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CYCLOPROPENYLCARBINYL-ALLENYL REARRANGEMENT

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Summary. An acid catalyzed rearrangement of vinylcyclopropenylcarbinols into vinylallenic alcohols and divinyl ketones (of the monoterpene series) is discussed.

The cyclopropylcarbinyl-homoallyl rearrangement has been investigated in considerable detail[1]. In contrast to that, the related transformation of cyclopropenyl derivatives still remains practically unexplored, cf.[2,3]. We report here three examples of the title rearrangement illustrating at the same time a new synthetic way to conjugated allenic alcohols as well as to divinyl ketones (Scheme).

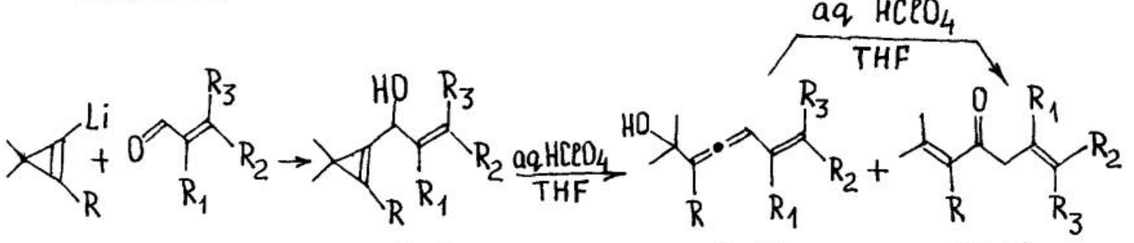
Reaction of the Li salt 1 (prepared by deprotonation of dimethylcyclopropene with 1.0 mol equiv. of LDA in the presence of 1.05 mol equiv. of TMEDA at -20° for 1 h in hexane-THF solution, 6:1) with THF solution of aldehydes 3 or 4 at -30° for 5 min gives rise to the respective carbinols 6 or 7 in ~90% yield. The carbinol 8 was prepared similarly from trimethylcyclopropenyl lithium 2 and methacrolein 5. Found for 6[4,5]: b.p. 53°/2 mm Hg;n_D^{22} 1.4621; $\delta^{CCl_4}_{TMS}$: 1.11, 1.17 (bs, 6H, C$\underline{H}_3$), 1.71 (bs, 6H, C$\underline{H}_3$), 5.19 (bs, 2H,C$\underline{H}$OH, $\underline{H}$C=C)[6], 6.87 ppm (bs, 1H, cyclopropene $\underline{H}$C=C). Found for 7[4,5]: b.p.49°/1 mm Hg; n_D^{22} 1.4641; $\delta^{CCl_4}_{TMS}$: 1.13, 1.17, 1.58 (bs, 9H, C$\underline{H}_3$), 1.70 (bd, J=6 Hz, 3H, C$\underline{H}_3$CH=C), 4.91 (bs, 1H, C$\underline{H}$OH), 5.52 (bq, J=6 Hz, 1H, $\underline{H}$C=C), 6.94 ppm (bs, 1H, cyclopropene $\underline{H}$C=C). Found for 8[4,5]: b.p.55°/2 mm Hg; n_D^{20} 1.4588; $\delta^{CCl_4}_{TMS}$: 1.08 (bs, 6H, C$\underline{H}_3$), 1.74, 2.01 (bs, 6H, C$\underline{H}_3$), 4.76, 4.86 (bs, 2H, $\underline{H}_2$C=C), 4.96 ppm (bs, 1H, C$\underline{H}$OH).

Vinylcyclopropenylcarbinols 6 or 7 in THF when treated with 30% $HClO_4$ (0.2-0.3 ml per 10 ml of the 5% carbinol solution) at room temperature for ~1h (TLC monitoring) afford ~2:1 mixtures[7] of the corresponding vinylallenic monoterpenols 9 or 10 and the known vinylallyl ketones 12[8] or 13[9] in 70-90% yield. The separation of the mixtures was achieved by flash chromatography[10] on silica gel (gradient elution from hexane to hexane-ether, 7:3 v/v). Found for 9[4,5]: b.p.61°/1 mm Hg; n_D^{20} 1,4998; $\delta^{CCl_4}_{TMS}$: 1.28 (s, 6H, $C\underline{H}_3$), 1.72, 1.76 (bs, 6H, $C\underline{H}_3$), 5.48 (bd, J=11 Hz, 1H, $\underline{H}$-C_6), 5.52 (d, J=9.5 Hz, 1H, $\underline{H}$-C_3), 6.01 ppm (dd, J=11 and 9.5 Hz, 1H, $\underline{H}$-C_5). Found for 10[4,5]: b.p.58°/1 mm Hg; n_D^{21} 1.5035; $\delta^{CCl_4}_{TMS}$: 1.30 (s, 6H, $C\underline{H}_3$), 1.65 (bs, 3H, $C\underline{H}_3$), 1.70 (d, J=7 Hz, 3H, $C\underline{H}_3CH{=}C$), 5.48 (bq, J=7 Hz, 1H, $\underline{H}$-C_7), 5.50 (d, J=7 Hz, 1H, $\underline{H}$-C_3), 5.90 ppm (d, J=7 Hz, $\underline{H}$-C_5). Found for 12[5]: b.p.72°/5 mm Hg; $\delta^{CCl_4}_{TMS}$: 1.61, 1.73, 1.85, 2.10 (bs, 12H, $C\underline{H}_3$), 2.96 (d, J=7 Hz, 2H, $C\underline{H}_2$), 5.22 (bt, J=7 Hz, 1H, $\underline{H}$-C_6), 5.90 ppm (bs, 1H, $\underline{H}$-C_3). Found for 13[5]: b.p.52°/2 mm Hg; $\delta^{CCl_4}_{TMS}$: 1.59, 1.85, 2.11 (bs, 9H, $C\underline{H}_3$), 1.65 (d, J=7 Hz, 3H, $C\underline{H}_3CH{=}C$), 2.93 (bs, 2H, $C\underline{H}_2$), 5.27 (bq, J=7 Hz, 1H, $\underline{H}$-C_7), 5.99 ppm (bs, 1H, $\underline{H}$-C_3).

Under the above conditions carbinol 8 nearly quantitatively rearranges into the separable ~5:1 mixture[7] of vinylallenic alcohol 11 and conjugated dienone 14a, respectively. The expected vinylallylic isomer 14 could not be found, probably due to its fast prototropic isomerization. Found for 11[4,5]: b.p.47°/1 mm Hg; n_D^{21} 1.5032; $^{CCl_4}_{TMS}$: 1.30 (S, 6H, $C\underline{H}_3$), 1.73, 1.78 (bs, 6H, $C\underline{H}_3$), 4.78, 4.86 (bs, 2H, $\underline{H}_2C{=}C$), 5.84 ppm (dd, J=2.5 and 2 Hz, 1H, $\underline{H}$-C_5). Found for 14a[4,5]: b.p. 65°/5 mm Hg; n_D^{20} 1.4902; $\delta^{CCl_4}_{TMS}$: 1.75 (bs, 9H, $C\underline{H}_3$), 1.89, 2.12 (bs, 6H, $C\underline{H}_3$), 5.99 ppm (bs, 1H, $\underline{H}C{=}C$).

The initial resonance stabilized divinyl carbonium ion 15 is probably responsible, cf.[2,3], for the rearrangement discussed[11] (Scheme). Disrotatory cleavage of the cyclopropene C-C bond in one of the forms of 15 would lead to the allylic carbocation 16 which further collapses[12] to the observed final products 9-14/14a. It should be noted that the carbonyl compounds 12 - 14/14a may be formed, at least partly, from the allenic carbinols 9-11 via the common cation 16. Indeed, we found (Scheme) that the rather unstable 9-11 give moderate yields of the respective ketones 12-14a under the conditions employed for the isomerization of alcohols 6-8. The same transformation of related allenic alcohols was described earlier[13].

Scheme



1-2 3-5 6-8 9-11 12-14

1: R=H

2: R=Me

3: R_1=H, R_2=R_3=Me

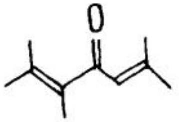
4: R_1=R_2=Me, R_3=H

5: R_1=Me, R_2=R_3=H

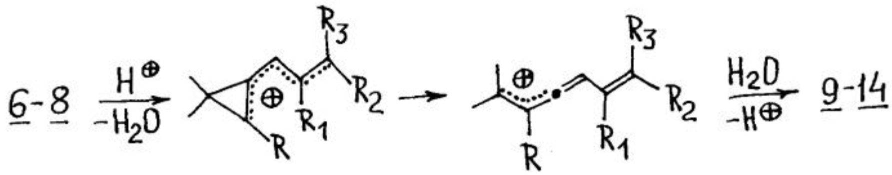
6, 9, 12: R=R_1=H, R_2=R_3=Me;

7, 10, 13: R=R_3=H, R_1=R_2=Me;

8, 11, 14: R=R_1=Me, R_2=R_3=H



14 a



15 16

Thus, the cyclopropenylcarbinyl-allenyl rearrangement represents a simple way to vinylallenic alcohols and isomeric divinyl ketones starting from cyclopropenes. Examination of the synthetic value of this approach to some other unsaturated isoprenoids is presently in progress in our laboratory.

References and Notes

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3. P.Dobrindt, Ph.D.Thesis, University of Ruhr, Bochum, 1979. The authors thank Prof. Ivan N.Domnin (Leningrad State University) who draw our attention to this work during the preparation of our manuscript.
4. Satisfactory elemental analyses data were obtained for this compound.
5. Satisfactory IR,UV, and mass spectral data were obtained for this compound.
6. Degenerated AB spin system; the signal transforms into dd, centered at 5.63 ppm (J_{AB}=8 Hz), in the presence of ca.1 wt.% of Eu $(dpm)_3$.
7. The ratio was determined by column chromatography. The main reaction byproducts are hydrocarbons which were not further investigated.
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11. It should be noted that attempts to perform the similar isomerization of dihydro-6 (prepared from 1 and isovaleraldehyde) met with failure: the reaction proceeds under rather drastic conditions and yields complex mixture containing only traces of dihydro-9 and -12 derivatives.
12. cf. G.Leandri, H.Monti, M.Bertrand, Tetrahedron, 30, 289 (1974).
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