

A Vinylogous Wolff Rearrangement; Copper Sulphate-catalysed Decomposition of Unsaturated Diazomethyl Ketones

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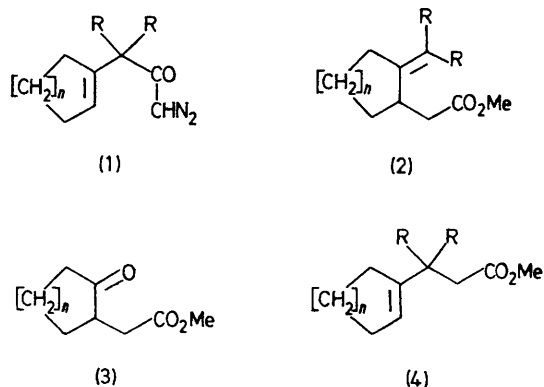
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Summary Copper sulphate-catalysed decomposition of the unsaturated diazomethyl ketones (**1a—c**) in the presence of methanol leads to the $\gamma\delta$ -unsaturated esters (**2a—c**), respectively.

ALTHOUGH copper-catalysed reactions of unsaturated diazomethyl ketones leading to intramolecular cyclopropane formation¹ have been widely employed in organic syntheses, few examples² exist where the site of unsaturation is $\beta\gamma$ to the carbonyl group. We report here the copper sulphate-catalysed decomposition of such diazomethyl ketones (**1a—c**), which in the presence of methanol leads *via* a novel skeletal rearrangement to the $\gamma\delta$ -unsaturated esters (**2a—c**). In addition, we draw attention to the contrast in reaction pathway followed when (**1a—c**) are subjected to photochemical decomposition.

Treatment of (**1a—c**), derived from the corresponding $\beta\gamma$ -unsaturated acid chloride,³ with anhydrous CuSO_4 suspended in boiling cyclohexane containing 2.5% methanol, affords (**2a—c**),[†] respectively in 31, 67, and 85% yield.[‡] The structures of (**2a—c**) were deduced from their spectroscopic properties; *e.g.* (**2a**) showed ν_{max} 3090w, 1740s, 1645w, 1165s, and 895m cm^{-1} ; τ (60 MHz) 0.90—2.83 (m, 11H), 3.58 (s, 3H), 4.51br (s, 1H), and 4.61br (s, 1H). Confirmation of structures (**2a—c**) was obtained by ruthenium tetroxide

oxidation⁴ to the respective ketone methyl esters (**3a**) and (**3b**), available from the known ethyl esters.⁵



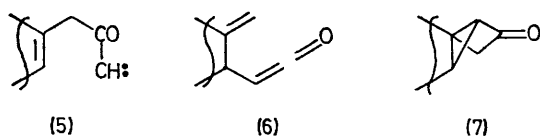
a; $n = 2$, $R = \text{H}$
 b; $n = 2$, $R = \text{Me}$
 c; $n = 1$, $R = \text{Me}$

Interestingly, irradiation (*ca.* 0.02M) $\lambda > 2800 \text{ \AA}$ of (**1a—c**) in methanol leads to the isomeric esters (**4a—c**) in

[†] All new compounds described had satisfactory microanalysis and spectroscopic properties.

[‡] Yields, determined by g.l.c. calibration and based on acid chloride, are not maximized.

79, 95, and 92% yields,⁶ respectively, with only the diazoketone (1c) yielding an appreciable amount (ca. 8%) of (2c). Thus, the photochemical Wolff rearrangement of such unsaturated diazoketones, leading to the expected



chain-lengthened ester, apparently proceeds normally, whilst CuSO_4 catalysis generates, *via* skeletal rearrangement, a new $\gamma\delta$ -unsaturated ester. This transformation, an extension of the Arndt-Eistert procedure, is formally a vinylogous Wolff rearrangement and its utility as a synthetic method is increased by the ready availability of $\beta\gamma$ -

unsaturated carboxylic acid derivatives. Recently the thermal decomposition of triphenylacetyldiazomethane, which appears to involve a similar skeletal rearrangement, was reported by Wilds and his co-workers.⁷

A possible pathway⁸ for these reactions is through an intermediate carbene or carbenoid (5) formed by decomposition of the diazoketone. Skeletal rearrangement of this intermediate can then lead to the ketene (6) which is trapped as an ester in the presence of methanol. The rearrangement leading to the postulated ketene can formally be envisaged to occur either by a [2,3]sigmatropic reaction or by the formation and subsequent fragmentation of a bicyclo[2,1,0]pentane derivative (7).

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¹ G. Stork and J. Ficini, *J. Amer. Chem. Soc.*, 1961, **83**, 4678.

² W. von E. Doering and M. Pomerantz, *Tetrahedron Letters*, 1964, 961.

³ The acid chlorides were prepared from the known carboxylic acids: O. Wallach, *Annalen.*, 1909, **365**, 255; O. Wallach and K. Fleischer, *Chem. Zentr.*, 1907, 53; O. Wallach and T. Mallison, *Annalen.*, 1908, **360**, 68.

⁴ S. W. Pelletier, K. N. Iyer, and C. W. J. Chang, *J. Org. Chem.*, 1970, **35**, 3535.

⁵ G. Stork, R. Terrell, and J. Szmuzkovicz, *J. Amer. Chem. Soc.*, 1954, **76**, 2029; A. Katz, *Annalen.*, 1906, **350**, 299.

⁶ A. B. Smith and W. C. Agosta, *J. Amer. Chem. Soc.*, 1973, **95**, 1961.

⁷ A. L. Wilds, R. L. von Trebra, and N. F. Woolsey, *J. Org. Chem.*, 1969, **34**, 2404; also see A. L. Wilds, J. Van der Berghe, C. H. Winestock, R. L. von Trebra, and N. F. Woolsey, *J. Amer. Chem. Soc.*, 1962, **84**, 1503, footnote 7.

⁸ At present it is impossible to exclude the possibility of diazoketone protonation followed by rearrangement as suggested by A. L. Wilds; see reference 7.