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CYCLIC SULPHONES. VII.[1]
ADDITION OF DIAZOMETHANE TO 3-PHENYL-2H-THIOPYRAN-1,1-DIOXIDE.

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Diazomethane reacts with sulphonyl derivatives containing active methylene[2] or methine[3] groups affording C-methylated products; however, it shows as well a 1,3-dipolarophilic[4] behaviour towards α,β-unsaturated sulphones.[5,6] The active methylene character of the CH_2 in 3-phenyl-2H-thiopyran-1,1-dioxide (I) is supported by the deuterium exchange of its protons in the absence of basic catalysis[7] and by the facile formation of the corresponding anion[8,9]; thiopyran-1,1-dioxide system shows as well the normal reactivity of α,β-unsaturated sulphones, as it undergoes addition of weakly basic nucleophiles in position 5 of the ring[8,10].

We have investigated the reaction of 3-phenyl-2H-thiopyran-1,1-dioxide (I) with diazomethane in order to ascertain if methylation or addition would be preferred.

Isomerically pure 3-phenyl-2H-thiopyran-1,1-dioxide (I) (m.p. 100-101°) reacts with diazomethane in ether to give the isopyrazoline (II) (m.p. 115-116° from AcOEt; sint. 96-100°) in 83% yield; (II) is readily isomerized by boiling methanol to the pyrazoline (III) [m.p. 145-147° from MeOH; PMR (DMSO d_6): 2.55 τ, 5H,m; 3.28 τ, 1H,d; 5.8-7.1 τ, 5H,m. N-Benzoyl derivative: m.p. 220-221° from C_6H_6] in 94% yield. Bromination of (III) with two moles of bromine in acetic acid affords the bromo-pyrazole (IV) [m.p. 211-212° from AcOH; PMR (DMSO d_6): 2.14 τ, 1H, s; 2.58 τ, 5H, m; 5.12 τ, 2H, s] in 63% yield.

The position of the attack of diazomethane on the ring has been demonstrated

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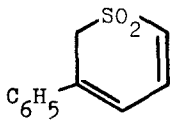
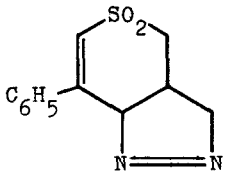
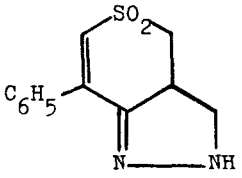
by cleavage of the bromo-pyrazole (IV) with potassium permanganate: the oxidation, carried out in NaOH 2N, gives in low yield the 3-benzoyl-4-carboxy-pyrazole (V) [m.p. 261-262° from MeOH-H_2O; PMR (DMSO d_6): 1.6 τ, 1H,s; 2.25 τ, 6H,m], not yet known in the literature. Pyrazole-carboxylic acid (V) was identified by comparison with the product obtained by thermal (180°) decarboxylation of the benzoyl-pyrazole-dicarboxylic acid (VI) (m.p. 221° from AcOH, lit.[11], m.p. 220°), obtained in turn by permanganate oxidation of 3-benzoyl-5-carboxy-4-methyl-pyrazole (VII)[11]. The above reaction sequence unequivocally assigns the structure of 3-benzoyl-4-carboxy-pyrazole (V)[12] to the product obtained by oxidation of the bromo-pyrazole derivative (IV).



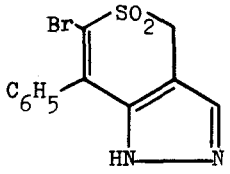
(I)



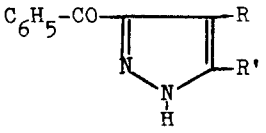
(II)



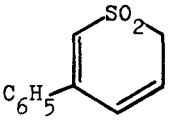
(III)



(IV)



(V) : R= CO_2H , R'= H.
(VI): R= R'= CO_2H.
(VII): R= CH_3 , R'= CO_2H



(VIII)

The structure of the isopyrazoline (II) is supported by the absence of absorptions in the NH stretching region: isomerisation of (II) to (III) occurs either in protic and aprotic dipolar media and appears to be considerably fast. Structure (III) for the obtained pyrazoline is supported by its PMR spectrum: remarkably the olefinic proton α to the sulphonyl group is present at unusually high field.

3-Phenyl-2H-thiopyran-1,1-dioxide (I) seems to be not sufficiently acidic for methylation to occur; addition of diazomethane however takes place smoothly,

apparently through the initial isomerisation of (I) to 3-phenyl-6H-thiopyran-1,1-dioxide (VIII). This isomerisation is supported by treatment of isomerically pure 3-phenyl-2H-thiopyran-1,1-dioxide (I) with a protic solvent at room temperature: for instance after 5 hr. of contact with methanol, (I) gave a mixture of (I) and (VIII) in the ratio 4:1, as revealed by PMR ($CDCl_3$: the two methylene are present, respectively, at 5.72 τ, 1.6H,d, J= 0.5 c.p.s. and at 6.05 τ, 0.4H,d, J= 4 c.p.s.). The mixture obtained (m.p. 74-88°) is analogous to that obtained by quenching the anion of (I) in methanol[8]. The above isomerisation of sulphone (I) in the reaction with diazomethane is presumably due to protic impurities contained in the ethereal solution of the reagent. The attack of the dipolarophile occurs at the end of the dienic chain of sulphone (VIII), which then appears to be more reactive than isomer (I).[14]

All new products gave satisfactory analyses.

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