Thermal Isomerisation of 1,1-Dichlorocyclopropanes

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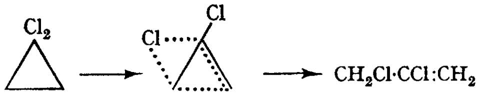
Thermal isomerisation of cyclopropane and its alkyl derivatives involves, as the major reaction, ring opening to the most stabilised diradical and migration of hydrogen, rather unselectively, to the radical sites.[1] Recently the kinetics of the gas-phase isomerisation of bromo- or chloro-cyclopropane,[2] and the isomerisation in kerosene solution of 1,1-dibromo-2,3-dimethylcyclopropane[3] were interpreted as involving a ring opening associated with halogen atom migration. Related studies now reported of the thermal isomerisation of a series of 1,1-dichlorocyclopropanes provide firm evidence for halogen migration during isomerisation.

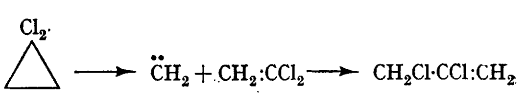
The product from the pyrolysis at 650° of 1,1-dichlorocyclopropane in a flow system at *ca.* 2 mm. pressure with a contact time of *ca.* 0·2 sec. clearly establishes that migration of chlorine has occurred during isomerisation; this is believed to occur by a mechanism of the following type:



(1)

2,3-Dichloropropene, unambiguously identified by comparison with authentic material, is formed in 75% yield based on the cyclopropane consumed. The minor products obtained, hydrogen chloride, allene, 3-chloropropyne, and possibly chloroallene, are those also found on pyrolysis of 2,3-dichloropropene under these reaction conditions.

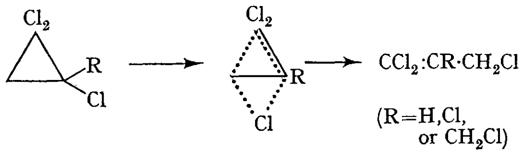
Ring-opening to give the most stable diradical, $\dot{C}H_2\cdot CH_2\cdot\dot{C}Cl_2$, followed by hydrogen migration, would have given 1,1- or 3,3-dichloropropene; the former is stable under the conditions used, and it is known that the latter is similarly stable, since it is formed by heating 1,3-dichloropropene at 400—600°, under conditions more severe than those used in the present work.[4] Neither 1,1- nor 3,3-dichloropropene were reaction products from the pyrolysis of 1,1-dichlorocyclopropane. Extrusion of methylene, analogous to carbene formation from fluorocyclopropanes,[5] followed by reinsertion of CH_2 into a C–Cl bond of the olefin could also have led to the product:



and the identification of 1,1-dichloroethylene as a minor product from the pyrolysis of 1,1-dichlorocyclopropane might be thought to provide support for this suggestion. The failure of this type of mechanism to account satisfactorily for the products formed by the pyrolysis of other 1,1-dichlorocyclopropanes (Table), the unusually high selectivity for C–Cl rather than C–H that would be required, and failure to obtain evidence for carbene intermediates in trapping experiments, lead us to reject this mechanism in favour of that of equation (1) with concerted ring opening and chlorine migration. The product distribution and conversion were substantially unaffected by the presence of 10 mole % of chlorine, toluene, or oxygen, and the implication that a radical chain mechanism is not involved is fully substantiated by kinetic studies carried out in this department.[6]

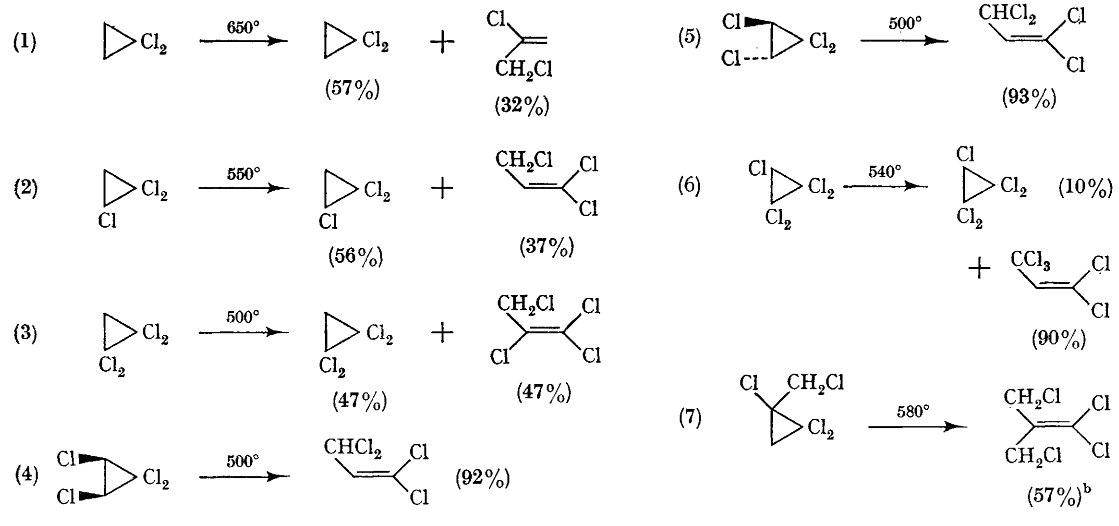
The isomerisation under similar conditions of a number of 1,1-dichlorocyclopropanes, prepared in good yield by the vapour-phase decomposition of trichloromethyltrifluorosilane in an excess of the appropriate olefin,[7] is summarised in the Table. The single olefin produced in high yield in each case is in accord with a mechanism involving halogen migration similar to that suggested for 1,1-dichlorocyclopropane.

It is noteworthy that in reactions 4—7 (Table), which take place at 70—150° below the temperature required for comparable conversion of 1,1-dichlorocyclopropane, the products require migration from the group CRCl rather than from CCl_2, with the CCl_2 group apparently stabilising the incipient double bond as in the isomerisation of 3,3,3-trichloropropene.[8] The same process could also account for the product in reactions 2 or 3.



TABLE

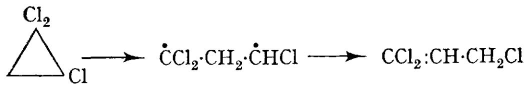
Thermal isomerisation of 1,1-*dichlorocyclopropanes*[a]



[a] At 2 mm. Hg in a silica tube, contact time 0·1—0·2 sec.

[b] The other product was a mixture of trichlorobutadienes (27%), probably the 1,2,3- and 1,1,3-isomers.

Only the isomerisation of 1,1,2-trichlorocyclopropane could have been interpreted *via* a diradical intermediate without chlorine migration:



The formation and pyrolysis of 1,1-dichlorocyclopropanes in this way forms an efficient two-stage synthesis for a number of polychloropropenes from accessible ethylene precursors. In some instances (*e.g.*, reactions 4 and 5) the overall yield (72%) is considerably greater than that obtained by the previously reported[9] route (24%).

The applicability of this reaction path to 1,1-dichlorocyclopropanes containing substituents other than chlorine will be reported shortly.

(*Received, August 29th,* 1967; *Com.* 919.)

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