**Tetrahedron Letters No.9, pp. 525-529, 1965. Pergamon Press Ltd.
Printed in Great Britain.**

THE BECKMANN CLEAVAGE OF
1,1 DIARYL-2-PROPANONE OXIMES.(1)

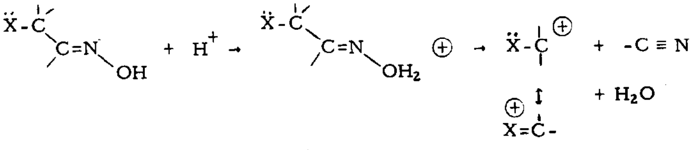
Alfred Hassner and E.G. Nash(2)

Department of Chemistry

University of Colorado, Boulder, Colorado

(Received 20 November 1964; resubmitted 4 January 1965)

Although the chemistry of oximes and in particular the Beckmann rearrangement has been studied extensively since the beginning of this century, reactions of oximes and their mechanism are still under active investigation.(3) Besides the normal Beckmann Rearrangement to amides, many oximes undergo cleavage to nitriles and some other fragment. This latter reaction, sometimes referred to as "second order" Beckmann rearrangement, has been observed for: α-hydroxy oximes, α-keto oximes, α-oximino acids, α-imino oximes, α-amino oximes, α,α-diaryl oximes, β-thioether oximes, bridged α,α-dialkyl oximes, α-trisubstituted oximes and α-ether oximes.(4) In all of these cases the α-substituents can stabilize the carbonium ion or the incipient positive charge formed during the cleavage. The reaction can be formalized as shown below although a direct displacement path has been suggested for the cleavage of α-keto oximes.(5,6)



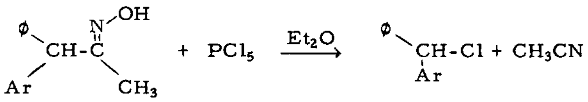
In most cleavage reactions, the two fragments consist of a nitrile and a double bond function, the latter presumably arising by proton elimination from a carbonium ion.(4, 7)

In connection with our effort to clarify the reaction path of oxime cleavage,(6) we were searching for oximes that might undergo cleavage with substitution at a tetrahedral α-carbon to the exclusion of elimination an/or rearrangement.

No such cases are recorded in the literature. In fact 1, 1-diphenyl-2-propanone oxime where elimination upon cleavage is impossible undergoes a normal Beckmann rearrangement on subjecting its tosylate to treatment with base.(8) Similarly 3-phenyl-2-propanone oxime undergoes rearrangement to an amide on treatment with acid.(9) Other α, α-diaryl oximes undergo cleavage with elimination.(10) In our work we obtained similar results in the Beckmann rearrangement of 2-phenylcyclohexanone oxime; the products being an unsaturated nitrile and a lactam. 1-Phenyl-2-indanone oxime under Beckmann rearrangement conditions gives nitrile as well as lactam products. The latter could arise by a cyclization of the intermediate nitrile as has been shown to occur in other cases.(11)

We would now like to report an oxime system which under Beckmann rearrangement conditions (PCl_5-ether) seems to give exclusively cleavage with displacement. In particular, the 1, 1-diaryl-2-propanone oxime system cleaves under Beckmann rearrangement conditions to alkyl chlorides in good yields. The cleavage is extremely facile, being complete within 5 min. at 0°. Organic halides have not been reported as products of

Beckmann cleavages, except in one case, as a minor product which was not identified.(12) The benzhydryl chlorides IIa-d were obtained crude in essentially quantitative yield. The infrared spectra of the crude halides indicated the presence of little or no amide products. The yield of pure benzhydryl chlorides obtained by careful distillation in vacuum is indicated below.(13)



Ia.	Ar: p-CH_3-C_6H_4-	IIa.	(64%)
b.	Ar: p-Cl-C_6H_4-	b.	(38%)
c.	Ar: 2,5$(CH_3)_2$-C_6H_3-	c.	(63%)
d.	Ar: 2,4,6$(CH_3)_3$-C_6H_2-	d.	(65%)

The starting oximes Ia-d were prepared in good yield from the corresponding ketones, which in turn were synthesized from α-bromo-α-phenylacetone and the corresponding aromatic hydrocarbon in a Friedel-Crafts reaction.(14) The structure of the products were proven by independent synthesis, IR, NMR and elemental analysis. For instance IIa and IIb respectively were identical to authentic material prepared from the corresponding benzhydrol.(15)

The NMR spectra of these compounds are of interest and served well in the elucidation of the structures of the products. For example, compound Id had NMR peaks (in $CHCl_3$) at τ4.8, 7.76, 7.88, 8.21 in the ratio 1:3:6:3 whereas compound IId showed absorption (in CCl_4 at 30^o) at τ 3.48, 7.82, 7.88 in the ratio 1:3:6. Surprisingly, the NMR spectra indicate that the two ortho methyl groups in the mesityl compounds Id and IId are equivalent at room temperature. On cooling free rotation of the mesityl group becomes restricted and absorption of one of the ortho methyl groups is shifted to slightly lower field, where the para methyl group is found.(16) This is indicated by the NMR spectrum of IId at -30°, in which the ratio of the peaks at τ 3.50, 7.81 and 7.90 has changed to approximately 1:6:3. It is interesting to note that the methine hydrogen in the benzhydryl chloride IId absorbs at a considerably lower field (τ3.48) than in the analogous compounds IIa-c. It appears that the ortho methyl groups are responsible for this downfield shift since in IIa and IIb the methine proton appears at τ 4.09 whereas in IIc it is found at τ3.83.

Work is currently in progress to obtain these compounds in optically active form and to elucidate the stereochemical course of this cleavage reaction.

Acknowledgement: We are grateful to the National Science Foundation for financial support of this work through Grant G24091.

References:

1. Paper IV, Chemistry of Oximes, for paper III see ref. 6b.
2. N.I.H. Predoctoral Fellow, 1963-64.
3. a. A.G. Donaruma and W.Z. Heldt, "Organic Reactions," Vol. XI, A.C. Cope, Ed., J. Wiley and Sons, New York (1960), pp. 1-156.
   b. C.A. Grob, H.P. Fischer, W. Raudenbusch and J. Zergenzi, Helv. Chem. Acta, 47, 1003 (1964).
   c. M. Kawakami and Y. Yukawa; Bull Chem. Soc. Japan, 37, 1050 (1964).

4. R.K. Hill, *J. Org. Chem.*, **27**, 29 (1962) and references cited therein.

5. J.P. Freeman, *J. Org. Chem.*, **26**, 3507 (1961) and references cited therein.

6. a. A. Hassner and I. Pomerantz, *J. Org. Chem.*, **27**, 1760 (1962).
   b. A. Hassner, W. Wentworth and I. Pomerantz; *J. Org. Chem.*, **28**, 304 (1963).
   c. A. Hassner and W. Wentworth, unpublished work.

7. R.T. Conley and M.C. Annis, *J. Org. Chem.*, **27**, 1961 (1962); R.T. Conley and B.E. Nowak, ibid, **27**, 1965 (1962).

8. M.J. Hatch and D.J. Cram, *J. Amer. Chem. Soc.*, **75**, 38 (1953).

9. A. Campbell and J. Kenyon, *J. Chem. Soc.*, 25 (1946).

10. C.C. Price and G.P. Mueller, *J. Amer. Chem. Soc.*, **60**, 634 (1934); W.L. Bencze and M.J. Allen, *J. Org. Chem.*, **22**, 352 (1957); S. Wawzouek and J.V. Hallum, *J. Org. Chem.* **24**, 364 (1959).

11. R.T. Conley, *J. Org. Chem.*, **28**, 278 (1963).

12. R.E. Lyle and G.G. Lyle, *J. Org. Chem.*, **18**, 1058 (1953).

13. These compounds are not very stable and oxidize or hydrolyze on standing.

14. E.J. Cragoe, C.M. Robb and A.M. Peitruszkiewicz, *J. Org. Chem.*, **23**, 971 (1958).

15. J.F. Norris and C. Banta, *J. Amer. Chem. Soc.*, **50**, 1804 (1928).

16. The p-methyl group in IIa absorbs at τ 7.79.