

THE REARRANGEMENT OF O-VINYLOXIMES  
A NEW SYNTHESIS OF SUBSTITUTED PYRROLES

Tuvia Sheradsky

Department of Organic Chemistry, the Hebrew University

Jerusalem, Israel.

(Received in UK 22 November 1969; accepted for publication 3 December 1969)

The big difference in bond energies between the carbon-carbon and the nitrogen-oxygen bonds should cause, in a suitably arranged molecule, a concerted cleavage of an N-O bond and formation of a new C-C bond. Rearrangement of this type is the postulated first step in the Fischer-like benzofuran synthesis (1,2).

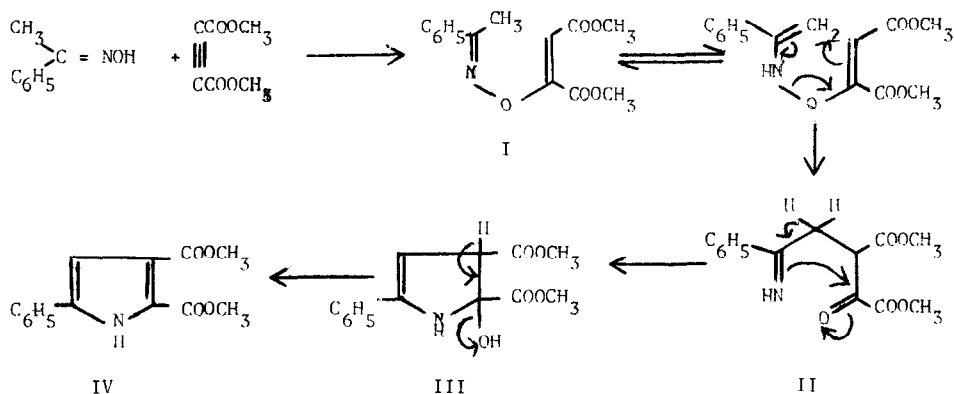
The enamine form of o-vinyloximes having a  $\alpha$ -methylene group seemed to be a suitable system, which might undergo such a rearrangement (3). For the preparation of a starting material we tried the addition of acetophenone oxime to dimethyl acetylenedicarboxylate.

The addition reaction was carried out in boiling methanol with basic ( $\text{NaOCH}_3$ ) catalysis, and yielded quantitatively the adduct I (oil). Its nmr spectrum indicates that it is a mixture of the cis and trans isomer in 1:2 ratio. (Vinylic hydrogen at  $\delta$ 5.14 for cis,  $\delta$ 6.20 for trans, C-CH<sub>3</sub> at  $\delta$ 2.52 for cis,  $\delta$ 2.25 for trans).

Heating of the mixture I at 170-160° for 30 min. yielded the product IV (80%) m.p. 140°,  $\lambda_{\text{EtOH}}^{\text{max}}$  242 ( $\epsilon=24200$ ), 276(23600), 294(25200), 306m $\mu$ (25800). The structure of IV was assigned as dimethyl 5-phenyl-pyrrole-2,3-dicarboxylate on the basis of elemental analyses ( $\text{C}_{14}\text{H}_{13}\text{NO}_4$ ), infrared spectrum (NH at 3270  $\text{cm}^{-1}$ , ester unconjugated to NH at 1730  $\text{cm}^{-1}$  conjugated at 1680  $\text{cm}^{-1}$ ) and nmr spectrum [NH at  $\delta$ 10.2 (broad, 1H), phenyl at  $\delta$ 7.3-7.7 (multiplet, 5H) H-3 at  $\delta$ 6.95 (doublet  $J_{1,3}=3.5$  Hz, 1H) and O-CH<sub>3</sub> at  $\delta$ 3.96 (singlet, 6H)].

On carrying out the same reaction sequence with cyclohexanone oxime, dimethyl 4,5,6,7-tetrahydroindole-1,2-dicarboxylate, m.p. 140°, was obtained in 45% yield. Analyses and spectral data were in accord with the assigned structure.

The formation of pyrroles in the reaction can be accounted for by the following mechanism:



The first step is the expected rearrangement to the imino-ketone II, which cyclizes to III. Dehydration of III yields the final product IV.

Further studies, mechanistic and synthetic, of this new pyrrole synthesis are in progress.

#### References

1. A. Mooradian and P.E. Dupont, Tetrahedron Letters 2867 (1967).
2. T. Sheradsky and A. Elyavi, Israel J. Chem. **6** 895 (1968).
3. A similar rearrangement, involving formation of a carbon-oxygen bond was recently reported. H.O. House and F.A. Richey, J. Org. Chem. **34** 1430 (1969).