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ORGANODIMAGNESIUM DERIVATIVES OF THIOPHENE.

3.* SYNTHESIS OF AN ORGANODIMAGNESIUM DERIVATIVE OF HEXABROMO-2,2'-DITHIENYL AND ITS REACTION WITH OXALIC ACID ESTERS

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It was established that the reaction of hexabromo-2,2'-dithienyl with magnesium in the presence of ethyl bromide gives an organodimagnesium derivative, which reacts with oxalic acid esters to give 3,3',4,4'-tetrabromo-5,5'-dithienyl-diglyoxalic acid esters. Reduction of the latter with ethylmagnesium bromide leads to 3,3',4,4'-tetrabromo-5,5'-dithienyl-2,2'-diglycolic acid esters.

In contrast to monomagnesium derivatives, organodimagnesium compounds are substances to which little study has been devoted both in a theoretical respect and with respect to their practical application; this is reflected in the amount of published data pertaining to these classes of compounds [2]. The formation of an organodimagnesium derivative of thiophene was established for the first time by Thomas [3] and was subsequently confirmed by others [4, 5]. After this, these compounds did not attract the attention of researchers for a long time, although the possibility of the simultaneous introduction of two functional groups in the thiophene ring by means of organodimagnesium compounds is of doubtless interest, as confirmed by research on dilithium compounds [6].

It was subsequently shown that 2,5-diiodothiophene [7] and 3,4-dibromo- and 3-bromo-2,5-diiodothiophenes in the presence of ethyl bromide smoothly form organodimagnesium compounds [8]. An organodimagnesium derivative was also obtained under the same conditions in the 2,2'-dithienyl series from 5,5'-dibromo-2,2'-dithienyl [1].

In a continuation of these studied we investigated the possibility of the preparation of an organodimagnesium derivative from hexabromo-2,2'-dithienyl (I) and its reaction with oxalic acid esters (II).

As in the case of 5,5'-dibromo-2,2'-dithienyl, attempts to obtain an organodimagnesium derivative (III) of hexabromo-2,2'-dithienyl by direct reaction between the components or "accompanied" by 1,2-dibromoethane (at a molar ratio of I to dibromoethane of 1:8) in ether

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*See [1] for Communication 2.

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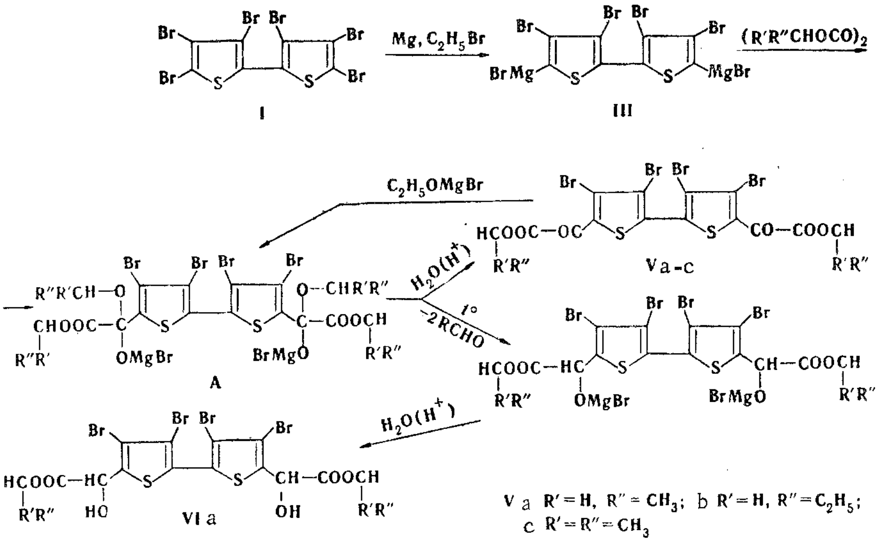
or tetrahydrofuran (THF) were unsuccessful. We were able to obtain III only with the "accompaniment" of ethyl bromide (IV) at a ratio of I to IV of 1:4.

Hence it may be assumed that the reaction between magnesium and I in the presence of accompanying agent IV proceeds via the Yurion exchange mechanism [2]. However, our attempt to obtain III by an exchange reaction between ethylmagnesium bromide and I at a ratio of 10:1 in absolute THF showed that the contribution of the exchange mechanism to the formation of III is extremely small. Despite prolonged heating and removal of IV by distillation, only 1% 3,3',4,4'-tetrabromo-2,2'-dithienyl was isolated after hydrolysis. The action of IV in this case evidently reduces to dissolving III in the resulting ethylmagnesium bromide to give etherates of the $xC_2H_5Br \cdot yR(MgBr)_2 \cdot zTHF$ type.

The reaction of III with esters II in ether gives carbinolate A, which upon hydrolysis gives 3,3',4,4'-tetrabromo-5,5'-dithienyl-2,2'-diglyoxalic acid esters (Va-c), whereas when carbinolate A is heated in toluene for 6 h, it undergoes decomposition with the liberation of two molecules of aldehyde and, after hydrolysis, gives 3,3',4,4'-tetrabromo-5,5'-dithienyl-2,2'-diglycolic acid esters (VIa). A higher yield of ester VIa can be obtained in the case of formation of carbinolate A from ester Va and ethylmagnesium bromide.



V a R'=H, R"=CH₃; b R'=H, R"=C₂H₅; c R'=R"=CH₃

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with an IKS-22 spectrometer. The PMR spectra of solutions of the compounds in deuteroacetone were recorced with a Tesla BS-467C spectrometer with hexamethyldisiloxane as the internal standard.

Hexabromo-2,2'-dithienyl (I). A solution of 10 g (0.06 mole) of 2,2'-dithienyl in 100 ml of dioxane was added dropwise with stirring in the course of 10 min to a solution of dioxane dibromide obtained from 22.4 g (0.14 mole) of bromine and 150 ml of dioxane. The flask was heated carefully until vigorous hydrogen bromide evolution commenced, after which heating was discontinued. Heating and subsequent cooling were repeated five to six times, after which the solution was refluxed until a straw-yellow coloration developed. Cooling of the solution precipitated 30 g (75%) of colorless acicular crystals of I with mp 257-258°C, in agreement with the data in [9].

An additional amount of I was obtained by evaporation of the mother liquor *in vacuo* and treatment of the residue with liquid bromine.

3,3',4,4'-Tetrabromo-5,5'-dithienyl-2,2'-diglyoxalic Acid Esters (Va-c). Two to three drops of ethyl bromide were added to a mixture of 1.2 g (0.05 mole) of magnesium and 75 ml of ether. After the reaction had begun, 3.2 g (0.005 mole) of I was added to the flask, and a solution of 3 ml (0.04 mole) of IV in 25 ml of ether was added dropwise at such a rate that the solution boiled evenly. To complete the reaction, the flask was heated on a water bath for 1-2 h (the yield of III was 80-85% and was determined by hydrolysis of III to 3,3',4,4'-tetrabromo-2,2'-dithienyl). The reaction mass was transferred to a dropping funnel and was added dropwise with stirring to a solution of 0.1 mole of ester II in 100 ml of ether, and the mixture was stirred for 2 h and allowed to stand overnight. It was then de-

TABLE 1. Characteristics of Va-c

Compound	R′	R″	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
				C	Br	S		C	Br	S	
Acid V	—	—	dec. 180	23,1	51,2	10,4	$C_{12}H_2Br_4O_6S_2$	23,0	51,1	10,2	—
Va	H	CH_3	199—200	28,2	47,0	9,5	$C_{16}H_{10}Br_4O_6S_2$	28,1	46,8	9,4	33
Vb	H	C_2H_5	156—158	30,3	45,0	9,2	$C_{18}H_{14}Br_4O_6S_2$	30,4	45,1	9,0	28
Vc	CH_3	CH_3	179—180	30,4	45,2	9,2	$C_{18}H_{14}Br_4O_6S_2$	30,4	45,1	9,0	30

composed with water and 10% hydrochloric acid. The ether layer was washed with water, sodium sulfate. The ether was removed by distillation, excess ester II and the products of its reaction with ethylmagnesium bromide were removed *in vacuo* (5 mm), and the residue was recrystallized from alcohol to give esters Va-c. Acid V was obtained by hydrolytic cleavage with a 5% alcohol solution of KOH. The constants and yields of the synthesized substances are presented in Table 1. Intense absorption bands of ketone and ester carbonyl groups at 1680 and 1730 cm^{-1} are observed in the IR spectra of esters Va-c. PMR spectra: Va, 1.30 (t, 3H, CH_2CH_3); 4.30 (q, 2H, OCH_2CH_3) , Vb, 1.29 (t, 3H, CH_2CH_3), 1.88 (m, 2H, $CH_2CH_2CH_3$) , 4.30 (t, 2H, OCH_2CH_2) , Vc, 1.35 [d, 6H $(CH_3)_2CH$] , 5.02 ppm [m, 1H, $OCH(CH_3)_2$].

Diethyl 3,3',4,4'-Tetrabromo-5,5'-dithienyl-2,2'-diglycolate (VIa). A 1-ml sample of ethyl bromide was added to 0.24 g (0.01 mole) of magnesium in absolute ether, and 1 ml of absolute ethanol was added after the initial reaction was complete. A 0.68-g (0.001 mole) sample of ester Va and 50 ml of absolute toluene were added to the solution of ethylmagnesium bromide, the diethyl ether was removed by distillation, and the residue was refluxed for 6 h. It was then decomposed with water and 10% hydrochloric acid and extracted with ether (two 50-ml portions). After the usual workup, the ether was removed by distillation, the toluene was removed *in vacuo*, and the residue was recrystallized from alcohol to give a product with mp 176-178°C in 70% yield. The IR spectrum did not contain a band of a ketone carbonyl group (1680 cm^{-1}) but did contain intense bands at 1740 (ester carbonyl) and 3500 cm^{-1} (OH stretching vibrations). PMR spectrum: 1.12 (t, 3H, CH_2CH_3) , 4.12 (q, 2H, OCH_2CH_3) , and 5.5 ppm (s, 1H, CHCO). Found: C 27.3; Br 47.0; S 9.5%. $C_{16}H_{14}Br_4O_6S_2$. Calculated: C 28.0; Br 46.6; S 9.4%.

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