

Beckmann Rearrangement Studies of $\alpha\beta$ -Acetylenic Ketoximes

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Summary It is demonstrated that the newly available $\alpha\beta$ -acetylenic ketoximes undergo Beckmann rearrangements and/or fragmentations with PCl_5 in ether, and, contrary to previous report, the products of the reaction are readily isolated and characterised.

THE long-elusive $\alpha\beta$ -acetylenic ketoximes (I) have recently been isolated and characterised.¹⁻³ Physical and chemical evidence available so far indicate that all the oximes prepared by the two different methods¹⁻³ have a configuration in which the hydroxy-group is *syn* with respect to the acetylenic function. The principal chemical evidence supporting this view comes from the fact that the oximes cyclise readily to the expected, isomerically pure, isoxazoles (III).^{1,2} According to a previous report² attempts to establish the configuration by the Beckmann rearrangement

procedure using PCl_5 in ether were unsuccessful. The proof of the configuration was therefore provided indirectly, by hydrogenating the acetylenic oximes to the corresponding saturated oximes and then subjecting these to the Beckmann rearrangement.

We now report that the $\alpha\beta$ -acetylenic ketoximes undergo interesting reactions under Beckmann rearrangement conditions using PCl_5 in anhydrous ether. Other reagents usually employed for the Beckmann rearrangement, such as sulphuric acid, polyphosphoric acid, and thionyl chloride were found to be unsatisfactory, as they gave either no reaction or caused extensive isoxazole formation. Our results indicate that, under the Beckmann rearrangement conditions involving PCl_5 , these oximes undergo reaction by two paths. Path A, which can be considered as the Beckmann rearrangement path, does not give the acetylenic

amide (II) expected from the normal rearrangement of the oxime, but instead gives products resulting from the addition of elements of HCl to the triple bond in (II). In cases where $R = \text{Ph}$, the product isolated is exclusively of the *trans*-type (IV) and, where $R = \text{Me}$, both *cis*-(V) and *trans*-(IV) products are isolated. Path B, which is the so-called Beckmann fragmentation reaction, gives rise to equal amounts of the acetylenic nitrile (VI) and the chloride (VII). Oximes with $R^1 = \text{Me}$, $R^2 = \text{Bu}^t$ and $R^1 = \text{Me}$, $R^2 = \text{Me}(\text{Ph})\text{CH}$ undergo reaction by both pathways under the conditions used. A summary of our preliminary results is given in the Table. The reaction products were

TABLE

R ¹	Oxime (I) R ²	Amides % (IV) (m.p.)	% (V) (m.p.)
Ph	Pr ^t	100 (96—97°)	—
Ph	Bu ^s	100 (84—86°) ^a	—
Ph	Bu ^t	^a	^a
Ph	Et	100 (107—108°)	—
Ph	Pr ⁿ	100 (57—58°)	—
Ph	Ph	100 (130—131°)	—
Ph	Me(Ph)CH	^a	^a
Ph	Me	100 (112—113°)	—
Me	Pr ^t	53 (74—75°)	47 (85—86°)
Me	Bu ^s	50 (62—63°)	50 (68—69°)
Me	Et	56 (54—55°)	44 (57—58°)
Me	Bu ^t	55 (83—84°) ^b	45 (94—95°) ^b
Me	Me(Ph)CH	60 (115—116° ^b)	40 (93—94°) ^b

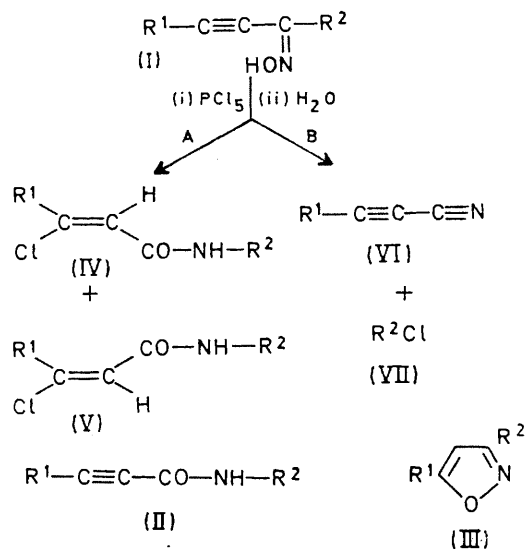
^a Products correspond to path B exclusively.

^b Products corresponding to path B have also been identified.

identified by comparison with authentic samples synthesized independently. All new products gave satisfactory elemental analyses and have the expected i.r. and n.m.r. spectral characteristics.

In no case were we able to identify the acetylenic amide

(II) in the products of the reaction of the oxime with PCl_5 . It is known that amides of the type (II; $R^1 = \text{Ph}$, $R^2 = \text{Ph}$ or Et) react with PCl_5 under conditions similar to those used



in the present study, to give products (IV).⁴ We have also shown that the amide (II; $R^1 = \text{Me}$, $R^2 = \text{Pr}^t$), under the conditions used for the reaction of the acetylenic oximes is transformed into products (IV) and (V) in nearly the same ratio as is obtained in the reaction of the corresponding acetylenic oxime.

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⁴ J. v. Braun and H. Ostermayer, *Ber.*, 1937, 70B, 1002.