# Silver Ion-catalysed Rearrangement of an Allylic Halide

By DENNIS N. KEVILL* and CHARLES R. DEGENHARDT
(*Department of Chemistry, Northern Illinois University, DeKalb, Illinois* 60115)

*Summary* When 3-chlorobut-1-ene reacts with an MeCN solution of $AgClO_4$, a silver ion-catalysed allylic rearrangement accompanies the silver ion-assisted reactions which proceed with precipitation of AgCl.

IT was proposed[1] several years ago that alkyl halides in MeCN react faster with $AgNO_3$ than with $AgClO_4$ because the more nucleophilic nitrate ion is better able to divert an alkyl halide–silver ion complex[2] away from the alternative loss of silver ion and return to reactant. Direct evidence[3] for internal return of halide within halide–silver ion complexes came from the observation, using $AgClO_4$ in MeOH, of a silver ion-catalysed rearrangement of 4,7,7-trimethyl-2-chloro-2-azabicyclo[2,2,1]heptane to *exo*-2-chloro-3,3,4-trimethyl-1-azabicyclo[2,2,1]heptane, which was postulated to involve simultaneous bond formation and rupture without formation of a free chloride ion. More recently, it has been suggested that silver ion can catalyse the decomposition of methyl chloroformate to MeCl.[4]

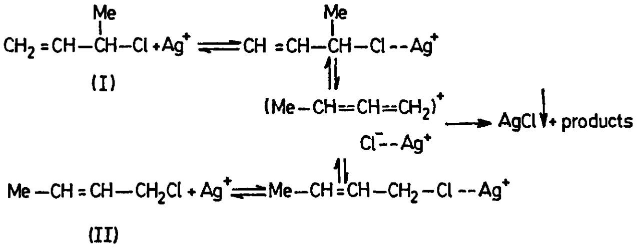

TABLE. Reactant and product concentrations[a] in an MeCN solution initially 0·190M in $AgClO_4$ and 0·197M in 3-chlorobut-1-ene at 45·1 °C

| Time[b]/ min | (I) | (II)[c] | (III)[d] | (IV)[e] | (V) | % Reaction[f] |
|---|---|---|---|---|---|---|
| 0 | 98 | 0·0 | 1·1 | 0·0 | 0·0 | 2·0 |
| 355 | 92 | 3·5 | 4·1 | 4·5 | 3·0 | 12·8 |
| 1449 | 64 | 8·2 | 4·8 | 6·8 | 3·6 | 31·8 |
| 1820 | 51 | 9·3 | 4·4 | 6·1 | 3·8 | 36·2 |
| 2823 | 39 | 9·7 | 5·0 | 6·2 | 4·2 | 44·8 |
| 4299 | 38 | 13·6 | 5·1 | 5·6 | 4·8 | 52·9 |
| 6244 | 32 | 14·0 | 5·0 | 3·7 | 5·1 | 59·4 |
| 8621 | 20 | 8·3 | 3·7 | 5·7 | 5·1 | 64·2 |
| 11,479 | 19 | 6·6 | 4·3 | 2·5 | 4·6 | 67·6 |
| 23,031 | 12 | 4·7 | 2·9 | 3·1 | 3·3 | 75·6 |

[a] Expressed as percentage of initial 3-chlorobut-1-ene concentration and relative to chloroform or *N*-t-butylacetamide as internal standard. [b] From arbitrary time zero, *ca.* 10 min after mixing. [c] *cis*- and *trans*-isomers. [d] Determined, after hydrolysis, as *N*-(1-methylallyl)acetamide. [e] Determined, after hydrolysis, as *N*-(3-methylallyl)acetamide. [f] Determined from potentiometric titration of unprecipitated silver-ion.

We present what is believed to be the first direct evidence that complexation of a carbon-bonded halogen with silver ion can indeed be followed by a reaction in which the halogen migrates from carbon to carbon. The reaction of 3-chlorobut-1-ene (I) with $AgClO_4$ in MeCN was monitored by g.l.c. and also by potentiometric titration of unprecipitated silver ion. Concurrent with silver ion-assisted reaction to give those products which are accompanied by AgCl precipitation, a silver ion-catalysed rearrangement to a mixture of *cis*- and *trans*-but-2-enyl chlorides (II) was observed. Compounds (II) are eventually also converted into products which are accompanied by AgCl precipitation and their concentration passes through a maximum; the results are in the Table. In the absence of $AgClO_4$ and either with or without solid AgCl present,† equivalent to a concentration of 0·100M if it was to pass in solution, no rearrangement (or other reaction) of the 3-chlorobut-1-ene was observed, even after much longer times than those in the Table.

$$\mathrm{MeC}\overset{+}{\mathrm{N}}\mathrm{CHMeCH{=}CH_2}\qquad \mathrm{MeC}\overset{+}{\mathrm{N}}\mathrm{CH_2CH{=}CHMe}$$

(III) (IV)

$$\mathrm{CH_2{=}CH{-}CH{=}CH_2}$$

(V)

Substitution reactions of allyl halides favour ionization processes and silver ion assistance is considered to increase the bias towards this mechanism.[5,6] Rearrangements have been formulated as involving internal return within an intimate ion pair.[5] Presumably, a silver ion-catalysed rearrangement would also proceed *via* an allylic carbonium ion.

The products were monitored by g.l.c. after hydrolysis of the solvolytically generated nitrilium ions (III) and (IV) to the corresponding *N*-substituted acetamides.[7] Compounds (III), (IV), and (V) are formed in roughly equal amounts (Table) and initially they account for almost all the products generated from the allylic chlorides. However, all three concentrations reach a maximum and then decrease with formation of, as yet, unidentified products. This situation parallels that reported for the reaction of $\mathrm{Pr^iI}$ with $\mathrm{AgClO_4}$ in MeCN;[8] dark unidentified nitrogeneous products were produced, possibly by reaction (1).

$$\mathrm{RI + AgClO_4 + MeCN \rightarrow (MeCNR)^+ \rightarrow CH_2{=}C{=}N{-}R} \xrightarrow{\mathrm{MeCN}} \text{condensation products} \qquad (1)$$

(*Received*, 16*th May* 1974; *Com.* 555.)

---

† From reaction of 3-chlorobut-1-ene and $\mathrm{AgClO_4}$ in MeCN at 45 °C.

[1] Y. Pocker and D. N. Kevill, *J. Amer. Chem. Soc.*, 1965, **87**, 4760.
[2] D. N. Kevill and V. V. Likhite, *Chem. Comm.*, 1967, 247.
[3] P. G. Gassman and R. L. Cryberg, *J. Amer. Chem. Soc.*, 1969, **91**, 2047.
[4] P. Beak, J. T. Adams, P. D. Klein, P. A. Szczepanik, D. A. Simpson, and S. G. Smith, *J. Amer. Chem. Soc.*, 1973, **95**, 6027.
[5] R. H. de Wolfe and W. G. Young, *Chem. Rev.*, 1956, **56**, 753.
[6] H. M. R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1973, **12**, 819.
[7] J. J. Ritter and P. Minieir, *J. Amer. Chem. Soc.*, 1948, **70**, 4045.
[8] G. S. Hammond, M. F. Hawthorne, J. H. Waters, and B. M. Graybill, *J. Amer. Chem. Soc.*, 1960, **82**, 704.