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# [2+2]-CYCLOADDITIONS OF ALKENES WITH THE TRIPHENYLALLENYL CATION

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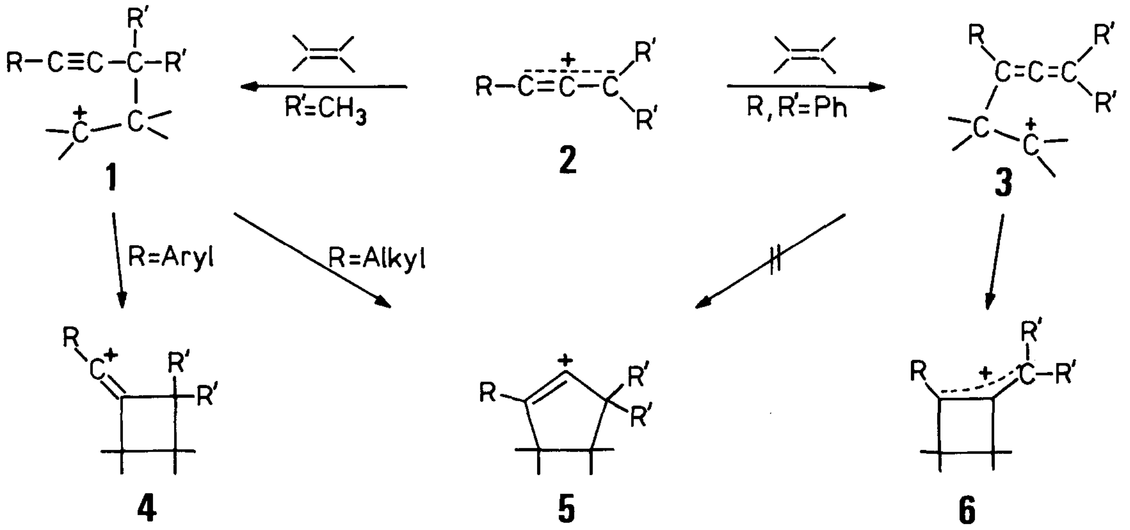
Summary. The triphenylallenyl cation (8), generated from triphenylpropynol (7) and $FSO_3H$, reacts with alkenes to give the allyl cations 12, which may be deprotonated to yield the methylenecyclobutenes 14. Alternatively, 12 can be converted into the 2-vinyl-indenes 13 *via* two subsequent electrocyclic reactions.

Allenyl cations (2) are ambident electrophiles.[1)] Nucleophilic attack at the $sp^2$ 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 1 and 3, which can undergo successive cyclization reactions as shown in Scheme 1.

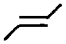
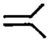
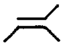
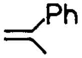
Scheme 1



Allenyl cations (2) with R' = $CH_3$ and alkenes were found to give the vinyl cations 4 (R = aryl) and 5 (R = alkyl) *via* the linear intermediate 1.[2)] We now report a novel type of reaction between alkenes and allenyl cations. A [2+2]-cycloaddition with formation of allyl cations 6 is observed if the triphenylallenyl cation (R, R' = Ph) is employed.

Since allyl cations **6** are better stabilized than their precursors **2**,3) 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.4) 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.

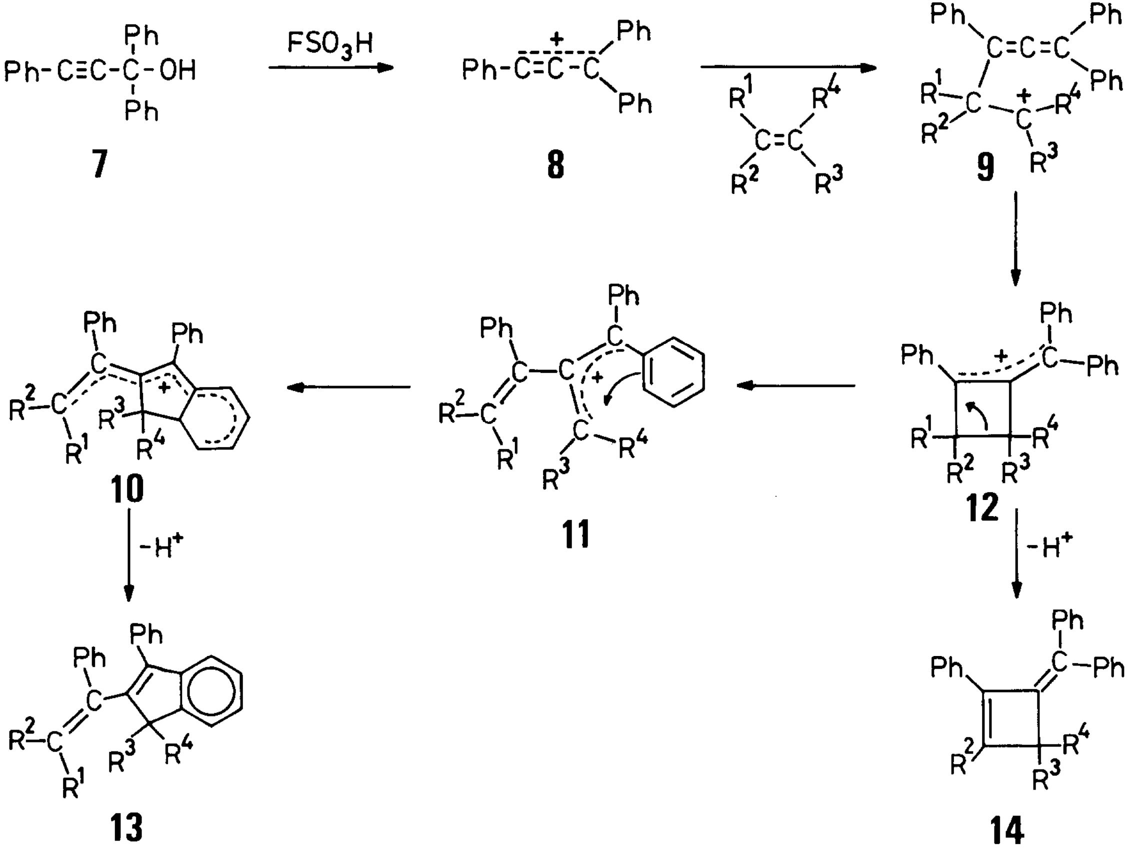
Table. Fluorosulfuric Acid Initiated Reactions of Triphenylpropynol (**7**) with Some Alkenes at -60°C

| | $R^1$ | $R^2$ | $R^3$ | $R^4$ | Alkene | **7**/Alkene/$FSO_3H$[a] | Time | Product | (Yield)[b] | mp (°C) |
|---|---|---|---|---|---|---|---|---|---|---|
| a) | H | $CH_3$ | H | $CH_3$ |  | 1 : 2.4 : 2.0 | 20 min | **14a** | (84 %) | 156-158 |
| b) | H | H | $CH_3$ | $CH_3$ |  | 1 : 1.4 : 1.2 | 30 min | **14b** | (63 %) | 113-115 |
| c) | H | $CH_3$ | $CH_3$ | $CH_3$ |  | 1 : 2.1 : 0.25 | 20 min | **14c** | (69 %) | 103-105 |
| | | | | | | 1 : 2.1 : 2.0 | 15 min | **13c** | (72 %) | 95- 97 |
| d) | $CH_3$ | $CH_3$ | $CH_3$ | $CH_3$ |  | 1 : 1.2 : 1.1 | 15 min | **13d** | (86 %) | 106-108 |
| e) | H | H | $CH_3$ | Ph |  | 1 : 1.1 : 2.0 | 15 min[c] | **13e** | (78 %) | 128-130 |
| f) | H | -$(CH_2)_4$- | | $CH_3$ |  | 1 : 1.2 : 1.2 | 20 min | **14f** | (41 %) | 138-140 |

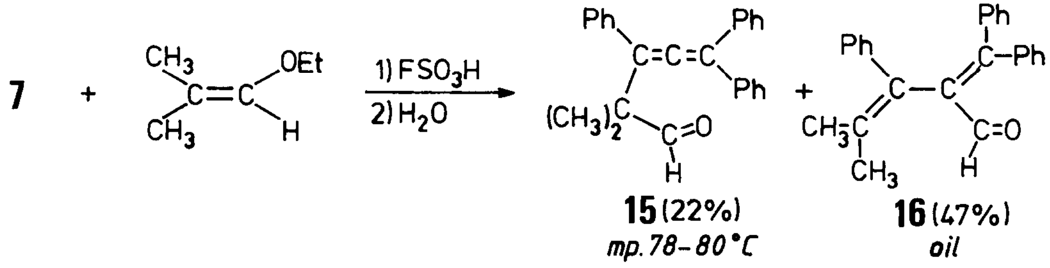
a) Molar ratio; b) Isolated yield of crystalline material; all compounds were structurally ascertained by $^{1}$H (ref. 9) and $^{13}$C-NMR, MS and elemental analyses; c) -35°C;

It is suggested (Scheme 2) that fluorosulfuric acid rapidly converts the alcohol **7** into the triphenylallenyl cation (**8**), 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.5) Furthermore, the reaction of **7** with 1-ethoxy-2-methylpropene yields aldehydes **15** and **16**,9) hydrolysis products of **9** and **11**.

Scheme 2



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 $FSO_3H$) 12c undergo rapid electrocyclic ring opening reactions at -60 to -30°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 13.



The activation barrier of the electrocyclic process 12 → 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.

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9) $^1$H-NMR ($CDCl_3$, $\delta$ ):
**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, 10 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).

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