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WARNING

Dear Readers

I note[1] that in a recent paper in Tetrahedron Letters 2-deuterio-1,3-benzodithiolium perchlorate is recommended as 'a useful synthon for the preparation of aldehydes-1-d'.

In the recent past we have examined the uses in organic synthesis of 2-alkoxy-1,3-benzodithioles and various salts[2]. 1,3-Benzodithiolium perchlorate is a well known compound[3] which is thermally stable and has indeed been referred to as 'the stable perchlorate salt' of the benzodithiolium ion.[4] In our laboratories the compound was made, following the procedure of Nakayama, some five times without incident. However when a larger batch was prepared the simple act of opening a desiccator containing the perchlorate led to an explosion which severely injured the technician carrying out the preparation and which led to a fire which gutted the laboratory.

Benzodithiolium perchlorate was subsequently examined independently at the Royal Armament Research and Development Establishment (Mr. J.R. Hughes) and by I.C.I. Nobel Explosives Co. Ltd. (Mr. T.A. Brown).

Mr. Hughes reported that the perchlorate had been subjected to the Koenen friction test and gave crepitation at 0.6Kg loading and a detonation at 0.8Kg loading. This compares with detonation of mercury fulminate at 0.5Kg and calcium azide at 1.0Kg, and Mr. Hughes commented that 'this compound has a friction sensitivity similar to that of initiatory compounds'.

Mr. Brown subjected the perchlorate to the 'fall hammer (0.5Kg)' and 'torpedo friction (1Kg)' tests. The 'fall hammer' test gave a value of <5cm (lead azide, lead styphnate, 10-15cm) and the friction test a value of 5-10cm. Mr. Brown stated that 'it is, if anything, more sensitive than some of the primary explosives used by us in detonator manufacture..... Materials of this sort of sensitivity should clearly be handled with the utmost care using every possible safeguard.'

Clearly 1,3-benzodithiolium perchlorate should be regarded a hazardous chemical, only to be used as a last resort and then with extreme care. However the corresponding fluoroborate is readily made,[2d] easily handled and behaves chemically in a similar fashion to the perchlorate.[5] We have modified the literature procedure for making the fluoroborate and will be happy to pass on details to anyone interested.

Readers may also be interested in the comments by Mr. Brown on the frequently used 2,4,6-triphenylpyrylium perchlorate (sample 2). 'Sample 2 was insensitive to initiation at maximum setting in the tests but when grit was added values of 120-160cm in the 'fall hammer' test and 20-30cm in the 'torpedo friction' test were obtained showing that although it is insensitive to initiation in the tests, nevertheless it does have explosive properties.

I think these results show that in general organic perchlorates are materials which can have explosive properties with varying degrees of sensitivity to initiation.'

To me it would seem wise that anyone wishing to prepare and use any organic perchlorate should have to show good cause to the head of the laboratory and to his colleagues.

A. PELTER

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