STUDIES ON FURAN DERIVATIVES. XIII.[1]
THERMOLYSIS OF METHYL 5-(2-AZIDOPHENOXY)-2-FUROATE

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Abstruct —— In thermolysis of methyl 5-(2-azidophenoxy)-2-furoate, the first conversion of this into 2-(2-methoxalylvinyl)benzoxazole has been found.

Meth-Cohn and co-workers[2] have proposed a new mechanism on the pyrrolo[2,1-b]-benzothiazole formations employing photolysis and thermolysis of 2-azidophenyl thienyl sulfides, which involves the cleavage of thiophene ring to α,β-unsaturated thioketones via a five membered ring intermediate by intramolecular insertion of nitrene. They also have emphasized the propriety of this ring opening mechanism rather than the 1,4-cycloaddition pathway of nitrene already suggested in other related reactions.[3] Jones and Mckinley[4] have also assumed similar α,β-unsaturated indolenyl ketone intermediates in the deoxygenation of ortho-nitrophenyl-di-(2-furyl)methanes to give diethyl 2-alkylfuro[3,2-c]carbazol-5-ylphosphates.

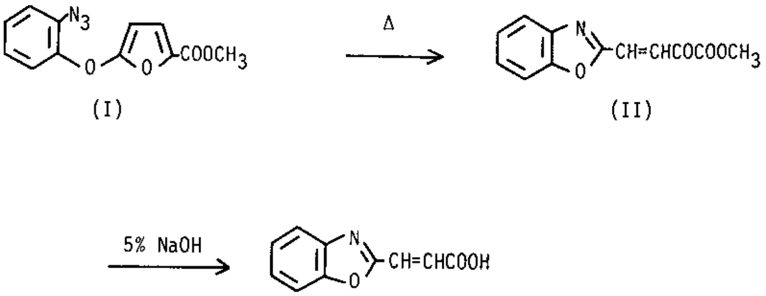
We now confirmed that the thermolysis of methyl 5-(2-azidophenoxy)-2-furoate (I) leads to the formation of 2-(2-methoxalylvinyl)benzoxazole (II) which corresponds to α,β-unsaturated ketones (or thioketones) as mentioned above.

Compound (I), prepared from methyl 5-(2-nitrophenoxy)-2-furoate[1] by the usual method,[5] was allowed to thermolyse in ortho-dichlorobenzene at 160-170° for 3 hr under nitrogen. After cooling, an excess of solvent was removed and the residue was chromatographed on silica gel, eluting with benzene, to give II; yield 22%; m.p. 134-136° (from petroleum benzin); ^{1}H-N.M.R. δ (acetone-d_6): 3.89 (3H, s, CH_3), 7.10-7.85 (6H, m, benzene ring and vinylene H); I.R. ν (nujol): 1725, 1695 (C=O), and 1625 cm^{-1} (C=N); mass spectrum m/e: 231 (40.5%), 203 (33), 172 (100), 144 (89), 116 (21.7), and 89 (23.4).

Hydrolysis of II in 5% sodium hydroxide solution gave 3-(2-benzoxazolyl)acrylic acid which was identified with a sample.[6]

From these data, the structure of II was assigned as 2-(2-methoxalylvinyl)benzoxazole. The elemental analysis of II supported a molecular formula of $C_{12}H_9NO_4$. Thus, we could be obtained the stable α,β-unsaturated ketone (II) which corresponds to the ring opening intermediate proposed by Meth-Cohn et al.[2] and a new synthetic rout for a benzoxazole ring system was also provided. More recently, α,β-unsaturated ketone and thioketone as minor components (~1.5%) were isolated by Jones et al.[7] in the reaction of 2-nitrenophenyl-di-(5-t-butyl-2-thienyl)methane.

Scheme



References and Notes

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