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A VERY SIMPLE SYNTHESIS OF DIVINYLKETONES.

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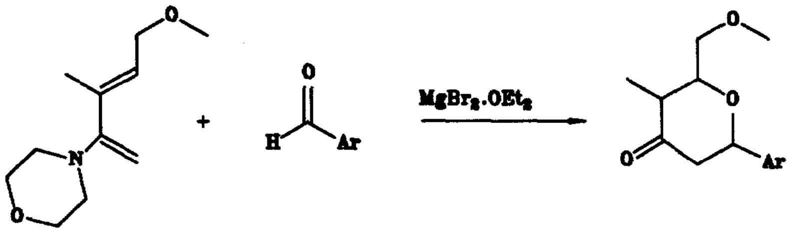
Summary: Divinylketones are synthesized from aromatic aldehydes and 2-morpholinobutadiene derivatives in good yields.

Divinylketones are important starting materials in synthetic organic chemistry. They have been extensively used not only in the Robinson annulation[1] and Michael addition reactions,but also as dienophiles in the Diels-Alder reaction [2]; moreover, the synthesis of substituted cyclopentanones and cyclopentenones from these compounds by the Nazarov reaction[3] is a versatile route for preparing of cyclopentanoid natural products.

Althougt there are several methods suitable for the preparation of simple systems[4],only a few number of them allow the synthesis of highly functionalized divinylketones[5]

On the other hand , we have described recently the preparation of 4-oxanone derivatives **2** [6] by reaction of the very easily available 2-morpholinobutadiene **1** with aromatic aldehydes and $MgBr_2 . OEt_2$ (Scheme I).

Scheme I

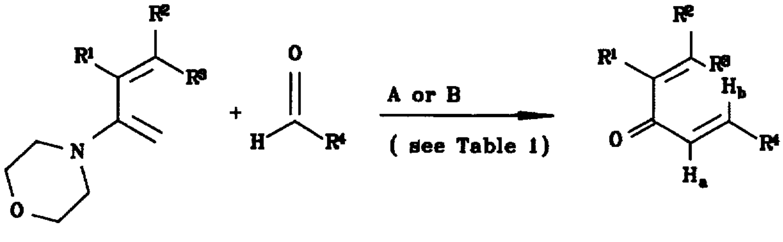


1 **2**

In this work we report that the treatment of 2-morpholinobutadienes **3** with aromatic aldehydes **4**[7] in the presence of $MgBr_2 \cdot OEt_2$ (Method A) or $ZnCl_2$ (Method B) leads after hydrolysis (50% AcOH/ H_2O solution) to the divinylketones 5 in a stereoselective fashion (Scheme II, Table I).

^{1}H-NMR data show compounds **5** to have the E configuration ($J_{Ha\text{-}Hb}$ = 15-17 Hz).

Scheme II



3 **4** **5**

Some representative examples of the divinylketones **5** prepared from 2-morpholinobutadienes **3** are summarized in *Table I*[8]. The divinylketones **5i** and **5j** are obtained from **3** when R^2= CH_2-O-Si(CH_3)$_3$.

Table 1. Preparation of divinylketones from 2-aminobutadienes.

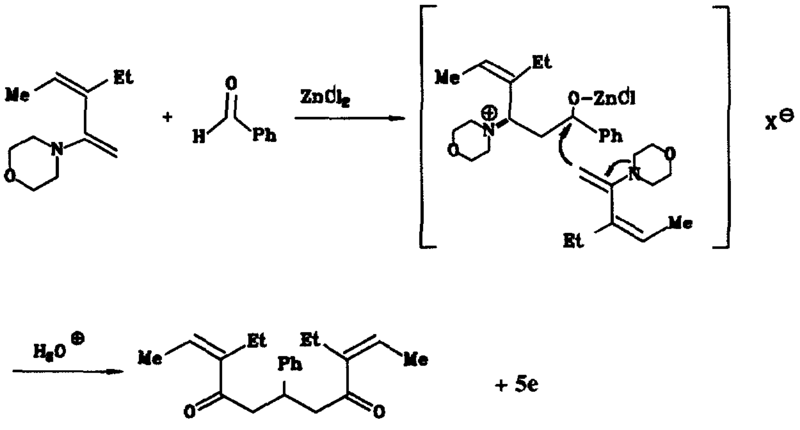
Divinylketone	R^1	R^2	R^3	R^4	Method^a (A or B)	Yield^b (%)
5a	$-CH_3$	$-CH_2-O-CH_3$	H	Phenyl	A	87
5b	$-CH_3$	$-CH_3-O-CH_3$	H	p-Cl-Phenyl	A	72
5c	$-CH_3$	$-CH_2-O-CH_3$	H	2-Furyl	A	84
5d	$-CH_3$	$-CH_2-O-CH_3$	H	2-Thienyl	A	62
5e	$-CH_2-CH_3$	H	$-CH_3$	Phenyl	B	64
5f	$-CH_2-CH_3$	H	$-CH_3$	p-Cl-Phenyl	B	65
5g	$-CH_2-CH_3$	H	$-CH_3$	2-Thienyl	B	45
5h	$-(CH_2)_4-$		H	2-Furyl	A	69
5i	$-CH_3$	$-CH_2-OH$	H	Phenyl	A	77
5j	$-CH_3$	$-CH_2-OH$	H	2-Furyl	A	87

a) Method A **3**:**4**:$MgBr_2 \cdot OEt_2$ (molar ratio 1:2:2, CH_3CN, 25 °C, 6h). Method B **3**:**4**:$ZnCl_2$(molar ratio 1:2:2, THF, 70 °C, 8h).b) Isolated yield after trap to trap high vacuum (10^{-5} Torr) condensation. All new compounds were characterized by high resolution NMR and mass spectral analysis.

It is noteworthy that the 2-morpholinobutadiene **3** (R^1 = Et, R^2= H, R^3 = Me) reacts with benzaldehyde in the presence of $ZnCl_2$ (molar ratio 3 : 1 : 1, CH_3CN, 25 °C, 6h.) affording after hydrolysis a 3:1 mixture of **6** and **5e** (Scheme III); the diketone **6** is rapidly isolated by destillation (65% yield based on benzaldehyde)[8]

The formation of **6** as the exclusive regioisomer can be understood by assuming that the initial addition reaction to the carbonyl group is followed by a nucleophilic attack of a second molecule of the 2-morpholinobutadiene at the oxygen-substituted carbon atom of the adduct. The structure of **6** has been deduced from its ^{1}H- and ^{13}C-NMR and MS spectra.

Scheme III



6

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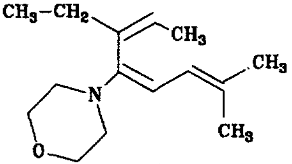
7. The reaction with aliphatic aldehydes under the same reaction conditions affords a very complex mixture. However, isobutylaldehyde is able to react with **3** (R^1=Et, R^2=H and R^3=Me) in the presence of $ZnCl_2$ (THF, 25°C, 6h) to give the enamine **7**.



7

8. **Spectroscopic data** *e. g.* **4c**. ^{1}H-NMR($CDCl_3$) δ= 1.8(s,3H), 3.4(s,3H), 4.2(d,2H), 6.4(dd,1H), 6.5(d,1H), 6.7(t,1H), 7.1(d,1H, *J*= 15.36 Hz), 7.3(d,1H,*J*= 15.36 Hz), 7.4(d,1H) ppm. ^{13}C-NMR (neat) δ= 11.8(q), 58.1(q), 69.5(t), 112.6(d), 115.5(d), 118.5(d), 128.2(d), 138.2(s), 138.4(d), 144.9(d), 151.7(s), 189.8(s) ppm. MS (m/e): 206 (M^+). **6** ^{1}H-NMR($CDCl_3$) δ= 0.9(t,6H), 1.6(d,6H), 2.1(t,4H), 2.9(d,4H), 3.7(m,1H), 5.6(q,2H), 7.3(s,5H) ppm. ^{13}C-NMR (CCl_4) δ= 13.9(q), 15.6(q), 27.7(t), 37.1(d), 40.8(t), 127.9(d), 128.3(d), 128.4(d), 129.0(d), 144.4(s), 144.8(s), 196.0(s) ppm. MS (m/e): 320 (M^+). **7** ^{1}H-NMR($CDCl_3$) δ= 0.8(t,3H), 1.4(d,3H), 1.7(s,3H), 1.72(s,3H), 2.1(t,2H), 2.6-2.9(m,4H), 3.5-3.7(m,4H), 5.3(d,1H), 5.5(q,1H), 5.6(d,1H) ppm. ^{13}C-NMR (neat) δ= 13.1(q), 15.2(q), 18.7(q), 26.9(q), 30.7(t), 49.5(t), 67.5(t), 102.5(d), 123.8(d), 124.8(d), 127.4(s), 138.7(s), 147.4(s) ppm. MS (m/e): 235 (M^+).

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