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PHOTOLYSIS OF 2-METHOXY- AND 2-ACETOXYFURAN

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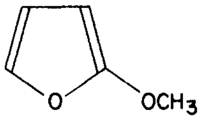
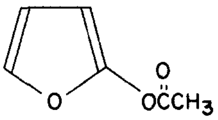
It has been shown that the primary photochemical process in furan[1)] and in a number of alkylfurans[2,3)] is the cleavage of one of the carbon-oxygen bonds in the ring. The behavior of these furans in these instances is similar to that of a vinylether[4)]. In 2-methoxyfuran (I) and 2-acetoxyfuran (II) there are ether linkages external to the ring and vinylic with respect to one of the double bonds in the ring. It was of interest to compare the photochemistry of these compounds with that of furan to see which of the ether links would cleave readily.


I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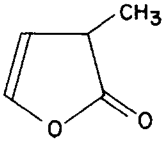
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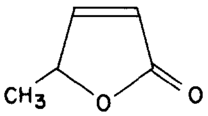
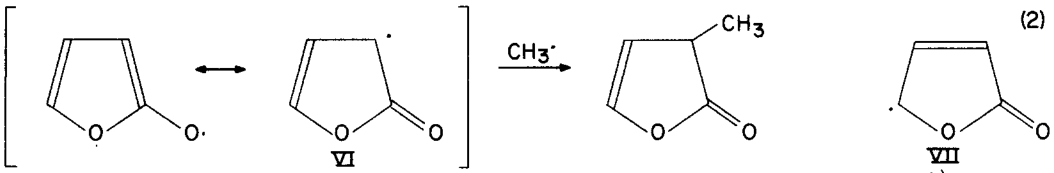

IV

The absorption spectrum of 2-methoxyfuran (Aldrich Chemical Co.) starts at 260 nm and has a maximum of 213 nm ($\epsilon = 4{\cdot}2 \times 10^4$ liter mol^{-1} cm^{-1}). Direct irradiation of the material in the gas phase and in solution in ether, or cyclohexane as well as sensitization by mercury ($^3P_1$)atoms gave essentially similar results but it was most convenient to study the reaction in the vapor phase with the mercury atom as sensitizer[5)].

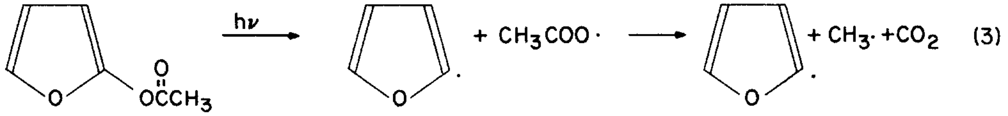
The complex photolyzate consisted of numerous products of which the only major one, formed to the extent of 10-20% of the 2-methoxyfuran that was converted, was an isomer $C_5H_6O_2$ (mol.wt.by mass spectrometry 98). It had an intense absorption at 1800 cm^{-1} (γ -lactone) and a weak absorption at 1370 cm^{-1} (CH_3) in its infrared spectrum. The nmr spectrum (CCl_4



(2)

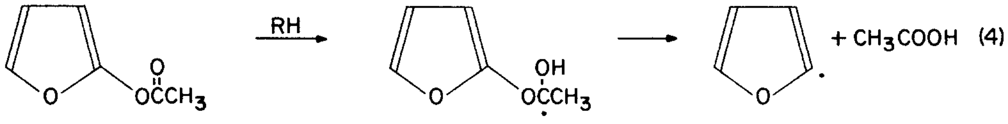
The overall reaction thus bears some resemblance to the photo-Fries rearrangement9) that has been observed in phenolate esters and enol acetates. The alternative structure VII for the oxyfuran radical can lead to IV by the addition of a methyl. But the favorable location of the unpaired electron in VI in comparison to VII must account for the predominance of III over IV in the photolysis of 2-methoxyfuran.

The photochemical processes in 2-acetoxyfuran seem to be quite complex. The furan ring appears intact in the products that were characterized so that the cleavage must occur on primarily in the side chain. By analogy to the photolysis of other acetates10) one primary process may ben



(3)

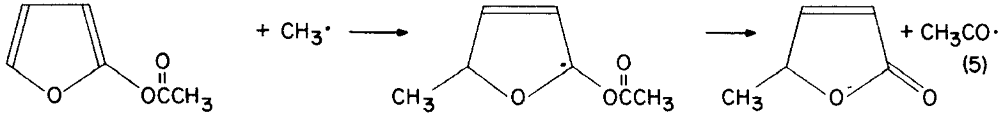
The abstraction of a hydrogen from the solvent by the furyl radical would give furan. Since $CH_3COO.$ is known to decarboxylate readily, it cannot be the source of acetic acid. The abstraction of a hydrogen from the solvent by an excited molecule of the ester can account for the acetic acid.



(4)

A similar reaction has been proposed in the photolysis of aliphatic esters in solution10).

The formation of IV is not easy to explain. It cannot originate in the addition of a methyl to the furyloxy radical V for the reason stated above. In any case the products of radical-radical reactions seem to be of minor importance in this system. A possible pathway is



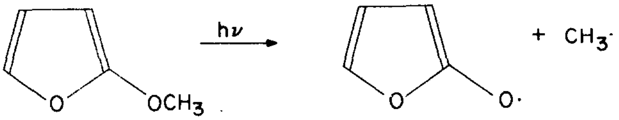
(5)

solun; TMS as internal reference) consisted of absorptions at 8.7T (3H, doublet - J = 7.5) 6.9T (1H, multiplet); 4.50T (1H, Quartet - J = 2,4); 3.25T (1H, Quartet - J = 2,4). The presence of a γ -lactone, two olefinic protons and a methyl group reduced the possible structures to III and IV. Since the carbonyl frequency indicated that the double-bond is not in conjugation with the >C = O group[6], structure III alone would fit all of the data.

Among the other products, the abundant formation of ethane indicated the presence of free methyl radicals in the system. During photolysis in the presence of a small (5%) quantity of oxygen, nearly all of the volatile products including III in its entirety were eliminated. There was a minor amount of CO that was formed in normal photolysis but there were several compounds which corresponded to the decarbonylated products. None of these was characterized. Other isomeric products of the formula C_5H_6O were also formed in traces.

Irradiation of 2-acetoxyfuran[7] was studied in ether (1% solun) at 253.7 nm. The solution was degassed with a stream of pure nitrogen. The photolyzate consisted of unreacted 2-acetoxyfuran along with two products in significant amount (10 and 15% respectively) and numerous others in minor amount. The first of the significant products was identified as acetic acid. The second was a compound of the formula C_5H_6O (mol.wt. by mass spectrometry: 98) with an intense absorption at 1760 cm^{-1} (γ -lactone with conjugation)[6] and a weak absorption at 1370 cm^{-1}(CH_3-) in its infrared spectrum. The nmr spectrum consisted of absorptions of 8.6T (3H, doublet - J = 6.5); 4.95T (1H-multiplet); 4.02T (1H, Quartet - J = 2,6); (1H, Quartet - J = 1.5,6). The presence of the γ -lactone, two olefinic protons, and a methyl group suggested structure IV in which the carbonyl group is in conjugation with the double bond. A comparison with the nmr spectrum of 2-butenoic acid-γ-lactone[8] indicated that this assignment was a reasonable one. Among the minor products, a second lactone (not III) and furan were detected. There was also evidence for free radical attack on the solvent.

These results suggest that in I the major point of photochemical cleavage is in the side chain at the first carbon-oxygen bond.



V

(I)

The oxyfuran radical V can react in its lactone form (VI) with a methyl radical to give III:

which can lead to a chain. Experiments to test this hypothesis are currently being undertaken.

Acknowledgement

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