Tetrahedron Letters Vol. 22, pp 583 - 584 0040-4039/81/0201-0583$02.00/0

CONCERNING THE STRUCTURE OF THE REACTION PRODUCTS FROM N-SULFINYLSULFONAMIDES AND DIMETHYLKETEN-N-PHENYLIMINE

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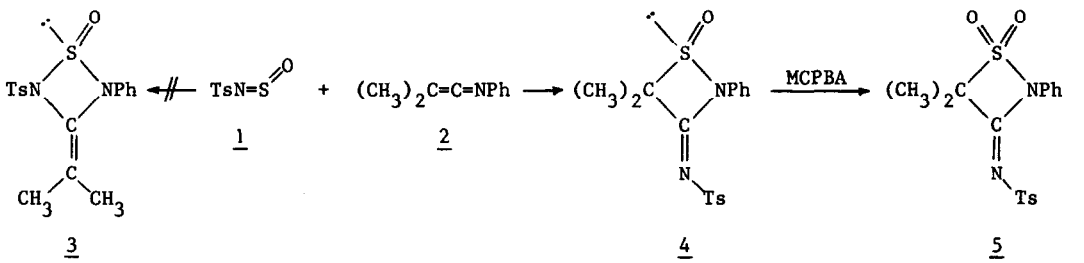
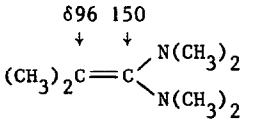
ABSTRACT. The reactions of N-sulfinylsulfonamides with dimethylketen-N-phenylimine furnish 3-sulfonylimino-1,2-thiazetidin-1-oxides (e.g. 4) instead of the previously reported 3-isopropylidene-1,2,4-thiadiazetidin-1-oxides (e.g. 3).

An interesting aspect of heterocumulene chemistry is the formation of four-membered heterocycles by ($2\pi + 2\pi$)-cycloaddition reactions. The non-linear N-sulfinylamines and N-sulfinylsulfonamides give cycloadducts which are unstable in most cases and even then only postulated as elusive intermediates.[1] Notable exceptions are the reactions with enol ethers,[2] ketenes,[3] carbodiimides,[4] and ketenimines[5] which afford stable cycloadducts. Thus, the reactions of N-sulfinylsulfonamides with dimethylketen-N-phenylimine in ether at ambient temperature give 1:1 adducts which were previously formulated as 3-isopropylidene-1,2,4-thiadiazetidin-1-oxides (e.g. 3).[5] Basic hydrolysis of 3 furnished N-phenyl-N'-tosylisobutyramidine.



3 1 2 4 5

In our hands, the reaction product obtained from 1 and 2 in 90% yield (mp 127-128°C) exhibited similar properties to those reported earlier.[5] However, the strong IR absorption at 1612 cm^{-1} (KBr) is hardly reconcilable with a C=C stretching vibration of the four-membered ring 3.[6] On the contrary, it occurs at the position expected[7] for a $C{=}NSO_2$ stretching vibration of 4, which would result from 3 by a Dimroth-rearrangement.[8] The non-equivalence of the two methyl groups in the ^1H NMR spectrum ($CDCl_3$, δ 1.93 and 1.99) is then attributed to the anisotropic effect of the sulfinyl function in structure 4, rather than to an isopropylidene grouping in structure 3. Also, the ^{13}C NMR spectrum ($CDCl_3$) confirms structure 4 with ring carbon absorptions at δ 75 and 163.9 ppm in agreement with expectation.[9] For structure 3, olefinic carbon absorptions similar to those of our model compound 6 would be expected.



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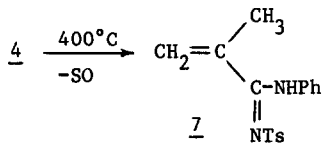
Finally, definite proof of structure 4 comes from oxidation of the cycloadduct with a three-fold excess of m-chloroperbenzoic acid in ether, giving 5 (40%, mp 150-151°C, C=NSO_2 at 1630 cm^{-1}) in addition to N-phenyl-N'-tosylisobutyramidine (the hydrolysis product of 4, 50%, mp 125-126°C) and N-phenyl-N'-tosyl-α-sulfoisobutyramidine (the hydrolysis product of 5, 10%, mp 196-201°C, dec). The sultam 5 possesses two identical ring-methyl groups which absorb at δ 2.16 in the ^1H NMR spectrum ($CDCl_3$), thus ruling out structure 3 as its precursor. In the ^{13}C NMR spectrum ($CDCl_3$) the ring carbon atoms of 5 resonate at δ 86.5 (C_4) and 157.1 ppm (C_3). Interestingly, compound 4 decomposes by flash thermolysis[10] at 400°C to give the methacrylic amidine 7 in 64% isolated yield (mp 124-125°C). This reaction proceeds by elimination of S=O followed by hydrogen shift.



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(Received in UK 19 November 1980)