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SYNTHESIS AND SOME REACTIONS OF HEXAHYDRO-3-OXO-1-ARYL-2-PHENANTHRENECARBOXANILIDES

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Treatment of 2-arylidene tetralone with acetoacetanilide gave the phenanthrenecarboxanilides 1a-b. 1a underwent condensation with 5-aminotetrazole, 3-amino-1,2,3-triazole and 2-amino-5-carboethoxythiazole to give compounds 2,3 and 5 respectively. The structures of these compounds were established by their IR, ^{1}H-NMR and mass spectral data.

Key words: Phenanthrenecarboxanilides; Synthesis; Reactions.

INTRODUCTION

Interest has been expressed in the pharmacological action and the synthetic potentialities of anilides [1]. From a synthetic point of view, such compounds are of considerable importance as intermediates in the synthesis of certain heterocycles carrying potential basic side-chains [2].

The reaction of such compounds with acetoacetanilide has been investigated to give β-ketoanilides [3].

The present work deals with the synthesis of some new hexahydrophenanthrenes (1a-b), their reactions with 5-aminotetrazole, 3-amino-1, 2,4-triazole, and 2-amino-5-carboethoxythiazole. Thus, treatment of 2-arylidene tetralone with acetoacetanilide gave (1a-b).

The assignment of structures (1a-b) are based on the IR, ^{1}H-NMR and mass spectral data. The IR spectrum of (1a) showed absorption bands at 3300 (NH), 1670(CO) and 1630 cm^{-1} (-CO-NH-). The ^{1}H-NMR spectrum of 1a displayed signals at δ 8.25 (s, 1H, -CO-NH-), 6.7 (s, 1H, olefinic) and 3.7 (s, 3H, OCH_3) in addition to aromatic and methylene protons. The mass spectrum of 1a gave an M^+ at 468 which conformed exactly with the molecular weight obtained.

The presence of the β-ketoanilide moiety in structures (1a-b) prompted us to undertake the synthesis of some new anilides carrying potential basic side-chains.

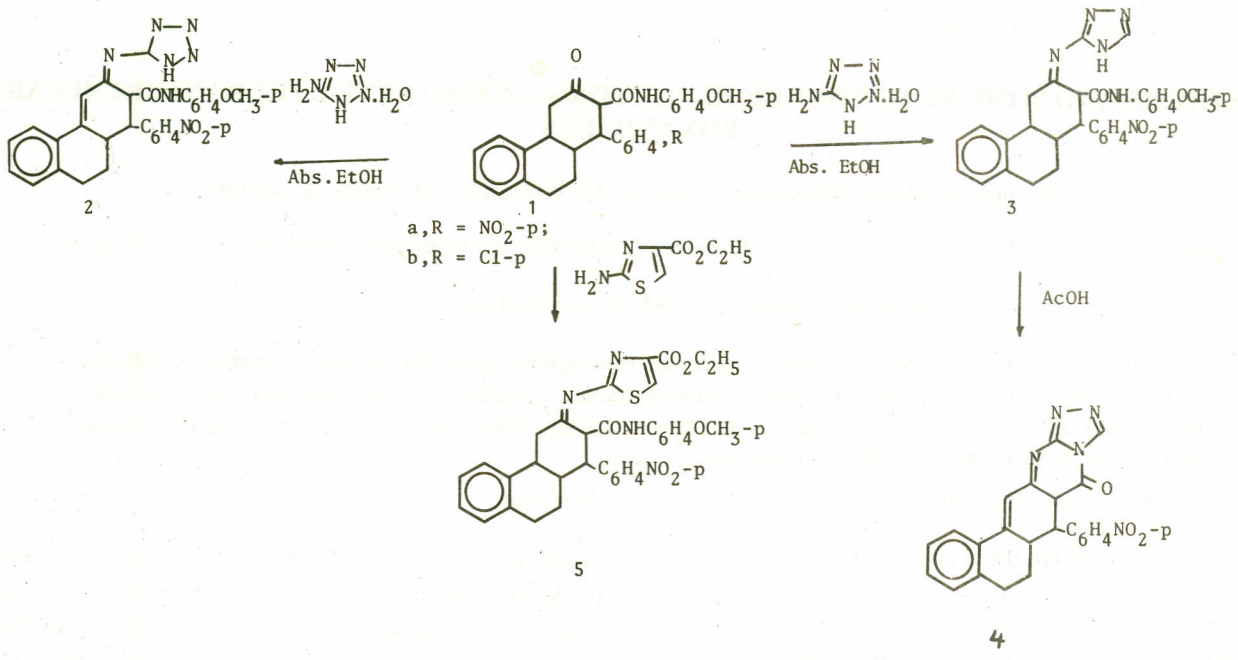
Thus the treatment of 1,2,3,9,10,10a-hexahydro-3-oxo-1-(p-nitrophenyl)-2-phenanthrenecarboxanilide (1a) with 5-aminotetrazole monohydrate in absolute ethanol afforded the tetrazole anil derivative (2). The assignment of structure (2) was based on the IR, ^{1}H-NMR and MS spectral data. The IR spectrum showed well-defined absorptions at 3325 (NH, tetrazole), 3035 (NH amide), 1630(CONH) and 1600 cm^{-1} (C=N). The ^{1}H-NMR spectrum displayed signals at δ 8.3(-CO-NH-), 7.7(N-H, tetrazole), 3.85(OCH_3). In the mass spectrum no molecular ion was noticed, but the observed fragment m/z 466, corresponding to $C_{28}H_{24}N_3O_4$, was obviously formed by the loss of the tetrazole fragment (CHN_4) from the parent ion.

In the same manner, condensation of (1a) with 3-amino-1,2,4-triazole in absolute ethanol afforded the anil derivative (3) as inferred from the ^{1}H-NMR spectrum, which displayed signals at δ 5.77 (s, 1H, olefinic phenanthrene), 7.72 (s, 1H, olefinic triazole). The mass spectrum showed no molecular ion, but upon loss of triazole fragment gave m/z 466. Boiling [3] with glacial acetic acid gave [4], as inferred from the absence of -NH- absorption in its IR spectrum.

In connection with the above condensation, treatment of (1a) with 2-amino-5-carboethoxythiazole under the same reaction conditions gave the anil derivative [5]. The IR spectrum showed absorption bands at 1630 (CONH), 1705 (CO ester) and 1605(C=N). The ^{1}H-NMR spectrum displayed signals at δ 7.17 (s, 1H, olefinic thiazole). The same behaviour in the mass spectrum has been noticed, namely, that the molecular ion upon the loss of 5-carboethoxythiazole gave a fragment at m/z 466.

EXPERIMENTAL

Melting points (uncorrected) were determined on a Gallenkamp electric melting point apparatus. Micro-analysis of the elements carbon, hydrogen and nitrogen were determined at the Institut fur Organishe Chemie, Tech. Hochschule Darmstadt, West Germany. IR spectra were recorded in KBr; ^{1}H-NMR spectra were determined with a Varian 90 MHz and MS were measured with an AET Ms-9 at 70 ev.



1,2,3,9,10, 10a-Hexahydro-3-oxo-1-laryl-2-phenanthrene carboxanilide (la and b). In a 250-ml flask was placed 0.002 mole of 2(p-nitro or p-chloro) arylidine-3, 4-dihydro-1 (2H) naphthalenone in 0.004 mole potassium methoxide and aceto-(*p*-methoxy) acetanilide (0.002 mole). The reaction mixture was refluxed for 8 hr, poured into ice cold dilute hydrochloric acid. The solid products that separated were filtered off, and crystallized from ethanol to give compounds (1 and b).

Compound (1a) formed pale-yellow crystals (91 % yield), m.p. 135°, IR(KBr), $\nu_{max}^{cm^{-1}}$: 3300(NH), 1670 (C=O) and 1630 (CO-amide), MS m/z (rel. int.) 468.49 [M^+] (4) (calcd for $C_{28}H_{24}N_2O_5$), 319(M-$C_8H_7NO_2$) (34), 215(319-C_8H_6) (7), 123(215-C_6H_6O) (100), ^{1}H-NMR(DMSO): δ 8.25(s, 1H,-CO-NH-), 6.7 (s, 1H, olefinic phenanthrene), 3.7 (s, 3H, OCH_3) and 7.2-8.1 (m, 12H, ARH).

Analysis: $C_{28}H_{24}N_2O_5$ (468.49)
Calcd : C, 71.77; H, 5.16; N, 5.98
Found : C, 71.88; H, 5.01; N, 6.33

Compound (1b): formed yellow crystals (82 % yield), m.p. 155°, IR(KBr), $\nu_{max}^{cm^{-1}}$: 3350 (NH), 1675(C=O) and 1645 (CO-amide).

Analysis: $C_{28}H_{24}NO_3Cl$(457.935)
Calcd : C, 73.43; H, 5.28; N, 3.05
Found : C, 73.66; H, 5.11; N, 3.21

Condensation of (1a) with 5-aminotetrazole monohydrate: Formation of the tetrazole anil derivative 2. A solution of (1a) (1x10^{-}≅ mole) and 5-aminotetrazole monohydrate (1x10^{-3} mole) in absolute ethanol (50 ml) was refluxed for 16 hr. The reaction mixture was left to stand for approximately 12 hr. when the solid product obtained was filtered off and recrystallized from ethanol to give compound (2) as brown crystals (50 % yield), m.p. 185°, IR(KBr), $\nu_{max}^{cm^{-1}}$: 3325(NH, tetrazole), 3035(NH, amide), 1630(CO-amide) and 1600(C=N), MS m/z(rel. int.) 466[MCN_4H] (1) (Calcd for: $C_{28}H_{24}N_3O_4$), 317(466-$C_8H_7NO_2$) (10), 123(317-$C_{20}H_{17}N_2O_2$) (80), 108(100), ^{1}H-NMR (DMSO) δ : 8.3(s, 1H, CO-NH), 7.7 (s, 1H,-NH, tetrazole), 3.85(s,3H,OCH_3) and 6.8-7.6 (m, 12H, Arh).
Analysis: $C_{29}H_{25}N_7O_4$(535.547)
Calcd : C, 65.03; H, 4.7; N, 18.3
Found : C, 65.58; H, 5.05; N, 17.91

Condensation of (1a) with 3-aminotriazole. Formation of the triazole anil derivative 3. This compound was synthesized in the same manner as above, from (1a) and 3-aminotriazole to give compound 3 in 60 % yield as brown crystals, m.p. 191-92°, IR(KBr), $\nu_{max}^{cm^{-1}}$: 3200 (NH, triazole), 3130(NH, amide), and 1600-1615(C=N), MS m/z (rel. int.) 466[M-$C_2H_2N_3$] (5) (Calcd for: $C_{39}H_{26}N_6O_4$), 317(466-$C_8H_7NO_2$) (3), 123(317-C_{20}≒$_{17}N_2O_2$) (100), ^{1}H-NMR(DMSO) δ : 8.2 (s, 1H, CO-NH), 7.8(s, 1H, -NH, triazole), 3.75(s,3H,)CH_3), 5.77(s, 1H, olefinic phenanthrene), 7.72 (s, 1H, olefinic triazole) and 6.85-7.65 (m, 12H, ArH).

Analysis : $C_{30}H_{26}N_6O_4$ (534.56)
Calcd : C, 67.4; H, 4.9; N, 15.72
Found : C, 67.48; H, 4.88; N, 15.95

Treatment of 3 with glacial acetic acid: Formation of 4. In glacial acetic acid (30 ml) was heated (0.25 g) of (3) under reflux for 3 hr. The reaction mixture was left to cool and poured into ice-cold water. The solid product that separated was filtered off, recrystallized from DMF to give compound 4 as brownish-black crystals in 45 % yield, m.p. 223°C, IR(KBr), $\nu_{max}^{cm^{-1}}$: 1675(C=O) and 1595-1615 (C=N).

Analysis : $C_{23}H_{17}N_5O_3$(411.41)
Calcd : C, 67.14; H, 4.16; N, 17.02
Found : C, 67.61; H, 4.51; N, 16.91

Condensation of 1a with 2-amino-5-carboethoxythiazole. Formation of 5. This compound was synthesized in the same manner as in (2), from (1a) and 2-amino-5-carboethoxythiazole to give compound 5 in 67 % yield, as brownish-red crystals, m.p. 126° IR(KBr), $\nu_{max}^{cm^{-1}}$: 3160 (NH, amide), 1705(C=O, ester), 1630 (C=O, amide and 1605(C=N), m/z (rel. int.) 466(M-$C_6H_6NSO_2$) (3), 317 (466-C_8H7NO_2) (2), 123(317-$C_{20}H_{17}N_2O_2$) (72), 43(100), ^{1}H-NMR (DMSO) δ : 8.35(s, 1H,-CO-NH), 7.17(s, 1H, olefinicthiazole), 3.6(s,3H,.CH_3) and 7.15-7.85 (m, 12H, ArH).

Analysis : $C_{34}H_{30}$(Å4SO_6(622.674).
Calcd : C, 65.57; H, 4.85; N, 8.99
Found : C, 65.83; H, 4.54; N, 8.63

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