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HALOGENATED KETENES. XXVI. MIXED DIMERS[1]

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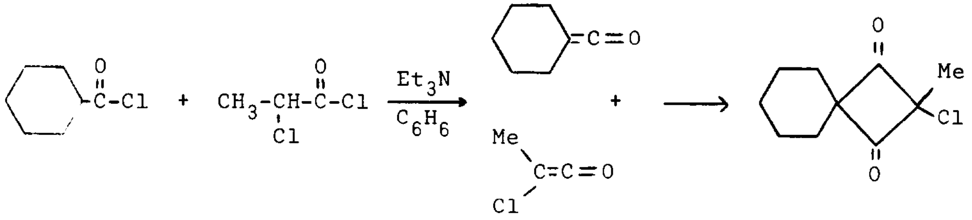
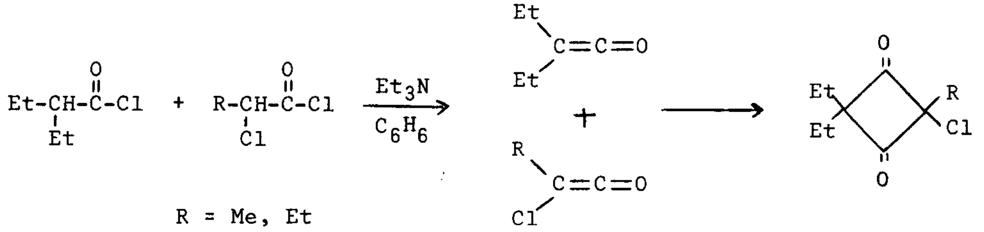
Most ketenes spontaneously dimerize on standing or upon heating.[2] However, no reports have appeared on the dimerization of halogenated ketenes although numerous papers on cycloaddition reactions of these ketenes are found.[3] We would now like to report the mixed dimerization of some halogenated ketenes with pentamethyleneketene and diethylketene.

The reaction of triethylamine with an equimolar mixture of cyclohexanecarboxyl chloride and α-chloropropionyl chloride in benzene at reflux yields the mixed dimer of methylchloroketene and pentamethyleneketene, 2-chloro-2-methylspiro[3.5]nona-1,3-dione. Thus, to a 0.1 m portion of cyclohexanecarboxyl chloride and 0.1 m of α-chloropropionyl chloride in 250 ml of benzene was added 0.2 m of triethylamine. This mixture was refluxed for 24 hrs. Upon cooling, the salt was removed by filtration and the solution concentrated on a rotatory evaporator. Vacuum distillation afforded the mixed dimer in 56% yield at 67-70° at 0.025 mm; mp, 67-69°; ir, 1750 cm.$^{-1}$ (C=O); nmr, a multiplet centered at 1.80 δ out of which there was a singlet at 1.70 δ. Calcd. for $C_{10}H_{13}ClO_2$: C, 59.85; H, 6.48; Cl, 17.71. Found: C, 59.60; H, 6.65; Cl, 17.45. Some dimer of pentamethyleneketene was also produced.



The pentamethyleneketene forms slowly under these conditions over a period of several hrs.[4] The α-chloropropionyl chloride reacts with triethylamine to form 1,2-dichloropropenyl 2-chloropropanoate which slowly produces methylchloroketene over a period of several hrs.[5] This ester could be used as a source of methylchloroketene in which case the mixed dimer was produced in 63% yield. The mixed dimers of ethylchloroketene and t-butylbromoketene with pentamethyleneketene were also prepared by the above procedure.

The mixed dimers of methylchloroketene and diethylketene and also ethylchloroketene and diethylketene, were prepared in a similar manner in 63 and 65% yields respectively except a 4-5 day reaction time was necessary.



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