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LETTERS TO THE EDITOR

Synthesis of *N*-Adamantoyl-*N*-acylanilines

E. V. Shishkin, V. A. Vasil'ev, and V. E. Shishkin

Volgograd State Technical University, Volgograd, Russia

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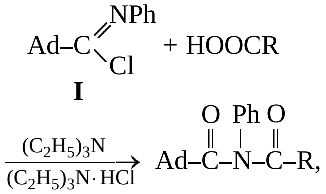
Imidoyl chlorides react with carboxylic acids and their salts, yielding *N*,*N*-diacylamines [1–3]. It is supposed that the reactions involve initial formation of unstable "acylimidates" which fast rearrange into *N*,*N*-diacylamines [4].

Proceeding with our research into adamantyl-containing imidoyl chlorides [5], we have studied utility of the above reaction for preparing new functionally substituted adamantane derivatives. It was found that *N*-phenyl-1-adamantanecarboximidoyl chloride (**I**) reacts both with aromatic and aliphatic carboxylic acids, yielding *N*-adamantoyl-*N*-acylanilines **IIa**–**IIc**.



$$\text{Ad–C}(=\text{NPh})\text{Cl} + \text{HOOCR} \xrightarrow[(C_2H_5)_3N\cdot HCl]{(C_2H_5)_3N} \text{Ad–C(O)–N(Ph)–C(O)–R},$$

I **IIa–IIc**

R = *o*-[$CH_3C(O)O]C_6H_4$ (**a**), C_6H_5 (**b**), CH_3 (**c**).

The reactions were performed in benzene at 20–80°C in the presence of triethylamine as hydrogen chloride acceptor. The triethylamine hydrochloride that formed was separated by hot filtration. Reaction completion was judged about by the amount of the precipitate.

Compound **IIb** was also synthesized by the reaction of 1-adamantanecarboxylic acid with *N*-phenylbenzimidoyl chloride. The results of this synthesis showed that the sizable adamantyl group creates no steric hindrances to the rearrangement of the "acylimidate" into the final structure.

Reactions of imidoyl chloride **I** with carboxylic acid salts give rise to compounds **IIb** and **IIc**.

$$\mathbf{I} + \text{NaOOCR} \longrightarrow \mathbf{IIb}, \mathbf{IIc} + \text{NaCl}.$$

The reactions were performed in diethyl ether under reflux, and the yields of the target products were 90–95%.

Compounds **IIa**–**IIc** are colorless crystals. Their composition and structure were established by their elemental analyses and IR and mass spectra.

N-Phenyl-1-adamantanecarboximidoyl chloride (**I**) was prepared as described in [5].

***N*-(2-Acetoxybenzoyl)-*N*-adamantoylaniline (IIa).** Acetylsalicylic acid, 2.29 g, and 1.5 g of triethylamine were added to a solution of 4.1 g of imidoyl chloride **I** in 15 ml of benzene. The mixture was heated under reflux for 6 h. The triethylamine hydrochloride precipitate was separated by hot filtration, and the precipitate that dropped from the filtrate was recrystallized from benzene. Yield 4.2 g (72%), mp 102–104°C. Mass spectrum, *m/e* (I_{rel}, %): 417 (2) $[M]^+$, 282 (6) $[M - Ph - OCOCH_3]^+$, 238 (2) $[M - OCOPhCOOCH_3]$, 135 (100) $[Ad]^+$, 77 (16) $[Ph]^+$. IR spectrum, ν, cm^{-1}: 1464, 1100, 920, 768 (Ad), 1228, 1266, 1288 (C–N), 1172 (C–O), 1608 (Ar), 1764, 1716, 1676 (C=O). Found, %: C 74.91; H 6.50; N 3.40. $C_{26}H_{27}NO_4$. Calculated, %: C 74.80; H 6.52; N 3.35.

***N*-Adamantoyl-*N*-benzoylaniline (IIb).** *a*. Compound **IIb** was prepared similarly to compound **IIa** from 5.2 g of imidoyl chloride **I**, 2.4 g of benzoic acid, and 1.93 g of triethylamine. Reaction time 1 h, purification was performed by recrystallization from benzene. Yield 6.3 g (92%), mp 132–134°C.

b. 1-Adamantanecarboxylic acid, 4.19 g, and 2.34 g of triethylamine were added to a solution of 5 g of *N*-phenylbenzimidoyl chloride in 23 ml. The mixture was heated under reflux for 2 h. The triethylamine hydrochloride precipitate was separated by hot filtration, and the precipitate that dropped from the filtrate was recrystallized from benzene. Yield 7.6 g (91%), mp 132–134°C.

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c. Sodium benzoate, 2.12 g, was added to a solution of 4 g of imidoyl chloride **I** in 15 ml of diethyl ether. The mixture was heated under reflux for 16 h. The sodium chloride precipitate was separated by hot filtration, and the precipitate that dropped from the filtrate was recrystallized from benzene. Yield 5 g (94%), mp 132–134°C. Mass spectrum, *m/e* (I_{rel}, %): 359 (6) [*M*], 282 (3) $[M - Ph]^+$, 282 (2) $[M - OCPh]^+$, 224 (5) $[M - Ad]^+$, 196 (6) $[M - OCAd]^+$, 163 (7) [*M* – PhCONPh], 135 (100) $[Ad]^+$, 92 (26) $[PhNH]^+$, 77 (59) [Ph]. IR spectrum, ν, cm^{-1}: 1380, 1100, 924, 768 (Ad), 1212, 1252, 1276 (C–N), 1580 (Ar), 1804, 1740 (C=O). Found, %: C 80.34; H 7.12; N 3.76. $C_{24}H_{25}NO_2$. Calculated, %: C 80.19; H 7.01; N 3.90.

***N*-Acetyl-*N*-adamantoylaniline (IIc).** *a*. Compound **IIc** was prepared similarly to compound **IIa** from 7.5 g of imidoyl chloride **I**, 1.65 g of acetic acid, and 2.78 g of triethylamine. The reaction was performed at 25°C; reaction time 2 h. The product was purified by recrystallization from hexane. Yield 7.2 g (91%), mp 65–67°C.

b. Compound **IIc** was prepared similarly to compound **IIb** (method *c*) from 5 g of imidoyl chloride **I** and 1.5 g of sodium acetate. The mixture was heated under reflux for 12 h. Purification was performed by recrystallization from hexane. Yield 4.9 g (91%), mp 65–67°C. Mass spectrum, *m/e* (I_{rel}, %): 297 (3) $[M]^+$, 254 (2) $[M - COCH_3]^+$, 163 (5) $[M - NPhCCOCH_3]^+$, 135 (100) $[Ad]^+$, 119 (4) $[M - AdCO - CH_3]^+$, 107 (5) $[M - COCH_3 - Ad]^+$, 92 (31) $[PhNH]^+$, 77 (26) [Ph]. IR spectrum, ν, cm^{-1}: 1116, 972, 752 (Ad), 1220, 1248, 1292 (C–N), 1488 (Ar), 1736, 1728 (C=O). Found, %: C 76.95; H 7.71; N 4.79. $C_{19}H_{23} \cdot NO_2$. Calculated, %: C 76.73; H 7.80; N 4.71.

The IR spectra were measured in mineral oil on a Specord M-82 spectrophotometer. The mass spectra were obtained on a Varian MAT-111 instrument.

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