Tetrahedron Letters No. 6, pp. 30-34, 1960. Pergamon Press Ltd. Printed in Great Britain.

SYNTHESIS OF CONDENSED THIOPHENES, DIARYLS AND DIALKYLS THROUGH ARYLLITHIUM AND ALKYLLITHIUM DERIVATIVES

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(Received 15 February 1960)

A FEW condensed thiophenes have been synthesised by the cyclization of diaryl sulphides by the action of arylsodium and/or aryllithium derivatives,[1,2] and by the action of sodamide on diaryl sulphoxides.[3,4] In view of the formation of diphenyl sulphone-2:2'-dilithium[5,6] (II) from diphenyl sulphone (I), and the synthesis of 2:2'-and 3:3'-dithionaphthenyls by the action of anhydrous cupric chloride on the corresponding Grignard reagents achieved earlier by us,[7] the cyclization of (I) by interaction of its dilithium

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derivative (II) with cupric chloride was investigated. It is of interest to record that dibenzothiophene (III) (20%) was formed along with the expected dibenzothiophene-5:5-dioxide (IV) (50%) (separation by chromatography over alumina using benzene as eluent). In later experiments, the mixture itself was reduced by treatment with lithium aluminium hydride, when (III) was obtained.

The above method which represents a new synthesis of condensed thiophenes from diaryl sulphones may prove to be of general interest for the preparation of other condensed thiophenes from diaryl sulphones. Thus the lithium derivative of 2:2'-dinaphthyl sulphone (V),[8] on treatment with anhydrous cupric chloride, gave a product which on treatment with lithium aluminium hydride gave dinaphtho-(2:1-b,1':2'-d)-thiophene (VI).

Conversion of diphenyl sulphoxide and diphenyl sulphide to (III) by the procedure was unsuccessful. In the case of diphenyl sulphoxide, interaction of butyllithium followed by treatment with anhydrous cupric chloride gave diphenyl sulphide. When diphenyl sulphide was treated with butyllithium or phenyllithium and then with cupric chloride, it remained unreacted.

When phenyllithium was treated with cupric chloride, diphenyl was obtained in nearly quantitative yield. Although a few diaryls and dialkyls have been prepared earlier by the interaction of the corresponding magnesium Grignard reagents with metal halides,[9-12] this method does not appear to have

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TABLE 1

Synthesis of Condensed Thiophenes, Diaryls and Dialkyls through Aryllithium and Alkyllithium Derivatives

Starting material	Reaction products, molecular formula, % yields.	m.p. or b.p.	Isolation and purification of reaction products	Analysis %						Refs.
				Found			Required			
				C	H	S	C	H	S	
I	III, $C_{12}H_8S$ (70%)	m.p. 99°	Reduction with $LiAlH_4$, chromatography, distillation, crystallization; compared with an authentic sample.	78.2	4.3	17.2	78.3	4.4	17.4	5
V	VI, $C_{20}H_{12}S$ (50%)	m.p. 208-9°	Reduction with $LiAlH_4$, chromatography, crystallisation, compared with an authentic sample.							8,13,14.
PhBr	Diphenyl, $C_{12}H_{10}$ (100%)	m.p. 70-1° b.p. 95-130° (bath temp)/ 6 mm	Distillation, crystallization.							15
α-Bromonaphthalene	1:1'-Dinaphthyl, $C_{20}H_{14}$ (18%)	m.p. 160-1°	Chromatography, distillation, crystallization.	94.2	5.7		94.5	5.5		16
	Naphthalene, $C_{10}H_8$ (31%)	m.p. 81°	Chromatography, distillation, crystallization.							
	Perylene, $C_{20}H_{12}$ (9%)	m.p. 275-7°	Chromatography, distillation, sublimation & crystallization.	95.5	4.4		95.2	4.8		17

Thionaphthene	2:2'-Dithionaphthenyl, $C_{16}H_{10}S_2$ (52%)					7
3-Iodothionaphthene	3:3'-Dithionaphthenyl, $C_{16}H_{10}S_2$ (11%)					7
n-C_4H_9 Br	n-Octane, C_8H_{18} (22%)	b.p.121-3° (bath temp)	Fractional distillation.	83.6 15.1	84.2 15.8	18
n-$C_{12}H_{25}Cl$	Tetracosane, $C_{24}H_{50}$ (33%)	m.p.53-4°	Fractional distillation, crystallization.	84.8 14.8	85.2 14.8	19
n-$C_{18}H_{37}Cl$	Hexatriacontane, $C_{36}H_{74}$ (32%)	m.p.76° b.p.220-35° (bath temp)/ 0.-005 mm	Fractional distillation, crystallization.	85.9 14.2	85.4 14.6	
	Octadecane, $C_{18}H_{38}$ (32%)	b.p.89-91° (bath temp)/ 0.005 mm	Fractional distillation.	85.4 14.6	85.1 15.0	
	Octadecylalcohol, $C_{18}H_{37}OH$ (36%)	m.p.58.5-59.5° b.p.115-123° (bath temp)/ 0.005 mm	Fractional distillation, crystallization.	80.2 14.2	80.0 14.1	

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been sufficiently exploited for the synthesis of these compounds. Symmetrical diaryls and dialkyls have now been synthesised by the interaction of aryllithium and alkyllithium derivatives with anhydrous cupric chloride and the results are summarised in Table 1, which also includes analytical data. Where the figures of analysis are not quoted, the products were identified by comparison with authentic specimens. The table also includes 2:2'- and 3:3'-dithionaphthenyls as examples of the present synthesis.

When octadecyl chloride was treated with lithium alone the yield of hexatriacontane was lower (7%) than when the lithium derivative was treated with cupric chloride when the hydrocarbon was obtained in 32% yield. By-products which often accompany diaryls and dialkyls consist of the corresponding hydrocarbons and in the case of dialkyls, the corresponding alcohols are also formed in some cases.

Application of this method for the synthesis of other compounds of the above and other types will form the subject of further communications. It is hoped that a full account of the work will be published shortly in Tetrahedron.

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