Tetrahedron Letters,Vol.30,No.43,pp 5919-5922,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

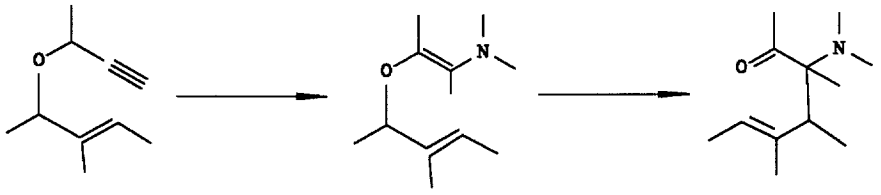
SYNTHESIS OF 2-MORPHOLINOPENTA-3,4-DIENAL DERIVATIVES AND PROPARGYLOXYENAMINES BY CATALYTIC AMINOMERCURATION OF DIPROPARGYL ETHERS.

José Barluenga*, Fernando Aznar, Miguel Bayod and José M. Alvarez.
Departamento de Química Organometálica, Universidad de Oviedo,
33071 Oviedo, Spain.

Summary : *Propargyloxyenamines and/or 2-morpholinopenta-3,4-dienal derivatives are obtained by catalytic aminomercuration of dipropargyl ethers depending on their substituents.*

We have previously reported the preparation of β-allyloxyenamines **1** by catalytic aminomercuration of allyl propargyl ethers. These enamino derivatives undergo [3,3] or [1,3] rearrangements, furnishing 2-morpholinopent-4-enals **2** almost quantitatively[1,2] (Scheme 1).

Scheme 1



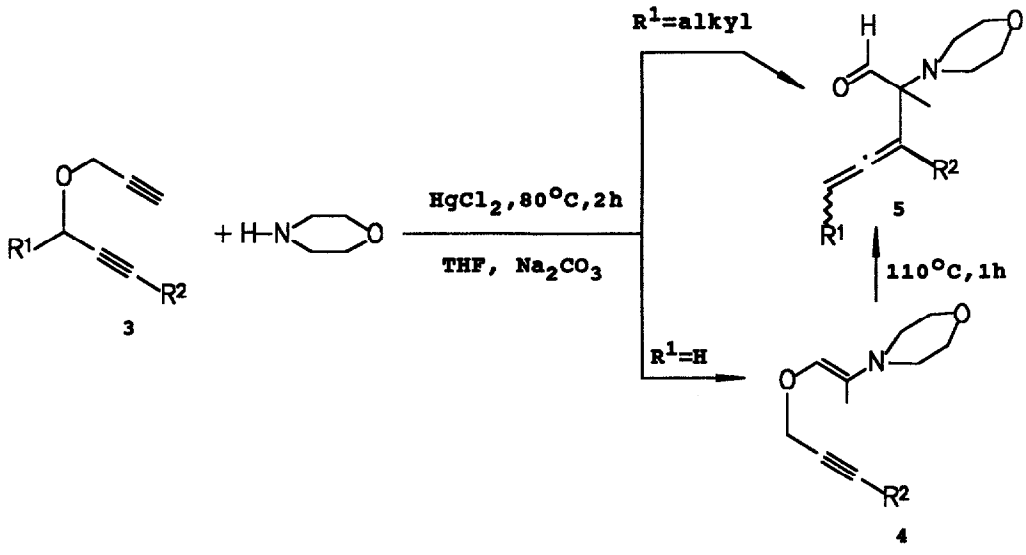
1 **2**

As it was shown, the rate and the stereochemistry of the Claisen rearrangements strongly depend on the position and type of the substituents, finding that the amino group always cause an increase in the reaction rate.[2]

These results encouraged us to extend the reaction to the easily available dipropargyl ethers **3**, having a terminal triple bond ($R^2 \neq H$). These systems would give the enamine derivatives since only the terminal triple bond is active in the catalytic aminomercuration process, as previously reported..[3] Thus, when the reaction was carried out under conventional conditions for catalytic aminomercuration in the presence of aliphatic amines (alkyne : $Hg(OAc)_2$: morpholine, 20 : 15: 60) the terminal triple bond was aminated, as expected . However, the other triple bond played a role because a complex between enamine and mercury (II) salts was formed instead of free enamine , and attempts to remove the mercury salts from the complex

led to the formation of furan derivatives.[4] This fact prompted us to explore new aminomercuration conditions in order to obtain the propargyloxyenamines **4** (Scheme 2).

Scheme 2



4	R^1	R^2
a	H	CH_3
b	H	$Si(CH_3)_3$

5	R^1	R^2
a	H	CH_3
b[6]	H	$Si(CH_3)_3$
c	CH_3	Ph
d	Et	Ph
e	^iPr	Ph

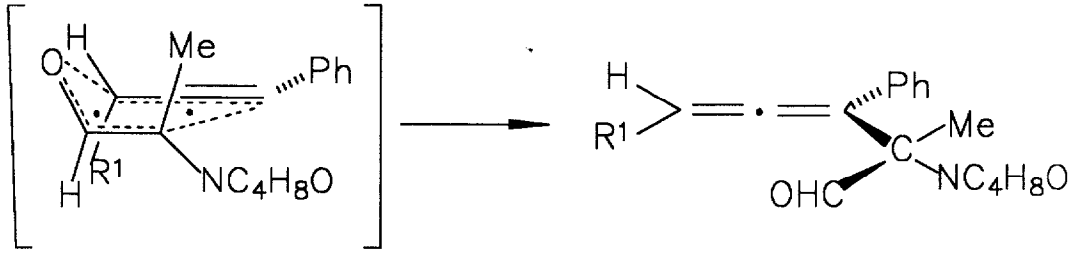
In this paper we wish to report a convenient method for the preparation of this kind of compounds **4** as well as their transformation into the corresponding α-allenic α-morpholino aldehydes **5**. (Scheme 2)

When dipropargyl ethers **3** (R^1 = H) and morpholine were allowed to react in the presence of catalytic amounts of $HgCl_2$ (molar ratio **3** : morpholine : $HgCl_2$, 10 : 100 : 2) at 80 °C[5] for 2h in a Na_2CO_3 satu rated solution of THF the enamines **4** were obtained in good yields (Scheme 2). These enamines undergo a [3.3] Claisen rearrangement by heating at 110 °C for 1 h giving rise to the aminoaldehydes **5**. On the other hand, the catalytic amination of the dipropargyl ethers **3** (R^1 = alkyl) in the above conditions directly yielded the corresponding aminoaldehydes **5(c-e)**. These results can easily be understood by taking into account that a donor substituent in the 4-position of the enamine increases the rate of the Claisen rearrangement.[2]

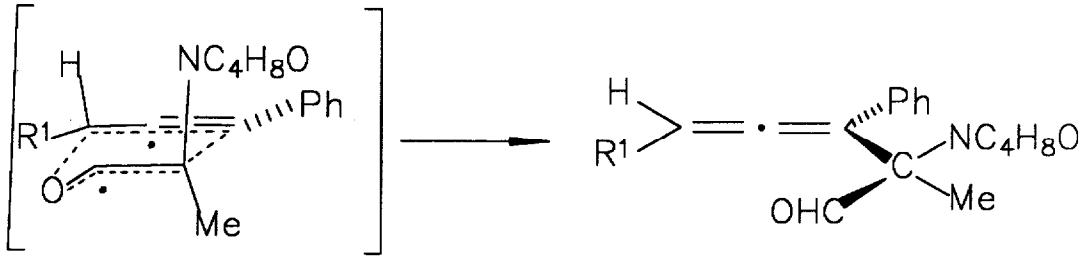
Finally, from the point of view of stereoselectivity, when $R^1 = CH_3, CH_3CH_2, (CH_3)_2CH$ a diaste-

reoisomeric mixture of **5A** and **5B** was formed in a molar ratio of about 1 : 2. These results can be rationalized by admiting that semichair transition states **A** and **B**, which would lead to **5A** and **5B** respectively, operate and that, unlike the latter transition state suffers from 1,3-pseudoaxial interactions; therefore, the formation of **5B**, as the major diastereoisomer, is easily understood as it arises from the more stable transition state **B**. The higher stereoselectivity found in the case of allyloxyenamines **1**[2], in which the rearrangement is completely stereoselective, compared to that observed in this case, should be clearly due to the more effective 1,3-diaxial intereactions in the corresponding chair-like transition state.

Scheme 3



A **5 A**



B **5 B**

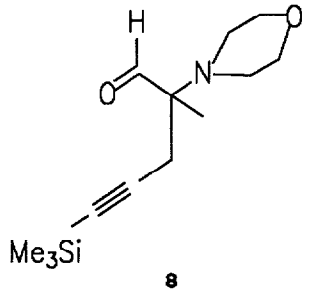
Experimental : In a typical run, to a solution of **3** (10 mmol) and morpholine (100 mmol) in anhydrous THF (15 ml) (saturated in Na_2CO_3 anh.) was added $HgCl_2$ (2 mmol). The mixture was allowed to warm to 80 °C, and stirred. After 2 h the reaction was cooled to room temperature and, filtered under argon. The volatile components were in vacuum eliminated and the reaction crude was trap-to-trap condensed in va-

cuum (0.001 torr, preheated oil bath temperature 100-110 °C) leading to the compounds **5 (c,d,e,f)** or **4 (a,b)**. [E.g. (**4a**) yield 67 %, **^{1}H-NMR** ($CDCl_3$/TMS) δ = 1.7 (d,3H,J = 1Hz); 1.8 (t,3H,J = 2.3Hz); 2.7-3.0 (m,4H); 3.5-3.8 (m,4H); 4.2 (q,2H,J = 2.3Hz); 5.7 (q,1H,J = 1Hz) ppm.[7] **^{13}C-NMR** ($CDCl_3$) δ = 3.3(q), 12.1(q), 49.5(t), 59.7(t), 66.3(t), 74.2(s), 83.5(s), 128.5(d), 132.4(s) ppm.[7]
Heating 1 g of **4a**,(110 °C, 1 h), and trap-to-trap condensation (0.001 torr)led to 0.95 g of **5a**. **^{1}H-NMR** ($CDCl_3$/TMS) δ = 1.1(s,3H); 1.6(t,3H,J = 3.2Hz); 2.3-2.45(m,2H); 2.5-2.6(m,2H); 3.6-3.8(m,4H); 4.7(q,2H,J = 3.2Hz); 9.4(s,1H) ppm.[7] **^{13}C-NMR** ($CDCl_3$) δ = 10.7(q), 14.3(q), 47.3(t), 67.3 (t),69.7 (s), 76.7(t) 98.2(s),201.1(d), 208.7(s) ppm.[7] **MS m/e** = 178 (M^+-15), 166 (M^+-28).

Acknowledgment : Financial Support of this work by Comisión Asesora de Investigación Científca y Técnica (CAICYT) is gratefully acknowledged.

REFERENCES AND NOTES

1.- J.Barluenga, F.Aznar, R. Liz, M. Bayod, *J.Chem.Soc.,Chem. Commun.*, **1984**, 1427.
2.- J.Barluenga, F.Aznar, R.Liz and M.Bayod, *J.Org.Chem.*, **1987**, *52*,, 5190.
3.- J.Barluenga, F.Aznar, R.Liz,and R.Rodes, *J.Chem. Soc., Perkin Trans I*, **1983**, 1087.
4.- J.Barluenga, F.Aznar, and M.Bayod,*Tetrahedron Lett.*, **1988**, *39*,, 5029.
5.- When the reaction was carried out at lower temperature only the dialkynylmercury compound was formed and the catalysis process did not progress.
6.- .In this case compound **8** resulting from a [1.3] sigmatropic rearrangement was always formed in ca 20 % yields.



8

7.- Recorded on a Bruker AC-300 Spectrometer.

(Received in UK 11 December 1988)