

INTRAMOLECULAR KETOCARBENE ADDITION TO FURAN: A NOVEL RING-OPENED PRODUCT

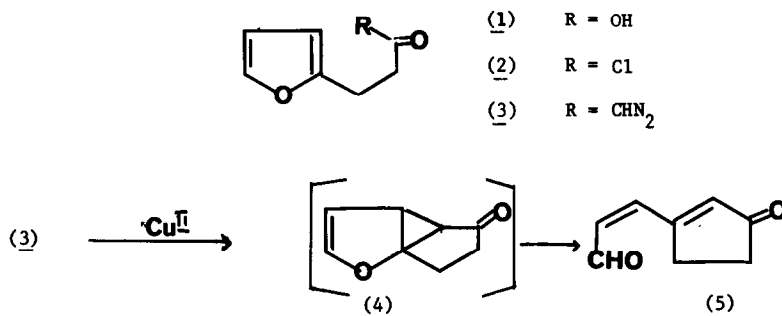
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Intramolecular carbene addition to aromatic hydrocarbons<sup>1,2,3</sup> and ketocarbene addition to benzene<sup>4</sup> are well established reactions. We now report that intramolecular ketocarbene addition to furan is followed by ring opening resulting in the cyclopentenoketo-aldehyde (5).

$\beta$ -(2-Furyl)-propionyl chloride (2) (prepared by treatment of the acid (1) with oxalyl chloride) was quantitatively converted into the diazoketone (3) by excess diazomethane. Anhydrous copper (II) sulphate catalysed decomposition of a 0.05M solution of the diazoketone (3) in refluxing cyclohexane then gave trans-3-(cyclopent-2-enone-3-yl) propenal (5), m.p. 65°, 60% yield.



The product (5) analysed satisfactorily for C<sub>8</sub>H<sub>8</sub>O<sub>2</sub> and its structure was readily established from its spectral properties. The field desorption mass spectrum showed the molecular ion at m/e 136, whilst the i.r. spectrum showed that it was an unsaturated dicarbonyl derivative i.e.  $\nu_{\text{max}}$  (nujol) 1665, 1682, 1707 cm<sup>-1</sup>. The n.m.r. spectrum (CDCl<sub>3</sub>) showed an aldehyde proton ( $\tau$  -0.18, d, J=8Hz), vinylic protons at

$\tau$  2.74 (1H d,  $J=13\text{Hz}$ ), 3.63 (1H, s) and 3.75 (1H, d d) and methylene protons at  $\tau 7.05$  (2H, m) and 7.4 (2H, m). The u.v. spectrum (ethanol),  $\lambda_{\text{max}}$  271 nm ( $\epsilon = 14, 100$ ) (calculated 272 nm using Woodward's rules) was consistent with the structure assigned.

Formation of the cyclopenteno-aldehyde (5) can be rationalised on the basis of an initial intra-molecular addition of the ketocarbene to the furan to give the intermediate (4) followed by ring opening of the heterocyclic system. The stereochemistry at the exocyclic carbon-carbon double bond is assigned as trans based on the coupling constant  $J$  (13Hz) of the attached protons, as well as characteristic bands in the i.r. spectrum at  $\nu_{\text{max}}$  985 and 1295  $\text{cm}^{-1}$ . A similar (intermolecular) reaction between furan and diazoanthrone has recently been described<sup>5</sup>.

#### REFERENCES

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