Aminoacids in the Synthesis of Heterocyclic Systems. The Synthesis of Methyl 2-Acetylamino-3-dimethylaminopropenoate and 2-(*N*-Methyl-*N*-trifluoroacetyl)amino-3-dimethylaminopropenoate and their Application in the Synthesis of Heterocyclic Compounds

Lucija Kralj, Aleš Hvala, Jurij Svete, Ljubo Golič, and Branko Stanovnik*

Faculty of Chemistry and Chemical Technology, University of Ljubljana, 1000 Ljubljana, Slovenia

Received May 29, 1996

Methyl (*Z*)-2-acetylamino-3-dimethylaminopropenoate (**3**) was prepared from *N*-acetylglycine (**1**), which was converted with *N,N*-dimethylformamide and phosphorus oxychloride into 4-dimethylaminomethylene-2-methyl-5(4*H*)-oxazolone (**2**), followed by treatment with methanol in the presence of potassium carbonate, into **3**. The compound **3** was shown to be a versatile reagent in the synthesis of various heterocyclic systems. With *N*-nucleophiles, such as heterocyclic amines **4**, either methyl 2-acetylamino-3-heteroarylaminopropenoates **5** or fused pyrimidinones **6** were formed, dependent on the reaction conditions and/or heterocyclic substituents: *C*-nucleophiles with an active or potentially active methylene group, such as 1,3-dicarbonyl compounds **7**, **8** and **9**, substituted phenols **10a,b**, naphthols **11**, **12a-c**, and substituted coumarin **13a**, afforded substituted pyranones **20** and **22**, and fused pyranones **21**, **23-26**. The nitrogen containing heterocycles **14-19** produced pyranoazines **27-31** and pyranoazole **32**. In all of these systems the acetylamino group is attached at position 3 of the newly formed pyranone ring. The orientation around the double bond for methyl (*Z*)-2-(*N*-methyl-*N*-trifluoroacetyl)-3-dimethylaminopropenoate (**36**) was established by X-ray analysis.

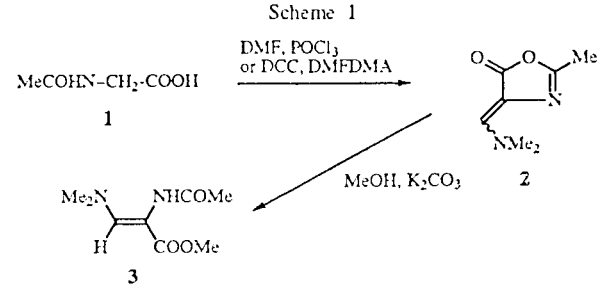
J. Heterocyclic Chem., **34**, 247 (1997).

In our systematic studies about β-dimethylamino-α,β-dehydro-α-amino acid derivatives in the synthesis of β-aryl- and β-heteroaryl- and β-arylamino and β-heteroarylamino substituted α,β-dehydro-α-aminoacids and their derivatives, as intermediates in the synthesis of heterocyclic systems, methyl (*Z*)-2-benzoylamino-3-dimethylaminopropenoate has been extensively studied [1].

Recently, we introduced ethyl (*Z*)-2-[2,2-bis(ethoxycarbonyl)vinyl]amino-3-dimethyl-aminopropenoate [2] and related compounds [3] as new reagents in the synthesis of heteroaryl substituted β-amino-α,β-dehydro-α-amino acid derivatives and some fused heterocyclic systems.

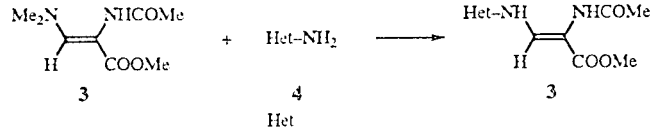
Now we report on the preparation of methyl (*Z*)-2-acetylamino-3-dimethylaminopropenoate (**3**), as a new reagent in this series. The starting compound, *N*-acetylglycine (**1**), was transformed either with a mixture of *N,N*-dimethylformamide and phosphorus oxychloride or with *N,N'*-dicyclohexylcarbodiimide into 4-dimethylaminomethylene-2-methyl-5(4*H*)-oxazolone (**2**) in 51% and 55% yield, respectively. This was then converted by gentle heating in methanol in the presence of potassium carbonate into methyl (*Z*)-2-acetylamino-3-dimethylaminopropenoate (**3**) (Scheme 1).

Scheme 1



In further experiments compound **3** was treated with *N*-nucleophiles such as heterocyclic amines, in a 1:1 molar ratio in acetic acid by heating under reflux for 1 to 7.5 hours. For this purpose a series of 5-membered and 6-membered heterocyclic amines were selected: 4-amino-5-carbamoylimidazole (**4a**), 3-aminoisoxazole (**4b**), 2-amino-4,6-dimethylpyrimidine (**4c**), 2-amino-5-nitropyridine (**4d**), 2-amino-4-methylpyrimidine (**4e**), 2-amino-4,6-dimethoxy-1,3,5-triazine (**4f**), 2-aminopyridine (**4g**), 2-amino-3-hydroxypyridine (**4h**), and 3-amino-1*H*-1,2,4-triazole (**4i**). The substitution of a dimethylamino group with a heterocyclic amino group took place to give methyl 3-heteroarylamino-2-acetylaminopropenoates **5a-f** (Scheme 2).

Scheme 2



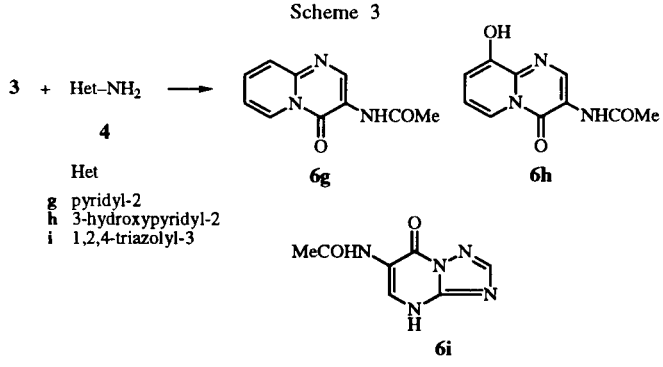
Het

- a 5-carbamoylimidazolyl-4
- b isoxazolyl-3
- c 4,6-demethylpyrimidinyl-2
- d 5-nitropyridyl-2
- e 4-methylpyrimidinyl-2
- f 4,6-dimethoxy-1,3,5-triazinyl-2

In some instances further cyclization of an ester group to the ring nitrogen at the α-position in the heterocyclic ring took place to yield the corresponding acetylaminoazolo- or azinopyrimidine derivatives **6g-i** (Scheme 3).

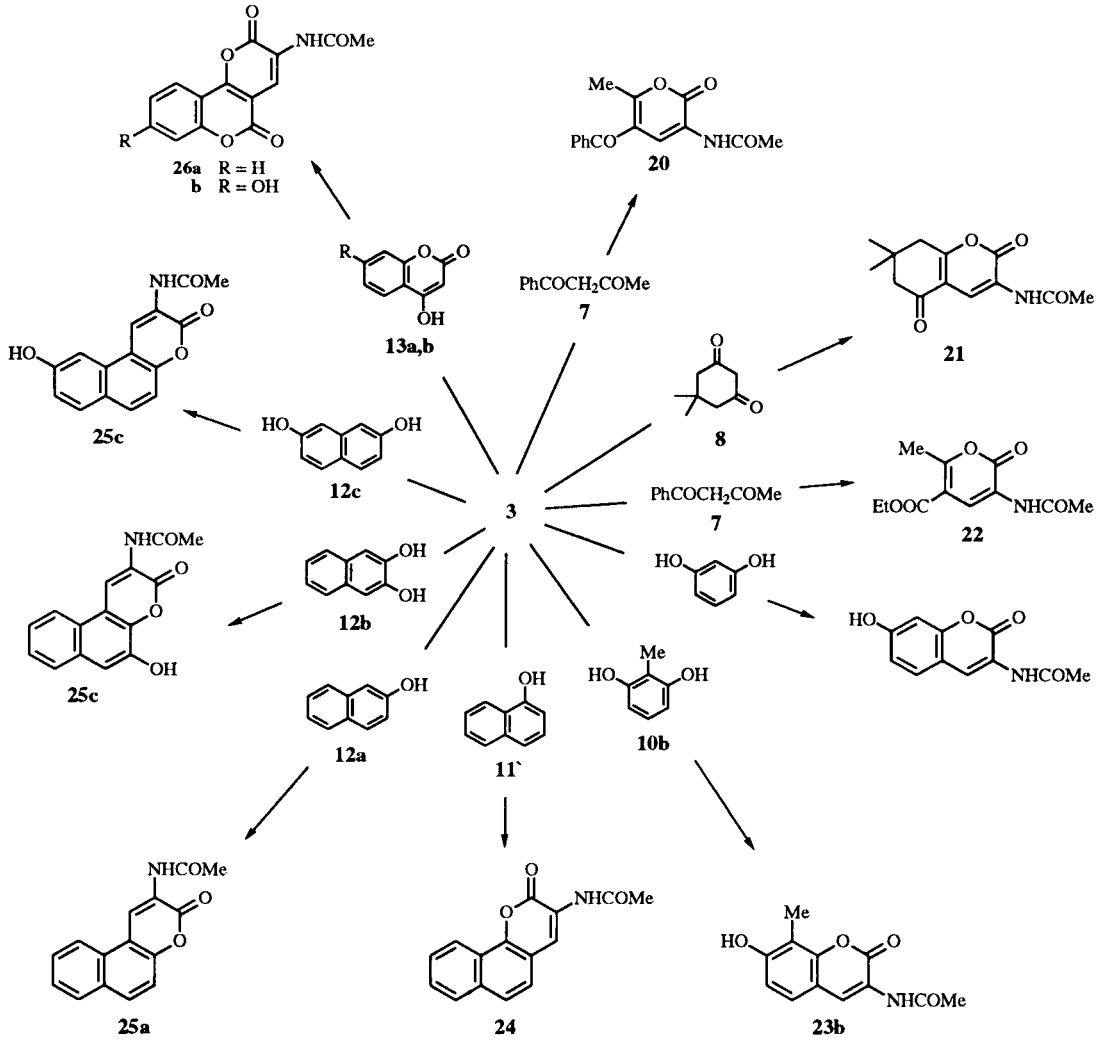
The second group of substrates were *C*-nucleophiles, *i.e.* compounds with an active methylene group such as benzoylacetone (**7**), dimedone (**8**) and ethyl benzoylacetate (**9**), which react with the compound **3** to give 3-acetylamino-5-

Scheme 3

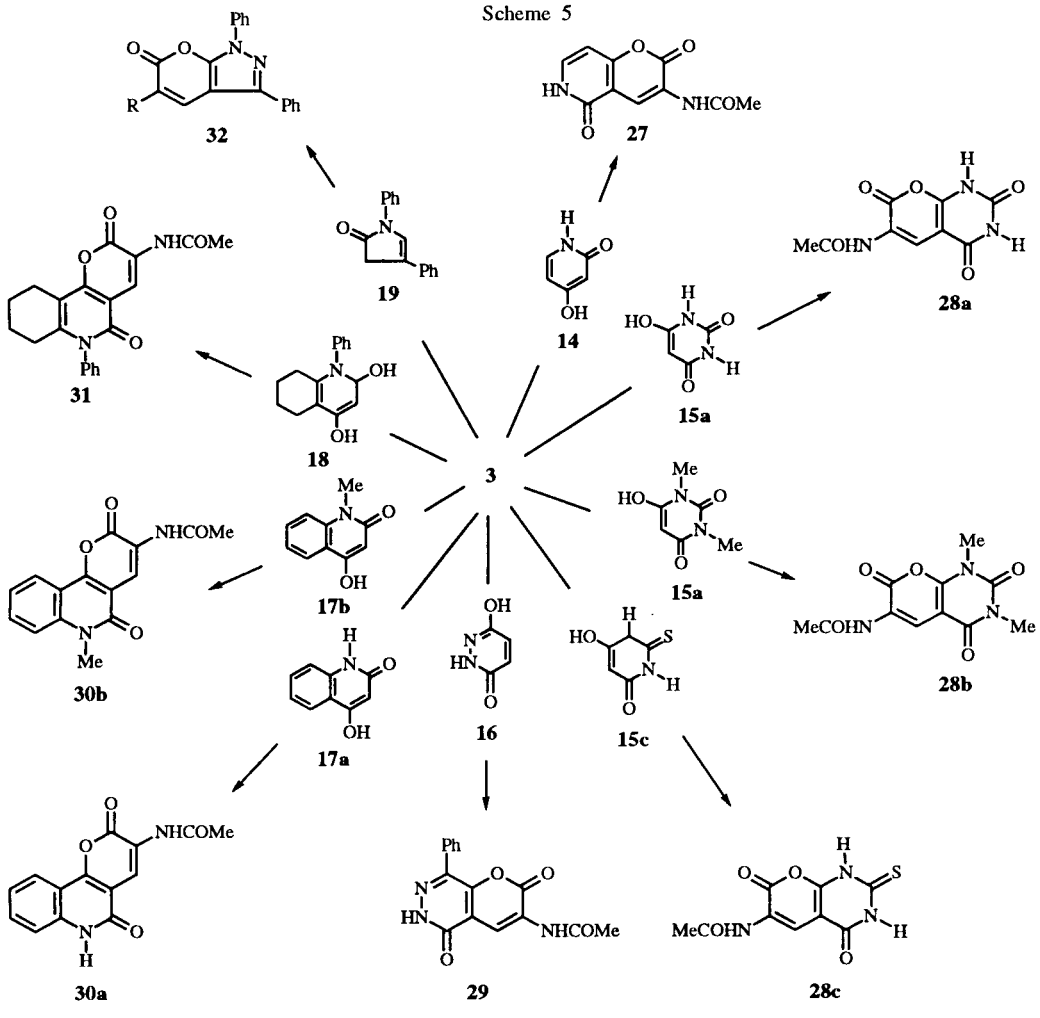


benzoyl (or 5-ethoxycarbonyl)-6-methyl (or 6-phenyl)-2*H*-pyran-2-ones **20** and **22** and 3-acetylamino-5-oxo-5,6,7,8-tetrahydro-2*H*-1-pyran-2-one (**21**), respectively. It turned out, that also the compounds with a potential methylene group, such as resorcinol (**10a**) and 2-methyl-1,6-dihydroxybenzene (**10b**), 1-naphthol (**11**) and 2-naphthol derivatives **12a-c** give the corresponding 3-acetylamino-2*H*-1-benzopyran-2-one derivatives **23a,b**, 3-acetylamino-2*H*-naphtho[1,2-*b*]pyran-2-one (**24**), and 2-acetylamino-3*H*-naphtho[2,1-*b*]pyran-3-one derivatives **25a-c**, respectively. Analogously, heterocyclic hydroxy compounds react also with an active or potentially active methylene group. In this manner, the following compounds were converted into fused pyranone systems: 4-hydroxycoumarins **13a,b** into 3-acetylamino-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-2,5-diones **26a,b**, 4-hydroxypyridin-2(1*H*)-one (**14**) into 2*H*-pyrano[3,2-*c*]pyridine-2,5-dione derivative **27**, barbituric acid and thiobarbituric acid derivatives **15a-c** into pyrano[2,3-*d*]pyrimidines **28a-c**, 5-hydroxy-6-phenylpyridazin-3(2*H*)-one (**16**) into 2*H*-pyrano[2,3-*d*]pyridazine-2,5-dione derivative **29**, 4-hydroxyquinolin-2(1*H*)-ones **17a,b** and their 5,6,7,8-tetrahydro derivative **18** into the corresponding 2*H*-pyrano[3,2-*c*]quinoline-2,5-diones **30a,b** and **31**, and pyrazolone **19** into 1*H*,6*H*-pyrano[2,3-*c*]pyrazol-6-one derivative **32** (Scheme 4 and 5).

Scheme 4

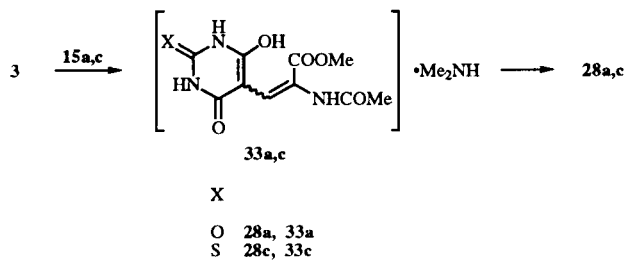


Scheme 5



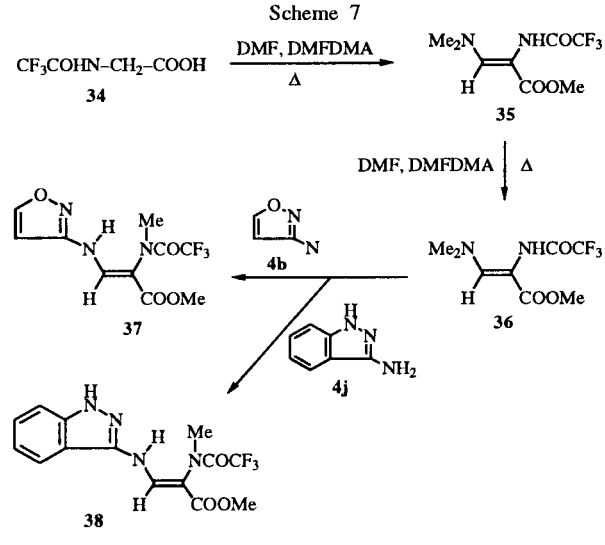
In the case of barbituric acid **15a** and thiobarbituric acid **15c** the corresponding propenoates, which form salts with dimethylamine, eliminated by the reaction, **33a,c** were isolated. They cyclize into pyrano[2,3-*c*]pyrimidines **28a,c** by heating (Scheme 6).

Scheme 6



We tried to establish the structure of the reagent **3**, especially the orientation of groups around the double bond. Namely, the compound exhibits two sets of peaks in the ^{1}H nmr spectrum in a ratio of 3:1; two singlets at δ = 2.09 ppm and δ = 2.22 ppm for the acetyl group, two singlets at δ = 3.01 ppm and δ = 3.08 ppm for the dimethylamino group, two singlets at δ = 3.65 ppm and δ = 3.69 ppm for the ester methyl group, two singlets at δ = 7.34 ppm and

Scheme 7



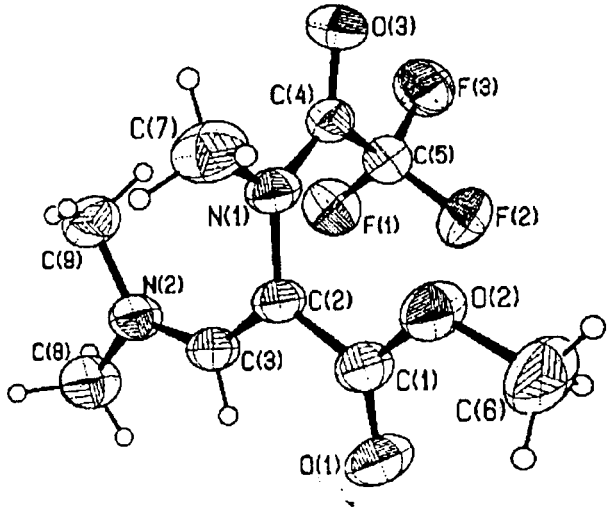


Figure 1. Ortep view of the molecule with labeling of non hydrogen atoms (elipsoids at 50% probability level).

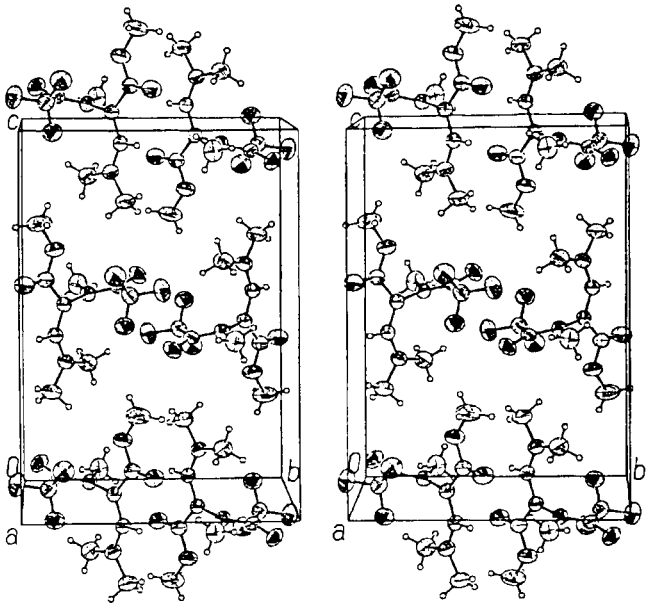


Figure 2. Ortep stereoview of molecular packing in the unit cell.

δ = 7.38 ppm for the proton attached to the double bond and two broad singlets at δ = 6.47 ppm and δ = 6.70 ppm for the NH group. The nmr studies show that this is due to two different orientations of the acetyl group, while the orientation around the double bond is in both rotamers (*Z*) [4]. However, we experienced some difficulties in the preparation of crystals for X-ray analysis, since compound **3** sublimes at room temperature forming tiny needles. Therefore, we prepared the corresponding methyl 3-trifluoroacetyl-2-dimetylaminopropenoate (**35**) by heating *N*-trifluoroacetylglycine (**34**) with *N*,*N*-dimethylformamide, which produces by prolonged reaction with an excess of

Table 1

Final Fractional Coordinates and Equivalent Isotropic Temperature Factors, U_{eq} (Å^2) with e.s.d.'s in parentheses

	x	y	z	U_{eq} [a]
F(1)	0.8374(2)	0.3793(1)	0.49020(7)	0.0672(5)
F(2)	0.9257(1)	0.3463(1)	0.62466(7)	0.0670(5)
F(3)	0.8114(2)	0.5178(1)	0.57999(9)	0.0762(7)
O(1)	0.8986(2)	0.0182(1)	0.60150(8)	0.0719(7)
O(2)	0.7252(2)	0.1267(1)	0.68234(7)	0.0627(6)
O(3)	0.4663(2)	0.4374(1)	0.59777(8)	0.0616(6)
N(1)	0.5206(2)	0.2493(1)	0.55341(7)	0.0451(5)
N(2)	0.6032(2)	0.1637(1)	0.37866(7)	0.0536(6)
C(1)	0.7736(2)	0.0940(1)	0.60691(8)	0.0505(6)
C(2)	0.6592(2)	0.1597(1)	0.53573(8)	0.0440(6)
C(3)	0.6886(2)	0.1276(1)	0.45612(8)	0.0465(6)
C(4)	0.5738(2)	0.3623(1)	0.57370(7)	0.0428(5)
C(5)	0.7894(2)	0.4011(1)	0.56601(9)	0.0514(7)
C(6)	0.8441(4)	0.0716(3)	0.7567(1)	0.086(1)
C(7)	0.3195(2)	0.2119(2)	0.5649(2)	0.069(1)
C(8)	0.6674(4)	0.1111(2)	0.3042(1)	0.071(1)
C(9)	0.4360(3)	0.2473(2)	0.3608(1)	0.0659(9)
C(9)	0.4360(3)	0.2473(2)	0.3608(1)	0.0659(9)
H(3)	0.788(3)	0.070(2)	0.454(1)	0.044(4)
H(61)	0.868(6)	-0.013(4)	0.748(2)	0.11(1)
H(62)	0.976(6)	0.101(3)	0.758(2)	0.10(1)
H(63)	0.812(5)	0.103(3)	0.801(3)	0.11(1)
H(71)	0.235(5)	0.276(3)	0.555(2)	0.11(1)
H(72)	0.270(5)	0.148(3)	0.526(2)	0.10(1)
H(73)	0.310(5)	0.181(3)	0.614(3)	0.11(1)
H(81)	0.778(5)	0.062(3)	0.322(2)	0.09(1)
H(82)	0.697(5)	0.174(3)	0.268(2)	0.10(1)
H(83)	0.544(5)	0.063(3)	0.270(2)	0.10(1)
H(91)	0.334(7)	0.217(4)	0.385(3)	0.13(1)
H(92)	0.416(5)	0.270(3)	0.306(3)	0.11(1)
H(93)	0.470(5)	0.322(3)	0.393(2)	0.10(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensors. Hydrogen atoms were refined with isotropic thermal parameters.

Table 2

Bond Lengths (Å) and Bond Angles (°) with e.s.d.'s in Parentheses

C(1) -O(1)	1.212(2)	C(2) -N(1)	1.434(2)
C(1) -O(2)	1.349(2)	N(1) -C(7)	1.465(2)
O(2) -C(6)	1.449(3)	N(1) -C(4)	1.341(2)
C(1) -C(2)	1.456(2)	C(4) -O(3)	1.216(2)
C(2) -C(3)	1.365(2)	C(4) -C(5)	1.546(2)
C(3) -N(2)	1.331(2)	C(5) -F(1)	1.326(2)
N(2) -C(8)	1.455(2)	C(5) -F(2)	1.342(2)
N(2) -C(9)	1.457(3)	C(5) -F(3)	1.330(2)
O(1) -C(1) -O(2)	122.2(1)	C(2) -N(1) -C(7)	118.5(1)
O(1) -C(1) -C(2)	125.6(1)	C(4) -N(1) -C(7)	117.2(1)
O(2) -C(1) -C(2)	112.2(1)	N(1) -C(4) -O(3)	125.3(1)
C(1) -O(2) -C(6)	115.2(2)	N(1) -C(4) -C(5)	117.6(1)
C(1) -C(2) -C(3)	116.5(1)	O(3) -C(4) -C(5)	117.0(1)
C(1) -C(2) -N(1)	118.6(1)	C(4) -C(5) -F(1)	113.8(1)
C(3) -C(2) -N(1)	124.9(1)	C(4) -C(5) -F(2)	111.1(1)
C(2) -C(3) -N(2)	132.1(1)	C(4) -C(5) -F(3)	110.0(1)
C(3) -N(2) -C(8)	119.2(1)	F(1) -C(5) -F(2)	107.6(1)
C(3) -N(2) -C(9)	125.0(1)	F(2) -C(5) -F(3)	106.9(1)
C(8) -N(2) -C(9)	115.6(1)	F(3) -C(5) -F(1)	107.2(2)
C(2) -N(1) -C(4)	123.4(1)		

Table 3

Intermolecular Contacts Less than 3.3 Å

	Distance (Å)	Symmetry operation of second atom
F(1) .....F(3)	3.023	2-x,1-y,1-z
F(1) .....O(3)	3.066	1-x,1-y,1-z
F(3) .....O(3)	3.154	1-x,1-y,1-z
F(3) .....C(6)	3.233	2-x,1/2+y,3/2-z

N,N-dimethylformamide dimethyl acetal the corresponding methyl 2-(*N*-methyl-*N*-trifluoroacetyl)-3-dimethylaminopropenoate (**36**) (Scheme 7). The X-ray analysis shows that both amino groups are in (*Z*)-orientation with respect to each other. The details are given in Figures 1 and 2 and also in Tables 1-3. This observation is in agreement with other examples of substituted β-amino-α,β-dehydro-α-aminoacid derivatives.

EXPERIMENTAL

Melting points were taken on a Kofler micro hot stage. The ^{1}H nmr spectra were obtained on a Varian EM 360 L or JEOL JNM FX 90Q FT spectrometers, ir spectra on a Perkin-Elmer 1310 instrument, microanalyses for C, H and N on a Perkin-Elmer Analyser 2400, and mass spectra on an Autospeck Q spectrometer.

The Synthesis of Methyl 2-Acetylamino-3-dimethylaminopropenoate (**3**).

4-Dimetylaminomethylene-2-methyl-5(4*H*)-oxazolone (**2**).

Method A.

To a mixture of *N*-acetylglycine **1** (1.17 g, 0.010 mole) and phosphorus oxychloride (2.9 ml, 0.025 mole) stirred at 0°, *N,N*-dimethylformamide (DMF) (1.9 ml, 0.025 mole) was added dropwise. The mixture was then stirred at 40-45° for 1 hour. The volatile components were evaporated *in vacuo* and the oily residue was poured into a mixture of aqueous ammonia (25%, 10 ml) and crushed ice (20 g). The product was collected by filtration, dissolved in chloroform (5 ml) and washed with water (5 ml). The organic layer was dried over anhydrous sodium sulphate and evaporated *in vacuo*. The solid residue was recrystallized from ethanol to give **2** in 78.5% yield, mp 153-155°; ^{1}H nmr (deuteriochloroform, 90 MHz): δ 2.19 (s, CH_3), 3.20 and 3.46 (2 br s, $N(CH_3)_2$), 6.98 (s, CH).

Anal. Calcd. for $C_7H_{10}N_2O_2$: C, 54.54; H, 6.54; N, 18.17. Found: C, 54.41; H, 6.58; N, 18.47.

Method B.

A mixture of *N*-acetylglycine **1** (0.586 g, 0.005 mole) and *N,N*-dicyclohexylcarbodiimide (1.032 g, 0.005 mole) in methylene chloride (10 ml) was stirred at room temperature for 3 hours. The mixture was cooled and filtrated. To the filtrate *N,N*-dimethylformamide dimethyl acetal (0.65 g, 0.0055 mole) was added and the mixture was left at room temperature for 18 hours. The solvent was evaporated *in vacuo* and water (2 ml) was added to the oily residue. The product was collected by filtration and recrystallized from ethanol to give **2** in 55% yield.

Methyl (*Z*)-2-Acetylamino-3-dimethylaminopropenoate (**3**).

A mixture of 4-dimetylaminomethylene-2-methyl-5(4*H*)-oxazolone (**2**, 1.54 g, 0.010 mole) in methanol (30 ml) and potassium carbonate (0.035 g, 0.0025 mole) was heated under reflux for 0.5 hour. The solvent was evaporated *in vacuo* and water (30 ml) was added and extracted with chloroform (5 times, 30 ml each time). The organic layer was dried over anhydrous sodium sulphate and evaporated *in vacuo*. The oily residue crystallised from diethyl ether and it was recrystallized from a mixture of chloroform and diethyl ether to give **2** in 78% yield, mp 98-99° (sublimation starts at 55° and recrystallisation occurs at 62°); ms: 186.100442 (M^+, $C_8H_{14}N_2O_3$); ^{1}H nmr (deuteriochloroform, 90 MHz): δ 2.09 and 2.22 (2 s, 2 $COCH_3$), 3.01 and 3.08 (2 s, 2 $N(CH_3)_2$), 3.65 and 3.69 (2 s, 2 OCH_3), 6.47 and 6.70 (2 br s, 2 NH), 7.34 and 7.38 (2 s, 2 CH).

Anal. Calcd. for $C_8H_{14}N_2O_3H_2O$: C, 47.05; H, 7.90; N, 13.72. Found: C, 47.35; H, 8.26; N, 13.71.

The Reaction between Heterocyclic Amines **4a-i** and Methyl 2-Acetylamino-3-dimethyl-aminopropenoate (**3**). The Synthesis of Methyl 2-Acetylamino-3-heteroaryl-aminopropenoates **5a-f** and Fused Pyrimidones **6g-i**.

Methyl 2-Acetylamino-3-(5-carbamoylimidazolyl-4)aminopropenoate (**5a**)

A mixture of **4a** hydrochloride (0.001 mole) and compound **3** (0.001 mole) in ethanol (3 ml) was heated under reflux for 2 hours. The volatile components were evaporated *in vacuo* and the solid residue was recrystallized from ethanol to give **5a**, in 66% yield, mp 173-175°; ^{1}H nmr (DMSO-d_6, 60 MHz): δ 2.02 (s, $COCH_3$), 3.79 (s, OCH_3), 7.28 (br s, $CONH_2$), 7.70 (s, H_2), 8.16 (d, C*H*NH), 8.92 (d, CHN*H*), 8.98 (br s, NHCO), H_1 exchanged, J_{CHNH} = 13.5 Hz.

Anal. Calcd. for $C_{10}H_{14}N_5O_4Cl$: C, 39.55; H, 4.65; N, 23.06. Found: C, 39.46; H, 4.79; N, 22.76.

General Procedure.

A mixture of compound **3** (0.001 mole) and the heterocyclic amine **4a-i** (0.001 mole) in acetic acid (3 ml) was heated under reflux for several hours. The reaction was followed by tlc (DC-Alufolien Kieselgel 60 F 254, 0.2 mm, E. Merck, and chloroform/methanol, 5:1, as solvent). The volatile components were evaporated *in vacuo* and the residue was recrystallized from an appropriate solvent to give **5a-f** or **6g-i** .

In the same manner the following compounds were prepared:

Methyl 2-Acetylamino-3-(isoxazolyl-3)aminopropenoate (**5b**).

This compound was prepared from **4b**, 4.5 hours of reflux, in 63% yield, mp 175-177° (from water); ^{1}H nmr (DMSO-d_6, 90 MHz): δ 1.97 (s, $COCH_3$), 3.64 (s, OCH_3), 6.40 (d, H_4), 7.74 (d, C*H*NH), 8.69 (d, H_5), 8.75 (br s, NHCO), 9.23 (d, CHN*H*), J_{CHNH} = 12.7 Hz, $J_{H4,H5}$ = 1.7 Hz.

Anal. Calcd. for $C_9H_{11}N_3O_4$: C, 48.00; H, 4.92; N, 18.66. Found: C, 47.85; H, 5.05; N, 18.50.

Methyl 2-Acetylamino-3-(4,6-dimethylpyrimidinyl-2-)aminopropenoate (**5c**).

This compound was prepared from **4c**, 7.5 hours of reflux, in 48% yield, mp 180-182° (from a mixture of ethanol and water); ^{1}H nmr (DMSO-d_6, 90 MHz): δ 2.20 (s, $COCH_3$), 2.37 (s, 4,6-di CH_3), 3.82 (s, OCH_3), 6.58 (s, H_5), 7.47 (br s, NHCO), 8.31 (d, C*H*NH), 9.00 (br d, CHN*H*), J_{CHNH} = 11.5 Hz.

Anal. Calcd. for $C_{12}H_{16}N_4O_3$: C, 54.54; H, 6.10; N, 21.20. Found: C, 54.23; H, 6.23; N, 20.91.

Methyl 2-acetylamino-3-(5-nitropyridyl-2)aminopropenoate (**5d**).

This compound was prepared from **4d**, 1 hour of reflux, in 47% yield, mp 228-230° (from a mixture of acetonitrile and water); ^{1}H nmr (DMSO-d_6, 90 MHz): δ 2.01 (s, $COCH_3$), 3.69 (s, OCH_3), 7.19 (d, H_3), 8.44 (dd, H_4 and H_1), 8.93 (s, C*H*NH), 9.12 (d, H_6), 9.89 (br s, CHN*H*), $J_{H4,H6}$ = 2.7 Hz, $J_{H3,H4}$ = 9.3 Hz.

Anal. Calcd. for $C_{11}H_{12}N_4O_5$: C, 47.14; H, 4.32; N, 19.99. Found: C, 47.39; H, 4.44; N, 20.09.

Methyl 2-Acetylamino-3-(4-methylpyrimidinyl-2)amino-propenoate (**5e**).

This compound was prepared from **4e**, 3.5 hours of reflux, in 26% yield, mp 163-165° (from a mixture of ethanol and water); ^{1}H nmr (deuteriochloroform, 60 MHz): δ 2.22 (s, $COCH_3$), 2.45 (s, 4-CH_3), 3.88 (s, OCH_3), 6.77 (d, H_5), 7.59 (br s, NHCO), 8.37 (d, C*H*NH), 8.38 (d, H_6), 9.29 (br d, CHN*H*), J_{CHNH} = 12.0 Hz, $J_{H5,H6}$ = 5.6 Hz.

Anal. Calcd. for $C_{11}H_{14}N_4O_3$: C, 52.79; H, 5.64; N, 22.39. Found: C, 53.18; H, 5.59; N, 22.03.

Methyl 2-Acetylamino-3-(4,6-dimethoxy-1,3,5-triazinyl-2)aminopropenoate (**5f**).

This compound was prepared from **4f**, 3.5 hours of reflux, in 50% yield, mp 216-217° (from acetonitrile); ^{1}H nmr (deuterio-chloroform, 90 MHz): δ 2.22 (s, $COCH_3$), 3.83 (s, $COOCH_3$), 4.01 (s, 4,6-di OCH_3), 7.59 (br s, NHCO), 8.09 (d, C*H*NH), 9.73 (br d, CHN*H*), J_{CHNH} = 11.2 Hz.

Anal. Calcd. for $C_{11}H_{15}N_5O_5$: C, 44.44; H, 5.09; N, 23.56. Found: C, 44.30; H, 5.25; N, 23.62.

3-Acetylamino-4-oxo-4*H*-pyrido[1,2-*a*]pyrimidine (**6g**).

This compound was prepared from **4g**, 4.5 hours of reflux, in 74% yield, mp 207-208° (from acetic acid); ^{1}H nmr (deuterio-chloroform, 90 MHz): δ 2.28 (s, $COCH_3$), 7.14 (ddd, H_7), 7.60-7.68 (m, H_8, H_9), 9.50 (s, H_1), 8.14 (br s, NH), 8.94 (ddd, H_6), 9.53 (s, H_2).

Anal. Calcd. for $C_{10}H_9N_3O_2$: C, 59.10; H, 4.46; N, 20.68. Found: C, 58.77; H, 4.23; N, 20.66.

3-Acetylamino-9-hydroxy-4-oxo-4*H*-pyrido[1,2-*a*]pyrimidine (**6h**).

This compound was prepared from **4h**, 1.5 hours of reflux, in 45% yield, mp 260-263° dec (from a mixture of ethanol and DMF); ^{1}H nmr (DMSO-d_6, 60 MHz): δ 2.17 (s, $COCH_3$), 7.06-7.38 (m, H_7, H_8), 8.51 (dd, H_6), 9.21 (s, H_2), 9.65 (br s, NH), OH exchanged.

Anal. Calcd. for $C_{10}H_9N_3O_3$: C, 54.79; H, 4.14; N, 19.17. Found: C, 54.43; H, 4.19; N, 19.25.

6-Acetylamino-7-oxo-4*H*,7*H*-1,2,4-triazolo[1,5-*a*]pyrimidine (**6i**).

This compound was prepared from **4i**, 1.75 hours of reflux, in 62% yield, mp 300° dec (from a mixture of ethanol and DMF); ^{1}H nmr (DMSO-d_6, 60 MHz): δ 2.11 (s, $COCH_3$), 8.28 (s, H_2), 8.62 (s, H_5), 9.48 (br s, NH), H_4 exchanged.

Anal. Calcd. for $C_7H_7N_5O_2$: C, 43.53; H, 3.65; N, 36.26. Found: C, 43.74; H, 3.78; N, 36.22.

According to the same procedure the reactions between the compounds containing an active methylene group **7-19** and methyl 2-acetylamino-3-dimethyl-aminopropenoate (**3**) were carried out.

3-Acetylamino-5-benzoyl-6-methyl-2*H*-1-pyran-2-one (**20**).

This compound was prepared from **7**, 6 hours of reflux, in 26% yield, mp 217-219° (from ethanol); ^{1}H nmr (DMSO-d_6, 60 MHz): δ 2.11 (s, $COCH_3$), 2.21 (s, CH_3), 7.35-7.97 (m, Ph), 8.20 (s, H_4), 9.70 (br s, NH).

Anal. Calcd. for $C_{15}H_{13}NO_4$: C, 66.41; H, 4.83; N, 5.16. Found: C, 66.24; H, 4.51; N, 5.17.

3-Acetylamino-7,7-dimethyl-5,6,7,8-tetrahydro-2*H*-1-benzopy-ran-2,5-dione (**21**).

This compound was prepared from **8**, 1.5 hours of reflux, in 78% yield, mp 186-187° (from ethanol); ^{1}H nmr (deuterio-chloroform, 60 MHz): δ 1.15 (s, 7,7-di CH_3), 2.21 (s, $COCH_3$), 2.42 (s, 8-CH_2), 2.71 (s, 6-CH_2), 7.84 (br s, NH), 8.60 (s, H_4).

Anal. Calcd. for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.07; N, 5.62. Found: C, 63.02; H, 5.79; N, 5.91.

3-Acetylamino-5-ethoxycarbonyl-6-phenyl-2*H*-1-pyran-2-one (**22**).

This compound was prepared from **9**, 4.5 hours of reflux, in 46% yield, mp 140-142° (from a mixture of ethanol and water); ^{1}H nmr (DMSO-d_6, 60 MHz): δ 0.90 (t, OCH_2CH_3), 2.16 (s, $COCH_3$), 4.09 (q, OCH_2CH_3), 7.52 (s, Ph), 8.55 (s, H_4), 9.87 (br s, NH).

Anal. Calcd. for $C_{16}H_{15}NO_5$: C, 63.78; H, 5.02; N, 4.65. Found: C, 63.41; H, 5.09; N, 4.75.

3-Acetylamino-7-hydroxy-2*H*-1-benzopyran-2-one (**23a**).

This compound was prepared from **10a**, 1 hour of reflux, in 24% yield, mp 305° (from ethanol); ^{1}H nmr (DMSO-d_6, 60 MHz): δ 2.15 (s, $COCH_3$), 6.78 (s, H_6), 6.85 (d, H_8), 7.59 (d, H_7), 8.58 (s, H_4), 9.63 (br s, NH), 10.50 (br s, OH).

Anal. Calcd. for $C_{11}H_9NO_4$: C, 60.27; H, 4.14; N, 6.39. Found: C, 59.89; H, 3.92; N, 6.32.

3-Acetylamino-7-hydroxy-8-methyl-2*H*-1-benzopyran-2-one (**23b**).

This compound was prepared from **10b**, 2.5 hours of reflux, in 67% yield, mp 256-257° (from ethanol); ^{1}H nmr (DMSO-d_6, 60 MHz): δ 2.17 (s, $COCH_3$), 2.20 (s, 8-CH_3), 6.88(d, H_6), 7.40 (d, H_5), 8.55 (s, H_4), 9.63 (br s, NH), $J_{H5,H6}$ = 9 Hz.

Anal. Calcd. for $C_{12}H_{11}NO_4$: C, 61.80; H, 4.75; N, 6.01. Found: C, 62.03; H, 4.73; N, 5.71.

3-Acetylamino-2*H*-naphtho[1,2-*b*]pyran-2-one (**24**).

This compound was prepared from **11**, 2 hours of reflux, in 23% yield, mp 258-259° (from ethanol); ^{1}H nmr (DMSO-d_6, 60 MHz): δ 2.23 (s, $COCH_3$), 7.50-8.50 (m, H_5, H_6, H_7, H_8, H_9, H_{10}), 8.83 (s, H_4), 9.88 (br s, NH).

Anal. Calcd. for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38; N, 5.53. Found: C, 70.79; H, 4.36; N, 5.51.

2-Acetylamino-3*H*-naphtho[2,1-*b*]pyran-3-one (**25a**).

This compound was prepared from **12a**, 3 hours of reflux, in 19% yield, mp 253-254° (from ethanol); ^{1}H nmr (DMSO-d_6, 60 MHz): δ 2.22 (s, $COCH_3$), 7.50-8.43 (m, H_5, H_6, H_7, H_8, H_9, H_{10}), 9.50 (s, H_1), 9.97 (br s, NH).

Anal. Calcd. for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38; N, 5.53. Found: C, 70.87; H, 4.36; N, 5.32.

2-Acetylamino-5-hydroxy-3*H*-naphtho[2,1-*b*]pyran-3-one (**25b**).

This compound was prepared from **12b**, 2.5 hours of reflux, in 56% yield, mp >310° (from DMF); ms: 269.0688 (M^+, $C_{15}H_{11}NO_4$), ^1H nmr (deuteriotrifluoroacetic acid, 60 MHz): δ 2.07 (s, $COCH_3$), 7.10-7.87 (m, H_6, H_7, H_8, H_9, H_{10}), 9.10 (s, H_1).

Anal. Calcd. for $C_{15}H_{11}NO_4$: C, 66.91; H, 4.12; N, 5.20. Found: C, 66.34; H, 4.04; N, 5.49.

2-Acetylamino-9-hydroxy-3*H*-naphtho[2,1-*b*]pyran-2-one (**25c**).

This compound was prepared from **12c**, 3 hours of reflux, in 38% yield, mp >360° (from a mixture of ethanol and DMF); ^1H nmr (DMSO-d_6, 60 MHz): δ 2.23 (s, $COCH_3$), 7.10-7.67 (m, H_6, H_7, H_9), 7.90 (d, H_5), 8.07 (s, H_4), 9.33 (s, H_1), 9.93 (br s, NH), 10.27 (br s, OH), $J_{H5,H6} = J_{H6,H9} = 2.5$ Hz, $J_{H6,H7} = 10.0$ Hz.

Anal. Calcd. for $C_{15}H_{11}NO_4$: C, 66.91; H, 4.12; N, 5.20. Found: C, 66.69; H, 4.13; N, 5.09.

3-Acetylamino-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-2,5-dione (**26a**).

This compound was prepared from **13a**, 0.5 hour of reflux, in 80% yield, mp 292-296° (from acetic acid); ^1H nmr (CF_3COOD, 60 MHz): δ 2.05 (s, $COCH_3$), 7.33-7.98 (m, H_7, H_8, H_9, H_{10}), 8.73 (s, H_4).

Anal. Calcd. for $C_{14}H_9NO_5$: C, 62.00; H, 3.34; N, 5.16. Found: C, 61.79; H, 3.20; N, 5.18.

3-Acetylamino-8-hydroxy-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-2,5-dione (**26b**).

This compound was prepared from **13b**, 1 hour of reflux, in 60% yield, mp >300° (from DMF); ^1H nmr (DMSO-d_6, 60 MHz): δ 2.15 (s, $COCH_3$), 6.80-7.10 (m, H_7, H_9), 7.80 (d, H_{10}), 8.60 (s, H_4), 9.93 (br s, NH), $J_{H9,H10} = 9.0$ Hz.

Anal. Calcd. for $C_{14}H_9NO_6$: C, 58.54; H, 3.16; N, 4.88. Found: C, 58.72; H, 2.96; N, 4.56.

3-Acetylamino-2,5-dioxo-5,6-dihydro-2*H*-pyrano[3,2-*c*]pyridine-2,5-dione (**27**).

This compound was prepared from **14**, 2.5 hours of reflux, in 66% yield, mp >360° (from acetic acid); ms: 220.048407 (M^+, $C_{10}H_8N_2O_4$), ^1H nmr (deuteriotrifluoroacetic acid, 60 MHz): δ 2.00 (s, $COCH_3$), 6.60 (d, H_7), 7.60 (d, H_8), 8.77 (s, H_4), $J_{H7,H8} = 7.0$ Hz.

Anal. Calcd. for $C_{10}H_8N_2O_4$: C, 54.55; H, 3.66; N, 12.72. Found: C, 54.30; H, 3.41; N, 12.65.

6-Acetylamino-2,4-dioxo-1,2,3,4-tetrahydro-7*H*-pyrano[2,3-*d*]-pyrimidin-7-one (**28a**).

This compound was prepared from **15a**, 4 hours of reflux, in 46% yield, mp >320° (from a mixture of DMF and water); ^1H nmr (DMSO-d_6, 60 MHz): δ 2.15 (s, $COCH_3$), 8.53 (s, H_5), 9.77 (br s, NH), 11.63 (br s, OH).

Anal. Calcd. for $C_9H_7N_3O_5$: C, 45.58; H, 2.98; N, 17.72. Found: C, 45.20; H, 2.78; N, 17.55.

6-Acetylamino-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydro-7*H*-pyrano[2,3-*d*]pyrimidin-7-one (**28b**).

This compound was prepared from **15b**, 1.5 hours of reflux, in 42% yield, mp 230-232° (from 1-propanol); ^1H nmr (deuteriochloroform, 60 MHz): δ 2.26 (s, $COCH_3$), 3.47 (s, 1-CH_3), 3.63 (s, 3-CH_3), 7,77 (br s, NH), 8.90 (s, H_5).

Anal. Calcd. for $C_{11}H_{11}N_3O_5$: C, 49.81; H, 4.18; N, 15.84. Found: C, 49.74; H, 3.99; N, 15.91.

6-Acetylamino-4-oxo-2-tiooxo-1,2,3,4-tetrahydro-7*H*-pyrano-[2,3-*d*]pyrimidin-7-one (**28c**).

This compound was prepared from **15c**, 4 hours of reflux, in 53% yield, mp >315° (from DMF); ^1H nmr (DMSO-d_6, 60 MHz): δ 2.13 (s, $COCH_3$), 8.47 (s, H_5), 9.80 (br s, NHCO), 12.83 (br s).

Anal. Calcd. for $C_9H_7N_3O_4S$: C, 42.69; H, 2.79; N, 16.59. Found: C, 42.33; H, 2.73; N, 16.41.

3-Acetylamino-8-phenyl-5,6-dihydro-2*H*-pyrano[2,3-*d*]pyridazine-2,5-dione (**29**).

This compound was prepared from **16**, 1 hour of reflux, in 34% yield, mp >310° (from a mixture of ethanol and DMF); ^1H nmr (DMSO-d_6, 60 MHz): δ 2.20 (s, $COCH_3$), 7.50-8.03 (m, Ph), 8.77 (s, H_4), 10.20 (br s, NHCO), 13.53 (br s, NH).

Anal. Calcd. for $C_{15}H_{11}N_3O_4$: C, 60.61; H, 3.73; N, 14.14. Found: C, 60.04; H, 3.69; N, 14.08.

3-Acetylamino-5,6-dihydro-2*H*-pyrano[3,2-*c*]quinoline-2,5-dione (**30a**).

This compound was prepared from **17a**, 1 hour of reflux, in 71% yield, mp >360° (from DMF); ^1H nmr (deuteriotrifluoroacetic acid, 60 MHz): δ 2.03 (s, $COCH_3$), 7.03-8.13 (m, H_7, H_8, H_9, H_{10}), 8.90 (s, H_4).

Anal. Calcd. for $C_{14}H_{10}N_2O_4$: C, 62.22; H, 3.73; N, 10.37. Found: C, 61.83; H, 3.41; N, 10.37.

3-Acetylamino-6-methyl-5,6-dihydro-2*H*-pyrano[3,2-*c*]quinoline-2,5-dione (**30b**).

This compound was prepared from **17b**, 1 hour of reflux, in 85% yield, mp 287-290° (from acetic acid); ^1H nmr (deuteriotrifluoroacetic acid, 60 MHz): δ 2.03 (s, $COCH_3$), 3.60 (s, 6-CH_3), 7.00-8.17 (m, H_7, H_8, H_9, H_{10}), 8.93 (s, H_4).

Anal. Calcd. for $C_{15}H_{12}N_2O_4$: C, 63.36; H, 4.25; N, 9.85. Found: C, 63.13; H, 4.03; N, 9.60.

3-Acetylamino-6-phenyl-5,6,7,8,9,10-hexahydro-2*H*-pyrano-[3,2-*c*]quinoline-2,5-dione (**31**).

This compound was prepared from **18**, 2 hours of reflux, in 67% yield, mp 297-298° (from acetic acid); ^1H nmr (deuteriotrifluoroacetic acid, 60 MHz): δ 1.47 (m, 8-CH_2, 9-CH_2), 2.00 (s, $COCH_3$), 2.00 (m, 10-CH_2), 2.50 (m, 7-CH_2), 6.77-7.50 (m, Ph), 8.93 (s, H_4).

Anal. Calcd. for $C_{20}H_{18}N_2O_4$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.67; H, 4.99; N, 7.97.

5-Acetylamino-1,3-diphenyl-1*H*,6*H*-pyrano[2,3-*c*]pyrazol-6-one (**32**).

This compound was prepared from **19**, 5 hours of reflux, in 47% yield, mp 275-277° (from acetic acid); ^1H nmr (DMSO-d_6, 60 MHz): δ 2.17 (s, $COCH_3$), 7.33-8.17 (m, 1,3-di Ph), 8.93 (s, H_4), 9.80 (br s, NH).

Anal. Calcd. for $C_{20}H_{15}N_3O_3$: C, 69.56; H, 4.38; N, 12.17. Found: C, 69.36; H, 4.15; N, 11.97.

Methyl 2-Acetylamino-3-(6-hydroxy-2,4-dioxo-1,2,3,4-tetrahydro-pyrimidinyl-5) propenoate (**33a**).

To a suspension of barbituric acid (**15a**, 0.128 g, 0.001 mole) in acetic acid (3 ml) compound **3** (0.186 g, 0.001 mole) was added in portions and heated until all dissolved. After 15 minutes the reaction was completed. The solvent was evaporated

in vacuo and the solid residue was recrystallized from water to give **33a** in 97% yield, mp >320°; ^{1}H nmr (DMSO-d_6, 60 MHz): δ 1.83 (s, $COCH_3$), 2.57 (br s, $N(CH_3)_2$), 3.60 (s, OCH_3), 7.07 (s, CH), 9.80 (br s, NH 2), 10.83 (br s, OH).

Anal. Calcd. for $C_{10}H_{11}N_3O_6 \cdot Me_2NH \cdot H_2O$: C, 43.37; H, 6.07; N, 16.86. Found: C, 43.39; H, 5.82; N, 16.91.

Compound **33a** was transformed by heating at reflux temperature into **28a**.

Methyl 2-Acetylamino-3-(6-hydroxy-4-oxo-1,2,3,4-tetrahydro-2-thiooxopyrimidinyl-5)propenoate (**33c**).

A mixture of thiobarbituric acid (**15c**, 0.144 g, 0.001 mole) and compound **3** (0.186 g, 0.001 mole) in acetic acid (3 ml) was stirred at room temperature for 24 hours. The precipitate was collected by filtration and recrystallized from ethanol to give **33c** in 90% yield, mp 215-216°; ^{1}H nmr (DMSO-d_6, 60 MHz): δ 1.93 (s, $COCH_3$), 2.60 (br s, $N(CH_3)_2$), 3.63 (s, OCH_3), 6.95 (s, CH), 10.70 (br s, NH).

Anal. Calcd. for $C_{10}H_{11}N_3O_5S \cdot Me_2NH$: C, 43.63; H, 5.49; N, 16.96. Found: C, 43.48; H, 5.78; N, 16.43.

Compound **33c** was transformed by heating at reflux temperature into **28c**.

Methyl (*Z*)-3-Dimethylamino-2-trifluoroacetylaminopropenoate (**35**).

A mixture of *N*-trifluoroacetylglycine (**34**, 0.855 g, 0.005 mole) and *N,N*-dimethylformamide dimethyl acetal (1.31 g, 0.011 mole) in *N,N*-dimethylformamide (DMF) (5 ml) was heated for 1.5 hours at 70°. The solvent was evaporated *in vacuo*. To the oily residue water (10 ml) was added and extracted with chloroform (3 times, 10 ml each time). The organic layer was dried over anhydrous sodium sulphate and evaporated *in vacuo*. The product was used without further purification in the following experiment.

Methyl (*Z*)-3-Dimethylamino-2-(*N*-methyl-*N*-trifluoroacetyl)-aminopropenoate (**36**).

A mixture of *N*-trifluoroacetylglycine (**34**, 0.855 g, 0.005 mole) and *N,N*-dimethylformamide dimethyl acetal (1.79 g, 0.015 mole) in *N,N*-dimethylformamide (DMF) (2.5 ml) was heated for 6 hours at 80°. The solvent was evaporated *in vacuo*. The oily residue was dissolved in diethyl ether (10 ml) and petroleum ether was added until the product precipitated. The product was washed with water (10 ml) and recrystallized from a mixture of diethyl ether and petroleum ether to give **36** in 66% yield, mp 63-65°,^{1}H nmr (deuteriochloroform, 60 MHz): δ 3.01 (s, $N(CH_3)_2$), 3.12 (s, N-CH_3), 3.69 (s, OCH_3), 7.34 (s, CH).

Anal. Calcd. for $C_9H_{13}N_2O_3F_3$: C, 42.52; H, 5.15; N, 11.02. Found: C, 42.92; H, 5.32; N, 11.10.

Methyl 3-(Isoxazolyl-3)amino-2-(*N*-methyl-*N*-trifluoroacetyl)-aminopropenoate (**37**).

A mixture of **4b** (0.001 mole) and compound **36** (0.001 mole) in ethanol (3 ml) and concentrated hydrochloric acid (0.1 ml) was heated under reflux for 4.5 hours. The volatile components were evaporated *in vacuo* and the solid residue was recrystallized from toluene to give **37**, in 26% yield, mp 143-145°; ^{1}H nmr (deuteriochloroform, 60 MHz): δ 3.26 (s, N-CH_3), 3.85 (s, OCH_3), 6.26 (s, H_4), 8.20 (d, C*H*NH), 8.30 (d, H_5), 8.80 (br d, CHN*H*), J_{CHNH} = 12.6 Hz, $J_{H4,H5}$ = 1.7 Hz..

Anal. Calcd. for $C_{10}H_{10}N_3O_4F_3$: C, 40.96; H, 3.44; N, 14.33. Found: C, 41.36; H, 3.43; N, 14.44.

Methyl 3-(Indazolyl-3)amino-2-(*N*-methyl-*N*-trifluoroacetyl)-aminopropenoate (**38**).

A mixture of **4j** (0.001 mole) and compound **36** in ethanol (2 ml) and acetic acid (1 ml) was heated under reflux for 4 hours. After cooling to room temperature the product was collected by filtration and recrystallized from ethanol to give **38** in 19% yield, mp 222-224°; ^{1}H nmr (DMSO-d_6, 60 MHz): δ 3.13 (s, N-CH_3), 3.71 (s, OCH_3), 6.90-8.08 (m, Ph), 8.34 (d, C*H*NH), 10.20 (d, CHN*H*), 12.50 (br s, H_1), J_{CHNH} = 12.0 Hz.

Anal. Calcd. for $C_{14}H_{13}N_4O_3F_3$: C, 49.13; H, 3.83; N, 16.37. Found: C, 49.18; H, 4.08; N, 16.38.

X-ray Structure Determination.

A well-formed crystal with approximate dimensions 0.80 x 0.76 x 0.53 mm was used for data collection and cell determination on an Enraf-Nonius CAD-4 diffractometer with graphite monochromatized MoKα radiation, λ = 0.71069 Å. Accurate unit-cell parameters were obtained from a least-squares refinement of the angular settings of 75 reflections with 10.0 < θ < 16.0°. Crystals are monoclinic with space group $P2_1/c$, $C_9H_{13}F_3NO_3$, M = 254.2, a = 6.764(1), b = 11.203(1), c = 15.920(2) Å, β = 99.98(1)°, V = 1188.1(5) Å^3, Z = 4, D_x = 1.421 M/gm^3, μ = 0.129 mm^{-1}, F(000) = 528, T = 293(2) K; intensities were collected in the ω-2θ scan mode with a scan width (0.7 + 0.3 tanθ)°, aperture (2.4 +0.9tanθ) mm, to $2\theta_{max}$ = 60° in one hemisphere h -9 to 9, k -15 to 15, l 0 to 22; three intensity check reflections (4,0,4; -4,3,8; 1,7,1) monitored periodically every 20000 seconds of scanning time and showed an intensity loss of 2.85% over the data collection; orientation control with three reflections (-5,2,2; 3,3,7; -3,-3,2) every 600 reflections, maximum and minimum scan speed 5.55 and 1.04°/min, absorption was ignored; 7214 total data measured, equivalent reflections merged into a set of 3461 independent reflections (R_{int} = 0.016), 2122 with I >2.5((I) as observed.

Structure was solved by MULTAN[5], full-matrix least-squares refinement minimizing $\Sigma w(|Fo| - |Fc|)^2$ with empirical weighting scheme; correction for secondary extinction[6] applied, g = 7.6(7)x10^{-6}; nonhydrogen atoms with anisotropic temperature factors, all H atoms from difference Fourier synthesis, refined with isotropic temperature factors. In the final least-square cycle were 2633 contributing reflections (included were those unobserved reflections for which F_c was greater than F_o) and 207 variables. The final R factors were R = 0.037, wR = 0.051; the maximum shift-to-esd ratio $(\Delta/\sigma)_{max}$ was 0.19 (extinction correction), average 0.002. The maximum and minimum residual electron densities in the final difference map were 0.27 and -0.20 e/Å^3, respectively. Atomic scattering factors for neutral nonhydrogen atoms from [7], dispersion correction from [8], for hydrogen atoms from [9] were used. All calculations were performed on the DEC-10 computer at RCU Ljubljana with the XRAY-76[10] system of crystallographic programs.

Fractional coordinates and equivalent isotropic thermal parameters are reported in Table 1. Intramolecular interatomic distances and angles for nonhydrogen atoms are given in Table 2. An ORTEP drawing [11] showing the atom-labelling scheme is presented in Figure 1 and molecular packing with outlined unit cell is illustrated in Figure 2.

Intermolecular contacts which result in the packing of the crystal are dominated by van der Waals interaction between adjacent asymmetric units. All intermolecular distances, excluding those listed in Table 3 are greater than 3.3 Å.

Acknowledgement.

The authors wish to express their gratitude to the Ministry of Science and Technology of Slovenia for financial support.

REFERENCES AND NOTES

[1] For a review see: B. Stanovnik, Methyl 2-Benzoylamino-3-dimethylaminopropenoate in the Synthesis of Heterocyclic Systems, Progress in Heterocyclic Chemistry, H. Suschitzky, E. F. V. Scriven, eds., Vol. **5**, Pergamon Press, Oxford 1993, pp 34-53.

[2] G. Soršak, A. Sinur, L. Golič, and B. Stanovnik, *J. Heterocyclic Chem.*, **32**, 921 (1995).

[3] S. Strah, J. Svete, and B. Stanovnik, *J. Heterocyclic Chem.*, **33**, (1996), in print

[4] The detailed nmr studies of this and other compounds of this type will be published elsewhere.

[5] T. Debaerdemaker, G. Germain, P. Main, L. S. Refaat, C. Tate and M. M. Woolfson, MULTAN**. A System of Computer Programs for the Automatic Solutions of Crystal Structures from X-ray Diffraction Data., Universities of York, England and Louvain, Belgium (1988).

[6] W. H. Zachariasen, *Acta Cryst.*, **23**, 558 (1967).

[7] D. T. Cromer and J. B. Mann, *Acta Cryst.*, **A24**, 321 (1968).

[8] D. T. Cromer and D. J. Liberman, *J. Chem. Phys.*, **53**, 1891 (1979).

[9] R. F. Stewart, E. R. Davidson and W. R. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

[10] J. M. Stewart, P. A. Machin, C. W. Dickinson, H. L. Amon, H. Heck and H. Flack, The XRAY-76 System. Tech. Rep. TR-446. Computer Science Center University of Maryland, College Park, Maryland (1976).

[11] C. K. Johnson, ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA (1976).