

INTRAMOLECULAR CYCLISATION OF α -DIAZO KETONES THROUGH
 CARBONYL YLIDE INTERMEDIATES. A NOVEL FORMATION OF
 THE FURAN-3(2H)-ONE SYSTEM

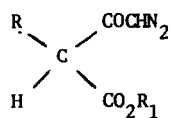
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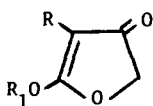
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Carbonyl ylides have been suggested recently as intermediates in some 1,3-dipolar cycloadditions.^{1,2} As an alternative route to carbonyl ylides, the reaction of an electrophilic ketocarbene species with carbonyl compounds may be considered. This pathway, however, has been realised only in few cases.²⁻⁵

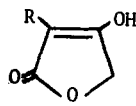
We now wish to report the catalytic decomposition⁶ of ethyl 2-phenyl-4-diazoacetate⁷ (1a) to give 5-ethoxy-4-phenyl-3(2H)-furanone (2a) in ca. 35% yield, m.p. 117-8°. A second product isolated in ca. 13% yield was identified as the already known⁹ 3-phenyl-tetronic acid (4-hydroxy-3-phenyl-2(5H)-furanone) (3a). Presumably, the tetronic acid represents a secondary product formed by hydrolysis of the furanone 2a during work-up. Indeed, the furanone 2a was converted into 3a in 75% yield when stirred overnight in a mixture of ether and aqueous HCl.^{10,11}



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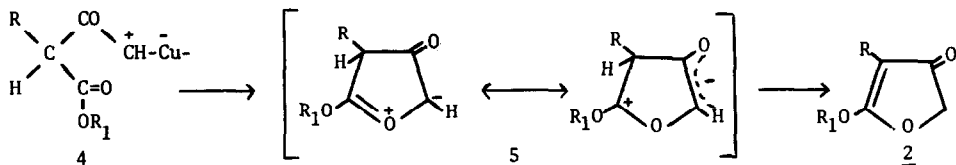


3

- a. R = C₆H₅; R₁ = C₂H₅
 b. R = R₁ = C₂H₅
 c. R = C₆H₅CH₂; R₁ = CH₃

Similarly, catalytic amounts of (MeO)₃P.CuI effected the smooth decomposition of the 2-ethyl- and 2-benzyl-4-diazoacetates (1b and 1c) in ether at room temperature. The oily furanone 2b was formed in 41% yield (glc) and could be purified by preparative glc (3/8 in x 5.5 ft column of 3% Se-30 on 60-80 mesh Gas-Chrom Q). The furanone 2c was isolated in 25% yield by preparative tlc on silica gel. All three furanones showed strong and characteristic ir absorption at ca. 1590 cm⁻¹ and a weaker band at ca. 1685 cm⁻¹.¹²

The course of the reaction may be rationalised by formation of the resonance stabilised five-membered cyclic carbonyl ylide (5), produced from the ketocarbene copper complex (4) reacting intramolecularly with the suitably located alkoxy carbonyl group. The intermediate



(5) collapses preferentially to the product by proton transfer. This reaction which represents a novel route to the 3(2H)-furanone system is now under further investigation.

All new compounds gave satisfactory elemental analysis and have been characterised spectroscopically.

REFERENCES and NOTES

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6. CuSO₄ in refluxing cyclohexane or (MeO)₃P.CuI complex in benzene at room temp. were used as catalysts.
7. This compound was obtained by diazomethane treatment of the corresponding acid chloride, which in turn was prepared by partial hydrolysis⁸ of commercial diethyl phenylmalonate followed by reaction with oxalyl chloride.
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10. All 5-alkoxyfuranones, prepared in this work were water sensitive and hydrolysed to tetronic acids, but could be stored unchanged at -5° in the absence of moisture.
11. 5-Alkoxy-3(2H)-furanones have been used recently as intermediates for the synthesis of tetronic acids.¹²
12. T.P.C. Mulholland, R. Foster, and D.B. Haydock, *J. Chem. Soc., Perkin I*, 1972, 1225