Synthesis of 3-Arylmethyl-*p*-tropoquinones from 5-Alkoxy-2-(arylmethoxy)-tropones via Homolytic Rearrangement and Oxidation

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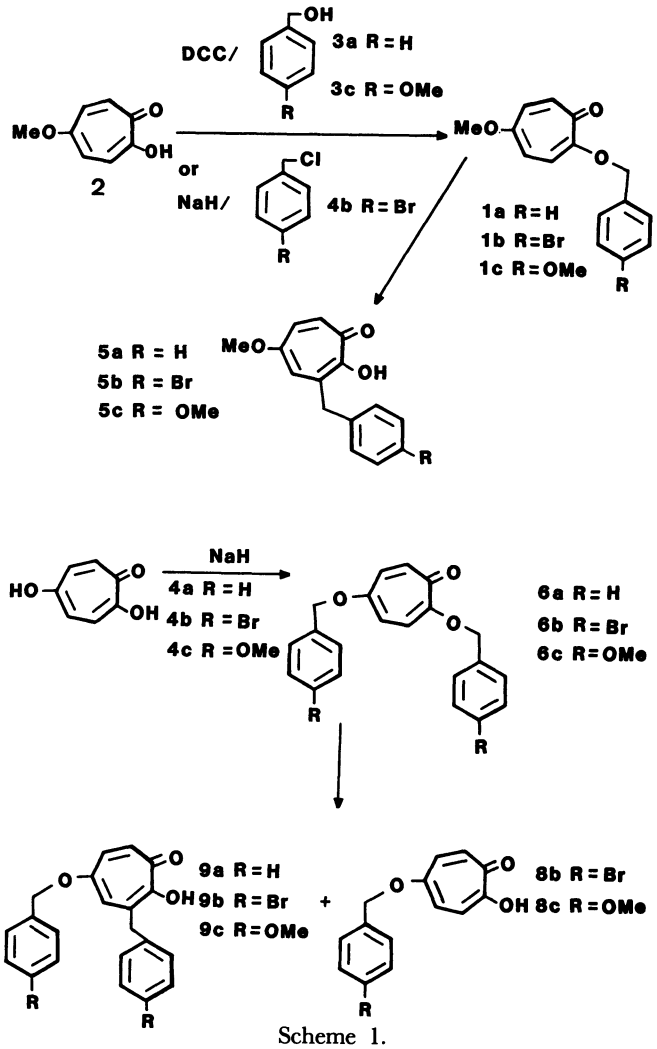
(Received November 11, 1985)

The 3-(arylmethyl)-*p*-tropoquinones were synthesized by starting from the homolytic thermal rearrangement of 2-(arylmethoxy)-5-methoxytropones or 2,5-bis(arylmethoxy)tropones, followed by hydrolysis and oxidation. The half-wave potentials of these tropoquinones were determined by cyclic voltammetry. A remote substituent effect was observed for 3-(4-hydroxybenzyl)-*p*-tropoquinone, which may be attributable to intermolecular hydrogen bonding.

Recently, we have synthesized several halo-, alkyl-, and alkenyl-substituted *p*-tropoquinones,[1] and have measured their reduction potentials by cyclic voltammetry (CV)[2] to show the typical quinone character of *p*-tropoquinones; indeed, tropoquinones revealed stronger oxidizing ability than the benzoquinone derivatives carrying similar substituents.[3] However, an additional oxidation wave appeared around zero V together with two pairs of reduction-oxidation waves. The appearance of these new waves was more or less common to *p*-tropoquinones, and relatively intense waves were observed in 3-substituted derivatives. We have now synthesized another group of derivatives, 3-(arylmethyl)-*p*-tropoquinones, by application of the recently-found homolytic rearrangement of 2-(arylmethoxy)tropones to 3-(arylmethyl)tropolones.[4] The CV measurement of these 3-(arylmethyl)tropoquinones disclosed intense waves in that region. The findings will be described herein.

Synthesis of 3-(Arylmethyl)-*p*-tropoquinones. 2-(Arylmethoxy)-5-methoxytropones (**1**) were prepared in good yields from 5-methoxytropolone (**2**) and appropriate arylmethanols (**3**) by the dicyclohexylcarbodiimide (DCC)-condensation[5] or by condensation of **2** and arylmethyl chloride (**4**) in the presence of sodium hydride in hexamethylphosphoric triamide (HMPA).[4] Thermolysis of **1** proceeded in a manner similar to that of 2-(arylmethoxy)tropones,[4] or in even better yields; the only by-product identified was the debenzylated tropolone, **2**. The structures of the products (**5**) were obviously 3-(arylmethyl)-5-methoxytropolones from the known reaction mechanism, and characterized by their ^{1}H- and ^{13}C NMR spectra. Particularly, there is a distinct long-range coupling between the protons on the C-4 and C-6 of each product and a regular change of the ^{13}C chemical shift from the parent **2** in the vicinity of the substituents.

In view of the specificity of the homolytic rearrangement for 2-benzyloxy group, 2,5-bis(arylmethoxy)-tropone (**6**) prepared directly from 5-hydroxytropolone (**7**), could also be used for the present purpose. However, for the preparation of the 3-(4-methoxybenzyl) derivative, **1c** was better than 2,5-bis(4-methoxybenzyloxy)tropone (**6c**), from which, the major product was the debenzylated 5-(4-methoxybenzyloxy)-tropolone (**8c**); the desired 3-(4-methoxybenzyl)-5-(4-methoxybenzyloxy)tropolone (**9c**) was obtained only in a 10% yield. The yield of rearrangement products from the other two pairs of reactants (**1a** vs. **6a** and **1b** vs. **6b**) were not significantly different. Subsequently, the hydrolysis of **5** or **9** with hydrobromic acid in acetic acid afforded the desired 3-(arylmethyl)-5-hydroxytropolone (**10**) in good yields. In the case of **5c**, the methoxyl group on the benzene ring was



Scheme 1.

Table 1. Half-Wave Potentials of **11**[a] and Reference *p*-Tropoquinones

	E_1	E_2	$\Sigma(E_1+E_2)$	$\Delta(E_1-E_2)$
11a	−0.26	−1.04	−1.30	+0.78
11b	−0.24	−0.80	−1.04	+0.56
11d	−0.19	−0.72	−0.91	+0.53
12	−0.21	−1.10	−1.31	+0.89
13	−0.28	−1.15	−1.43	+0.87

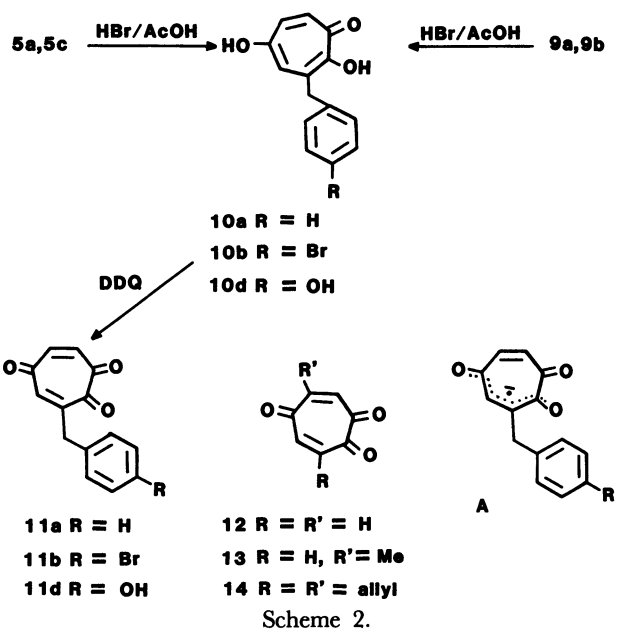
a) CV measurements were carried out at the concentrations of 1.09×10^{-3} mmol cm^{-3} for **11a**, 1.03×10^{-3} mmol cm^{-3} for **11b**, and 8.18×10^{-4} mmol cm^{-3} for **11d**.

simultaneously demethylated to form 5-hydroxy-3-(4-hydroxybenzyl)tropolone (**10d**). By the DDQ (2,3-dichloro-5,6-dicyano-*p*-benzoquinone)-oxidation, **10** yielded corresponding quinones (**11**).

Measurement of the Cyclic Voltammetry. The half-wave potentials were determined by the CV and are summarized in Table 1 together with those of *p*-tropoquinone (**12**) and 4-methyl-*p*-tropoquinone (**13**).[2] The values were corrected with an internal standard for the redox potential of ferrocenium/ferrocene couple, +0.465 V vs. Ag/AgCl. Similar to other 3-substituted tropoquinones,[2] the CV of all **11** disclosed oxidation waves around +0.11 to +0.135 V. The intensities of these waves, which indicated an electrochemical formation of a different species, were as large as that of 3,6-diallyl-*p*-tropoquinone (**14**)[1b] and were even comparable to their first oxidation waves. The responsibility of the anion radical species (**A**) for these waves was verified by scanning between +0.3 to −0.5 V for CV of **11d**. It is likely that the species responsible for the waves are coupling products derived from **A**. As previously reported, treatment of 5-hydroxy-2-methoxytropones or 5-hydroxytropolones with a one-electron oxidation agent, such as cerium(IV) ammonium nitrate or silver acetate, led to a facile formation of several dimerization products.[2,6,7] For elucidation of the structures of the coupling products, preparative electrolytic study is being undertaken.

As in the benzoquinones,[8] a hydroxyl group of **11d** at a remote position caused an enhancement of the reduction potential. Although the mesomeric electron transmission through the benzene ring was blocked by the methylene group as has been indicated by the similar first reduction potentials of **11a**, **11b**, and **13**,[1b] the potential of **11d** exceeded the value not only of **11a** but also of unsubstituted **12**. Since intramolecular hydrogen bonding was sterically prohibited, this enhancement of the reduction potential may be attributed to intermolecular hydrogen bonding[8] to increase the electron affinity of the quinonoid carbonyl groups.

In conclusion, since the *p*-tropoquinones are stronger oxidizing agents than benzoquinones, it is interesting to prepare *p*-tropoquinone derivatives having stronger oxidizing ability than DDQ. In this respect, the present observations on the substituent effects suggested an approach. Furthermore, this easy method for the synthesis of benzyl-*p*-tropoquinones should be applicable to preparation of the polymer-supported tropoquinones, which is our current interest.



Scheme 2.

Experimental

All the mps, measured with a Yanagimoto Micro-mp apparatus, are uncorrected. Elemental analyses were performed by Miss S. Hirashima of the Research Institute of Industrial Science, Kyushu University. The CV were measured by Yanaco Polarographic Analyzer Model P-1100 apparatus in a standard three-electrode cell with a standard Ag/AgCl reference electrode in anhydrous *N*,*N*-dimethylformamide (DMF) solutions in the presence of 0.1 M† Bu_4NBF_4 under N_2. The scan rate was 100 mV/s at 22—23 °C. The NMR spectra were measured by means of a JEOL FX 100 Spectrometer in $CDCl_3$ solutions unless otherwise specified, and the chemical shifts were expressed in δ units from the internal Me_4Si. The mass spectra were measured by means of a JEOL OISG-2 Spectrometer.

2-Benzyloxy-5-methoxytropone (1a). A mixture of **3a** (0.3 cm^3) and DCC (663 mg) was kept at 60 °C for 14 h with CuCl (5 mg). Then, a benzene solution (0.5 cm^3) of **2** (301 mg) was added and kept at 60 °C for 16 h. After removal of the precipitates, the mixture was chromatographed on a silica-gel column with AcOEt–benzene (1:5) to give **1a** [yellow crystals, mp 102—103 °C, 441.5 mg; 92%. Found: C, 74.46; H, 5.90%. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.83%. ^{1}H NMR δ=3.68 (3H, s), 5.16 (2H, s), 6.18 (1H, dd, J=11, 2.5 Hz), 6.99 (1H, dd, J=13.5, 2.5 Hz), 7.18 (1H, d, J=13.5 Hz), and 7.25—7.5 (6H, m). ^{13}C NMR δ=55.5, 71.0, 107.1, 117.6, 127.2 (2C), 128.0, 128.5 (2C), 132.6, 136.2, 137.8, 158.6, 159.7, and 179.7. IR ν: 1570 and 1202 cm^{-1}. UV λ_{max}^{MeOH}: 227 nm (ε=24000), 252 (7500, sh), 328 (11200), 347 (10200), 361 (9300, sh), and 376 (6400, sh)].

2-(4-Bromobenzyloxy)-5-methoxytropone (1b). To an

† 1 M=1 mol dm^{-3}.

HMPA solution (3 cm³) of **2** (203 mg) and NaH (50%, 81 mg), **4b** (341 mg) was added at 60 °C. The mixture was kept at 60 °C for further 13 h, the reaction mixture was poured into water to precipitate **1b** [yellow crystals, mp 157—159 °C, 329 mg; 77%. Found: C, 55.80; H, 4.06%. Calcd for $C_{15}H_{13}O_3Br$: C, 56.09; H, 4.08%. ^1H NMR δ=3.72 (3H, s), 5.10 (2H, s), 6.18 (1H, dd, J=11, 2.5 Hz), 6.78 (1H, d, J=11 Hz), 7.06 (1H, dd, J=13, 2.5 Hz), 7.18 (1H, d, J=13 Hz), 7.26 (2H, d, J=8.5 Hz), and 7.46 (2H, d, J=8.5 Hz). ^{13}C NMR δ=55.5, 70.3, 106.8, 118.3, 121.9, 128.9 (2C), 131.7 (2C), 132.7, 135.3, 138.1, 158.3, 160.0, and 179.7. IR ν: 1570 and 1200 cm^{-1}. UV λ_{max}^{MeOH}: 227 nm (ε=16500), 252 (4100, sh), 327 (5900), 332 (5900), 341 (5600), 362 (4800, sh), and 376 (3400, sh)].

2-(4-Methoxybenzyloxy)-5-methoxytropone (1c). To a mixture prepared from **3c** (380 mg), DCC (615 mg), and CuCl (5 mg) by warming at 60 °C for 10 h a benzene solution (0.5 cm³) of **2** (297 mg) was added. After standing at 60 °C for 30 min, the precipitates were removed by filtration, the filtrate was heated in vacuo to remove the volatile material, and the residue was recrystallized from a mixture of benzene and hexane (2:1) to give **1c** [yellow needles, mp 157—158.5 °C, 527 mg; 99%. Found: M. W., 272.1033. Calcd for $C_{16}H_{16}O_4$: 272.1048. ^1H NMR δ=3.72 (3H, s), 3.78 (3H, s), 5.12 (2H, s), 6.20 (1H, dd, J=11, 2.8 Hz), 6.82 (1H, d, J=11 Hz), 6.86 (2H, d, J=9 Hz), 7.00 (1H, dd, J=13, 2.8 Hz), 7.18 (1H, d, J=13 Hz), and 7.52 (2H, d, J=9 Hz). ^{13}C NMR δ=55.3, 55.5, 70.8, 107.3, 114.0 (2C), 118.1, 128.2, 129.0 (2C), 132.6, 137.8, 158.7, 159.5, 159.8, and 179.8. IR ν: 1610, 1573, 1520, 1237, 1200, 1108, and 825 cm^{-1}. UV λ_{max}^{MeOH}: 229 nm (ε=15200), 252 (4200, sh), 274 (1300), 282 (1500), 327 (5400), 332 (5400), 348 (4900), 362 (4200, sh), and 378 (3100, sh)].

2,5-Bis(benzyloxy)tropone (6a). To an HMPA solution (12 cm³) prepared from **7** (500 mg) and NaH (392 mg) by warming at 60 °C for 3 h, **4a** (1.2 cm³) was added. After 13 h, the mixture was poured into water, and the resultant precipitates were collected by filtration. Recrystallizations from a mixed solution of benzene and hexane yielded **6a** [yellow crystals, mp 114—115 °C, 915 mg; 80%. Found: C, 79.30; H, 5.67%. Calcd for $C_{21}H_{18}O_3$: C, 79.22; H, 5.70%. ^1H NMR δ=4.95 (2H, s), 5.18 (2H, s), 6.30 (1H, ddd, J=11, 2, 1 Hz), 6.78 (1H, d, J=11 Hz), 7.07 (1H, dd, J=13, 2 Hz), 7.25 (1H, dd, J=13, 1 Hz), and 7.35 (10H, br s). ^{13}C NMR δ=70.4, 71.0, 108.7, 117.3, 127.2 (2C), 127.4 (2C), 128.0, 128.4, 128.6 (2C), 128.7 (2C), 132.8, 135.4, 136.1, 137.9, 158.8 (2C), and 179.7. IR ν: 1601, 1566, 1233, 1193, 1126, 849, and 759 cm^{-1}. UV λ_{max}^{MeOH}: 227 nm (ε=13300), 253 (5200, sh), 327 (6300), 332 (6300), 344 (5700), 360 (4900, sh), and 370 (3400, sh)].

2,5-Bis(4-bromobenzyloxy)tropone (6b). Similarly, **7** (276 mg) in HMPA (4 cm³) with NaH (218 mg) was treated with **4b** (1070 mg) in HMPA (4 cm³) to give **6b** [yellow crystals, mp 142—143 °C, 903 mg; 95%. Found: C, 52.87; H, 3.44%. Calcd for $C_{21}H_{16}O_3Br_2$: C, 52.97; H, 3.39%. ^1H NMR δ=4.88 (2H, s), 5.08 (2H, s), 6.24 (1H, d, J=11 Hz), 6.72 (1H, d, J=11 Hz), 7.12 (2H, s), 7.20 (2H, d, J=9 Hz), 7.22 (2H, d, J=9 Hz), 7.42 (2H, d, J=9 Hz), and 7.44 (2H, d, J=9 Hz). ^{13}C NMR δ=69.6, 70.2, 108.6, 117.6, 122.0, 122.4, 129.0 (4C), 131.7 (2C), 131.8 (2C), 132.8, 134.4, 135.1, 138.1, 158.7 (2C), and 179.6. IR ν: 1630, 1595, 1570, 1516, 1245, 1190, and 1010 cm^{-1}. UV λ_{max}^{MeOH}: 228 nm (ε=38700), 254 (9600, sh), 327 (11700), 346 (10300, sh), 360 (8900, sh), and 376 (5900, sh)].

2,5-Bis(4-methoxybenzyloxy)tropone (6c). In a similar manner to **6b**, **7** (411 mg) was converted to **6c** [yellow needles, mp 145—148 °C, 1060 mg; 94%. Found: C, 73.02; H, 5.85%. Calcd for $C_{23}H_{22}O_5$: C, 73.00; H, 5.86%. ^1H NMR δ=3.76 (3H, s), 3.78 (3H, s), 4.86 (2H, s), 5.10 (2H, s), 6.30 (1H, ddd, J=11, 2.5, 1 Hz), 6.78 (1H, d, J=11 Hz), 6.84 (2H, d, J=9 Hz), 6.88 (2H, d, J=9 Hz), 7.04 (1H, dd, J=13, 2.5 Hz), 7.20 (1H, dd, J=13, 1 Hz), 7.26 (2H, d, J=9 Hz), and 7.30 (2H, d, J=9 Hz). ^{13}C NMR δ=55.3 (2C), 70.3, 70.8, 108.7, 114.0 (2C), 114.1 (2C), 117.7, 124.1, 127.4, 128.9 (2C), 129.2 (2C), 132.8, 137.9, 158.9, 159.4, 159.7, 168.3, and 179.8. IR ν: 1612, 1518, 1252, 1232, 1185, and 1175 cm^{-1}. UV λ_{max}^{MeOH}: 229 nm (ε=41200), 253 (10700, sh), 330 (12200), and 382 (6100, sh)].

3-Benzyl-5-methoxytropolone (5a). A decalin solution (9 cm³) of **1a** (225 mg) was refluxed for 4.5 h. The mixture was then chromatographed on a silica-gel column to give **5a** [yellow needles, mp 86—88 °C, 98 mg; 44%. Found: C, 74.46; H, 5.64%. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.83%. ^1H NMR δ=3.70 (3H, s), 4.13 (2H, s), 6.70 (1H, dd, J=11, 2.5 Hz), 7.09 (1H, d, J=2.5 Hz), 7.24 (5H, s), and 7.26 (1H, d, J=11 Hz). ^{13}C NMR δ=40.8, 55.8, 117.4, 120.3, 126.8, 128.8 (2C), 129.4 (2C), 129.5, 139.2, 141.7, 158.7, 162.9, and 171.3. IR ν: 1608, 1529, and 1210 cm^{-1}. UV λ_{max}^{MeOH}: 227 nm (ε=11900), 253 (7500), 322 (3400), 372 (2900), and 386 (2800)] and **2** (16.7 mg; 12%).

3-(4-Bromobenzyloxy)-5-methoxytropolone (5b). Similarly, **1b** (148 mg) was converted to **5b** [yellow crystals, mp 109—111 °C, 84.5 mg; 57%. Found: M.W., 319.9975 and 322.0017. Calcd for $C_{15}H_{13}O_3Br$: 320.0028 and 322.0048. ^1H NMR δ=3.73 (3H, s), 4.08 (2H, s), 6.70 (1H, dd, J=11.5, 3 Hz), 7.08 (1H, d, J=3 Hz), 7.18 (2H, d, J=9 Hz), 7.26 (1H, d, J=11.5 Hz), and 7.38 (2H, d, J=9 Hz). ^{13}C NMR δ=40.5, 55.8, 116.7, 119.8, 129.9, 130.9 (2C), 131.6 (2C), 135.0, 138.0, 141.1, 158.5, 162.2, and 171.4. IR ν: 1609, 1515, 1484, 1450, 1400, and 1207 cm^{-1}. UV λ_{max}^{MeOH}: 228 nm (ε=21100), 241 (21100), 271 (6700, sh), 330 (7600), 370 (5400), and 384 (4800, sh)]. In this case, **2** could not be isolated.

3-(4-Methoxybenzyloxy)-5-methoxytropolone (5c). Similarly, **1c** (54 mg) was converted to **5c** [yellow crystals, mp 78—80 °C, 30 mg; 56%. Found: C, 70.80; H, 6.08%. Calcd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92%. ^1H NMR δ=3.72 (3H, s), 3.78 (3H, s), 4.10 (2H, s), 6.72 (1H, dd, J=11, 3 Hz), 6.82 (2H, d, J=8.5 Hz), 7.10 (1H, d, J=3 Hz), 7.18 (2H, d, J=8.5 Hz), and 7.28 (1H, d, J=11 Hz). ^{13}C NMR δ=40.0, 55.2, 55.7, 114.0 (2C), 116.9, 119.9, 129.3, 130.2 (2C), 130.8, 142.0, 158.3, 158.5, 162.4, and 171.1. IR ν: 1605, 1508, 1453, 1397, 1247, 1040, and 740 cm^{-1}. UV λ_{max}^{MeOH}: 227 nm (ε=24300), 240 (21200, sh), 251 (14900, sh), 276 (4200), 330 (7300), 371 (6100), and 387 (6100)] and **2** (5.4 mg; 18%).

3-Benzyl-5-benzyloxytropolone (9a). Similarly, **6a** (727 mg) was converted to **9a** [pale yellow crystals, mp 79—80 °C, 361 mg; 50%. Found: C, 79.38; H, 5.71%. Calcd for $C_{21}H_{18}O_3$: C, 79.22; H, 5.70%. ^1H NMR δ=4.12 (2H, s), 4.94 (2H, s), 6.83 (1H, dd, J=11.5, 3 Hz), 7.23 (6H, br s), 7.24 (1H, d, J=11.5 Hz), and 7.30 (5H, s). ^{13}C NMR δ=40.8, 70.8, 120.1, 121.0, 126.7, 127.6 (2C), 128.4, 128.7 (2C), 128.8 (2C), 129.2 (2C), 129.5, 135.6, 139.0, 141.1, 157.8, 163.9, and 170.3. IR ν: 1608, 1548, 1458, 1400, and 1192 cm^{-1}. UV λ_{max}^{MeOH}: 237 nm (ε=22600), 250 (18800, sh), 332 (8600), 370 (6100), and 387 (5900)].

Thermolysis of 6b to 3-(4-Bromobenzyl)-5-(4-bromobenzyloxy)-tropolone (9b) and 5-(4-Bromobenzyloxy)tropolone (8b). Similarly, **6b** (80.6 mg) was heated. Silica-gel column chromatography of the mixture yielded **9b** [yellow crystals, mp 62 °C, 32.8 mg; 41%. Found: M.W., 473.9484, 475.9440, and 477.9440. Calcd for $C_{21}H_{16}O_3Br_2$: 473.9466, 475.9447, and 477.9427. ^1H NMR δ=4.04 (2H, s), 4.90 (2H, s), 6.80

(1H, dd, J=11, 3 Hz), 7.06 (2H, d, J=9 Hz), 7.12 (1H, d, J=3 Hz), 7.17 (2H, d, J=9 Hz), 7.22 (1H, d, J=11 Hz), 7.35 (2H, d, J=9 Hz), and 7.47 (2H, d, J=9 Hz). ^{13}C NMR δ=40.4, 70.2, 119.4, 120.4, 120.7, 122.6, 129.2 (2C), 130.0, 131.0 (2C), 131.8 (2C), 132.1 (2C), 134.7, 138.1, 140.8, 157.4, 163.5, and 171.1. IR ν: 1608, 1555, 1488, 1456, 1398, 1367, 1259, 1015, 1188, and 804 cm^{-1}. UV λ_{max}^{MeOH}: 227 nm (ε=29300), 241 (24100, sh), 250 (19700, sh), 332 (8300), 370 (5800), 387 (5600), and 422 (1400)] and **8b** [yellow crystals, mp 121—123 °C. 8.7 mg; 11%. Found: M.W., 305.9878 and 307.9871. Calcd for $C_{14}H_{11}O_3Br$: 305.9889 and 307.9871. ^{1}H NMR δ=4.98 (2H, s), 7.00 (2H, d, J=12 Hz), 7.24 (2H, d, J=9 Hz), 7.28 (2H, d, J=12 Hz), and 7.52 (2H, d, J=9 Hz)].

Thermolysis of 6c to 3-(4-Methoxybenzyl)-5-(4-methoxybenzyloxy)tropolone (9c) and 5-(4-Methoxybenzyloxy)-tropolone (8c). Similarly, **6c** (549.5 mg) was converted to **9c** [a yellow oil, 55.6 mg; 10%. Found: M.W., 378.1462. Calcd for $C_{23}H_{22}O_5$: 378.1464. ^{1}H NMR δ=3.74 (3H, s), 3.80 (3H, s), 4.06 (2H, s), 4.88 (2H, s), 6.7—7.0 (6H, m), and 7.05—7.3 (5H, m). ^{13}C NMR δ=40.4, 55.2 (2C), 70.7, 113.7, 114.0 (2C), 114.1 (2C), 119.5, 120.5, 127.6, 129.3 (2C), 129.6, 130.2 (2C), 130.9, 141.4, 157.7, 158.3, 163.5, and 170.5] and **8c** [colorless crystals, mp 181.5 °C (decomp), 274.5 mg; 73%. Found: C, 69.86; H, 5.47%. Calcd for $C_{15}H_{14}O_4$: C, 69.75; H, 5.46%. ^{1}H NMR δ=3.80 (3H, s), 4.94 (2H, s), 6.90 (2H, d, J=9 Hz), 7.00 (2H, d, J=12 Hz), 7.26 (2H, d, J=12 Hz), and 7.30 (2H, d, J=9 Hz). ^{13}C NMR δ=40.0, 55.3, 114.1 (2C), 124.1 (2C), 124.2 (2C), 127.4, 129.3 (2C), 158.8, 159.7, and 168.3 (2C). IR ν: 1618, 1547, 1454, 1269, 1254, 1190, and 1173 cm^{-1}].

Demethylation of 5a to 3-Benzyl-5-hydroxytropolone (10a). A 1:1-mixture of conc HBr–AcOH (1.2 cm^3) and **5a** (30.6 mg) were heated. The product mixture was then poured into water, and extracted with AcOEt. Recrystallizations from a mixed solution of acetone and ether yielded **10a** [yellow crystals, mp 192 °C (decomp), 12 mg; 42%. Found: M.W., 228.0787. Calcd for $C_{14}H_{12}O_3$: 228.0787. ^{1}H NMR (DMF-d_7) δ=4.11 (2H, s), 6.96 (1H, dd, J=11, 3 Hz), 7.23 (1H, d, J=3 Hz), and 7.28 (6H, br s). ^{13}C NMR δ=40.9, 120.3, 121.2, 126.9, 129.0 (2C), 129.8 (2C), 130.3, 140.6, 143.6, 158.2, 159.4, and 171.3. IR ν: 1605, 1376, 1277, 1215, and 962 cm^{-1}. UV λ_{max}^{MeOH}: 239 nm (ε=21200), 270 (3900, sh), 342 (8700), 380 (7300, sh), 393 (7700), and 422 (2600, sh)].

Debenzylation of 9a to 10a. Similarly, **9a** (48.3 mg) was hydrolyzed to **10a** (25.2 mg; 73%).

Debenzylation of 9b to 10b. Similarly, **9b** (284 mg) was converted to **10b** [yellow needles, mp 161 °C (decomp), 78 mg; 42%. Found: C, 54.51; H, 3.76%. Calcd for $C_{14}H_{11}O_3Br$: C, 54.75; H, 3.61%. ^{1}H NMR (CD_3OD) δ=4.07 (2H, s), 6.94 (1H, dd, J=11, 2.5 Hz), 7.15 (2H, d, J=8.5 Hz), 7.16 (1H, d, J=2.5 Hz), 7.28 (1H, d, J=11 Hz), and 7.39 (2H, d, J=8.5 Hz). ^{13}C NMR δ=41.0, 121.2, 123.9, 124.8, 129.8, 132.0 (2C), 132.6 (2C), 140.0, 142.5, 159.3, 166.1, and 169.6. IR ν: 1605, 1370, 1277, and 1214 cm^{-1}. UV λ_{max}^{MeOH}: 230 nm (ε=23700, sh), 237 (23800), 336 (8100), 379 (7200), and 394 (7400)].

Demethylation of 5c to 10d. Similarly, **5c** (110 mg) was converted to **10d** [yellow crystals, mp 191 °C (decomp), 54.4 mg; 55%. Found: M.W., 244.0733. Calcd for $C_{14}H_{12}O_4$: 244.0733. ^{1}H NMR (CD_3OD) δ=4.01 (2H, s), 6.70 (2H, d, J=9 Hz), 6.94 (1H, dd, J=11.5, 3 Hz), 7.05 (2H, d, J=9 Hz), 7.12 (1H, d, J=3 Hz), and 7.24 (1H, d, J=11.5 Hz). ^{13}C NMR δ=40.7, 116.6 (2C), 124.0, 125.2, 129.7, 131.5 (3C), 144.3, 157.3, 159.7, 166.4, and 169.7. IR ν: 1610, 1518, 1373, 1214, and 1201 cm^{-1}. UV λ_{max}^{MeOH}: 229 nm (ε=21000), 239 (20800), 280 (3900, sh), 344 (8500), 395 (6800), and 422 (3100, sh)].

3-Benzyl-*p*-tropoquinone (11a). An acetone solution (10 cm^3) of **10a** (104.5 mg) was treated with DDQ (121 mg) at 20—25 °C for 2 to 5 h. Silica-gel column chromatography of the mixture afforded **11a** [a yellow oil, 93.8 mg; 91%. Found: M.W., 226.0630. Calcd for $C_{14}H_{10}O_3$: 226.0630. ^{1}H NMR δ=3.84 (2H, d, J=1.5 Hz), 6.57 (1H, br s), 6.77 (2H, s), and 7.0—7.4 (5H, m). ^{13}C NMR δ=38.8, 127.3, 129.0 (2C), 129.3 (2C), 133.6, 135.6, 136.9, 139.5, 147.7, 187.7, 189.1, and 189.9. IR ν: 1680, 1644, and 1615 cm^{-1}. UV $\lambda_{max}^{CHCl_3}$: 252 nm (ε=12600) and 272 (7600)].

3-(4-Bromobenzyl)-*p*-tropoquinone (11b). Similarly, **10b** (101.7 mg) was oxidized to **11b** [yellow crystals, mp 97.5—99.5 °C, 76.7 mg; 76%. Found: M.W., 303.9758 and 305.9729. Calcd for $C_{14}H_9O_3Br$: 303.9735 and 305.9715. ^{1}H NMR δ=3.80 (2H, d, J=1.5 Hz), 6.57 (1H, q, J=1.5 Hz), 6.80 (2H, s), 7.03 (2H, d, J=9 Hz), and 7.42 (2H, d, J=9 Hz). ^{13}C NMR δ=38.3, 121.4, 131.0 (2C), 132.2 (2C), 133.7, 134.7, 137.1, 139.4, 147.0, 187.5, 188.7, and 189.4. IR ν: 1665, 1630, and 1600 cm^{-1}. UV $\lambda_{max}^{CHCl_3}$: 253 nm (ε=19200), 258 (19800), 265 (19200), and 271 (16700)].

3-(4-Hydroxybenzyl)-*p*-tropoquinone (11d). Similarly, **10d** (37.4 mg) was oxidized with DDQ (39.7 mg) to give **11d** [a yellow oil, 35.2 mg; 95%. Found: C, 68.12; H, 4.68%.[9] Calcd for $C_{14}H_{10}O_4 \cdot C_{14}H_{12}O_4 + 1/3H_2O$: C, 68.29; H, 4.61%. m/z, 278 (M^++36), 244 (M^++2), and 242 (M^+). ^{1}H NMR δ=3.78 (2H, d, J=1.5 Hz), 6.57 (1H, q, J=1.5 Hz), 6.74 (2H, d, J=9 Hz), 6.80 (2H, s), and 7.01 (2H, d, J=9 Hz). ^{13}C NMR δ=38.1, 116.0 (2C), 127.5, 130.6 (2C), 133.6, 136.7, 139.7, 148.2, 154.9, 187.9, 189.2, and 190.0. IR ν: 1680, 1640, 1615, and 1515 cm^{-1}].

The authors thank the Ministry of Education, Culture, and Science for a financial support with the Grant-in-Aid for Scientific Research to A. M. (No. 60470025).

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