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Rearrangement of 4-(Phenylthio)(1,1-D_2)butyl Radical: Mechanistic Implications for Homolytic Substitution on Sulfur

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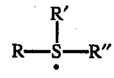
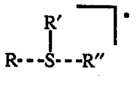


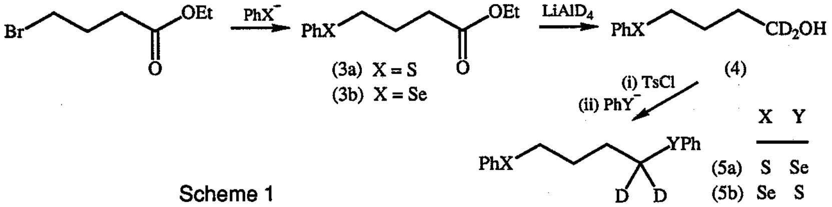
(1)



(2)

The mechanism of homolytic substitution by an alkyl radical at the sulfur atom in alkyl sulfides is still not well understood. Hypervalent (9-S-3) sulfuranyl radicals have been observed in e.s.r. experiments when a peroxy ester containing a neighbouring sulfenyl group is photolysed,[1] and when sulfonium salts containing radical-stabilizing groups are electrochemically reduced,[2] these results suggesting that 9-S-3 species, such as (1), might be involved in homolytic substitution on sulfur, although there appears to be little evidence in favour of an intermediate in the absence of stabilizing groups.[3] Other workers have suggested that a transition state, such as (2), or an intermediate (1), in which the rate of pseudo-rotation is slow with respect to the rate of departure of the leaving group, is involved, in order to explain the strict inversion of configuration observed when chiral sulfoxides are involved in homolytic substitution.[4]

In an attempt to shed some light on this problem we have examined the rearrangement of the title radical, which cannot achieve the colinear requirement of either (1) or (2).



Scheme 1

To avoid any possible ambiguity that might arise due to formation of trialkylsufonium salts, we chose to use the phenyl selenide (5a) (as opposed to the halide) as the radical precursor in this study. To that end, phenyl 4-(phenylseleno)(4,4-D_2)butyl sulfide† (5a) was prepared according to Scheme 1.

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† All compounds gave satisfactory n.m.r. and mass spectral data.

[1] Perkins, C. W., Martin, J. C., Arduengo, A. J., Lau, W., Alegria, A., and Kochi, J. K., *J. Am. Chem. Soc.*, 1980, **102**, 7753.

[2] Beak, P., and Sullivan, T. A., *J. Am. Chem. Soc.*, 1982, **104**, 4450; Perkins, C. W., Clarkson, R. B., and Martin, J. C., *J. Am. Chem. Soc.*, 1986, **108**, 3206; Perkins, C. W., and Martin, J. C., *J. Am. Chem. Soc.*, 1986, **108**, 3211; Saeva, F. D., and Morgan, B. P., *J. Am. Chem. Soc.*, 1984, **106**, 4121.

[3] Franz, J. A., Roberts, D. H., and Ferris, K. F., *J. Org. Chem.*, 1987, **52**, 2256.

[4] Beckwith, A. L. J., and Boate, D. R., *J. Chem. Soc., Chem. Commun.*, 1985, 189.

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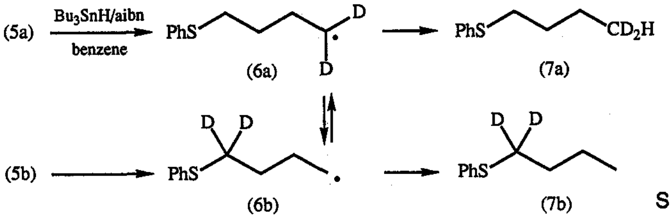
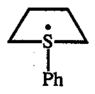
Reaction of ethyl 4-bromobutanoate with sodium benzenethiolate (NaH/PhSH) in dimethylformamide yielded ethyl 4-(phenylthio)butanoate (3a) which was reduced with lithium aluminium deuteride in ether to give 4-(phenylthio)(1,1-D_2)butan-1-ol (4a) in 75% overall yield. Coversion into the tosylate and subsequent displacement with phenyl selenide ($NaBH_4$/PhSeSePh) in ethanol afforded the radical precursor (5a) in 34% yield after recrystallization from ethanol.



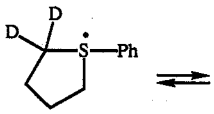
Scheme 2

Reaction of (5a) with 1 equiv. of tributyltin hydride in benzene (0·017 M) [azobisisobutyronitrile (aibn) initiator] yielded, after 84 h, a mixture of (4,4-D_2)butyl phenyl sulfide (7a) (90%) and (1,1-D_2)butyl phenyl sulfide (7b) (10%) (Scheme 2) as determined by 41-MHz ^{2}H n.m.r. spectroscopy of the product after chromatography. At substantially higher stannane concentration, reduction of (5a) gave exclusively (7a), while lower concentrations resulted in a lack of reaction, presumably due to an inefficient radical chain. The reverse product distribution [(7a) (10%) and (7b) (90%)] was obtained when precursor (5b), prepared according to Scheme 1, was used in this study.

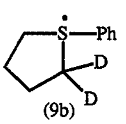
The formation of (7b) from (5a) under these conditions is likely due to intramolecular homolytic substitution by labelled primary alkyl radical on sulfur with the loss of unlabelled primary radical. Given the geometrical constraints in this reaction, homolytic substitution is unlikely to occur through a colinear structure (8). Rearrangement must therefore occur through a transition state in which the attacking and leaving groups substantially deviate from linearity, or a hypervalent (9-S-3) intermediate (9a) which, by analogy with phosphorus and silicon chemistry, undergoes pseudo-rotation to (9b) prior to stannane reduction, thereby ensuring that the leaving group is in the required axial position.[5]



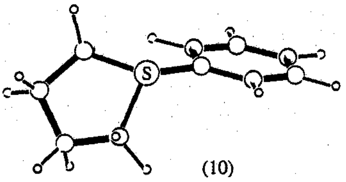
(8)



(9a)



(9b)



(10)

In an attempt to resolve the question of reaction mechanism, the proposed hypervalent intermediate in this reaction was modelled by molecular orbital theory. PM3/UHF calculations[6] suggest that a 9-S-3 species (10) does correspond to a

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[5] Holmes, R. R., *Chem. Rev.*, 1990, **90**, 17, and references cited therein.

[6] Stewart, J. J. P., *J. Comput. Chem.*, 1988, **10**, 209, 221 (implemented on a Sun SparcStation 1+ as MOPAC 6.0).

minimum on the potential-energy surface and resembles a distorted T-shape with a structure similar to that calculated by INDO for the propyltetramethylenesulfuranyl radical.[3] *Ab initio*[7] calculations (UHF/3-21G(*)),[8] however, failed to locate any intermediate that might be involved in the rearrangement of (6a). (All calculations were performed on a Sun SparcStation 1+.)

While we have not resolved the question of transition state *versus* intermediate, we have shown that homolytic substitution can occur on sulfur by a mechanism that does not involve a colinear arrangement of attacking and leaving radicals.

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[7] Frisch, M. J., Head-Gordon, M., Trucks, G. W., Foresman, J. B., Schlegel, H. B., Raghavarchari, K., Robb, M., Binkley, J. S., Gonzalez, C., Defrees, D. J., Fox, D. J., Whiteside, R. A., Seeger, R., Melius, C. F., Baker, J., Martin, R. L., Kahn, L. R., Stewart, J. J. P., Topiol, S., and Pople, J. A., *Gaussian 90*, Revision F, Gaussian Inc., Pittsburgh PA, 1990.

[8] Dobbs, K. D., and Hehre, W. J., *J. Comput. Chem.*, 1986, 7, 359.