NEW COMPOUNDS

A Convenient Synthesis and Spectral Properties of Some New Iminium and 2-Azaallenium Salts

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Disubstituted iminium hexachloroantimonate salts 1a–c and 1,1-diamino-substituted 2-azaallenium salts 2a–d have been synthesized. The structures of these new compounds were established by IR, ^{1}H NMR, ^{13}C NMR, and elemental analysis data.

Recent advances in 2-azaallenium salts chemistry in the past few years have called attention to the development of new methods to synthesize these versatile compounds (*1–4*). We now report a simple method for the synthesis of some new 2-azaallenium salts. The procedure involves the initial preparation of iminium hexachloroantimonate salts. Treatment of the latter salt with dialkylcarbodiimide affords 2-azaallenium salts **2a–d** in excellent yields (Scheme I).

Experimental Section

The melting points are uncorrected. Infrared spectra were recorded on Pye-Unicam SP3-100 spectrophotometer. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were determined on an NIC instrument in CD_3CN with Me_4Si as internal standard. Elemental analysis was carried out by M.H.W. Laboratories, Phoenix, AZ. The found elemental analysis data for carbon, hydrogen, and nitrogen were in good agreement with those calculated and submitted for review (Table I). Disubstituted imines were prepared by a literature procedure (*5*). Diisopropylcarbodiimide and dicyclohexylcarbodiimide were purchased from Fluka.

General Procedure for the Preparation of Iminium Salts 1a–c. Dry hydrogen chloride was bubbled through a solution of the imine (0.20 mol) in dry hexane (40 mL) at 0 °C. A white precipitate was formed. Antimony pentachloride (0.20 mol) was added dropwise to the reaction mixture which resulted in dissolution of the precipitate. The reaction mixture was stirred for 1 h at room temperature. The product was precipitated by slow addition of dry ether (30 mL). The stable salts **1a–c** were collected and recrystallized from dichloromethane/ether.

General Procedure for the Preparation of 2-Azaallenium Salts 2a–d. Iminium hexachloroantimonate (**1a,b**) (10 mmol) was suspended in anhydrous dichloromethane (20 mL) at room temperature. Dialkylcarbodiimide (10 mmol) in dichloromethane (20 mL) was added dropwise. The reaction mixture was stirred for 2 h, during which time the iminium salts (**1a,b**) were dissolved. The product was precipitated by slow addition of dry ether. 2-Azaallenium salts **2a–d** were collected and recrystallized from dichloromethane/ether.

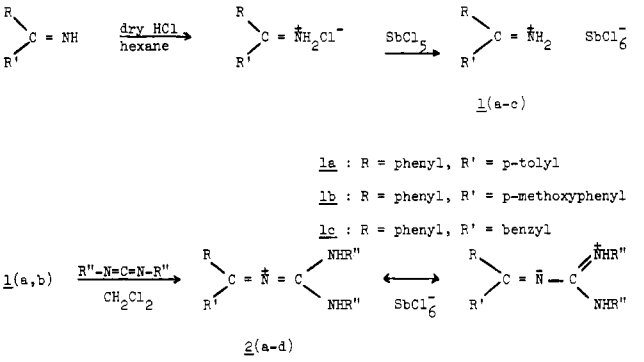
(Phenyl-p-tolylmethylene)ammonium Hexachloroantimonate (1a). Yield 97%, pale yellow powder, mp 146–148 °C. IR (KBr): 1580, 1650, 3240, 3320, 3380 cm^{-1}. ^{1}H NMR: δ 2.52 (s, CH_3, 3 H), 7.42–7.78 (m, aromatic, 9 H), 10.08 (t, NH_2, 2 H; J = 6.4 Hz). ^{13}C NMR: δ 22.2 (CH_3), 128.1, 130.5, 131.3, 133.0, 133.4, 137.3, 150.2 (aromatic), 185.4 (C=N).

{(p-Methoxyphenyl)phenylmethylene}ammonium Hexachloroantimonate (1b). Yield 98%, yellow crystals, mp 135–137 °C. IR (Kbr): 1590, 1640, 3240, 3320, 3400 cm^{-1}. ^{1}H NMR: δ 3.97 (s, CH_3O, 3 H), 8.02–7.42 (m, aromatic, 9 H), 10.12 (broad, NH_2, 2 H). ^{13}C NMR: δ 57.3 (CH_3O), 116.5, 122.8, 130.5, 131.8, 132.8, 136.5, 136.9, 168.5 (aromatic), 183.9 (C=N).

(Benzylphenylmethylene)ammonium Hexachloroantimonate (1c). Yield 95%, yellow crystals, mp 144–146 °C. IR (KBr): 1660, 3270, 3360 cm^{-1}. ^{1}H NMR: δ 4.60 (s, CH_2, 2 H), 7.25–8.05 (m, aromatic, 9 H), 10.35 (broad, NH_2, 2 H). ^{13}C NMR: δ 42.3 (CH_2), 129.8, 130.2, 130.7, 130.8, 130.9, 131, 132.2, 138.1 (aromatic), 191.1 (C=N).

{N,N'-Diisopropyl-N''-(phenyl-p-tolylmethylene)}guanidinium Hexachloroantimonate (2a). Yield 88%, pale yellow crystals, mp 126–128 °C. IR (KBr): 1600, 3335, 3370 cm^{-1}. ^{1}H NMR: δ 0.93 (d, $(CH_3)_2CH$, 6 H; J = 6.4 Hz), 1.22 (d, $(CH_3)_2CH$, 6 H; J = 6.4 Hz), 2.42 (s, CH_3, 3 H), 3.56 (m, CH, 1 H), 3.86 (m, CH, 1 H), 6.57 (d, NH, 1 H; J = 7.7 Hz), 6.70 (d, NH, 1 H; J = 8.1 Hz), 7.10–7.85 (m, aromatic, 9 H). ^{13}C NMR: δ 21.6, 22.5 ($CH_3)_2CH$), 21.7 (CH_3), 45.7, 48.1 (CH), 129.7, 130.5, 133.3, 135.9, 145.2 (aromatic), 160.8, 178.9 (C=N).

Scheme I. The Reaction of Disubstituted Iminium Hexachloroantimonate with Dialkylcarbodiimides



R" = isopropyl or cyclohexyl

Table I. Elemental Analysis

compd	analysis calcd (found) C%	H%	N%
1a	31.67 (31.90)	2.64 (2.83)	2.64 (2.63)
1b	30.74 (30.72)	2.20 (2.08)	2.56 (2.54)
1c	31.67 (31.40)	2.64 (2.88)	2.64 (2.76)
2a	38.38 (38.51)	4.26 (4.20)	6.40 (6.36)
2b	44.00 (44.12)	4.92 (4.92)	5.70 (5.74)
2c	37.50 (37.62)	4.19 (4.16)	6.24 (6.13)
2d	43.06 (42.25)	4.82 (4.80)	5.58 (5.47)

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{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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