

Tritylium ions as initiators and co-initiators in cationic polymerizations

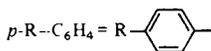
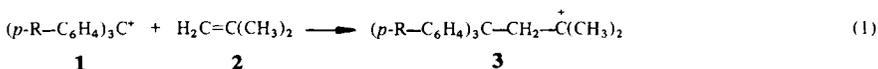
Christian Schade, Herbert Mayr*

Institut für Chemie der Medizinischen Universität zu Lübeck,
Ratzeburger Allee 160, D-2400 Lübeck, Federal Republic of Germany

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Introduction

The unsubstituted tritylium cation (**1a**) does not initiate the cationic polymerization of isobutene (**2**)¹. This observation was attributed to the difference of the carbenium ion stabilization of **1a** and **3a**, which cannot be compensated by the free energy, gained from the conversion of a π - into a σ -bond [Eq. (1)]².



1a, 3a: R = H
b: R = Cl

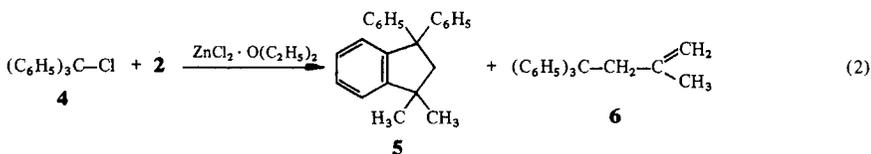
On the other hand, the less stabilized tris(4-chlorophenyl)methyl cation (**1b**) was reported to initiate the polymerization of isobutene³. In accordance, *p*-methoxy and *p*-methyl substituted tritylium ions do not initiate the polymerization of α -methylstyrene, in contrast to the less stable **1a** and **1b**⁴. Only for few reactive monomers, however, the initiation was proven to proceed via addition of trityl cations **1** to the monomer⁵, and in most of these cases the site of attack at the trityl cation has not been determined⁶. As some nucleophiles were shown to attack the para-position of trityl cations⁷, the reaction might occur either at the central carbon or at one of the aromatic rings. Due to their sluggish addition towards alkenes, tritylium ions have been introduced as Lewis acidic catalysts for the addition of acetals and aldehydes to (silyl) enol ethers and allyltrimethylsilanes by Mukaiyama et al.⁸.

In this work, we have studied electrophilic alkylations of isobutene (**2**) and allyltrimethylsilane, in which tritylium ions alternatively act as electrophilic alkylating agents or as Lewis acidic catalysts. As in previous investigations, conditions were used under which the reactions terminate after the inclusion of one alkene unit⁹.

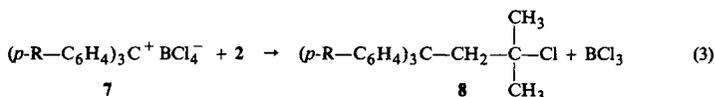
Initiation by tritylium ions

The reaction of tritylium perchlorate with isobutene (**2**) in acetonitrile at 30°C was reported to yield 28% of 1,1-dimethyl-3,3-diphenylindane (**5**) along with polymeric material¹⁰. The corresponding $\text{ZnCl}_2 \cdot \text{Et}_2\text{O}$ catalyzed reaction of trityl chloride (**4**)

with **2** in CH_2Cl_2 at 0°C gave **5** and 2-methyl-4,4,4-triphenyl-1-butene (**6**) in small yield^{9b}.

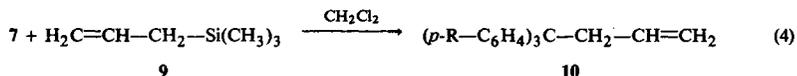


We found now that tritylium tetrachloroborate (**7a**) does not react with isobutene in CH_2Cl_2 at -10°C . Under the same conditions, the less stabilized chloro derivative **7b** gave 79% of the regular addition product **8b**, when treated with 70 equivalents of isobutene.



	7a, 8a	7b, 8b
R	H	Cl

Allyltrimethylsilane (**9**) is more reactive than **2** and gives the expected 4,4,4-triaryl-1-butenes **10a, b** with both trityl tetrachloroborates **7a**¹¹ and **7b**. The structures of compounds **5**, **6**, **8b** and **10** indicate that both π -nucleophiles **2** and **9** attack tritylium ions at the central carbon atom, not in *p*-position of the aromatic rings.



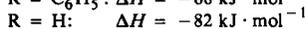
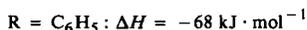
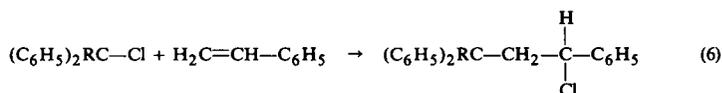
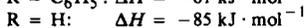
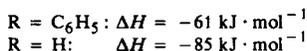
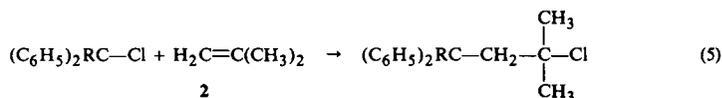
10a: R = H
10b: R = Cl

In contrast to the common viewpoint¹⁾, the sluggishness of tritylium ion additions towards π -systems cannot be explained by the inherent stability of these carbenium ions. Whereas the unsubstituted trityl cation ($\text{p}K_{\text{R}^+} = -6,63$)¹² does not react with **2** below 0°C , the even better stabilized bis(*p*-anisyl)methyl cation ($\text{p}K_{\text{R}^+} = -5,71$)¹³ reacts with **2** even at -70°C ^{11, 14}.

This conclusion is corroborated by kinetic experiments. When the consumption of **7b** by **2** was followed photometrically by monitoring the absorbance at 490 nm, the rate of the reaction was found to decrease considerably after a small degree of conversion. In contrast, the decrease of [**7b**] in presence of a large excess (770 equivalents) of **9** followed a pseudo first order rate law up to 80% conversion of **7b**. The resulting second order rate constant $k_2 = 0,44 \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ (at -10°C in CH_2Cl_2) is 5000 times smaller than k_2 of the corresponding reaction of α -(*p*-methoxyphenyl)benzyl tetrachloroborate (BMMT) with **9** (k_2 (at -10°C) = 2040)¹¹, although both

carbenium ions are of similar stability (pK_{R^+} of **7b** = $-7,74^{12}$) and pK_{R^+} of α -(*p*-methoxyphenyl)benzyl tetrachloroborate = $-7,9^{13}$). Steric strain, therefore, accounts for the relatively low reactivity of the trityl cation **7b**.

Force field calculations (MMPMI)¹⁵ have been used to estimate the steric strain generated in such reactions¹⁶.

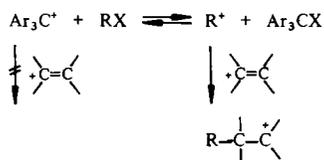


Eqs. (5) and (6) show that the addition reactions of trityl chloride to **2** and styrene are less exothermic than the corresponding diarylmethyl chloride additions. The difference is much more pronounced in the additions to **2** ($\Delta\Delta H = 24 \text{ kJ} \cdot \text{mol}^{-1}$) than in the additions to styrene ($\Delta\Delta H = 14 \text{ kJ} \cdot \text{mol}^{-1}$), indicating that steric hindrance is more important in additions to isobutene. Therefore, styrene polymerization in contrast to isobutene polymerization can be initiated by the unsubstituted trityl cation^{5,17}, although diarylcarbenium ions were shown to react faster with isobutene than with styrene¹⁸.

Co-initiation by tritylium ions

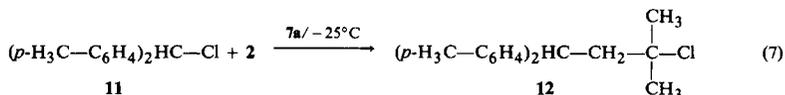
The discussion in the previous section has shown that trityl cations, though not having an extraordinarily high stability (pK_{R^+}), exhibit a very low reactivity towards olefinic π -systems. They can, therefore, act as Lewis acids and accept halide anions from other alkyl halides. Since the carbenium ions, thus generated, may be capable of attacking olefins, trityl salts can act as co-initiators for the carbocationic polymerization of alkenes (*Scheme 1*).

Scheme 1:



Experimental evidence for these conclusions comes from the formation of 94% of **12** from **11** and **2** in presence of tritylium tetrachloroborate (**7a**). Whereas **11** and **2** do

not react in dichloromethane in absence of a Lewis acid, the reaction proceeds at considerably lower temperatures (-78°C) when **7a** is replaced by the stronger Lewis acid BCl_3 ¹⁴⁾.



Since the rates of electrophilic alkylations of alkenes (*Scheme 1*) depend on the equilibrium concentration of R^+ , the co-initiating efficiency of trityl salts can be controlled by appropriate substituents in the tritylium ions. Co-initiation by tritylium tetrachloroborates may either proceed via direct Cl^- abstraction of tritylium ions from $\text{R}-\text{Cl}$ or via the small equilibrium concentration of BCl_3 ($\text{7a} \rightleftharpoons \text{4} + \text{BCl}_3$). Assuming fast Cl^- transfer processes, both mechanisms are in agreement with our conclusions.

Experimental part

CH_2Cl_2 was dried with CaCl_2 , washed with conc. H_2SO_4 , stirred over K_2CO_3 , distilled over P_2O_5 and finally CaH_2 .

3-Chloro-3-methyl-1,1,1-tris(4-chlorophenyl)butane (8b): Isobutene (**2**) (28,1 g; 500 mmol) was condensed into a flask which contained 2,64 g (6,91 mmol) of the chloride of **1b**. After dilution with 100 ml of CH_2Cl_2 , 50 ml (2,0 mmol) of gaseous BCl_3 was added. The reaction mixture was stored for 70 h at -10°C , washed with 6N HCl, dried over CaCl_2 , and the solvent was evaporated. The residue (3,02 g; 6,89 mmol; 99%) was purified by recrystallization from petroleum ether; colorless crystals, which decompose at $159-160^{\circ}\text{C}$ with elimination of HCl. Yield: 2,4 g (79%).

¹H NMR (90 MHz, CDCl_3): $\delta = 1,18$ (s; 6H, CH_3), 3,33 (s; 2H, CH_2), 7,27 (mc; 12H, Ar-H).

¹³C NMR (CDCl_3): $\delta = 34,55$ (q; 2 CH_3), 52,34 (t; C-2), 55,58 (s; C-1), 70,10 (s; C-3), 128,10, 130,56 (2d; ortho-C, meta-C), 132,28 (s; para-C), 144,51 (s; ipso-C).

MS (70 eV): $m/z = 402, 400$ (3%, 3%, $M^+ - 36$), 349 (31), 348 (20), 347 (94), 346 (21), 345 (100), 277 (6), 275 (17), 239 (20), 235 (10), 233 (15).

4,4,4-Tris(4-chlorophenyl)-1-butene (10b): Gaseous BCl_3 (100 ml; 4,0 mmol) and 1,0 ml (6,3 mmol) of **9** were successively added to a solution of 1,11 g (2,90 mmol) of the chloride of **1b** in 50 ml of CH_2Cl_2 at -20°C . After 24 h, another 1 ml of **9** was added, and the solution was kept at -20°C for 24 h. The mixture was washed with 25% aq. NH_4Cl , dried over CaCl_2 , and the solvent was evaporated. Purification was done by MPLC (Merck Lichroprep Si 60 RP-18, MeOH, 12,5 ml/min, 12 bar, $t_R = 16,3$ min). Yield: 0,94 g (84%) of a colorless oil.

¹H NMR (200 MHz, CDCl_3): $\delta = 3,33$ (br. d; $J = 6,6$ Hz, 2H, 3-H), 4,94–5,08 (m; 2H, 1-H), 5,47–5,67 (m; 1H, 2-H), 7,01, 7,27 (AA'BB' system; $J_{AB} = 8,8$ Hz, 12H, Ar-H).

¹³C NMR (CDCl_3): $\delta = 45,33$ (t; C-3), 55,26 (s; C-4), 118,45 (t; C-1), 128,15, 130,51 (2d; ortho-C, meta-C), 132,33 (s; para-C), 134,58 (d; C-2), 144,85 (s; ipso-C).

MS (70 eV): $m/z = 349, 347, 345$ (5%, 13%, 14%, $M^+ - \text{C}_3\text{H}_5$), 88 (12), 86 (77), 84 (100), 75 (15), 73 (45).

IR (neat): 3065, 3025, 2960, 2919, 1660, 1588, 1570, 1490, 1444, 1400, 1094, 1011, 975, 916, 811, 748, 732 cm^{-1} .

4,4,4-Triphenyl-1-butene (10a): It was prepared as described by R. Schneider¹¹⁾ in an analogous manner; m. p. $68-68,5^{\circ}\text{C}$.

^1H NMR (200 MHz, CDCl_3): $\delta = 3,43$ (br. dt; $J = 6,6$ Hz, $J = 1,5$ Hz, 2H, 3-H), 4,89–5,07 (m; 2H, 1-H), 5,55–5,75 (m; 1H, 2-H), 7,21 (mc; 15H, Ar-H).

*Kinetic experiment*¹⁴⁾: Compound **9** (3,16 mmol) was added to a solution of **7b** (0,0041 mmol) in 100 ml of CH_2Cl_2 , and the decreasing absorbance of **7b** was subsequently monitored at 490 nm. The reaction followed a pseudo first order rate law, and the second order rate constants k_2 were derived from the pseudo first order rate constants $k_{1\psi}$, using the equation $k_2 = k_{1\psi} / [\text{Alkene}]$. Two independent experiments gave $k_2 = 0,436$ and $0,453 \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$.

Tritylium tetrachloroborate catalyzed additions of bis(p-tolyl)methyl chloride (11) towards isobutene (2): Compound **11** (258 mg; 1,12 mmol) was added to a solution of **7a** prepared from **4** (52,2 mg; 0,187 mmol) and BCl_3 (4 ml; 0,16 mmol) in 100 ml of CH_2Cl_2 . After the addition of isobutene (50 ml; 2,3 mmol), the mixture was kept at -25°C for 24 h and worked up with 6 M HCl. After removal of the solvent, 144 mg (1,33 mmol) of anisole was added as internal standard. ^1H NMR analysis showed the formation of 94% of **12**.

Conclusion

Tritylium ions can attack at the double bond of isobutene and thus are potential initiators of the polymerization of isobutene. Their additions to alkenes are considerably retarded, however, by the steric strain, generated during the addition reactions. Diarylcarbenium ions attack alkenes with rate constants several orders of magnitude higher than trityl cations of similar stability (derived from $\text{p}K_{\text{R}^+}$).

Because of their Lewis acidity and low reactivity towards CC π -bonds, tritylium ions may also act as co-initiators of alkene polymerizations. They may ionize other types of alkyl halides to give less bulky carbenium ions, which add to CC π -bonds and thus initiate polymerization. The main advantage of such initiating systems is the well-defined character of the individual steps, for which thermodynamic and kinetic data are frequently available¹⁹⁾.

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