LETTERS TO THE EDITOR

THE FURAN RING AS A NUCLEOFUGE IN THE AROMATIZATION OF 2-CYCLOHEXEN-1-ONES

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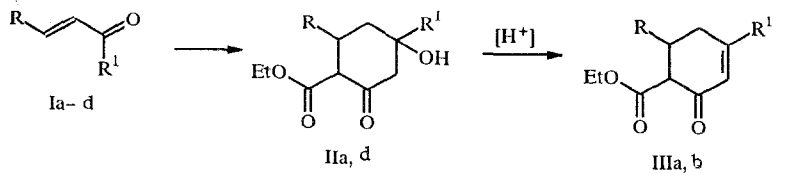
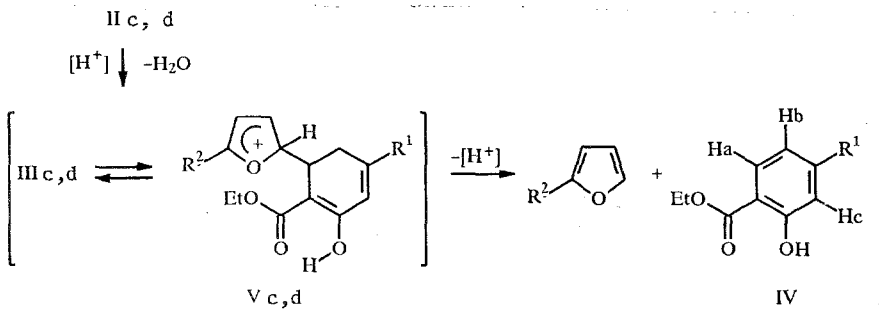
β-Ketols are products of cyclization of 1,5-dicarbonyl compounds with a methyl or methylene group in position 6 relative to one of the carbonyl groups. In acid media, these compounds are readily dehydrated to give cyclohexenones [1, 2].

We have found that ketols II obtained by the addition of ethyl acetoacetate to chalcones I are transformed in acid media depending on the nature of substituent R. Thus, heating IIa and IIb, in which R = C_6H_5, at reflux in benzene in the presence of catalytic amounts of perchloric acid gives the expected cyclic chalcones IIIa and IIIb.



I-III a,b) R = C_6H_5, c) R = 2-furyl, d) R = 5-methyl-2-furyl; a) R^1 = 2-furyl, b) R^1 = 5-methyl-2-furyl, c,d) R^1 = C_6H_5

In the case of ketols IIc and IId, the reaction does not stop after dehydration, but rather also involves the subsequent conversion of IIIc and IIId into salicylic acid derivative IV.



The aromatization of IIIc and IIId likely proceeds through electrophilic *ipso* attack by a proton at C^2 of the furan ring, which is readily protonated due to its high π-basicity in comparison with the unsubstituted benzene ring.

5-Phenyl-3-(2-furyl)-6-ethoxycarbonyl-2-cyclohexen-1-one (IIIa, $C_{19}H_{18}O_4$), mp 108-109°C. IR spectrum (Nujol mull): 1715 (C=O), 1660 (C=O), 1640 cm^{-1} (C=C). PMR spectrum in $CDCl_3$: 1.0 (3H, t,CH_3CH_2, J = 7.0 Hz), 2.83 (1H, d.d.d.d, 4-H, J = 17.5, J = 2.5, J = 3.5, J = 7.0 Hz), 3.02 (1H, br.d.d, 4-H, J = 17.5, J = 3.5 Hz), 3.77 (2H, m, 5-H, 6-H), 4.50 (2H, q, CH_3H_2, J = 7.0 Hz), 6.61 (1H, d, 2-H, J = 2.0 Hz), 7.3 (5H, s, C_6H_5), furan ring protons: 6.53 (1H, d.d, 4-H, J_{34} = 3.6, J_{45} = 2.0 Hz), 6.78 (1H, d, 3-H, J_{34} = 3.6 Hz), 7.58 ppm (1H, 5-H, J_{54} = 2.0 Hz).

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3-(5-Methyl-2-furyl)-5-phenyl-6-ethoxycarbonyl-2-cyclohexen-1-one (IIIb, $C_{20}H_{20}O_4$), mp 98-100°C. IR spectrum (Nujol mull): 1715 (C=O), 1660 (C=O), 1640 cm^{-1} (C=C). PMR spectrum in $CDCl_3$: 1.05 (3H, t, CH_3CH_2, J = 7.0 Hz), 2.78 (1H, d.d.d.d, 4H, J = 17.5, J = 2.5, J = 3.5, J = 7.0 Hz), 3.0 (1H, br.d.d, 4-H), J = 17.5, J = 3.5 Hz), 3.77 (2H, m, 5-H, 6-H), 4.03 (2H, q, CH_3CH_2, J = 7.0 Hz), 6.68 (1H, d, 2-H, J = 2.5 Hz), 7.3 (5H, s, C_6H_5), furan ring protons: 6.16 (1H, m, 4-H), 6.56 ppm (1H, d, 3-H, J_{34} = 3.6 Hz).

Ethyl ester of 2-hydroxy-4-phenylbenzoic acid (IV, $C_{15}H_{14}O_3$), mp 55-56°C. IR spectrum (Nujol mull): 1660 cm^{-1} (C=O). PMR spectrum in CCl_4: 1.27 (3H, t, CH_3CH_2, J = 7.0 Hz), 3.93 (2H, q, CH_3CH_2, J = 7.0 Hz), 6.85 (1H, d.d, H_B), 7.03 (1H, d, H_C), 7.62 (1H, d, H_A, J_{AB} = 8.0, J_{BC} = 2.0 Hz), 7.07-7.48 (5H, m, C_6H_5), 10.07 ppm (1H, s, OH).

REFERENCES

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