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Boron Trifluoride-Etherate Induced Rearrangement of Bicyclo[2.2.2]octenediones: An Efficient Synthesis of Bicyclo[3.2.1]octenediones

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Abstract—A facile transformation of bicyclo[2.2.2]octenediones to bicyclo[3.2.1]octenediones mediated by BF_3-etherate is described.

o-Benzoquinones constitute a unique class of conjugated 1,2 diones and their chemistry, especially cycloaddition, has attracted the attention of synthetic organic chemists.[1–10] Potentially they can function as carbodienes, heterodienes or dienophiles in Diels–Alder reactions. Our own investigations in this area have contributed to a deeper understanding of their reactivity towards electron rich cyclic and acyclic dienes and also aryl alkenes and aryl alkynes.[11–17] With electron rich dienes, *o*-benzoquinones react as heterodienes leading to the formation of novel benzodioxin derivatives whereas the reaction of pentafulvenes, phenylacetylenes and styrenes afforded bicyclo[2.2.2]octenediones by participation of the quinone as carbodiene. The HOMO–LUMO energy calculations show that all the above reactions may be defined as inverse electron demand Diels–Alder reactions.

Bicyclo[2.2.2]octenediones can potentially undergo a number of synthetically useful transformations. For example, photolytic extrusion of carbon monoxide from these compounds constitutes an efficient method for the synthesis of highly substituted benzene derivatives.[18] Recently we have observed a facile BF_3-etherate catalysed rearrangement of bicyclo[2.2.2]octenediones to bicyclo[3.2.1]octenediones.[19] Only an isolated example of such a rearrangement involving the cycloadduct of cyclooctyne and 3,5-di-*tert*-butyl-*o*-benzoquinone is known in the literature.[20]

It is worthy of note that the principal methods available for the construction of bicyclo[3.2.1]octene system consist of: (i) the reaction of alkenes with 3-alkoxy-4-alkylcyclohexa-2,5-diene-1-one-4-yl cation generated in situ by different methods[21,22] affording the bicyclo[3.2.1]octenyl cation which on dealkylation yields the bicyclic[3.2.1]octenedione,[23] (ii) carbonylating ring enlargement of cyclohexadienes under the influence of $Fe(CO)_5$[24,25] and (iii)

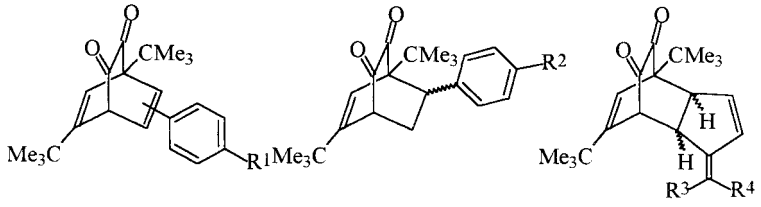

Figure 1.

Keywords: bicyclic aliphatic compounds; diones; rearrangements.
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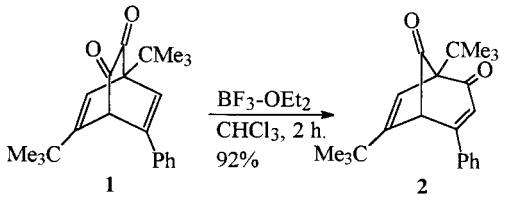


Scheme 1.

Lewis acid promoted reaction of (*E*) propenyl benzenes with 2-alkoxy-1,4-benzoquinones.[26,27]

In view of the efficiency and facility of the rearrangement of bicyclo[2.2.2]octenediones to bicyclo[3.2.1]octenediones,[19] we have carried out an extensive investigation of this rearrangement and the results are presented here.

Results and Discussion

The bicyclo[2.2.2]octenediones required for our studies (Fig. 1) were prepared by the Diels–Alder reactions of *o*-benzoquinones with phenylacetylenes, styrenes and fulvenes, respectively.

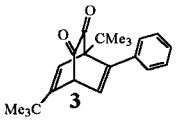
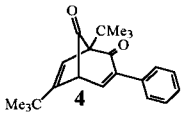
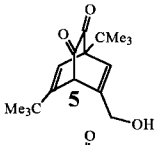
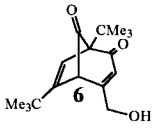
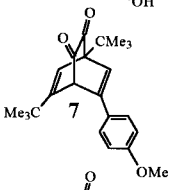
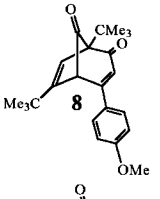
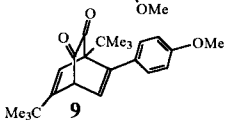
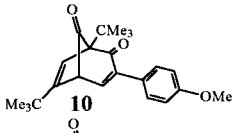
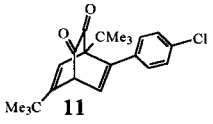
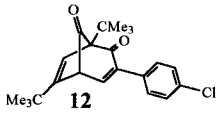
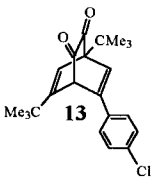
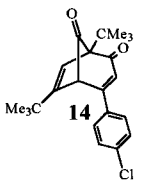
The bicyclo[2.2.2]octenedione **1**, readily obtained from phenylacetylene and 3,5-di-*tert*-butyl-*o*-benzoquinone, when refluxed with BF_3-etherate in chloroform afforded the bicyclo[3.2.1]octene-2,8-dione **2** in 92%yield (Scheme 1).

The structure of the product **2** and proposed mechanism was established by spectral analysis and ultimately by single crystal X-ray determination.[19]

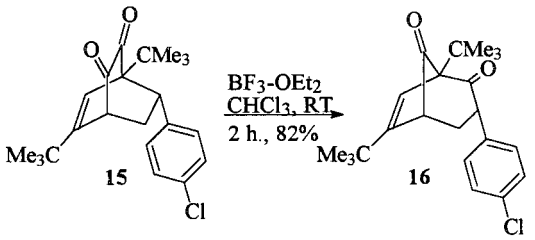
The reaction of other bicyclo[2.2.2]octenediones proceeded in a similar fashion yielding bicyclo[3.2.1]octenediones in good yields and these results are summarized in Table 1. The diones **3–9** were obtained by the cycloaddition of 3,5-di-*tert*-butyl-*o*-benzoquinone with corresponding phenylacetylenes.

Subsequently we investigated the BF_3–OEt_2 induced rearrangement of bicyclo[2.2.2]octenediones derived from the cycloaddition reaction of 3,5-di-*tert*-butyl-*o*-benzoquinone

Table 1. Rearrangement of bicyclo[2.2.2]oct-5,7-diene 2,3 dione

Entry	Bicyclo[2.2.2] octene dione	Condition[a]	Product	Yield[b] (%)
1		Reflux, 4 h.		89
2		RT, 4 h.		82
3		RT, 1 h.		100
4		RT, 1 h.		90
5		Reflux, 6 h.		92
6		Reflux, 6 h.		90

[a] All the reactions were carried out in chloroform.
[b] Isolated yield.



Scheme 2.

and styrenes.[28] A solution of 7-(4-chlorophenyl)-1,5-bis(1,1-dimethylethyl) bicyclo[2.2.2]octene-2,3-dione (*exo* **15**) in chloroform at room temperature in the presence of BF_3-etherate smoothly rearranged to afford 3-(4-chlorophenyl)-1,6-bis(1,1-dimethylethyl) bicyclo[3.2.1]oct-6-ene-2,8-dione (Scheme 2).

The structure of the product **16** was confirmed on the basis of spectral data. The IR spectrum of **16** showed two strong absorptions at 1769 and 1701 cm^{-1} indicating the presence of two carbonyls. In the ^1H NMR spectrum, the bridgehead protons resonated at δ 3.65 as a multiplet and the benzylic proton appeared at 3.17 as a doublet. In the ^{13}C NMR spectrum the two carbonyl carbons resonated at δ 210.37 and 200.38. Final proof for the structure was obtained by single crystal X-ray determination of **16** (Fig. 2).

Similar BF_3-etherate induced rearrangement occurred with a variety of 1,2-diones resulting from the Diels–Alder reactions of 3,5-di-*tert*-butyl-*o*-benzoquinone and styrenes and the results are summarized in Table 2.

The dione **27** readily obtained by the Diels–Alder reaction of 3,5-di-*tert*-butyl-*o*-benzoquinone and 6,6-diphenyl fulvene was selected for our further studies.[15] A solution of the dione **27** in chloroform on treatment with BF_3-etherate followed by heating under reflux afforded the product **28** in 69% yield (Scheme 3).

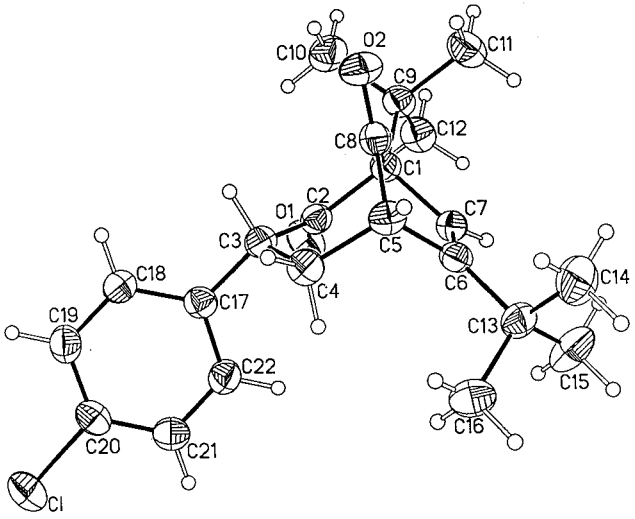
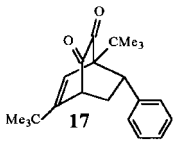
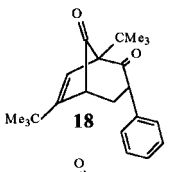
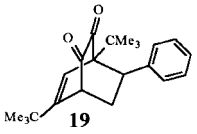
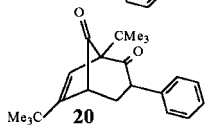
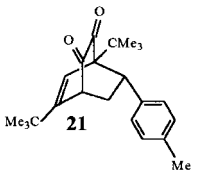
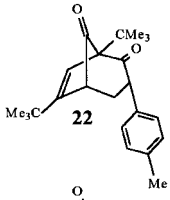
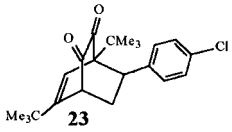
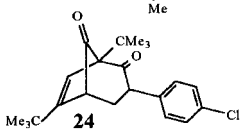
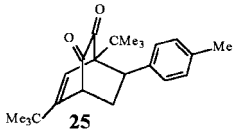
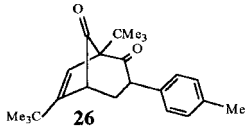


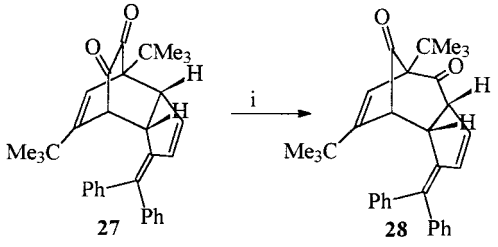
Figure 2. X-Ray crystal structure of **16**.

Table 2. Rearrangement of bicyclo[2.2.2]oct-5-ene 2,3-dione

Entry	Bicyclo[2.2.2] octene dione	Product[a]	Yield[b] (%)
1	 **17**	 **18**	80
2	 **19**	 **20**	95
3	 **21**	 **22**	100
4	 **23**	 **24**	90
5	 **25**	 **26**	95

[a] Reaction conditions: $CHCl_3$, RT, 2 h.
[b] Isolated yield.

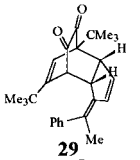
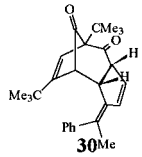
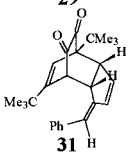
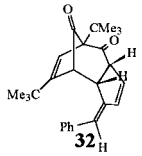
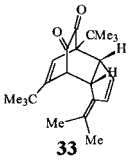
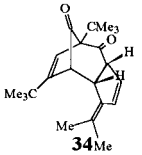
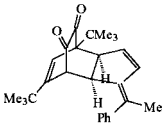
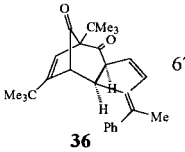
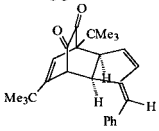
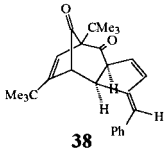
The structure of the product was ascertained from its spectral data. The IR spectrum of **28** exhibited two absorptions at 1699 and 1752 cm^{-1} due to the presence of two carbonyl groups. In the ^1H NMR spectrum the two olefinic protons on the fulvene moiety appeared at δ 5.83 and 6.49 as doublet of a doublet. The bridgehead proton and the proton α to the carbonyl group appeared together as a multiplet at δ 3.92. The molecular ion peak at *m/z* 450 is also in agreement with the assigned structure.



i, BF_3-OEt_2, $CHCl_3$, reflux, 20 h., 69%

Scheme 3.

Table 3. Rearrangement of the adduct of 3,5-di-*tert*-butyl-*o*-benzoquinone

Entry	Bicyclo[2.2.2] octene dione	Reaction condition[a]	Product	Yield[b] (%)
1	 **29**	4 h.	 **30**	70
2	 **31**	22 h.	 **32**	45
3	 **33**	18 h.	 **34**	32
4	 **35**	4 h.	 **36**	67
5	 **37**	6 h.	 **38**	43

[a] Chloroform reflux.
[b] Isolated yield.

In a similar fashion a number of other diones also underwent rearrangement when refluxed with BF_3-etherate in dry chloroform and these results are summarized in Table 3.

In conclusion, we have developed a facile method for the synthesis of bicyclo[3.2.1]octenediones by the BF_3-etherate induced rearrangement of bicyclo[2.2.2]octenediones.

Experimental

All reactions were carried out in oven-dried glassware (120°C) under an atmosphere of argon. Analytical thin layer chromatography was performed on silica gel TLC plates. Chloroform was dried over P_2O_5 prior to use. The various substituted styrenes were prepared from the corresponding aryl aldehydes by the Wittig reaction. Different substituted phenylacetylenes were prepared from the corresponding aromatic aldehydes. The fulvenes were obtained by the condensation of cyclopentadiene with the appropriate carbonyl compound in the presence of pyrrolidine. The quinones were prepared by the routine oxidation of the corresponding catechols. On completion of the reaction, the mixture was stirred with water (20 mL) and extracted with dichloromethane (4×15 mL). The extract was dried over anhydrous Na_2SO_4 and concentrated. The crude product was then purified by column chromatography on silica gel (100–200 mesh). Mixtures of ethyl acetate and hexane were used as eluents. Melting points are uncorrected. The IR spectra were recorded on a Perkin–Elmer model 882 infrared spectrometer and Nicolet impact 400 D infrared spectrometer using potassium bromide pellets. NMR spectra were recorded on Jeol EX-90 and Bruker-300 spectrometers using chloroform-d as the solvent. The chemical shifts are given in δ scale with tetramethylsilane as internal standard. Elemental analysis were done using Perkin–Elmer 2400 CHN analyzer. High-resolution mass spectra were obtained using Finnigan MAT model 8430. All of the adducts were purified by recrystallisation in dichloromethane/hexane solvent system.

1,6-bis(1,1-Dimethylethyl)-4-phenylbicyclo[3.2.1]oct-3,6-diene-2,8-dione (2). A solution of **1** (500 mg, 1.55 mmol) in dry chloroform (20 mL) was refluxed with BF_3-etherate (0.22 mL, 254 mg, 1.79 mmol) for 2 h. The usual work-up followed by chromatographic purification on a silica gel column using 1% ethyl acetate in hexane as eluent afforded the product **2** (458 mg, 92%) as a colorless crystalline solid; recrystallized from hexane. Mp 151–153°C. IR (KBr) 2959, 2871, 1769, 1662, 1359, 1212 cm^{-1}. ^1H NMR δ 7.55–7.43 (m, 5H), 6.24 (s, 1H), 5.92 (s, 1H), 4.29 (s, 1H), 1.26 (s, 9H), 0.97 (s, 9H). ^{13}C NMR δ 199.77, 191.60, 161.13, 157.76, 135.56, 129.45, 128.43, 125.45, 125.36, 121.69, 74.94, 57.34, 33.59, 31.98, 27.65, 25.89. EIMS *m/z* 322 (M^+, 8), 266 (100), 251 (33), 57 (12). HRMS calcd for $C_{22}H_{26}O_2$: 322.1932; Found 322.1927.

1,6-bis(1,1-Dimethylethyl)-3-phenylbicyclo[3.2.1]oct-3,6-diene-2,8-dione (4). A solution of **3** (500 mg, 1.55 mmol) in dry chloroform (20 mL) was refluxed with BF_3-etherate (0.22 mL, 254 mg, 1.79 mmol) for 4 h. The usual work-up followed by purification of the product by chromatography on a silica gel column using 1% ethyl acetate in hexane as eluent afforded **4** (445 mg, 89%) as a colorless crystalline solid; recrystallized from hexane. Mp 133–134°C. IR (KBr) 2952, 2871, 1763, 1675, 1366 cm^{-1}. ^1H NMR δ 7.42–7.22 (m, 6H), 5.87 (s, 1H). 3.85(d, J=7.7 Hz, 1H), 1.27 (s, 9H), 1.15 (s, 9H). ^{13}C NMR δ 199.62, 191.60, 162.83, 144.84, 139.83, 135.45, 128.70, 127.99, 127.90, 120.89, 75.57, 56.17, 33.74, 33.17, 28.01, 26.64. EIMS *m/z* 322 (M^+, 8), 307 (9), 266 (100), 251 (36), 57 (33). Anal. Calcd For $C_{22}H_{26}O_2$: C, 81.95; H, 8.13. Found: C, 81.76; H, 8.08.

1,6-bis(1,1-Dimethylethyl)-4-(hydroxymethyl)bicyclo-[3.2.1]oct-3,6-diene-2,8-dione (6). A solution of **5** (400 mg, 1.45 mmol) in dry chloroform (10 mL) was stirred at room temperature with BF_3-etherate (0.2 mL, 231 mg, 1.63 mmol) for 4 h. The usual work-up followed by chromatographic purification of the product on a silica gel column using 10% ethyl acetate in hexane as eluent afforded **6** (327 mg, 82%) as an amorphous solid. IR (KBr) 3468, 2970, 2884, 1779, 1675, 1475, 1369 cm^{-1}. ^1H NMR δ 6.10 (br s, 1H), 5.87 (br s, 1H), 4.51 (d, J=7.2 Hz, 2H), 4.32 (br s, 1H), 3.87 (br s, 1H), 1.21(s, 9H), 1.10 (s, 9H). ^{13}C NMR δ 192.73, 170.65, 162.77, 161.10, 151.56, 124.97, 124.35, 122.17, 56.56, 32.69, 28.28, 27.62, 26.49. EIMS *m/z* 276 (M^+, 12), 261 (72), 57 (100). HRMS calcd for $C_{17}H_{24}O_3$: 276.1725; Found 276.1712.

1,6-bis(1,1-Dimethylethyl)-4-(4-methoxyphenyl)bicyclo-[3.2.1]oct-3,6-diene-2,8-dione (8). A solution of **7** (352 mg,

1 mmol) in dry chloroform (20 mL) was stirred at room temperature with BF_3-etherate (0.15 mL, 170 mg, 1.2 mmol) for 1 h. The usual work-up followed by chromatographic purification of the product on silica gel column using 2% ethyl acetate in hexane as eluent afforded **8** quantitatively as a pale yellow solid. Mp 103–105°C. IR (KBr) 2967, 2878, 1773, 1666, 1367, 1232 cm^{-1}. ^1H NMR δ 7.53–6.93 (m, 4H), 6.19 (s, 1H), 5.91 (s, 1H), 4.25 (s, 1H), 3.85 (s, 3H), 1.23 (s, 9H), 0.98 (s, 9H). ^{13}C NMR δ 200.51, 192.14, 161.32, 157.62, 128.04, 127.67, 124.14, 122.73, 144.54, 113.96, 77.33, 57.49, 55.21, 24.32, 32.63, 28.40. Anal. Calcd For $C_{23}H_{28}O_3$: C,78.38; H, 8.01. Found: C, 78.12; H, 8.08. EIMS *m/z* 352 (M^+, 10), 296 (65), 281(60), 225 (42), 210 (17), 57 (100).

1,6-bis(1,1-Dimethylethyl)-3-(4-methoxyphenyl)bicyclo-[3.2.1]oct-3,6-diene-2,8-dione (10). A solution of **9** (352 mg, 1 mmol) in dry chloroform (20 mL) was stirred at room temperature with BF_3-etherate (0.15 mL, 170 mg, 1.2 mmol) for 1 h. The usual work-up followed by chromatographic purification of the product on silica gel column using 2% ethyl acetate in hexane as eluent afforded **10** (317 mg, 90%) as a pale green liquid. IR (KBr) 2962, 2872, 1770, 1674, 1364, 1178 cm^{-1}. ^1H NMR δ 7.33–6.83 (m, 5H), 5.83 (s, 1H), 3.78 (s, 4H), 1.12 (s, 18H). ^{13}C NMR δ 199.61, 191.80, 162.81, 159.58, 143.58, 139.41, 130.02, 127.92, 120.98, 113.48, 79.44, 56.21, 55.14, 33.85, 33.27, 28.16. Anal. Calcd For $C_{23}H_{28}O_3$: C, 78.38; H, 8.01. Found: C, 78.56; H, 8.14. EIMS *m/z* 352 (M^+, 9), 296 (32), 281(30), 225 (24), 210 (13), 57 (100).

1,6-bis(1,1-Dimethylethyl)-3-(4-chlorophenyl)bicyclo[3.2.1]-oct-3,6-diene-2,8-dione (12). A solution of **11** (356 mg, 1 mmol) in dry chloroform (20 mL) was refluxed with BF_3-etherate (0.15 mL, 170 mg, 1.2 mmol) for 6 h. The usual work-up followed by chromatographic purification of the product on silica gel column using 2% ethyl acetate in hexane as eluent afforded **12** (327 mg, 92%) as a colorless solid. Mp 181–183°C. IR (KBr) 2969, 2874, 1782, 1681, 1485, 1101 cm^{-1}. ^1H NMR δ 7.39 (d, J=7.6 Hz, 1H), 7.31–7.16 (m, 4H), 5.84 (s, 1H), 3.84 (d, J=7.6 Hz, 1H), 1.26 (s, 9H), 1.14 (s, 9H). ^{13}C NMR δ 199.04, 191.10, 162.76, 144.84, 138.87, 134.25, 133.79, 130.07, 128.18, 121.02, 79.60, 56.18, 33.83, 33.25, 28.11. Anal. Calcd For $C_{22}H_{25}O_2Cl$: C, 74.04; H, 7.06. Found: C, 73.70; H, 7.6. EIMS *m/z* 358 (M^++2, 18) 356 (M^+, 54), 341 (100), 313 (95), 293 (33), 149 (13), 125 (11). HRMS calcd for $C_{22}H_{25}O_2Cl$: 356.1543; Found 356.1532.

1,6-bis(1,1-Dimethylethyl)-4-(4-chlorophenyl)bicyclo-[3.2.1]oct-3,6-diene-2,8-dione (14). A solution of **13** (356 mg, 1 mmol) in dry chloroform (20 mL) was refluxed with BF_3-etherate (0.15 mL, 170 mg, 1.2 mmol) for 6 h. The usual work-up followed by chromatographic purification of the product on silica gel column using 2% ethyl acetate in hexane as eluent afforded **14** (320 mg, 90%) as a colorless solid. Mp 140–142°C. IR (KBr) 2962, 2874, 1775, 1667, 1600, 1411 cm^{-1}. ^1H NMR δ 7.44–7.41 (m, 2H), 6.17 (s, 1H), 5.89 (s, 1H), 4.17 (s, 1H), 1.23 (s, 9H), 0.96 (s, 9H). ^{13}C NMR δ 199.92, 191.74, 161.61, 156.97, 136.44, 134.85, 129.45, 127.27, 126.41, 122.50, 77.74, 57.87, 34.29, 32.71, 28.39. Anal. Calcd For $C_{22}H_{25}O_2Cl$: C, 74.04; H, 7.06. Found: C, 73.79; H, 7.53. EIMS *m/z* 358 (M^++2, 18) 356 (M^+, 56), 341 (100), 313 (98), 293 (32). HRMS calcd for $C_{22}H_{25}O_2Cl$: 356.1543; Found 356.1547.

1,6-bis(1,1-Dimethylethyl)-3-(4-chlorophenyl)bicyclo-[3.2.1]oct-6-ene-2,8-dione (*endo* 16). A solution of **15** (358 mg, 1 mmol) in dry chloroform (20 mL) was stirred at room temperature with BF_3-etherate (0.15 mL, 170 mg, 1.2 mmol) for 2 h. The usual work-up followed by chromatographic purification of the product on silica gel column using 2% ethyl acetate in hexane as eluent afforded **16** (294 mg, 82%) as a colorless solid. Mp 132–135°C. IR (KBr) 2969, 2881, 1769, 1701, 1472, 1243, 1081 cm^{-1}. ^1H NMR δ 7.32–6.96 (m, 4H), 5.88 (s, 1H), 3.65 (m, 1H), 3.17 (d, J=6.5 Hz, 1H), 2.70–2.61 (m, 1H), 2.02–1.94 (m, 1H), 1.14 (s, 18H). ^{13}C NMR δ 210.37, 200.38, 159.28, 138.19, 132.97, 130.15, 128.82, 121.19, 75.21, 55.85, 49.53, 35.60, 34.53, 33.07, 28.94, 26.58. EIMS *m/z* 360 (M^+, 9), 358 (41), 343 (10), 274 (20), 177 (26), 149 (100), 108 (52), 91 (30), 57 (64). Anal. Calcd for $C_{22}H_{27}O_2Cl$: C, 73.62; H, 7.58; Cl, 9.88. Found; C, 73.42; H, 7.35; Cl, 9.98.

Crystal data of 16. $C_{22}H_{27}O_2Cl$. F_w 358.89. Crystal size 0.40×0.40×0.38 mm. Orthorhombic. Space group *Pbca*. Unit cell dimensions a=14.2854(6) Å, α=90°; b=12.5511(6) Å, β=90°; c=21.9950(11) Å, γ=90°. Final R indices [$I>2\sigma$ (I)] R_1=0.0328, wR_2=0.0826. R indices (all data) R_1=0.0516, wR_2=0.0869. Volume Z=3943.6(3) $Å^3$, 8. D calcd=1.209 mg/m^3. F (000)=1536. Absorption coefficient=0.205 mm^{-1}. Reflections collected=41799. (Sheldrick, G. M., Siemens, Analytical X-ray Division, Madison, WI, 1995.)

1,6-bis(1,1-Dimethylethyl)-3-phenylbicyclo[3.2.1]oct-6-ene-2,8-dione (*endo* 18). A solution of **17** (324 mg, 1 mmol) in dry chloroform (20 mL) was stirred at room temperature with BF_3-etherate (0.15 mL, 170 mg, 1.2 mmol) for 2 h. The usual work-up followed by chromatographic purification of the product on silica gel column using 2% ethyl acetate in hexane as eluent afforded **18** (260 mg, 80%) as a colorless solid. Mp 147–149°C. IR (KBr) 2962, 2874, 1769, 1708, 1472, 1364, 1243 cm^{-1}. ^1H NMR δ 7.33–7.02 (m, 5H, Ar), 5.88 (s, 1H), 3.66 (m, 1H), 3.15 (d, J=6.9 Hz, 1H), 2.70–2.60 (m, 1H), 2.08–2.01 (m, 1H), 1.18 (s, 9H), 1.13 (s, 9H). ^{13}C NMR δ 210.77, 200.82, 159.08, 139.73, 128.66, 128.56, 127.07, 121.22, 75.21, 56.53, 49.66, 35.61, 34.50, 33.06, 28.94, 26.59. Anal. Calcd for $C_{22}H_{28}O_2$: C, 81.44; H, 8.70. Found; C, 80.92; H, 8.78. EIMS *m/z* 324 (M^+, 88), 309 (24), 281 (33), 266 (13), 240 (51), 149 (100), 108 (53), 91 (86), 57 (87).

1,6-bis(1,1-Dimethylethyl)-3-phenylbicyclo[3.2.1]oct-6-ene-2,8-dione (*exo* 20). A solution of **19** (324 mg, 1 mmol) in dry chloroform (20 mL) was stirred at room temperature with BF_3-etherate (0.15 mL, 170 mg, 1.2 mmol) for 2 h. The usual work-up followed by chromatographic purification of the product on silica gel column using 2% ethyl acetate in hexane as eluent afforded **20** (292 mg, 90%) as a colorless solid. Mp 157–159°C. IR (KBr) 2969, 2867, 1762, 1708, 1458, 1357, 1236, 1047 cm^{-1}. ^1H NMR δ 7.31–6.99 (m, 5H), 6.02 (s, 1H), 4.00 (dd, J=8.9, 11.9 Hz, 1H), 3.37 (m, 1H), 2.32 (m, 1H), 1.94 (m, 1H), 1.20 (s, 18H). ^{13}C NMR δ

208.47, 202.68, 154.00, 138.09, 129.38, 128.69, 127.39, 124.66, 78.50, 61.07, 53.08, 40.01, 35.00, 31.28, 29.34, 28.49. Anal. Calcd for $C_{22}H_{28}O_2$: C, 81.44; H, 8.70. Found; C, 81.44; H, 8.67. EIMS *m/z* 324 (M^+, 80), 309 (17), 281 (22), 240 (36), 177 (25), 149 (100), 136 (18), 108 (63), 91 (93), 57 (71).

1,6-bis(1,1-Dimethylethyl)-3-(4-methylphenyl)bicyclo-[3.2.1]oct-6-ene-2,8-dione (*endo* 22). A solution of **21** (338 mg, 1 mmol) in dry chloroform (20 mL) was stirred at room temperature with BF_3-etherate (0.15 mL, 170 mg, 1.2 mmol) for 2 h. The usual work-up followed by chromatographic purification of the product on silica gel column using 2% ethyl acetate in hexane as eluent afforded **22** quantitatively as a colorless solid. Mp 57–59°C. IR (KBr) 2962, 2874, 1769, 1715, 1472, 1371, 1256, 1088 cm^{-1}. ^1H NMR δ 7.12–6.88 (m, 4H), 5.86 (s, 1H), 3.60 (m, 1H), 3.13 (d, *J*=6.7 Hz, 1H), 2.66–2.56 (m, 1H), 2.30 (s, 3H), 2.04–1.97 (m, 1H), 1.17 (s, 9H), 1.13 (s, 9H). ^{13}C NMR δ 210.36, 200.55, 158.94, 136.75, 136.49, 129.29, 128.61, 121.25, 75.11, 56.15, 49.64, 35.63, 34.46, 33.03, 28.98, 26.63, 21.05. Anal. Calcd for $C_{23}H_{30}O_2$: C, 81.61; H, 8.93. Found; C, 81.52; H, 8.98. EIMS *m/z* 338 (M^+, 12), 337 (49), 309 (10), 294 (12), 253 (34), 177 (12), 149 (36), 118 (100), 91 (14).

1,6-bis(1,1-Dimethylethyl)-3-(4-chlorophenyl)bicyclo-[3.2.1]-oct-6-ene-2,8-dione (*exo* 24). A solution of **23** (358 mg, 1 mmol) in dry chloroform (20 mL) was stirred at room temperature with BF_3-etherate (0.15 mL, 170 mg, 1.2 mmol) for 2 h. The usual-work up followed by chromatographic purification of the product on silica gel column using 2% ethyl acetate in hexane as eluent afforded **24** (323 mg, 90%) as a colorless solid. Mp 167–169°C. IR (KBr) 2962, 2881, 1769, 1708, 1485, 1357, 1249, 1094 cm^{-1}. ^1H NMR δ 7.29–6.92 (m, 4H), 6.01 (s, 1H), 3.98 (dd, *J*=8.8, 11.8 Hz, 1H), 3.37–3.36 (m, 1H), 2.34–2.25 (m, 1H), 1.93–1.84 (m, 1H), 1.19 (s, 18H). ^{13}C NMR δ 207.62, 202.38, 153.88, 136.42, 133.18, 130.60, 128.72, 124.55, 79.99, 52.81, 50.75, 34.36, 32.94, 31.21, 28.40. Anal. Calcd for $C_{22}H_{27}O_2Cl$: C, 73.62; H, 7.58; Cl, 9.88. Found; C, 73.41; H, 7.59; Cl, 9.71. EIMS *m/z* 360 (M^++2, 9), 358 (M^+, 26), 274 (18), 177 (28), 149 (100), 108 (53), 91 (28), 57 (85).

1,6-bis(1,1-Dimethylethyl)-3-(4-methylphenyl)bicyclo-[3.2.1]oct-6-ene-2,8-dione (*exo* 26). A solution of **25** (338 mg, 1 mmol) in dry chloroform (20 mL) was stirred at room temperature with BF_3-etherate (0.15 mL, 170 mg, 1.2 mmol) for 2 h. The usual work-up followed by chromatographic purification of the product on silica gel column using 2% ethyl acetate in hexane as eluent afforded **26** (321 mg, 95%) as a colorless solid. Mp 114–116°C. IR (KBr) 2963, 2876, 1764, 1708, 1471, 1366, 1245, 1049 cm^{-1}. ^1H NMR δ 7.11–6.87 (m, 4H), 6.01 (s, 1H), 3.95 (dd, *J*=8.9, 11.7 Hz, 1H), 3.35 (m, 1H), 2.34–2.25 (m, 4H), 1.96–1.87 (m, 1H), 1.19 (s, 18H). ^{13}C NMR δ 207.90, 202.82, 153.69, 136.62, 134.79, 129.15, 129.01, 124.42, 79.82, 52.84, 50.84, 34.23, 32.80, 31.15, 28.32, 21.00. Anal. Calcd for $C_{23}H_{30}O_2$: C, 81.61; H, 8.93. Found; C, 81.57; H, 8.96. EIMS *m/z* 338 (M^+, 15), 337 (57), 294 (14), 253 (36), 149 (32), 118 (100), 91 (13), 57 (8).

1,2-bis(1,1-Dimethylethyl)-6-(1,1-diphenylmethylene)tricyclo[6.2.2.0^{3,7}]undec-4,9-diene-2,11-dione (28). A solution of dione **27** (300 mg, 0.67 mmol) in dry chloroform (15 mL) was refluxed with BF_3-etherate (0.1 mL, 115 mg, 0.81 mmol) for 20 h. Work-up followed by chromatographic purification of the product on silica gel column using 1% ethyl acetate in hexane as eluent to afford **28** (206 mg, 69%) as colorless crystals; recrystallized from hexane. Mp 218–220°C. IR (KBr) 2947, 2902, 1752, 1699, 1471, 1444, 1359 cm^{-1}. ^1H NMR δ 7.29 (m, 10H), 6.49 (dd, *J*=5.4, 2.7 Hz, 1H), 5.83 (dd, *J*=5.4, 2.7 Hz, 1H), 5.70 (s, 1H), 3.92 (m, 2H), 2.85 (d, *J*=1.7 Hz, 1H), 1.12 (s, 9H), 0.76 (s, 9H). ^{13}C NMR δ 199.83, 188.50, 158.24, 144.31, 142.64, 142.34, 137.00, 136.10, 129.96, 129.69, 128.97, 128.08, 127.39, 127.15, 121.66, 59.13, 53.70, 43.97, 34.28, 32.40, 28.43, 26.58. EIMS *m/z* 450 (M^+, 12), 230 (100), 57 (25). HRMS calcd for $C_{32}H_{34}O_2$: 450.2558; Found 450.2551. Anal. Calcd for $C_{32}H_{34}O_2$: C, 85.28; H, 7.61. Found; C, 85.60; H, 7.68.

1,9-bis(1,1-Dimethylethyl)-6-(1-methyl-phenylmethylene)-tricyclo[6.2.1.0^{3,7}]undec-4,9-diene-2,11-dione (30). A solution of **29** (200 mg, 0.51 mmol) in dry chloroform (15 mL) was refluxed with BF_3-etherate (0.08 mL, 92 mg, 0.65 mmol) for 4 h. The usual work-up followed by chromatographic purification on silica gel column using 1% ethyl acetate in hexane as eluent afforded **30** (140 mg, 70%) as colorless crystals; recrystallized from *n*-pentane. Mp 154–155°C. IR (KBr) 2970, 2878, 1761, 1707, 1488, 1450, 1363, 1294 cm^{-1}. ^1H NMR δ 7.38–7.15 (m, 5H), 6.18 (m, 2H), 5.80 (s, 1H), 3.76–3.52 (m, 3H), 2.24 (s, 3H), 1.18 (s, 9H), 1.05 (s, 9H). ^{13}C NMR δ 207.54, 197.49, 157.53, 143.57, 143.12, 138.24, 132.59, 128.53, 128.17, 127.62, 124.32, 59.54, 55.58, 54.92, 44.53, 33.17, 30.11, 26.56, 21.22. EIMS *m/z* 388 (M^+, 9), 168 (100), 153 (54), 57 (9). HRMS calcd for $C_{27}H_{32}O_2$: 388.2402; Found 388.2419.

1,9-bis(1,1-Dimethylethyl)-6-benzylidenetricyclo[6.2.1.0^{3,7}]-undec-4,9-diene-2,11-dione (32). BF_3-etherate (0.2 mL, 231 mg, 1.63 mmol) was added to a solution of **31** (500 mg, 1.34 mmol) in dry chloroform (15 mL) and refluxed for 20 h. Work-up followed by chromatographic purification of the product on silica gel column using 1% ethyl acetate in hexane as eluent to afford **32** (225 mg, 45%) as colorless crystals; recrystallized from *n*-pentane. Mp 118–119°C. IR (KBr) 2968, 2937, 1771, 1743, 1657, 1460, 1392, 1216 cm^{-1}. ^1H NMR δ 7.38–7.17 (m, 7H), 6.27 (s, 1H), 5.89 (s, 1H), 3.95–3.75 (m, 3H), 1.21 (s, 9H), 1.08 (s, 9H). ^{13}C NMR δ 197.59, 188.16, 161.58, 161.43, 143.53, 141.06, 138.01, 137.21, 128.70, 126.70, 122.92, 75.57, 54.92, 37.56, 34.54, 33.98, 32.99, 28.28, 26.73. EIMS *m/z* 374 (M^+, 10), 318 (15), 91 (100), 57 (66). Anal. Calcd For $C_{26}H_{30}O_2$: C, 83.38; H, 8.07. Found: C, 82.89; H, 8.25. HRMS calcd for $C_{26}H_{30}O_2$: 374.2245; Found 374.2227.

1,9-bis(1,1-Dimethylethyl)-6-(dimethylmethylene)tricyclo-[6.2.1.0^{3,7}]undec-4,9-diene-2,11-dione (34). To a solution of dione **33** (170 mg, 0.52 mmol) in dry chloroform (10 mL) was added BF_3-etherate (0.08 mL, 92 mg, 0.65 mmol) and refluxed for 18 h. The usual work-up followed by column chromatography on silica gel using 1% ethyl acetate in hexane as eluent afforded **34** (54 mg, 34%) as pale yellow crystals; recrystallized from hexane. Mp 186–187°C. IR

(KBr) 2972, 2879, 1770, 1665, 1465, 1392, 1365, 1220 cm^{-1}. ^1H NMR δ 6.42 (s, 1H), 5.90 (s, 1H), 4.11 (s, 1H), 3.14 (br s, 2H), 2.80 (t, J=6.7 Hz, 1H), 1.27 (s, 9H), 1.14 (s, 3H), 1.11 (s, 3H), 1.06 (s, 9H). ^{13}C NMR δ 198.07, 188.11, 161.76, 161.58, 151.35, 140.70, 132.34, 122.83, 54.93, 37.35, 34.04, 32.93, 28.16, 27.00, 26.70, 24.46, 20.82. EIMS *m/z* 326 (M^+, 40), 270 (100), 255 (90), 254 (70), 57 (36). HRMS calcd for $C_{22}H_{30}O_2$: 326.2245; Found 326.2233.

3Hα,7Hα-1,9-bis(1,1-Dimethylethyl)-6-(1-methyl-1-phenylmethylene)tricyclo[6.2.1.0^{3,7}]undec-4,9-diene-2,11-dione (36). A solution of **35** (200 mg, 0.51 mmol) in dry chloroform (15 mL) was refluxed with BF_3-etherate (0.08 mL, 92 mg, 0.65 mmol) for 4 h. The usual work-up and subsequent purification by chromatography on a silica gel column using 1% ethyl acetate in hexane as eluent afforded **36** (134 mg, 67%) as an amorphous solid. IR (KBr) 2967, 2878, 1765, 1707, 1367 cm^{-1}. ^1H NMR δ 7.45–7.10 (m, 5H), 6.64 (m, 1H), 5.83 (m, 1H), 5.65 (s, 1H), 3.79–3.52 (m, 3H), 2.21 (s, 3H), 1.17 (s, 9H), 1.03 (s, 9H). ^{13}C NMR δ 207.94, 200.12, 158.11, 144.02, 135.51, 134.22, 131.52, 129.53, 128.04, 127.12, 122.08, 59.14, 53.65, 43.82, 32.51, 28.33, 26.21. EIMS *m/z* 388 (M^+, 8), 168 (100), 153 (52), 57 (10). HRMS calcd for $C_{27}H_{32}O_2$: 388.2402; Found 388.2415.

3Hα,7Hα-1,9-bis(1,1-Dimethylethyl)-6-(benzylidine)tricyclo[6.2.1.0^{3,7}]undec-4,9-diene-2,11-dione (38). A solution of **37** (300 mg, 0.80 mmol) in dry chloroform (15 mL) was refluxed with BF_3-etherate (0.12 mL, 138 mg, 0.97 mmol) for 6 h. The usual work-up and subsequent purification by chromatography on a silica gel column using 1% ethyl acetate in hexane as eluent afforded **38** (130 mg, 43%) as colorless amorphous solid. IR (KBr) 2968, 2879, 1767, 1706, 1367 cm^{-1}. ^1H NMR δ 7.64–7.18 (m, 6H), 6.50–6.19 (m, 2H), 5.85 (s, 1H), 4.00–3.50 (m, 3H), 1.20 (s, 9H), 0.98 (s, 9H). ^{13}C NMR δ 210.02, 199.04, 157.12, 147.33, 147.05, 142.43, 138.91, 128.12, 127.80, 123.04, 59.90, 53.05, 43.11, 34.03, 37.51, 28.57, 24.82. EIMS *m/z* 374 (M^+, 10), 318 (15), 91 (100), 57 (66). Anal. Calcd For $C_{26}H_{30}O_2$: C,83.38; H, 8.07. Found: C, 82.88; H, 8.63. HRMS calcd for $C_{26}H_{30}O_2$: 374.2245; Found 374.2236.

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28. Nair, V.; Maliakal, D; Treesa, P. M.; Rath, N. P.; Eigendorf, G. K., *Synthesis* **2000**, in press. ^1H NMR ($CDCl_3$) of **15**: δ 7.12–7.27 (m, 4H), 6.15 (d, J=2 Hz, 1H), 3.68–3.65 (m, 1H), 3.50–3.30 (dd, J=10.0, 6.1 Hz, 1H), 2.88–2.60 (m, 1H), 1.95–1.70 (m, 1H), 1.21 (s, 18H).