preparative method of orthothioborates, offers a new, simple and rapid technique of preparation of thioacetals, under neutral conditions. The side reactions resulting from acid catalysis, as required by the standard methods of preparation of thioacetals, can be avoided with this new procedure.

Experimental

In a dry 500 ml flask, a mixture of 7.6 g (0.2 mole) of sodium borohydride and 19.2 g (0.6 mole) of sulfur was stirred with 50 ml of anhydrous tetrahydrofuran (slow addition). After the initial reflux had subsided, heat was applied, for a total reflux time of 1½ h. The tetrahydrofuran was then evaporated under vacuum at room temperature and 200 ml of dry petroleum ether, b.p. 30–60° was added to the hydride, with 137 g (1.8 mole) of 1-propanethiol. The reaction mixture was then refluxed overnight.

The crude mixture was then filtered on a carefully dried sintered glass filter (medium porosity). It is advantageous to keep the system dry during the filtration, using a stream of dry nitrogen flowing through an inverted funnel over the filter. After evaporation of the solvent at atmospheric pressure under dry nitrogen, the residue (56.0 g) was then fractionated under vacuum. The first fraction was di-*n*-propyl disulfide, 20.3 g, b.p. 44°/0.5 mm, n_D^{29} 1.4980. Reported for di-*n*-propyl disulfide, b.p. 193.5°/750 mm, n_D^{20} 1.4981. The second fraction, 25.8 g (55% yield based on $NaBH_4$) was *n*-propyl orthothioborate, b.p. 110–118° /0.6 mm, n_D^{29} 1.5341. Reported (5) for *n*-propyl orthothioborate, b.p. 110°/0.6 mm, n_D^{25} 1.5346. This second fraction had an infrared spectrum showing the typical B—S bands at 910 cm^{-1}.

In a dry 250 ml flask, 6.7 g (0.93 mole) of butanone were mixed with 16.1 g (0.82 mole) of ethyl orthoborate. Upon warming, the mixture assumed a gel-like appearance. After a 1h- contact, the mass was extracted with petroleum ether. The boric anhydride was filtered off, the solvent evaporated, and the crude thioacetal distilled. The main fraction was the ethyl thioacetal of butanone, b.p. 73°/0.15 mm, n_D^{28} 1.4959. Reported (2), b.p. 205–208°/750 mm, n_D^{25} 1.4955. The yield of thioacetal was 86%. The reaction could be reproduced with other simple orthothioborates, such as propyl, butyl, and pentyl, with similar yields.

1. F. Bessette, J. Brault, and J. M. Lalancette. Can. J. Chem. **43**, 307 (1965).
2. J. Brault and J. M. Lalancette. Can. J. Chem. **42**, 2903 (1964).
3. B. M. Mikhailov, T. A. Schegoleva, E. M. Shashkova, and V. D. Sheludyakov. Bull. Acad. Sci. USSR, Div. Chem. Sci. English Transl. **7**, 1143 (1962).
4. J. M. Lalancette, A. Frêche, and R. Monteux. Can. J. Chem. **46**, 2754 (1968).
5. A. Cabana, J. Brault, and J. M. Lalancette. Spectrochim. Acta, **22**, 377 (1966).

α-Metallation and subsequent alkylation of alkyl alkanesulfonates

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Strong bases affect α-metallation of alkyl alkanesulfonates; subsequent alkylation offers a useful approach to esters of the higher sulfonic acids.

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In further pursuing the synthesis utility of sulfur group-stabilized carbanions as in alkylations (1), acylations (2), halogenations (3), nitrations (4), and sulfonylations,[1] it has been found that alkyl alkanesulfonates can be metallated and subsequently alkylated in fair to excellent yields.[2,3]

Interest in this area was cultivated by the discovery in this laboratory (6) that the azasultone **1** could be alkylated to yield two different products depending on the conditions employed. Also, the related 1,3-diphenyl-1,4-butanesultone was methylated under the first set of conditions (6).

Following this, attention was turned to a series of neopentyl alkanesulfonates (**2–4** in Table I), the neopentyl group being used initially to preclude the possibility of such undesirable side reactions on the alkyl unit as elimination and displacement. With neopentyl α-toluenesulfonate (**2**), where a benzylic carbanion is formed, *n*-

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[1] W. E. Truce and L. W. Christensen. Unpublished results.

[2] E. J. Corey and T. Durst (5) have studied the formation of $LiCH_2SO_3CH_3$ and its reaction with carbonyl compounds.

[3] We were recently made aware of related work by T. Durst and J. du Manoir on reactions of α-metallated sultones with alkyl halides and with carbonyl compounds.

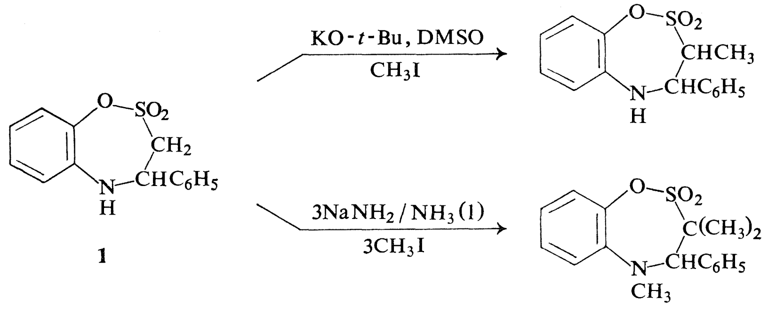

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TABLE I

$RCH_2SO_3CH_2R'' + R'X \rightarrow RR'CHSO_3CH_2R''$

$RCH_2SO_3CH_2C(CH_3)_3$	R′X	Base	$RR'CHSO_3CH_2C(CH_3)_3$		
R = C_6H_5 (**2**)	CH_3I	n-BuLi	73%	b.p.	110–113°/0.25 mm
R = C_6H_5	$(CH_3)_2CHI$	n-BuLi	86%	b.p.	112–115°/0.25 mm
R = H (**3**)	p-$CH_3C_6H_4CH_2Br$	n-BuLi/TMEDA	40% by n.m.r. 15% isolated	m.p.	51–52°
R = H	$C_6H_5CH_2Cl$	KH	38%	b.p.	131–137°/0.45 mm
R = CH_3 (**4**)	CH_3I	KH	46%	b.p.	51–52°/0.20 mm
$C_6H_5CH_2SO_3CH_2CH_3$ (**5**)	CH_3I	n-BuLi	$C_6H_5CH(CH_3)SO_3CH_2CH_3$ 79%	b.p.	99–101°/0.20 mm

butyllithium in hexane was found to be a satisfactory metallating agent. Subsequent reaction of the α-metallated species with methyl or isopropyl iodide led to alkylation product in excellent yield.

With neopentyl methanesulfonate (**3**) or neopentyl ethanesulfonate (**4**), where the α-position being metallated is not benzylic, best yields were obtained with potassium hydride in tetrahydrofuran or *n*-butyllithium complexed with *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (7–9) as metallating agent.

Most recently,[4] ethyl-α-toluenesulfonate (**5**) has been prepared, and shows, by its conversion to its α-methyl derivative in high yield, that the presence of the neopentyl "protective group" is not necessary to obtain high yields when a benzylic position is being alkylated. That is, α-metallation is preferred over elimination or displacement in these systems.

Experimental

All reactions described herein were carried out in thoroughly dried apparatus under an atmosphere of nitrogen. *n*-Butyllithium in hexane was purchased from the Foote Mineral Co., and potassium hydride, as a 50% suspension in mineral oil, from Alfa Inorganics. Starting sulfonates were prepared by the reaction of the appropriate sulfonyl chloride and alcohol in the presence of triethylamine in benzene or diethyl ether solvent. These consisted of: neopentyl α-toluenesulfonate, m.p. 71–73°; neopentyl methanesulfonate, b.p. 94–96°/10 mm; neopentyl ethanesulfonate, b.p. 58–60°/0.15 mm; and ethyl α-toluenesulfonate, b.p. 129–130°/0.04 mm. Infrared (i.r.) spectra were recorded on an Infracord spectrophotometer and nuclear magnetic resonance (n.m.r.) spectra on a Varian Associates A-60A spectrophotometer. Microanalyses were carried out by Dr. C. S. Yeh and staff.

Neopentyl 1-Phenylethanesulfonate

A solution of 7.27 g (0.030 mole) of neopentyl α-toluenesulfonate dissolved in 40 ml of tetrahydrofuran was added dropwise to 20.7 ml of a 1.6 *M* solution (0.033 mole) of *n*-butyllithium in hexane at −65 °C over a 35 min period. As soon as the addition was complete, 4.69 g (0.033 mole) of methyl iodide were added portionwise resulting in the precipitation of finely divided lithium iodide. After 15 min stirring at −65°, the reaction mixture was allowed to warm to room temperature, was quenched with 100 ml of H_2O, and the resulting suspension was extracted with chloroform. The chloroform

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[4] Recently, we extended the use of α-metallated sulfonate esters to the preparation of cyclopropanesulfonates from γ-chloropropanesulfonates by internal alkylation, e.g., neopentyl cyclopropanesulfonate from γ-chloropropanesulfonate, see ref. 10.

extracts were combined, dried, and evaporated *in vacuo* yielding a yellow oil which was chromatographed on a 3 × 25 cm column of alumina with chloroform as eluent. The neopentyl 1-phenylethanesulfonate thus obtained was distilled yielding 5.62 g (73.1%) of pure material, b.p. 110–113°/0.25 mm; i.r. (neat): 2950 (s), 1470 (s), 1360 (s), 1175 (s), 980 (b), 840 (b), and 700 $\mathrm{cm^{-1}}$ (s); n.m.r. ($CDCl_3$): δ 0.84 (s, 9H, $C(CH_3)_3$), 1.77 (d, 3H, CH—CH_3) J = 7 c.p.s., 3.62 (sym m, 2H, O—$CH_2C(CH_3)_3$), 4.37 (quartet, 1H, $CHCH_3$) J = 7 c.p.s., and 7.35 (m, 5H, ArH).

Anal. Calcd. for $C_{10}H_{14}O_3S$: C, 60.90; H, 7.86; S, 12.51. Found: C, 61.10; H, 8.14; S, 12.52.

Neopentyl 2-Methyl-1-phenylpropanesulfonate

In a manner completely analogous to that above, the title compound was prepared from neopentyl α-toluenesulfonate and isopropyl iodide in 86% yield, b.p. 112–115°/0.25 mm; i.r. (neat): 3000 (s), 1460 (s), 1180 (s), 975 (b), and 704 $\mathrm{cm^{-1}}$ (s); n.m.r. ($CDCl_3$): δ 0.75 (s, 9H, $C(CH_3)_3$), 0.98 (d, 3H), and 1.22 (d, 3H), the two nonequivalent methyl groups of the isopropyl group, δ 2.62 (m, 1H, $CH(CH_3)_2$), 3.51 (sym m, 2H, $OCH_2C(CH_3)_3$), 3.98 (d, 1H, C_6H_5CH), and 7.35 (s, 5H, C_6H_5).

Anal. Calcd. for $C_{15}H_{24}O_3S$: C, 63.34; H, 8.51; S, 11.28. Found: C, 63.55; H, 8.81; S, 11.64.

Neopentyl 2-p-Tolylethanesulfonate

To 0.050 mole of the *n*-butyllithium – TMEDA complex prepared as described by Peterson (9), were added 8.31 g (0.050 mole) of neopentyl methanesulfonate. After 2.25 h stirring, a solution of 9.25 g (0.050 mole) of *p*-methylbenzylbromide in 30 ml of tetrahydrofuran was added. After 1.5 h additional stirring, the reaction was quenched with 100 ml of H_2O and extracted with chloroform. The chloroform extracts were combined, dried, and evaporated *in vacuo* yielding a yellow oil. The oil was dissolved in a small amount of 95% ethanol, and the solution cooled to −78°. The white solid that separated was recrystallized from isopropanol–water yielding 2.05 g (15.1%) of the title compound, m.p. 51–52°; i.r. (solid film): 3000 (s), 1530 (s), 1370 (s), 1170 (s), and 970 $\mathrm{cm^{-1}}$ (b); n.m.r. ($CDCl_3$): δ 0.98 (s, 9H, $C(CH_3)_3$), 2.28 (s, 3H, $ArCH_3$), 3.20 (sym m, 4H, CH_2CH_2), 3.82 (s, 2H, OCH_2), and 7.08 (s, 4H, ArH).

Neopentyl 2-Phenylethanesulfonate

A solution of 7.07 g (0.0425 mole) of neopentyl methanesulfonate dissolved in 20 ml of tetrahydrofuran was added to a suspension of 0.0425 mole of potassium hydride in 30 ml of tetrahydrofuran. The reaction mixture was stirred at room temperature for 5.5 h, and then heated to 60° until hydrogen evolution ceased. The reaction mixture was then cooled to 0°, and 5.37 g (0.0425 mole) of benzyl chloride were added dropwise. After 12 h stirring, 200 ml of water were added, and the resulting suspension was extracted with chloroform. The chloroform extracts were combined, dried, and evaporated *in vacuo* yielding a light oil. Upon distillation, 4.0 g (38%) of the title compound, contaminated with a small amount of mineral oil was obtained, b.p. 131–137°/0.45 mm; i.r. (neat): 2950 (s), 1360 (s), 1175 (s), 970 (b), and 700 $\mathrm{cm^{-1}}$ (s); n.m.r. ($CDCl_3$): δ 0.94 (s, 9H, $C(CH_3)_3$), 3.19 (sym m, 4H, CH_2CH_2), 3.78 (s, 2H, OCH_2), and 7.21 (s, 5H, ArH).

Neopentyl 2-Propanesulfonate

To 0.105 mole of potassium hydride suspended in tetrahydrofuran were added 9.5 g (0.052 mole) of neopentyl ethanesulfonate, and the reaction mixture was stirred for 48 h. After this time, 15 g of methyl iodide (0.105 mole) were added and stirring continued for 24 h before the reaction mixture was quenched with 100 ml of water and extracted with chloroform. The chloroform extracts were combined, dried, and evaporated *in vacuo* leaving a light oil that was chromatographed on acid-washed alumina with chloroform as eluent. The product obtained was distilled under vacuum yielding 4.72 g (46.2%) of neopentyl 2-propanesulfonate, b.p. 51–52°/0.20 mm; i.r. (neat): 3020 (s), 1370 (s), 1190 (s), 1170 (s), 975 (b), and 835 $\mathrm{cm^{-1}}$ (b); n.m.r. ($CDCl_3$): δ 0.98 (s, 9H, $C(CH_3)_3$), 1.43 (d, 6H, $(CH_3)_2CH$), 3.37 (septet, 1H, $(CH_3)_2CH$), and 3.89 (s, 2H, OCH_2).

Ethyl 1-Phenylethanesulfonate

In a manner completely analogous to that used for the preparation of neopentyl 1-phenylethanesulfonate, the title compound was prepared in 79% yield from ethyl α-toluenesulfonate and methyl iodide with *n*-butyllithium as metallating agent, b.p. 99–101°/0.20 mm; i.r. (neat): 3000 (w), 1350 (s), 1175 (s), 1005 (s), 920 (b), and 700 $\mathrm{cm^{-1}}$ (s); n.m.r. ($CDCl_3$): δ 1.17 (t, 3H, CH_2CH_3), 1.76 (d, 3H, $CHCH_3$), 3.98 (m, 2H, CH_2CH_3), 4.33 (m, 1H, $CHCH_3$), and 7.37 (m, 5H, ArH).

Anal. Calcd. for $C_{10}H_{14}O_3S$: C, 56.05; H, 6.58; S, 14.97. Found: C, 55.77; H, 6.54; S, 15.12.

1. W. E. Truce and L. B. Lindy. J. Org. Chem. **26**, 1463 (1961).
2. W. E. Truce and F. E. Roberts. J. Org. Chem. **28**, 961 (1963).
3. W. E. Truce and R. W. Lagally. Abstr. 153rd Meeting Amer. Chem. Soc. Miami Beach, Florida. April 1967. No. O 102.
4. W. E. Truce and L. W. Christensen. Tetrahedron, To be published.
5. E. J. Corey and T. Durst. J. Am. Chem. Soc. **90**, 5548 (1968).
6. J. W. Fieldhouse. Ph.D. Thesis, Purdue University. Lafayette, Indiana. June 1968.
7. G. G. Eberhardt and W. A. Butte. J. Org. Chem. **29**, 2928 (1964).
8. A. W. Langer, Jr. Trans. New York Acad. Sci. [II], **27**, 741 (1965).
9. B. J. Peterson. J. Org. Chem. **32**, 1717 (1967).
10. C. T. Goralski. Ph.D. Thesis, Purdue University. Lafayette, Indiana. January 1969.