{N,N'-Dicyclohexyl-N''-(phenyl-p-tolylmethylene)}guanidinium Hexachloroantimonate (2b). Yield 92%, yellow crystals, mp 215–218 °C. IR (KBr): 1585 (broad), 3340 cm^{-1}. ^1H NMR: δ 0.95–1.91 (m, CH_2, 20 H), 3.25 (m, CH, 1 H), 3.46 (m, CH, 1 H), 2.43 (s, CH_3, 3 H), 6.58 (d, NH, 1 H; J = 8.7 Hz), 6.69 (d, NH, 1 H; J = 8.7 Hz), 7.12–7.85 (m, aromatic, 9 H). ^{13}C NMR: δ 21.8 (CH_3), 25.0, 25.8, 32.3, 33.4 (CH_2), 52.2, 55.1 (CH), 129.8, 130.3, 130.5, 131.0, 133.4, 136.0, 145.2 (aromatic) 160.9, 178.8 (C=N).

{N,N'-Diisopropyl-N''-((p-methoxyphenyl)phenylmethylene)}guanidinium Hexachloroantimonate (2c). Yield 86%, deep yellow crystals, mp 142–144 °C. IR (KBr): 1580 (broad), 3325, 3360 cm^{-1}. ^1H NMR: δ 0.94 (d, $(CH_3)_2CH$, 6 H; J = 6.5 Hz), 1.25 (d, $CH_3)_2CH$, 6 H; J = 6.5 Hz), 3.58 (m, CH, 1 H), 3.84 (m, CH, 1 H), 3.87 (s, OCH_3, 3 H), 6.58 (d, NH, 1 H; J = 7.8 Hz), 6.71 (d, NH, 1 H; J = 7.5 Hz), 7.18–8.02 (m, aromatic, 9 H). ^{13}C NMR: δ 22.5, 22.7 $(CH_3)_2CH$, 45.8, 48.2 (CH), 56.8 (OCH_3), 129.8, 130.5, 132.9, 133.7, 135.8, 136.6, 136.9, 165.1 (aromatic), 161.0, 178.0 (C=N).

{N,N'-Dicyclohexyl-N''-((p-methoxyphenyl)phenylmethylene)}guanidinium Hexachloroantimonate (2d). Yield 90%, deep yellow crystals, mp 159–161 °C. IR (KBr): 1585 (broad), 3335, 3380 cm^{-1}. ^1H NMR: δ 0.96–1.90 (m, CH_2, 20 H), 3.27 (m, CH, 1 H), 3.45 (m, CH, 1 H), 3.86 (s, OCH_3, 3 H), 6.58 (d, NH, 1 H; J = 8.6 Hz), 6.68 (d, NH, 1 H; J = 8.6 Hz), 7.10–7.95 (m, aromatic, 9 H). ^{13}C NMR: δ 25.8, 26.0, 32.5, 32.9, 33.6 (CH_2), 52.2, 55.2 (CH), 56.9 (OCH_3), 115.6, 128.9, 130.0, 133.8, 135.9, 136.7, 165.2 (aromatic), 161.0, 178.1 (C=N).

Registry No. **1a**, 110117-53-8; **1b**, 110117-54-9; **1c**, 110117-55-0; **2a**, 110142-41-1; **2b**, 110142-43-3; **2c**, 110142-45-5; **2d**, 110142-47-7; PhC(=NH)-p-C_6H_4Me, 22632-90-2; PhC(=NH)-p-C_6H_4OMe, 5291-46-3; PhC(=NH)CH_2Ph, 35183-09-6; i-PrN=C=NPr-i, 693-13-0; c-C_6H_{11}N=C=N-c-C_6H_{11}, 538-75-0.

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Steroidal Pyrazoline and Pyrazole

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A synthetic method for the preparation of steroidal pyrazoline and steroidal pyrazole is described.

We report here the preparation of 3-oxo-4-pregneno[20,21-*c*]-1'-phenyl-5'-(pyridinyl)pyrazole (IV), according to Scheme I.

We thought it would be of interest to combine the pyrazole and pyrazoline rings out of the steroid skeleton and to study the biological action.

5-Pregnen-3β-ol-20-one acetate condensed with pyridine-2-carboxaldehyde yields a mixture of *cis*- and *trans*-21-(2-pyridylmethylene)-5-pregnen-3β-ol acetate (II). The structure was deduced from their ^1H NMR spectrum which is shown in Table I.

The condensation of phenylhydrazine with 21-(21-pyridylmethylene)-5-pregnen-3-ol acetate in the presence of hydrochloric acid gave the corresponding pyrazoline (III) (*1*). The structure of pyrazoline was deduced from its ^1H NMR spectrum which is shown in Table I.

Basic hydrolysis of the pyrazoline acetate, IIIa, following Oppenauer oxidation gave the 3-oxo-4-pregneno[20,21-*c*]-1'-phenyl-5'-(2-pyridinyl)pyrazole (IV).

A variety of conditions and reagents have been used for cyclizing α,β-unsaturated carbonyl compounds with phenylhydrazine to produce pyrazolines, through phenylhydrazone formation (*2*).

Experimental Section

Melting points were determined on a Fisher-Jones melting point apparatus and are uncorrected. The IR spectra were recorded with a Perkin-Lmer 298 in solid-phase potassium bromide (KBr). NMR spectra were determined with a Varian XL-100 instrument, using deuteriochloroform as a solvent and tetramethylsilane as the internal standard.

Elemental analyses were performed by the Analytical Laboratory of Nuclear Research Center "Demkocritos". All of the compounds gave elemental analyses (C, N, H) within ±0.45 of the calculated values.

21-(2-Pyridylmethylene)-5-pregnen-3β-ol. To a solution of 3β-acetoxy-5-pregnen-20-one (I; 11.11 g) and pyridine-2-carboxaldehyde (2.255 g) in absolute ethanol (260 mL) a solution of sodium–ethanol (6.3 g, of sodium in 190 mL of absolute ethanol) is added. The mixture is agitated at room temperature

Table I Proton NMR Data in Deuteriochloroform Solution[a]

	chemical shifts (δ)		
protons	IV	IIIa	II
18-CH_3	0.62	0.64	0.68
19-CH_3	1.12	0.98	1.00
3-CH_3COO–		2.00	1.99
17-H	2.76		
4-H	5.66		
6-H		5.34	5.39
21-H	6.56	2.83 (A), 3.22 (B)	6.20 (cis), 6.48 (trans)
22-H		5.15	6.70 (cis), 7.08 (trans)
α-pyridyl	8.55	8.57	8.56 (cis), 8.66 (trans)

	coupling const, Hz		
IV	J_{AB} = 17.5	J_{AX} = 7.5	J_{BX} = 12
II	J_{trans} = 17	J_{cis} = 12	

[a] The cis and trans isomers of II are present at a ratio 40:60 as estimated from the intensities of the α-pyridyl from resonances 8.56 and 8.66, respectively. The assignment is based on the relative size of the coupling between 21-H and 22-H.

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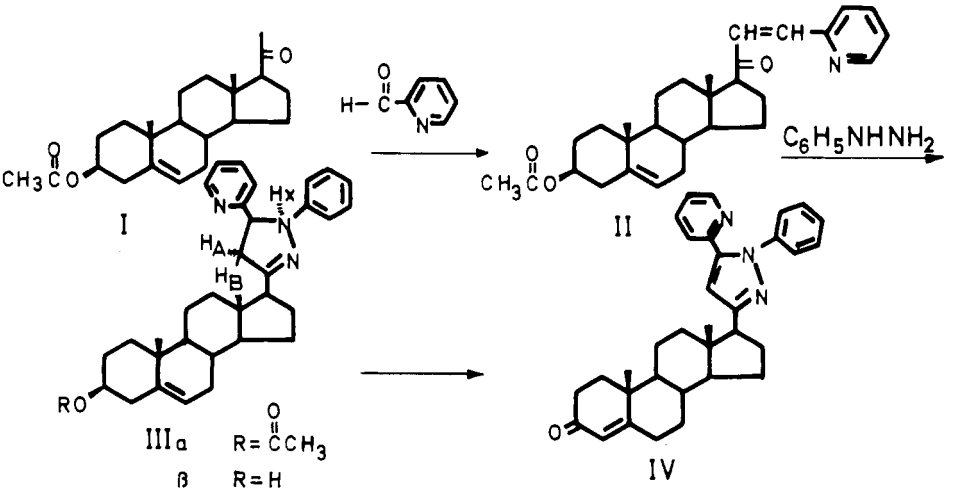
Scheme I



for 24 h. Then water was added and extracted several times with chloroform. After evaporation of the solvent the residue was acetylated with pyridine–acetic anhydride; yield 7.5 g; mp 132–134 °C (acetone–water); IR V_{max} 1730 cm^{-1}; 1240 cm^{-1} (CH_3CO); 1610 cm^{-1} (C=C).

3β-Acetoxy-5-pregneno[20,21-c]-1′-phenyl-5′-(2-pyridinyl)pyrazoline (III). To a solution of II (4.7 g) in ethanol (100 mL) containing hydrochloric acid (3 mL), phenylhydrazine (1.2 g) is added. The resultant solution is refluxed for 24 h. Then water was added and neutralized with ammonium hydroxide. The precipitate was collected by filtration, dried, and acetylated with pyridine–acetic anhydride at room temperature. Then the usual work up and column chromatography from silica gel (eluent chloroform) gave 4.0 g of III. Recrystallization from methanol gives mp 115–117 °C; IR V_{max} 1730 cm^{-1}; 1250 cm^{-1} (CH_3CO).

3-Oxo-4-pregneno[20,21-c]-1′-phenyl-5′-(2-pyridinyl)-pyrazole (IV). Pyrazoline (III) (1.5 g) was dissolved in 200 mL of methanol containing 2 g of sodium hydroxide. The mixture was refluxed for 1.5 h. The reaction mixture was poured into water and the precipitate, collected by filtration, was washed several times with water and dried to yield IIIβ (1.3 g).

To a solution of IIIβ (0.5 g) in 7 mL of cyclohexanone, 20 mL of dry dioxane and 20 mL of dry toluene was distilled slowly as a solution of aluminum isopropylate (0.8 g) in dry toluene (6 mL) was added. Distillation was continued for 2 h as 15 mL of toluene was added and 30 mL of distillate was collected. Then the mixture was refluxed for 4 h and left to stand at room temperature overnight. The mixture was filtered to remove the precipitate containing the aluminum. The filtrate was distilled, extracted with chloroform, and evaporated. The volatile constituents were removed by steam distillation. The residue was extracted with chloroform and evaporated. Column chromatography from silica gel (eluent chloroform:methanol, 98:2) gave pyrazole IV (1.15 g), which was recrystallized from chloroform–methanol; mp 249–251 °C; IR V_{max} 1670 cm^{-1}; 1615 cm^{-1} (C=C).

Registry No. I, 1778-02-5; (*E*)-II, 110027-50-4; (*Z*)-II, 110027-56-0; (*E*)-II·AcOH, 110027-51-5; (*Z*)-II·AcOH, 110027-57-1; IIIa, 110027-52-6; IIIa·AcOH, 110027-53-7; IIIb, 110027-54-8; IV, 110027-55-9; pyridine-2-carboxaldehyde, 1121-60-4.

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2-Pyrazinyl-2-arylalkanenitriles

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A series of new 2-alkyl-2-(3,4-dialkylphenyl)-2-pyrazineacetonitriles (3) was prepared from readily available starting materials by a simple, efficient, two-step sequence. The products are potential herbicides.

Compounds of the type **2** and **3** have been reported in the patent literature (*1*, *2*) to possess sedative and anticonvulsive activity. Pyrazineacetonitriles (**3**) (Scheme I) were prepared in our lab for testing as herbicides.

2-Substituted acetonitriles were reacted at room temperature with 2-chloropyrazine under basic conditions (NaOH) in dimethyl sulfoxide (DMSO) (*3*, *4*) to afford **2** in high yields. Syntheses of these compounds previously reported (*1*) used drastic conditions ($NaNH_2$/toluene, reflux or liquor ammonia/dioxane) and the yields were lower (27–80%) than ours (70–90%). Compounds **2** with base (see Table I) and the appropriate alkyl halide gave **3** in fair to very good yields, usually by simple workup. Thus, quenching of the reaction mixture with water

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