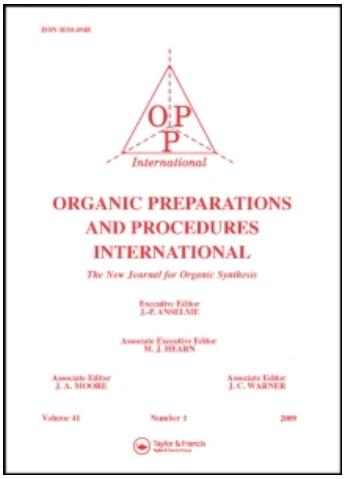

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A SIMPLE SYNTHESIS OF SOME NOVEL OXIME ETHERS

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3361r, 1970.

6. It is interesting to note that under the reaction conditions described (1.0 molar equivalent of acylating reagent), no appreciable amount of product resulting from the Friedel-Crafts acylation of the solvent (toluene) was observed.

A SIMPLE SYNTHESIS OF SOME NOVEL OXIME ETHERS†

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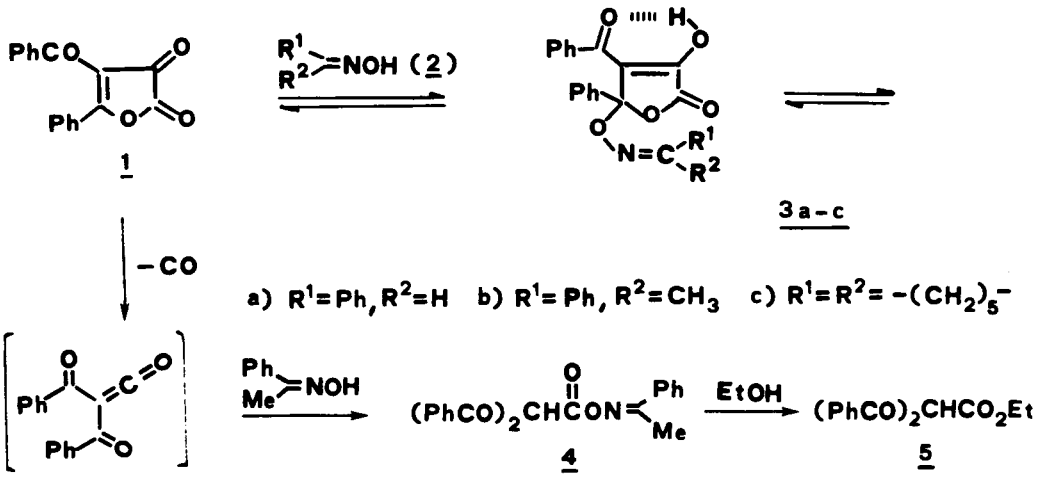
The reaction of 4-benzoyl-5-phenylfuran-2,3-dione (1) with phenylhydrazones or phenylhydrazine leads to pyrazolecarboxylic acids.[1] The use of oximes instead of phenylhydrazones would be expected to give the corresponding isoxazolecarboxylic acids. Surprisingly however, the oximes 2 add to 1 to yield the 1:1 adducts which were identified as oxime ethers (3) containing an acetal group; oxime ethers of this type had not been described previously.[2,3] The formation of these oxime ethers may be viewed as occurring *via* a Michael addition to 1; a very similar attack of phenylhydrazine on 1 was discussed in a previous paper.[1] There are only a few known examples of the synthesis of oxime ethers *via* Michael addition of oximes to activated olefins.[3]

This addition is a thermally reversible process. Thus at 150° (or in boiling xylenes), an acylated oxime 4 is obtained, starting either from 3b or from the corresponding starting materials 1 and 2b themselves. In both



cases, 4 is obviously derived from a nucleophilic addition[4] of the oxime 2 to the dibenzoylketene intermediate,[5] formed by decarbonylation of 1. In quite a similar fashion, the ketene intermediate adds phenylhydrazones to afford the dibenzoylacetic acid hydrazides.[1]

Compounds 3a and 3b show characteristic IR absorption bands at 1770(s), 1700(m) and 1660(s) cm^{-1}, 3c at 1805, 1690 and 1660 cm^{-1} in the solid state (KBr). In chloroform, these absorption bands of 3a-c shift to 1720 and 1630 cm^{-1}. A possible explanation could be the tautomerism of these compounds which is dependent on their physical state.

From the ^{1}H and ^{13}C-NMR spectra of 3b, it is evident that two stereoisomeric forms must exist in a molar ratio of approximately 70:30. This could be due either to rotational barriers of the oxime group or to E/Z-isomerism of the oximes.[6] The shift differences of 0.1 ppm (^{1}H-NMR spectrum) and of 2-4 ppm (^{13}C-NMR spectrum) agree well with correponding literature data of E/Z oxime isomerism.[6,7] Complete assignment of carbon

atoms of 3b is given in the Experimental Section. The fragmentation pattern in the MS spectra of 3 demands a thermally initiated primary elimination of the oxime. This is made evident from peaks with highest intensities, assigned to the corresponding oxime itself and the fragmentation pattern of pure 1 (m/e = 250, M^+-CO; 105, PhCO). The IR and ^{1}H-NMR spectra (no OH, NH-absorption bands, CH-signal at 6.6 ppm) confirmed the diketo form of 4. This agrees well with earlier results obtained from various dibenzoylacetic acid derivatives,[1,8] which again show no tendency toward enolization under the measurement conditions. Compound 4 is easily converted into the ester 5[9] by ethanolysis.

EXPERIMENTAL SECTION

^{1}H NMR, ^{13}C NMR and Mass spectra were determined on Varian EM-360L and XL 200 and MAD 111 spectrometers respectively.

O-(3-Benzoyl-2,5-dihydro-4-hydroxy-5-oxo-2-phenyl-2-furyl)oximes (3). General Procedure.- A mixture of 0.5 g (1.8 mmol) of 1 and 1.8 mmol of the corresponding oxime was warmed up to 50-60° for 5 min. After cooling, the products crystallized upon addition of 5 ml dry ether. Recrystallization was avoided because of partial decomposition of the thermally unstable compounds.

3a: 63% yield as yellow needles, mp. 122-124°.

^{1}H NMR ($CDCl_3$): δ 7.2-8.1 (m, ArH), 8.3 (s, CH). IR(KBr): 3350 cm^{-1} (OH, broad), 1770, 1710, 1670 cm^{-1}. MS (80 eV): m/e (rel. intensities) 250 (M^+ -CO, -oxime, 20), 222(8), 121(15), 105(100).

Anal. Calcd for $C_{24}H_{17}NO_5$: C, 72.12; H, 4.29; N, 3.50

Found: C, 71.88; H, 4.26; N, 3.45

3b: 81% yield as yellow needles, mp. 134-135°.

^{1}H NMR ($CDCl_3$): δ 2.3 (s, Me), 2.4 (s, Me), 7.2-8.0 (m, ArH).

^{13}C NMR ($CDCl_3$): 14, 16 (q, 130 Hz, Me), 110.4 (t, 3Hz, C-2), 123.0 (s, C-3), 150.8 (s, C-4), 156, 160 (m, oxime-C), 165, 168 (s, C-5), 190.0 (t,

4Hz, benzoyl-C). IR(KBr): 3360 cm^{-1} (broad), 1770, 1700, 1660 cm^{-1}; ($CHCl_3$): 3380 cm^{-1} (broad), 1720, 1620, 1575 cm^{-1}. MS (80eV): m/e (rel. intensities) 250 (M^+-CO, -oxime, 10), 222(5), 135(15), 105(100).

Anal. Calcd for $C_{25}H_{19}NO_5$: C, 72.63; H, 4.63; N, 3.39

Found: C, 72.69; H, 4.65; N, 3.34

3c: 60% yield as orange needles, mp. 96-97°.

^1H NMR ($CDCl_3$): δ 1.5, 2.2, 2.5 (broad, CH_2), 7.0-8.0 (m, ArH). ^{13}C NMR ($CDCl_3$): 10.3, 11.6, 14.4 (t, 120 Hz, CH_2), 109.0 (t, 4 Hz, C-2), 121.2 (s, C-3), 151.2 (s, C-4), 158.0 (m, oxime-C), 166.0 (s, C-5), 188.4 (t, 4 Hz, benzoyl-C). IR(KBr): 3000 (broad), 1805, 1690, 1660 cm^{-1}; ($CHCl_3$): 3330 cm^{-1} (broad), 1720, 1615, 1570 cm^{-1}.

Anal. Calcd for $C_{23}H_{21}NO_5$: C, 70.57; H, 5.41; N, 3.58

Found: C, 70.48; H, 5.46; N, 3.50

O-Dibenzoylacetyl Acetophenone Oxime (4)

a) Thermolysis of 0.6 g 3b at 145-150° for 10 min. gave, after cooling and treatment with dry ether, 0.4 g (72%) of 4 recrystallized from ethanol, mp. 140-141°.

b) To a solution of 0.24 g (1.8 mmol) of 2b in 6 ml xylene heated at reflux, was added a solution of 0.5 g (1.8 mmol) of 1 in 30 ml xylene dropwise over 2 hrs. The solvent was then removed *in vacuo* and the residue treated with dry ether to yield 0.23 g (33%) of 4, recrystallized from ethanol, mp. 140-141°.

^1H NMR ($CDCl_3$): δ 2.25 (s, CH_3), 6.6 (s, CH), 7.2-8.1 (m, ArH). IR(KBr): 1770, 1690, 1680 cm^{-1}. MS (80 eV): m/e (rel. intensities) 251, 250(5), 223, 224(15), 135(10), 105(100).

Anal. Calcd for $C_{24}H_{19}NO_4$: C, 74.79; H, 4.97; N, 3.63

Found: C, 74.58; H, 4.87; N, 3.57

Dibenzoylacetic Acid Ethyl Ester (5).- Compound 4 (0.1 g) was refluxed in a

mixture of 4 ml ethanol and 1 ml water for 1 hr. After cooling, 0.06 g (78%) of 5 crystallized from the solution; it was identified by its mp. 112°, mixture melting point with an authentic sample[9] and comparison in TL chromatography.

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