REACTIONS OF α-CHLOROETHERS IN PRESENCE OF ZINC. X†. DITHIENYL- AND DIFURYLALKANE DERIVATIVES

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Reaction of α-chloroethers with zinc in the presence of thiophene and furan derivatives gives the corresponding diheterylalkanes.

α-Chloroethers react vigorously with metals, especially zinc [2]. The present paper gives the results of an investigation of this reaction in the presence of furan and thiophene derivatives. The corresponding dithienyl- and difurylalkanes were obtained (Tables 1 and 2).

The yields of the products reached 30-60% (60-70% based on the furan or thiophene reacted). Halothiophenes gave somewhat poorer yields. In this case, the halogen deactivated the thiophene ring, as has also been observed in the case of benzene derivatives. For example, bromobenzene fails altogether to react under these conditions.

The mechanism of the reaction, which is of the free radical type, has been described in detail [3].

The method described differs from those already known for the preparation of diheterylalkanes [4,5].

EXPERIMENTAL

General Method. 0.2 mole of the thiophene of furan and 0.05 g-atom of zinc in the form of fine turnings were placed in a flask fitted with a stirrer, reflux condenser, and dropping funnel. The α-chloroether (0.1 mole) was then added with ice-water cooling. When all the α-chloroether had been added, water was introduced to hydrolyze unreacted ether, followed by diethyl ether. The ether layer was separated, washed with water, and dried over anhydrous magnesium sulfate. After removal of the solvent, the product was distilled in vacuo, or recrystallized from alcohol, if crystalline.

All the furans containing ester groups were hydrolyzed with 10% alcoholic KOH. The two acids obtained were: di-(5-carboxy-2-furyl)methane, mp 238° [6], and 1, 1-di-(5-carboxy-2-furyl)ethane, mp 214° [6].

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† For Part IX, see [1].

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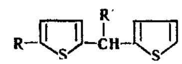
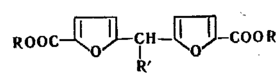
TABLE 1



R	R′	Bp, °C (press, mm)	n_D^{20}	d_4^{20}	Molecular formula	Found		Calculated		Yield, %
						MR_D	S, %	MR_D	S, %	
H	i-C_3H_7	135—138 (7)	1,5690	1,1176	$C_{12}H_{14}S_2$	65,17	28,65	65,86	28,87	36
Cl	i-C_3H_7	140—142 (5)	1,5789	1,2738	$C_{12}H_{12}Cl_2S_2$	76,19	22,17	75,59	22,01	16
Br	i-C_3H_7	m.p. 54°			$C_{12}H_{12}Br_2S_2$		16,66		16,75	30
CH_3	i-C_3H_7	m.p. 45°			$C_{14}H_{18}S_2$		25,64		25,60	46
C_2H_5	i-C_3H_7	160—162 (5)	1,5506	1,0520	$C_{16}H_{22}S_2$	84,31	22,83	84,34	23,04	50
n-C_3H_7	i-C_3H_7	170—175 (5)	1,5435	1,0368	$C_{18}H_{26}S_2$	93,18	20,93	93,57	20,90	50
H	n-C_3H_7	128—130 (4)	1,5702	1,1090	$C_{12}H_{14}S_2$	65,76	29,09	65,86	28,87	30
C_2H_5	n-C_3H_7	162—164 (4)	1,5488	1,0572	$C_{16}H_{22}S_2$	83,70	23,29	84,34	23,07	61
Br	n-C_3H_7	160—164 (5)	1,5781		$C_{12}H_{12}Br_2S_2$		16,86		16,78	34

TABLE 2



R	R′	Bp, °C (press, mm)	n_D^{20}	d_4^{20}	Molecular formula	Found			Calculated			Yield, %
						MR_D	C, %	H, %	MR_D	C, %	H, %	
CH_3	H	m.p. 121° [7]			$C_{13}H_{12}O_6$		58,64	4,88		59,12	4,54	64
C_2H_5	H	m.p. 40° [6]			$C_{15}H_{16}O_6$		61,13	5,60		61,64	5,52	45
n-C_3H_7	H	225—230 (7)	1,5215	1,1930	$C_{17}H_{20}O_6$	81,72	63,42	6,64	81,03	63,75	6,25	30
n-C_4H_9	H	225—227 (5)	1,5085	1,1320	$C_{19}H_{24}O_6$	91,64	65,21	6,97	90,26	65,51	6,89	30
CH_3	CH_3	Т. пл. 83° [8]			$C_{14}H_{14}O_6$		60,37	5,27		60,43	5,03	35
C_2H_5	CH_3	210—212 (5) [6]	1,5251	1,2070	$C_{16}H_{18}O_6$	77,46	62,26	5,95	76,41	62,77	5,87	30
n-C_3H_7	CH_3	215—217 (5)	1,5163	1,1520	$C_{18}H_{22}O_6$	87,17	64,13	6,76	85,65	64,67	6,58	50