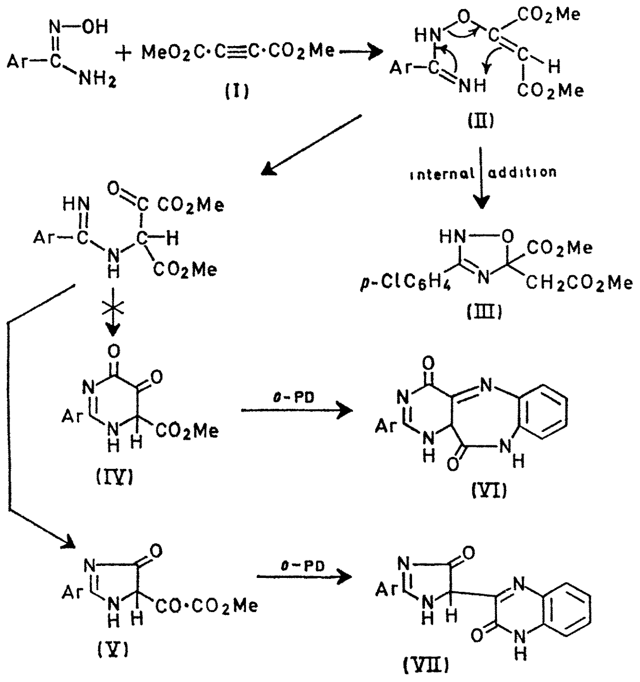
Claisen Rearrangement of Amide Oxime–Dimethyl Acetylenedicarboxylate Adducts as a Route to Imidazolinones

By NED D. HEINDEL*
(*Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania* 18015)
and MARIA C. CHUN
(*Department of Chemistry, Cedar Crest College, Allentown, Pennsylvania* 18104)

Summary Pyrolysis of the vinyl ether adducts obtained by condensation of arylamide oximes and dimethyl acetylene dicarboxylate affords a new class of substituted imidazolinones, probably by a Claisen-type rearrangement with subsequent cyclisation.

RECENT work[1-5] has shown that the condensation of difunctional nucleophiles with dimethyl acetylenedicarboxylate (I) is a versatile heterocyclic synthesis. Accordingly, we heated equimolar amounts of amide oximes and the ester (I) under reflux for 3 h in methanol and isolated the 1 : 1 adducts (II) in excellent yields. In view of the addition of ketoximes to (I)[6] and our observation that *O*-methylamide oximes did not react with (I), it was apparent that the adducts were formed by addition of O–H across the alkyne bond. After 4 days under reflux in methanol, the adduct (IIb) gave the oxadiazoline (III) in 27% yield, m.p. 157—158°.



a; Ar = Ph
b; Ar = *p*-ClC$_6$H$_4$
c; Ar = *p*-MeC$_6$H$_4$

In an attempt to improve this conversion, the adducts were heated under reflux in diphenyl ether for 0·5 h but this gave new products which elemental and mass spectral analysis established as (II) — MeOH. These products did not arise by the direct displacement of an ester group by the amide oxime imino-group, for the i.r. spectra (3250—3050 cm^{-1}, broad OH), solubility in dilute bases, and positive FeCl$_3$ tests all indicated a highly enolic system. In accord with similar observations on enolic heterocycles, the very broad tautomeric proton resonance could not be precisely located in the n.m.r. spectrum.[7] A single methoxy-group signal at τ 6·15 and the Ar*H* and N*H* resonances at τ 1·5—2·7 were present in the spectrum of each product.

A Claisen-type rearrangement, as recently reported by Sheradsky[6] for ketoxime adducts of (I), would generate either the pyrimidinedione (IV) or the imidazolinone (V), both of which would be expected to be highly enolic. The chemical and spectral data supports either of these alternatives except that intense mass spectral fragment ion at *M* —87 (CO·CO$_2$Me) favours structure (V). Condensation of the hitherto unknown phenyl-analogue (Ar = Ph) with *o*-phenylenediamine (*o*-PD) gave a compound, m.p. 367—368°, which mass spectrometry (M^+, 304) and combustion analysis indicated was the product of (IV) or (V) and *o*-PD with loss of methanol and water. This product, *i.e.* (VI) or (VII), showed base peaks at *m/e* 145 and 159 in its mass spectrum, corresponding to the scission of the single bond joining the imidazolinone portion (*m/e* 159) and the quinoxalone portion (*m/e* 145) in compound (VII). These fragment ions cannot be readily rationalized from (VI) and hence the initial rearrangement products are believed to be the imidazolinones (V). Some data for three such imidazolinones are given in the Table.

TABLE[a]

Compound	Yield (%)	M.p. (°C)	Product	Yield (%)	M.p. (°C)
(IIa)	61	78—79	(Va)	68	240—242
(IIb)	64	57—58	(Vb)	63	256—257
(IIc)	59	69—70	(Vc)	41	256—258

[a] Satisfactory i.r., ^{1}H n.m.r. (CDCl$_3$; 60 MHz), and mass spectra and combustion analyses were obtained for all compounds described.

We thank the National Institute of Mental Health for a grant.

(*Received, March* 18*th*, 1971; *Com.* 351.)

---

[1] N. D. Heindel and L. A. Schaeffer, *J. Org. Chem.*, 1970, **35**, 2445.
[2] N. D. Heindel, P. D. Kennewell, and M. Pfau, *J. Org. Chem.*, 1970, **35**, 80.
[3] N. D. Heindel, V. B. Fish, and T. F. Lemke, *J. Org. Chem.*, 1968, **33**, 3997.
[4] A. F. Cameron, N. J. Hair, N. F. Elmore, and P. J. Taylor, *Chem. Comm.*, 1970, 800.
[5] Y. Iwanami, *Nippon Kagaku Zasshi*, 1962, **83**, 100; (*Chem. Abs.*, 1963, **59**, 3916b).
[6] T. Sheradsky, *Tetrahedron Letters*, 1970, 25.
[7] N. D. Heindel, V. B. Fish, M. F. Ryan, and A. R. Lepley, *J. Org. Chem.*, 1967, **32**, 2678.