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THE REACTION OF 2-ACETYLFURAN OXIME p-TOLUENESULPHONATE WITH METHANOL

by

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The reaction which occurs when 2-acetylfuran oxime p-toluenesulphonate is allowed to stand with methanol at room temperature was first investigated by Vargha, Ramonczai and Bite (1). Subsequently Vargha and Ocskay (2) extended this work and showed that the reaction was dependent on the geometry of the oxime toluenesulphonate, the anti derivative undergoing rearrangement in the cold while the syn derivative was stable under comparable conditions but on heating formed products of a Beckmann type reaction.

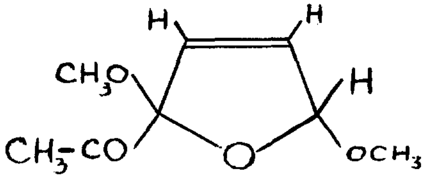
On the basis of chemical degradations, all of which involved reactions under aqueous and eventually acidic conditions, Vargha et al. assigned structure (I), cis-hex-2-ene-4,5-dion-1-al dimethyl acetal to the product which they isolated from the rearrangement of the anti-toluenesulphonate of 2-acetylfuran oxime in methanol.

$$CH_3-CO-CO-CH=CH-CH(OMe)_2$$

(I)

The cis geometry of the product was assigned because of the isolation of maleic acid when (I) was oxidized by 15% hydrogen peroxide in refluxing glacial acetic acid. No ultraviolet or infrared spectral measurements were recorded in support of structure (I).

We have repeated the rearrangement of the toluenesulphonate under the conditions used by Vargha et al. (1) and have isolated a liquid having similar properties to those reported previously (1,2). The spectral properties of our product were, however, incompatible with structure (I). In the ultraviolet there was no intense absorption around 225 mμ as would be expected for a β-substituted α,β-unsaturated ketone (3), the product showing only end absorption (λ 220 mμ, ε 280; λ 210 mμ, ε 800), compatible with the presence of an isolated disubstituted ethylene system (3). In the infrared spectrum the product showed a single strong carbonyl peak at 1733 cm^{-1} (C = O) and a weak peak at 1634 cm^{-1} (C = C). The infrared spectrum showed a marked similarity, apart from the carbonyl band, to that of 2,5-dimethoxy-2,5-dihydrofuran, and we suggest that the actual structure of the product formed by rearrangement of the oxime toluenesulphonate is 2-acetyl-2,5-dimethoxy-2,5-dihydrofuran (II), a formulation which



(II)

agrees with the spectral results and accommodates equally well the chemical evidence of Vargha <u>et al</u>. (1), in particular the oxidation to form maleic acid. It is well known (4) that 2,5-dimethoxy-2,5-dihydrofurans can exist in <u>cis</u> and <u>trans</u> forms and in the present case gas chromatography indicated that the product (II) was a mixture of two components. Fractional distillation using a spinning band column yielded two substantially pure fractions ($C_8H_{12}O_4$) having similar u.v. and i.r. spectral properties but showing some differences in the i.r. fingerprint region. The n.m.r. spectra of the two isomers showed similar absorption characteristics, the lower boiling isomer showing peaks at δ 2.18 (singlet, 3H, $CH_3.CO$), δ 3.20 (singlet, 3H, OCH_3), δ 3.45 (singlet, 3H, OMe), round δ 5.58 (triplet, 1H, $^{O}\searrow CH \swarrow^{O}$), δ 6.0 (quartet, 1H, vinyl) and δ 6.19 (quartet, 1H, vinyl). The three latter groups of signals analysed as an ABX system with δ_{AB} = 9.2 c/s, δ_{AX} = 35.4 c/s; J_{AB} 5.7 c/s, J_{AX} 1.1 c/s and J_{BX} - 1.1 c/s. The couplings in this system exclude a trans arrangement for the vinyl protons and the couplings of AB, AX and BX agree very well with those observed for the 2,5-dimethoxy-2,5-dihydrofuran system (5).

Synthesis of 2-acetyl-2,5-dimethoxy-2,5-dihydrofuran (II) following Elming (6) gave a product having infrared spectrum and other properties indistinguishable from those of the product derived from the methanolysis of 2-acetylfuran oxime p-toluenesulphonate.

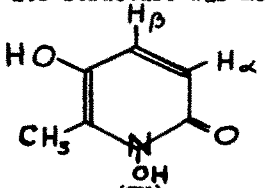
Vargha <u>et al</u>. (1,2) found that treatment of their product with aqueous hydroxylamine hydrochloride yielded a product

($C_6H_7NO_3$) to which they assigned the structure

$$CH_3\text{-}CO\text{-}CO\text{-}CH{=}CH\text{-}CH{=}N\text{-}OH$$

(III)

Nielsen *et al.* (7) prepared a substance having properties identical with those of the oxime isolated by Vargha *et al.* and suggested that its structure was more probably (IV).



(IV)

The hydroxylamine product isolated in our work showed u.v. and i.r. absorption properties in agreement with the above structure (IV) (8,9) and this structure was further confirmed by the n.m.r. spectrum which revealed two exchangeable protons and a simple AB quartet centred on δ 6.8 (δ_{AB} 46.6 c/s; J_{AB} 9 c/s) for protons H_α H_β in addition to the CH_3 signal at δ 2.32.

N.m.r. spectra were measured on a Varian A60 spectrometer at the University of Sydney by Mr. D.C. Dehlsen and Dr. A.V. Robertson whom we thank for their kind assistance.

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