.): 160 (45.2) M^+ ($C_3H_6Cl_2OS$); 125 (14.3) $(M - Cl)^+$; 82 (9.1) CCl_2^+; 78 (66.8) $C_2H_6OS^+$; 63 (100.0) CH_3OS^+; 61 (20.9) $C_2H_5S^+$; 48 (10.1) SO^+; 47 (8.3) CCl^+; 45 (62.3) CHS^+; 35 (6.9) Cl^+; 15 (18.2) CH_3^+.

Reaction of S-methyl-S-phenylsulfoximine (I, R = CH_3, R' = Ph) with phenyl(tribromomethyl)mercury

A solution of 1.55 g (10 mmol) of *S*-methyl-*S*-phenylsulfoximine and 5.29 g (10 mmol) of phenyl(tribromomethyl)mercury was heated at 80°C in 50 ml of benzene for 2 h. The mixture was filtered, leaving 3.11 g (87%) of PhHgBr, m.p. 282—284°C. The usual work-up of the filtrate afforded 1.54 g of a crude semisolid product from which on chromatographic separation was obtained 0.085 g (6%) of methyl phenyl sulfoxide (III, R = CH_3, R' = Ph), 0.172 g (5%) of tetrabromoethylene (IV, X = Br), and 1.279 g (41%) of pure, white, solid methylphenyloxosulfonium ylide (II, R = CH_3, R' = Ph, X = Br), m.p. 94—96°C. Anal.: Found: C, 30.69; H, 2.50, Br, 51.10. Calcd. for $C_8H_8Br_2OS$: C, 30.79; H, 2.58; Br, 51.21%. NMR ($CDCl_3$): δ 3.76 (3H, s, SCH_3) and 7.70—7.95 ppm (5H, m, Ph—H). IR (Nujol): 756s cm^{-1} (CBr_2). Mass spectrum (^{79}Br), *m/e* (rel. int.): 310 (59.8) M^+ ($C_8H_8Br_2OS$); 231 (17.9) $(M - Br)^+$; 170 (3.1) CBr_2^+; 140 (100.0) $C_7H_8OS^+$; 125 (92.9) $C_6H_5OS^+$; 112 (4.8) $C_6H_8S^+$; 97 (40.2) $C_5H_5S^+$; 94 (11.3) $C_6H_6O^+$; 91 (2.7) CBr^+; 79 (2.2) Br^+; 77 (53.1) $C_6H_5^+$; 51 (46.1) $C_4H_3^+$; 48 (2.4) SO^+.

Reaction of S-methyl-S-phenylsulfoximine (I, R = CH_3, R' = Ph) with phenyl(bromodichloromethyl)mercury

This reaction was carried out similarly with 1.55 g (10 mmol) of *S*-methyl-*S*-phenylsulfoximine and 4.40 g (10 mmol) of phenyl(bromodichloromethyl)mercury in 45 ml of benzene at 80°C for about 3 h. The usual work-up gave 2.69 g (83%) of PhHgBr, m.p. 280—283°C, and 1.39 g of a crude semisolid material, from which on chromatographic separation was obtained 0.085 g (6%) of methyl phenyl sulfoxide (III, R = CH_3, R' = Ph), 0.066 g (4%) of tetrachloroethylene (IV, X = Cl), and 0.937 g (42%) of methylphenyloxosulfonium ylide (II, R = CH_3, R' = Ph, X = Cl) as a white solid, m.p. 89—90°C. Anal.: Found: C, 42.99; H, 3.53; Cl, 31.75. Calcd. for $C_8H_8Cl_2OS$: C, 43.06; H, 3.61; Cl, 31.78%. NMR ($CDCl_3$): δ 3.78 (3H, s, SCH_3) and 7.73—8.00 ppm (5H, m, Ph—H). IR (Nujol): 847s cm^{-1} (CCl_2). Mass spectrum (^{35}Cl), *m/e* (rel. int.): 222 (61.2) M^+ ($C_8H_8Cl_2OS$); 187 (19.4) $(M - Cl)^+$; 140 (100.0) $C_7H_8OS^+$; 125 (93.0) $C_6H_5OS^+$; 112 (4.9) $C_6H_8S^+$; 97 (40.1) $C_5H_5S^+$; 94 (11.2) $C_6H_6O^+$; 82 (2.3) CCl_2^+; 77 (53.1) $C_6H_5^+$; 51 (46.4) $C_4H_3^+$; 48 (2.2) SO^+; 47 (2.1) CCl^+; 35 (1.8) Cl^+.

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