SYNTHESIS OF DICARBOXYLIC ACIDS AND DIESTERS OF THE DIFURYLMETHANE SERIES

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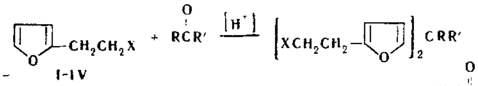
The condensation with saturated aliphatic carbonyl compounds of furan acids and esters having a functional group not conjugated with the furan nucleus has been carried out. Symmetrical bifunctional derivatives of the difurylmethane series have been synthesized.

The reaction of furan or its alkyl derivatives with aliphatic aldehydes or ketones in the presence of catalytic amounts of mineral acid is a convenient method for the synthesis of compounds containing two furan nuclei in the molecule [1, 2]. In the condensation of furan nuclei with the carbonyl group of an aliphatic compound, only the α-hydrogen atoms of the furan nuclei are involved [3, 4]. As a rule, an electron-donating substituent in the furan ring favors and an electron-accepting substituent inhibits this reaction [4–6]. When the weakly electron-accepting alkoxycarbonyl group is present in the furan nucleus, its condensation with the carbonyl group of an aliphatic aldehyde takes place only under severe conditions with large amounts of mineral acid [5, 6]. The diesters of the difurylmethane series obtained in this way, and also the products of their hydrogenation, are of interest as starting materials for the production of polyamide fibers, plasticizers for poly(vinyl chloride)s and for other purposes [7].

In the present investigation it was found that furan acids and esters in which the electron-accepting groups are not conjugated with the furan nucleus react even in the presence of a catalytic amount of sulfuric acid both with aliphatic aldehydes and with ketones, forming the corresponding dicarboxylic acids and diesters with a yield of 50–60%.



I-IV

I $X = COOH$; II $X = COOCH_3$; III $X = COOC_2H_5$; IV $X = CH_2O\overset{O}{\overset{\|}{C}}CH_3$

$R, R' = H, H$; H, CH_3; CH_3, CH_3

If the nuclei are separated by a methylene group, they can be hydrogenated on a Raney nickel catalyst to compounds of the tetrahydrofuran series even at a temperature of 100–110° C. If R and R' are alkyls, more severe conditions are necessary for the hydrogenation of the furan nuclei.

EXPERIMENTAL

1,1-Bis[2'-(β-ethoxycarbonylethyl)-5'-furyl]ethane. With stirring, 11 g (0.25 mole) of acetaldehyde was added over 1 hour to 16 g (0.095 mole) of III, 0.1 g of hydroquinone, and 0.07 ml of 50% sulfuric acid. The reaction mixture was stirred for another 2 hr at 25° C and was then treated with water; the aqueous layer was extracted with ether and the ethereal extracts were neutralized with $NaHCO_3$ solution, washed with water, and distilled. Yield 10.5 g (61%). Bp 182–183° C (3 mm); n_D^{20} 1.4905; d_4^{20} 1.1073. Found, %: C 65.82, 65.65; H 7.43, 7.20; MR_D 94.71. Calculated for $C_{20}H_{26}O_6$, %: C 66.27; H 7.23; MR_D 94.83.

1,1-Bis[2'-(β-methoxycarbonylethyl)-5'-furyl]ethane. This was obtained similarly from 113 g (0.73 mole) of II and 46 g (1.05 mole) of acetaldehyde in the presence of 0.2 g of hydroquinone and 0.7 ml of 50% sulfuric acid. Yield 74 g (60%). Bp 170–171° C (2 mm); n_D^{20} 1.4988; d_4^{20} 1.1486. Found, %: C 64.34, 64.25; H 6.65, 6.71; MR_D 85.44 g. Calculated for $C_{18}H_{22}O_6$, %: C 64.65; H 6.63; MR_D 85.65.

2,2-Bis[2'-β-methoxycarbonylethyl)-5'-furyl]propane. A mixture of 25 g (0.16 mole) of II, 0.2 g of hydroquinone, 0.4 ml of 50% sulfuric acid, and 22 g (0.38 mole) of acetone was stirred for 3 hr at 65° C. After the usual working up, 17 g (60%) of reaction product was obtained. Bp 170–172° C (3 mm); n_D^{20} 1.4964; d_4^{20} 1.1293. Found, %: C 66.32, 66.39; H 7.05, 7.12; MR_D 90.17. Calculated for $C_{16}H_{24}O_6$, %: C 65.49; H 6.94; MR_D 90.12.

2,2-Bis[2'-(β-ethoxycarbonylethyl)-5'-furyl]propane. With stirring, 20 g (0.34 mole) of acetone was added to 25 g (0.15 mole) of III, 0.1 g of hydroquinone, and 0.4 ml of 50% sulfuric acid. After the working-up procedure described above, 16.7 g (60%) of reaction product was obtained. Bp 171–172° C (2 mm); n_D^{20} 1.4893; d_4^{20} 1.0953. Found, %: C 66.40, 66.41; H 7.37, 7.31; MR_D 99.23, Calculated for $C_{21}H_{28}O_6$, %: C 67.00; H 7.49; MR_D 99.50.

Bis[2'-(β-methoxycarbonylethyl)-5'-furyl]methane. To 143 g (0.93 mole) of II, 0.2 g of hydroquinone, and 2 ml of 50% sulfuric acid was added 45 g (0.6 mole) of a 40% formalin solution. After stirring at 50° C for 3 hr and the usual working-up procedure, 63.5 g (42%) of product was obtained. Bp 175–176° C (4 mm); mp 36.5–37° C. Found, %: C 63.71, 63.83; H 6.25, 6.28. Calculated for $C_{17}H_{20}O_6$, %: C 63.73; H 6.29.

1,1-Bis[2'-(β-carboxyethyl)-5'-furyl]ethane. With stirring, 11 g (0.25 mole) of acetaldehyde was added over an hour to 21 g (0.15 mole) of I, 20 ml of CH_3COOH and 0.2 ml of 50% sulfuric acid. After being stirred for 2 hr at a temperature not exceeding 30° C, the reaction mixture was poured into water. The precipitate that deposited was twice recrystallized from water, giving 11.5 g (50%) of a product with mp 127.5–128° C. The same acid was obtained in quantitative yield by the saponification with 20% aqueous alcoholic alkali of 1,1-bis[2'-carboxyethyl)-5'-furyl]ethane or 1,1-bis[2'-(β-methoxycarbonylethyl)-5'-furyl]ethane. Found, %: C 62.41, 62.62; H 5.93, 5.83; acid number 296. Calculated for $C_{16}H_{18}O_6$, %: C 62.73; H 5.92; acid number 295.

1,1-Bis[3'-(γ-acetoxypropyl)-5'-furyl]ethane. With stirring, 22 g (0.5 mole) of acetaldehyde was added to 67 g (0.4 mole) of IV, 0.15 ml of 50% sulfuric acid, and 0.1 g of hydroquinone. After the usual working up, 43 g (60%) of product was obtained with bp 196° C (3 mm); n_D^{20} 1.4938; d_4^{20} 1.1076. Found, %: C 66.00, 66.02; H 7.25, 7.29; MR_D 95.05. Calculated for $C_{20}H_{26}O_6$, %: C 66.27; H 7.23%; MR_D 94.89.

Bis[2'-(β-carboxyethyl)-5'-furyl]methane was obtained by saponifying bis[2'-(β-methoxycarbonylethyl)-5'-furyl]methane with 8% NaOH solution. Mp 141°–141.5° C. Found, %: C 61.71, 61.69; H 5.48, 5.47; acid number 270, 282. Calculated for $C_{15}H_{16}O_6$, %: C 61.63; H 5.52; acid number 276.

2,2-Bis[2'-(β-carboxyethyl)-5'-furyl]propane was obtained by saponifying 2,2-bis[2'-(β-methoxycarbonylethyl)-5'-furyl]propane with 9% NaOH solution. Mp 117.5–118° C. Found, %: C 63.52, 63.89; H 6.38, 6.28; acid number 250, 260. Calculated for $C_{17}H_{20}O_6$; acid number 252.

Bis[2'-(methoxycarbonylethyl)-5'-tetrahydrofuryl]methane was obtained by the hydrogenation of bis[2'-(β-methoxycarbonylethyl)-5'-furyl]methane over Raney nickel at 100–110° C and an initial pressure of hydrogen of 200 atm with a yield of 70%. Bp 164–165° C (3 mm); n_D^{20} 1.4737; d_4^{20} 1.1119. Found, %: C 62.06, 62.30; H 8.48, 8.23; MR_D 82.95. Calculated for $C_{17}H_{28}O_6$, %: C 62.17; H 8.59%; MR_D 82.90.

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NITROGEN-CONTAINING ORGANOSILICON COMPOUNDS

XIV. N-Morpholyl-, N-Thiamorpholyl-, N-Methylpiperazinyl-, and N-Perhydroazepinylalkylsilanes*

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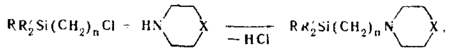
By the reaction of trialkylsilanes and dialkoxy- or di(chloroalkyl)alkylsilanes with morpholine, thiamorpholine, N-methylpiperazine, and hexamethyleneimine, 14 new organosilicon derivatives of these heterocycles have been synthesized. The addition of perhydroazepine to diethylmethylvinylsilane has been performed.

The usual method for obtaining morpholylsilanes [2] and piperazinylsilanes [3–7] containing the Si—N bond is the reaction of organylchlorosilanes with morpholine and piperazine, respectively. Their triphenylsilyl derivatives have been obtained by the reaction of the heterocycles mentioned with triphenylsilyl-lithium [8].

N-Piperazinylsilanes are also formed by the transamination of piperazine with alkylaminosilanes [9], dehydrocondensation with triorganylsilanes in the presence of potassium [10], and the thermal rearrangement of N-aziridinylsilanes [11]. N-Morpholinylmethylsilanes have been synthesized by the reaction of triorganylchloromethylsilanes with morpholine [12]. N-Piperazinylalkylsilanes containing the $Si—C_n—N$ grouping have been obtained by the addition of piperazine to trialkylvinylsilanes in the presence of alkali metals [13] and also by the thermal rearrangement of aziridinylalkylsilanes [13, 14]. Triphenoxy-N-perhydroazepinylsilane is formed by the reaction of chlorotriphenoxysilane with hexamethylenediamine. Di-n-butoxy(methyl)-(N-perhydroazepinylmethyl)silane has been obtained by the reaction of hexamethyleneimine with di-n-butoxy-(chloromethyl)methylsilane [16]. Organosilicon derivatives of thiamorpholine were not previously known.

By heating trialkylsilanes, dialkoxyalkyl- and di(chloromethyl)alkylsilanes, and (3-chloropropyl)silanes with morpholine, thiamorpholine, N-methylpiperazine, and hexamethyleneimine (perhydroazepine) in toluene in the presence of triethylamine for 15–20 hr, we have obtained the corresponding alkyl-N-heterylsilanes with yields of 40–60%:



$R = CH_3, C_2H_5, C_3H_7, C_2H_5O$; $R' = C_2H_5$, $_3H_7, C_2H_5O, i\text{-}C_4H_9O$;
$X = O, S, NCH_3, CH_2CH_2$; n- 1, 3

By the addition of hexamethyleneimine to diethylmethylvinylsilane in the presence of lithium, we have obtained diethylmethyl(2-N-perhydroazepinylethyl) silane:

$$CH_3(C_2H_5)_2SiCH=CH_2 + H\underline{N(}CH_2)_6 \longrightarrow CH_3(C_2H_5)_2SiCH_2CH_2\underline{N(}CH_2)_5$$

The method of performing the syntheses was similar to that described previously [17]. The physicochemical constants, the analytical data, and the yields of the compounds synthesized are given in the table. A

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*For part XIII, see [1].