A SIMPLE ROUTE TO 3-(DIHALOMETHYLENE)CYCLO-ALKENES

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Abstract: Thermolysis of a number of bicyclic trihalocyclopropanes (1; X, Y = halogen) in the presence of quinoline leads either to 3-(dihalomethylene)cyclo-alkenes (8,9,10) with loss of halogen X or to ring expanded 1,2-dihalocycloalka-1,3dienes (11,13) with loss of halogen Y, depending on ring size and on the nature of the halogen.

The thermolysis of dihalocyclopropanes (1; X = H, Y = halogen) in solution and their reaction with silver ion in, e.g., methanol generally lead to ring expanded products by concerted loss of halide ion and disrotatory cyclopropyl-allyl rearrangement to a (formal) allyl cation (2; X = H, Y = halogen), the stereochemistry of which depends on which halogen is lost.^{1,2} Trihalocyclopropanes (1; X, Y = halogen) can react in the same manner to give products derived formally from (2; X, Y = halogen); thus compound (3) reacts with silver nitrate - aq. acetone to produce (4).⁴ In principle, trihalocyclopropanes (1; X, Y = halogen) may also react by loss of X^{Θ} to produce the allyl ion (5) by cleavage of the bond adjacent to the gem-dihalide.³



Treatment of (1; n = 4, X = Cl, Y = Br)⁵ with $AgClo_4$ -methanol for 45 hrs at 20° leads to (6) (73%). However, similar reaction of (1; n = 4, X = Br, Y = Cl) leads to the loss of the 1-bromine and formation of 2-methoxy-1-(dichloromethylene)cyclohexane (7; Y = Cl) (70%) in 19 hrs at 20°, while the tribromide (1; n = 4, X = Y = Br)⁵ reacts by loss of 1rather than 7-bromine to produce (7; Y = Br) (90%). Moreover, when (1; n = 4, X = Br, Y = Cl)⁵ was heated for 2 hr at 100° in quinoline, 3-dichloromethylenecyclohexene (8; Y = Cl) was obtained in 90% yield.⁸ In the same way, heating compounds (1; n = 4, X = Y = Br) and (1; n = 4, X = Cl, Y = Br) for 3 hr and for 10 min respectively at 200° in quinoline led to (8; Y = Br) (80, 86%).



The bicyclic homologues (1; n = 5, X = Y = C1) and (1; n = 6, X = Br, Y = C1) behaved in an analogous manner leading to (9; Y = Cl) (70%) and (10) (65%) when heated in quinoline (1hr 220° , 0.5 hr 200° respectively). The mechanisms of these processes are as yet unknown, but may involve loss of halide ion and concerted ring opening to the dihalo-allylcation (5), and deprotonation by the base. A concerted rearrangement to a 2-halo-1-(dihalomethylene)cycloalkane followed by dehydrochlorination is also possible. Whatever the mechanism, the ready accessibility of compounds (1; X, Y = halogen) by dihalocarbene additions to 1-halo-alkenes² makes this a quick and straightforward route to 3-(dihalomethylene)cyclo-alkenes.



The loss of the 1-halogen as in the above reactions of compounds of type (1) is not, however, completely general. Thus trichloride (1; n = 3, X = Y = Cl) reacts in 2 hr at 160° in quinoline to give 1,2-dichlorocyclohexa-1,3-diene (11) (40%) rather than 3-(dichloromethylene)cyclopentene: + a minor product of this reaction was characterised as o-dichlorobenzene. Moreover, reaction of 1-chlorocyclopentene with CHBr₃-aq. NaOH-cetrimide under phase transfer conditions at 60-80° leads directly to the ring expanded dibromide (12) (46%) in 2 hrs, in keeping with the known easy rearrangement of 6,6-dibromobicyclo[3.1.0]hexane to 2,3-dibromocyclohexene.^{1a} In addition, (1; n = 6, X = C1, Y = Br) rearranges in 10 min at 230° by loss of bromine to give (13), of unknown stereochemistry about the tetra-substituted alkene (38%).

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References

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- 2.
- Pyrolysis of monocyclic trichlorocyclopropanes in the gas phase leads to allylic 3. chlorides, e.g. 1,1,2-trichlorocyclopropane is converted to 1,1,3-trichloropropene. In this case the non-geminal chlorine migrates.apparently in a process involving unimolecular chlorine atom migration and cleavage of the cyclopropane bond adjacent to the gem-dichloride. (R. Fields, R.N. Haszeldine and D. Peters, <u>J.Chem.Soc.(C)</u>, 1969, 165).
- 4.
- H. Sadlo and W. Kraus, <u>Tetrahedron</u>, <u>34</u>, 1965 (1978). Treatment of l-chlorocyclohexene with CHCl₃- aq. NaOH cetrimide under phase transfer conditions⁶ leads to (1; n = 4, X = Y = Cl)⁷ and similar reactions of l-chloro- or 5. L-bromo-cycloalkenes with :CCl₂ or :CBr₂ lead to (1; n = 4, X = Y = Br) (50%), (1; n = 4, X = Br, Y = Cl) (61%), (1; n = 4, X = Cl, Y = Br) (37%), (1; n = 3, X = Y = Cl) (71.5%), (1; n = 5, X = Y = Cl) (74%), (1; n = 5, X = Cl, Y = Br) (70%), (1; n = 6, X = Br, Y = Cl) (50%) and (1; n = 6, X = Cl, Y = Br) (55%).
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- 0.M. Nefedov and R.N. Shafran, <u>Izv.Akad.Nauk.SSSR Ser.Khim</u>., 1965, 538. H N.M.R.: δ 1.74 (m, 2H), 2.2 (m, 2H), 2.5 (m, 2H), 5.95 (dt, J = 10, 4, 4 Hz, 1H), 8. 6.45 (dt, J = 10, 2, 2 Hz, 1H). This was identical to a second sample obtained by dehydrochlorination of 2-chloro-l-(dichloromethylene)cyclohexane on heating in quinoline.9
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⁺An authentic sample of 3-(dichloromethylene)cyclopentene was prepared from cyclopentan-one by treatment with (i) NaOH-NH₃-CHCl₃ (ii) SOCl₂ and then (iii) heating in quincline. ⁺Under the same conditions (1; n = 5, X = Cl, Y = Br) also reacted completely, but after extraction only a trace of product remained and the n.m.r. of this did not correspond to either 1-chloro-2-bromocyclo-octa-1,3-diene or 3-(dibromomethylene)cycloheptene.

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