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A NEW SYNTHESIS OF FURANS[1a]

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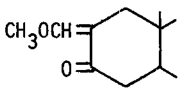
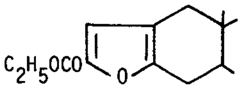
The recent report by Storm and Spencer of the copper-catalyzed addition of ethyl diazoacetate to 2-methoxymethylenecholestan-3-one (I) to form furan II[2] prompts us to report results we have obtained in the addition of sulfur ylides to enol ethers of β-dicarbonyl compounds.

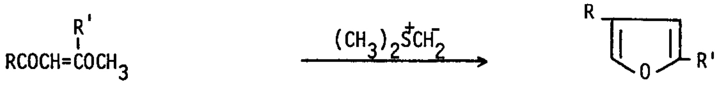


I



II

Enol ether IIIa[3] of dibenzoylmethane in tetrahydrofuran was added to a solution of dimethylsulfonium methylide in dimethyl sulfoxide. After 45 min. at 0° the reaction mixture was poured into water. Ether extraction afforded 42% of 2,4-diphenylfuran (IVa), m.p. 108-109.5° (Lit.[4] m.p. 109°).[5]



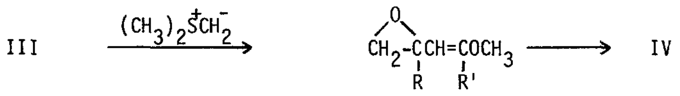
$$RCOCH{=}\overset{R'}{C}OCH_3 \xrightarrow{(CH_3)_2\overset{+}{S}\overset{-}{C}H_2}$$

IIIa, R, R' = C_6H_5
b, R = CH_3, R' = C_6H_5
c, R = C_6H_5, R' = H

IVa, R, R' = C_6H_5
b, R = CH_3, R' = C_6H_5
b', R = C_6H_5, R' = CH_3
c, R = C_6H_5, R' = H
c', R = H, R' = C_6H_5

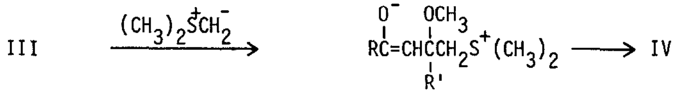
Furan IVa might conceivably have arisen either by attack of the ylide at the carbonyl group to form an epoxide, which cationically rearranged and lost methanol (Path A), or by conjugate addition of the ylide to the double bond followed by intramolecular nucleophilic displacement of dimethyl sulfide and loss of methanol (Path B).

Path A



V

Path B

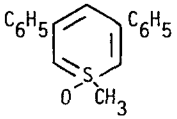


The known preference of this ylide to attack α,β-unsaturated ketones at the carbonyl group[6] provides support for Path A. The acid-catalyzed rearrangements of derivatives of 3,4-epoxybutyraldehyde acetal to furans by Burness[7] and by Cornforth[8] provide additional support. Epoxy enol ether V would be expected to undergo rearrangement more readily than the related acetals. However, it should be mentioned that the furan was isolated from the present reaction mixture without acidification.

Evidence for Path A was obtained by submitting enol ethers IIIb[9] and IIIc[10] to this reaction. From enol ether IIIb the only isolable product (41%) was 4-methyl-2-phenylfuran (IVb), m.p. 38-40° (Lit.[11] m.p. 42-43°).[5] Isomeric furan IVb' was not detected. Enol ether IIIc afforded 8% of 3-phenylfuran (IVc), m.p. 57-58° (Lit.[12] m.p. 58.5-59°).[5] No trace of IVc' could be detected by n.m.r. or g.l.c.[13]

The present procedure provides a new route to 3-substituted furans from readily available enol ethers. Alkyl and aryl groups cannot generally be introduced at the 3-position of furan directly because of the high reactivity of the 2-position. Alternative procedures include rearrangements of epoxy acetals[7,8] and condensations of tetrahydrofuran-3-one with Grignard reagents.[12]

The use of dimethyloxosulfonium methylide with IIIa did not afford furan IVa but instead gave thiabenzene derivative VI, m.p. 147.5-149° (Lit.[14] m.p. 148-148.5°) in 56% yield.[5] Compound VI was previously prepared by Hortmann by the condensation of this ylide with 1,4-diphenyl-2-propyn-1-one.[14]



VI

References:

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5 Infrared and n.m.r. spectra were consistent with structural assignments.

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13 Another product resulting from the addition of two equivalents of ylide to IIIc was also isolated. It will be the subject of a later paper.

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