

SYNTHESIS OF NEW NORBORNENONES WITH THE AMINOESTER GROUP

METHYL BICYCLO [2-2-1] HEPT 5-ENE 7-ONE 1-AMINO 2-CARBOXYLATES

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**SUMMARY.** Amino norbornenonecarboxylates were synthesized from methyl acrylate and amino butadienecarboxylates. This result is equivalent of amino cyclopentadienones Diels-Alder reaction. Amino butadienecarboxylates were prepared by prototropic transposition of the  $\beta$ -allenic aminoesters.

Many norbornenones, with the carbonyl group in the 7-position, can be obtained by the Diels-Alder reaction between suitable cyclopentadienones and dienophiles.<sup>1</sup> Norbornenone carboxylates have been prepared in the same way;<sup>2</sup> in this case the electronic demand may be inverted.<sup>3</sup> However, there exists no description of the representatives of this group of compounds bearing an amino function.

It must be noted that only a few representatives of amino cyclopentadienones have been obtained, and that they have been prepared from ynamines.<sup>4</sup> Moreover, the 2-dialkylamino phenyl cyclopentadienones are not stable.<sup>5</sup> The tetrakis-dialkylamino cyclopentadienones have been stabilized by an iron carbonyl complex.<sup>6</sup> But in none of these cases have the corresponding amino norbornenones been obtained.

We now wish to report a particularly convenient method for the synthesis of bicyclic terpenoid aminoesters. We have observed an unexpected and original enaminoester cyclisation.

Previous studies performed in our laboratory have focused on the synthesis of unsaturated aminoesters under mild conditions.<sup>7</sup> In particular, the first two authors have described some  $\beta$ -allenylaminoesters.<sup>8</sup>

The 2-amino butadienecarboxylates studied in this paper were prepared by prototropic transposition of the  $\beta$ -allenic aminoesters: treatment of 0,025 mole by HMPT solution (30 ml) of *t*-BuOK (0,0025 mole) in an ice bath. Total migration of the double bond took ten minutes. The reaction mixture was poured into ice cold water and extracted with ether.



The structure of 3 was assigned on the basis of elemental analysis, mass spectra and  $^1\text{H}$  and  $^{13}\text{C}$  NMR.<sup>11</sup> In order to confirm these structural assignments, a single crystal x-ray analysis was performed on adduct 3a.<sup>12</sup> An ORTEP drawing of the molecular structure is shown in figure 1.

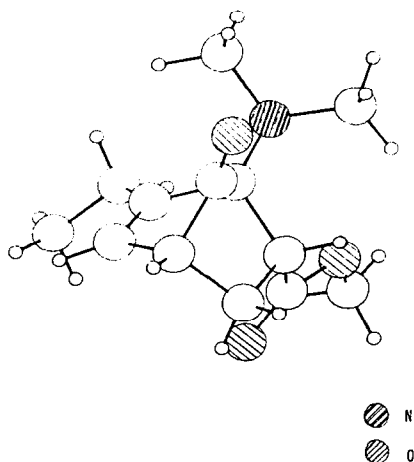


Figure 1

Everything occurs as though the amino butadienecarboxylate is first transformed through cyclisation in amino cyclopentadienone. The latter, which is undoubtedly very reactive, might be trapped by the methyl acrylate.

Both mechanistic and synthetic studies of this reaction are continuing.

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9. (a) Amino alkylbutadienecarboxylates  $\text{RCH}=\text{CH}-\text{CH}=\text{C}-\text{CO}_2\text{Me}$  ( $\text{R} \neq \text{H}$ ) have been described  

$$\begin{array}{c} | \\ \text{N(Me)Ph} \end{array}$$
  
 cf. Ahlbrecht, H.; Simon, H.; Synth. Comm. 1983, 61.  
 (b) 2b has previously been obtained by Stevens rearrangement of ammonium compounds  
 cf. Babayan, A. T.; Kocharyan, S. T.; Ogandzhanyan, S. M.; Dokl. Akad. Nauk Arm.  
 1974, 58, 100; C. A. 1974, 81, 359.
10. Yields are not optimised.
11. The NMR and IR spectral properties of all new compounds 2 (a, c-f) and 3 (a, b, c) are consistent with the assigned structures. Correct elemental analyses and parent ion exact mass spectral data were also obtained for all new compounds.
12. The crystals of 3a are triclinic, space group  $\bar{P}1$ ,  $a = 7.295(5) \text{ \AA}$ ,  $b = 7.925(8) \text{ \AA}$ ,  $c = 12.303(4) \text{ \AA}$ ,  $\alpha = 87.26(7)^\circ$ ,  $\beta = 93.51(5)^\circ$ ,  $\gamma = 113.81(9)^\circ$ ,  $V = 649.3(9) \text{ \AA}^3$ .  $\rho_c = 1.21 \text{ Mg.m}^{-3}$ , for 2 formula units per cell.. A total of 1928 independent reflections were collected of which 1700 were accepted as statistically above background on the basis that  $I \geq 3\sigma(I)$ . The structure was determined by direct methods using the Multan-80 program (Main, Hull, Lessinger, Germain, Declercq & Woolfson) and refined to a final  $R = 0.065$ .

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