5.68 g (81%) and had m.p. 120–121°. A mixture melting point with an authentic specimen of *N*-methylhomophthalimide was undepressed.

N-Methylphthalonimide

The following procedure was typical for the oxidation of isocarbostyrils.

A magnetically stirred solution of *N*-methylisocarbostyril (20.0 g, 125.8 mmoles) in 200 ml of glacial acetic acid was titrated with 0.649 *M* sodium dichromate in 2.5 *M* sulfuric acid (194 ml, 377.7 m eq.) at a rate such that the reaction temperature did not exceed 30°. When the addition was completed the mixture was stirred for an additional $\frac{1}{2}$ h at room temperature, and then it was poured with stirring into ca. 1.5 l of ice-cold water. The precipitated yellow solid was collected by filtration, washed well with ice-cold water, and dried *in vacuo*. The yellow solid obtained in this way had m.p. 185–186° (lit. (7), m.p. 186–187°), and weighed 19.2 g (81%).

1. A. von Baeyer and C. Knop. Ann. Chem. **140**, 1 (1866).
2. A. von Baeyer. Chem. Ber. **11**, 582 (1878).
3. P. L. Julian, E. W. Meyer, and H. C. Printy. Heterocyclic compounds. Vol. III. *Edited by* R. C. Elderfield. John Wiley and Sons, Inc., New York. 1952. pp. 126–130.
4. B. Sakurai. J. Chem. Soc. Japan, **17**, 269 (1942); Chem. Abstr. **41**, 4486 (1947).
5. N. P. Buu-Hoi, G. Saint-Ruf, and J. C. Bourgeade. J. Heterocyclic Chem. **5**, 545 (1968).
6. B. R. Harriman, R. S. Shelton, M. G. Van Campen, and M. R. Warren. J. Am. Chem. Soc. **67**, 1481 (1945).
7. M. Freund and H. Beck. Chem. Ber. **37**, 1942 (1904).
8. S. Gabriel and J. Coleman. Chem. Ber. **35**, 2421 (1902).
9. W. Findeklee. Chem. Ber. **38**, 3542 (1905).
10. R. Stolle, R. Bergdoll, M. Luther, A. Auerhahn, and W. Wacker. J. Prakt. Chem. **128**, 1 (1930).
11. J. M. Muchowski. Tetrahedron Letters, 1773 (1966).
12. A. H. Beckett, R. W. Daisley, and J. Walker. Tetrahedron, **24**, 6093 (1968).
13. T. A. Foglia and D. Swern. J. Org. Chem. **33**, 4440 (1968).

Facile preparation of thioacetals in neutral medium starting from sodium borohydride

J. M. Lalancette and A. Lachance

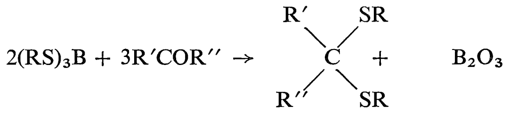
Department of Chemistry, Faculty of Sciences, University of Sherbrooke, Sherbrooke, Quebec

Received October 23, 1968

Sodium borohydride can be sulfurated to give $NaBH_2S_3$. The sulfurated hydride, when treated with a mercaptan, gives an orthothioborate: $(RS)_3B$. The orthoborates react with aldehydes and ketones to give the corresponding thioacetals with quantitative yields, in neutral medium.

Canadian Journal of Chemistry, 47, 859 (1969)

We have reported (1) the preparation of thioacetals in neutral media (benzene or petroleum ether) using alkyl orthothioborates (eq. [1]).

[1] 

$$2(RS)_3B + 3R'COR'' \rightarrow R'R''C(SR)_2 + B_2O_3$$

The orthothioesters can be prepared from boron sulfide (2) or boron halides (3) but in both cases, these preparations are somewhat tedious. Recently, we have reported the partial sulfuration of sodium borohydride to give a sulfurated borohydride formulated as $NaBH_2S_3$ (4).

This sulfurated borohydride reacts very easily with mercaptans to give the corresponding orthothioborates, according to eq. [2]:

$$[2]\quad NaBH_2S_3 + RSH \rightarrow (RS)_3B + H_2 + RSSR + NaS_3H$$

The sulfuration of the borohydride is an extremely simple reaction; a mixture of $NaBH_4$ (1 mole) and sulfur (3 moles) is treated by anhydrous tetrahydrofuran and the solvent is evaporated under vacuum after a short contact. This sulfurated hydride is then treated with an excess of the selected mercaptan in petroleum ether. The use of a stoichiometric amount of mercaptan gives rather low yields of orthothioborate (10–20%) but a 100% excess of mercaptan brings the yield in the 50–60% range. In petroleum ether the sodium polysulfide is insoluble and the organic fraction can be filtered off. Due care must be exercized in the course of this filtration since orthothioborates are very hygroscopic. The orthothioborate is then separated from the disulfide by distillation and can be used for the preparation of the thioacetal.

This sequence of reactions besides giving a new 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

W. E. Truce and D. J. Vrencur
Purdue University, Lafayette, Indiana 47907

Received October 3, 1968

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

Canadian Journal of Chemistry, 47, 860 (1969)

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*-

---

[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.