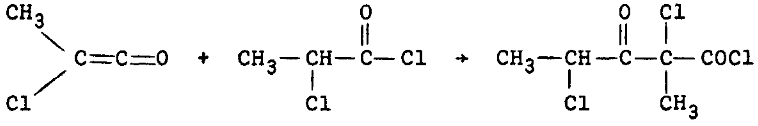
Tetrahedron Letters No.16, pp. 1977-1980, 1968. Pergamon Press. Printed in Great Britain.

HALOGENATED KETENES VI. THE ADDITION OF α-CHLOROPROPIONYL CHLORIDE TO METHYLCHLOROKETENE[1]

William T. Brady and Robert Roe, Jr.[2]
Department of Chemistry
North Texas State University,
Denton, Texas

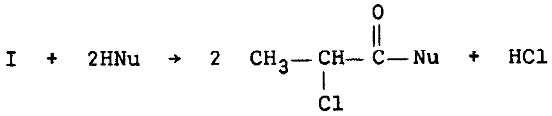
(Received in USA 4 December 1967)

One of us has recently reported on the preparation and cycloaddition of methylchloroketene (3,4). In our continuing studies on the chemistry of halogenated ketenes, we attempted the preparation and dimerization of methylchloroketene by the dehydrochlorination of α-chloropropionyl chloride with triethylamine. However, instead of isolating the dimer, we obtained a good yield of a 1:1 adduct of methylchloroketene and α-chloropropionyl chloride (I). This communication describes this reaction and the proof of structure of I. 2,4-Dichloro-2-methyl-3-ketopentanoyl chloride (I) as prepared from methylchloroketene and α-chloropropionyl chloride, is a mixture of diastereomers in the ratio of 5:4 as determined by pmr and vpc. This compound reacted with three equivalents of base thus establishing an equivalent weight of 74.5 (theory 72.5). Several attempts to form a derivative of I



I

resulted in cleavage of the molecule and formation of a propionyl derivative as illustrated below:



$$\mathrm{I} + 2\mathrm{HNu} \rightarrow 2\ CH_3{-}\underset{\substack{|\\ Cl}}{CH}{-}\overset{\substack{O\\ \|}}{C}{-}Nu + HCl$$

HNu = water, methanol, benzylamine

The optimum conditions for the formation of I are described below: Triethylamine (0.2 m.) in 50 ml. of dry hexane was added dropwise to a solution of α-chloropropionyl chloride (0.3 m.) in 250 ml. of dry hexane at 0-5° over a 30 min. period. After the addition was complete, the reaction mixture was stirred an additional hour as it warmed to room temperature. Only half the stoichiometric amount of amine salt (0.15 m.) was removed by filtration, and distillation at reduced pressure afforded I in 64% yield (5). b.p. 48-50° at 0.8 mm.; infrared absorption (smear): 5.6μ (s) and 6.04μ (m); pmr spectrum ($CHCl_3$): quartet centered at 5.5 ppm; singlet at 7.8 ppm; singlet at 7.9 ppm; doublet at 8.25 ppm. These peak areas were in the ratio of 1:1.5:1.5:3. Calcd. for $C_6H_7Cl_3O_2$: C, 33.10; H, 3.22; Cl, 49.0. Found: C, 33.28; H, 3.57; Cl, 48.91.

The acid halide (I) can also be produced by the stoichiometric addition of acid halide to amine. Consequently, to prevent the formation of I, it is necessary to add the acid halide to a 200-300% *excess* of triethylamine *slowly*. In *in situ* cycloaddition reactions with olefinic compounds where less than a stoichiometric amount of salt is produced, yields can be raised considerably by taking precautions against this reaction.

If the dehydrochlorination described above is conducted in the presence of cyclopentadiene, I is not significantly produced; instead a good yield of the methylchloroketene-cyclopentadiene adduct is obtained (3). Also in the presence of the diene, a stoichiometric amount of the amine salt is obtained rather than just half the stoichiometric amount. Consequently, this is considered ample evidence that this reaction is proceeding via methylchloroketene.

The infrared band at 6.04μ is surprising and perhaps is due to a portion of the β-keto group existing in the enol form (6).

Staudinger and coworkers have reported the reaction of diphenylketene with acid halides and more recently reports have indicated that this reaction occurs only with activated acid halides such as α-haloacid halides (7,8). Consequently, this problem of the ketene reacting with the acid halide from which it was prepared is much more likely to occur in the preparation of halogenated ketenes and precautions should be taken to prevent this side reaction from occurring (9).

ACKNOWLEDGMENTS

Support of this investigation by a National Science Foundation Grant (GP-7386) is gratefully acknowledged.

REFERENCES

1. Paper V. W. T. Brady and O. H. Waters, J. Org. Chem., 32, 3703 (1967).
2. High School Science teacher on National Science Foundation Research participation Program. Grant GW-559.
3. W. T. Brady and B. M. Holifield, Tetrahedron Letters, No. 45, 5511 (1966).

4. W. T. Brady and B. M. Holifield, *Tetrahedron*, **23**, 4251 (1967).

5. Half the stoichiometric amount based on formation of the ketene. The amount of salt produced is indicative of the extent of reaction between ketene and acid halide.

6. The corresponding adduct of dimethylketene and trichloroacetyl chloride has just been prepared by us and while there is a strong band in the infrared at 5.6μ there is no absorption at 6.04μ.

7. H. Staudinger, O. Gohring and M. Scholler, *Chem. Ber.*, **47**, 40 (1914).

8. F. Sorm, J. Smrt and J. Beranek, *Chem. Listy*, **48**, 679 (1954); through *Chem. Abstr.*, **49**, 9545 (1955).

9. We have observed this same side reaction in other halogenated ketene preparations.