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DIAZOALKANE INDUCED SULPHOXIDE ELIMINATION: ACCESS TO THE PYRANO[3,4-c]PYRAZOLE SYSTEM.

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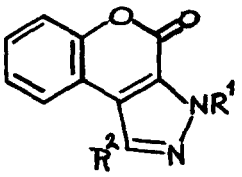
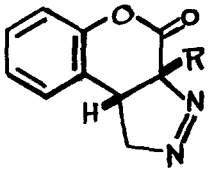
During studies on the reactions of coumarins with diazoalkanes we examined 3(4-methylphenylsulphinyl)coumarin since the literature appeared to contain scant reference to the reactions of diazoalkanes with simple α,β-unsaturated sulphoxides.[1] The starting coumarin was obtained from salicylaldehyde and methyl 4-methylphenylsulphinylacetate and had m.p. 208-209° and ν_{max}(KBr) 1725 and 1052 cm^{-1}. With diazomethane at 0° for 1 h it gave the pyranopyrazole derivative 1 (92%), m.p. 160-162°, ν_{max} 1736 and 1592 cm^{-1}, $\tau(CDCl_3)$ 2.03 (s, 1H), 2.2-2.8 (mm, 4H), and 5.71 (s, 3H). With diazomethane it gave the corresponding derivative 2, m.p. 164°, along with a small amount (ca. 2%) of the non-ethylated pyrazole 3, m.p. 225-230° (subl.), ν_{max} 1735 and 1590 cm^{-1}, $\tau(CF_3.CO_2H)$ 1.9-2.4 (mm, 4H), 7.00 (s, 3H), which was different from a sample of the isomeric 1-methylchromeno[4,3-c]pyrazole[2] thus confirming the orientation of addition.

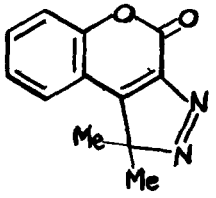
Evidently diazomethane adds to the coumarin giving 4 which then eliminates the sulphoxide residue and tautomerises to the 1H-pyrazole system. Elimination of sulphoxide must precede tautomerism because with 2-diazopropane the coumarin rapidly forms the stable 3H-pyrazole derivative 5 (91%), m.p. 240-241°, ν_{max} 1750, 1610, and 1560 cm^{-1}; $\tau(CDCl_3)$ 2.2-2.8 (mm, 4H), 8.29 (s, 6H).

Thus the ease of sulphoxide elimination is such that it supersedes the nitrogen elimination that is normally spontaneous and rapid in systems such as 6.

Usually the extrusion of sulphoxide is effected at temperatures greater than 100° and even the closest parallels to our examples (in chromone/flavone chemistry,[4] for example) are conducted in refluxing toluene. Presumably the 1,3-dipolar cycloaddition of diazoalkane produces exactly the cis ring fusion needed for the syn-elimination of sulphenic acid while the re-development of conjugation between the carbonyl group and the aryl ring simultaeously provides a driving force. This useful extension of pyrazole syntheses also shows that the sulphoxide group does activate the normal 1,3-dipolar cycloaddition of diazoalkanes and offers further evidence for believing that the alkylation of 3-acylcoumarins does involve adducts similar to 6 notwithstanding the fact that they cannot be isolated.[3]







1; R^1 = Me; R^2 = H
2; R^1 = Et; R^2 = Me
3; R^1 = H; R^2 = Me

4; R = $SO.C_7H_7$
6; R = Ac

5

References

1. L. Veniard and G. Pourcelot, Bull. Soc. Chim. France, 1973, 1746.

2. A. Mustafa, O. H. Hishmat, A. A. Nawar, and K. M. A. Khalil, Annalen, 1965, 684, 194.

3. R. Clinging, F. M. Dean, and L. E. Houghton, J.C.S. (Perkin I), 1974, 66.

4. B. N. Trost and T. N. Salzmann, J. Amer. Chem. Soc., 1973, 95, 6840; M. von Strandtman, S. Klutchko, M. P. Cohen, and J. Shavel, J. Heterocylic Chem., 1972, 9, 171.

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