

Note

Beckmann rearrangement of α -oximinoketones

B N Hitesh Kumar^{ab}, T Prakasam^{ab}, P S Srinivasan^a,
Bhanumathi Arabindoo^b & D V Ramana*^a

^aResearch and Development, Malladi Drugs and Pharmaceuticals Ltd., No. 52, Jawaharlal Nehru Road, Ekkattuthangal, Chennai 600 097, India

^bDepartment of Chemistry, College of Engineering, Anna University, Chennai 600 025, India
E-mail: dvramana@malladiinc.com

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The Beckmann rearrangement of α -oximinoketones gives benzoic acids as chief isolable products. Both first order and second order Beckmann rearrangements have been observed. The occurrence of first order Beckmann rearrangement in these oximinocarbonyl compounds is confirmed through the identification of the products obtained.

Keywords: First order, second order Beckmann rearrangements, oximinoketones, imide-like intermediate, substituted benzoic acids

The acid-mediated conversion of oximes to amides, the Beckmann rearrangement, is one of the oldest and well known transformations¹⁻⁹ in organic chemistry. Both normal (first order) and abnormal (second order) Beckmann rearrangement products are obtained when α -oximinoketones are treated with acid¹⁰. It has been demonstrated that α -oximinoketones in the presence of alcohol give the corresponding esters as one of the products during Beckmann rearrangement indicating that the reactions follow the second order mechanism with the formation of aroyl cations subsequently reacting with alcohol to produce the esters¹¹.

This mechanism involves the cleavage of the carbon-carbon bond with concomitant formation of nitrile and an acylium cation which forms the ester in the presence of alcohol. Both normal and abnormal Beckmann rearrangement products are reported to have been obtained from α -oximinoketones, but the mechanisms for these reactions have not been clearly established. Hence, the concise study of the mechanism of Beckmann rearrangement reactions of α -oximinoketones (compounds **1-10**, Table I) is now being undertaken. The melting points of these compounds are given in Table I.

Results and Discussion

The α -chloriminocarbonyl compounds formed *in situ* from the corresponding oximinoketones are refluxed with water to obtain the Beckmann products in all the cases. The products isolated in all these reactions are the corresponding benzoic acids. Three possible mechanisms are envisaged for the formation of benzoic acids in these reactions. In the first mechanism, the cleavage of the bond between the two sp^2 hybridised carbons leads to the formation of the aroyl cation which reacts with water to afford substituted benzoic acid (**Scheme I**).

In the second mechanism, water attacks the carbonyl group with the concomitant cleavage of the carbon-carbon bond giving rise to substituted benzoic acid as the isolable product (**Scheme II**).

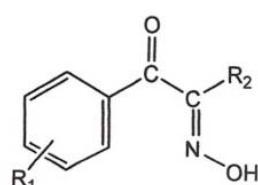
Table I—Compounds **1-10** and their melting points

Compd	R ₁	R ₂	Observed m.p. (°C)	Reported m.p. (°C)
1	H	H	126-28	127-28
2	* <i>m</i> -OCH ₂ -C ₆ H ₅	H	127-31	-
3	<i>p</i> -Cl	H	131-33	135
4	<i>m</i> -OCH ₃	H	127-31	117-18
5	<i>p</i> -CH ₃	H	85-87	98-100
6	H	CH ₃	112-14	113-15
7	<i>p</i> -OCH ₃	CH ₃	114-18	131
8	<i>p</i> -O-CH ₂ -C ₆ H ₅	CH ₃	142-45	138-39
9	* <i>p</i> -OCOCH ₃	CH ₃	128-30	-
10	<i>p</i> -Cl	CH ₃	114-18	116-17

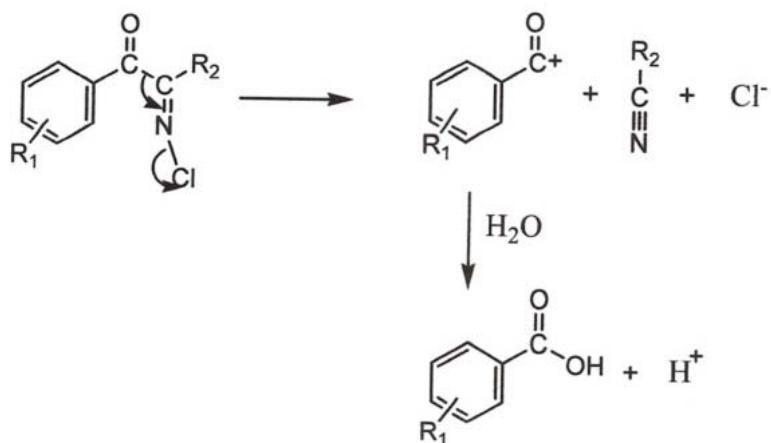
* Compounds are not reported in the literature. Microanalytical data for these compounds are given below:

Compd **2**: Anal. Calcd. for C₁₅H₁₃NO₃: C, 70.58; H, 5.09; N, 5.49. Found: C, 70.36; H, 5.40; N, 5.34%.

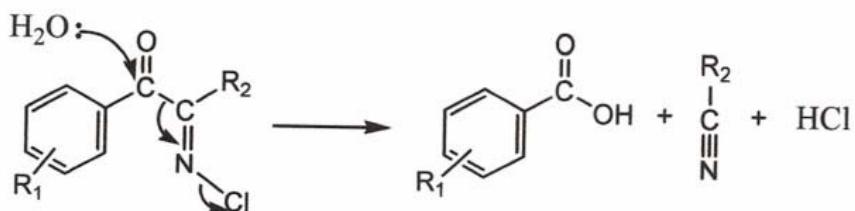
Compd **9**: Anal. Calcd. for C₁₁H₁₁NO₄: C, 59.72; H, 4.97; N, 6.33. Found: C, 59.42; H, 5.37; N, 6.12%.



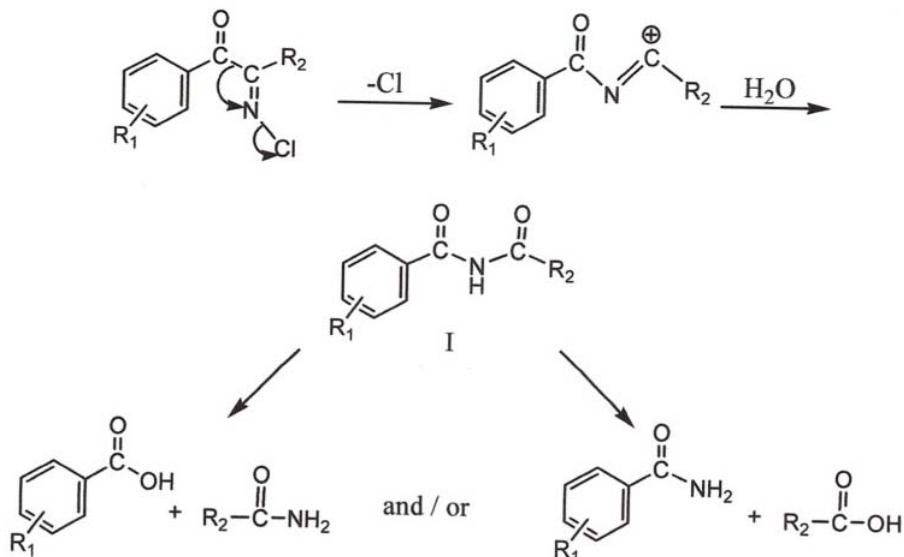
Compounds **1-10**



Scheme I



Scheme II



Scheme III

In the third mechanism, the migration of the aryl moiety from the carbon to the oximino nitrogen alongwith the bonding pair of electrons is postulated during the Beckmann rearrangement. Water attacks the resulting carbonium ion affording an imide-like intermediate I. The hydrolysis of the imide intermediate can take place by reaction of water molecule on either of the two carbonyl functions. The reaction

of water on the aryl carbon can lead to benzoic acid and acetamide or formamide. If water attacks the acyl or formyl carbons the two products that can form are benzamide and acetic or formic acids. All the four products can form in principle (**Scheme III**).

The following experiment is carried out to adduce evidence for the operation of the third mechanism proposed. α -chloriminopropiophenone is stirred with

Table II — Percentage profile of the products of hydrolysis of α -chloriminopropiophenone at different temperatures

Reaction condition (°C)	α -Chlorimino propiophenone(%)	Benzoic acid (%)	Benzamide (%)	Acetic acid (%)
RT (30°C)	47.15	43.37	9.18	0.18
60	23.43	55.23	21.21	0.13
80	6.52	64.25	29.01	0.04
90	1.85	71.93	26.18	0.02
100 (for 1hr)	nil	80.23	19.02	0.42
100 (for 3hr)	nil	92.99	7.00	0.01

water at RT and the temperature is gradually increased while analysing the products formed by HPLC at each temperature region. The products identified are benzoic acid, benzamide and acetic acid and the percentage of their formation is given in **Table II**.

It is noticed from **Table II** that the amount of benzamide increases with temperature of the reaction and decreases with further increase in the reaction temperature. On the contrary, benzoic acid keeps increasing with the increase in temperature. These observations support the proposed mechanisms while benzamide is formed through the third mechanism only. Furthermore, benzamide is hydrolysed to benzoic acid at higher temperatures.

Experimental Section

The α -oximinoketones were prepared¹² from the corresponding propiophenones and acetophenones by treating with *n*-butyl nitrite in ether in the presence of hydrogen chloride gas. The oximinocarbonyl compounds were isolated by neutralising the reaction mixture with alkali. The α -oximino compounds were refluxed with thionyl chloride in diethyl ether to obtain the α -chloriminoketones which were used for the Beckmann rearrangement reactions.

The benzoic acids obtained as Beckmann products were identified through physical and spectroscopic characterization data.

Conclusion

It can be observed from this study that α -oximinoketones undergo Beckmann rearrangement reaction through both first order and second order processes giving rise to benzoic acid or substituted benzoic acid as the main isolable product.

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