Acid-catalysed Decomposition of βγ-Unsaturated Diazomethyl Ketones: A New Cyclopentenone Annelation

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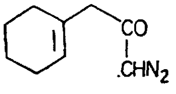
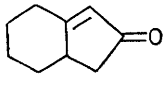
Summary The acid-catalysed decomposition of the unsaturated diazomethyl ketones (**1**—**3**) leads to the cyclopentenone derivatives (**4**—**6**), respectively; this reaction, in conjunction with the Reformatsky addition–dehydration sequence, leading to βγ-unsaturated acids, represents a new cyclopentenone annelation scheme.

Although the Robinson annelation[1] yielding cyclohexenones has been widely employed, no comparable simple method exists for cyclopentenone annelation.[2] Recently, we have studied βγ-unsaturated diazomethyl ketones,[3] and now report their conversion into cyclopentenones. The diazoketones (**1**—**3**), derived from the corresponding βγ-unsaturated acid chlorides,[4] were treated with BF_3–Et_2O in nitromethane† (room temp., 1·5 h), followed by 10% aqueous HCl and then heated at reflux for 1 h to give (**4**—**6**)‡ respectively in 50—68% yield.§ The structures of (**4**—**6**) were deduced from their spectroscopic properties. Structure (**4**) was confirmed by comparison with an authentic sample prepared by Deno's method.[5]

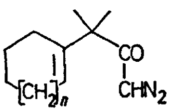
A reasonable pathway for these reactions involves BF_3 complexation with the diazoketone at either the O or C atom. Cyclization of this intermediate, involving π-bond participation in the displacement of nitrogen, leads to the carbocation (**7**) which eliminates a proton to yield a mixture



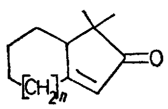
(1)



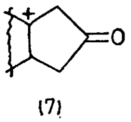
(4)



(2) (n=1)
(3) (n=2)



(5) (n=1)
(6) (n=2)



(7)

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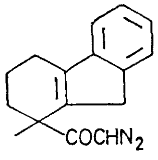
† Similar conditions have recently been employed by L. N. Mander and co-workers, see ref. 6.

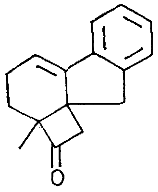
‡ All new compounds described had satisfactory micro-analyses and spectroscopic properties.

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

of the αβ and/or the βγ isomers. Subsequent aqueous acid treatment gives (**4**—**6**) respectively. This transformation, an extension of the acid-catalysed intramolecular carbon-alkylation of γδ-unsaturated diazoketones introduced by Mander[6] and Erman,[7] represents a new cyclopentenone synthesis, which when combined with the improved Reformatsky addition–dehydration sequences[8] leading to βγ-unsaturated acids, yields a new synthetic cyclopentenone annelation procedure.



(8)



(9)

Ghatak reported recently that βγ-unsaturated diazoketones such as (**8**) give cyclobutanone derivatives (**9**) exclusively upon acid-catalysed decomposition.[9] This apparent departure from the above reaction pathway is explicable in terms of formation of the most stable carbocation intermediate.

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[2] For a recent cyclopentanone annelation sequence see B. M. Trost and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, 1973, **95**, 289, 5311.

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[4] The acid chlorides were prepared from the known carboxylic acids: O. Wallach, *Annalen*, 1909, **365**, 255; O. Wallach and T. Mallison, *Annalen*, 1908, **360**, 68; F. Korte, T. Falbe, and A. Zschocke, *Tetrahedron*, 1959, **6**, 201.

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