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[2,3] vs [3,3] : THE NOVEL [2,3] SIGMATROPIC REARRANGEMENT OF OXIME-O-ALLYL ETHERS

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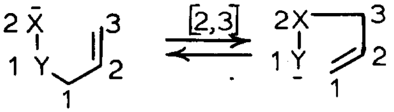
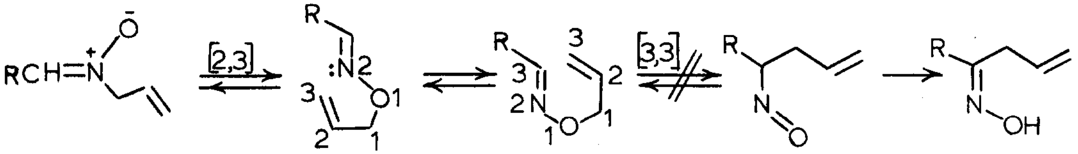
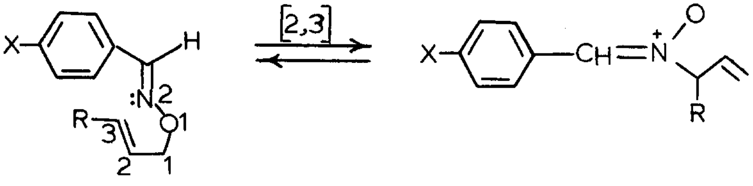
The rearrangement of several heterocyclic systems such as Sommelet rearrangement, the Wittig, Stevens and Meisenheimer rearrangements of allyl systems, the rearrangement of allyl sulfonium ylids, sulfenates and the rearrangement of nucleophilic carbenes have all been recently catalogued as [2,3] sigmatropic changes [1]:



We highlight the ubiquitous nature of the [2,3] shift in the present communication which reports the exhibition of the [2,3] shift over the more popularized [3,3] [2]. Thus, aldoxime-O-allyl ethers are transformed thermally to nitrones by a [2,3] process. The alternate [3,3] that would have resulted in α-homologation by a 3 carbon unit was not, alas, even detected!



The E-aldoxime-O-ethers 1a-1c , prepared by alkylation of the oximes with allyl iodide/ crotyl bromide in MeOH-MeONa [3,4,5] were pyrolysed in boiling o-dichlorobenzene(bp 180°) for 10 hr. The reaction as monitored by tlc was found to be clean giving rise to substantially more polar product appearing as a twin-spot. Careful chromatography gave nitrones 2a-2c as a nearly 1:1 mixture of isomers in 50-80% yields, based on recovered starting material[6]. The



a: $X = NO_2$; R= H
b: X= H ; R= H
c: X= H ; R=Me

1 2

structural assignment for 2 is based on analytical and spectral data [4,7] and transformation to the corresponding aldehyde 2,4,-dinitrophenylhydrazones in excellent yields($\sim$80%). No other product could be detected in the pyrolysis experiment. Thus, the oxime-O-crotyl ether 1c was transformed to nitrone 2c only, establishing thereby the concerted nature of the $1 \rightarrow 2$ change. Whilst the [2,3]shift results in $1 \rightleftarrows 2$, the [3,3] would irreversibly lead to homologous ketoxime. The fact that no such product was observed strongly suggests a virtual exclusion of the [3,3] path. The distict preference for a [2,3] demonstrates the assertion of the nitrogen lone pair which finds expression in the more favoured transition state leading to nitrones wherein the lone pair- lone pair interactions are also minimum.

REFERENCES AND FOOTNOTES

1. See, V.Rautenstrauch, Chem.Comm., 4 (1970) for an extensively referenced communication; R.A.W. Johnstone, "Mechanisms of Molecular Migrations", B.S.Thyagarajan(ed), Vol.II, Interscience, New York, 1969, p.249; J.E.Baldwin and J.A.Walker, Chem.Comm., 354(1972).

2. S.J. Rhodes, "Molecular Rearrangements", P.DeMayo(ed), Vol.I, Interscience, New York, 1963, p.655; A.Jefferson and F.Scheinmann, Quart.Rev., 22, 391(1968); E.Winterfeldt, Fort. Chem.Forsch., 16, 75(1970).

3. O.L.Brady and F.H. Peakin, J.Chem.Soc., 226(1930)

4. Satisfactory analytical and ir data have been obtained.

5. 1a: 35%; mp 75°; nmr: δ(CDCl$_3$) 4.7(d, J=5 Hz, allylic CH$_2$), 5.3 (t, methylene), 5.9 (m, vinyl), 7.9(q, aromatic), 8.1(s, ArCH). 1b: 54%; bp 90°/8 mm; nmr: δ(CDCl$_3$) 4.7 (d, J=5 Hz, allylic CH$_2$), 5.4(t, methylene), 6.1(m, vinyl), 7.6(m, aromatic), 8.2(s,ØCH). 1c: 80%, bp 52°/0.5 mm; nmr: δ(CDCl$_3$) 1.7(d,d, J=4 Hz, J=1 Hz, methyl), 4.65(d, J=5 Hz, allylic CH$_2$), 5.8(m, vinyl protons), 7.45(m, aromatic), 8.1(s, ØCH).

6. The 1:2 ratio under the same reaction conditions are : 1a, 1:2; 1b, 7:2; 1c, 6:1, based on actual amounts isolated by chromatography. Brief heating of nitrones 2a and 2c in o-dichlorobenzene produced the oxime ethers 1a and 1c. In expectations with a concerted process, the oxime ether-nitrone system exists in equilibrium and it is interesting to note, from the above ratios, that the nitro substitution does indeed change the direction under conditions tried here.

7. 2a: 77%; nmr: δ(CDCl$_3$) 3.5(d, J=5 Hz), 4.4(d, J=5 Hz) ($\sim$1:1, allylic CH$_2$), 5.2(t, methylene of one isomer); 2b: 70%; nmr: δ(CDCl$_3$) 3.5(d, J=5 Hz) (allylic CH$_2$ of one of the isomers); 2c: 50%; nmr: δ(CDCl$_3$) 1.2(d, J=6 Hz), 1.4(d, J=6 Hz) ($\sim$1:1, saturated methyl), 4.2(m, methylene), 5.1(m, vinyl).