

## Elimination Reaction over Solid Supports under Microwave Irradiation : Synthesis of Functionalized Alkenes

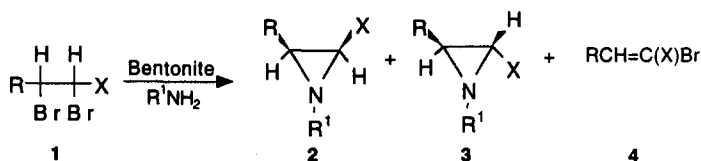
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**Abstract:** Treatment of 1,2-dibromocompounds with KF supported on alumina, or bentonite/Et<sub>3</sub>N under microwave irradiation leads to an elimination reaction which produces functionalized alkenes in fair yields.  
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The use of alumina and bentonite as heterogeneous catalysts for various organic reactions is well documented<sup>1,2</sup>. We have previously reported the synthesis of aziridines by reacting dibromo compounds with amines over bentonite<sup>3</sup>. These early results have shown that coupling bentonite supported reaction with microwave irradiation promoted the formation of  $\alpha$ -bromo alkenes (Scheme 1).

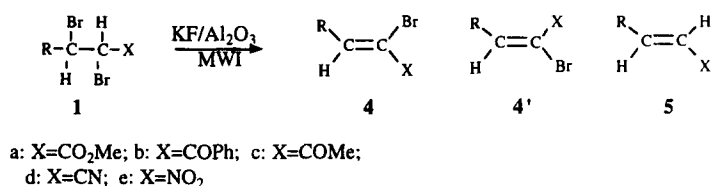


Scheme 1

In order to obtain exclusively functionalized alkenes, which are useful intermediates in organic synthesis<sup>4</sup>, we decided to study this reaction in details. The present paper describes the behaviour of the 1,2-dibromo compounds 1 under various conditions.

Elimination from dibromide 1 carried out over KF-Alumina under microwave irradiation led to an isomeric mixture of  $\alpha$ -bromo alkenes, and in some cases debromination occurs to give 5 (Scheme 2). The reaction with a series of dibromides was examined and the results are summarized in Table 1.

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Scheme 2

Table 1: Formation of alkenes over KF/Al<sub>2</sub>O<sub>3</sub> under MW irradiation or classical heating<sup>5</sup> within 30 minutes

Entry	R	X	Reaction Solvent	Conditions Temp(°C)	%4	Alkenes %4'	(%) %5	Ref
1	Ph	CO <sub>2</sub> Me	CH <sub>3</sub> CN	80	57	43		6
2	//	//	(b)	80	32 <sup>c</sup>	15	7	
3	//	//	(b)	130	55		45	
4	//	//	CH <sub>3</sub> CN <sup>d</sup>	80	40	60		
5	//	COPh	CH <sub>3</sub> CN	80	(e)			7
6	//	COMe	CH <sub>3</sub> CN	80	93		7	8
7	//	//	(b)	80	34 <sup>c</sup>		10	
8	//	//	(b)	130	80		20	
9	//	//	CH <sub>3</sub> CN <sup>d</sup>	80	90	10		
10	CH <sub>3</sub>	CN	CH <sub>3</sub> CN	80	60	40		9
11	//	//	(b)	80	60	40		
12	//	//	(b)	130	78	22		
13	//	//	CH <sub>3</sub> CN <sup>d</sup>	80	57	43		
14	Ph	NO <sub>2</sub>	CH <sub>3</sub> CN	80	55 <sup>c</sup>			10
15	//	//	(b)	80	70 <sup>f</sup>		15	
16	//	//	(b)	130	20 <sup>f</sup>		20	
17	//	//	CH <sub>3</sub> CN <sup>d</sup>	80	100			

<sup>a</sup>Yields estimated by <sup>1</sup>H NMR. <sup>b</sup>Reaction without solvent. <sup>c</sup>Reaction is not quantitative, starting materials are detected.

<sup>d</sup>Classical heating. <sup>e</sup><sup>1</sup>H NMR does not allow the percentage estimation. <sup>f</sup>Formation of benzaldehyde.

Table 1 shows that the ratio of the corresponding alkenes is highly dependent on the experimental conditions. The conversion of dibromides **1** was complete when acetonitrile was used as solvent. A series of experiments were performed without solvent under various temperatures. At 80°C, dibromides gave partial dehydrohalogenation, but when the temperature increased the reaction afforded alkene **5**, the debromination product. To our knowledge this is the first example of debromination in dry media under microwave irradiation. Usually debromination of dibromides to alkenes is performed using various reducing agents<sup>11</sup>. The generation of alkenes was also observed when alumina was used alone, but after 30 minutes the reactions were not quantitative and the selectivity was the same. Under classical heating the elimination of dibromide gave a different composition of isomers (entries 1,4 and 6,9) which could result from a microwave effect. The

obtention of two isomers Z and E may be explained by a E1cB mechanism, the intermediate carbanion undergoing a C-C bond rotation. In the case of dibromide **1d** (starting from the mixture of erythro and threo isomers) elimination gave Z and E isomers.

The exception was dibromonitrophenylethane **1e**, when the temperature increased (130°C) elimination reaction gave 60% of benzaldehyde which results probably from hydrolysis of  $\alpha$ -bromo nitroalkene. KF-Alumina was found to promote the hydrolysis of  $\alpha$ -bromo nitroalkene in these conditions.

We also examined the elimination reaction over bentonite in the presence of triethylamine under microwave irradiation at 80°C for 30 minutes. The experimental results are reported in Table 2

Table 2: Formation of alkenes over bentonite/Et<sub>3</sub>N under MWI<sup>12</sup>

Entry	R <sup>1</sup>	X	%4	% 4'	% 5
1	Ph	CO <sub>2</sub> Me	45	55	
2	Ph	COMe	75	25	
3	CH <sub>3</sub>	CN	58	42	
4	Ph	NO <sub>2</sub>	100		

The above results show that reaction with bentonite proceeds more selectively, without debromination products. The ratio of Z and E isomers is nearly equivalent with KF-Alumina.

In conclusion our experimental procedure provides an easy and efficient way to prepare  $\alpha$ -bromo alkenes. We are currently exploring the debromination in these various conditions.

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## References and Notes

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- 5 *General procedure for the dehydrohalogenation by KF/Al<sub>2</sub>O<sub>3</sub>* : The KF-Alumina reagent prepared from alumina (5g) and KF (1.2 g) dried in a kitchen microwave oven in an open 50 ml becker (500 W) during 5 mn, was mixed with dibromide **1** (1.5 10<sup>-3</sup> mol). The reaction mixture with acetonitrile or without solvent was introduced in a Synthewave 402® (Prolabo) single mode apparatus (4 cm, Ø, reactor). After irradiation at the temperature given in Table 1 (temperature is monitored either at 80 or 130°C by continuous adjustment of the power between 15 and 240 Watts) for 30 minutes, the products were extracted with dichloromethane. Thermal reactions were carried out in an oil bath previously set at the

temperature monitored in the microwaves oven. The crude mixture was analyzed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR and compared with the literature data.

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- 11 March, J.; *Advanced Organic Chemistry: Reactions, Mechanism, and Structures*, 2<sup>nd</sup> Ed.; Mc Graw Hill International; New York, **1977**, p 946-7 and references cited therein.
- 12 *Reaction with bentonite/Et<sub>3</sub>N*:  $5 \cdot 10^{-3}$  mole of dibromocompound **1** are mixed with bentonite (2g) and triethylamine (1eq) is added at room temperature. The reaction mixture was stirred for 30 minutes, under microwave irradiation. After usual work up, the products were identified by their spectroscopic data.