
PREFERENTIAL *cis*-OLEFIN FORMATION: A STRIKING RESEMBLANCE BETWEEN ALKALI-ALKOXIDE AND ALUMINA PROMOTED ELIMINATIONS IN LOW POLAR SOLVENTS*

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Olefin-isomer distribution has been investigated in the Woelm alumina promoted elimination from a series of 2-decyl and 5-decyl derivatives (X = F, Cl, Br, I, OTs) in ether. From the observed effect of leaving group it has been inferred that the heterogeneous reaction is a concerted process. A comparison has been made with corresponding results from homogeneous, alkali-alkoxide promoted eliminations in low polar solvents. A striking similarity in steric course between the two reactions has been noted and explained in terms of acid-base co-catalysis.

As we pointed out earlier¹, selectivity of homogeneous, metal alkoxide promoted elimination from alkyl halides and tosylates is in low polar solvents remarkably anomalous. Contrary to a simple expectation, distribution of olefin isomers in the reaction is concentration-dependent^{2,3}. Proportion of *cis* and terminal alkenes increases with increasing concentration of metal alkoxide in the reaction. Prevalence of the less stable isomers is frequently observed at high base concentrations⁴⁻⁶. We have shown in the preceding paper⁷ that concentration-dependent solvation of leaving group by metal ion is the responsible factor.

Notably, a preferential *cis*-olefin formation was noted earlier also by Posner⁸ in a heterogeneous elimination of 2-octyl tosylate promoted by Woelm neutral alumina in ether; no explanation for the steric outcome has been however offered.

Aiming to explore possible mechanistic analogies between the homogeneous and heterogeneous reactions, we have investigated in a more detail steric course of the Woelm promoted elimination with a wider structural range of substrates. In this paper we report the results obtained from a homologous series of 2-decyl and 5-decyl halides and tosylates (X = F, Cl, Br, I, OTs).

* Part LI in the series Elimination Reactions; Part L: Collect. Czech. Chem. Commun. 55, 695 (1990).

EXPERIMENTAL

Materials: 2-Decyl and 5-decyl halides and tosylates were prepared as described previously^{4,5}. Woelm neutral alumina (W-200-N) was dried at 400°C for 6 h and stored in an exiccator over P₂O₅. Ether was distilled and stored over sodium.

General procedure for elimination runs: Reaction flasks were dried in oven (120°C), filled with Woelm alumina (1.5 g) and closed with rubber septum caps. A solution of a substrate (0.2 mmol) and internal standard (decane, dodecane) was added and the contents were shaken occasionally (25°C). Aliquots were withdrawn with a syringe in appropriate time intervals and analyzed by gas-chromatography^{4,5}.

Control experiments: Within limits of experimental error no isomerisation of the investigated olefins was observed on the Woelm alumina under conditions of the elimination runs. It was found moreover that olefin-isomer distribution remained practically constant up to completion in the elimination runs.

RESULTS AND DISCUSSION

Olefin-isomer distribution data obtained in the Woelm alumina promoted elimination from 2-decyl halides and sulphonates in ether are summarized in Table I. A very pronounced effect of leaving group takes place in the reaction. It is found that percentage of 1-alkene and, at the same time, also the value of *cis*-2-alkene/*trans*-2-alkene ratio decrease in the elimination series in the order F > OTs > Cl > Br > I. This pattern of results provides a strong evidence that the alumina-promoted elimination does not proceed via carbenium ion (E1) but represents rather a concerted E2-like process⁹. The corresponding data we obtained previously⁴ from the homogeneous E2 reaction of 2-decyl derivatives with potassium tert-butoxide in benzene are included for a comparison in Table I. A striking resemblance between the hetero-

TABLE I

Olefin-isomer distribution in heterogeneous and homogeneous eliminations from 2-decyl derivatives in low polar solvents

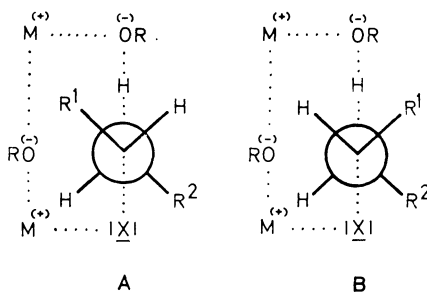
X	Woelm-N-Alumina/Ether		t-C ₄ H ₉ OK/Benzene ^a	
	% 1-decene	<i>cis/trans</i> ^b	% 1-decene	<i>cis/trans</i> ^b
F	42.3	4.8	94.0	2.0
OTs	28.5	3.3	88.2	1.5
Cl	19.2	3.3	68.0	1.5
Br	15.5	2.8	79.9	1.25
I	12.2	1.5	66.1	0.68

^a Taken from ref.⁴; ^b *cis*-2-decene/*trans*-2-decene ratios.

geneous and the homogeneous elimination is apparent; with a single exception ($X = I$; $t\text{-C}_4\text{H}_9\text{OK}/\text{C}_6\text{H}_6$), *cis*-olefin prevails always over *trans*-isomer in the reaction.

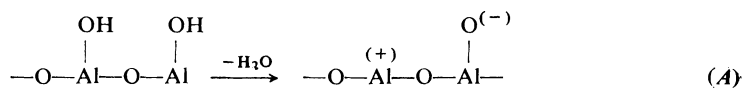
A quite analogous situation has been found in the elimination reaction of the positionally-isomeric 5-decyl derivatives (Table II).

As we already pointed out in the preceding paper⁷, a cooperation of an "active" and "passive" base species is anticipated in the alkali alkoxide promoted eliminations performed in low polar solvents as visualized in Scheme 1. As the "active" base we denote the alkoxide species which is involved in proton abstraction from $\text{C}_\beta\text{—H}$ bond, whereas the metal alkoxide which solvates leaving group and participates electrophilically in $\text{C}_\alpha\text{—X}$ bond breaking is referred to as the "passive" base. In accord with Scheme 1 it is assumed that steric interference between the "passive" base and alkyl portion of the substrate creates a selective hindrance to the metal ion solvation of leaving group in the transition state for *trans*-alkene formation (A). In the transition state for the *cis*-isomer (B), the solvation is unaffected because the metal ion has a free access to the leaving group from that side where only hydrogen atoms are placed.



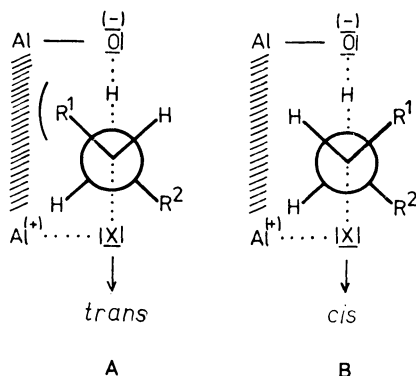
SCHEME 1

An entirely analogous steric situation can be portrayed for the alumina promoted elimination proceeding on the solid surface. Pairwise formation of acidic and basic sites by dehydration of surface hydroxyl group on alumina has been suggested by Pines and Manassen¹⁰, in accordance with the general equation (A).



A cooperative action of the neighbouring acidic and basic sites may therefore take place in the heterogeneous elimination, with the acidic aluminium ($\text{Al}^{(+)}$) site inter-

acting electrophilically with leaving group (X) whilst the basic oxygen atom (O^-) attacks nucleophilically the hydrogen on the $C_\beta-H$ bond (Scheme 2). A pseudo-cyclic transition state accordingly arises which is sterically more shielded in the arrangement leading to *trans*- (A) than to *cis*- (B) olefin formation.



SCHEME 2

Comments on Some Related Results Reported in Literature

Dehydration of alcohols on alumina¹¹⁻¹³ is a well-known contact process which is conducted routinely at high temperatures. According to available evidence, the reaction involves *anti*-elimination of the elements of water from the α - and β -carbon

TABLE II

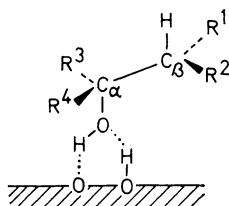
Olefin-isomer distribution in heterogeneous and homogeneous eliminations from 5-decyl derivatives in low polar solvents

X	Woelm-N-Alumina/Ether	t-C ₄ H ₉ OK/Benzene
	<i>cis/trans</i> ^a	<i>cis/trans</i> ^{a,b}
F	3.5	1.35
OTs	1.2	1.5
Cl	1.2	2.1
Br	1.2	1.8
I	0.63	— ^c

^a *Cis*-4- and 5-decene/*trans*-4- and 5-decene ratios. ^b The overall elimination consists of the *syn*- and *anti*-elimination pathways. The figures given correspond to the *anti*-pathway; cf. ref.⁵.

^c Not determined.

atoms. Whenever simultaneous formation of *cis*- and *trans*-olefins is possible, the *cis*-isomer is usually the predominant product. Taking into account these facts, Knözinger with coworkers¹³ have arrived to a mechanistic explanation which in main features is similar to Scheme 2. According to their proposal, a molecule of alcohol is adsorbed to alumina surface by means of a double hydrogen bond between hydroxyl groups located on substrate and alumina. The most favourable conformation is considered to be that in which the C_α—O bond in the alcohol molecule is directed perpendicularly to the surface of alumina (Scheme 3). In this arrange-



SCHEME 3

ment, the antiperiplanar hydrogen on C_β is too remote for interaction with the surface basic site. According to the authors, however, the molecule as a whole exercises vibrational motions by which the O—C_α—C_β—H plane may incline to the surface which is a prerequisite for the reaction. It is expected that the inclination may be opposed by steric interference between bulky alkyl substituents and the surface. Therefore, formation of the *cis*-isomer (R¹ and R³ = alkyl, R² and R⁴ = = hydrogen) is preferred since in course of the inclination both alkyl substituents remain in a position which is diverted away from the surface.

In this way it appears that hindrance to acid-base co-catalysis is a factor of a more general significance which controls steric course of a wide range of homogeneous as well as heterogeneous olefin-forming reaction.

REFERENCES

1. Bartsch R. A., Závada J.: *Chem. Rev.* **80**, 453 (1980).
2. Bartsch R. A., Pruss G. M., Cook D. M., Buswell R. L., Bushaw B. A., Wiegiers K. E.: *J. Am. Chem. Soc.* **95**, 6745 (1973).
3. Závada J., Pánková M., Bartsch R. A., Cho B. R.: *Collect. Czech. Chem. Commun.* **46**, 850 (1981).
4. Pánková M., Závada J.: *Collect. Czech. Chem. Commun.* **42**, 1981 (1977).
5. Závada J., Pánková M., Svoboda M.: *Collect. Czech. Chem. Commun.* **41**, 3778 (1976).
6. Závada J., Pánková M.: *Collect. Czech. Chem. Commun.* **42**, 3421 (1977).
7. Závada J., Pánková M., Vitek A.: *Collect. Czech. Chem. Commun.* **55**, 695 (1990).
8. Posner G. H., Gurria G. M., Babiak K. A.: *J. Org. Chem.* **42**, 3173 (1977).

9. Saunders W. H., Cockerill A. M.: *Mechanisms of Elimination Reactions*. Wiley, New York 1977.
10. Pines H., Manassen J.: *Adv. Catal. Relat. Subj.* 16, 49 (1966).
11. Noller H., Kladning G.: *Catal. Rev.* 13, 149 (1976).
12. Noller H., Andreau P., Hunger M.: *Angew. Chem.* 83, 185 (1971).
13. Knözinger H., Bühl H., Kochloefl K.: *J. Catal.* 24, 57 (1972).

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