THE CYCLOPROPENYL CARBINARY ALLENYL REARRANGEMENT AS A METHOD OF SYNTHESIZING VINYL ALLENYL ALCOHOLS AND DIVINYL KETONES*

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In contrast to the well-known cyclopropylcarbinyl homoallyl rearrangement [2-4], the related conversion in the cyclopropene series has not attracted the attention of investigators. Thus there is in the literature [5] only the mention of the possibility of such a reaction, which could lead to allenyl alcohol derivatives. The present communication considers three examples of the cyclopropenylcarbinyl allenyl rearrangement (CPAR) and demonstrates a new simultaneous synthesis of vinylallenyl alcohols and divinyl ketones.

The starting compounds were 3,3-dimethyl- [6] and 1,3,3-trimethylcyclopropene [7]; deprotonation by lithium diisopropylamide (LDA) in the presence of an equimolar amount of tetramethylethylene diamine (TMEDA) yielded the respective lithium derivatives I and II. The latter can react with various electrophilic reagents; we used isovaleric, dimethyl acrylic, and tiglic aldehyde as C₂ synths for reaction with I, and methylacrolein as a C₂ synthon for II. As a result, this choice enabled us to synthesize some isoprenoid alcohols of the monoterpene series.

By the high-yield condensation of these components we obtained the respective, hitherto unknown isoprenoid cyclopropenylcarbinols III-VI. Their structure was confirmed by spectral methods:

The mass spectra contain the molecular ion peaks. The PMR spectra of alcohols III-V contain the characteristic singlets of the cyclopropene protons with δ ~ 6.9 ppm, and for VI the CH₂ at the cyclopropene double bond with δ 2.0 ppm. In the PMR spectrum (60 MHz) of carbinol IV, the signals of the vicinal methylene protons at the hydroxyl and the divinyl protons have identical chemical shifts; they form a broad singlet which upon addition of Eu(dpm)₃ is transformed to a classical AB system with spin-spin coupling constant (SSCC) of J = 8 Hz.

Treatment of the THF solutions of the cyclopropenylvinyl carbinols IV and V with a catalytic amount of 30% HClO₄ at room temperature gives a 70-90% yield of a mixture of the respective vinylallenyl monoterpenols VII and VIII and the known vinyl allyl ketones X and XI, in a ~ 2:1 ratio. Under analogous conditions carbinol VI was converted to a ~ 5:1 mixture of vinylallenyl alcohol, IX, and the doubly conjugated ketone XII; the

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expected vinylallyl isomer of the latter was not found. An attempt to isomerize carbinol III was successful. Under more drastic conditions a complex mixture was obtained that according to spectral data did not contain the expected rearrangement product:

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\begin{align*}
R &= H, R^1 = Me (VII), (X); R = Me, R^1 = H (VIII), (XI).
\end{align*}
\]

All the obtained mixtures were separated by column chromatography. The structures of the new synthesized, extremely labile terpenols VII-IX and ketone XII follow reliably from their spectral data. Thus, e.g., the PMR spectra of VII and VIII contain the doublet signals of the allenic protons with \( J = 7-9 \) Hz, while the IR spectra of VII-IX show the 1950 cm\(^{-1}\) absorption bands that are typical of allenes. The structures of the known ketones X [8] and XI [9] were confirmed by comparison of their boiling points and PMR and IR spectra with those previously described.

The isomerization of carbinols IV-VI is apparently attributable to the primary formation of a resonance-stabilized divinylcarbonium ion, XIII (compare [5]). Dysrotatory scission of the C-C cyclopropene bond in one of the forms of XIII ought then lead to an allyl carbocation, XIV, which is further stabilized (see [10]) by the addition of an external nucleophile at two centers to form the final products, VII-XII.

Apparently the allylic double bond in the side chain substantially facilitates the formation of the carbonium ion like XIII and its subsequent rearrangement. This apparently explains why the expected isomerization products could not be obtained from III.

The carbonyl compounds X-XII can originate in part from the respective allenic carbinols VII-IX through a common carbonium ion XIV; evidence for this is the conversion of IX in 20% yield to the divinyl ketone XII under the conditions for the rearrangement of alcohols IV-VI given above. Such an acid-catalyzed conversion has been described for the related allenic alcohols [11].

These CPAR examples illustrate a quite simple synthesis of tertiary vinylallenic alcohols and the isomeric divinyl ketones. Since these compounds have the structure of irregular monoterpenoids, it can be expected that they will subsequently be discovered in natural sources.

**EXPERIMENTAL**

IR spectra were obtained in CCl\(_4\) solution in a UR-20 apparatus. UV spectra of alcoholic solutions were obtained on a Specord UV-VIS spectrophotometer. PMR spectra were measured relative to TMS in CCl\(_4\) solution in Varian DA-60-IL or Tesla ES-497 (100 MHz) spectrometers. Mass spectra were obtained on Varian MAT CH-6 or LKB-2091 spectrometers at 70-eV ionization voltage. GLC analysis was carried out on an LKhM-SMD apparatus (column 2 m x 3 mm, with 15% Carbowax 20M on Chromaton N-AW); TLC was carried out on plates with an attached layer of Silufol grade SiO\(_2\) in 1:1 ether–hexane.

1-(1'-Hydroxy-3'-methylbutyl)-3,3-dimethylcyclopropene (III). To 23 ml of 1 N n-BuLi (28 mmole) in hexane at \(-30^\circ\)C was added over 10 min 3 g (30 mmole) of disopropylamide in 5 ml of THF. After 0.5 h stirring at this temperature, 3.5 g (30 mmole) of TMEDA was added in one portion, and the mixture was held for 15 min at 25\(^\circ\)C. The mixture was cooled to \(-30^\circ\)C, and 2.1 g (31 mmole) of 3,3-dimethylcyclopropene was bubbled in over 45 min, after which stirring was continued for 1 h. Without raising the temperature, 2.41 g of