Journal of Organometallic Chemistry, 134 (1977) 151—163

THE STEREOCHEMISTRY OF THE PETERS REACTION ($RSO_2HgX \rightarrow RHgX$)

LAWRENCE C. COSTA, G. BRENT YOUNG and GEORGE M. WHITESIDES *

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.S.A.)

(Received September 2nd, 1976)

Summary

Thermal decomposition of either *exo*- or *endo*-2-norbornylsulfinatomercuric chloride (*exo*-A or *endo*-A) in DMF at 100°C yields only *exo*-2-norbornylmercuric chloride. Under similar conditions, *erythro*-3,3-dimethylbutyl-1-sulfinatomercuric chloride-1,2-d_2 yields a 1/1 mixture of *erythro*- and *threo*-3,3-dimethylbutyl-1-mercuric chloride-1,2-d_2. *endo*-2-Norbornylmercuric chloride is not epimirized under the reaction conditions, and *endo*-A is recovered from partial decompositions without detectable epimerization. These results suggest that the product-forming step proceeds via a stereochemically labile intermediate. Although several qualitative experiments provide evidence against a free radical chain mechanism, the detailed pathway of the reaction has not been established.

Introduction

A number of methods are available for generating carbon—mercury bonds [1]. One of the less frequently employed routes is the Peters reaction [2], in which organomercury(II) chlorides are obtained on heating a mixture of mercuric chloride and a sulfinic acid or its sodium salt. A variety of arylmercuric

$$RSO_2H(Na) + HgCl_2 \xrightarrow{\Delta} RHgCl + SO_2 + (Na)HCl \qquad (1)$$

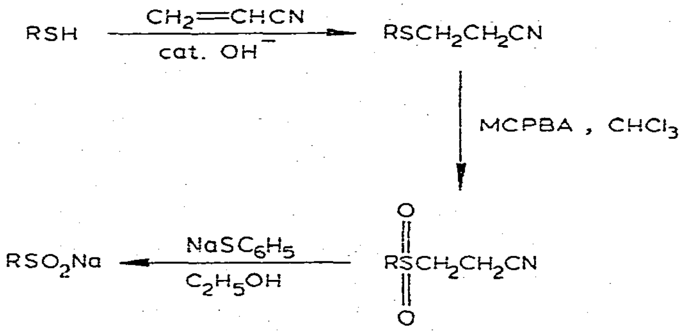
R = alkyl, aryl, heteroaryl

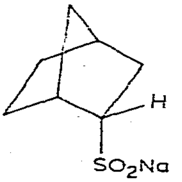
chlorides have been synthesized using this reaction, but only a few alkylmercuric chlorides have been prepared. Although yields for the synthesis of alkylmercuric halides by the Peters reaction are modest (<50%), it seemed possible that this reaction might have useful stereoselectivity. There are presently no generally applicable procedures for the preparation of organomercury compounds with defined stereochemistry. Although tris(3,3-dimethylbutyl)boron is converted by mercuric acetate to the corresponding organomercury compound with inversion of stereochemistry [3], secondary alkylboranes are not cleaved by mercuric acetate [4], and the methods available for the conversion of secondary alkylboranes to organomercury compounds are not stereospecific [5,6]. Other methods available for the preparation of diastereomerically and enantiomerically pure organomercury compounds [7,8] are laborious, specialized, and do not always yield stereochemically pure product.

Results and discussion

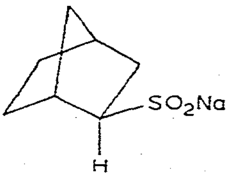
Preparation of starting materials. The required sulfinic acid salts were synthesized by two methods (free alkylsulfinic acids disproportionate rapidly [9]). The achiral salts employed as model compounds were obtained by reaction of the appropriate Grignard reagent with sulfur dioxide [9,10]. The sodium salts used for stereochemical studies, *exo*-2-norbornylsulfinate (*exo*-I), *endo*-2-norbornylsulfinate (*endo*-I), and *erythro*-3,3-dimethylbutane-1-sulfinate-1,2-d_2 (II), were obtained by adaptation of the method of Truce and Roberts (Scheme 1) [11].

SCHEME 1. Synthesis of sodium alkyl sulfinate.

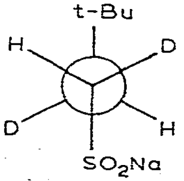




endo-I



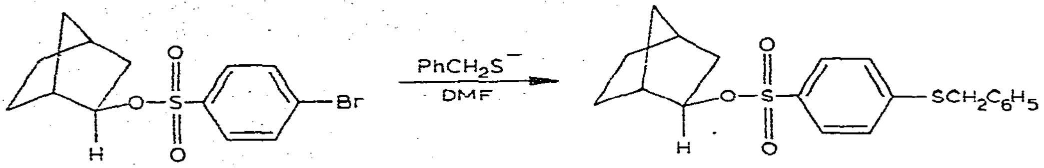
exo-I

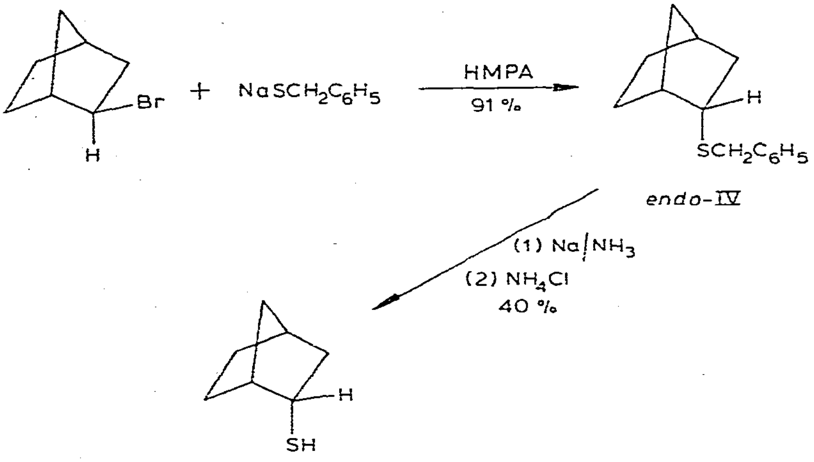


II

Attempts to oxidize thiols directly to sulfinic acids using *m*-chloroperbenzoic acid (MCPBA) [12] were unsuccessful.

Both *exo*-2-norbornanethiol (*exo*-III) and *erythro*-3,3-dimethylbutane-1-thiol-1,2-d_2 were prepared by base-catalyzed transesterification of the corresponding thioacetates [13]. The thioacetates in turn were obtained by unambiguous routes: *exo*-2-norbornylthioacetate was prepared directly from norbornene and thiolacetic acid [14]; *erythro*-3,3-dimethylbutyl-1-thioacetate-1,2-d_2, a particularly convenient substrate for NMR determinations of stereochemistry [3,15], was prepared by S_N2 displacement of the *threo*-*p*-bromobenzenesulfonate by thioacetate in *N*,*N*-dimethylformamide (DMF). The preparation of *endo*-2-norbornanethiol (*endo*-III) was not so straightforward. A variety of sulfur-containing nucleophiles (thioacetate, thiocyanate, and thiourea) were found to be unreactive toward *exo*-2-norbornyl bromide and/or the corresponding *p*-bromobenzenesulfonate and *p*-toluenesulfonate. In fact, reaction of *exo*-2-norbornyl *p*-bromobenzenesulfonate with the sodium salt of benzyl mercaptan in DMF resulted only in displacement of bromide from the aromatic ring. The reaction of *exo*-2-norbornyl bromide with the sodium salt of benzyl mercaptan in HMPA proceeded readily, however, and gave *endo*-2-norbornyl benzyl sulfide (*endo*-IV) in good yield. The benzyl group was cleaved with sodium in liquid ammonia [16] and yielded *endo*-2-norbornanethiol (*endo*-III).





endo-III

The NMR spectra of *endo*-III and *exo*-III were distinct; in particular, the C(2) methine proton resonance of *endo*-III appeared as a six-component multiplet centered at 3.2 ppm, while the C(2) methine proton resonance of *exo*-III appeared as a four-component multiplet centered at 2.8 ppm. Verification of the stereochemical assignment for *endo*-IV was obtained similarly by comparison of the NMR spectra of *endo*-IV and *exo*-IV. The latter was prepared by the addition of benzyl mercaptan to norbornene [14].

Authentic samples of alkylmercuric chlorides were prepared by reaction of the appropriate Grignard reagent with mercuric chloride. *endo*-2-Norbornylmercuric chloride (*endo*-V) was obtained by reaction of *endo*-2-norbornylmagnesium bromide [17] with mercuric chloride. *exo*-2-Norbornylmercuric chloride (*exo*-V) was obtained by adaptation of the preparative procedure for *exo*-2-norbornylmercuric bromide [18].

Model reactions. The Peters reaction has normally been effected by mixing aqueous or alcoholic solutions of mercuric chloride and the sulfinic acid or its salt, and heating the resulting insoluble organosulfinatomercuric chloride [19] as a suspension in the solvent employed at 80—100°C for several hours [2]. The intermediate *S*-mercury(II) sulfinato complexes can be identified by characteristic strong IR absorptions at 1000—1100 cm^{-1} and 1100—1250 cm^{-1} [19].

When this procedure was applied to sodium cyclohexane sulfinate in absolute ethanol, the intractable solid that was obtained showed weak IR absorption bands due to cyclohexylmercuric chloride, but the product could not be isolated. Similar results were obtained from a mixture of *endo*-I and *exo*-I. These difficulties could be avoided by running the Peters reaction in the polar, aprotic solvents pyridine, dimethylsulfoxide (DMSO), DMF, and *N*-methylpyrrolidone (NMP), in which the alkylsulfinatomercuric chlorides were soluble. When these solutions were heated to ca. 100°C for several minutes, they rapidly became opaque. The desired alkylmercuric chlorides precipitated on quenching with water, and could be isolated in yields of 30—60%. The highest yields were obtained in DMF, and this solvent was employed for further studies. Application of this procedure to representative sodium alkyl sulfinates gave alkylmercuric chlorides in the yields summarized in Table 1.

Thermal decomposition of n-hexylsulfinatomercuric chloride in the solid state also produced alkylmercury compound. When a portion of the former compound was heated in a sublimator at 150°C and 0.01 Torr, crystals of n-hexylmercuric chloride slowly grew on the cold finger. The IR spectrum of this material also contained weak sulfur—oxygen stretching bands of the starting material. This procedure was not preparatively useful.

Stereochemical results. Treatment of aqueous solutions of *exo*-I, *endo*-I and II with an aqueous solution of a 50—100% excess of mercuric chloride resulted in the precipitation of the corresponding alkylsulfinatomercuric chlorides: *exo*-2-norbornylsulfinatomercuric chloride (*exo*-VI), *endo*-2-norbornylsulfinatomercuric chloride (*endo*-VI), and *erythro*-3,3-dimethylbutyl-1-sulfinatomercuric chloride-1,2-d_2 (VII). The stereochemical assignments for *exo*-VI, *endo*-VI and VII were based on NMR analyses analogous to those described above for *exo*-III, *endo*-III, and *erythro*-3,3-dimethylbutyl-1-thioacetate-1,2-d_2.

When solutions of either *exo*-VI or *endo*-VI in DMF were heated to 100°C (5—30 min) and the resulting crude mercurial precipitated with water, only *exo*-2-norbornylmercuric chloride (*exo*-V) could be detected by IR. The stereochemical assignment was based on comparison of the IR spectrum of the product with the IR spectra of mixtures of *exo*-V and *endo*-V of known composition.

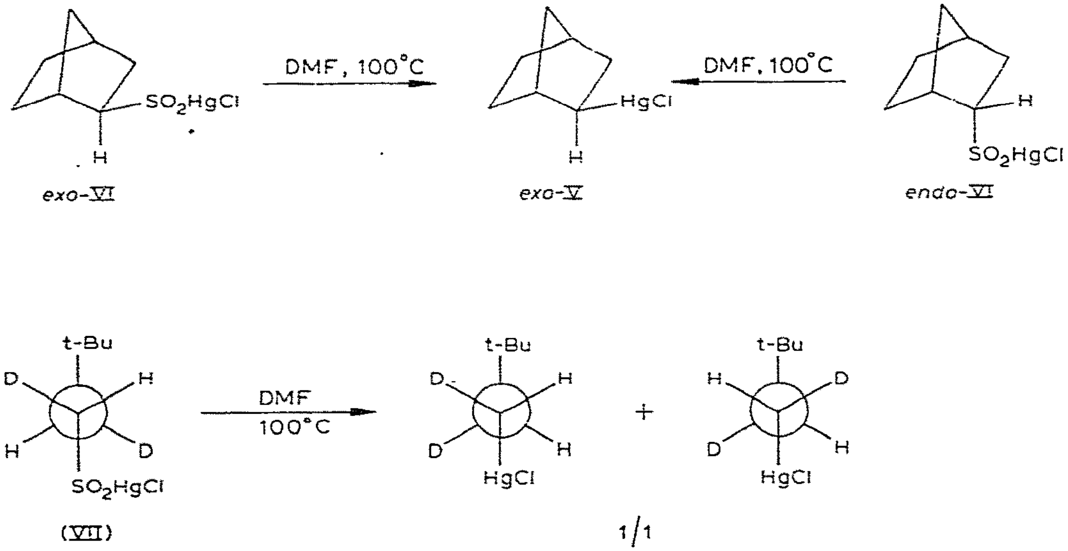
TABLE 1

ALKYLMERCURIC CHLORIDES PREPARED BY THE PETERS REACTION

Product	Isolated yield (%)
2,2-Dimethylpropylmercuric chloride	35
n-Hexylmercuric chloride	58
Cyclohexylmercuric chloride	45
3,3-Dimethylbutylmercuric chloride	48
exo-2-Norbornylmercuric chloride	39

An epimeric mixture containing only 20% of the minor component could have easily been identified. Attempts to confirm these assignments by conversion of V to norbornyl bromides by reaction with bromine gave erratic results [7,20]. A report that *endo*- and *exo*-2-norbornyl(methyl)mercury(II) can be separated by GLPC appeared too late to be used in this work [21]. Using similar reaction conditions, a solution of VII in DMF gave products identified on the basis of coupling constants to be a 1/1 mixture (±5%) of *erythro*- and *threo*-3,3-dimethylbutyl-1-mercuric chloride-1,2-d_2. These results indicate that, under the conditions employed, the product of the Peters reaction is completely epimerized (Scheme 2).

SCHEME 2. The Peters reaction proceeds with loss of stereochemistry.



The Peters reaction might follow a concerted or a nonconcerted mechanism. If the reaction is concerted, it should be stereospecific. The observed loss of stereochemistry should then occur prior to or subsequent to reaction. If the reaction is not concerted, it might involve a stereochemically labile intermediate: viz., a carbonium ion, a carbanion, or a free radical. A rigorous mechanistic study of the reaction has not been performed, and the questions of where and how the stereochemistry is lost cannot be answered precisely. Several experiments have, however, been performed which provide qualitative evidence against some of the various possibilities.

When the Peters reaction was run in the presence of *endo*-V using cyclohexylsulfinatomercuric chloride as the reactant (DMF, 100°C, 30 min), the product mixture consisted only of cyclohexylmercuric chloride and *endo*-V. No *exo*-V was detected by IR. In addition, when the Peters reaction was run in the presence of 5-hexenylmercuric chloride with n-hexylsulfinatomercuric chloride as the reactant (DMF, 100°C, 30 min), the product mixture consisted only of n-hexylmercuric chloride and 4-hexenylmercuric chloride. No cyclopentylmethylmercuric chloride was detected by IR. These results preclude the intervention of carbonium ions [23] or free radicals [24,25] derived from the product mercurials as the agents responsible for their loss of stereochemistry *.

When a solution of *endo*-VI in DMF was heated briefly at 100°C (3—4 min) and then rapidly quenched by pouring into ice/water, the recovered starting material was found not to have undergone any detectable epimerization by NMR. The observation that both the starting sulfinatomercuric chloride and the product alkylmercuric chloride are configurationally stable under the reaction conditions indicates that loss of stereochemistry occurs during the Peters reaction itself.

Carbanions do not seem likely as intermediates, since the reaction can be carried out successfully in protic solvents and in DMF. A free radical chain mechanism, or a mechanism involving free radical intermediates in other capacities, is also unlikely. The qualitative rate of reaction and the yield of product were insensitive to the presence of radical scavengers such as oxygen [26], bromotrichloromethane, and hydroquinone. Reaction of VII in the presence of 1 mol% of hydroquinone gave a 1/1 mixture of *erythro*- and *threo*-3,3-dimethylbutyl-1-mercuric chloride-1,2-d_2. Reaction of n-hexylsulfinatomercuric chloride in the presence of 1 equiv of hydroquinone gave n-hexylmercuric chloride in ca. 40% yield. The same reaction run in the absence of hydroquinone gave ca. 45% yield. The difference is not significant. No difference could be discerned if the reaction was run in anhydrous, distilled DMF under nitrogen, or in reagent DMF taken directly from the bottle under air. Addition of 1—2% water by volume to these DMF solutions also had no effect on the reaction.

Experimental evidence that would definitely rule out carbonium ions or solvent-caged radicals as intermediates has not been obtained. The facility with which primary alkylsulfinatomercuric chlorides undergo the reaction would, however, argue against carbonium ion formation. Alkylsulfonyl radicals, generated by radiolysis of alkylsulfonyl chlorides in cyclohexane, do not undergo significant decomposition to sulfur dioxide and alkyl radicals [27]. If alkylsulfonyl radicals are formed during the Peters reaction, their behavior under these conditions need not necessarily parallel that which was observed in cyclohexane.

It is thus not clear what the detailed mechanism of the Peters reaction is, but it appears that the reaction is not applicable to the stereoselective synthesis of alkylmercuric halides. Since the starting materials are difficult to obtain, and since the reaction does not proceed in high yield, it seems unlikely that the Peters reaction will find application in routine synthesis of alkylmercury compounds, although it may prove useful in specialized instances in which other polar functionality in the molecule precludes the use of the more conventional Grignard- or organolithium-based procedures.

Experimental

General methods. All reactions involving organometallic compounds were conducted under nitrogen using standard techniques for handling air-sensitive

---

* An effort to check this conclusion by studying the loss of sulfur dioxide from 5-hexenylsulfinatomercuric chloride was abandoned when it was established that reaction of sodium-5-hexenylsulfinate with mercuric chloride yielded only a compound tentatively identified as 2-chloromercurimethylthiane-1,1-dioxide.

compounds [28]. Diethyl ether and tetrahydrofuran were distilled under nitrogen from solutions of sodium benzophenone dianion. Pyridine, *N,N*-dimethylformamide, and *N*-methylpyrrolidone were distilled under nitrogen from calcium hydride. Melting points were recorded on a Thomas—Hoover capillary melting point apparatus and are uncorrected. Boiling points are uncorrected. Proton NMR spectra were obtained at 60 MHz on a Varian T-60 instrument. Chemical shifts are reported in ppm downfield from internal tetramethylsilane. Deuterium-decoupled proton NMR spectra were recorded on a Varian HA-100 instrument which was modified for heteronuclear decoupling. Infrared spectra were obtained on a Perkin—Elmer Model 237, 237B, or 567 instrument. Liquid samples were run as thin films between potassium bromide plates; solid samples were run in potassium bromide pellets (3% w/w). Elemental analyses were carried out by Robertson Laboratory, Florham Park, N.J.

A sample of *threo*-3,3-dimethylbutan-1-ol-1,2-d_2 was provided by Dr. Paul L. Bock [15]. *exo*-2-Norbornyl bromide [29], *endo*-2-norbornylmagnesium bromide [17], and *exo*-2-norbornyl thioacetate [14] were prepared using literature procedures. *threo*-3,3-Dimethylbutan-1-ol-1,2-d_2 was converted to the corresponding *p*-bromobenzene sulfonate by a literature procedure for the non-deuterated material [22]. Commercial samples of *p*-bromobenzenesulfonyl chloride and *p*-toluenesulfonyl chloride were recrystallized from light petroleum ether. All other reagents were from commercial sources and were used without further purification.

Sodium alkylsulfinates from Grignard reagents. General procedure [10]. The Grignard reagent solution was cooled with a Dry Ice/acetone bath so that the internal temperature of the solution was —30°C. Anhydrous sulfur dioxide was passed into the mechanically stirred solution through a 15-gauge hypodermic needle, and the internal temperature was maintained below —20°C. A white solid formed immediately, and sulfur dioxide addition was continued until no more solid precipitated. The mixture was diluted with an equal volume of ether, and then sufficient aqueous, 10% HCl was cautiously added to dissolve the solids and bring the aqueous phase to pH 1. The yellow ether layer was removed and washed with small portions (10—20 ml) of saturated, aqueous sodium carbonate solution until the pH of the collected washings was 7—8. If the washings had a pH > 8, the product sulfinate was contaminated with sodium carbonate, and reaction of these contaminated sulfinates with mercuric chloride produced alkylsulfinatomercuric chlorides which were contaminated with mercuric carbonate. Evaporation of the water at room temperature under reduced pressure left the sodium alkylsulfinate as a white powder which was not purified further. The following sodium alkylsulfinates were prepared in this manner (alkyl group, yield): n-hexyl (76%), cyclohexyl (68%), 2-butyl (50%), 2,2-dimethylpropyl (83%), 3,3-dimethylbutyl (81%), 5-hexenyl (42%).

Alkylmercuric chlorides from Grignard reagents. General procedure. The Grignard reagent solution (typically 15 mmol) was cooled to 0°C and treated with 1 equiv of mercuric chloride. The mixture was stirred at 0°C for 4 h, and then quenched with 50 ml of water. The crude product was collected by filtration, dried, and recrystallized from ethanol/water (2/1). The following compounds were prepared by this procedure: *endo*-2-norbornylmercuric chloride (*endo*-V) (35%, m.p. 119—120°C), 2-norbornylmercuric chloride (ca. 1/1 mixture of epimers, 65%, m.p. 169—171°C), n-hexylmercuric chloride (77%, m.p. 119—120°C, lit. [4], m.p. 121—122°C), cyclohexylmercuric chloride (64%, m.p. 161—162°C, lit. [30], m.p. 163—164°C), 5-hexenylmercuric chloride (68%, m.p. 100—101°C), cyclopentylmethylmercuric chloride (48%, m.p. 57—58°C, lit. [31] m.p. 55°C), 3,3-dimethylbutylmercuric chloride (73%, m.p. 132—134°C, lit. [22] m.p. 132—134°C), 2,2-dimethylpropylmercuric chloride (68%, m.p. 113—114°C, lit. [32] m.p. 117—118°C). Elemental analyses for new alkylmercuric chlorides are given in Table 2.

exo-2-Norbornylmercuric chloride (exo-V). This compound had a m.p. 193—194°C and was prepared by the procedure for *exo*-2-norbornylmercuric bromide [18].

Potassium thioacetate. A non-aqueous preparation which is superior to the literature procedure [33] was developed. To a suspension of 18.0 g (130 mmol) of anhydrous potassium carbonate in 25 ml of absolute methanol was added 5.0 g (65 mmol) of thioacetic acid in small portions. When carbon dioxide evolution had ceased, the mixture was stirred an additional 10 min and filtered. The unreacted potassium carbonate was triturated with 10 ml of methanol, and the combined methanolic solutions were transferred to a 1-liter Erlenmeyer flask. Ether was slowly added to this solution until it became cloudy, and the mixture was cooled slowly to —78°C. The white needles of potassium thioacetate that crystallized were collected by suction filtration, washed with 100 ml of ether, and dried under reduced pressure. The yield was 6.85 g (93%).

erythro-3,3-Dimethylbutyl-1-thioacetate-1,2-d_2. To a stirred solution of 8.00 g (70 mmol) of freshly prepared potassium thioacetate in 75 ml of DMF was added a solution of 20.3 g (63 mmol) of *threo*-3,3-dimethylbutyl-1-*p*-bromobenzenesulfonate in 50 ml of DMF. Within a few minutes, the mixture had become warm and a white solid had precipitated. The mixture was stirred over-

TABLE 2

ELEMENTAL COMPOSITIONS

Compound	Formula	Analysis calcd. (found) (%)	
		C	H
endo-2-Norbornylmercuric chloride	$C_7H_{11}ClHg$	25.38 (25.19)	3.35 (3.30)
exo-2-Norbornylmercuric chloride	$C_7H_{11}ClHg$	25.38 (25.61)	3.35 (3.36)
5-Hexenylmercuric chloride	$C_6H_{11}ClHg$	22.57 (22.23)	3.47 (3.27)
n-Hexylsufinatomercuric chloride	$C_6H_{13}SO_2ClHg$	18.70 (18.75)	3.40 (3.34)
Cyclohexylsulfinatomercuric chloride	$C_6H_{11}SO_2ClHg$	18.80 (18.74)	2.89 (2.88)
exo-2-Norbornylsulfinatomercuric chloride	$C_7H_{11}SO_2ClHg$	21.27 (21.37)	2.81 (2.69)
2,2-Dimethylpropylsulfinatomercuric chloride	$C_5H_{11}SO_2Hg$	16.17 (15.67)	2.99 (2.85)
erythro-3,3-Dimethylbutyl-1-sulfinatomercuric chloride-1,2-d_2	$C_6H_{11}D_2SO_2ClHg$	18.70 (18.75)	3.40 (3.34)

night at room temperature, and then poured into 600 ml of water. The aqueous mixture was extracted with four 50-ml portions of ether. The combined ethereal extracts were washed with two 50-ml portions of water, dried ($MgSO_4$), and the ether was removed at reduced pressure. The remaining yellow oil was distilled through a 10-cm Vigreux column, and yielded 7.90 g (78%) of *erythro*-3,3-dimethylbutyl-1-thioacetate-1,2-d_2, b.p. 83—84° (21 Torr); NMR (100 MHz, deuterium-decoupled, CCl_4) 2.81 (1H, doublet, J 12.3 Hz) 2.30 (3H, singlet), 1.42 (1H, doublet), 0.93 (9H, singlet); IR 1685 cm^{-1} (s).

exo-2-Norbornanethiol (exo-III), A mixture of 9.32 (55 mmol) of *exo*-2-norbornyl thioacetate and 0.30 g (0.5 mmol) of sodium methoxide in 25 ml of absolute methanol was refluxed under nitrogen. After 6 h, the mixture was allowed to cool, and was poured into 100 ml of 5% aqueous HCl. This aqueous mixture was extracted with three 50-ml portions of ether. The combined ethereal extracts were washed with two 50-ml portions of water, dried ($MgSO_4$), and the ether was removed under reduced pressure. The remaining clear, foul-smelling oil was distilled through a 10-cm Vigreux column, and yielded 5.90 g (83%) of *exo*-2-norbornanethiol (*exo*-III), b.p. 67—68°C/18 Torr; NMR (CCl_4) 1.0—2.2 (1H, complex), 2.8 ppm (1H, multiplet).

erythro-3,3-Dimethylbutane-1-thiol-1,2-d_2. This compound was prepared in a fashion analogous to the preparation of *exo*-III in 88% crude yield; NMR (CCl_4) 2.4 (1H, multiplet), 1.5 (1H, multiplet), 1.1 (1H, doublet), 0.9 ppm (9H, singlet). This sample was not purified further. The b.p. of a non-deuterated sample was 45—48°C/20 Torr.

endo-2-Norbornyl benzyl sulfide (endo-IV). To a solution of 14.6 g (100 mmol) of sodium benzyl mercaptide (prepared from benzyl mercaptan and sodium hydride in ether) in 75 ml of HMPA was added 16.0 g (91 mmol) of *exo*-2-norbornyl bromide. Within a few minutes, the mixture had become warm, and sodium bromide had begun to precipitate. After 2 h, the mixture was poured into 500 ml of water, and extracted with three 50-ml portions of ether. The combined organic phases were washed with three 50-ml portions of water, dried ($MgSO_4$), and the ether was removed at reduced pressure to leave 18.1 g (91%) of crude *endo*-2-norbornyl benzyl sulfide as a light yellow oil; NMR (CCl_4) 7.2 (5H, singlet), 3.6 (2H, singlet), 2.8 (1H, multiplet), 0.8—2.2 ppm (10H, complex). This material was homogeneous by NMR and TLC, and was not purified further.

endo-2-Norbornanethiol (endo-III). Ammonia (100 ml) was condensed into a 250-ml three-necked flask equipped with a Kel-F coated stirring bar and a Dry Ice condenser. The flask was then charged with 18.1 g (83 mmol) of crude *endo*-2-norbornyl benzyl sulfide. Diethyl ether (75 ml) was added as a cosolvent and gave a clear, two-phase system. Sodium (0.46 g, 200 mg-atom) was then added in small pieces to the well-stirred mixture. The blue color was rapidly discharged at first, and then more slowly as a solid precipitated. The color of the mixture changed from blue to yellow to green to brown. When all the sodium had been consumed, the ammonia was allowed to evaporate, while powdered ammonium chloride was added to the mixture to destroy any unreacted sodium and sodium amide. The residue was triturated with 50 ml of 10% aqueous HCl and extracted with two 100-ml portions of ether. The combined ethereal extracts were washed once with 50 ml of water, dried ($MgSO_4$), and the ether was removed at reduced pressure. The remaining oil was distilled through a 10-cm Vigreux column to yield 4.15 g (40%) of *endo*-2-norbornanethiol (*endo*-III), b.p. 73—74°C/20 Torr; NMR (CCl_4) 3.2 (1H, multiplet), 0.8—2.2 ppm (11H, complex).

Reactions of thiols with acrylonitrile. General procedure. To 1 equiv of the cooled (0°C), neat thiol containing three drops of Triton B (A 40% solution of benzyltrimethylammonium hydroxide in methanol) was added slowly two equiv of acrylonitrile. The mixture was stirred under nitrogen at 0°C for 1 h, and then allowed to warm to room temperature and stirred overnight. The mixture was treated with three drops of aqueous 10% HCl and diluted with an equal volume of ether. Insoluble material was removed by filtration, the filtrate was dried ($MgSO_4$), and the volatile materials were removed at reduced pressure to yield the crude alkyl 2-cyanoethyl sulfide. The following compounds were so obtained: *erythro*-3,3-dimethylbutyl-1,2-d_2 2-cyanoethyl sulfide (83%); NMR (CCl_4) 2.7 (5H, multiplet), 1.4 (1H, multiplet), 0.9 ppm (9H, singlet). This material was not purified further, but a non-deuterated sample had b.p. 72—73° C/0.10 Torr. Also, *exo*-2-norbornyl 2-cyanoethyl sulfide (82%) was obtained as a glass, m.p. ca. 25°C; NMR (CCl_4) 1.1—2.3 (10H, complex), 2.8 ppm (5H, multiplet); *endo*-2-norbornyl 2-cyanoethyl sulfide was obtained as a viscous syrup (66%); NMR (CCl_4) 0.8—2.3 (10H, complex), 2.6 (4H, multiplet), 3.2 ppm (1H, multiplet). These latter two compounds were homogeneous by NMR and TLC, and were not purified further.

Oxidation of alkyl 2-cyanoethyl sulfides. General procedure. To a cooled solution of 2 equiv of MCPBA, (85%) in chloroform was added slowly a solution of 1 equiv of the alkyl 2-cyanoethyl sulfide in chloroform. The oxidation is very exothermic. The mixture was stirred overnight at room temperature, and the insoluble *m*-chlorobenzoic acid was removed by filtration. The filtrate was washed once with a 50-ml portion of saturated, aqueous sodium bisulfite solution, and then repeatedly with small portions (20—40 ml) of saturated, aqueous sodium bicarbonate until carbon dioxide evolution ceased. The mixture was washed once with 100 ml of water, dried ($MgSO_4$), and the chloroform was removed at reduced pressure. The remaining oil was taken up in a minimum amount of hot chloroform, and the solution was treated with hexane until cloudy. Sufficient chloroform was added to clarify the solution, and it was allowed to cool. The product alkyl 2-cyanoethyl sulfone crystallized on standing. The following compounds were obtained in this manner: *erythro*-3,3-dimethylbutyl-1,2-d_2-2-cyanoethyl sulfone (90%), m.p. 88—89°C; NMR ($CDCl_3$) 3.1 (5H, multiplet), 1.7 (1H, multiplet), 1.0 ppm (9H, singlet); IR 2240 (m), 1250(s), 1100 cm^{-1} (s); *exo*-2-norbornyl 2-cyanoethyl sulfone (94%, viscous oil); NMR ($CDCl_3$) 1.1—2.4 (10H, complex), 2.8—3.3 ppm (5H, multiplet); IR 2235 (m), 1300 (s), 1125 cm^{-1} (s); *endo*-2-norbornyl 2-cyanoethyl sulfone (83%, viscous syrup); NMR ($CDCl_3$) 0.9—2.4 (10H, complex), 2.8 (4H, multiplet), 3.4 (1H, multiplet); IR 2240 (m), 1310 (s), 1110 cm^{-1} (s).

Conversion of alkyl 2-cyanoethyl sulfones to sodium alkylsulfinates. General procedure. To a solution of 1 equiv of the alkyl 2-cyanoethyl sulfone in 50 ml of absolute ethanol was added 1 equiv of sodium thiophenoxide (prepared from thiophenol and sodium hydride in THF), and the mixture was refluxed for 4—6 h under nitrogen. The ethanol was removed at reduced pressure, and the remaining sodium alkylsulfinate was triturated with 50 ml of ether, collected by suction filtration, washed with 100 ml of ether, and allowed to dry. The following sodium alkylsulfinates were prepared in this manner: *erythro*-3,3-dimethylbutyl-1-sulfinate-1,2-d_2 (II) (100%); *exo*-2-norbornylsulfinate (*exo*-I) (88%) *endo*-2-norbornylsulfinate (*endo*-I) (95%).

Preparation of alkylsulfinatomercuric chlorides. General procedure. A solution of 1 equiv of the sodium alkylsulfinate in water was slowly added to a solution of mercuric chloride (2 equiv) in water. A white precipitate formed immediately. The mixture was stirred at room temperature for 10 min, and the product was collected by suction filtration and dried. The following compounds were prepared by this method: n-hexylsulfinatomercuric chloride (71%); IR 1180 (s), 1060 cm^{-1} (s); cyclohexylsulfinatomercuric chloride (59%); IR 1185 (s), 1050 cm^{-1} (s); *endo*-2-norbornylsulfinatomercuric chloride (*endo*-VI) (50%): NMR (pyr) 0.8—2.4 (10H, complex), 2.9 (1H, multiplet); IR 1180 (s), 1030 cm^{-1} (s); *exo*-2-norbornylsulfinatomercuric chloride (*exo*-VI) (56%); NMR (pyr) 1.0—2.3 (10H, complex), 3.0 (1H, multiplet); IR 1170 (s), 1030 cm^{-1} (s); 2,2-dimethylpropylsulfinatomercuric chloride (60%); NMR (DMSO-d_6) 1.1 (9H, singlet), 3.0 (2H, singlet); IR 1200 and 1175 (doublet, s), 1060 and 1000 cm^{-1} (doublet, s); *erythro*-3,3-dimethylbutyl-1-sulfinatomercuric chloride-1,2-d_2 (VII) (62%); NMR (pyr, 100 MHz, deuterium-decoupled) 0.79 (9H, singlet), 1.80 (1H, doublet, *J* 12.6 Hz), 2.36 (1H, doublet); IR 1180 (s), 1050 cm^{-1} (s). Cyclic alkylsulfinato mercurials did not melt but decolorized steadily from ca. 150°C to brown-grey residues; acyclic compounds melted with decomposition and release of gas: n-hexyl, 140—142°C; 2,2-dimethylpropyl, 129—130°C, *erythro*-3,3-dimethylbutyl-1,2-d_2, 142—143°C. Elemental analyses for these materials are listed in Table 2. The analysis of the sample of *endo*-VII was approximately 2% low in carbon; this sample was used in further experiments without purification. Where necessary analytically pure samples of alkylsulfinatomercurials could be obtained by dissolution in DMF and precipitation by addition of water at 0°C.

General procedure for the Peters reaction. The alkylsulfinatomercuric chloride (1 mmol) was dissolved in DMF (10 ml). The solution was purged with nitrogen and the flask was placed into an oil bath heated to 100°C. Within a few minutes, the clear solution rapidly became milky-white. Heating was continued for the desired length of time (most reactions were complete in 5—10 min), and the mixture was filtered while hot through Celite to remove small amounts of insoluble material and elemental mercury. The filtrate was treated with 100 ml of water, and the crude alkylmercuric chloride was collected by filtration. Purified product was obtained after recrystallization from ethanol/water (2/1). The yields of crude product were consistently 40—60%, while the yields of purified product were 30—50%.

Infrared analyses. IR spectra were obtained in potassium bromide pellets (3% w/w). The IR spectrum of *exo*-2-norbornylmercuric chloride (*exo*-V) shows characteristic absorption bands at 1100, 995, 949, and 865 cm^{-1}; *endo*-2-norbornylmercuric chloride (*endo*-V) has characteristic bands at 1118, 959, 890, and 754 cm^{-1} (see also ref. 18). Cyclopentylmethylmercuric chloride has characteristic IR absorption bands at 1150, 931, and 735 cm^{-1}, and 5-hexenylmercuric chloride has characteristic bands at 990 and 910 cm^{-1}. The IR spectra were recorded using either samples of crude or recrystallized mercurials isolated from the Peters reaction as described in the previous section with indistinguishable results. Control experiments established that the isolation procedure did not result in epimerization of *endo*-V, and recrystallization of a 1/1 mixture of *exo*-V and *endo*-V as described in the previous section led to no detectable fractionation of the mixture.

Acknowledgments

A sample of *threo*-3,3-dimethylbutan-1-ol-1,2-d_2 was kindly provided by Dr. Paul L. Bock. Special thanks go to Dr. Bock and Mr. Jim Simms for assistance in obtaining 100 MHz deuterium-decoupled proton NMR spectra. This research was supported by the National Science Foundation, Grant MPS 74-20946. The award of a NATO Postdoctoral Fellowship (1975—77) by the (British) Science Research Council to G.B. Young is gratefully.

References

1 Reviews: (a) E. Mueller (Ed.), Houben-Weyl, Methoden der Organischen Chemie, 13/2b, Georg Thieme Verlag, Stuttgart, 1974, p. 11—276; (b) L.G. Makarova and A.N. Nesmeyanov, Methods of Elemento-Organic Chemistry, Vol. 4, Noth-Holland Publ. Co., Amsterdam, 1976, p. 1—336.
2 W. Peters, Ber., 38 (1905) 2567; Ref. 1a, p. 123—129; Ref. 1b, p. 254—257.
3 M. Gielen and R. Fosty, Bull. Soc. Chim. Belg., 83 (1974) 333.
4 R.C. Larock and H.C. Brown, J. Amer. Chem. Soc., 92 (1970) 2467.
5 R.C. Larock and H.C. Brown, J. Organometal. Chem., 26 (1971) 35; R.C. Larock, ibid., 67 (1974) 353; 72 (1974) 35.
6 D.S. Matteson and R.A. Bowie, J. Amer. Chem. Soc., 87 (1965) 2587.
7 F.R. Jensen and B. Rickborn, Electrophilic Substitution of Organomercurials, McGraw-Hill, New York, 1968, p. 32—35.
8 D.E. Bergbreiter and G.M. Whitesides, J. Amer. Chem. Soc., 96 (1974) 4937.
9 E. Wellisch, E. Gipstein and O.J. Sweeting, J. Org. Chem., 27 (1962) 1810; W.E. Truce and A.M. Murphy, Chem. Rev., 48 (1951) 69.
10 P. Allen, Jr., J. Org. Chem., 7 (1942) 23.
11 W.E. Truce and F.E. Roberts, J. Org. Chem., 28 (1963) 593.
12 W.G. Filby, K. Gunther and R.D. Penzhorn, J. Org. Chem., 38 (1973) 4070.
13 E.E. Reid, Organic Chemistry of Bivalent Sulfur, Vol. 1, Chemical Publishing Co., New York, 1958, p. 30.
14 D.I. Davies, L.T. Parfitt, C.K. Alden and J.A. Claisse, J. Chem. Soc. C, (1969) 1585.
15 G.M. Whitesides and D.J. Boschetto, J. Amer. Chem. Soc., 91 (1969) 4313; 93 (1971) 1529; P.L. Bock, D.J. Boschetto, J.R. Rasmussen, J.P. Demers and G.M. Whitesides, ibid., 96 (1974) 2814; P.L. Bock and G.M. Whitesides, ibid., 96 (1974) 2826; H.L. Fritz, J.H. Espenson, D.A. Williams and G.A. Molander, ibid., 96 (1974) 2378; D.E. Bergbreiter and D.P. Rainville, J. Org. Chem., 41 (1976) 3031.
16 J.F.W. McOmie, in Advances in Organic Chemistry, Vol. 3, Wiley, New York, 1963, p. 252.
17 F.R. Jensen and K.L. Nakamaye, J. Amer. Chem. Soc., 88 (1966) 3437.
18 G.M. Whitesides and J. San Filippo, J. Amer. Chem. Soc., 92 (1970) 6611.
19 J.R. Brush, P.G. Cookson and G.B. Deacon, J. Organometal. Chem., 34 (1972) C1; G. Vitzhum and E. Linder, Angew. Chem. Internat. Ed., 10 (1971) 315.
20 C.P. Casey, Ph.D. Thesis, Massachusetts Institute of Technology, 1967, p. 202—203.
21 W.A. Nugent, M. Wu, T.P. Fehlner and J.K. Kochi, Chem. Commun., (1976) 456.
22 G.M. Whitesides, J.P. Sevenair and R.W. Goetz, J. Amer. Chem. Soc., 89 (1967) 1135.
23 G.D. Sargent, in G.A. Olah and P. v. R. Schleyer (Eds.), Carbonium Ions, Vol. III, Wiley—Interscience, New York, 1971, p. 1099 ff.
24 P.D. Bartlett, G.N. Fickes, F.C. Haupt and R. Helgeson, Accounts Chem. Res., 3 (1970) 177.
25 D. Lal, D. Griller, S. Husband and K.U. Ingold, J. Amer. Chem. Soc., 96 (1974) 6355.
26 C.L. Hill and G.M. Whitesides, J. Amer. Chem. Soc., 96 (1974) 870.
27 A. Horowitz and L.A. Rajbenbach, J. Amer. Chem. Soc., 97 (1975) 10.

28 D.F. Shriver, The Manipulation of Air-Sensitive Compounds, McGraw-Hill, New York, 1969; H.C. Brown, G.W. Kramer, A.B. Levy and M.M. Midland, Organic Synthesis via Boranes, Wiley, New York, 1975.
29 J.D. Roberts, E.R. Trumbull, Jr., N. Bennett and R. Armstrong, J. Amer. Chem. Soc., 72 (1950) 3116.
30 G. Grüttner, Chem. Ber., 47 (1914) 1651.
31 Yu.A. Ol'dekop, N.A. Maier, Yu.D. But'ko and M.S. Mindel, Zh. Obsch. Khim., 41 (1971) 1066.
32 F.C. Whitmore, E.L. Wittle and B.R. Harriman, J. Amer. Chem. Soc., 61 (1939) 1585.
33 C. Ulrich, Ann., 109 (1859) 272.