SYNTHESIS OF DIVINYL COMPOUNDS OF TYPE OF BIS-(p-VINYLPHENYL)ALKANES

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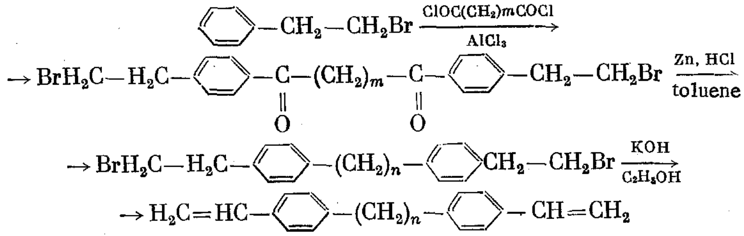
The synethesis of bis-(p-vinylphenyl)alkanes, with n = 1-4, is described in the literature according to the scheme: diphenyl compound (acetylation) → diacetyl compound (reduction) → dicarbinols (dehydration) → divinyl compound [1]. The results on the synthesis of bis-(p-vinylphenyl)alkanes, with n = 6 and 10, are given in the present communication. The synthesis was accomplished by the acylation of β-bromoethylbenzene (BEB) with the diacid chlorides of aliphatic acids and subsequent reduction of the obtained diketones to the halohydrocarbons and their dehydrohalogenation



The acylation of aromatic compounds with the acid chlorides of the higher dicarboxylic acids has been described by a number of authors [2-5]. Information is lacking in the literature regarding the acylation of either β-bromo- or chloroethylbenzene with the acid chlorides of dicarboxylic acids.

The acylation of BEB was run with the dichlorides of either adipic or sebacic acid in the presence of anhydrous $AlCl_3$ in a stream of a dry inert gas. Dichloroethane (DCE) was used as the solvent, in which the complex: $AlCl_3$–acid chloride–diketone is readily soluble. $AlCl_3$ dissolves only partially in DCE. In nitrobenzene, which is usually used for acylation, in which both the $AlCl_3$ and the acyl chloride complexes are readily soluble, a large amount of tarry products is obtained, and the yield of the diketone drops by half. The direction of the reaction is also affected by the order in which the reactants are added. In order to increase the yield of the diketone it is necessary to add the β-bromoethylbenzene to a solution of the acid chloride in DCE, and then to gradually add the $AlCl_3$ at 0°C. A large amount of tarry products is obtained when adipoyl chloride is added to a mixture of $AlCl_3$ and BEB in DCE, which is evidently caused by the formation of the complex with BEB and the progress of polycondensation. The addition of the BEB to a solution of the $AlCl_3$–acid chloride complex in DCE is responsible for a large excess of the adipoyl chloride at the moment of reaction, which facilitates the formation of δ-(1,4-β-bromoethylbenzoyl)valeric acid.

The reaction was studied at various molar ratios of BEB and adipoyl chloride (ranging from 4 to 2), at a temperature ranging from −12 to 0° and a variation in the amount of $AlCl_3$ ranging from 2 to 2.4 mole per mole of adipoyl chloride, with a variation in the reaction time ranging from 2 to 12 h. It was established that the predominant formation of the diketone is observed at a molar ratio of BEB to acid chloride equal to 2.05 : 1, at 0°, in the presence of 2.03 M of $AlCl_3$ per mole of acid chloride, for 5 h. The acid chloride should be freshly distilled and added in a stream of a dry inert gas; the entrance of atmospheric moisture should also be completely excluded during the addition of the acid chloride.

The reduction of the bis-(p-β-bromoethylbenzoyl)alkanes was run by the Martin modification of the Clemmensen method, in a heterogeneous medium using toluene. The maximum concentration of the diketone

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should not exceed 20%. A tendency for the diketone to precipitate from solution is observed at a higher concentration, especially at the start of reaction. On the average, the reaction time is 5 h. With a longer reaction time the yield decreases due to an increase in the amount of tarry substances.

EXPERIMENTAL METHOD

1,4-bis(p-β-Bromoethylbenzoyl)butane. To a solution of 15 ml of adipoyl chloride in 250 ml of dry DCE, in an argon stream, were added 31 ml of BEB, and then gradually 30 g of $AlCl_3$ in such a manner that the temperature of the reaction mixture did not exceed 0°. The reaction mass was stirred at 0° for 5 h and then decomposed with 1 N HCl solution. The dichloroethane layer was separated, and the DCE and unreacted BEB were steam-distilled. The residue was treated with 100 ml of ethanol, then with 10% Na_2CO_3 solution, and recrystallized from isopropanol; yield 33 g (70%), mp 130°. Found: C 55.30; H 5.23; Br 33.37; $>C=O$ 11.43%. $C_{22}H_{24}Br_2O_2$. Calculated: C 55.06; H 5.00; Br 33.34; $>C=O$ 11.67%. Infrared spectrum (KBr, ν, cm^{-1}): 1680 and 1410 ($Ar-CO-$ and $-CH_2-CO-$).

δ-(1,4-β-Bromoethylbenzoyl)valeric Acid. The acidification of the soda solution obtained in working up the synthesis product of 1,4-bis-(p-β-bromoethylbenzoyl)butane gave δ-(1,4-β-bromoethylbenzoyl)valeric acid with mp 95° (from alcohol). Found: C 53.47; H 5.54; Br 25.56%. $C_{14}H_{17}BrO_3$. Calculated: C 53.70; H 5.43; Br 25.55%.

1,8-bis-(p-β-Bromoethylbenzoyl)octane. To a solution of 21.5 ml of sebacoyl chloride in 250 ml of DCE, cooled to −10°, in an argon stream, were added 31 ml of BEB and 30 g of $AlCl_3$. The reaction mass was stirred at −10° for 6 h. After hydrolysis, followed by steam-distillation of the DCE and unreacted BEB, the product was recrystallized from methanol; yield 35 g (60%), mp 93°. Found: C 58.11; H 5.94; Br 29.73; $>C=O$ 10.43%. $C_{26}H_{32}Br_2O_2$. Calculated: C 58.22; H 6.01; Br 29.80; $>C=O$ 10.44%.

θ-(1,4-β-Bromoethylbenzoyl)pelargonic Acid. The mother liquor from the recrystallization of 1,8-bis-(p-bromoethylbenzoyl)octane was diluted with water to give θ-(1,4-β-bromoethylbenzoyl)pelargonic acid, which was recrystallized from 80% ethanol; mp 78°. Found: C 58.43; H 6.82; Br 21.38%. $C_{18}H_{25}BrO_3$. Calculated: C 58.53; H 6.78; Br 21.68%.

1,6-bis-(p-β-Bromoethylphenyl)hexane. Into a flask equipped with a glass-packed column were loaded 70 ml of HCl solution, 100 g of zinc amalgam and 9.6 g of 1,4-bis-(p-β-bromoethylbenzoyl)butane in 50 ml of toluene. The reduction was run at 100° for 5 h. The toluene layer was separated and dried over $CaCl_2$. After distilling off the solvent the residue was recrystallized from 90% ethanol; yield 6 g (66.3%), mp 72°. Found: Br 35.38%. $C_{22}H_{28}Br_2$. Calculated: Br 35.39%.

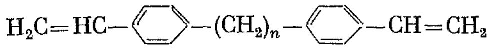
1,10-bis-(p-β-Bromoethylphenyl)decane. The compound was obtained in the same manner as 1,6-bis-(p-β-bromoethylphenyl)hexane, mp 60°. Found: Br 31.33%. $C_{26}H_{36}Br_2$. Calculated: Br 31.44%.

1,6-bis-(p-Vinylphenyl)hexane. A mixture of 9 g of 1,6-bis-(p-β-bromoethylphenyl)hexane and 2.24 g of KOH in 200 ml of ethanol was heated on the water bath for 5 h. The hot solution was decanted from the KBr precipitate and cooled. The filtrate was diluted with 25 ml of water, and the obtained precipitate was filtered and recrystallized from 80% ethanol; yield 3.2 g (64%), mp 52°. Found: C 90.91; H 9.13%. $C_{22}H_{26}$. Calculated: C 91.03; H 8.97%. Infrared spectrum (in KBr, ν, cm^{-1}): 1645, 990, and 910 ($-C=C-$).

1,10-bis-(p-Vinylphenyl)decane. The compound was obtained in the same manner as bis-(p-vinylphenyl)hexane; mp 40°. Found: C 90.00; H 9.98%. $C_{26}H_{34}$. Calculated: C 90.17; H 9.83%.

CONCLUSIONS

Some new divinyl compounds of general formula



where n = 6 and 10, were synthesized by the acylation of β-bromoethylbenzene with the acid chlorides of dibasic aliphatic acids and subsequent reduction of the obtained diketones to the halohydrocarbons, followed by their dehydrohalogenation.

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