New Synthesis for norbornene from 4-amoniantipyrine

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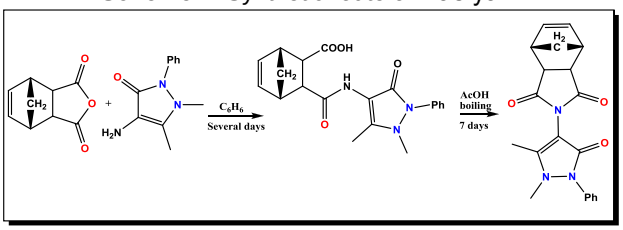
INTRODUCTION

In 2006, Kas'yan[1] et al. reported the synthesis of several bicycle [2.2.1] hept-5-ene-endo, endo-2, 3-dicarboxilic anhydride (endic anhydride) with cyclic non-aromatic amines.

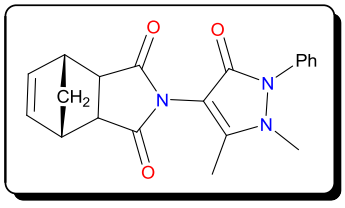
It is known that these compounds were used as components of repellent compositions[2] and as agents endowed with sedative activity[3]. One of the products formed was *N*-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-4 pyrazolyl) bicyclo [2.2.1] hept-5-ene-endo, endo-2,3-dicarboximide (**1**) (**Figure 1**) derived from 4-aminoantipyrine.

Scheme 1. Synthetic route of Kas'yan.



To prepare the compound **1** is required two steps: a) formation of a derivative norbornene acid and b) closure of imidic ring (Scheme 1) using several days with yields of 86% and 74%, respectively.

Figure 1. Structure of compound (**1**).

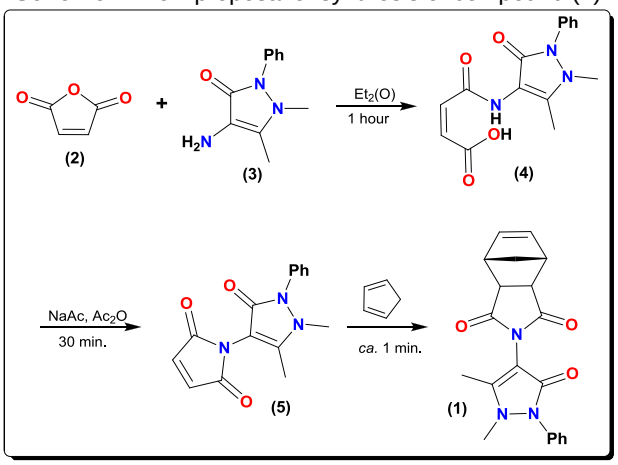


In view of the synthetic and biological relevance, we proposed the synthesis of the compound (**1**) in 90 min. (Scheme 2), using three steps: a) synthesis of maleamic acid (**4**) derived from 4-aminoantypirine (**3**), b) synthesis of maleimide derived from compound (**4**) and c) 4+2 coupling reaction (Diels-Alder) using cyclopentadiene.

RESULTS AND DISCUSSION

In the first step the maleamic acid derivative (**4**) was synthetized in 70% yield and was used in the formation of dienophile (**5**) in the second step in 60% yield.

Scheme 2. New proposal of synthesis of compound (**1**).



To purify the compound (**4**) we used just filtration followed by washing with diethyl ether. In the next step the compound (**5**) was purified by recrystallization in ethanol and water 1:1.

The Diels-Alder reaction (step 3), at room temperature, produced just the *endo* adduct (**1**) in 80% yield.

The proposed synthetic route was performed in *ca.* 90 min. in good yield being faster than that proposed by Kas'yan which use days to synthetize the same compound (**1**).

The compounds were characterized by ^{1}H e ^{13}C NMR.

CONCLUSION

The new synthetic route proposed to produce the compound (1) was performed withsuccess in lesser time than the existing methodology in the literature.

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CAPES

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