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STUDIES IN CLAISEN REARRANGEMENT

CLAISEN REARRANGEMENT OF 2-PROPARGYLTHIOBENZIMIDAZOLES

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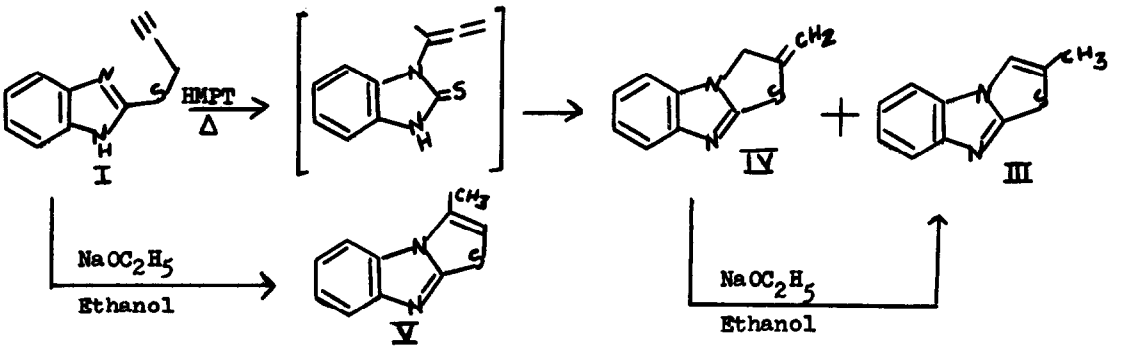
Thioclaisen rearrangement of 2-allylthioimidates[1] and 2-allylthiobenzimidazoles[2,3] is well known. However similar 3,3-sigmatropic rearrangement of propargylthioimidates has not been reported in literature so far[4]. In this communication we report a few examples of 3,3-sigmatropic rearrangement of 2-propargylthiobenzimidazoles.

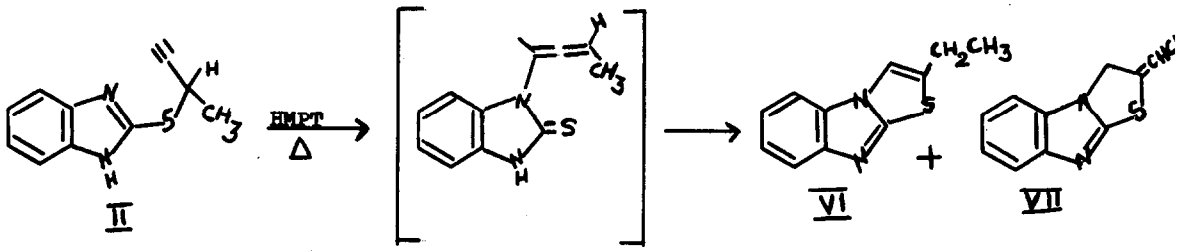
Reaction of 2-mercaptobenzimidazole with propargyl bromide in acetone in the presence of sodium acetate and a few drops of acetic acid furnished the known 2-propargylthiobenzimidazole, I (79%), m.p.151-2° (lit.[5] m.p.151-2°), while 2-(but-3-yn-2-ylthio)benzimidazole, II, m.p.129-30° (20%) was prepared by refluxing a mixture of 2-mercaptobenzimidazole and but-3-yn-2yl tosylate in ethanol in the presence of sodium bicarbonate.

When 2-propargylthiobenzimidazole, I, was refluxed in hexamethylphosphoric triamide (HMPT) for 40 minutes in a nitrogen atmosphere or heated in a sealed tube at 160° in benzene for 40 minutes, a smooth rearrangement was observed. The crude product, m.p.152-5° (85%) showed two very closely moving spots in tlc (chloroform-benzene, 1:1) and its infrared spectrum exhibited no N-H or ≡C-H band. Its n.m.r. spectrum showed signals at δ2.2 (d, J=1.5 Hz), δ4.75 (t, J=1.5Hz) δ5.4 (m) and δ7.6 (m). The n.m.r. data clearly indicated that it is a mixture of 2- or 3-methylthiazolo(2,3-b)benzimidazole and one of the exomethylene isomers ($N-CH_2$ at δ4.75 and $=C\begin{smallmatrix}H\\H\end{smallmatrix}$ at δ5.4). By preparative tlc it was possible to isolate one of the products, viz.III, in a pure state, m.p.161-2° . From its analytical, spectral and melting point data as well as by comparison with an authentic sample of V,[6] the product III has been identified as 2-methylthiazolo(2,3-b)benzimidazole[7].

The other product IV, isolated from preparative tlc, was found to be contaminated with a little of 2-methylthiazolo(2,3-b)benzimidazole, III, as could be seen from its n.m.r. It was shown to be the exomethylene isomer of III by isomerising it to the latter under the influence of sodium ethoxide in ethanol.



2-(But-3-yn-2-ylthio)benzimidazole, II, also underwent a 3,3-sigmatropic rearrangement when refluxed in HMPT for fifteen minutes in a nitrogen atmosphere, affording a brown solid, m.p.82-90° (37.5%) consisting of a mixture of 2-ethylthiazolo(2,3-b)benzimidazole VI and the isomeric exoolefnic compound VII, as indicated by the n.m.r. spectra 1.35 (t, J=7 Hz, $-CH_2-CH_3$), 1.8(d, J=7 Hz, $=CH-CH_3$), 2.8 (q, J=7Hz, $-CH_2-CH_3$), 4.8 ($-N-CH_2-$) and 7.4 (m, ring protons and $=CH-CH_3$) . By preparative tlc one of the two products, viz. 2-ethylthiazolo (2,3-b)benzimidazole VI was isolated in about 90% purity, m.p.103-5°.



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