[2+2]-Cycloadditions of Alkenes with the Triphenylallenyl Cation

Herbert Mayr* and Englbert Bäuml
Institut für Organische Chemie der Universität Erlangen-Nürnberg
Henkestr. 42, D-8520 Erlangen

Summary. The triphenylallenyl cation (3), generated from triphenylpropynol (7) and FSO3H, reacts with alkenes to give the allyl cations (8), which may be deprotonated to yield the methylenecyclobutenes (9). Alternatively, (8) can be converted into the 2-vinyl-indenes (10) via two subsequent electrocyclic reactions.

Allenyl cations (2) are ambident electrophiles. 1) Nucleophilic attack at the sp2 carbon yields propargyl derivatives, whereas allenic compounds are formed via attack at the sp terminus. If the nucleophile is an alkene, reaction at these two positions yields carbenium ions (11) and (12), which can undergo successive cyclization reactions as shown in Scheme 1.

Scheme 1

Allenyl cations (2) with R' = CH3 and alkenes were found to give the vinyl cations (13) (R = aryl) and (14) (R = alkyl) via the linear intermediate (11). 2) We now report a novel type of reaction between alkenes and allenyl cations. A [2+2]-cycloaddition with formation of allyl cations (15) is observed if the triphenylallenyl cation (R, R' = Ph) is employed.
Since allyl cations are better stabilized than their precursors, complex mixtures would be expected, if the reactions were carried out in our usual way by combining propargyl or allenyl halides with alkenes in the presence of a weak Lewis acid. Good yields of the 1:1 products 13 and 14 are obtained, however, by simultaneous addition of triphenylpropynol (7) and alkenes to solutions of fluorosulfuric acid in dichloromethane and subsequent workup with aqueous sodium carbonate solution (Table). Obviously, protonation of the alkenes does not play an important role under these conditions.

Table. Fluorosulfuric Acid Initiated Reactions of Triphenylpropynol (7) with Some Alkenes at -60°C

<table>
<thead>
<tr>
<th>R¹</th>
<th>R²</th>
<th>R³</th>
<th>R⁴</th>
<th>Alkene</th>
<th>Z/Alkene/FSO₃H²</th>
<th>Time</th>
<th>Product (Yield)³</th>
<th>mp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) H</td>
<td>CH₃</td>
<td>H</td>
<td>CH₃</td>
<td>1 : 2.4 : 2.0</td>
<td>20 min</td>
<td>14a (84%)</td>
<td>156-158</td>
<td></td>
</tr>
<tr>
<td>b) H</td>
<td>H</td>
<td>CH₃</td>
<td>CH₃</td>
<td>1 : 1.4 : 1.2</td>
<td>30 min</td>
<td>14b (63%)</td>
<td>113-115</td>
<td></td>
</tr>
<tr>
<td>c) H</td>
<td>CH₃</td>
<td>CH₃</td>
<td>CH₃</td>
<td>1 : 2.1 : 0.25</td>
<td>20 min</td>
<td>14c (69%)</td>
<td>103-105</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1 : 2.1 : 2.0</td>
<td>15 min</td>
<td>13c (72%)</td>
<td>95-97</td>
<td></td>
</tr>
<tr>
<td>d) CH₃</td>
<td>CH₃</td>
<td>CH₃</td>
<td>CH₃</td>
<td>1 : 1.2 : 1.1</td>
<td>15 min</td>
<td>13d (86%)</td>
<td>106-108</td>
<td></td>
</tr>
<tr>
<td>e) H</td>
<td>H</td>
<td>CH₃</td>
<td>Ph</td>
<td>1 : 1.1 : 2.0</td>
<td>15 min</td>
<td>13e (78%)</td>
<td>128-130</td>
<td></td>
</tr>
<tr>
<td>f) H</td>
<td>-(CH₂)₄-</td>
<td>CH₃</td>
<td>Ph</td>
<td>1 : 1.2 : 1.2</td>
<td>20 min</td>
<td>14f (41%)</td>
<td>138-140</td>
<td></td>
</tr>
</tbody>
</table>

a) Molar ratio; b) Isolated yield of crystalline material; all compounds were structurally ascertained by ¹H (ref. 9) and ¹³C-NMR, MS and elemental analyses; c) -35°C;

It is suggested (Scheme 2) that fluorosulfuric acid rapidly converts the alcohol into the triphenylallenyl cation (9), which undergoes a [2+2]-cycloaddition with alkenes. Though the intermediacy of 9 has not been proven for the examples quoted in the Table, we suggest a stepwise cycloaddition mechanism for the formation of 12 in analogy to the reaction of 8 with cyclopentadiene. Furthermore, the reaction of 7 with 1-ethoxy-2-methylpropene yields aldehydes 15 and 16, hydrolysis products of 9 and 11.
Deprotonation of $12$ affords methylenecyclobutenes $14$, which are analogous to the products obtained from vinyl cation cycloadditions with alkenes.$^6$ The allyl cations $12d$, $e$ and (in the presence of excess $\text{FSO}_3\text{H}$) $12c$ undergo rapid electrocyclic ring opening reactions at $-60$ to $-30^\circ\text{C}$. The resulting carbenium ions $11$, like other 1-arylallyl cations,$^7$ undergo a pentadienyl cation type cyclization with formation of $10$, which is finally deprotonated to give $12$.

The activation barrier of the electrocyclic process $12 \rightarrow 11$ is unusually low, compared to cyclobutene - butadiene isomerizations of neutral systems.$^8$ In subsequent work, we are trying to elucidate the mechanism of this rapid ring opening reaction.
We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for support of this work.

3) For a comparison of solvolysis rates of allyl and propargyl halides see:
9) $^1$H-NMR (CDCl$_3$, δ):
   13c: 1.11 (s, 6 H), 1.68 (d, 6.8 Hz, 3 H), 5.62 (q, 1 H), 7.13-7.70 (m, 14 H).
   13d: 0.72 (s, 3 H), 1.30 (s, 3 H), 1.39 (s, 3 H), 1.67 (s, 3 H), 7.10-7.90 (m, 14 H).
   13e: 1.77 (s, 3 H), 4.73 (d, 1.4 Hz, 1 H), 5.37 (d, 1.4 Hz, 1 H), 7.03-7.70 (m, 19 H).
   14a: 0.87 (d, 6.8 Hz, 3 H), 2.10 (d, 1.6 Hz, 3 H), 3.58 (qq, 6.8 Hz, 1.6 Hz, 1 H), 6.68-7.20 (m, 14 H), 7.30 (s, 5 H).
   14b: 1.20 (s, 6 H), 6.70-7.23 (m, 11 H), 7.30 (s, 5 H).
   14c: 1.13 (s, 6 H), 1.95 (s, 3 H), 6.93 (br. s, 10 H), 7.30 (s, 5 H).
   14f: 0.92 (s, 3 H), 1.07-2.93 (m, 8 H), 6.40-7.07 (m, 10 H), 7.17 (s, 5 H).
   15: 1.37 (s, 6 H), 7.17-7.63 (m, 15 H), 9.72 (s, 1 H).
   16: 1.70 (s, 3 H), 1.75 (s, 3 H), 6.70-7.70 (m, 15 H), 9.68 (s, 1 H).

(Received in Germany 5 December 1983)