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Claisen Rearrangement of 4-Allyloxytropones and Cerium(IV) Ammonium Nitrate-Oxidation of 4-Hydroxytropones

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Heating 4-allyloxytropones gave Claisen rearrangement products together with oxidation products such as C–C coupling dimers. The products were sensitive to oxygen. Some of the dimeric products were obtained from the cerium(IV) ammonium nitrate-oxidation of 4-hydroxytropones.

The Claisen rearrangement is a method to introduce alkyl substituents to troponoids. It is used in the syntheses of cycloheptafurans and cycloheptadifurans[1)] and in total syntheses of natural products, nootokatin[2)] and procerin.[3)] But a synthetic restriction was also pointed out: in Claisen rearrangements of 2-(2-alkenyloxy)tropones,[4)] an alternative elimination process occurs from the Claisen intermediate, in which the tropone carbonyl group abstracts an allylic hydrogen atom to generate tropolones. In this paper, we report the results of the Claisen rearrangements of 4-hydroxytropones as one of the series of our studies on thermal rearrangements of troponoids.[1,4,5)]

When a xylene solution of 4-allyloxytropone (**1**), prepared from 4-hydroxytropone (**2**)[6)] and allyl bromide in the presence of sodium hydride in *N*,*N*-dimethylformamide (DMF), was refluxed, four products (**3**—**6**) were obtained after purification by column chromatography and HPLC separation. Their structures were elucidated by the ^{1}H NMR spectroscopic analysis; the major product **3**, obtained in 43% yield, was a Claisen rearrangement product, 5-allyl-4-hydroxytropone[7)] since the ^{1}H NMR spectrum showed the presence of an allyl group and four proton signals of a tropone nucleus.

The second product **4** was the cyclized cyclohepta[*b*]pyran-7(2*H*)-one since it had two olefinic and four aromatic protons but no methyl group. The position of the double bond of the pyran ring was determined by the comparison with the chemical shifts [δ=4.85 (2H, dd, J=3.7, 1.8 Hz), 5.78 (1H, dt, J=9.9, 3.7 Hz), 6.25 (1H, dt, J=9.9, 1.8 Hz)] with those of cycloheptapyran **7** [δ=4.77 (2H, dd, J=4, 2 Hz), 5.95 (1H, dt, J=10, 4 Hz), 6.60 (1H, dt, J=10, 2 Hz)].[1d)]

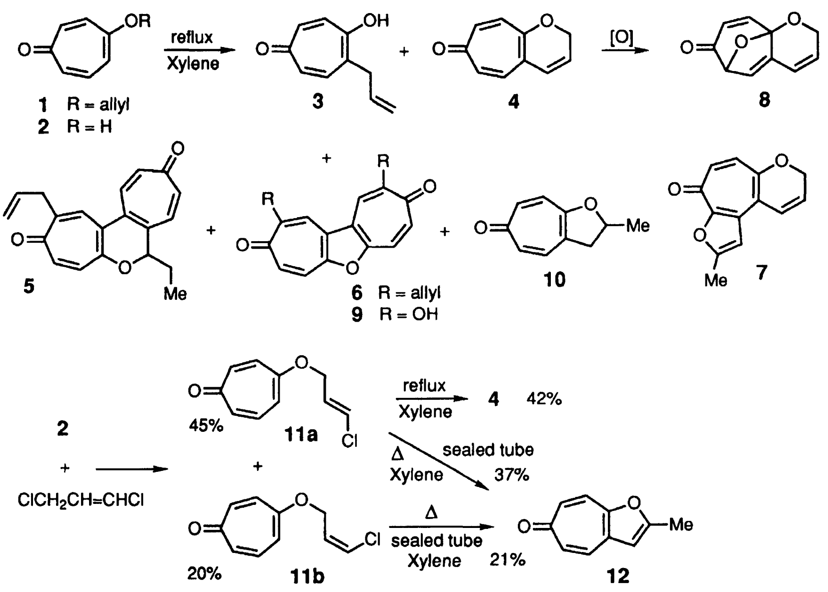
The molecular composition of **4** corresponds to a dehydro derivative of **3**. It was also noticed that **4** was susceptible to an autooxidation; even at room temperature **4** in a chloroform solution caused a change to compound **8**, which was too unstable to be isolated and gradually gave polymeric materials. This process, **4** to **8**, could be monitored by NMR spectroscopy. The ^{1}H NMR data of **8** indicated five olefinic proton signals and a methine and two methylene proton signals. The ^{13}C NMR spectrum showed six sp^2-carbons and a carbonyl signals as well as three signals of saturated carbons at δ=62.6, 87.5, and 102.4, which indicated the presence of an acetal carbon. The mass spectrum of **8** showed an incorporation of one oxygen atom to **4**. Therefore, the structure of **8** is 6,9a-dihydro-6,9a-epoxycyclohepta[*b*]pyran-7-one (Scheme 1).

The remaining two products (**5** and **6**) were dimeric condensates of **3**, as judged from the mass spectral analyses. The NMR spectrum of **6** showed an element of symmetry and the chemical shifts of the signals were quite similar to those of 2,10-dihydroxydicyclohepta[*b*,*d*]furan-3,9-dione (**9**), an oxidation product of 2,5-dihydroxytropone.[8)] The structure of **6** was thus assigned to be 2,10-diallyldicyclohepta[*b*,*d*]furan-3,9-dione. Because the other dimer **5** had seven proton signals of tropone nuclei as well as an ethyl and an allyl groups, its structure was determined to be 11-allyl-6-ethyldicyclohepta[*b*,*d*]pyran-3,10-dione.

While a xylene solution of **1** was heated at 140—145 °C for 6 h in a sealed tube, a small amount of a new product **10** was obtained together with **3** (72%) and **4** (1%). The NMR spectrum of **10** was consistent with that of 2-methyl-2,3-dihydro-6*H*-cyclohepta[*b*]furan-6-one showing a doublet methyl signal, three saturated proton signals, and four aromatic proton signals. The formation of **4** from **1** in an open vessel was facilitated by oxygen, whereas a thermal reaction of **3** afforded **10** by preventing an oxidation process, as summarized in Table 1.

Next, we observed a facile oxidation of the reaction products from **1**; this prompted us to investigate the Claisen rearrangement of 4-(3-chloro-2-propenyloxy)tropone (**11**), since it will give the products having the same oxidation state with **4**. Thus, (*E*)-4-(3-chloro-2-propenyloxy)tropone (**11a**), by refluxing in xylene, gave **4** in 42% yield. On the other hand, heating **11a** in a sealed tube resulted in a formation of a known 2-methyl-6*H*-cyclohepta[*b*]furan-6-one **12**[9)] in 37% yield. Similarly, heating a (*Z*)-isomer **11b** in a sealed tube afforded **12** in 21% yield.

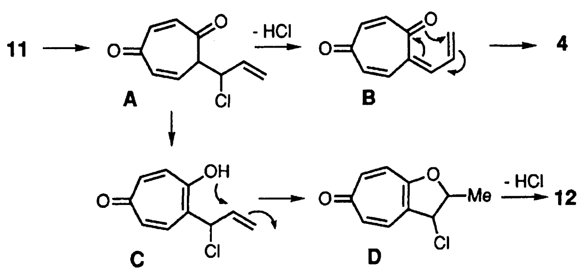
Under aerobic conditions, elimination of hydrogen chloride from an intermediate **A** of the Claisen rearrangement occurred to give **B**, which cyclized to **4** (Scheme 2). In a sealed tube, however, liberated hydrogen chloride would serve as a proton source to cause enolization of **A** to **C** and **D**. Then, elimination of hydrogen chloride from **D** would occur during work-up to



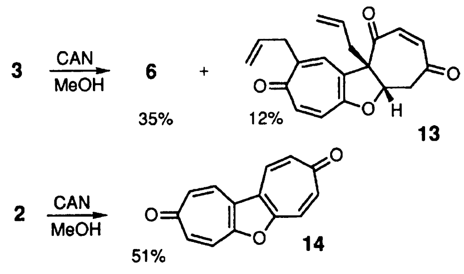
Scheme 1.

Table 1. Product Distributions (%) of the Thermal Reactions of **1** and **3**

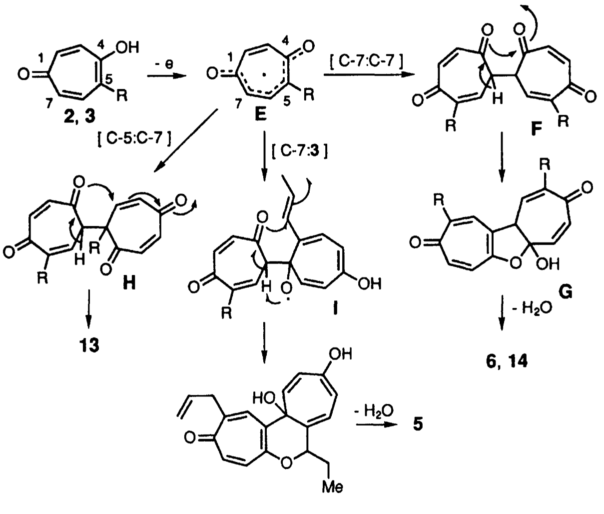
Starting material	Conditions	**3**	**4**	**5**	**6**	**10**	Recovery
1	Reflux, 4 h 140—145 °C	43	5	6	1	—	4
1	140—145 °C, 6 h sealed tube	55	2	—	—	—	32
1	140—145 °C, 8 h sealed tube	72	1	—	—	Trace	24
3	Reflux, 10 h 140—145 °C	25	21	—	16	13	—



Scheme 2.



Scheme 3.



Scheme 4.

give **12**. A facile dehydrogenation of **3** prompted us to carry out oxidation reactions of **3** or **2** with appropriate agents.

CAN-Oxidation of 4-Hydroxytropones. It is known that the CAN-oxidation of 5-hydroxy-2-methoxytropone gives C–C coupling products.[10] A methanol solution of **3** was treated by CAN to give **6** and a new product **13** in 35 and 12% yields, respectively (Scheme 3). The structure of **13** was determined by the NMR data, which showed two kind of allyl groups and an enedione chromophore. Similarly, the CAN-oxidation of **2** gave a parent dicyclohepta[*b*,*d*]furan-3,9-dione **14** in 51% yield.

Since CAN is known to be a one-electron oxidation agent, a radical intermediate **E** would be formed to give a symmetrical C–C coupling product **F**, which gave **6** and **14** via **G** (Scheme 4). When **E** coupled between C-5 and C-7, an intermediate **H** was formed. A subsequent ring closure gave **13**. **E** coupled with **3**, however, along with a migration of the double bond, to give **I**, which was followed by ring closure and dehydration to give **5**.

Conclusion 4-Hydroxytropone, once designated as γ-tropolone,[11] and its derivatives are quite different from tropolone and its derivatives as regards the chemical properties. It is much more reactive with radical species than tropolones so as to suffer attacks at C-1, C-5, and C-7 positions. Formation of dimeric condensates is all derived from an attack at these reactive carbons. Dicyclohepta[*b*,*d*]furan-3,9-dione (**14**) is a promising precursor of redox compounds and will be an independent research subject.

Experimental

Elemental analyses were performed by Mrs. Y. Hatozoe of this Institute, Kyushu University. The mps were measured with a Yanagimoto Micro mp apparatus and are not corrected. The NMR spectra were measured by JEOL FX 100 and GSX 270H spectrometers in $CDCl_3$, unless otherwise specified, and the chemical shifts expressed were in δ units. Mass spectra were measured with a JEOL 01SG-2 spectrometer. The IR spectra were taken as KBr disks for crystalline compounds or as liquid films inserted between NaCl plates for oily materials using a JASCO IR-A 102 spectrometer. The UV spectra were measured using Hitachi U-3200 and U-3410 spectrophotometers. The stationary phase for the column chromatography was Wakogel C-300 and the elution solvents were mixtures of hexane and ethyl acetate.

Reaction of 2 with Allyl Bromide. To a DMF solution (11 cm^3) of **2** (200 mg, 1.64 mmol) and 60%-NaH (209 mg, 5.2 mmol) was added allyl bromide (388 mg, 3.2 mmol) at 0 °C. The resultant mixture was heated at 60 °C for 6 h. Aqueous 2 M (1 M=1 mol dm^{-3}) HCl solution was then added carefully to the mixture and this new mixture was extracted with $CHCl_3$. The extract was dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was chromatographed on silica gel (AcOEt : hexane=3 : 1) to give **1** as a yellow oil (190 mg, 72%): ^{1}H NMR δ=4.48 (2H, d, *J*=5.1 Hz), 5.35 (1H, dd, *J*=10.6, 1.5 Hz), 5.43 (1H, dd, *J*=17.2, 2.2 Hz), 6.01 (1H, ddt, *J*=17.2, 10.6, 5.1 Hz), 6.24 (1H, d, *J*=9.9 Hz), 6.74 (1H, dd, *J*=12.1, 0.7 Hz), and 7.02—7.10 (3H, m). ^{13}C NMR δ=69.1, 109.5, 118.8, 131.5, 134.3 (2C), 136.5, 141.3, 163.2, and 186.9. IR (KBr) 1569, 1526, 1223, 1196, and 858 cm^{-1}. UV (MeOH) 224 nm (ε=19900), 252 (5000), 264 (700), and 325 (12800). MS *m/z* 163 (18, M^++1), 162 (49, M^+), 134 (57), 119 (48), 94 (100), 65 (84), and 51 (56). Found: *m/z* 162.0684 (M^+). Calcd for $C_{10}H_{10}O_2$: M, 162.0680.

Claisen Rearrangement of 1. 1) A xylene solution (10 cm^3) of **1** (145 mg, 0.9 mmol) was refluxed for 4 h. The mixture was cooled to room temperature to form precipitates, which were filtered off and washed with hexane to isolate **3** as yellow crystals (43%, mp 164—165 °C): ^{1}H NMR δ=3.37 (2H, d, *J*=6.6 Hz), 5.14 (1H, br d, *J*=11.0 Hz), 5.15 (1H, br d, *J*=17.2 Hz), 5.93 (1H, ddt, *J*=17.2, 11.0, 6.6 Hz), 6.57 (1H, dd, *J*=10.6, 2.6 Hz), 7.07 (1H, dd, *J*=12.8, 2.6 Hz), 7.16 (1H, d, *J*=12.8 Hz), and 7.18 (1H, d, *J*=10.6 Hz). ^{13}C NMR (CD_3OD) δ=39.4, 116.8, 137.0, and 140—142.[12] IR (KBr) 3074, 2886, 2684, 2562, 1451, 1414, 1264, and 1222 cm^{-1}. UV (MeOH) 213 nm (ε=21200), 227 (22300), 351 (13600), and 367 (14500). MS *m/z* 163 (9, M^++1), 162 (56, M^+), 147 (100), 91 (48), and 77 (53). Found: C, 73.85; H, 6.28%. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21%.

The filtrate was chromatographed on silica gel to give **4**, **5**, and **6**. **4**[13] (a yellow oil, 5%): ^{1}H NMR δ=4.85 (2H, dd, *J*=3.7, 1.8 Hz), 5.78 (1H, dt, *J*=9.9, 3.7 Hz), 6.25 (1H, dt, *J*=9.9, 1.8 Hz), 6.76 (1H, dm, *J*=12.5 Hz), 6.86 (1H, d, *J*=12.5 Hz), and 6.94 (2H, s). ^{13}C NMR δ=65.5, 121.3, 122.0, 126.5, 133.3, 134.7, 137.9, 140.6, 158.5, and 186.0. IR (KBr) 1614, 1555, 1500, and 1401 cm^{-1}. UV (MeOH) 236 nm (ε=13300), 252 (10000), and 354 (6800). MS *m/z* 161 (2, M^++1), 160 (19, M^+), 132 (7), 131 (16), 32 (19), and 28 (100).

5 (a yellow oil, 6%): ^{1}H NMR δ=0.85 (3H, t, *J*=7.4 Hz), 1.73 (2H, qd, *J*=7.4, 5.9 Hz), 3.40 (2H, br d, *J*=6.7 Hz), 3.49 (1H, t, *J*=5.9 Hz), 5.13—5.20 (2H, m), 5.94 (1H, ddt, *J*=17.6, 9.9, 6.7 Hz), 6.92 (2H, d, *J*=1.6 Hz), 7.01 (1H, dm, *J*=12.8 Hz), 7.01 (1H, br s), 7.03 (1H, d, *J*=13.2 Hz), 7.12 (1H, d, *J*=13.2 Hz), and 7.14 (1H, d, *J*=12.8 Hz). ^{13}C NMR δ=9.5, 31.2, 38.9, 46.8, 117.7, 122.9, 123.9, 130.6, 132.0, 135.1, 136.7, 136.9, 138.1, 138.4, 139.9, 149.3, 152.2, 153.8, 184.5, and 185.9. IR (KBr) 2964, 2924, 1633, 1573, 1517, 1415, and 1203 cm^{-1}. UV (MeOH) 237 nm (ε=27400), 283 (5200), and 329 (16100). MS *m/z* 307 (6, M^++1), 306 (27, M^+), 278 (22), 277 (100), 249 (22), and 221 (56). Found: *m/z* 306.1268 (M^+). Calcd for $C_{20}H_{18}O_3$: M, 306.1255.

6 (yellow needles, 1%, mp 162.0—163.0 °C): ^{1}H NMR δ=3.52 (4H, dd, *J*=7.0, 1.1 Hz), 5.22—5.28 (4H, m), 6.04 (2H, ddt, *J*=16.5, 9.9, 7.0 Hz), 7.12 (2H, d, *J*=12.5 Hz), 7.58 (2H, d, *J*=12.5 Hz), and 7.73 (2H, s). ^{13}C NMR δ=39.0 (2C), 117.9 (2C), 124.6 (2C), 125.1 (2C), 125.7 (2C), 135.2 (2C), 136.8 (2C), 148.3 (2C), 154.1 (2C), and 185.6 (2C). IR (KBr) 1575 and 1554 cm^{-1}. UV (MeOH) 239 nm (ε=17000), 256 (24800), 282 (20600), 293 (21500), 308 (15000), 327 (13500), 355 (21100), 368 (32300), and 386 (35400). MS *m/z* 305 (23, M^++1), 304 (100, M^+), 289 (80), and 261 (52). Found: C, 79.24; H, 5.20%. Calcd for $C_{20}H_{16}O_3$: C, 78.93; H, 5.30%.

2) A xylene solution (3 cm^3) of **1** (36 mg, 0.22 mmol) was heated at 140—145 °C for 8 h in a sealed tube. The mixture was cooled to room temperature to form precipitates, which were filtered off and washed with hexane to isolate **3** [72%], **4** [1%], and a small amount of **10** as yellow crystals (mp 46.5—47.5 °C): ^{1}H NMR δ=1.47 (3H, d, *J*=6.2 Hz), 2.86 (1H, dd, *J*=16.5, 8.4 Hz), 3.38 (1H, dd, *J*=16.5, 9.9 Hz), 4.94 (1H, ddq, *J*=9.9, 8.4, 6.2 Hz), 6.77 (1H, dd, *J*=12.1, 2.6 Hz), and 6.97—7.10 (3H, m). ^{13}C NMR δ=21.7, 40.4, 78.9, 124.4, 127.1, 134.4, 134.7, 142.4, 162.0, and 186.2. IR (KBr) 1556, 1520, and 1214 cm^{-1}. UV (MeOH) 215 nm (ε=11900), 234 (11600), 269 (4800), and 349 (11200). MS *m/z* 163 (7, M^++1), 162 (52, M^+), 134 (100), 133 (63), 119 (74), and 91 (98). FAB-MS Found: *m/z* 163.0754 (M+H^+), 162.0680 (M^+). Calcd for $C_{10}H_{11}O_2$: M+H, 163.0758 and for $C_{10}H_{10}O_2$: M, 162.0680.

Autoxidation of 4 to 8. When **4** was kept in $CDCl_3$ solution at room temperature, it changed to a yellow oil of **8**,[13] ^{1}H NMR δ=4.37 (1H, ddd, *J*=16.1, 4.4, 0.7 Hz), 4.46 (1H, ddd, *J*=16.1, 2.6, 2.0 Hz), 5.06 (1H, dd, *J*=7.3, 2.0 Hz), 5.98 (1H, dd, *J*=11.4, 2.0 Hz), 6.18 (1H, d, *J*=7.3 Hz), 6.27 (1H, ddd, *J*=10.3, 4.4, 2.6 Hz), 6.43 (1H, dt, *J*=10.3, 1.1 Hz), and 6.95 (1H, d, *J*=11.4 Hz). ^{13}C NMR δ=62.6, 87.5, 102.4, 116.1, 122.2, 127.6, 130.0, 140.7, 148.7, and 193.7. IR (KBr) 1691 cm^{-1}. MS *m/z* 176 (1, M^+), 160 (86), 132 (41), and 131 (100).

Thermal Reaction of 3. A xylene solution (10 cm^3) of **3** (21 mg, 0.13 mmol) was heated at 140—145 °C for 10 h under nitrogen stream. After evaporating the solvent, the residue was chromatographed on silica gel to give **6** (3 mg, 16%), **4** (4.5 mg, 21%), **10** (3 mg, 13%), and recovered **3** (5 mg, 25%).

Reaction of 2 with 1,3-Dichloropropene. To an HMPA solution (12 cm^3) of **2** (150 mg, 1.23 mmol) and 60%-NaH (88 mg, 2.2 mmol) was added 1,3-dichloropropene (a 1 : 2.24-mixture of *cis*- and *trans*-isomers, 267 mg, 2.4 mmol) at room temperature. The mixture was heated at 60 °C for 6 h. Water and 2 M HCl solution were added slowly to stop the reaction and the mixture was extracted with AcOEt. The organic layer was washed with saturated NaCl solution and was dried over Na$_2$SO$_4$. The solvent was removed in vacuum and the residue was chromatographed on silica gel to give yellow crystals of **11a** (109.3 mg, 45%, mp 69.0—70.5 °C): ^{1}H NMR δ=4.47 (2H, dd, J=6.2, 1.5 Hz), 6.14 (1H, dt, J=13.2, 6.2 Hz), 6.21 (1H, dm, J=9.5 Hz), 6.42 (1H, dt, J=13.2, 1.5 Hz), 6.76 (1H, dd, J=12.5, 2.0 Hz), 6.95—7.05 (2H, m), and 7.06 (1H, dd, J=12.5, 9.5 Hz). ^{13}C NMR δ=66.4, 109.3, 123.5, 126.8, 134.0, 134.7, 136.2, 141.4, 162.7, and 186.8. IR (KBr) 1563, 1527, 1375, 1196, and 809 cm^{-1}. UV (MeOH) 223 nm (ε=23700), 254 (5900, sh), and 323 (14200). MS m/z 198 (3, M$^+$ for ^{37}Cl), 197 (1), 196 (10, M$^+$ for ^{35}Cl), 75 (100), and 65 (27). Found: C, 60.93; H, 4.67%. Calcd for $C_{10}H_9O_2Cl$: C, 61.08; H, 4.61%.

A yellow oil of **11b** (48.6 mg, 20%): ^{1}H NMR δ=4.71 (2H, dd, J=5.9, 1.8 Hz), 6.04 (1H, dt, J=7.3, 5.9 Hz), 6.24 (1H, dm, J=9.5 Hz), 6.32 (1H, dt, J=7.3, 1.8 Hz), 6.77 (1H, dd, J=12.1, 1.8 Hz), 6.95—7.06 (2H, m), and 7.08 (1H, dd, J=12.1, 9.5 Hz). ^{13}C NMR δ=64.0, 109.4, 122.1, 126.0, 134.1, 134.5, 136.3, 141.3, 162.8, and 186.9. IR (NaCl) 1571, 1526, 1222, 1194, and 858 cm^{-1}. UV (MeOH) 224 nm (ε=19900), 247 (6700), 265 (700), and 324 (12200). MS m/z 198 (4, M$^+$ for ^{37}Cl), 197 (2), 196 (14, M$^+$ for ^{35}Cl), 77 (42), and 75 (100). Found: C, 61.32; H, 4.79%. Calcd for $C_{10}H_9O_2Cl$: C, 61.08; H, 4.61%.

Claisen Rearrangement of 11a. a) A xylene solution (12 cm^3) of **11a** (66.5 mg, 0.33 mmol) was refluxed at 140—145 °C for 12 h. After the removal of the solvent, the residue was chromatographed on silica gel to give **4** (23 mg, 42%).

b) A xylene solution (6 cm^3) of **11a** (64.4 mg, 0.34 mmol) was heated in a sealed tube at 140—145 °C for 10 h. After the removal of the solvent, the residue was chromatographed on silica gel to give **12** (19.6 mg, 37%).

Claisen Rearrangement of 11b. A xylene solution (6 cm^3) of **11b** (14.8 mg, 0.075 mmol) was heated in a sealed tube at 140—145 °C for 10 h. After the removal of the solvent, the residue was chromatographed on silica gel to give **12** (2.6 mg, 21%).

CAN-Oxidation of 3. To a MeOH solution (2 cm^3) of **3** (44 mg, 0.27 mmol) was added CAN (154 mg, 0.28 mmol) at 0 °C and this mixture was stirred at room temperature for 30 min. The stirred mixture was diluted with water (50 cm^3) and extracted with CHCl$_3$. The organic layer was dried over Na$_2$SO$_4$ and the solvent was removed in vacuum to obtain the residue, which was chromatographed to give **6** (35%) and a yellow oil of **13** (12%): ^{1}H NMR δ=2.80 (2H, dd, J=13.9, 7.3 Hz), 2.93 (1H, dd, J=15.8, 1.1 Hz), 3.29—3.39 (3H, m), 5.00 (1H, dd, J=7.3, 1.1 Hz), 5.06—5.24 (4H, m), 5.65 (1H, ddt, J=16.5, 10.6, 6.6 Hz), 5.87 (1H, ddt, J=16.5, 10.6, 6.6 Hz), 6.36 (1H, dd, J=12.5, 1.1 Hz), 6.69 (1H, d, J=12.5 Hz), 6.76 (1H, br s), 6.96 (1H, d, J=12.5 Hz), and 7.10 (1H, d, J=12.5 Hz). ^{13}C NMR δ=38.6, 38.9, 44.8, 67.9, 81.5, 117.5, 121.3, 123.2, 125.1, 129.6, 131.2, 135.1 (2C), 140.9, 142.5, 147.4, 162.1, 184.4, 194.6, and 197.2. IR (KBr) 1695, 1682, 1623, 1567, 1556, 1538, 1505, 1404, and 1227 cm^{-1}. UV (MeOH) 227 nm (ε=19800), 345 (10000), 351 (10000), and 376 (4900, sh). Found: m/z 322.1208 (M$^+$). Calcd for $C_{20}H_{18}O_4$: M, 322.1204.

CAN-Oxidation of 2. To a MeOH solution (5 cm^3) of **2** (40 mg, 0.33 mmol) was added CAN (180 mg, 0.33 mmol) at 0 °C and this mixture was stirred at room temperature for 30 min. The stirred mixture was diluted with water (50 cm^3) and extracted with CHCl$_3$. The organic layer was dried over Na$_2$SO$_4$ and the solvent was removed in vacuo to obtain the residue, which was chromatographed to give the crude product. Sublimation of the crude product gave crystals of **14** (mp>300 °C): ^{1}H NMR δ=7.08 (2H, dd, J=12.5, 4.0 Hz), 7.10 (2H, dd, J=12.5, 4.0 Hz), 7.60 (2H, d, J=12.5 Hz), and 7.61 (2H, d, J=12.5 Hz). ^{13}C NMR δ=125.6, 125.9, 126.8, 137.9, 138.1, 155.0, and 186.8. IR (KBr) 1629, 1571, 1547, 1212, and 862 cm^{-1}. UV (MeOH) 203 nm (ε=12200), 227 (14800), 235 (17400), 244 (18900), 251 (20600), 275 (18100), 286 (17100), 306 (9900), 325 (10800), 349 (18300), 366 (28800), and 384 (28300). FAB-MS Found: m/z 225.0542 (M+H$^+$), 224.0473 (M$^+$). Calcd for $C_{14}H_9O_3$: M+H, 225.0551 and for $C_{14}H_8O_3$: M, 224.0473. Found: C, 74.77; H, 3.83%. Calcd for $C_{14}H_8O_3$: C, 75.00; H, 3.60%.

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