Tetrahedron Letters No.57, pp. 4967-4970, 1970. Pergamon Press. Printed in Great Britain.

# ADDITION OF HYDROGEN CHLORIDE TO AN ALLYLIDENECYCLOPROPANE; SURVIVAL OF THE CYCLOPROPANE RING

Marvin L. Poutsma and Pedro A. Ibarbia

Union Carbide Research Institute, Union Carbide Corp.
Tarrytown, New York

**(Received in USA 20 October 1970; received in UK for publication 9 November 1970)**

Recently we described (1) the acid-catalyzed rearrangement of allene 1 to form a mixture of ring-opened isomers 2 (major) and 3 (minor); these conversions were rationalized as proceeding by the carbonium ion pathways shown. In particular, acid-catalyzed rearrangement of 2-methyl-3-(tetramethylcyclopropylidene)-propene (4), available from base-catalyzed isomerization of allene 1, gave triene 3 cleanly. Thus protonation of either allene 1 or diene 4 offered routes to cation 5 which could reasonably give triene 3 after electrocyclic ring opening to form cation 6 followed by proton loss. However, since solvolysis of most cyclopropyl derivatives gives allylic cations in a concerted fashion without the intervention of discrete cyclopropyl cations (2), it was of interest to determine whether cation 5, one resonance structure of which is a vinyl-substituted cyclopropyl cation, represents an energy minimum in the conversion of diene 4 to triene 3. We now report evidence for trapping of a product retaining the skeleton of cation 5 during electrophilic addition of hydrogen chloride to diene 4 (3).

Treatment of diene 4 in carbon tetrachloride solution with anhydrous hydrogen chloride at ambient temperature led to gradual formation of three products in a ratio of 3.5:1:1 as determined by nmr analysis. Treatment of the evaporated residue with excess 4-phenyl-1,2,4-triazoline-3,5-dione in benzene solution to remove dienic products (see below) (1,4) followed by trituration of the new residue with hexane and retention of the soluble portion allowed isolation of the major product in 50% yield. It was a thermally-unstable adduct [m/e 188 and 186 in correct isotopic ratio] whose nmr spectrum ($CCl_4$) [$\delta$ 5.48 (m, area 1), 1.75 (br t, $J \sim 1.8$ Hz, area 6), 1.20 (s, area 6), and 0.98 ppm (s, area 6)] showed four saturated methyl groups. The assignment as a 1,4 adduct with the cyclopropane ring intact [1-(1'-chloro-2',2',3',3'-tetramethylcyclopropyl)-2-methylpropene (7)] rather than a 1,2 adduct was confirmed by ozonization to form 1-chloro-2,2,3,3-tetramethylcyclopropanecarboxylic acid (8). Authentic acid 8 was prepared by photolysis of ethyl chlorodiazoacetate in tetramethylethylene

solution (5) followed by saponification of the crude ester product; it has mp 155-156°, nmr ($CH_2Cl_2$) δ 10.55 (br s, area 1), 1.27 (s, area 6), and 1.24 ppm (s, area 6), and elemental analytical values within usual limits. One of the two minor hydrochlorination products of diene 4 was triene 3. The residual nmr absorption in the crude product, after accounting for 3 and 7, suggested that the second minor product was 5-chloro-2,5-dimethyl-4-isopropylidene-2-hexene (9) but this assignment has not been confirmed.

Attempted glpc analyses of the crude product mixture suggested that products 7 and 9 were converted to triene 3 in the heated inlet. Attempted chromatography over Florisil led to isolation of a crystalline alcohol [mp 68-70°; m/e 168] whose nmr spectrum showed, in addition to one olefinic proton (δ 5.67, m) and six identical saturated protons (1.27, s), four weakly coupled allylic methyl doublets at 1.95 ($J$ = 1.7 Hz), 1.92 ($J$ = 1.4 Hz), 1.54 ($J$ = 1.2 Hz) and 1.49 ppm ($J$ = 1.3 Hz). Comparison of this pattern with that of triene 3 (1) supports the assignment as 2,5-dimethyl-3-isopropylidene-4-hexen-2-ol (10); attempted glpc analysis of 10 again gave only triene 3.

The conversion of diene 4 to chloride 7 can be added to the rather small list of examples of reactions in which cyclopropyl structures are the major products of conversions proceeding, at least formally, through cyclopropyl cations. These include solvolysis of 1-chlorobicyclopropyl where the cation is stabilized by an adjacent cyclopropane ring (6) rather than by a double bond as in 5 (7) and solvolysis of bicyclic compounds where the stereochemistry for symmetry-allowed ring opening is highly unfavorable (8).

Acknowledgement - We wish to thank Professor L. Friedman, Case Western Reserve University for performing the ozonization of 7.

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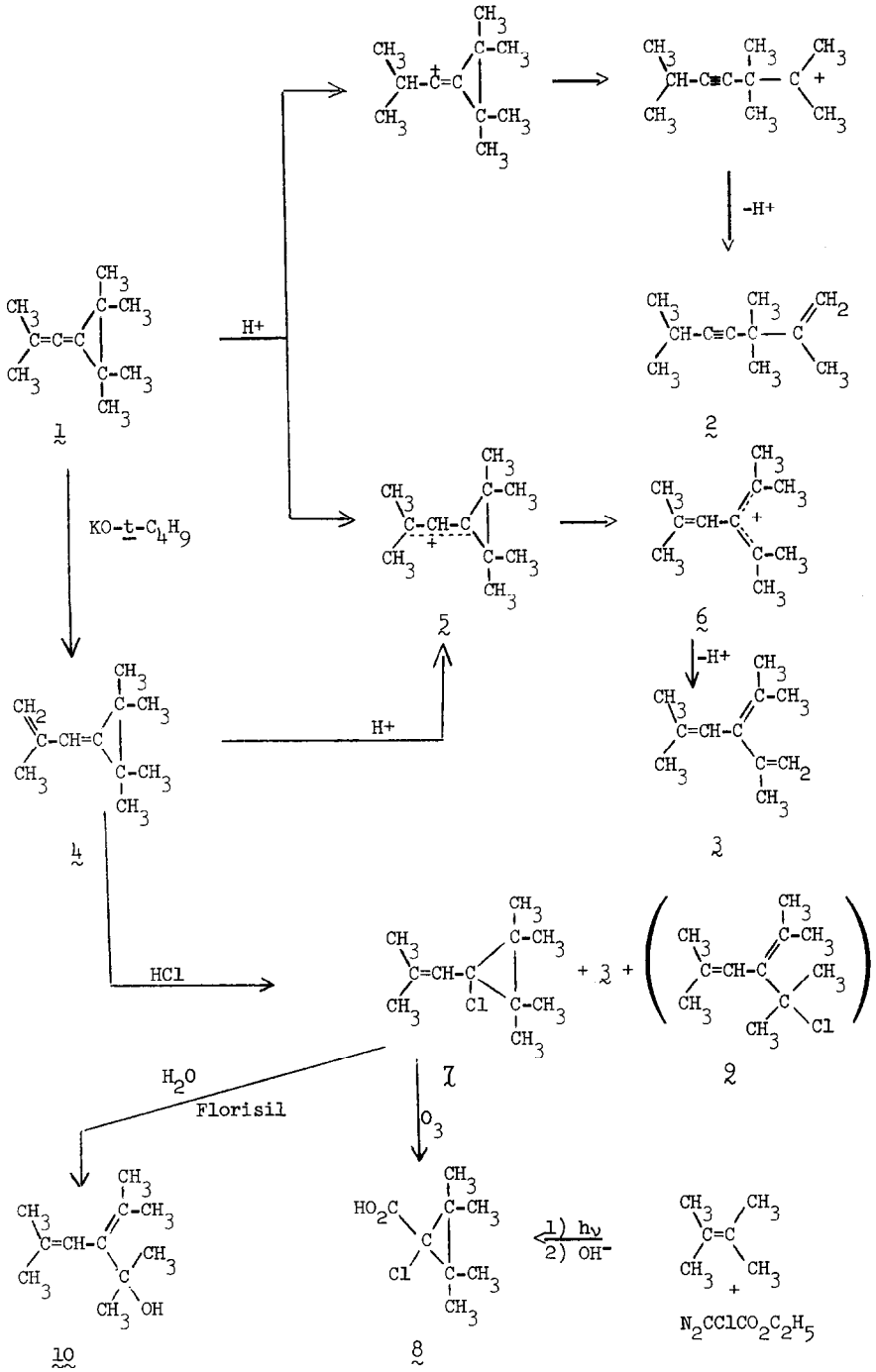
H+
KO-t-C4H9
H+
-H+
-H+
HCl
+ 3 +
H2O
Florisil
O3
1) hν
2) OH-
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