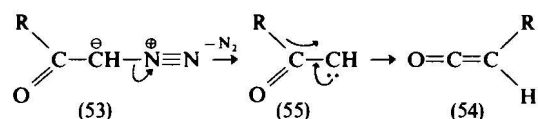


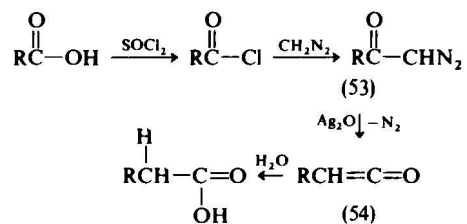
### 5.4.2.5 Wolff rearrangements

This rearrangement has been separated from carbocationic rearrangements proper as it involves migration to an uncharged, albeit electron-deficient, carbene-like carbon (*cf.* p. 266) atom rather than to a positively charged one. The reaction involves the loss of nitrogen from  $\alpha$ -diazoketones (53), and rearrangement to highly reactive *ketenes* (54):



The ketenes will then react readily with any nucleophiles present in the system, e.g.  $\text{H}_2\text{O}$  below. The reaction can be brought about by photolysis, thermolysis, or by treatment with silver oxide. In the first two cases an actual carbene intermediate (55) is probably formed as shown above, in the silver catalysed reaction loss of nitrogen and migration of R may be more or less simultaneous. In the case where R is chiral, e.g.  $\text{C}_4\text{H}_9\text{C}^*\text{MePh}$ , it has been shown to migrate with retention of its configuration (*cf.* p. 117).

Diazoketones (53) may be obtained by the reaction of diazomethane,  $\text{CH}_2\text{N}_2$ , on acid chlorides, and a subsequent Wolff rearrangement in the presence of water is of importance because it constitutes part of the Arndt-Eistert procedure, by which an acid may be converted into its homologue:



As well as in water, the reaction can be carried out in ammonia or in an alcohol when addition again takes place across the  $\text{C}=\text{C}$  bond of the ketene to yield an amide or an ester, respectively, of the homologous acid.

The Wolff rearrangement has a close formal resemblance to the Hofmann and related reactions (p. 122), in which migration takes place to an electron-deficient nitrogen atom to form an isocyanate,  $\text{RN}=\text{C}=\text{O}$ , intermediate.

## 5.5 DIAZONIUM CATIONS

The nitrosation of primary amines,  $\text{RNH}_2$ , with, for example, sodium nitrite and dilute acid (*cf.* p. 107) leads to the formation of diazonium