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ADDITIONS TO HEXAFLUOROBUT-2-YNE

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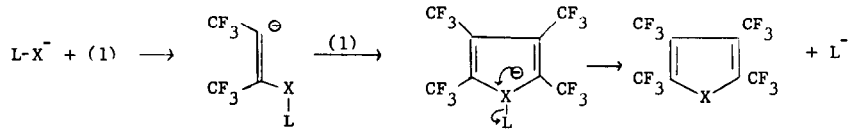
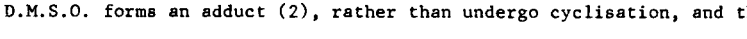
Earlier in our laboratory[1], we have shown that hexafluorobut-2-yne (1) reacts with sulphur, in an aprotic solvent, to give F-tetramethylthiophene and the reaction was formulated as a nucleophilic cyclisation process. Here we will describe attempts to obtain cyclised products via the generalised process shown below and using a variety of systems.



D.M.S.O. forms an adduct (2), rather than undergo cyclisation, and the



properties of (2) will be discussed.

Other additions to (1) will be described.

1 R.D. Chambers and D.B. Speight, unpublished results.

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NEW CONVENIENT AND EFFICIENT ROUTES TO LONG-CHAIN (PERFLUORO-ALKYL) ALKYNES

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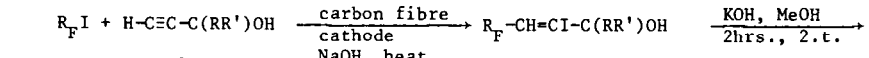
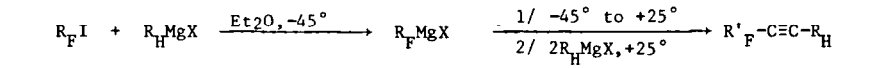
Perfluorinated alkynes are potential intermediates for the introduction of perfluoroalkyl chains in organic compounds. We report here new convenient and efficient preparations of various long-chain (perfluoroalkyl) acetylenes. (Perfluoroalkyl) alkynes R_F-C≡C-H (R_F=C_8F_{17}, C_6F_{13}, C_4F_9) are obtained from perfluoroalkyl iodides in excellent yields (80-90%) by means of a simple electrochemical technique (electrocatalysis at a carbon fibre cathode), according to :



The corresponding 1-substituted alkynes R_F-C≡C-R_H (R_H=C_2H_5, C_4H_9, C_8H_{17}, C_6H_5, O-CH_3-C_6H_4, O-CH_3O-C_6H_4) are obtained in good yields (70%), in a one-pot reaction, from the thermal decomposition of perfluoroalkyl grignard reagents in the presence of excess alkyl or aryl magnesium halides, according to :



The syntheses are described and mechanisms of the reactions are discussed.