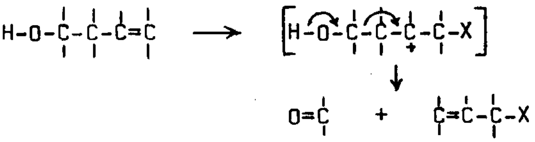
Tetrahedron Letters No. 2, pp 201 - 204, 1977. Pergamon Press. Printed in Great Britain.

CLEAVAGE OF HOMOALLYLIC ALCOHOLS —— A NOVEL FRAGMENTATION REACTION[1]

J.S. Yadav, H.P.S. Chawla and Sukh Dev
Malti-Chem Research Centre, Nandesari, Vadodara, India

(Received in UK 22 November 1976; accepted for publication 29 November 1976)

Fragmentations of Y-C-C-C-X systems, where X is a nucleofuge[2] which leaves as :X, and Y is a hetero atom with p-electrons, to -C=C- and $\overset{+}{Y}$=C moieties have been extensively studied[3] and frequently made use of in organic synthesis[4]. We wish to report a related, yet novel cleavage of homoallylic alcohols I, II, III and IV, under conditions of electrophilic addition of chlorine or acid-catalysed ring-opening of the corresponding epoxides. In generalised terms, this fragmentation can be depicted as follows:

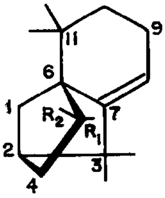


X = Cl, OH

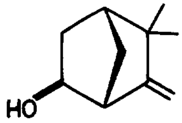
This cleavage was first encountered while studying reactions of I. The reaction differs from Grob fragmentations[3] in producing allylic halides or alcohols, instead of olefins and, in appropriate cases, this can be of distinct value for synthetic operations

Treatment of I[5] (m.p. 89-90.5°) in CCl_4 (~3%, w/v) with 1 molar equivalent of Cl_2 (5% soln in CCl_4, added dropwise at 0° over 5 min) in presence of excess Li_2CO_3, yielded V (Tetranitromethane, yellow color . PMR[6]: -C-Me, 0.99, 1.0, 1.01, 1.03 ppm; CHCl, b sig., 4.56 ppm, W_H = 7 Hz; CHO, t, 9.78 ppm, J = 1.5 Hz. IR: CHO, 2720, 1730 cm^{-1}) in almost quantitative yield. The compound is labile and its properties had to be studied in CCl_4 soln only, as attempts at purification through distillation or chromatography (silica gel) led to decomposition. The stereochemistry of C-Cl bond in V follows from the known propensity for endo attack (with reference to norbornyl part) in isolongifolene derivatives[7].

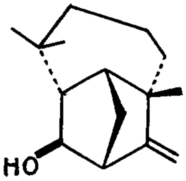
Exposure of epoxide VIII (m.p. 102-103°) to 0.5% $HClO_4$ in 90% aqueous dioxane (10°, 15 min) furnished, in almost quantitative yield, a mixture of epimeric alcohols VI (PMR: -C-Me, 0.95, 0.95, 0.98, 1.06 ppm; CHOH, b sig., 4.14 ppm, W_H = 9 Hz; CHO, t, 9.76 ppm, J = ~1.5 Hz) and VII (PMR: -C-Me 0.79, 0.89, 1.05, 1.13 ppm; $C\underline{H}OH$, b sig. 4.04 ppm, W_H = 8 Hz; $C\underline{H}O$, t, 9.76 ppm, J = ~ 1.5 Hz), in which VI predominated. The formation of both epimers, rather than only VI, is ascribed to acid-catalysed epimerisation (to some extent) at C-8 under the reaction conditions. The same epimeric mixture, but in which now VII predominates, is obtained by solvolysis (aq. dioxane, Li_2CO_3, 42°) of the chloro-aldehyde (V). The epimeric mixture of alcohols from both the reactions, on Jones oxidation[8], furnished the same keto acid IX (m.p. 162-164°; λ_{max}^{EtOH} 250.5 nm, ϵ 15150). These transformations also serve to further support the structures of the fragmentation products V, VI.



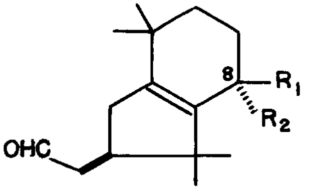
I: R_1=H, R_2=OH
II: R_1=OH, R_2=H



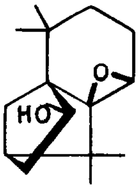
III



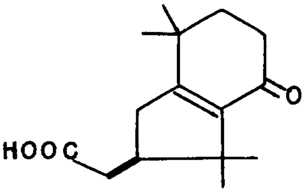
IV



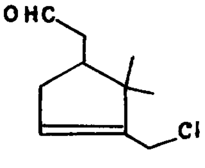
V: R_1=Cl, R_2=H
VI: R_1=OH, R_2=H
VII: R_1=H, R_2=OH



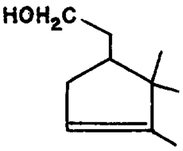
VIII



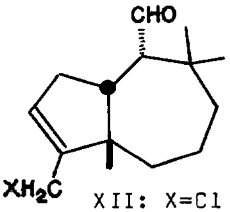
IX



X



XI



XII: X=Cl
XIII: X=OH

Similarly, reaction of camphene alcohol[9] (III) with Cl_2 in CCl_4, yielded quantitatively the cyclopentene derivative X (PMR: $-\overset{|}{\underset{|}{C}}-\underline{Me}$, 0.92, 1.12 ppm; $C\underline{H}_2Cl$, bs, 4.04 ppm; $C{=}C\underline{H}$ b sig., 5.76 ppm, W_H = 6 Hz; $C\underline{H}O$, t, 9.75 ppm, $J = \sim 1.5$ Hz. IR: CHO, 2710, 1725 cm^{-1}), which was further characterised by reduction (LAH) to the known[10,11] α-campholenic alcohol (XI).

Likewise, the homoallylic alcohol IV[12] (m.p. 171.5-172.5°) on exposure to Cl_2 yielded (~90%) the expected chloroaldehyde XII (PMR: $-\overset{|}{\underset{|}{C}}-\underline{Me}$, 0.97, 1.05, 1.18 ppm; $C\underline{H}_2Cl$, bs, 4.01 ppm, $C{=}C\underline{H}$, b sig. 5.72 ppm, W_H = 9 Hz; $C\underline{H}O$, d, 9.80 ppm, $J = 4$ Hz. IR: CHO, 2705, 1705 cm^{-1}), while the derived epoxide on acid (0.5% $HClO_4$ aq) cleavage furnished (~95%) the anticipated hydroxyaldehyde XIII (PMR: $-\overset{|}{\underset{|}{C}}-\underline{Me}$ 0.97, 1.06, 1.13 ppm; $C\underline{H}_2OH$, bs, 4.14 ppm, $C{=}C\underline{H}$, b sig., 5.50 ppm, W_H=7Hz; $C\underline{H}O$, d, 9.91 ppm, $J = 4$ Hz).

The substrates, investigated for this fragmentation reaction, in the present study, are all based on bicyclo[2,2,1]heptane system. Work is in progress to determine the geometrical requirements, if any, for this reaction and to delineate its scope. Configuration of the OH group, appears to be inconsequential, as the epimeric alcohol II (m.p. 48.5-49.5°) fragments with equal ease to give the same product (V).

All new compounds for which spectral data have not been given have spectral characteristics consistent with the assigned structures. Satisfactory elemental analysis were obtained for all new compounds.

References and Notes

1. MRC Communication No. 7

2. J. Mathieu, A. Allais and J. Valls, Angew. Chem. 72, 71 (1960).

3. See e.g.: C.A. Grob and P.W. Schiess, Angew. Chem. Internat. Edit. 6, 1 (1967); C.A. Grob, ibid. 8, 535 (1969); C.A. Grob, B. Schmitz, A. Sutter and A.H. Weber, Tetrahedron Letters 3551 (1975).

4. Inter alia see: E.J. Corey, R.B. Mitra and H. Uda, J. Am. Chem. Soc. 85, 485 (1964); P.S. Wharton and G.A. Hiegel, J. Org. Chem. 30, 3254 (1965); R. Zurfluh, E.N. Wall, J.B. Siddall and J.A. Edwards, J. Am. Chem. Soc. 90, 6224 (1968); J.A. Marshal, Rec. Chem. Progr. 30, 3 (1969).

5. E.H. Eschinasi, G.W. Shaffer and A.P. Bartles, Tetrahedron Letters 3523 (1970).

6. All PMR spectra were taken in CCl_4 soln on Perkin-Elmer model R32 (90 MHz) NMR spectrometer; b = broad, sig. = signal.

7. J.A. McMillan, I.C. Paul, U.R. Nayak and Sukh Dev, Tetrahedron Letters 419 (1974).

8. R.G. Curtis, I. Heilbron, E.R.H. Jones and G.F. Woods, J. Chem. Soc. 457 (1953).

9. M. Gaitonde, P.A. Vatakencherry and Sukh Dev, Tetrahedron Letters 2007 (1964).

10. V.S. Joshi, N.P. Damodaran and Sukh Dev, Tetrahedron 24, 5817 (1968).

11. A.F. Thomas, Helv. Chim. Acta 55, 815 (1972).

12. This compound has been synthesised from longicyclene; the details will be reported elsewhere.