Halogenated Ketens. Formation of Allenes by the Pyrolysis of Halogenated Oxetan-2-ones

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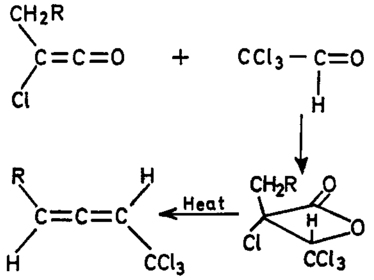
Summary Cycloadducts derived from the cycloaddition of alkylchloroketens and chloral were decarboxylated over a hot wire to produce trichloromethylallenes.

THE cycloaddition of ketens to chloral to produce oxetan-2-ones has been recently described.[1–3] Although these oxetan-2-ones are resistant to decarboxylation under the normal conditions when refluxed over a hot wire a double elimination yields allenes.



(I) R = H
(II) R = Me
(III) R = Et

Thus the oxetan-2-one derived from methylchloroketen and chloral, (I), when pyrolysed in a keten generator apparatus[4] at 1·5—2 mm gave, after *ca.* 2 h, trichloromethylallene (trapped in a solid CO_2–acetone trap). Distillation afforded the allene (60%) at 80—82°; λ_{max} 1601vs cm^{-1} and 1965w cm^{-1}; τ (CCl_4) 5·36 (d, 2H) and 6·03 (s, 1H).

The cycloadducts (II) and (III) upon pyrolysis gave the corresponding allenes in yields of 50 to 40%. Apparently, the decarboxylation of the oxetan-2-one is retarded by the presence of the electronegative substituent and thermal dehydrochlorination accompanies the decarboxylation.

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[2] W. T. Brady and L. Smith, *Tetrahedron Letters*, 1970, 2963.
[3] W. T. Brady and L. Smith, *J. Org. Chem.*, 1971, **36**, 1637.
[4] Org. Reactions, 1947, **3**, 137.