THE UNCATALYZED CYCLOADDITION OF A SILOXYDIENE TO N-ACYLIMINES. THE SYNTHESIS OF 4-PYRIDONES

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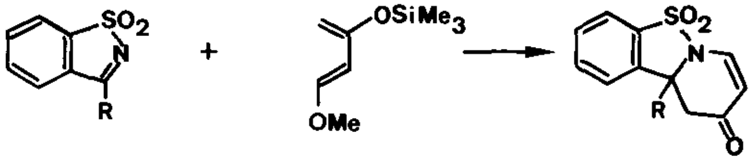
Astract - The (4 + 2) cycloaddition of 1-methoxy-3-trimethylsilyloxy-1,3-butadiene to cyclic and open-chain N-sulfonylimines leads to 5,6-dihydro-1,1-sulfonyl-4-pyridones. The presence of a good leaving group at C-6 leads to elimination and the formation of the corresponding 4-pyridone.

In recent years, several electron rich dienes have been used in Diels-Alder reactions. The best know of these is Danishefsky's diene (1-methoxy-3-trimethylsiloxy-1,3-butadiene (1), a siloxydiene).[1] Recently, this has been used to synthesize heterocycles e.g. thiazinones,[2] and 5,6-dihydro-γ-pyrones.[3] We have developped an uncatalyzed synthesis of 4-pyridones using this reagent with activated imines.[4] The publication[5] of a synthesis of 4-pyridones by the Lewis acid catalyzed cyclocondensation of imines with Danishefsky's diene prompts us to report our preliminary results.

Condensation of 1 with 3-methyl-1,2-benzisothiazole 1,1-dioxide (2)[6] in boiling toluene gave 5a-methyl-5,5a-dihydro-4-oxopyrido[1,2-b]-1,2-benzisothiazoline 1,1-dioxide (3) (45 %), mp 164-166°C [IR 1580 (C = O), 1600 (C = C), 1330 and 1180 cm^{-1} (SO$_2$) ; NMR 8.0 - 7.4 (m, 5H, ArH + -CH=), 5.6 (d, 1H, J = 8 Hz, -CH=),



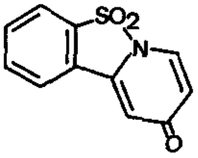
2 R = Me
4 R = Cl

1

3 R = Me
5 R = Cl

2.8 (s, 2H, CH_2CO), 1.7 (s, 3H, CH_3)].[7] On the other band, 3-methoxy- and 3-phenythio-1,2-benzisothiazole 1,1-dioxide did not react with **1**, presumably owing to the deactivation of the imine function by the +M substituent. It would be of interest to determine whether or not zinc chloride catalysis[5] would permit reaction to occur with these compounds. It should be noted that, in contrast to **2**, 3-methoxy-1,2-benzisothiazole 1,1-dioxide only reacts with 1-diethylaminopropyne at elevated temperature. The 3-phenylthio compound does react with the ynamine at room temperature, however.[4]

It was hoped that since a chlorine substituent is a net electron-attractor (-I > +M), saccharin pseudochloride (**4**) would undergo (4 + 2)-cycloaddition with **1** to give **5**, which would then dehydrohalogenate readily to **6**. Indeed, reaction occurred readily in toluene at room temperature to yield a product tentatively identified as **6** (75 %) [IR 1650, 1630 and 1590 cm^{-1} (4-pyridone), 1345 and 1180 cm^{-1} (SO_2N) ; NMR ($CDCl_3$) δ 8.45 (d, 1H, *J* = 7 Hz, C_2-H), 8.4 - 7.9 (m, 2H), 7.75 - 7.1 (m, 4H)]. Attempted recrystallization of this compound from 95 % ethanol effected its hydrolysis to 2-(4-oxo-1*H*-2-pyridyl)benzenesulfonic acid (**7**), mp > 300°C [IR (KBr) 3300-2200 (br), 1615, 1470, 1150 cm^{-1} (SO_3H). NMR could not be determined owing to the insolubility of the compound in normal solvents].[7]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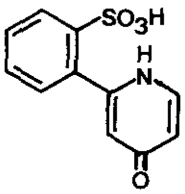
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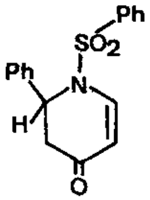
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That such cycloadditions can be extended to open chain sulfonylimines was shown by the reaction of **1** with *N*-(benzenesulfonyl)phenylimine[8] in boiling toluene to give *N*-(benzenesulfonyl)-2-phenyl-2,3-dihydro-4-pyridone (**8**) (80 %), mp 145°C [IR 1660, 1595, 1365, 1290, 1160 cm^{-1} ; NMR ($CDCl_3$) δ 8.1-7.2 (m, 11H), 5.75-5.4 (m, 2H) ; *m/e* 313 ($M^{+\cdot}$)]. The scope and applications of this 4-pyridone synthesis are being investigated.

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