Tetrahedron Letters No. 37, pp. 3483 - 3484, 1971. Pergamon Press. Printed in Great Britain.

REACTIONS OF 2-LITHIO-1,3-DITHIANES WITH AROMATIC SUBSTRATES

W. H. Baarschers and T. L. Loh

Department of Chemistry, Lakehead University, Thunder Bay, Ontario

(Received in USA 28 June 1971; received in UK for publication 16 August 1 71)

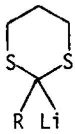
The lithium derivatives (I) of 1,3-dithianes, which have established their value as nucleophilic acylating agents, react with a variety of alkyl halides and carbonyl compounds. In addition to the original reports1), an increasing number of papers describes the application of these reactions to synthetic problems, and the topic has recently been reviewed2). We had occasion to study the reactions of (I) with some aromatic substrates which so far have received little or no attention.

The compound (I,R=C_6H_5), generated from the 1,3-dithiane derivative of benzaldehyde was allowed to react with 2,4-dinitrobromobenzene (at -20° for 2 hr, then at 0° for 1 hr) in tetrahydrofuran. The product was a white crystalline solid, $C_{20}H_{22}S_4$, m.p. 204°, obtained in nearly quantitative yield, to which structure (II) was assigned on spectral evidence (n.m.r., m.s.) and analytical results. Desulfurization with hydrazine3) yielded a homogeneous (t.l.c.) oil, identical in all respects with commercial bibenzyl. Mononitrohalobenzenes as well as nitrobenzene were also found to be sufficiently strong oxidizing agents to lead to this kind of oxidative dimerization. It is interesting to note that this dimerization reaction1a) was not observed in the reactions of various compounds with structure (I) with substituted ω-nitrostyrenes, which were reported4) to lead to 1,4-addition.

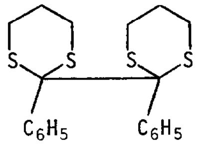
The lithium compound (I,R=C_6H_5) did, however, react with 2-bromopyridine to give (III), which had spectral properties in accordance with its expected structure, in approx. 50% yield. Purification of (III) by column chromatography, followed by treatment with silver nitrate and N-chlorosuccinimide in acetonitrile5) gave phenyl 2-pyridyl ketone, identical in all respects with a sample prepared by permanganate oxidation of 2-benzyl pyridine6).

Under the same conditions 2-bromopyridine did not react with the lithium compound (I,R=CH_3). As expected, 3- and 4-bromopyridine did not react with either (I,R=CH_3) or (I,R=C_6H_5), since these compounds are unlikely to be strong enough bases to lead to the benzyne type intermediate through which substitution of 3- and 4-halopyridines frequently takes place[7].

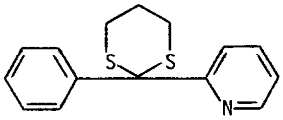
The successful coupling of 2-halopyridines with certain lithium compounds of type (I), although of limited scope, may be useful in synthetic procedures where acid sensitive groups prevent the formation of the aryl pyridyl ketone moiety by means of the usual Friedel-Craft process[8].



(I)



(II)



(III)

Acknowledgement: The authors wish to thank the National Research Council, Ottawa, Ont., for financial support.

References

1. a) E.J. Corey and D. Seebach, *Angew. Chem. Int. Eng. Ed.*, *4*, 1075 (1965), b) *ibid.*, *4*, 1077 (1965), c) D. Seebach, *ibid.*, *8*, 639 (1969).
2. D. Seebach, *Synthesis*, *1*, 17 (1969).
3. V. Georgian, R. Harrison and N. Gubish, *J. Am. Chem. Soc.*, *81*, 5834 (1959).
4. D. Seebach and H.F. Leitz, *Angew. Chem. Int. Eng. Ed.*, *8*, 983 (1969).
5. E.J. Corey and D. Crouse, *J. Org. Chem.*, *33*, 298 (1968).
6. E.H. Hintress and H.S. Walker, *J. Am. Chem. Soc.*, *70*, 3072 (1948).
7. L.A. Paquette, *"Principles of Modern Heterocyclic Chemistry"*, Benjamin, Inc., New York 1968, p. 242.
8. F.J. Villani and M.S. King, in *"Org. Synth. Coll. Vol. III"*, John Wiley & Sons, Inc., New York 1957, p.88.