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# PHOTOCHEMICAL TRANSFORMATIONS. XVII.
# STEREOCHEMISTRY OF THE ACETONE-SENSITIZED PHOTOCYCLIZATIONS OF THE CROTYL CHLORIDES TO 2-CHLORO-1-METHYLCYCLOPROPANES[1]

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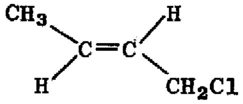
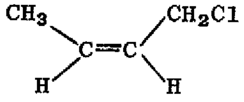
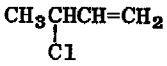
Photosensitized rearrangement of allylic chlorides to chlorocyclopropanes has been shown[2,3,4] to be a general phenomenon. Preliminary results[3] on the conversion of isomers of 1,3-dichloropropene to isomers of 1,2-dichlorocyclopropane indicated that the photoreactions were stereoselective. However, these reactions were run to high conversions, with attendant *cis*-*trans* and allylic isomerization of the reactants, so that the question of stereospecificity remained open. We decided, therefore, to look at the question of stereochemistry in somewhat more detail, choosing to work with crotyl chloride isomers **1** and **2**.



**1**

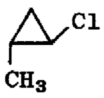


**2**



$CH_3\underset{Cl}{C}HCH=CH_2$

**3**



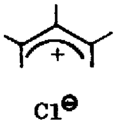
**4**

**5**

Although these compounds photointerconvert and photorearrange *via* a 1,3-sigmatropic (allylic) rearrangement to α-methylallyl chloride (**3**) somewhat more rapidly than they photocyclize to **4** and **5**, use of gas chromatography with flame-ionization detection enabled us to study the initial portion of the photocyclization reactions and thus to establish, within reasonable limits, the stereospecificity and/or stereoselectivity, if any, of the photoprocesses.

The photoreactions were studied using acetone (2.5 *M*) as sensitizer, 0.5 *M* of **1** or **2** as substrate, acetonitrile as solvent, nonane as internal standard, and GC analysis on a β,β-thio-bis-propionitrile column. *cis*-Crotyl chloride (**2**) was prepared from *cis*-crotyl alcohol[5] by the method of Meyers.[6] As reported,[6] this method gives replacement without substantial rearrangement. Our product was a mixture of 99% of 2, 0.9% of 1 and 0.1% of 3 (starting alcohol contained 1% of *trans*-crotyl alcohol). *trans*-Crotyl alcohol was prepared by lithium aluminum hydride reduction of crotonaldehyde (98% *trans*, 2% *cis*, Matheson, Coleman and Bell) and contained about 2% of the *cis* alcohol. Conversion of the alcohol by Meyer's method gave a sample of 1 with about 3.5% of 2. The irradiations were carried out, after degassing the solutions by freeze-pump-thaw cycles, in Pyrex test tubes sealed under vacuum, in a 300-nm Rayonet reactor merry-go-round apparatus using cyclopentanone actinometry,[7] and using $\phi = 0.37$ for this reaction. Typical results are shown in Tables I and II. Average quantum yield values for production of 3, 4 and 5 were 0.14, 0.015 and 0.008 respectively from 1 and 0.13, 0.006 and 0.030 respectively from 2.[8] Thus the ratio of the yield of 4 to that of 5 from 1 is about 2, and within the limits of our experimental error, independent of reaction extent (<10% conversion of 1), while the ratio of 4 to 5 yields from 2 is about 0.2. Thus the reactions are not stereospecific, although they are fairly stereoselective.

The reactions have been shown[2,3,4] to involve sensitization by triplet acetone and are thus apparently initiated by triplet excitation transfer.[9] It has previously been suggested[2,3] that vibrationally excited ion pairs of type 6 could be intermediates in both the 1,3- and 1,2-migrations. Were this the case, ion pair 7 would be formed from 1 and 8 from 2 (while both 7 and 8 could form from 3).



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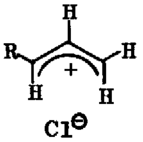

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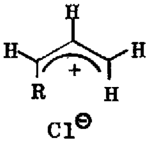
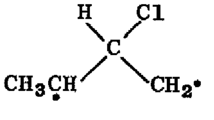


8

$CH_3\dot{C}H\text{-}\dot{C}HCH_2Cl$

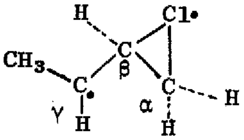
9



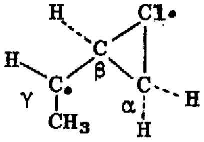
10

The electronic ground-state ring opening of cyclopropyl derivatives to allylic derivatives is known to proceed stereospecifically in an anti-disrotatory fashion,[10,11,12] when the allyl cation is formed concerted with departure of nucleofuge, and the principle of microscopic reversibility teaches that the coordination and ring closure of the reverse reaction should have the same stereochemistry. If this path is followed, the failure to observe stereospecificity makes it necessary to assume that the normal high stability[12] of allylic cations to geometric isomerism is partially lost when they are formed photochemically (i.e., with excess energy).

Lack of stereoconvergence makes clear that the triplet excitation transfer leads neither to species (9) similar to the triplets produced from *cis*-*trans* olefin pairs by sensitization in solution, which are assumed[13] to relax to more stable and identical "twist triplets," nor to long-lived triplet freely rotating 1,3-biradicals 10. An alternative, of some attraction to us, conceives the formation of 11 directly by excitation of 1 and that of 12 from 2 (that is, interaction of the chlorine with the double bond at the time of excitation[3]).



11



12

Intersystem crossing and $C_\gamma$-$C_\alpha$ bond formation with inversion in the radical displacement at $C_\alpha$ would give 4 from 11 and 5 from 12, in agreement with the principal product observed. The interconversion of 11 and 12, which requires a rotation around the $C_\beta$-$C_\gamma$ bond, would mix the two systems and provide the mechanism for partial loss of stereospecificity.[14]

Table I. Acetone-Photosensitized Conversion of *trans*-Crotyl Chloride (1) to α-Methylallyl Chloride (3), *trans*-(4) and *cis*-2-Chloro-1-methylcyclopropane (5)

(Solvent: acetonitrile, $[1]_0$ = 0.5 *M*, [acetone] = 2.5 *M*)

| time (hrs) | % 3 present | quantum yield 3 | 4 | 5 | $\phi_4/\phi_5$ |
|---|---|---|---|---|---|
| 0 | 1.00 | - | - | - | |
| 3 | 1.35 | 0.14 | 0.010 | | |
| 5 | 1.57 | .13 | .009 | | |
| 7 | 1.79 | .13 | .012 | .0048 | 2.5 |
| 12 | 2.14 | .11 | .012 | .0059 | 2.0 |
| 19 | 3.00 | .13 | .015 | .0074 | 2.0 |
| 39 | 5.79 | .14 | .019 | .010 | 1.9 |

Table II. Acetone-Photosensitized Conversion of *cis*-Crotyl Chloride (2) to α-Methylallyl Chloride (3), *trans*-(4) and *cis*-2-Chloro-1-Methylcyclopropane (5)

(Solvent: acetonitrile, $[2]_0$ = 0.5 *M*, [acetone] = 2.5 *M*)

| time (hrs) | % 3 present | quantum yield 3 | 4 | 5 | $\phi_4/\phi_5$ |
|---|---|---|---|---|---|
| 0 | 0.20 | | | | |
| 3 | 0.35 | 0.08 | 0.003 | 0.023 | 0.13 |
| 5 | 0.53 | .09 | .004 | .021 | .19 |
| 7 | 0.91 | .15 | .007 | .046 | .15 |
| 12 | 1.31 | .13 | .005 | .031 | .16 |
| 19 | 1.94 | .13 | .006 | .030 | .20 |
| 39 | 3.7 | .13 | .007 | .032 | .22 |

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8. The *cis*-*trans* interconversion of **1** $\rightleftarrows$ **2** proceeds at about 2/3 the rate of formation of **3**, and **3** gives almost equal quantities of **4** and **5** (R. P. Micheli, Ph.D. Thesis, University of Colorado, 1975).
9. The formation of sensitizer-substrate excited state complexes may be assumed from the sensitizer sensitivities of product ratios (C. S. Ilenda, Ph.D. Thesis, University of Colorado, 1974). However, we are ignoring the sensitizer component in the discussion at this stage.
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13. For a discussion, see N. J. Turro in "Technique of Organic Chemistry," Vol. XIV., P. A. Leermakers and A. Weissberger, Ed., Wiley-Interscience, New York, N. Y., 1969, p 133ff.
14. Intersystem crossing in **11** and **12** may be expected to be fast, as one of the unpaired electrons is directly on chlorine.