Quadricyclane Radical Cation Isomerizations

Rainer Herges,*[a] Felix Starck,[a] Torsten Winkler,[a] and Michael Schmittel[b]

Dedicated to Professor Armin de Meijere on the occasion of his 60th birthday

Abstract: Isopropylidene quadricyclane **1** upon oxidation with catalytic amounts of the electron transfer catalyst tris(*p*-tolyl)aminium hexafluoroantimonate ($TTA^{\bullet+}$ SbF_6^-) gives bicycloheptadiene **2** spontaneously and in quantitative yields. Epoxidation of the isopropylidene group drastically changes the reactivity of the quadricyclane framework. Under the same reaction conditions (catalytic amounts of $TTA^{\bullet+}$ SbF_6^-) norbornadiene **4** is formed spontaneously and quantitatively according to an NMR study. Theoretical calculations on the model compounds quadricyclane **5a** and isopropylidene quadricyclane **5b** at the B3LYP/3-21G and MP2/3-21G level of density functional theory (DFT) and ab initio theory reveal the mechanism of both reactions. In the parent quadricyclane system the concerted (but not synchronous) three-electron cycloreversion is favored, and by hyperconjugation with the π^* orbital the isopropylidene derivative prefers a simultaneous cleavage of a „lateral" bond and a cyclobutane bond to give the intermediate **9b**. Starting from **9b** there are two pathways to the product bicycloheptadiene **12b**. The pathway involving the trimethylenemethane intermediate **11b** turns out to be a dead end because the system has to overcome a very high activation barrier to give the bicycloheptadiene. Much more favorable and consistent with the reaction conditions is a 1,2-shift, which has a barrier of only 1.7 kcal mol^{-1}, leading directly to the bicycloheptadiene radical cation **10b** and subsequently upon reduction to the neutral product **12b**. A number of known quadricyclane rearrangements can be explained by these mechanisms.

Keywords: electron transfer · hyperconjugation · isomerizations · quadricyclane · radical ions

Introduction

Numerous mechanistic investigations have been carried out on the isomerization reactions of quadricyclane. Because of potential applications as solar energy storage systems the quadricyclane/norbornadiene system is of practical interest. In our investigations on norbornadiene/quadricyclane-based photoswitchable systems we have been looking for an efficient catalyst for the [2+2] cycloreversion of **1**.[1a,b] Probably because of the sterically hindered 1,5,6,7-positions, the well-known transition metal catalysts exhibit only low or no activity. To reduce steric problems, we have used thermally[2] and photochemically[3–5] oxidizing electron-transfer catalysts.[6]

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Results and Discussion

Surprisingly, the reaction of **1** with the oxidizing agent tris(*p*-tolyl)aminium hexafluoroantimonate ($TTA^{\bullet+}$ SbF_6^-)[7] does not lead to the expected norbornadiene. Within the NMR detection limit, the bicycloheptadiene **2** is formed immediately and quantitatively (Scheme 1). This means that instead of the "lower" four-membered ring bonds 1–7 and 5–6, the "lateral" three-membered ring bonds 2–7 and 4–6 (and one four-membered ring bond) are broken. It is known that π systems of suitable symmetry exhibit conjugation with "α,β-conjugated" cyclopropane bonds,[8] especially in quadricyclane.[9] In order to suppress this conjugation and to be finally able to isomerize the quadricyclane to the norbornadiene, we epoxidized the isopropylidene group.[10] Indeed, the epoxide reacts in the desired way and (according to NMR spectroscopy) gives the corresponding norbornadiene quantitatively within a few seconds.

The spontaneous reaction process and the drastic change in reactivity induced by a rather small change in the structure of the reactant prompted us to perform a detailed theoretical study of these reactions. The results explain our own observations as well as a large number of other well-known isomerization reactions of quadricyclanes.

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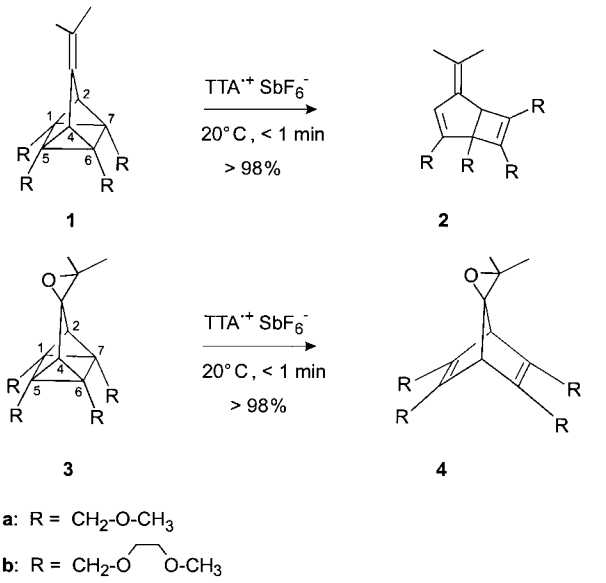


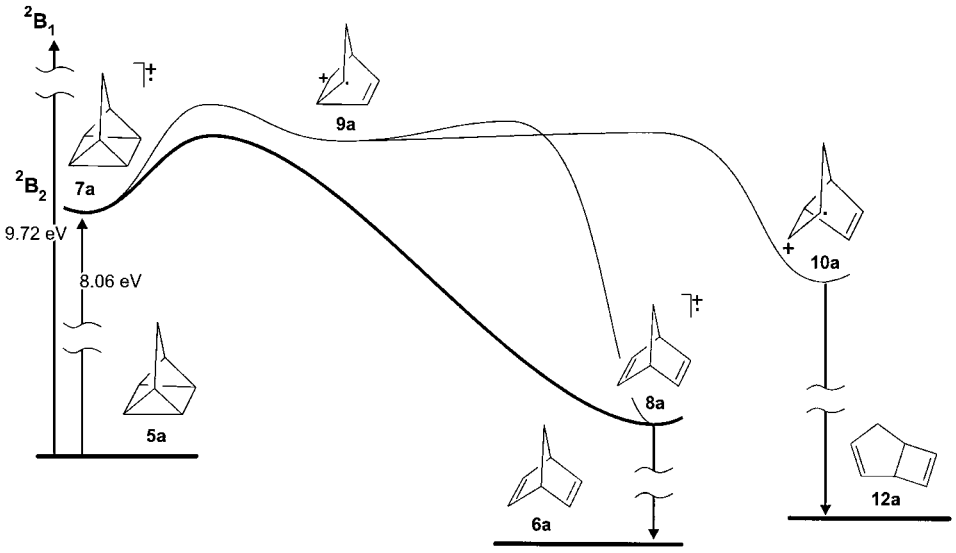
Scheme 1. Scheme 1.

To elicit the details of the mechanism of these isomerizations, we examined the energy hypersurface starting from the radical cations of the quadricyclane **5a** and the isopropylidene quadricyclane **5b** as model compounds (for the epoxide **3** and the isopropylidene quadricyclane **1**, respectively) using density functional methods (B3LYP/3-21G)[11,12] and ab initio (MP2/3-21G).[13,14]

Ionization energies were calculated by using the OVGF method[15] (ROVGF/3-21G//B3LYP/3-21G).[16] Several different mechanisms have been proposed for the conversion of quadricyclanes into bicycloheptadienes (analogous to Scheme 1, (**1**→**2**)).[17–19] During the isomerization, at least three bonds are broken and three new ones are formed. Therefore, there is a large number of conceivable pathways and intermediates that can neither be excluded nor confirmed by experimental data. For an exhaustive treatment of the problem, we first assumed a concerted mechanism and subsequently searched systematically for intermediates in the hypothetical least-motion process. There are two possibilities for such a process: formation of bonds 1–2, 4–7, and 6–7 while 1–7, 2–7, and 4–6 are broken, or formation of 1–2, 4–7, and 5–6 while 2–7, 4–6, and 1–5 are broken, or symmetrically equivalent reactions. The stationary points (see Schemes 2 and 3 and Table 1) were checked by harmonic frequency analysis, and the transition states were characterized by intrinsic reaction coordinate (IRC) calculations. Energies and geometries in the following are given at the B3LYP/3-21G level of theory if not stated otherwise.

The vertical ionization of quadricyclane **5a** leads to the $^2B_2$ state[20] **7a** of the radical cation (IE = 8.06 eV, exp. 8.43 eV[21])(Scheme 2). The ionization energy for the $^2B_1$ state (9.72 eV, exp. 9.78 eV[]) is remarkably higher. Starting from **7a**-$^2B_2$ two possible reaction paths branch out: the first route leads to the norbornadiene radical cation ($\Delta H^{\neq}$ = 8.3 kcal mol^{-1}[22]; exp. $\Delta G^{\neq}$ = 9.3 kcal mol^{-1}[23, 24]), the second gives **9a** ($\Delta H^{\neq}$ = 10.5 kcal mol^{-1}). The latter structure is formed by simultaneously breaking a lateral bond and a four-membered ring bond. For structure **9a** again two pathways are open that lead either to the norbornadiene **8a** ($\Delta H^{\neq}$ = 2.4 kcal mol^{-1}) or to the bicycloheptadiene **10a** ($\Delta H^{\neq}$ = 1.1 kcal mol^{-1}). The concerted (but asynchronous) cycloreversion therefore is kinetically more favorable than the two steps via **9a** and the isomerization to **10a** (Scheme 2). While only norbornadiene is formed by chemically, electrochemically, or photochemically induced oxidation of quadricyclane, **12a** can be detected as a product by matrix ESR under radiolysis conditions.[19] Presumably the excess energy induced by the oxidation is sufficient to open the energetically less favorable path. The calculated reaction profile explains the formation of **12a** from **8a** by irradiation at 620 nm.[19] Probably **9a** is formed as the first intermediate which surmounts a very low energy barrier (1.1 kcal mol^{-1}) to give **10a** and finally **12a** by reduction.

Unlike in the parent system **5a**, the $^2B_1$ state is formed instead of the $^2B_2$ state by vertical ionization of the isopropylidene quadricyclane. The electronic $^2B_1$ state (**7b**-$^2B_1$, C_{2v} symmetry) is a stationary point of second order. Following the two trajectories of imaginary frequency leads to the intermediate **9b** by breaking a lateral bond and a four-membered ring bond to or to the $^2B_2$ state (**7b**-$^2B_2$) which is a minimum according to a frequency calculation (Scheme 3 and Figure 1).



Scheme 2. B3LYP/3–21G-calculated energy hypersurface starting from the quadricyclane radical cation. Energy values for minima and transition states are true to scale unless specifically marked. The favorable reaction path is shown as a bold line. Ionization energies were calculated by ROVGF/3–21G using a B3LYP/3–21G geometry. Absolute energy values are listed in Table 1. The valence bond structures with the largest contribution to the overall wavefunction are shown.[25]

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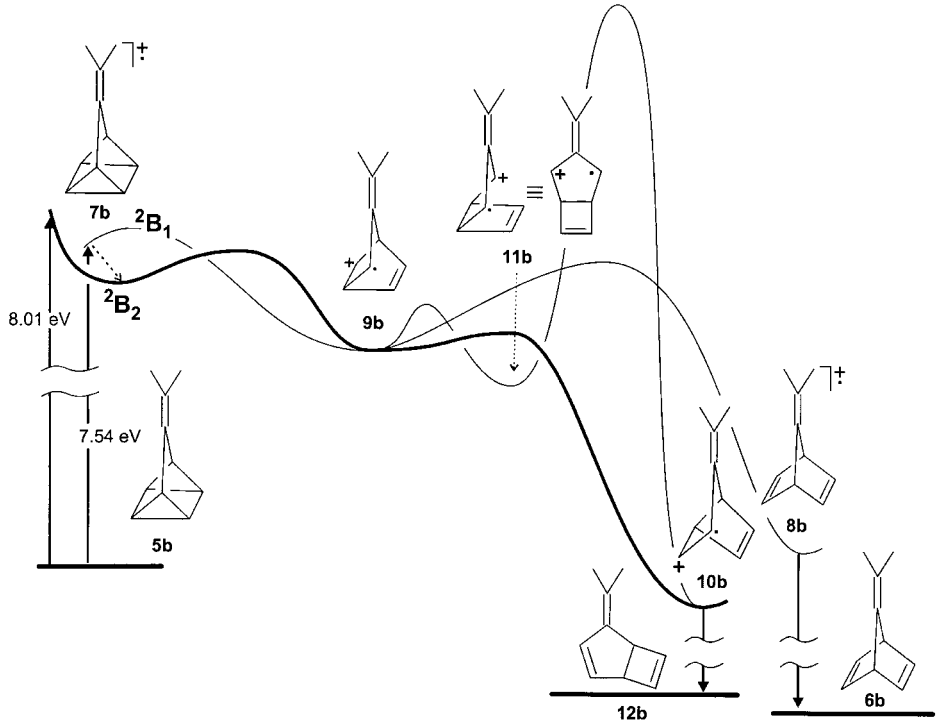

Scheme 3. B3LYP/3–21G-calculated energy hypersurface starting from the isopropylidene quadricyclane radical cation. Energy values for minima and transition states are true to scale unless specifically marked. The favorable reaction path is shown as a bold line. Ionization energies were calculated by ROVGF/3–21G using a B3LYP/3–21G geometry. Absolute energy values are listed in Table 1. The VB structures with the largest contribution to the overall wavefunction are shown.[25]

Starting from **9b** there are two paths leading to the bicyloheptadiene **10b**: either directly by a Wagner–Meerwein type rearrangement (breaking bond 5–6 and forming bond 1–6) with an activation barrier 1.7 kcal mol^{-1} or via a trimethylenemethane intermediate **11b** ($\Delta H^{\neq}$ = 4.7 kcal mol^{-1}) which has been proposed for similar systems. The activation barrier for the formation of the bicycloheptadiene **10b** from **11b** ($\Delta H^{\neq}$ = 37.1 kcal mol^{-1}) is considerably higher than the one for direct formation from **9b**. This is in agreement with experimental observations according to which trimethylenemethanes derived from quadricyclanes do not rearrange but dimerize.[26,27] Bicycloheptadienes can only be obtained by reverse reaction to laterally opened quadricyclanes (analogous to **9b**).[17] The formation of the bicycloheptadiene **10b** from **9b** by breaking bond 2–7 and forming bond 4–7 would be a conceivable alternative. However, we did not find a transition state for this "1,3-shift". The only plausible reaction path for the formation of the bicycloheptadiene **12b** from the quadricyclane **5b** therefore involves the laterally opened intermediate **9b** (bold line in Scheme 3). In agreement with the experimental observations, this path is kinetically more favorable than the isomerization to the norbornadiene **8b**. In the isopropylidene system, there is no concerted mechanism for the isomerization of quadricyclane **5b** to norbornadiene **8b**, and the stepwise reaction via **9b** is clearly less favorable ($\Delta H^{\neq}$ = 8.9 kcal mol^{-1}) than the formation of the bicycloheptadiene **10b**.

Thus, our theoretical calculations do not only reproduce the drastic change in reactivity induced by the exocyclic double bond, but also explain several other experimental observations. The reason for the large impact of the isopropylidene group can be explained using a simple MO diagram (Scheme 4).

The HOMO of the parent quadricyclane is a b_2 orbital which exhibits bonding properties in the four-membered ring (1–7 and 5–6). Removal of an electron from this orbital therefore weakens these bonds and favors a cycloreversion to norbornadiene. The second highest orbital in quadricyclane which is of b_1 symmetry interacts with the exocyclic double bond, and by a fairly large splitting the antibonding combination becomes the HOMO in the isopropylidene derivative.

Table 1. B3LYP/3–21G calculated stationary points on the potential energy hypersurface starting from the quadricyclane radical cation **7a** and the isopropylidene quadricyclane radical cation **7b**. E_{abs} in au, E_{rel} in kcal mol^{-1} related to **7a** or **7b** in the $^2B_2$ state; N_{imag} number of imaginary frequencies according to normal coordinate analysis; ν_{imag} frequencies of the imaginary vibrations in cm^{-1}.

	7–$^2B_2$	**7**–$^2B_1$	(**7**→**8**)$^+$	**8**	(**7**→**9**)$^+$	**9**	(**9**→**10**)$^+$	**10**	(**9**⇌**11**)$^+$	**11**	(**11**⇌**10**)$^+$	(**9**⇌**8**)$^+$
parent system												
E_{abs} −269	0.678069	0.605409	0.664781	0.711484	0.661392	0.667287	0.665548	0.688814	–	–	–	0.66339
E_{rel}		0.0	45.6	8.3	−21.0	10.5	6.8	7.9	−6.7	–	–	–
9.2												
N_{imag}	0	2	1	0	1	0	1	0	–	–	–	1
ν_{imag}	−8925, −1622	−1025		−266		−289					−224	
$<S^2>$		0.753	0.762	0.752	0.758	0.754	0.755	0.757				0.766
isopropylidene derivative												
E_{abs} −385.	0.761813	0.754965	–	0.805299	0.75772	0.772863	0.770030	0.812654	0.765314	0.778375	0.719248	0.758555
E_{rel}	0	4.3	–	−27.3	2.6	−6.9	-5.2	−31.0	−2.2	−10.4	26.7	2.0
N_{imag}	0	2	–	0	1	0	1	0	1	0	1	1
ν_{imag}		−160, −66	–		-370		−334		−363		−553	−484
$<S^2>$	0.754	0.752	–	0.753	0.753	0.774	0.770	0.759	0.764	0.772	0.769	0.756

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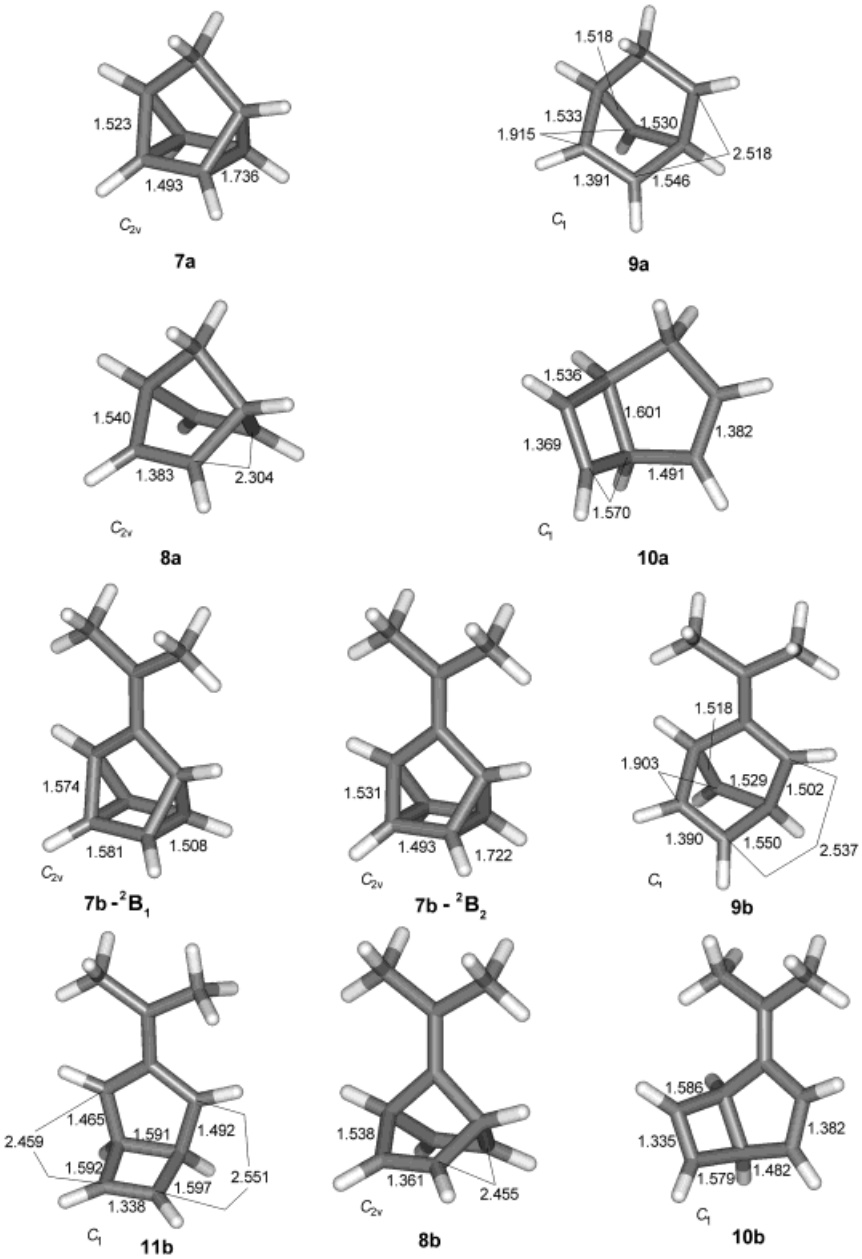
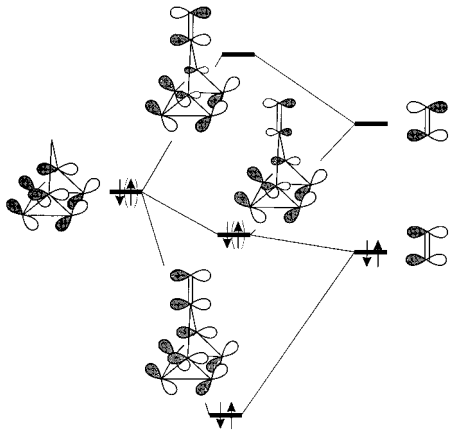


Figure 1. B3LYP/3–21G calculated structures and selected bond lengths [Å] of stationary points on the reaction hypersurface of quadricyclane **5a** to norbornadiene **6a** and the isopropylidene derivative **5b** to bicycloheptadiene **12b**.



Scheme 4. Conjugation of a double bond with a b_1 quadricyclane orbital.

Ionization of this b_1 orbital has the opposite effect on the reactivity of the quadricyclane framework than removing an electron from the b_2 orbital in the parent system. Because of the antibonding interactions in the cyclobutane bonds 1–7 and 5–6 and the bonding properties in the lateral bonds 1–2, 4–5, 2–7, and 4–6, the cycloreversion of the radical cation is discriminated against lateral bond cleavage. The same effect, but less pronounced, is also operative in the neutral quadricyclane system. By conjugation of the quadricyclane b_1 orbital with the π^* orbital, charge is transferred to the exocyclic double bond. Therefore the lateral bonds become more reactive, while the four-membered ring bonds are strenghtened. In dicyanomethylene quadricyclane, this effect is so large that the neutral system does not thermally isomerize to the norbornadiene but to the bicycloheptadiene.[18]

Experimental Section

Compounds 3a, **3b**: **1a** (100 mg, 0.32 mmol) or **1b**[1] (157 mg, 0.32 mmol) was dissolved in dichloromethane (30 mL) and a dimethyl dioxirane solution (3.8 mL, 0.33 mol) was added dropwise.[28] After the mixture was stirred at room temperature for 15 min the solvent was removed under vacuum. The product was obtained in quantitative yield. **3a**: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 3.87$, 3.73 (2d, ^2J(H,H) = 11.7 Hz, 8H; OCH_2), 3.85, 3.58 (2d, ^2J(H,H) = 11.4 Hz, 8H; OCH_2), 3.35, 3.33 (2s, 12H; OCH_3), 1.51 (s, 6H; CH_3), 1.26 (s, 2H; CH); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 79.76$ (C_q), 68.55, 68.51 (CH_2), 61.49 (C_q), 58.01, 57.94 (CH_3), 33.95, 32.12 (C_q), 32.99 (CH), 22.57 (CH_3); IR (film): $\tilde{\nu} = 3061$ (w), 2986, 2979, 2926, 2879, 2857, 2820 (s), 2739, 1720 1654, 1649, 1639, 1508 (w), 1452 (m), 1422, 1377 (s), 1293, 1259 (m), 1231, 1193 (s), 1156 (m), 1103 (ss), 1064 (s), 984 (w), 957 (m), 908 (s), 860, 751 (w), 710 (m) cm^{-1}; MS (CI negative-ion mode, NH_3): *m/z* (%): 323 (100) [$M - H^+$]. **3b:** ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 3.98$, 3.84 (2d, ^2J(H,H) = 11.9 Hz, 4H; OCH_2), 3.96, 3.71 (2d, ^2J(H,H) = 11.9 Hz, 4H; OCH_2), 3.65–3.50 (m, 16H; CH_2CH_2), 3.37 (2s, 12H; OCH_3), 1.49 (s, 6H; CH_3), 1.28 (s, 2H; CH); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 79.80$ (C), 72.01, 69.24, 69.02, 66.97 (CH_2), 61.47 (C_q), 58.94, 58.86 (CH_3), 34.15, 32.26 (C), 32.84 (CH), 22.54 (CH_3); IR (film): $\tilde{\nu} = 2980$ (m), 2926, 2978 (s), 2826, 1456, 1377, 1356, 1231, 1200 (m), 1133, 1102 (ss), 1035 (m), 981, 850, 732 (w) cm^{-1}; MS (CI positive-ion mode, NH_3): *m/z* (%): 518 (100) [M+NH_4^+], 500 (14) [M^+], 483 (14), 442 (11), 425 (53), 407 (14), 349 (29), 327 (14), 286 (17), 268 (17); HR-MS

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(CI negative-ion mode): calcd. for $C_{26}H_{43}O_9$: 499.2907, found: 499.2907 ± 10.

Compound 2a: 1a (143 mg, 0.46 mmol) and tris(*p*-tolyl)amine (66 mg, 0.23 mmol) were dissolved in dry acetonitrile (15 mL). A solution of tris(p-tolyl)aminium hexafluoroantimonate ($TTA^{\bullet+}SbF_6^-$) in acetonitrile (1.22×10^{-2} M; 32 mg, $TTA^{\bullet+}SbF_6^-$ dissolved in acetonitrile (5 mL)) was added dropwise. At the beginning the blue color of the catalyst rapidly vanished, after the addition of 2.0 mL (2.4×10^{-5} mol) $TTA^{\bullet+}SbF_6^-$ the color remained visible. After the solution was stirred for 15 min at room temperature, the color changed to green. The mixture was evaporated under vacuum to a quarter of its original volume and then filtered through a short silica gel column (hexane/ethyl acetate 1/1). The product **2a** (111 mg, 78%) was obtained by flash liquid chromatography (silica gel, $R_f = 0.44$). **2a:** ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 6.28$ (s, 1H; 3-H), 4.12, 4.08 (2d, ^2J(H,H) = 13.4 Hz, 2H; OCH_2), 4.01, 3.91 (2d, ^2J(H,H) = 12.8 Hz, 2H; OCH_2), 3.99 (s, 2H; OCH_2), 3.75, 3.56 (2d, ^2J(H,H) = 9.8 Hz, 2H; OCH_2), 3.36 (s, 3H; OCH_3), 3.34 (s, 3H; OCH_3), 3.32 (s, 3H; OCH_3), 3.29 (s, 3H; OCH_3), 1.76 (s, 3H; 10-H), 1.75 (s, 3H; 9-H); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 146.89$, 142.64 (C_q), 144.28 (C_q), 134.17, 125.16 (C_q), 129.06 (CH), 73.80 (CH_2), 70.25 (CH_2), 67.19 (CH_2), 66.80 (CH_2), 62.46 (C_q), 59.22 (CH_3), 58.18 (CH_3), 58.08 (CH_3), 58.06 (CH_3), 51.06 (CH), 21.53 (CH_3), 20.32 (CH_3); IR (film): $\tilde{\nu}$ = 3041 (w), 2980, 2921,2889, 2873, 2852, 2820 (s), 2728 (w), 1468 (m), 1450, 1374, 1193 (s), 1157 (m), 1108 (ss), 1020, 998 (w), 952, 912, 871, 733 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 308 (38) [M^+], 276 (58), 244 (100), 231 (50), 229 (27), 213 (16), 201 (22), 199 (40), 169 (21), 115 (15), 75 (59), 44 (83); HR-MS: calcd. for $C_{18}H_{28}O_4$: 308.1988, found: 308.1988 ± 6.

NMR experiment: Compound 2a: A solution of $TTA^{\bullet+}SbF_6^-$ in acetonitrile (3.1×10^{-2} M; $TTA^{\bullet+}SbF_6^-$ (12 mg) dissolved in dry CD_3CN (0.75 mL)) was added dropwise to a solution of **1a** (15 mg, 4.9×10^{-5} mol), tris(*p*-tolyl)amine (4.3 mg, 1.5×10^{-5} mol) and 2,6-di-*tert*-butylpyridine (1 drop) in CD_3CN (0.75 mL) until the blue color of the catalyst remained visible (10–15 mol% of the catalyst). The reaction mixture was immediately analyzed by NMR spectroscopy (^{1}H NMR: 400 MHz, $CDCl_3$, 25 °C, TMS; ^{13}C NMR: 100.6 MHz, $CDCl_3$, 25 °C, TMS). According to the NMR spectrum, the formation of **2a** was quantitative. The rearrangement of **1b** was carried out under analogous conditions, and a quantitative formation of **2b** was observed.

Compound 4a: A 0.01 M solution of $TTA^{\bullet+}SbF_6^-$ in acetonitrile was slowly added to a solution of **3a** (60 mg, 0.185 mmol) in dry acetonitrile (7 mL) using a syringe. At the beginning the blue color of the catalyst rapidly disappeared, after the addition of 1.3 mL (0.013 mmol, 7.0 mol%) $TTA^{\bullet+}SbF_6^-$ a blue-gray color remained visible. After further stirring at room temperature for 15 min the solution was quenched with $NaHCO_3$ solution (5 mL) and dichloromethane (15 mL). After phase separation the aqueous phase was extracted with dichloromethane (3 × 15 mL). The organic phase was dried with Na_2SO_4 and the solvent was removed under vacuum. The product was purified by flash liquid chromatography (florisil, hexane/ethyl acetate 1/2, $R_f = 0.25$). Compound **4a** (29 mg, 48%) was obtained as a colorless oil. **4a**: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 4.16$ (s, 4H; OCH_2), 4.11, 4.08 (2d, J(H,H) = 12.0 Hz, 4H; OCH_2), 3.41 (s, 2H; 1,4-H), 3.29, 3.27 (2s, 12H; OCH_3), 1.29 (s, 6H; CH_3); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 145.17$, 144.79 (C_q), 99.28 (C_q), 67.54, 67.47 (CH_2), 64.85 (C_q), 57.92, 57.53 (CH_3), 55.46 (CH), 20.75 (CH_3); IR (film): $\tilde{\nu}$ = 2987, 2926, 2892, 2854, 2819 (s), 1721, 1647, 1505 (w), 1455 (m), 1377 (s), 1356 (m), 1284, 1258 (w), 1236 (m), 1216, 1194 (s), 1154 (m), 1130 (s), 1096, 1086 (ss), 957, 920 (m), 899 (s), 733 (w), 699 (m) cm^{-1}; MS (CI positive-ion mode, NH_3): *m/z* (%): 342 (10) [M+NH_4^+], 325 (9) [M+H^+], 307 (97), 293 (82), 275 (35), 261 (100), 235 (25), 222 (12), 203 (57), 110 (19).

Compound 4b: A $TTA^{\bullet+}SbF_6^-$ solution (0.2 mL, 1.57×10^{-2} M) was added dropwise to a solution of **3b** (188 mg, 0.38 mmol), tris(*p*-tolyl)amine (51 mg, 0.18 mmol) and 2,6-di-*tert*-butylpyridine (0.05 mL, 0.22 mmol) in dry acetonitrile (25 mL). After the addition of several drops of the solution the blue color of the oxidizing agent already remained visible. The solution was evaporated to a quarter of its original volume and then filtered through a short florisil column. The product was further purified by liquid chromatography, but probably because of partial decomposition on the column only 18 mg (10%) of **4b** was obtained. **4b**: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 4.21$ (s, 4H; OCH_2), 4,16, 4,12 (2d, J(H,H) = 12.2 Hz, 4H; OCH_2), 3.46–3.43 (m, 16H; CH_2CH_2), 3.36 (s, 2H; 1,4-H), 3.30 (2s, 12H; OCH_3), 1.20 (s, 6H; CH_3); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 145.14$, 144.54 (C_q), 99.39 (C_q), 71.97 (CH_2), 69.43, 68.55 (CH_2), 66.38, 66.19 (CH_2), 64.89 (C_q), 59.02, 58.89 (CH_3), 55.43 (CH), 20.74 (CH_3).

NMR experiment: **Compound 4a**: Compound **3a** (16 mg; 0.05 mmol) was dissolved in CD_3CN (0.75 mL). A solution of $TTA^{\bullet+}SbF_6^-$ in CD_3CN (0.16 mL, 5 mol%; 0.015 M) was slowly added and the blue reaction mixture was immediately analyzed by NMR spectroscopy (^{1}H NMR: 400 MHz, $CDCl_3$, 25 °C, TMS; ^{13}C NMR: 100.6 MHz, $CDCl_3$, 25 °C, TMS). A quantitative formation of **4a** was observed.

NMR experiment: **Compound 4b**: Compound **3b** (15 mg, 0.03 mmol), tris(*p*-tolyl)amine (4.3 mg, 0.015 mmol) and one drop of 2,6-di-*tert*-butylpyridine were dissolved in CD_3CN (0.75 mL). A solution of $TTA^{\bullet+}SbF_6^-$ in CD_3CN (0.13 mL, 4 mol%; 0.015 M) was slowly added. The blue solution was immediately analyzed by NMR spectroscopy (^{1}H NMR: 400 MHz, $CDCl_3$, 25 °C, TMS; ^{13}C NMR: 100.6 MHz, $CDCl_3$, 25 °C, TMS). A quantitative formation of **4b** was observed.

Acknowledgment

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie (scholarship for T.W.) for support.

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Received: May 28, 1999 [F 1814]

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