

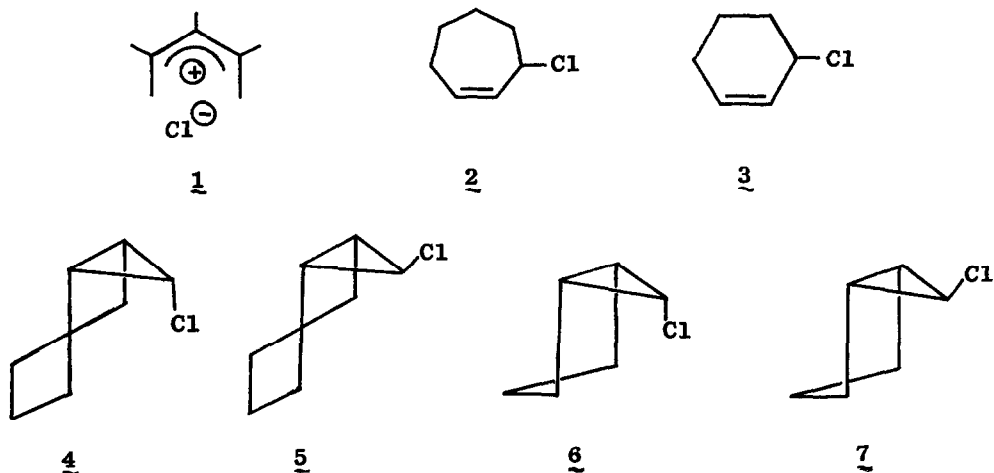
PHOTOCHEMICAL TRANSFORMATIONS. XVIII.
STEREOCHEMISTRY OF THE PHOTOSENSITIZED REARRANGEMENTS
OF SOME CYCLIC ALLYLIC CHLORIDES TO BICYCLIC (CYCLOPROPYL) CHLORIDES¹

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Some time ago^{2a} it was reported that acyclic allylic halides undergo rearrangement-cyclization to chlorocyclopropanes under irradiation with triplet photosensitizers, and extensions of this reaction were described in detail later.^{2b} We wish now to report the further extension of this useful photoreaction to cyclic allylic chlorides. We now describe the production of bicyclic cyclopropyl chlorides from 3-chlorocyclohexene and 3-chlorocycloheptene, note the stereochemistry of these reactions and discuss these results in mechanistic terms.

When the discovery was made² that photosensitization of allylic chlorides led to cyclopropyl chlorides, a number of plausible mechanisms were suggested. Of these, one involved the decay of an excited triplet species to an ion pair (of type 1) which was in the electronic ground state, but vibrationally excited, and which, among other fates, could recombine at the β carbon atom with concomitant ring closure to give the chlorocyclopropane product. The reverse of this latter process is well-known,³ and has been shown to proceed cleanly by an antidisrotatory process.^{4,5} One might anticipate, using the principle of microscopic reversibility, that the ring-opening and ring-closure reactions would have the same stereochemical requirements. We therefore decided to investigate some compounds where stereochemistry could be observed. Among these, we studied 3-chlorocycloheptene (2), which on photocyclization-rearrangement might give either or both of the epimers of 7-chloronorcarane (7-chlorobicyclo[4.1.0]heptane, 4 and 5) and 3-chlorocyclohexene (3) which might lead to 6-chlorobicyclo[3.1.0]hexane epimers (6 and/or 7). An early example⁵ of the stereochemical



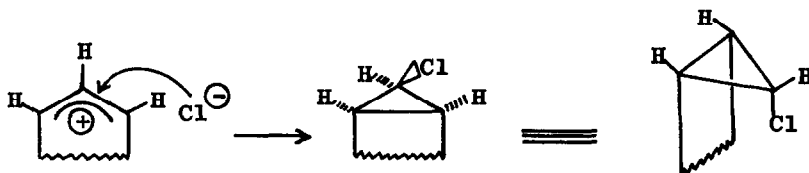
requirements for the ring-opening thermal transformation was in the ready formation of the cationic intermediate from endo-7-chloronorcarane (4), while 5 (the exo epimer) was inert, and similar observations were made⁶ with 6 (endo, reactive) and 7 (exo, inert). Based on these results and the carbonium-ion theory for the photochemical transformations, one would predict that the sensitized irradiation of 2 would give 4 and that of 3 would give 6.

3-Chlorocycloheptene (2) was prepared from the corresponding alcohol⁷ with thionyl chloride using the general procedure of Goering.⁸ It distilled with some decomposition at about 50° (40 Torr). Samples always contained some 1,3-cycloheptadiene. ¹H NMR (of 2 in CCl₄): δ 5.75 (m, H-1, H-2), 4.62 (m, H-3), 1.3-2.4 (m, 8 H). 3-Chlorocyclohexene (3) was prepared by the method of Theilacker and Wessel.⁹

When a 0.4 M solution of 2 (containing some 1,3-cycloheptadiene) in acetone was irradiated at 300 nm, the diene reacted rapidly to give 6-bicyclo[3.2.0]heptene, as is known.^{10,11} After an induction period due to this reaction, 4 was formed in about 20% chemical yield and with a quantum yield of about 0.024. In some experiments, 5 was not observed; in others, small peaks in the gas chromatograph were observed which could have been due to 5 (these were always substantially less than 10% of the 4 peak, and confirming ¹H NMR evidence for 5 was not adduced under conditions where the signal for 4 was observed). In like fashion, 3, dissolved in acetone, gave the endo epimer 6 in about 20% chemical yield and with a quantum yield of about 0.013, after an initial induction period, presumably also due to diene. Again, in most experiments, no exo isomer (7) peaks were seen in the gas chromatographic analysis, but, in a few, there was a peak with a retention time corresponding to 7. In a separate experiment, photoisomerization of 6 to 7 was found to occur slowly.

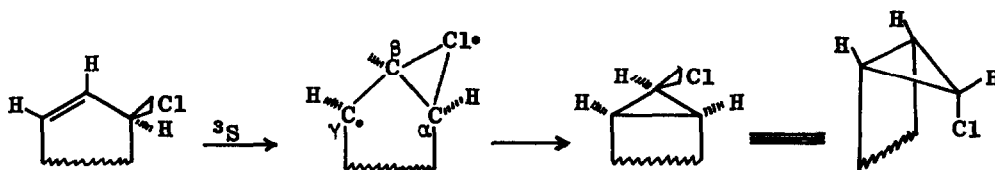
The stereochemical outcomes of these experiments are thus consistent with the assumption² of an ionic mechanism involving coordination of chloride ion at the β -carbon atom of the allylic cation and concomitant anti-disrotatory ring closure (Scheme I). However, the results are also

Scheme I



consistent (Scheme II) with the intervention¹ of a chlorine-bridged biradical

Scheme II



intermediate formed by triplet excitation transfer. Intersystem crossing and C_Y-C_α bond formation, with inversion in the radical displacement at C_α , would give 4 from 2 and 6 from 3, in accord with the results observed. We presently favor the latter explanation. These results, combined with those reported previously,¹ would appear to rule out simple unbridged 1,3-biradicals² as important intermediates in the cyclization rearrangements.

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