Tetrahedron Letters,Vol.24,No.8,pp 821-824,1983 0040-4039/83/080821-04$03.00/0
Printed in Great Britain

REACTION OF DIPHENYL DISULPHIDE WITH 1,8-DEHYDRONAPHTHALENE

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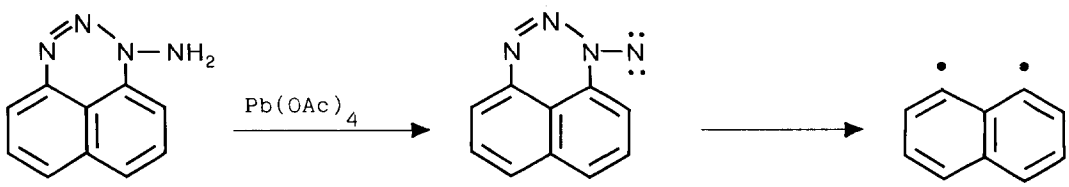
Summary: The reaction of diphenyl disulphide with 1,8-dehydronaphthalene gives benzo[kl] thioxantene(5), 1-naphthyl-phenyl-sulphide(6) and naphtho-[1,8-bc] thiet(7). Formation of these compounds is explained *via* the intermediacy of the radical species (8).

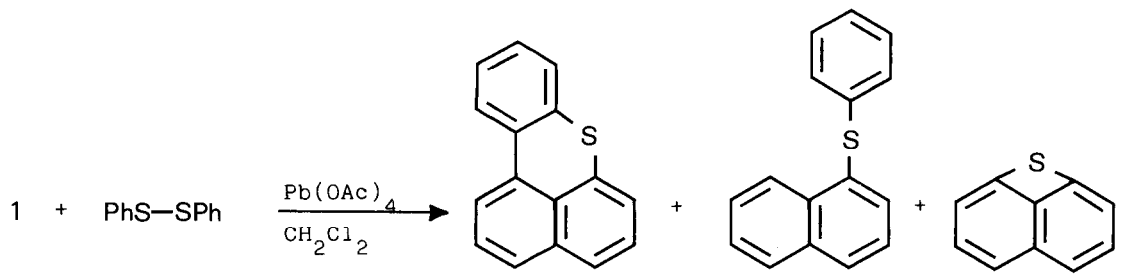
Lead tetraacetate oxidation[1] of 1-amino-naphtho[1,8-de]triazine(1)[2] gives the nitrene(2), whose subsequent fragmentation is expected to give the highly reactive intermediate 1,8-dehydronaphthalene(3):



The singlet diradical character of 1,8-dehydronaphthalene is supported by the stereospecific 1,2-additions to olefins[1], the reactions with halogenated hydrocarbons[1], and by theoretical arguments[3]. Recently, Nakayama et al.[4] published their work on a reaction of (3) with carbon disulphide which involves initial addition of 1,8-dehydronaphthalene to a sulphur atom; the tendency of (3) to act as an aryl radical is shown.

In the remainder of this paper, as a further step in our studies[5] of the radical acceptor character of the S atom, the results obtained investigating the 1,8-dehydronaphthalene behaviour towards diphenyl disulphide(4) will be presented

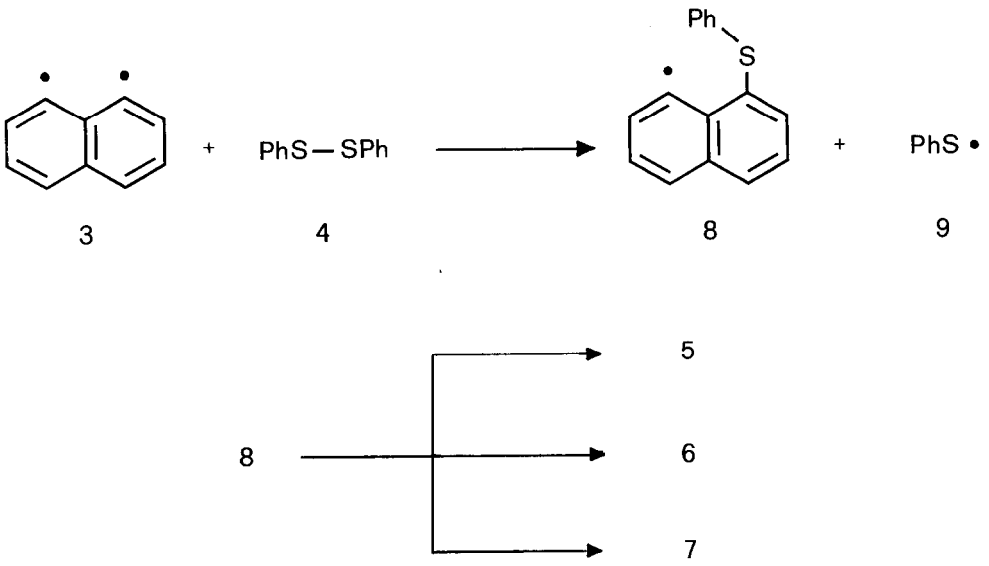
When to a stirred suspension of lead tetraacetate(5,32 g, 12 mmol) in methylene chloride(150 ml) is added a solution of the amine(1)(1,84 g, 10 mmol) and (4) (4,36 g, 20 mmol) in the same solvent(150 ml) rapid evolution of nitrogen occurred and the products (5)-(7) are formed (40 min at room temperature).



4 5 6 7

Lead salts are filtered off and the methylene chloride is distilled under reduced pressure. Column chromatography on alumina by elution with light petroleum/benzene yields naphtho [1,8-bc] thiet(7)(1%),m.p. 40°C[6], 1-naphthyl-phenyl-sulphide(6) (13%),m.p. 39°C[7], and benzo [kl] thioxantene(5)(6%),m.p. 79°C[8]. More polar eluants gives discrete amounts of tarry materials. About 50% of the starting diphenyl disulphide(4) is recovered. These compounds are subsequently identified by the usual spectroscopic methods (infrared, n.m.r. and u.v. spectra) and by comparison of g.l.c.[9] retention times with those of authentic samples.

The first step of this reaction is very likely the attack of 1,8-dehydronaphthalene on the sulphur atom of the diphenyl disulphide leading to the radical (8). Supporting evidence for the intervention of (8) as radical intermediate comes from the fact that the thermolysis[10] of benzoyl peroxide in the presence of naphtho [1,8-cd] 1,2-dithiol 1,1-dioxide gives (5), (6) and (7) in a ratio which is similar to that observed in the present reaction. Accordingly, the reaction products can be easily rationalized in terms of the following reactions:



The radical (8) can lead to compound (5) by intramolecular cyclization[10,11], to compound (6) by hydrogen abstraction and to (7) by loss of phenyl radical and subsequent 1,4-cyclization[4]. Phenylthio radical(9) can dimerize to yield the starting diphenyl disulphide. Traces of naphthalene and 1-chloronaphthalene are also isolated according to the well-known oxidation reactions[1,2] of 1-amino-naphtho-[1,8-de]triazine in methylene chloride.

The work reported here show another interesting example of radical-displacement reaction (SH_2) on disulphides[12], moreover obtained at very mild conditions of temperature.

References and Notes

1. C.W.Rees and R.C.Storr, J.Chem.Soc.(C), 760 (1969); R.W.Hoffmann, G.Guhn, M. Preiss and B.Dittrich, J.Chem.Soc.(C), 769 (1969).

2. C.W.Rees and R.C.Storr, J.Chem.Soc.(C), 756 (1969).

3. R.Hoffmann, A.Imamura and W.J.Hehre, J.Am.Chem.Soc., 90, 1499 (1968).

4. J.Nakayama, S.Dan and M.Hoshino, J.C.S.Perkin Trans.I, 413 (1981).

5. G.De Luca, G.Renzi, R.Cipollini and A.Pizzabiocca, Gazz.Chim.Ital., 107, 357 (1977); ibidem , J.C.S.Perkin Trans.I, 2022 (1977).

6. J.Meinwald and S.Knapp, J.Am.Chem.Soc., 96, 6532 (1974).

7. J.H.Uhlenbroek, Rec.Trav.Chim.Pays Bas, 80, 1060 (1961). Peracetic acid oxidation of 1-naphthyl-phenyl-sulphide(6) yields 1-naphthyl-phenyl-sulphone m.p. 99°C.

8. W.Davies, Q.N.Porter and J.R.Wilmshurst, J.Chem.Soc., 3366 (1957). Peracetic acid oxidation of benzo[kl]thioxantene(5) yields benzo[kl]thioxantene dioxide m.p. 196°C.

9. G.l.c. analysis (Hewlett-Packard 5730A - FID unit) are carried out on a 2m x 1/8in column packed with Silicone gum rubber E 301 (2,5%) on Chromosorb G AW-DMCS (80-100 mesh); column temperature 100-220°C at 4°C min^{-1}; 30 minute post hold; carrier gas N_2, 20 ml min^{-1}.

10. G.De Luca, G.Renzi, R.Cipollini and A.Pizzabiocca, Chem.Ind.(London), 661 (1977).

11. D.C.De Jongh and G.N.Evenson, J.Org.Chem., 37, 2152 (1972).

12. J.L.Kice in 'Free Radicals', vol.II, J.K.Kochi Ed., Wiley;New York, (1973), Chapter 24, p. 719.

(Received in UK 26 November 1982)