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1-ACYLDEOXYVASICINONE SALTS AS EFFECTIVE INTERMEDIATE C- AND N-ACYLATING AGENTS FOR ALKALOIDS AND AMINO ACIDS

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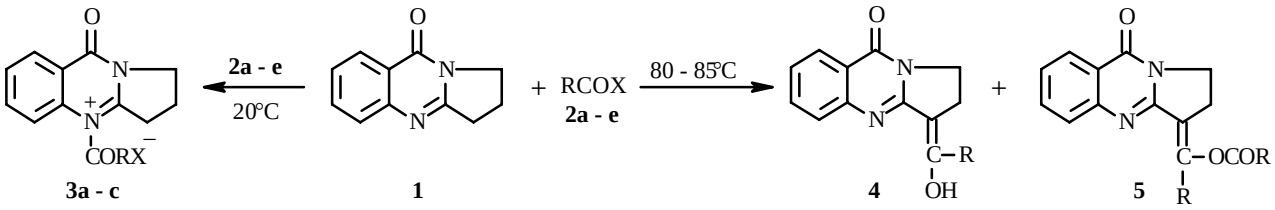
The reaction of deoxyvasicinone with acid chlorides of aliphatic (acetylbromide) and aromatic (benzoyl-, o-, p-*methoxy-,* p-*nitrobenzoylchlorides) acids was studied. It was shown that 1-deoxyvasicinone salts were formed at room temperature;α-aroyloxymethylidenedeoxyvasicinones, in the presence of triethylamine at 80-85°C. It was found that acid chlorides cause 1-acyldeoxyvasicinone salts to transform into α-hydroxy- or α-aroyloxyarylidenedeoxyvasicinones, which indirectly confirmed their acylating properties. It was found that 1-acyldeoxyvasicinone salts were effective acylating agents for alkaloids (cytisine, 1,2-dihydrodeoxyvasicinone) and amino acids (glycine, β-alanine, α-aminobutyric acid) and can be used to acylate primary and secondary aliphatic and heterocyclic amines.*

Key words: deoxyvasicinone, 1-acyldeoxyvasicinone salts, 1,2-dihydrodeoxyvasicinone, cytisine, amino acids, acylation, acetylbromide, *p*-nitro-, *o*-, *p*-methoxybenzoylchlorides.

We demonstrated previously that deoxyvasicinone (**1**) and its substituted derivatives and homologs undergo bromination, formylation, and other reactions [1-4]. It was found that complicated molecules can form at the N atom (bromination in glacial acetic acid, reaction with SO_3, etc.) [1, 3], on the aromatic ring (nitration, sulfochlorination, bromination by potassium bromate in acidic medium) [2, 4], and at the α-C atom [1, 3].

Herein we report the acylation of **1** and its 1-acyl derivatives by acid chlorides of aliphatic and aromatic acids and acylation of cytisine and amino acids (glycine, β-alanine, α-aminobutyric acid) by 1-acyldeoxyvasicinone salts.

Acylation of **1** by benzoylchloride (BC, **2a**) in a 1:1 ratio at room temperature both with and without triethylamine (TEA) gave the 1-benzoyl derivative, 1-benzoyldeoxyvasicinone (**3a**).



a: R = C_6H_5, X = Cl; **b:** R = *n*-$O_2NC_6H_4$; X = Cl; **c:** R = CH_3, X = Br; **d:** R = CH_3, X = Cl; **e:** R = *n*-$CH_3OC_6H_4$, X = Cl

The reaction of **1** with *p*-nitrobenzoylchloride (**2b**) and acetylbromide (**2c**) proceeded analogously to form **3b** and **3c**.

A mixture of two compounds was obtained by reaction of **1** with **2a** at 80-85°C and a reagent ratio **1**:**2a**:TEA = 1:2:1.3. These were the product from acylation of the α-C atom, α-benzoyl-**1**, which exists as the more stable enol form **4a**, and the product from its further benzoylation, α-benzoyloxybenzylidene-**1** (**5a**).

The reaction of **1** with substituted (*p*-nitro, *o*-, *m*-methoxy) benzoylchlorides (**2b**, **d**, **e**) proceeded analogously. The reaction for **1**:**2b**, **d**, **e** = 1:1 stopped with formation of salts **3b**, **d**, **e** [3]. If TEA was used for **1**:**2b**, **d**, **e**:TEA = 1:4:2, the diacylation products **5b**, **d**, **e**, respectively, were formed exclusively.

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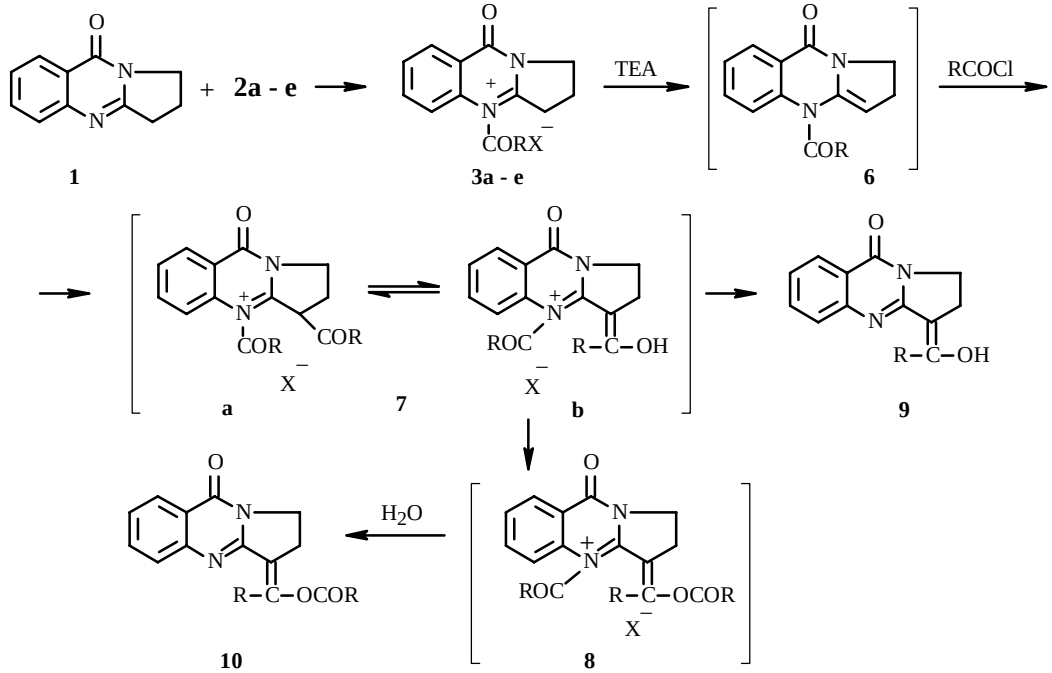
It was assumed that a salt of type **3** was also formed initially during acylation of **1** and its six-membered homolog [3]. Therefore, it was expected that the salts would be acylated easier than deoxyvasicinone itself and its homologs. In this instance, the acyl groups in the 1-position with a relatively large electronegativity should enhance the reaction. Furthermore, use of type **3** salts as an acylating agent might allow less reactive acyl groups to be added to the α-position of **1**. **1** did not react with acid chlorides of aliphatic acids even with heating for a long time. Acylation of **1** with acetylbromide or other aliphatic acylating agents gave starting **1**, which was also isolated pure from **3a-c** by the action of water.



The initially formed salts **3a-e** lost a molecule of HCl by the action of TEA and formed a double bond between C_2 and C_α. This formed intermediate 1-acyldehydrodeoxyvasicinone (**6**). Attack of **6** by another molecule of acylating agent gave salts of **1**,α-diacyldeoxyvasicinone (**7a**), which exist as the enols **7b**.

If an excess of acid chloride was used, **7** could be acylated to form 1-acyl-α-acyloxymethylidenedeoxyvasicinone salts (**8**). The intermediates **7** and **8** transformed into the corresponding α-monoacyl- (**9**) or their further acylation products, α-acyloxymethylidene-**1** (**10**), through intermediate **8** upon work up of the reaction mixture with water.

This pathway was explained by the exclusive formation of **3a-c** for **1**:**2a** = 1:1 with or without TEA. An excess of acid chloride was required to add an acyl group to the α-position and form intermediate **7** and to acylate its hydroxyl to give **10**. The need to use an excess of TEA was explained by the fact that it binds HCl released during the reaction from **3** to **7**.

Considering that the reaction proceeded through intermediates **3a-e**, we decided to use them as starting materials for acylation. Therefore, we studied the reaction of **3a-c** with benzoyl-, *p*-nitrobenzoyl-, and acetylchloride.

Chloride salt **3a** reacted with benzoylchloride in the presence of TEA (1:1:1 ratio) to form a mixture of α-hydroxybenzylidene-**1** (**4a**) and α-benzoylhydroxybenzylidene-**1** (**5a**) in a 1:10 ratio, respectively.

Chloride salt **3b** reacted with BC to give exclusively the *bis*-product **5a**. Such behavior of **3b** was explained by the apparently stronger electron-accepting effect of the *p*-nitrobenzoyl group, which causes the hydroxyl of intermediate **7b** (R = $C_6H_4NO_{2\text{-}n}$) to become more acidic and undergo acylation to a greater extent. This effect was observed even more for chloride salt **3a** upon acylation by *p*-nitrobenzoylchloride. Thus, even for **3a**:**2b**:TEA = 1:1:1 a mixture (1:2.2) of α-*p*-nitrobenzoyl-**1** (**4b**) and α-*p*-nitrobenzoyloxybenzylidene-**1** (**5c**) was produced.

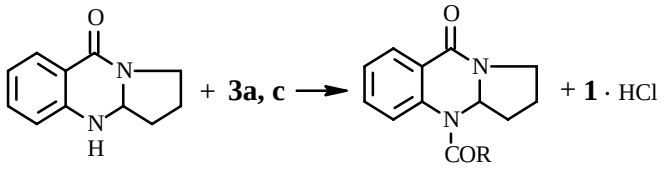
A similar effect was also observed using **3a**:**2b**:TEA = 1:4:2, where exclusively **5b** was formed.

The nature of the acylating agent played an important role in the acylation of **3a-c**. Thus, chloride salt **3a** did not react with benzenesulfonylchloride. Appropriate work up of the reaction mixture afforded **1**. Bromide salt 1-acetyl-**1** (**3c**) behaved similarly upon reaction with acetylbromide and even with benzoylchloride. Attempts to acylate even such an effective acylating agent as 1-*p*-nitrobenzoyldeoxyvasicinone (**3b**) with acetylbromide at 1:1 and even 1:2 ratios were unsuccessful. In all instances **1** was isolated. These facts were explained by the relatively low acylating ability of the acetyl cation formed from acetylbromide by TEA compared with the benzoyl cation and even more the *p*-nitrobenzoyl cation.

The results indicated that the acyl group in the 1-position of **3a-c** was not replaced with another acyl moiety during the acylation.

Because **3a-c** were effective acylating agents, it should have been possible to use them to acylate primary and secondary amines, which was recently demonstrated [5, 6]. In this regard, we studied the reaction of **3** with certain natural amines and amino acids.

Acylation of 1,2-dihydrodeoxyvasicinone (**11**) by **3a** and **-c** proceeded readily and gave 1-benzoyl- and 1-acetyl-1,2-dihydrodeoxyvasicinones (**12a** and **-c**).

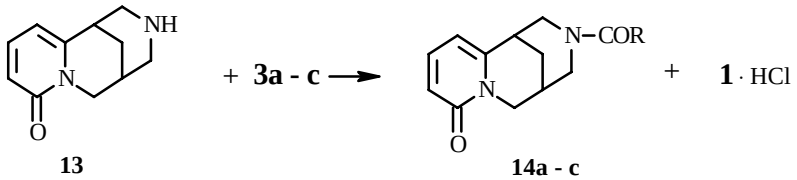


11 **12a, c**

a: R = C_6H_5; **c:** R = CH_3

It is well known that acylation of amines usually produces anhydrides or acid chlorides [7, 8]. This method is often used for relatively large quantities of reagents but is inconvenient when working with microscopic quantities of starting materials.

Our research showed that using **3a-c** to acylate small quantities of cytisine (**13**) gave high (94-95%) yields of the corresponding *N*-acyl cytisine derivatives (**14**):



13 **14a - c**

a: R = C_6H_5; **b:** R = $O_2NC_6H_5$; **c:** R = CH_3

Acylation of glycine, β-alanine, and α-aminobutyric acid by **3a** also proceeded smoothly to form the corresponding benzoylamino acids in good yields. The reaction was carried out in absolute benzene to produce **15a-c** in 77-95% yield. The relatively low (77%) yield of α-benzoylaminobutyric acid (**15b**) compared with **15a** and **-c** was apparently due to a slight steric effect of the *n*-propyl radical next to the amino group.

The structures of the synthesized compounds were confirmed by spectral (IR, PMR, mass) methods and by comparison of their physicochemical characteristics with authentic samples.

Thus, a simple method for acylating microscopic quantities of cytisine and amino acids was developed. The method is general in nature and can be used for *N*-acylation of primary and secondary aliphatic and heterocyclic amines.

EXPERIMENTAL

IR spectra were recorded on an IR-20 spectrometer; mass spectra, on a MX-1303 instrument; PMR spectra, on a JNM-4H-100 instrument (TMS and HMDS internal standards, CF_3COOH, $CDCl_3$, and deuteropyridine solvents). The purity of products was monitored on Silufol UV-254 plates. Deoxyvasicinone was prepared as before [9]. 1,2-Dihydrodeoxyvasicinone was synthesized by the literature method [10].

Acylation of 1 by: a) Benzoylchloride (1:2a:TEA = 1:2:1.3). A solution of **1** (930 mg, 5 mmol) in absolute benzene (5 mL) was stirred, treated first with a solution of TEA (0.9 mL, 6.4 mmol) in absolute benzene (3 mL) and then benzoylchloride (1.2 mL, 10 mmol) in the same solvent (5 mL), boiled for 8 h, cooled, and treated with water (20 mL). The organic layer was separated. The aqueous layer was extracted with benzene. The combined benzene solutions were washed twice with water and dried over Na_2SO_4. Solvent was distilled. Chromatography over a column of alumina ($CHCl_3$:hexane eluent) isolated α-hydroxybenzylidene-**1** (**4a**, 50 mg), mp 155-156°C, R_f 0.68 (Al_2O_3, $CHCl_3$).

PMR spectrum ($CDCl_3$, ppm): 3.257 (2H, t, β-CH_2), 4.155 (2H, t, γ-CH_2), 6.648-8.250 (aromatic protons). Mass spectrum (*m*/*z*, %): 290 (50) $[M]^+$, 262 (26), 213 (8), 185 (59), 155 (4), 130 (8), 105 (41), 77 (100).

Elution by $CHCl_3$ gave α-benzoyloxybenzylidene-**1** (**5**, 560 mg), mp 181-183°C (hexane), R_f 0.74 (Al_2O_3, $CHCl_3$).

IR spectrum (ν, cm^{-1}): 1588 (C=N), 1688 (C=O), 1740, 1794 (COO). PMR spectrum (Py-d_5, ppm): 2.915 (2H, t, β-CH_2), 3.935 (2H, t, γ-CH_2), 6.75-8.10 (aromatic protons). Mass spectrum: 394 (100) $[M]^+$, 290 (5), 262 (5), 223 (3), 185 (6). **1**:**2a**:TEA = 1:1:1.

Analogously, boiling **1** (653 mg, 2 mmol), benzoylchloride (0.3 mL, 2 mmol), and TEA (0.25 mL, 2 mmol) in absolute benzene (18 mL) for 8 h produced **4a** (30 mg, mp 155-156°C) and **5a** (400 mg, mp 181-183°C) (from hexane).

1:**2a**:TEA = 1:4:2.

Analogously, **1** (930 mg, 5 mmol), benzoylchloride (2.3 mL, 20 mmol), and TEA (1.4 mL, 10 mmol) produced **5a** (420 mg, mp 182-183°C from acetic anhydride);

b) *o*-Methoxybenzoylchloride. **1** (930 mg, 5 mmol), *o*-methoxybenzoylchloride (340 mg, 20 mmol), and TEA (1.4 mL, 10 mmol) produced α-(*o*-methoxybenzoyl-*o*-methoxybenzylidene)-**1** (**5d**, 1.24 g, 55%), mp 246-248°C (hexane), R_f 0.36 (Al_2O_3, $CHCl_3$).

IR spectrum (ν, cm^{-1}): 1600 (C=N), 1670 (C=O), 1730 (COO). PMR spectrum (CF_3COOH, ppm): 2.70 (2H, t, β-CH_2), 4.00 (2H, t, γ-CH_2), 3.45, 3.53 (3H, 2s, CH_3, CH_3), 6.4-8.1 (m, aromatic protons).

The aqueous solution remaining after separation of the benzene extracts was made basic with NH_4OH solution (25%) and extracted with $CHCl_3$. The organic layer was dried over Na_2SO_4. Solvent was distilled. The solid was recrystallized from cyclohexane to afford **1** (0.3 g), mp 110-111°C;

c) *p*-Methoxybenzoylchloride. **1** (930 mg, 5 mmol), *p*-methoxybenzoylchloride (340 mg, 20 mmol), and TEA (1.4 mL, 10 mmol) afforded α-(*p*-methoxybenzoyloxy-*p*-methoxybenzylidene)-**1** (**5e**, 640 mg, 25%), mp 205-207°C (hexane), R_f 0.41 (Al_2O_3, $CHCl_3$).

IR spectrum (ν, cm^{-1}): 1610 (C=N), 1680 (C=O), 1788 (COO). PMR spectrum (CF_3COOH, ppm): 2.80 (2H, t, β-CH_2), 4.10 (2H, t, γ-CH_2), 3.45 (6H, C, OCH_3, OCH_3), 6.5-8.2 (m, aromatic protons);

d) *p*-Nitrobenzoylchloride. **1** (930 mg, 5 mmol), *p*-nitrobenzoylchloride (370 mg, 20 mmol), and TEA (1.4 mL, 10 mmol) afforded α-(*p*-nitrobenzoyloxy-*p*-nitrobenzylidene)-**1** (**5b**, 70 mg, 3%), mp 227-229°C, R_f 0.36 (Al_2O_3, $CHCl_3$).

IR spectrum (ν, cm^{-1}): 1608 (C=N), 1700 (C=O), 1798 (COO). Mass spectrum: 422 (3), 412 (4), 379 (20), 363 (5), 352 (17), 344 (56), 335 (100), 320 (7), 314 (9), 307 (24), 298 (16), 185 (32).

Benzoylation of α-(Hydroxybenzylidene)-1 (4a). Synthesis of 5a. A mixture of **4a** (30 mg, 0.16 mmol) and benzoic anhydride (50 mg, 0.22 mmol) was heated at 95-98°C for 10 min. The temperature was increased to 110-115°C. The reaction mixture was held at this temperature for 1 h. The solidified mass was dissolved in a small amount of ether and treated with hexane until cloudy. The mixture was held at 0°C for 18-24 h. The resulting precipitate was filtered off, washed with hexane, and dried. Yield of **5a**, 30 mg (75%), mp 181-182°C.

Hydrolysis of 5a. Preparation of 4a. A mixture of **5a** (120 mg, 0.3 mmol) and dilute HCl (1:1, 4 mL) was boiled for 30 min, cooled, and filtered. The filtrate was diluted with water. The crystals that formed on standing were filtered off, thoroughly washed with water, and dried to afford **4a**, 70 mg (79%), mp 155-156°C.

Synthesis of 3a-c. 1-Benzoyldeoxyvasicinone chloride (3a) was prepared by a modified method [6]:

a) A mixture of **1** (1.86 g, 10 mmol) and benzoylchloride (1.2 mL) in absolute benzene (10 mL) was stirred at 0-5°C for 3 h. The resulting precipitate was filtered off, washed with cold benzene, and dried in a vacuum desiccator to afford **3a** (2.8 g, 86%), mp 278-280°C (acetone). IR spectrum (ν, cm^{-1}): 1670 (C=N), 1710 (C=O), 1850 (N–C=O);

b) reaction of **1** (0.93 g, 5 mmol), benzoylchloride (0.6 mL, 5 mmol), and TEA (0.6 mL, 6.4 mmol) at 20-23°C afforded **3a** (0.58 g, 36%), mp 278-280°C.

1-*p*-Nitrobenzoyldeoxyvasicinone chloride (3b) was prepared by a modified method [6]: A mixture of **1** (0.93 g, 5 mmol) and *p*-nitrobenzoylchloride (0.95 g, 5 mmol) in absolute benzene (10 mL) was held at 3-5°C for 30 min. The resulting crystals were filtered off, washed with cold benzene, and dried to afford **3b** (1.8 g, 97%), mp 209-210°C. IR spectrum (ν, cm^{-1}): 1614 (C=N), 1700 (C=O), 1847 (N–C=O).

Performing the reaction at room temperature analogously as above produced **3b** (1.2 g, 65%), mp 209-210°C.

1-Acetyldeoxyvasicinone Bromide (3c). **1** (0.37 g, 20 mmol) was dissolved in absolute benzene (15 mL), treated with acetylbromide (3 mL) in benzene (3 mL), and stirred for 1 h. The resulting precipitate was filtered off, washed with benzene, and dried to afford **3c** (5.6 g, 91%), mp 269-271°C. IR spectrum (ν, cm^{-1}): 1643 (C=N), 1707 (C=O), 1846 (N–C=O).

Acylation of 3a-c. Acylation of 3a by Benzoylchloride. 3a (650 mg, 2 mmol) was susspended in absolute benzene (10 mL), treated with benzoylchloride (260 mg, 2 mmol) and then TEA (0.3 mL, 2 mmol), and boiled for 3 h. Solvent was distilled. The solid was worked up with water. The insoluble precipitate was extracted with $CHCl_3$. The organic layer was washed with water and dried over Na_2SO_4. Solvent was distilled. Fractional crystallization from hexane afforded **4a** (30 mg, 5.4%), mp 156-158°C, and **5a** (420 mg, 54%), mp 181-183°C.

Acylation of 3b by Benzoylchloride. 3b (370 mg, 1 mmol), benzoylchloride (150 mg, 1 mmol), and TEA (100 mg, 1 mmol) afforded **5a** (290 mg, 78%), mp 181-182°C.

Reaction with *p*-Nitrobenzoylchloride (3a:2b = 1:1). 3a (370 mg, 1 mmol), *p*-nitrobenzoylchloride (190 mg, 1 mmol), and TEA (100 mg) analogously to the above afforded **4b** (100 mg, 3%), mp 192-195°C, and **5b** (330 mg, 68%), mp 227-229°C. IR spectrum (ν, cm^{-1}): (**4b**) 1598 (C=N), 1652 (C=O), 3326 (OH).

***p*-Nitrobenzoylation of 3a. 3a** (330 mg, 1 mmol) and *p*-nitrobenzoylchloride (750 mg, 4 mmol), and TEA (250 mg, 2 mmol) afforded **5b** (290 mg, 60%), mp 226-228°C.

Reaction of 3c with Acetylbromide. 3c (130 mg, 0.5 mmol), acetylbromide (20 mg, 0.5 mmol), and TEA (0.1 mL, 0.5 mmol) under analogous conditions after the appropriate work up afforded **1** (80 mg), mp 110-111°C (hexane).

Analogous results were obtained for the reaction of **3c** with benzoylchloride, 1-benzoyl-**1** chloride (**3a**) with benzenesulfonylchloride, and 1-*p*-nitrobenzoyl-**1** chloride (**3c**) with acetylbromide for **3a-c**:acid halide:TEA = 1:1:1. Deoxyvasicinone was isolated in all instances.

Benzoylation of 11 by 3a Chloride. A solution of **11** (190 mg, 1 mmol) in absolute benzene (5 mL) was treated with **3a** (330 mg). The resulting suspension was stirred at 40-50°C for 1 h and cooled to room temperature. The resulting precipitate of **1** hydrochloride was filtered off. The benzene layer was washed three times with water and dried over Na_2SO_4. Solvent was distilled. The solid was recrystallized from hexane to afford **12a** (290 mg, 82%), R_f 0.55 (Silufol, $CHCl_3$:CH_3OH, 10:1), mp 127-129°C. The melting point of a sample mixed with an authentic sample was not depressed.

1-Acetyl-1,2-dihydrodeoxyvasicinone (12b). Analogously to the above, **11** (190 mg, 1 mmol) and **3c** (270 mg, 1 mmol) afforded **12b** (0.21 g, 87%), mp 120-122°C (lit. [10] mp 120-122°C), R_f 0.30 (Silufol, $CHCl_3$:CH_3OH, 10:1).

***N*-Benzoylcytisine (14a).** A suspension of **3a** chloride (330 mg, 1 mmol) in dry acetone (3 mL) was stirred, treated dropwise with a solution of cytisine (190 mg, 1 mmol) in acetone (3 mL), stirred for 10 min, treated with water (10 mL), and stirred for 5-10 min. The resulting precipitate was filtered off, washed with water, and dried to afford **15a** (280 mg, 95%), mp 115-116°C (lit. [11] mp 116°C), R_f 0.53 (Silufol, acetone:$CHCl_3$, 1:1).

Compounds **14b**, **c**, and **15a-c** were prepared analogously.

***N*-*p*-Nitrobenzoylcytisine (14b)**, yield 94%, mp 206°C (acetone:hexane).

IR spectrum (ν, cm^{-1}): 1652, 1634 (CO). PMR spectrum (acetone-d_6, ppm, J/Hz): 6.0 (1H, br.s, H-5), 6.40 (1H, dd, H-3), 7.12 (2H, br.s, H-2′,6′), 7.33 (1H, dd, H-4), 8.18 (2H, d, J = 8, H-3′,5′). R_f 0.51 (Silufol, acetone:$CHCl_3$, 1:1).

***N*-Acetylcytisine (14c)**, yield 95%, mp 209-210°C (acetone) (lit. [11] mp 209°C), R_f 0.12 (Silufol, acetone:$CHCl_3$, 1:1).

***N*-Benzoylglycine (15a)**, yield 88.5%, mp 186-187°C (water) (lit [12] mp 187°C).

***N*-Benzoyl-α-aminobutyric acid (16b)**, yield 77%, mp 145-146°C (water) (lit. [8] mp 145°C).

***N*-Benzoyl-β-alanine (15c)**, yield 88.5%, mp 118-119°C (water) (lit. [13] mp 120°C).

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