Functionalized Oxatriquinanes and Their Structural Equilibrium in Protic Solvent

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We synthesized oxatriquinane hexafluorophosphate bearing an ethoxycarbonylmethyl group 7 or a 2-oxopropyl group 11. Both of these organic oxonium cation compounds were obtained as stable solids. However, 1H-NMR analysis showed that oxatriquinane 7 was present as the oxonium cation in aprotic solvent CD3CN, but was in rapid equilibrium with ring-opened bicyclic compound 8 in protic solvent CD3OD. The oxatriquinane 11 also showed similar behavior in protic solvent. Phenyl-substituted oxatriquinanes 12 and 14 were also obtained as stable solids, and showed similar properties to 7 and 11.

Key words oxatriquinane; organic oxonium cation; equilibrium; protic solvent

There have been few reports on stable organic oxonium salts, though alkyl oxonium salts such as triethyl oxonium tetrafluoroborate 1 (known as Meerwein’s reagent) have been utilized in organic synthesis as powerful alkylation reagents for alcohol or amine (2,3) (Fig. 1). However, they are chemically unstable and sensitive to moisture, so they are difficult to handle. Recently, Mascal et al. reported the synthesis of oxatriquinane 2 and oxatriquinacene 3, which have a tricyclic condensed ring structure with an oxygen cationic center.4 Compound 2 was isolated as a crystalline solid suitable for X-ray crystal structure analysis. Interestingly, 2 could be purified by column chromatography and was stable under reflux in alcohol or water. Subsequently, they synthesized several oxatriquinanes with simple alkyl groups and carried out X-ray crystal structure analysis.5,6 A unique S$_2$2 reaction at tertiary carbon in the α-position to the oxygen center was also reported.7 Most recently, oxatriquinane having a hydroxy group at the α-position to oxygen (4) was found to have the longest C–O bond length so far reported among organic compounds.8 We became interested in these stable oxonium cation species, and set out to synthesize further examples for examination of their potential utility in materials science or medicinal chemistry.

First, we focused on oxatriquinane having a simple ester group, to see whether such a group is compatible with the oxonium cation. As shown in Chart 1, the starting ketone 5,7 which was synthesized from 1,5-cyclooctadiene, was subjected to Reformatsky reaction to afford β-hydroxyester 6 in good yield. Compound 6 was obtained as nearly a single stereoisomer, and its stereochemistry was determined by examination of the nuclear Overhauser effect (NOE) between methine proton at C1 and methylene protons at the α-position to the carbonyl group. Next, 6 was treated with trifluoromethanesulfonic acid (TfOH) in acetonitrile to give oxatriquinane trifluoromethanesulfonate, but we could not obtain this in crystalline form, so the salt was purified by simple anion exchange using sat. aqueous KPF$_6$ to afford oxatriquinane hexafluorophosphate 7 in an excellent yield as a stable off-white solid after usual work-up. Recrystallization from CH$_2$Cl$_2$/Et$_2$O afforded colorless fine needles. Compound 7 showed good solubility in acetonitrile, dichloromethane, acetone, and lower alkyl alcohols such as methanol or ethanol, but was hardly soluble in chloroform, ethyl acetate, and diethyl ether.

Though the 1H-NMR spectrum of 7 in CD$_3$CN showed symmetric proton signals consistent with oxatriquinane structure, the spectrum in CD$_3$OD solution showed another set of signals in addition to the original oxatriquinane signals. The new signals indicated that 7 was predominantly cleaved to bicyclic compound 8 in CD$_3$OD. The 1H-NMR spectra in CD$_3$OD at two concentrations (0.02 M and 0.2 M) are shown in Fig. 2. At 0.02 M almost all the oxatriquinane signals were lost, except for weak signals at δ 5.5, 4.15–4.22, and 3.14. On the other hand, at 0.2 M, peaks due to 7 were more marked. These results suggest that oxatriquinane 7 and bicyclic compound 8 exist in equilibrium in CD$_3$OD solution (Fig. 3). The structure of 8 was confirmed by isolation and by 1H-NMR measure-

Reagents and conditions: (a) Zn, BrCH$_2$CO$_2$Et, PhH, reflux (1 h); (b) TfOH, CH$_3$CN, rt (15 min), then sat. KPF$_6$ aq.

Chart 1. Synthesis of Oxatriquinane with Ester Functionality 7

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ments after potassium carbonate treatment of 7 in CD$_3$OD (Chart 2).

The stereochemistry at C4 was determined on the basis of NOE between a methine proton at C4 and methylene protons at the α-position to the carbonyl group in the ester functionality. Cleavage on the side of the ethoxycarbonylmethyl substituent was not detected. The $^1$H-NMR spectrum of oxatriquinane 7 in D$_2$O showed a similar signal pattern to that in CD$_3$OD. In addition, the $^1$H-NMR signals of the ring-opened bicyclic compound were also recognized in DMSO-$d_6$ or acetone-$d_6$ containing a small amount of water. However, the $^1$H-NMR spectrum in aprotic CD$_3$CN afforded only the signals of 7, even though a little water was present (Fig. 2). This suggests that the acidity of protic solvent present in the organic solvent greatly affects the equilibrium. Mascal et al. reported that oxatriquinane is stable in alcohol or water, but is present as an equilibrium mixture in a protic solvent, and is almost entirely present as the bicyclic compound in highly dilute solution. We found that the original oxatriquinane could be recovered from the equilibrium mixture by concentrating the solution to dryness. We also confirmed that Mascal’s oxatriquinane 2 was in an equilibrium state in a protic solvent such as CD$_3$OD or D$_2$O. Thus, it is reasonable that oxatriquinane 7 could be purified by column chromatography without any problem using an aprotic solvent system of CH$_3$CN/CH$_2$Cl$_2$ as the eluent.

We next aimed to synthesize oxatriquinane bearing a ketone functionality. Namely, compound 7 was ring-opened with methanol and base followed by hydride reduction to give bicyclic ether 9 (Chart 3). The side chain unit in 9 was converted to an acetomethyl group in three steps (oxidation, Grignard reaction, and oxidation) to afford bicyclic ketone 10. Finally, compound 10 was treated with TfOH in CH$_3$CN and anion exchange afforded oxatriquinane 11 in an excellent yield as a stable white powder. Thus, a carbonyl group is compatible with oxonium cation structure. The $^1$H-NMR spectra of 11 in CD$_3$OD at two concentrations (0.02 M and 0.2 M) are also shown in Fig. 4. The behavior of 11 was similar to that of oxatriquinane 7.

Next, we focused on oxatriquinane bearing a phenyl group, since aromatically substituted derivatives might have potential for materials chemistry. As shown in Chart 4, the starting ketone 5 was treated with phenylmagnesium bromide to give...
a crude adduct, which was treated with TfOH in CH$_3$CN and subjected to anion exchange to afford the desired oxatriquinane 12 in modest yield. Phenylation at the α-position to the oxygen center in 12 was also performed. Compound 12 was hydrolyzed with aqueous potassium carbonate solution to afford bicyclic alcohol, which was oxidized to ketone 13 using Collins reagent. The same procedures used in the synthesis of oxatriquinane 12 then afforded oxatriquinane 14, which has two phenyl groups. Oxatriquinanes 12 and 14 showed similar properties to 7, and purification by column chromatography or recrystallization afforded a stable white powder. Finally, further phenylation of oxatriquinane 14 was examined. The same reaction sequence as above provided ketone 15 and its Grignard adduct. Treatment of the crude Grignard adduct with excess TfOH afforded a product that showed the $^1$H-NMR and $^{13}$C-NMR signals of oxatriquinane 16 in CD$_3$CN, although usual isolation failed, probably because the instability of 16 except under strongly acidic conditions. The usual work-up resulted in yielding an olefin 17. The geometry of the C=C double bond in 17 was determined to be (E) based on NOE between the C=C double bond and phenyl group protons. The $^1$H-NMR spectrum of 16 derived from 17 in the presence of excess TfOH in CD$_3$CN is shown in Fig. 5. Clear symmetrical peaks of aliphatic and aromatic protons were observed.

In summary, we synthesized several organic oxonium cation species, i.e., oxatriquinane hexafluorophosphate derivatives, bearing carbonyl or phenyl groups. These compounds were obtained as stable solids. $^1$H-NMR analysis suggested that ethoxycarbonylmethyl-substituted oxatriquinane 7 is stable in aprotic solvent, but is in rapid equilibrium with the ring-opened bicyclic compound in protic solvent. Oxatriquinanes 12 and 14 bearing a phenyl group at the α-position to the oxygen center were also synthesized and isolated as stable solids. Oxatriquinane 16 bearing three phenyl groups could not be isolated, though its formation was confirmed by $^1$H-NMR studies in excess TfOH/CD$_3$CN. Our findings demonstrate that a carbonyl or phenyl group is compatible with oxonium cation structure, and further synthetic studies aimed at novel functional or bioactive oxatriquinane molecules are in progress.

**Experimental**

**General** Melting points (mp) were determined on a Yanagimoto micro melting point apparatus (hot plate) and are uncorrected. Low-resolution electron-ionization mass spectra (LR-El-MS) and high-resolution (HR)-El-MS were recorded on a JEOL JMS-AX505HA. Proton nuclear magnetic resonance ($^1$H-NMR) spectra and carbon nuclear magnetic reso-
nance (\(^{13}\)C-NMR) spectra were measured with a Varian Mercury instrument at 300 MHz and at 75 MHz, respectively. The chemical shifts are recorded in ppm, and coupling constants (\(J\)) in Hz. \(^{1}H\) and \(^{13}\)C-NMR chemical shifts are given relative to that of either tetramethylsilane (0.00 ppm for \(^{1}H\)-NMR in CDCl\(_3\) and CD\(_3\)OD) or residual solvent (1.94 ppm for \(^{13}\)C-NMR in CDCl\(_3\)). Fluorine NMR (\(^{19}\)F-NMR) spectra and phosphorus NMR (\(^{31}\)P-NMR) spectra were measured with a Varian Mercury instrument at 282 MHz and at 121 MHz, respectively.

To a solution of ethyl bromoacetate (0.36 mL, 3.255 mmol) and LiAlH\(_4\) (55.1 mg, 1.452 mmol) was carefully added. The suspension was stirred for 15 min and then quenched with H\(_2\)O (0.1 mL) and 3 M NaOH (0.1 mL). The mixture was extracted with CH\(_2\)Cl\(_2\) (5 mL). The combined organic layer was dried. The solvent was evaporated and the residue was chromatographed on silica gel (10% to 15% AcOEt/hexane) to give 8 (68.3 mg, 0.263 mmol, 97%) as a colorless oil. \(^{1}H\)-NMR (CD\(_2\)OD) \(\delta\): 1.24 (3H, t, \(J=7.0\) Hz), 1.57–1.92 (9H, m), 1.50–2.12 (3H, m), 2.47 (1H, d, \(J=14.1\) Hz), 2.51 (1H, d, \(J=14.1\) Hz), 3.46–3.55 (2H, m), 4.10 (2H, q, \(J=7.0\) Hz), 4.25–4.34 (1H, m); \(^{13}\)C-NMR (CD\(_2\)OD) \(\delta\): 14.52, 30.46, 30.57, 31.24, 33.71, 35.11, 38.02, 47.12, 61.38, 79.46, 83.70, 84.27, 172.57; LR-EL-MS \(m/z\): 259 (M\(^{+}\))

\(\text{(4-Hydroxy-10-oxa-bicyclo[5.2.1]dec-4-yl)acetic Acid Ethyl Ester (7)}\) To a solution of \(\text{(100.5 mg, 0.271 mmol)}\) in CH\(_2\)Cl\(_2\) was added K\(_2\)CO\(_3\) (39.4 mg, 0.285 mmol). The mixture was stirred for 30 min, and then diluted with Et\(_2\)O. The resulting suspension was filtered on Celite pad, which was well washed with Et\(_2\)O. The filtrate was evaporated and the residue was chromatographed on silica gel (10% to 15% AcOEt/hexane as the eluent) to give 9 (296.5 mg, 1.154 mmol, 95%) as a colorless oil. \(^{1}H\)-NMR (CD\(_2\)OD) \(\delta\): 1.58–2.00 (1H, m), 2.00–2.12 (1H, m), 2.38 (1H, s), 3.46–3.62 (2H, m), 4.30–4.39 (1H, m); \(^{13}\)C-NMR (CD\(_2\)OD) \(\delta\): 28.89, 29.59 (2C), 30.19, 32.06, 34.52, 36.04, 42.09, 55.44, 59.31, 77.77, 81.51, 85.01; LR-EL-MS \(m/z\): 214 (M\(^{+}\)); HR-EL-MS \(m/z\): 214.1570 (Calcd for C\(_{11}\)H\(_{19}\)O\(_{3}\); 214.1569).

\(\text{(4-Methoxy-10-oxa-bicyclo[5.2.1]dec-1-yl)ethanol (9)}\) To a solution of \(\text{(350.7 mg, 1.447 mmol)}\) in CH\(_2\)Cl\(_2\) (5 mL) was added K\(_2\)CO\(_3\) (210.5 mg, 1.523 mmol). The resulting suspension was stirred for 30 min, then concentrated in vacuo and the residue was diluted with Et\(_2\)O. The suspension was filtered on a Celite pad, and the pad was well washed with Et\(_2\)O. The filtrate was evaporated to afford a crude product (358.6 mg). This product was dissolved in tetrahydrofuran (THF) (5 mL), and LiAlH\(_4\) (55.1 mg, 1.452 mmol) was carefully added. The suspension was stirred for 15 min and then quenched with H\(_2\)O (0.1 mL) and 3 M NaOH (0.1 mL). The suspension was filtered on a Celite pad, and the pad was well washed with Et\(_2\)O. The filtrate was concentrated in vacuo and the residue was chromatographed on silica gel (40% to 80% AcOEt/hexane as the eluent) to give 9 (296.5 mg, 1.384 mmol, 95%) as a colorless oil. \(^{1}H\)-NMR (CD\(_2\)OD) \(\delta\): 1.58–2.00 (1H, m), 2.00–2.12 (1H, m), 2.38 (1H, s), 3.46–3.62 (2H, m), 4.30–4.39 (1H, m); \(^{13}\)C-NMR (CD\(_2\)OD) \(\delta\): 28.89, 29.59 (2C), 30.19, 32.06, 34.52, 36.04, 42.09, 55.44, 59.31, 77.77, 81.51, 85.01; LR-EL-MS \(m/z\): 214 (M\(^{+}\)); HR-EL-MS \(m/z\): 214.1570 (Calcd for C\(_{11}\)H\(_{19}\)O\(_{3}\); 214.1569).

\(\text{1-(4-Methoxy-10-oxa-bicyclo[5.2.1]dec-1-yl)propan-2-one (10)}\) Compound 9 (247.3 mg, 1.154 mmol) was taken up in CH\(_2\)Cl\(_2\) (5 mL) and added to a stirred solution of Collins reagent, which had been prepared from CrO\(_3\) (579.2 mg, 5.793 mmol) and pyridine (0.93 mL, 11.56 mmol) in CH\(_3\)Cl\(_2\) (15 mL). After 1 h, 3 M NaOH (20 mL) was added, and the mixture was extracted with CH\(_3\)Cl\(_2\)\(_{3}\). The combined organic phase was washed with 2 M HCl (20 mL) and brine (20 mL), and dried. The solvent was evaporated and the residue (218.8 mg) was taken up in CH\(_2\)Cl\(_2\) (5 mL). This solution was added dropwise methylmagnesium bromide (3.0 M solution in Et\(_2\)O; 0.58 mL, 1.740 mmol) and stirring was continued for 15 min. 1H-NMR (CD\(_2\)OD) \(\delta\): 1.24 (3H, t, \(J=7.0\) Hz), 1.57–1.92 (9H, m), 1.50–2.12 (3H, m), 2.47 (1H, d, \(J=14.1\) Hz), 2.51 (1H, d, \(J=14.1\) Hz), 3.46–3.55 (2H, m), 4.10 (2H, q, \(J=7.0\) Hz), 4.25–4.34 (1H, m); \(^{13}\)C-NMR (CD\(_2\)OD) \(\delta\): 14.52, 30.46, 30.57, 31.24, 33.71, 35.11, 38.02, 47.12, 61.38, 79.46, 83.70, 84.27, 172.57; LR-EL-MS \(m/z\): 259 (M\(^{+}\)); HR-EL-MS \(m/z\): 259.1858 (Calcd for C\(_{14}\)H\(_{21}\)D\(_{3}\)O\(_{4}\); 259.1860).
To a stirred solution of 10 (173.7 mg, 0.768 mmol) in CH3CN (3 mL) was added dropwise TIOH (204 µL, 2.305 mmol). Stirring was continued for 15 min, then the reaction mixture was concentrated in vacuo, and the resulting residue was treated with sat. KPF6aq. (10 mL). The mixture was extracted with AcOEt, and the resulting mixture was evaporated and the residue was dissolved in a small amount of CH2Cl2, and then precipitated with Et2O. The resulting precipitate was collected on a filter and washed with Et2O to give 11 (236.1 mg, 0.694 mmol, 90%) as an off-white solid. Colorless needles (CH2Cl2/Et2O); mp 124.73 (2C), 126.40, 127.88 (2C), 146.60, 210.49; LR-EI-MS m/z: 230 (M+); HR-EI-MS m/z: 226.1559 (Calcd for C15H18O2; 226.1569).

2-(2-Oxopropyl)oxatriquinanium Hexafluorophosphate (11) To a stirred solution of 10 (173.7 mg, 0.768 mmol) in CH3CN (3 mL) was added dropwise TIOH (112 µL, 1.230 mmol). The solution was stirred in THF; 1.76 mL, 1.901 mmol). The solution was stirred for 15 min, then the reaction mixture was concentrated in vacuo, and the resulting mixture was extracted with AcOEt. The mixture was extracted into CH2Cl2/Et2O; mp 101.5–103.5°C; 1H-NMR (CD3CN): δ: 2.07–2.23 (4H, m), 2.12 (3H, s), 2.25–2.50 (8H, m), 3.22 (2H, s), 5.34 (2H, apparent quint, J=5.8 Hz); 13C-NMR (CD3CN): δ: 30.15 (2C), 30.50 (2C), 31.09, 35.14 (2C), 49.12, 102.24 (2C), 114.77, 205.02; 19F-NMR (CD3CN): δ: −73.12 (d, JF-P=708 Hz); 31P-NMR (CD3CN): δ: −143.21 (sept, JP-P=708 Hz); LR-EI-MS m/z: 195 (M+); HR-EI-MS m/z: 195.1387 (Calcd for C15H18O2F6: 195.1380).

2-Phenyloxatriquinanium Hexafluorophosphate (12) To a solution of 5 (195.4 mg, 1.267 mmol) in THF (2 mL) was added dropwise phenylmagnesium bromide (1.08 M solution in THF; 1.76 mL, 1.901 mmol). The solution was stirred for 30 min, then sat. NH4Cl aq. (5 mL) was added, and the mixture was extracted with AcOEt×3. The combined organic layer was dried. The solvent was evaporated and the residue was dissolved in CH3CN (3 mL). To this solution was added dropwise TIOH (112 µL, 1.266 mmol). Stirring was continued for 15 min, then the reaction mixture was concentrated in vacuo, and the resulting residue was treated with sat. KPF6aq. (10 mL). The mixture was extracted with CH2Cl2×6, and the combined organic layer was dried. The solvent was evaporated and the residue was dissolved in a small amount of CH2Cl2, and then precipitated with Et2O. The resulting precipitate was collected on a filter and washed with Et2O to give 12 (230.1307). The combined organic layer was dried. The solvent was evaporated and the residue was dissolved in CH3CN (3 mL). To this solution was added dropwise TIOH (150 µL, 1.695 mmol), and stirring was continued for 15 min. The reaction mixture was concentrated in vacuo, and the resulting residue was treated with sat. KPF6aq. (10 mL). The mixture was extracted with CH2Cl2×5, and the combined organic layer was dried. The solvent was evaporated and the residue was dissolved in a small amount of CH2Cl2, and then precipitated with Et2O. The resulting precipitate was collected on a filter and washed with Et2O to give 14 (275.9 mg, 0.632 mmol, 67%) as an off-white solid. White powder (CH2Cl2/Et2O); mp=153–155°C; 1H-NMR (CD3CN): δ: 2.36–2.62 (6H, m), 2.63–2.97 (6H, m), 5.98 (1H, apparent quint, J=5.8 Hz), 7.27–7.55 (10H, m); 13C-NMR (CD3CN): δ: 30.78 (2C), 36.86 (2C), 38.76 (2C), 104.46, 118.58 (2C), 126.07 (4C), 130.21 (4C), 130.57 (2C), 139.27 (2C); 19F-NMR (CD3CN): δ: −73.21 (d, JF-P=708 Hz); 31P-NMR (CD3CN): δ: −143.15 (sept, JP-P=708 Hz); LR-EI-MS m/z: 291 (M+); HR-EI-MS m/z: 291.1742 (Calcd for C15H18O2F6: 291.1743).

1,7-Diphenyl-10-oxa-bicyclo[5.2.1]decane-4-one (15) To a solution of 14 (275.9 mg, 0.632 mmol) in acetone (6 mL) was added 20% K2CO3 aq. (3 mL). The biphasic mixture was stirred for 15 h, and then concentrated in vacuo. The residue was extracted with CHCl3×4, and the combined organic extracts were dried. The solvent was evaporated and the residue was taken up in CH2Cl2 (6 mL). This solution was added to a stirred solution of Collins reagent, which had been prepared from CrO3 (385.5 mg, 3.855 mmol) and pyridine (6.02 mL, 7.705 mmol) in CH2Cl2 (12 mL). After 1 h, 3 mL NaOH (30 mL) was added, and the solution was extracted with CH2Cl2×3. The combined organic phase was washed with 2 mL HCl (30 mL) and brine (30 mL), and dried. The solvent was evaporated and the residue was chromatographed on silica gel (20% to 40% AcOEt/n-hexane as the eluent) to give 15 (212.1 mg, 0.415 mmol, 66%) as an off-white solid. Colorless needles (EtO/n-hexane); mp=66.5–67.5°C; 1H-NMR (CDCl3): δ: 1.88–2.27 (7H, m), 2.32–2.49 (4H, m), 2.67 (1H, ddd, J=3.6, 10.6, 13.8 Hz), 4.41–4.51 (1H, m), 7.15–7.38 (5H, m); 13C-NMR (CDCl3): δ: 29.14, 34.25, 35.02, 37.37, 37.59, 40.32, 77.25, 85.65, 124.73 (2C), 126.40, 127.88 (2C), 146.60, 210.49; LR-EI-MS m/z: 230 (M+); HR-EI-MS m/z: 230.1305 (Calcd for C15H18O2F6: 230.1307).

1,4,7-Triphenyl-10-oxa-bicyclo[5.2.1]decane-3-ene (17) To
a solution of 15 (96.0 mg, 0.313 mmol) in THF (1 mL) was added dropwise phenylmagnesium bromide (1.08 M solution in THF; 0.58 mL, 0.626 mmol) and the solution was stirred for 30 min. Additional phenylmagnesium bromide (1.08 M solution in THF; 0.29 mL, 0.313 mmol) was added dropwise. Stirring was continued for 2 h, then sat. NH₄Cl aq. (5 mL) was added, and the mixture was extracted with AcOEt × 3. The combined organic layer was dried. The solvent was evaporated and the residue was dissolved in CH₃CN (1 mL). To this solution was added dropwise TfOH (42 µL, 0.475 mmol), and stirring was continued for 15 min. The reaction mixture was concentrated in vacuo to dryness. The 1H-NMR spectrum of the crude product in CD₃CN indicated the presence of a bicyclic compound bearing three phenyl groups as the main component. The crude product was taken up in sat. NaHCO₃ aq. (10 mL), and the mixture was extracted with CH₂Cl₂ × 3. The combined organic layer was dried and then evaporated, and the residue was chromatographed on silica gel (10% to 30% benzene/n-hexane as the eluent) to give 17 (44.0 mg, 0.120 mmol, 38%) as a colorless oil. 1H-NMR (CDCl₃) δ: 2.03–2.22 (3H, m), 2.31–2.47 (2H, m), 2.61–2.84 (4H, m), 3.14 (1H, br t, J = 11 Hz), 6.15 (1H, dd, J = 7.3, 8.5 Hz), 7.13 (1H, tt, J = 1.4, 7.3 Hz), 7.19–7.29 (4H, m), 7.30–7.42 (6H, m), 7.51 (2H, br d, J = 7 Hz), 7.58 (2H, br d, J = 7 Hz); 13C-NMR (CDCl₃) δ: 26.78, 37.34, 39.29, 41.38, 43.68, 86.67, 89.73, 124.31, 124.42 (2C), 125.05 (2C), 125.95 (2C), 126.28, 126.88, 127.89 (2C), 128.04 (2C), 128.32, 128.36 (2C), 142.79, 143.66, 148.84, 151.59; LR-EI-MS m/z: 366 (M⁺); HR-EI-MS m/z: 366.1996 (Calcd for C₂₇H₂₆O: 366.1984).

2,4,6-Triphenyloxatriquinanium Trifluoromethanesulfonate (16) To a stirred solution of 17 (33.1 mg, 0.090 mmol) in CD₃CN (0.6 mL) was added dropwise TfOH (40 µL, 0.452 mmol). Stirring was continued for 15 min, then the reaction mixture was transferred into an NMR tube, and 1H- and 13C-NMR spectra were recorded. Both spectra indicated that compound 17 had been completely converted to oxatriquinane 16. 1H-NMR (CD₃CN) δ: 2.78–2.91 (6H, m), 2.92–3.05 (6H, m), 7.11 (6H, dt, J = 7.1, 1.8 Hz), 7.36 (6H, tt, J = 1.8, 7.1 Hz), 7.44 (3H, tt, J = 1.8, 7.1 Hz); 13C-NMR (CD₃CN) δ: 37.89 (6C), 120.45 (3C), 127.30 (6C), 130.36 (6C), 131.14 (3C), 137.74 (3C).

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