View Article Online / Journal Homepage / Table of Contents for this issue

Published on 01 January 1974. Downloaded by Universiteit Utrecht on 25/10/2014 00:24:01.

Benzophenonethio-oximate Ion

By Charles Brown, B. Terry Grayson, and Robert F. Hudson*
(*University Chemical Laboratory, Canterbury, Kent* CT2 7NH)

Summary The reaction between bis-(diphenylmethylenamino) disulphide and n-butyl-lithium gives the anion of benzophenone thio-oxime which can be trapped with 2,4-dinitrofluorobenzene to give *N*-(2,4-dinitrophenylthio)diphenylmethylenamine.

In an extension of our work on hydroxylamine derivatives we have attempted to prepare and isolate thio-oximes.[1] The $>$N–SH system is unknown,[2] although *S*-substituted derivatives of hydrosulphamines (sulphenamides,[3] $RSNH_2$) and thio-oximes[3,4] ($R^1_2C{=}NSR^2$) have been prepared, usually from imines, *e.g.* (**1**). Hunger postulated[5] the transient existence of a thio-oximate anion (**2**) during the alkaline hydrolysis of a phosphorylated thio-oxime but he was unable to substantiate this. We now report the generation and trapping of this anion.

Our approach involves the reaction of butyl-lithium with bis(diphenylmethylenamino) disulphide (**3**) (prepared according to the method of Exner[6]†) which should result in the cleavage of the disulphide bond,[7] (see Scheme).

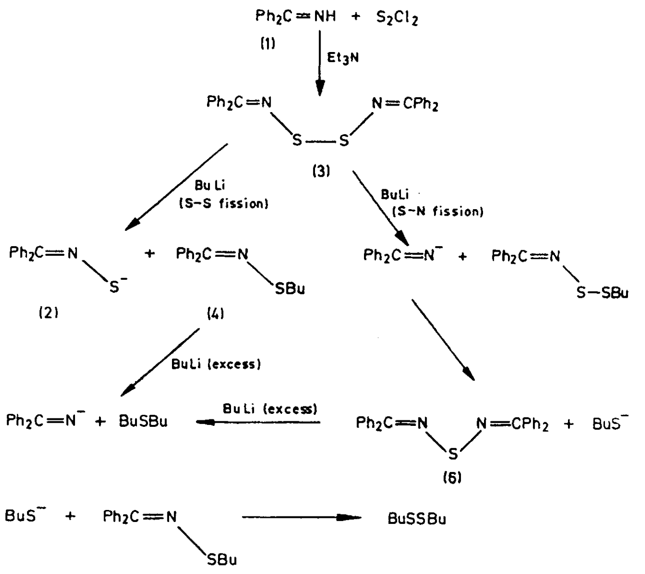
Addition of Bu^nLi (1 mol. equiv.) to (**3**) in benzene under nitrogen, followed by the addition of 2,4-dinitrofluorobenzene to trap the anion (**2**) if formed, gave a number of products. These included the *N*-(n-butylthio)diphenyl-

† In our hands this compound melted at 164—166°, then recrystallised on further heating and remelted at 178—180°. Exner[6] reports a m.p. of 176°.

View Article Online

Published on 01 January 1974. Downloaded by Universiteit Utrecht on 25/10/2014 00:24:01.

methyleneamine (**4**) [50%, based on starting material (**3**) consumed], and the *N*-(2,4-dinitrophenylthio)diphenylmethylenamine, (**5**) (10%) as yellow crystals, m.p. 224—226°, identical to authentic material,‡ confirming the presence of the thio-oxime anion (**2**) in the reaction mixture.§ However, although the isolation of (**5**) together with (**4**) strongly implies that S–S cleavage is an important reaction in this system, other processes clearly play a major part also. Thus, in addition to (**4**) and (**5**) we also isolated the following by p.l.c.: dibutyl disulphide, dibutyl sulphide, benzophenone (from decomposition of diphenylmethylenamine on the p.l.c. plate) and the sulphide (**6**). These products, especially (**6**), clearly indicate the possibility of S–N bond cleavage in (**3**), and this possibility was firmly substantiated by the observation that reaction of *S*-alkyl thio-oximes with butyl-lithium gave imine anions and alkyl butyl sulphide. Furthermore, the monosulphide (**6**) itself was converted by excess of butyl-lithium into the imine anion (isolated as benzophenone, 96%) and dibutyl sulphide (88%).



SCHEME

We found also that addition of 3 mol. equiv. of butyl-lithium to (**3**) gave only dibutyl disulphide, dibutyl sulphide, and imine anion, characterised as the *N*-(2,4-dinitrophenyl) derivative, m.p. 126—128° (52%). We postulate a reaction mechanism of the type in the Scheme to explain the products obtained.

Although the yield of the thio-oximate anion (**2**) is low, these experiments show that it is sufficiently stable to be trapped, and therefore capable of being used for reactions *in situ*. They also show that further experiments to improve the yield and to provide methods of isolating the salt are warranted.

One of us (B.T.G.) thanks Shell Research, Sittingbourne, for financial support.

(*Received*, 29*th August* 1974; *Com.* 1105.)

---

‡ All compounds reported had satisfactory elemental analyses and/or correct values for precise mass spectrometrically determined molecular weights. Their i.r. and n.m.r. spectra, where appropriate, were in accord with the assigned structures.

§ 2,4-Dinitrofluorobenzene does not react with (**3**) under these conditions.

[1] C. Brown, B. T. Grayson, and R. F. Hudson, *Tetrahedron Letters*, 1970, 4925.
[2] See however, F. Tiemann, *Ber*, 1891, **24**, 369.
[3] C. Brown and B. T. Grayson, *Mech. Reactions Sulphur Compounds*, 1970, **5**, 93; J. Almog, D. H. R. Barton, P. D. Magnus, and R. K. Norris, *J.C.S. Perkin I*, 1974, 853.
[4] F. A. Davis and E. B. Skibo, *J. Org. Chem.*, 1974, **39**, 807 and references therein.
[5] K. Hunger, *Ber.*, 1967, **100**, 2214.
[6] O. Exner, *Coll. Czech. Chem. Comm.*, 1963, **28**, 3150.
[7] A. Schonberg, A. Stephenson, H. Kaltschmidt, E. Peterson, and H. Schulten, *Ber.*, 1933, **66**, 237.

Printed by Heffers Printers Ltd Cambridge England