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# PHOTOCHEMISTRY OF α-ACYLAMINO-β-THIOALKYLACRYLAMIDES

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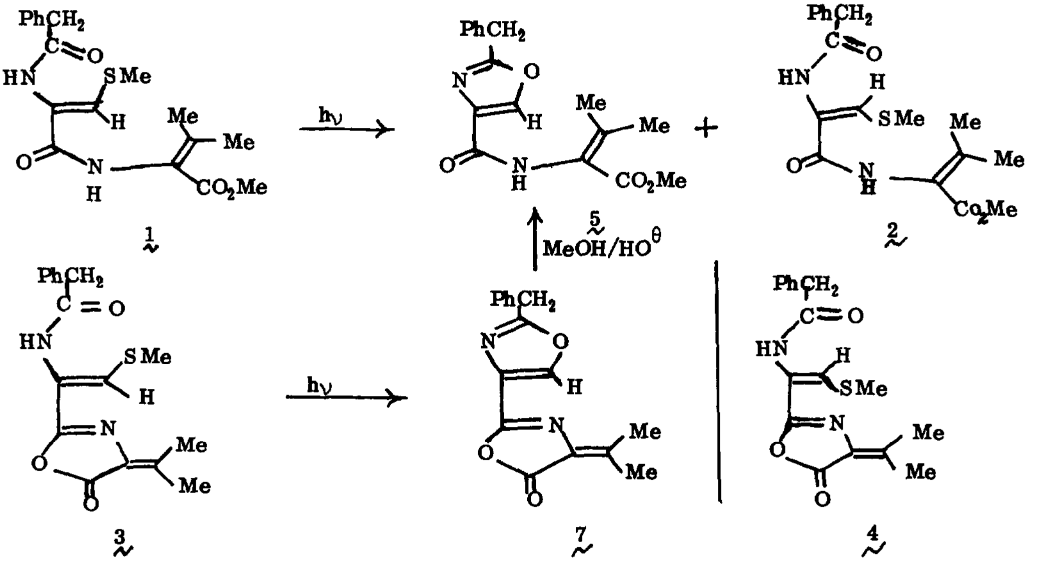
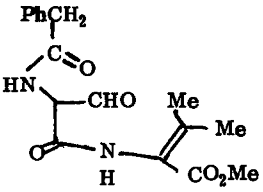
There has recently been interest in the photochemistry of penicillins and cephalosporins[1] and their degradation products[2]. We have obtained[3] the penicillin degradation products (1) and (3) and their stereoisomers (2) and (4) by stereospecific synthesis and now wish to report the results of studies on the photochemistry of these compounds.

The Z-acrylamide (1) was dissolved in degassed pyridine and photolysed using a Hanovia 125 watt medium pressure lamp made up in M84 quartz. Chromatographic separation of the product yielded the starting acrylamide (1, 34%), the E-isomer (2, 14%) identical with a synthetic sample[3], and a compound $C_{17}H_{18}N_2O_4$, mp 106° (13%) which had an nmr spectrum compatible with the structure (5). This oxazole proved identical to a sample synthesised independently by reacting the aldehyde (6)[4] with thionyl chloride. Almost identical results were obtained from photolysis of the E-isomer (2).

When the Z-oxazolone (3) was photolysed, the oxazole-oxazolone (7) was obtained in 23% yield and treatment of this compound with basic methanol yielded the oxazole (5).





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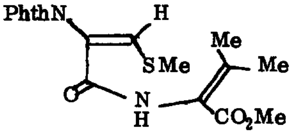

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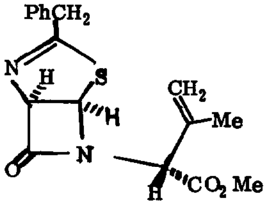

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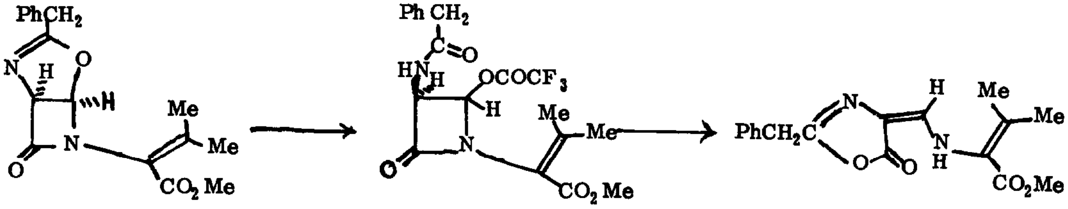
Since the major photochemical reaction appeared to be attack of the amide oxygen on the acrylamide system, it was of interest to see what would happen when this was prevented. The E-phthalimido-derivative (8) was, therefore, photolysed. No reaction was observed with the medium-pressure lamp, and a high-pressure lamp caused rearrangement to the corresponding Z-isomer as the only observable reaction.

It is of interest to record that during attempts at independent synthesis of the oxazole (5), the oxazoline-β-lactam (10)[5] was treated with TFA. It was hoped that this compound would rearrange in a similar manner to the thiazoline (9)[6] to yield (5) but the product (12) was, in fact, obtained. This compound could be synthesised by condensation of 2-benzyl-4-ethoxymethylene-5-oxazolone[7] and methyl dehydrovalinate[4]. A short-lived intermediate could be isolated from the TFA reaction and this was assumed from its spectra to be the β-lactam (11)[8].



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