

with Dicarboxylic Acid Imides

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Nitrogen-containing adamantane derivatives exhibit various kinds of biological activity due to lipophilic properties of the adamantane fragment. Studies in the field of synthesis of such compounds are performed with a view to obtain new structures and improve procedures for the preparation of known adamantane derivatives [1, 2].

Known methods for the synthesis of *N*-(1-adamantyl)imides are based on reactions of functionalized adamantane derivatives with cyclic amides, such as phthalimide, succinimide, and maleimide. *N*-Adamantylphthalimide was prepared in 38% yield from 1-adamantan-1-ol and phthalimide in trifluoroacetic acid [3], as well as from adamantan-1-amine and phthalic anhydride in dimethylformamide (yield 45%) [4] or in molten phthalic anhydride (59%) [5]. *N*-Adamantylsuccinimide was synthesized in 33% yield from 1-trimethylsilylpyrrolidine-2,5-dione and 1-chloroadamantane in the presence of TiCl₄ [6]. Thus the known methods for the preparation of *N*-adamantyl imides ensure fairly poor yields of the target products.

A promising starting compound for the synthesis of *N*-adamantyl imides may be 1,3-dehydroadamantane (tetracyclo[$3.3.1.1.^{3,7}.0.^{1,3}$]decane) (I) which is a representative of a class of interesting and unusual compounds, [3.3.1]propellanes containing small rings [7].

1,3-Dehydroadamantane (I) has been widely used for the introduction of an 1-adamantyl substituent into various molecules via addition to O–H, S–H, and other groups with a labile hydrogen atom [8, 9]. However, reactions of I with N–H compounds have been poorly studied. We previously reported [10] on the reaction of I with lactams derived from ω -amino acids and demonstrated prospects in using this compounds in the synthesis of amino derivatives of adamantane.

The present communication reports on the reactions of propellane (I) with dicarboxylic acid imides, namely succinimide and phthalimide. The yields of adducts **IIa** and **IIb** attained 85%. Mixing of a solution of **I** in diethyl ether with phthalimide was accompanied by a weak heat evolution. No adamantylation products at the aromatic ring or α -carbon atom with respect to the carbonyl group were detected, which may be rationalized by higher reactivity of the N–H proton in dicarboxylic acid imides as compared to the corresponding C–H protons.

Compounds **IIa** and **IIb** were purified by recrystallization from propan-2-ol, and their structure was confirmed by ¹H NMR and IR spectra and elemental analyses; the physical constants and spectral parameters of **IIa** and **IIb** were consistent with published data [3–6]. Compounds **IIa** and **IIb** displayed no IR



absorption bands in the region $3200-3500 \text{ cm}^{-1}$, which are typical of NH stretching vibrations in the initial imides.

Thus we have developed a convenient procedure for the preparation of *N*-adamantyl-substituted dicarboxylic acid imides under mild conditions with high yields.

N-(Adamantan-1-yl)succinimide (IIa). A mixture of 5 g (0.051 mol) of succinimide and 2 g (0.015 mol) of 1,3-dehydroadamantane (I) in 20 ml of anhydrous diethyl ether was heated for 3 h at 34–35°C. The solvent was distilled off, excess succinimide was distilled off under reduced pressure, and the residue was subjected to vacuum distillation. Yield 2.82 g (0.012 mol, 81%), bp 169–171°C (3 mm), mp 119–120°C; published data [6]: mp 118–119°C. ¹H NMR spectrum, δ , ppm: 1.60–2.02 m (15H, Ad), 2.49 d (4H, COCH₂CH₂CO). Found, %: C 72.13; H 8.15; N 6.05. C₁₄H₁₉NO₂. Calculated, %: C 72.07; H 8.21; N 6.00.

N-(Adamantan-1-yl)phthalimide (IIb) was synthesized in a similar way from 5 g (0.034 mol) of phthalimide and 2 g (0.015 mol) of I in 20 ml of anhydrous diethyl ether. Yield 3.73 g (0.013 mol, 85%), mp 138–139°C; published data: mp 140°C [4], 138–139°C [3]. ¹H NMR spectrum, δ, ppm: 1.52–2.06 m (15H, Ad), 7.30–7.70 m (4H, C₆H₄). Found, %: C 76.78; H 6.73; N 5.02. C₁₈H₁₉NO₂. Calculated, %: C 76.84; H 6.81; N 4.98.

The ¹H NMR spectra were recorded from solutions in carbon tetrachloride on a Varian Mercury-300 spectrometer operating at 300 MHz; hexamethyldisiloxane was used as internal reference. The IR spectra were measured on a Specord-82 spectrometer (KBr prism) from samples dispersed in mineral oil.

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