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NEW METHOD FOR THE PREPARATION OF 2-(1-ADAMANTYL)THIOPHENE

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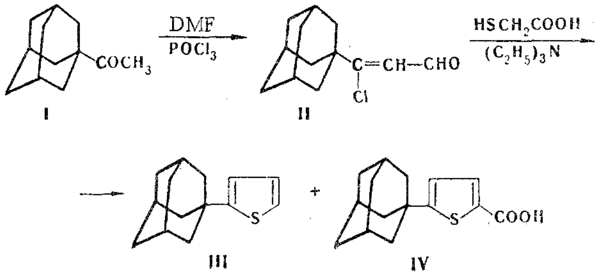
Among the numerous derivatives of adamantane [1] that have been of interest to researchers in the last 20 years owing to their high and diversified biological activity, compounds with a thiophene ring have received rather little study [2, 3]. This is due primarily to the lack of convenient methods for the synthesis of thienyladamantanes. The use of the alkylation of thiophene with bromo-substituted adamantanes in the presence of stannic chloride for this purpose gives a mixture of α- and β-thienyladamantanes in a ratio of 2:1, from which one can isolate individual thienyladamantanes, although additional treatment of the mixture with mercuric chloride and subsequent hydrolysis of the resulting monochloromercuri derivatives are required for this [2].

We have developed a different method for the preparation of individual 2-(1-adamantyl)thiphene (III), which consists in construction of the thiophene ring on the basis of a functionally 1-substituted adamantane and is illustrated by the following scheme:



A 4.4-g sample of thioglycolic acid was added at 20°C to a solution of 7.5 g of β-(1-adamantyl)-β-chlorovinyl aldehyde (II), obtained in 70% yield by Vilsmeier formylation of 1-acetyladamantane (I), in 30 ml of ethanol, after which 8.7 ml of triethylamine was added at 0-10°C, and the mixture was refluxed for 5 h. It was then worked up, the solvent was removed by distillation, and the residue was subjected to flash chromatography [with a 2 by 25 cm column filled with silica gel (40-100 mesh) by elution with CHCl$_3$—heptane (1:1)] to give 2.67 g (34%) of 2-(1-adamantyl)thiophene (III) with mp 61.5-62°C (mp 62-62.5°C [2]). The aqueous layer, after extraction with ether, was acidified with concentrated HCl to give 0.4 g (4.5%) of 2-(1-adamantyl)thiophene-5-carboxylic acid (IV) with mp 267-269°C (dec., from benzene) (mp 266-268°C [3]). The compositions and structures of II-IV were confirmed by the results of elementary analysis and the IR, PMR, and mass spectra.

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