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AMINOAZOLES IN HETEROCYCLIC SYNTHESIS
Synthesis of some pyrrolo Heterocycles[+]

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Condensation of 4-carbomethoxy-2,3-dioxopyrrolidines [1] with aminoazoles gave the linearly fused pyrroloheterocycles [2-6]. The structure of the hitherto unknown ring systems have been established by analytical and spectral data.

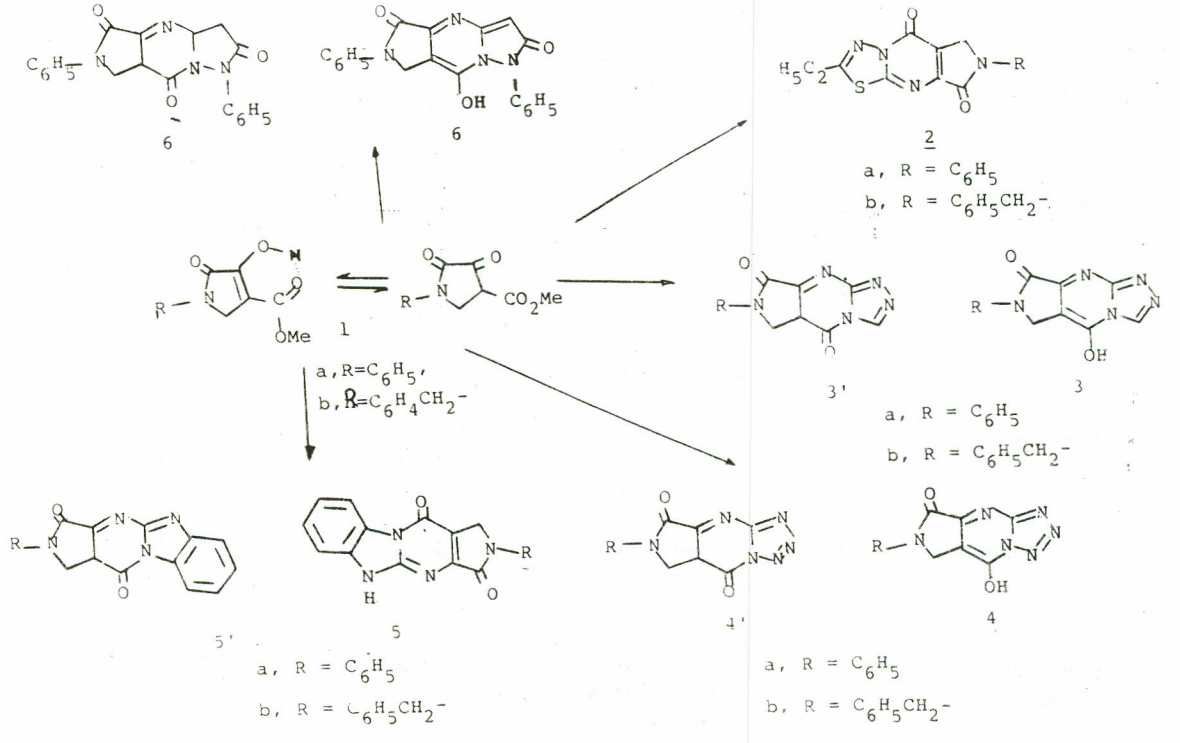
Key words: Aminoazoles, Pyrroloheterocycles.

INTRODUCTION

Cyclic β-keto ester reported to react with aminoazoles to give a linearly fused heterocycles [1-3]. A survey of the literature showed that condensed heterocycles having a fused pyrrolo nucleus have attracted little attention. Interest in the synthesis of fused heterocycles of potential biological activity [2] has prompted us to use 4-carbomethoxy-2,3-dioxopyrrolidines 1a & b [6] as heterocyclic β-keto esters.

It was found that 1 on reaction with 2-amino-5-ethylthiadiazole yielded pyrrolopyrimidones 2, as inferred from their IR spectra. The condensation of 2-amino-5-ethylthiadiazole with ethyl cyclohexanon-2-carboxylates as previously noted by us [2] and supported the formation of 2.

Compound 1 condensed with 3-amino-1,2,4-triazole, 5-aminotetrazole, 2-aminobenzimidazole and 3-amino-1-phenyl-2-pyrazolin-5-one to give 3,4,5– and 6 rather than



[+]Part 6 in the series of heterocyclic compounds with bridgehead nitrogen, for part 5 see, E.M. Kandeel and M.A. Metwally, Pakistan J. Sci. Ind. Res., 1988, in press.

3′, 4′, 5′ and 6′ depending on their correct analytical data their IR spectra and our previous work [3-5], (cf. Table 1)

EXPERIMENTAL

The melting points are uncorrected. The IR spectra were determined by KBr pellets on a Pye Unicam SP 2000 spectrophotometer.

Condensation of 1 with 2-amino-5-ethyl-1,3,4-thiadiazole: Formation of (2a&b). A mixture of 1 (1 x 10^{-3} mol) and 2-amino-5-ethyl-1,3,4-thiadiazole (1 x 10^{-3} mol) in dry xylene was refluxed for 4 hrs. After cooling a solid material was precipitated, which when crystallized with acetone gave compounds (2a&b) (Table 1).

Reaction of 1 with 3-amino-1,2,4-triazole: Formation of (3a&b). A solution of 1 (1 x 10^{-4} mol) and 3-amino-1,2,4-triazole (1 x 10^{-4} mol) in absolute ethanol (50 ml) containing few drops of piperidine was refluxed for 4 hrs. The reaction mixture was left to stand over-night. The solid product obtained was filtered off and recrystallized from ethanol to give compounds (3a&b) (Table 1).

Interaction of 1 with 5-aminotetrazole monohydrate: Formation of (4a&b). In 50 ml NaOMe 0.015 mol of Na-metal in 50 ml of dry methanol containing 1 x 10^{-3} mol of 1 was added (0.01 mol) to 5-aminotetrazole monohydrate. The reaction mixture was refluxed for 6 hrs., diluted with ice-cold water and acidified with dilute acetic acid (pH $\simeq$ 4). The solid product that separated was crystallized with ethanol to give compounds (4a&b) (Table 1).

Table 1. Characterization data of compounds (2-6).

Compd. No.	Col- our	M.P. °C	Yield %	IR cm^{-1}	Mol. F (M. Wt.)	Analysis Found (%) C	Analysis Calcd. (%) H
2a	White	180	60	1690, 1680 (C=O) & 1610 (C=N)	$C_{15}H_{12}N_4SO_2$ (312.34)	57.42 57.67	3.91 3.87
2b	White	250	65	1695, 1675 (C=O) & 1605 (C=N)	$C_{16}H_{14}N_4SO_4$ (326.36)	58.66 58.87	4.41 4.32
3a	White	179	70	3380 (OH) 1710 (C=O) & 1600 (C=N)	$C_{13}H_9N_5O_2$ (267.24)	58.35 58.42	3.59 3.39
3b	White	>250	60	3405 (OH) 1695 (C=O) & 1610 (C=N)	$C_{14}H_{11}N_5O_2$ (281.27)	60.01 59.77	4.21 3.94
4a	Brown	>250	55	3390 (OH) 1690 (C=O) & 1605 (C=N)	$C_{12}H_8N_6O_2$ (268.23)	53.91 53.72	2.95 3.00
4b	White	204	62	3395 (OH) 1695 (C=O) & 1615 (C=N)	$C_{13}H_{10}N_6O_2$ (282.26)	55.41 55.31	3.81 3.57
5a	White	>250	50	3160 (NH) 1700 (C=O) & 1600 (C=N)	$C_{18}H_{12}N_4^4O_2$ (316.31)	68.11 68.34	3.93 3.82
5b	Light orange	225	64	3100 (NH) 1695 (C=O) & 1610 (C=N)	$C_{19}H_{14}N_4O_2$ (330.33)	69.21 69.07	3.93 4.27
6	Pale yellow	186	53	3360 (OH), 1700, 1680 (C=O) & 1605 (C=N)	$C_{20}H_{14}N_4O_3$ (358.34)	66.61 67.03	4.61 3.93

Condensation of 1 with 2-aminobenzimidazole: Formation of (5a&b). These compounds were synthesized from 1 and 2-aminobenzimidazole in the same manner as (3a&b) and crystallized with DMF (Table 1).

Reaction of 1 with 3-amino-1-phenyl-2-pyrazolin-5-one: Formation of 6b. This compound was synthesized from 1 and 3-amino-1-phenyl-2-pyrazolin-5-one as (4a&b) and crystallized with ethanol (Table 1).

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