Tetrahedron Letters,Vol.29,No.10,pp 1139-1142,1988 0040-4039/88 $3.00 + .00
Printed in Great Britain Pergamon Press plc

CAPTODATIVE DIENES IN CYCLOADDITION CONDITIONS:

SYNTHESIS OF NEW BICYCLO (3.2.0) HEPT-3-ENE-2-ONES

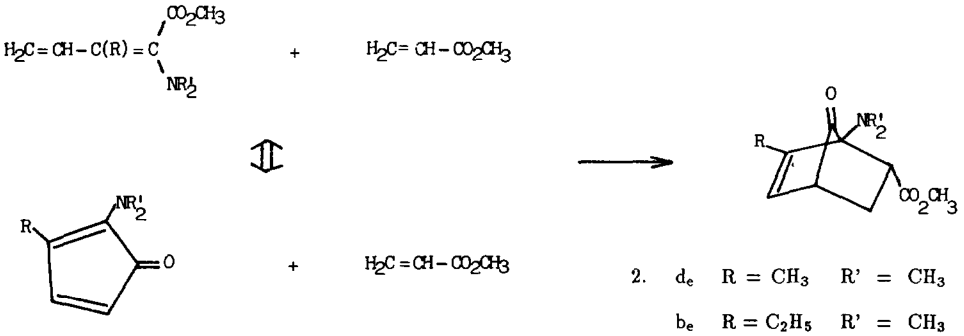
Mireille Bourhis*, René Golse, Edwige Adjanohoun, Jean-Jacques Bosc,
Michel Goursolle (UA 605)
Laboratoire de Chimie Générale, Université de Bordeaux II, 33000
Philippe Picard
Laboratoire de Cristallographie (UA 144), Université de Bordeaux I, 33400

SUMMARY : Aminobicyclo (3.2.0) heptenones and aminonorbornenones were obtained from methylacrylate or acrylonitrile and captodative dienes. They result from respectively (2+2) and (4+2) cycloadditions.

Very few functionalized derivatives of bicyclo (3.2.0) hept-3-ene-2-ones are known; such a compound bearing an acetal function in the 6- position has been described and is of some interest for prostaglandin synthesis[1]. We have found no reference to representatives of this group bearing an amino function.

We report the synthesis of bicyclo (3.2.0) hept-3-ene-2-ones bearing two other functions, one of which is an amino function in the 3-position. Conjugate dienic aminoesters are at the origin of these new bicycloheptenones.

Indeed, in a previous note[2], we pointed out the unexpected chemical behaviour of conjugate dienes of type 1. When the derivatives 1 for which R = CH_3, R' = CH_3; R = C_2H_5, R' = CH_3; R = C_2H_5, R'_2 = $(CH_2)_5$ are heated with a large excess of methylacrylate, they yield a large proportion of a product 2, an aminonorbornenone. Norbornenones usually result from a (4+2) cycloaddition involving a neutral or electron-deficient cyclopentadienone and a dienophile having a suitable electronic character[3]. Aminonorbornenones were unknown. Those aminonorbornenones could result from a (4+2) cycloaddition between methylacrylate and an aminocyclopentadienone formed by intramolecular cyclisation of the dienaminoester. The new results that we describe here speak in favour of this hypothesis.

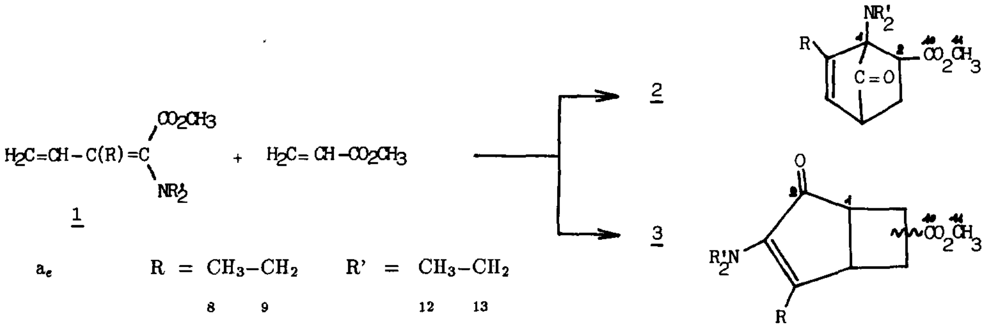


2. d_e $R = CH_3$ $R' = CH_3$

b_e $R = C_2H_5$ $R' = CH_3$

c_e $R = C_2H_5$ $R'_2 = (CH_2)_5$

Indeed we consider now the case of a diene 1a for which $R = C_2H_5$, $R'_2 = (CH_2)_5$. The diene 1a (0.025 mole) is heated up to 90°C with 30 cm^3 of methylacrylate for 72 hours. The excess methylacrylate is evaporated. The polymers are precipitated with Et_2O. After an analytical HPLC of the remaining oil, separation is performed by preparative HPLC. Two products are obtained. The first is the N,N-diethylaminonorbornenone $2a_e$ and comes from a (4+2) cycloaddition. Structural study of the second product reveals a N,N-diethylaminobicyclo (3.2.0) hept-3-ene-2-one $3a_e$ resulting from a (2+2) cycloaddition.



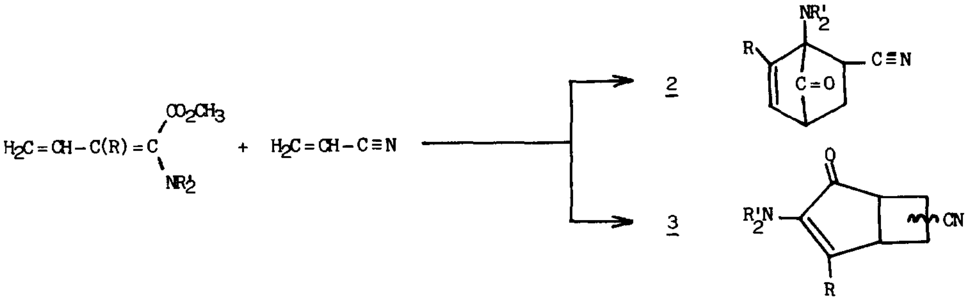
a_e $R = CH_3{-}CH_2$ $R' = CH_3{-}CH_2$

8 9 12 13

$2a_e/3a_e$ 60/40 $2a_e+3a_e$ 55%

The nature of the substituted amino function orientates the reaction toward a (4+2) or a (2+2) cycloaddition. Some authors have noticed this influence with respect to the reaction of aminocyclopentadienones on acetylenedicarboxylates[4]. They indicate that the unstable (4+2) and (2+2) adducts are the precursors of phtalates and tropones that they have isolated.

We then proceeded with acrylonitrile as a dienophile. Dienes 1 (0.025 mole) and acrylonitrile (30 cm^3) are heated up to 80^0C for 36 hours. The excess acrylonitrile is evaporated, the polymers are precipitated with ether. The remaining oil is purified by preparative HPLC. For all the dienes 1, $R = C_2H_5$, a $R'_2 = (CH_2)_5$, b $R' = CH_3$, c $R'_2 = C_2H_5$, we isolated (2+2) and (4+2) cycloadducts. It is known that, in the special cases described in ref.[5], (4+2) and (2+2) cycloaddition reactions can be of comparable energetic levels.



a_n	$R = C_2H_5$	$R' = C_2H_5$	2/3	50/50	2 + 3	60%
b_n	$R = C_2H_5$	$R' = CH_3$	2/3	65/35	2 + 3	40%
c_n	$R = C_2H_5$	$R'_2 = (CH_2)_5$	2/3	80/20	2 + 3	50%

Like many captodative compounds[6], conjugate dienic aminoesters have specific chemical properties. This special reactivity allows the synthesis of new bicyclic molecules[7]: nitrile or carboxylate aminoketones.

ACKNOWLEDGEMENTS : The authors wish to thank Mss. Petraud, B. Barbe and G. Bourgeois (CESAMO Bordeaux I) for the recording and assignment of ^1H NMR, ^{13}C NMR and Mass spectra.

REFERENCES AND NOTES.

1. Vandewalle, M.; Claeys, M.; De Keukeleire, D.; De Wilde, H.; Mijngheer, R.; Termont, D.; Chem. Biochem. Pharmacol. Act. Prostanoids, Incl. Proc. Symp. 1978, (Pub. 1979), 149.

2. Bourhis, M.; Golse, R.; Goursolle, M.; Picard, P.; Tetrahedron Lett. 1985, 25, 3445.

3. a) Ogliaruso, M. A.; Romanelli, M. G.; Becker, E. I.; Chem. Rev. 1965, 65, 261.
   b) Sasaki, T.; Kanematsu, K.; Iisuka, K.; J. Org. Chem. 1976, 41, 1105.
   c) Yasuda, M.; Harano, K.; Kanematsu, K; J. Org. Chem. 1980, 45, 659.
   d) Mori, M.; Hayamizu, A.; Kanematsu, K.; J. Chem. Soc. Perkin Trans. 1981, 4, 1259.

4. Eicher, T.; Urban, M.; Chem. Ber. 1980, 113, 408.

5. a) Epiotis, N. D.; J. Am. Chem. Soc. 1972, 94, 1924.
   b) Houk, K. N.; Acc. Chem. Res. 1975, 8, 361.

6. a) Viehe, H. G.; Merenyi, R.; Stella, L.; Janousek, Z.; Angew. Chem. Int. Ed. Engl. 1979, 18, 917.
   b) Viehe, H. G.; Janousek, Z.; Merenyi, R.; Stella, L.; Acc. Chem. Res. 1985, 18, 148.
   c) Creary, X.; Mehrsheikh-Mohammadi, M. E.; J. Org. Chem. 1986, 51, 2664.
   d) Stevenart-De Mesmaeker, N.; Merenyi, R.; Viehe, H. G.; Tetrahedron Lett. 1987, 28, 2591.

7. a) All new compounds $2a_e$, $3a_e$, $2a_n$, $3a_n$, $2b_n$, $3b_n$, $2c_n$, $3c_n$, gave consistent IR, ^1H, ^{13}C NMR, mass spectra and elemental analysis.

   b) Radiocristallographic study shows (Goursolle, M.; Bourhis, M.; H'Naifi, A.; Acta Crist. 1986, (C) 42, 1641) that methylacrylate (4+2) cycloaddition is regio and stero specific. An analogous study of (4+2) and (2+2) acrylonitrile adducts is underway.

   c) Selected spectral data IR film $2a_e$ 1780, 1740; $3a_e$ 1730, 1690, 1610, 1600; $2a_n$ 2220, 1780; $3a_n$,2210, 1690, 1610, 1590 cm^{-1};

   NMR ^{13}C ($CDCl_3$) ppm $2a_e$ C_7 207.9, C_{10} 176.0, C_6 149.5, C_5 123.9, C_1 78.6, C_{11} 52.0, C_4 42.3, C_{12} 45.7, C_2 38.2, C_3 30.1, C_8 21.7, C_{13} 13.8, C_9 10.5; $2a_n$ C_7 205.0, C_6 151.2, C_5 125.7, C_{10} 120.6, C_1 77.3, C_4 43.0, C_{12} 44.0, C_3 31.8, C_2 26.5, C_8 21.9, C_{13} 14.9, C_9 10.4; $3a_e$ C_2 209.0, C_3 174.4, C_{10} 170.4, C_4 147.3, C_{11} 51.9, C_{12} 46.1, C_1 C_5 41.6, 41.3, C_6 C_7 39.6, 23.7, C_8 21.5, C_{13} 13.7, C_9 11.4; $3a_n$ C_2 207.1, C_3 164.9, C_4 148.3, C_{10} 121.2, C_{12} 45.5, C_1 C_5 42.6, 39.6, C_6 C_7 25.9, 24.9, C_8 21.9, C_{13} 13.7, C_9 11.6.

(Received in France 22 October 1987)