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Novel Base-Promoted Rearrangement of 2-(4-Cyano-, 2-Nitro-, and 4-Nitrobenzyloxy)tropones and 2-(2-Oxo-2-phenethyloxy)tropone to 2-[(4-Cyano-, 2-Nitro-, and 4-Nitrophenyl)hydroxymethyl]-tropones and 2-(1-Hydroxy-2-oxo-2-phenethyl)tropone

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The base-catalyzed rearrangement of 2-(2-nitro-, 4-nitro-, and 4-cyanobenzyloxy)tropones smoothly yielded corresponding 2-[(aryl)hydroxymethyl]tropones, while their thermolysis gave 3-(arylmethyl)tropolones. This reaction has no precedent analogy in troponoid chemistry, and this rearrangement is widely applicable to the 2-troponyl ethers of alcohols carrying an electron-attractive substituent on the α-position, as was verified by the occurrence of 2-(1-hydroxy-2-oxo-2-phenethyl)tropone from 2-(2-oxo-2-phenethyloxy)tropone.

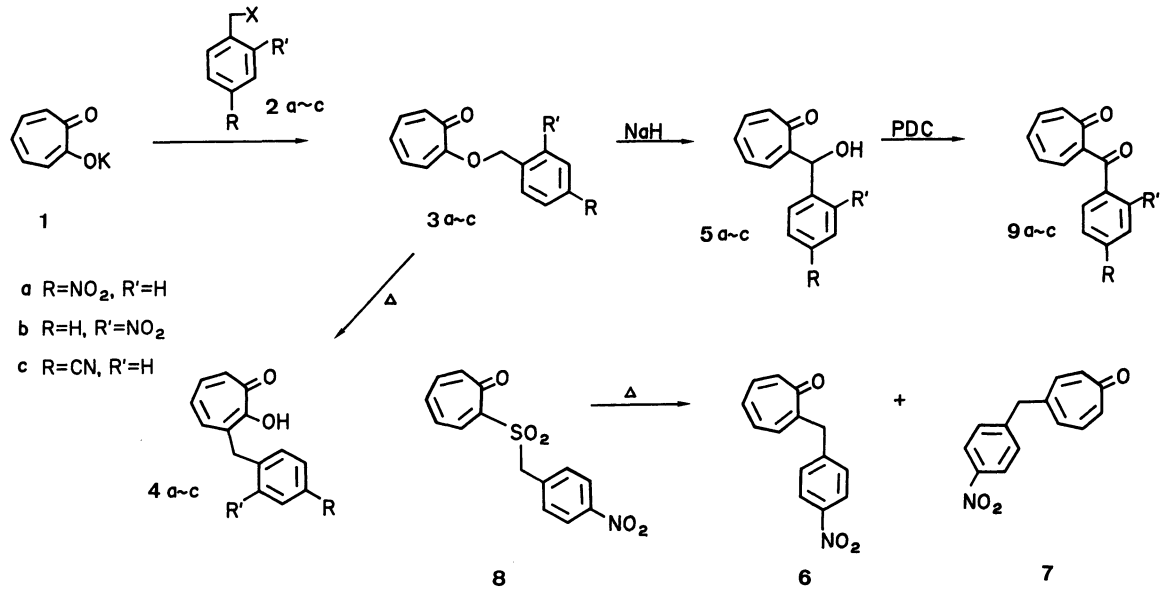
Among the chemical properties of troponoids, base-promoted ring-contraction to benzenoid derivatives from various functionalized tropone derivatives has been one of the most outstanding features.[1] However, to overcome this disadvantage has been a synthetic problem. In the course of our study on the thermal reaction of troponoids, we have found a new radical reaction of 2-troponyl benzyl ethers to the 3- and 5-(arylmethyl)tropolones.[2] The rearrangement mechanism could be clarified by a kinetic analysis and isotope-labelling experiments. Similar rearrangements also occurred when 2-(2-furyl- and 2-thienylmethoxy)tropones were heated in decalin; i.e., 2-(2-furylmethoxy)tropone gave 3- and 5-(2-furylmethyl)-tropolones and 3- and 5-(5-methyl-2-furyl)tropolones,[3] and 2-(2-thienylmethoxy)tropones gave 3- and 5-(2-thienylmethyl)tropolones.[4] During the preparation of 2-(2- and 4-nitrobenzyloxy)tropones from tropolone and nitrobenzyl halides under basic conditions, we found an unprecedented rearrangement in the troponoid chemistry to form a C-C bond. We will, herein, describe this novel base-catalyzed reaction of 2-troponyl ethers of alcohols having an electron-attractive substituent on their α-position, such as 2-(2- and 4-nitrobenzyloxy)tropones and 2-(2-oxo-2-phenethyloxy)tropone (2-phenacyloxytropone).

Results and Discussion

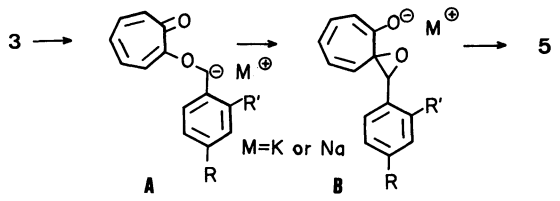
When a hexamethylphosphoric triamide (HMPA) solution of potassium tropolonate (**1**) and 4-nitrobenzyl chloride (**2a**) was stirred at 50 °C for 10 h, three products (**3a**, **4a**, and **5a**) were isolated by silica-gel column chromatography in 69, 0.3, and 8% yields, respectively. The structures of **3a** and **4a** were identified to be 2-(4-nitrobenzyloxy)tropone and 3-(4-nitrobenzyl)tropolone; i.e., the ^{1}H NMR of **3a** revealed a methylene signal at a lower field, δ=5.24, and nine aromatic protons, while the ^{1}H NMR spectrum of **4a**, showed a methylene signal at a higher field, δ=4.21, and eight aromatic protons. The ^{13}C NMR spectral comparison of **3a** and **4a** with a series of previously prepared derivatives[2] supported this conclusion.

The third product, **5a**, had a secondary hydroxyl group and the tropone ring was retained. In the ^{1}H NMR, a singlet signal ascribable to the newly-formed methine proton appeared at δ=5.86. It was further noticed that its ^{13}C NMR spectrum closely resembled, except for an sp^3-carbon, those of 2-benzyltropones.[5] Following our previous method, the model compounds, 2-(4-nitrobenzyl)tropone (**6**) and 4-(4-nitrobenzyl)tropone (**7**), could be prepared by a thermolysis of 2-(4-nitrobenzylsulfonyl)tropone (**8**).[5,6] The chemical shift differences, $\Delta\delta$(**5a**−**6**), between **5a** and **6**, thus prepared, showed a good correlation: For the seven-membered ring carbons, they were 1.4 (C-1), 0.6 (C-2), 1.3 (C-3), 1.8 (C-4), 1.0 (C-5), 1.0 (C-6), and 0.2 (C-7). In addition, the benzoyl derivative **9a**, a pyridinium dichromate(PDC)-oxidation product of **5a**, showed no singlet proton signal in the region of δ=7 to 7.5. This eliminated the alternative 3-substituted tropone structures;[7] therefore, **5a** must be the α-hydroxylated derivative of **6**, 2-[hydroxy(4-nitrophenyl)methyl]tropone.

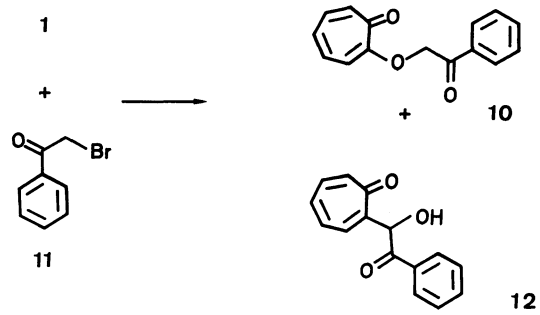
When **3a** was kept at room temperature in HMPA, no reaction occurred after 5 h; but when **3a** was refluxed in 1,2-dichlorobenzene (DCB), **4a** was formed in good yield. Furthermore, when **3a** was added to an HMPA solution of sodium hydride, the mixture instantly caused a change in color to yield **5a** in 72%, but no **4a**. Therefore, **3a** is not the precursor of **4a** already formed during preparation, and **4a** is likely to be formed by a direct C-attack. Clearly, the base was responsible for the formation of **5a**. For the rearrangement, the presence of an electron-attractive substituent, such as a nitro group, might be essential in order to generate a delocalized benzyl anion, since the unsubstituted 2-benzyloxytropone (**3d**)[2] gave no rearrangement product under comparable conditions. Such a stable anion (**A**) can be converted to the epoxide (**B**) by the assistance of a coordination with alkali metal ions to the carbonyl group. The following C-O bond cleavage should give **5** by another electrocyclic recombination.



Scheme 1.



Scheme 2.



Scheme 3.

This base-promoted reaction was also applicable to the corresponding 2-isomer, **3b**: By a reaction of **1** with 2-nitrobenzyl chloride (**2b**) in HMPA, 2-(2-nitrobenzyloxy)tropone (**3b**) was obtained in 88% yield together with 2-[hydroxy(2-nitrophenyl)methyl]tropone (**5b**). An alkali treatment of **3b** with sodium hydride in HMPA afforded **5b** in 95% yield, but the thermolysis of **3b** in DCB slowly produced **4b**; its yield was ca. 44% at 32% conversion after 13-h period. This low reactivity of thermolysis might be attributable to a steric hindrance of the bulky 2-nitro group. An attempted purification of **4b** resulted in an extensive decomposition of the material. The PDC-oxidation of **5b** yielded 2-(2-nitrobenzoyl)tropone (**9b**).

The rearrangement must be applicable to other derivatives whose ethereal carbon can generate a stable carbanion. This was verified when 2-(4-cyanobenzyloxy)tropone (**3c**), prepared from **1** and 4-cyanobenzyl bromide (**2c**), was converted to 2-[(4-cyanophenyl)-hydroxymethyl]tropone (**5c**). Furthermore, **3c** was thermolyzed to 3-(4-cyanobenzyl)tropolone (**4c**) in good yield.

Moreover, 2-(2-oxo-2-phenethyloxy)tropone (**10**), prepared similarly by condensation of **1** with phenacyl bromide (**11**, ω-bromoacetophenone), disclosed similar features. Thus, the attempted preparation of **10** resulted in a rearrangement product, 2-(1-hydroxy-2-oxo-2-phenethyl)tropone (**12**) in 59% yield; the isolated yield of **10** was only 17%.

Therefore, this base-promoted rearrangement has a considerable utility for introducing functionalized carbon side chains into the tropone system; particularly, there is no versatile method of C-C bond formation on the tropone system. Namely, a Grignard reaction has been generally employed to prepare 2-substituted tropones,[8] but its utility was severely restricted by the low yields of the desired products and a formation of ring-contracted phenyl derivatives; e.g., triphenylmethanol formation from phenylmagnesium bromide and 2-methoxytropone is inevitable.[9] It is also well known that 2-alkoxytropones are unstable under basic conditions and cause a ring-contraction to benzenoids.[1] The sole occurrence of substitution without ring-contraction under the present conditions is rather surprising. The marked difference should primarily be attributed to the different nature of the solvent used; one for protic solvents, such as alcohols which are sufficiently nucleophilic, and another for a bulky and polar-aprotic HMPA, being weakly nucleophilic. This newly-recognized property of 2-alkoxytropones[10] will make various reactions under basic conditions promising.

Experimental

The elemental analyses were performed by Miss S. Hirashima, the Research Institute of Industrial Science, Kyushu University. The mps were measured with a Yanagimoto Micro mp Apparatus and are uncorrected. The NMR spectra were measured with a JEOL FX 100 Spectrometer in $CDCl_3$ solution, and the chemical shifts expressed were in δ units. The mass spectra were measured with a JEOL 01SG-2 Spectrometer. The IR spectra were taken as KBr disks using a Jasco IR-A 102 Spectrometer. The UV spectra were taken with a Hitachi 124 Model Spectrophotometer.

Condensation Reactions of Potassium Tropolonate with Benzyl Halides under Basic Conditions. Following our previous method,[2] to anhydrous HMPA (2 cm^3) of **1** (ca. 1 mmol), an HMPA solution (2 cm^3) of **2a—c** (ca. 1 mmol) was added dropwise at room temperature and kept at 50—100 °C under an N_2 atmosphere. The mixture was then diluted with water, acidified with dil HCl, and extracted with ether. Silica-gel column chromatography of the extracts afforded **3a—c**, **4a**, and **5a, b**.

3a: Colorless plates, mp 164—166 °C, 69%. Found: C, 65.25; H, 4.30; N, 5.61%. Calcd for $C_{14}H_{11}O_4N$: C, 65.36; H, 4.31; N, 5.45%. ^1H NMR δ=5.24 (2H, s), 6.6—7.0 (3H, m), 7.1—7.2 (2H, m), 7.60 (2H, d, J=9 Hz), and 8.19 (2H, d, J=9 Hz). ^{13}C NMR δ=69.7, 115.5, 124.1 (2C), 127.8 (2C), 129.3, 132.5, 136.8, 138.0, 141.3, 148.0, 164.1, and 180.8. IR ν: 1620, 1600, 1570, and 1510 cm^{-1}. UV λ_{max}^{MeOH}: 265 nm (ε=11000) and 317 (9900).

4a: Yellow crystals, mp 167—169 °C, 0.3%. Found: C, 65.26; H, 4.29; N, 5.87%. ^1H NMR δ=4.21 (2H, s), 6.99 (1H, ddd, J=9.5, 6, 5 Hz), 7.2—7.6 (3H, m), 7.38 (2H, d, J=9 Hz), and 8.08 (2H, d, J=9 Hz). ^{13}C NMR δ=40.9, 120.5, 123.9 (2C), 127.7, 130.0 (2C), 136.9, 139.5, 140.1, 147.0, 147.3, 167.9, and 173.6. IR ν: 1600, 1545, and 1340 cm^{-1}. UV λ_{max}^{MeOH}: 244 nm (ε=24000), 269 (11600), 322 (7400), 356 (6200), 372 (5900), and 401 (1700).

5a: Yellow crystals, mp 170—172 °C, 8%. Found: C, 65.48; H, 4.37; N, 5.73%. ^1H NMR δ=3.40 (1H, br s, OH), 5.86 (1H, s), 6.9—7.2 (4H , m), 7.46 (1H, d, J=5.5 Hz), 7.58 (2H, d, J=9 Hz), and 8.12 (2H, d, J=9 Hz). ^{13}C NMR δ=75.2, 123.7 (2C), 127.5 (2C), 134.4, 135.4, 135.9, 137.0, 142.2, 147.5, 149.5, 153.3, and 187.5. IR ν: 3250, 1620 and 1595 cm^{-1}. UV λ_{max}^{MeOH}: 275 nm (ε=14000) and 315 (10500).

3b: Yellow needles, mp 151—153 °C, 88%. Found: C, 65.26; H, 4.29; N, 5.87%. Calcd for $C_{14}H_{11}O_4N$: C, 65.36; H, 4.31; N, 5.45%. ^1H NMR δ=5.55 (2H, s), 6.7—7.3 (5H, m), 7.4—7.8 (2H, m), and 8.0—8.2 (2H, m). ^{13}C NMR δ=67.7, 114.9, 125.2, 128.5, 128.8 (2C), 132.7, 134.8, 136.8 (2C), 137.9, 146.7, 164.2, and 180.8. IR ν: 1622, 1590, 1565, and 1515 cm^{-1}. UV λ_{max}^{MeOH}: 237 nm (ε=28600), 319 (9800), 347 (7300), and 362 (4400).

5b: Brown crystals, mp 165—167 °C, 5%. Found: C, 65.12; H, 4.46; N, 5.88%. ^1H NMR δ=6.36 (1H, s) and 6.9—8.0 (9H, m). ^{13}C NMR δ=70.4, 124.8, 128.8, 129.2, 133.5, 134.2, 134.5, 134.9, 136.7, 141.7, 148.9, 153.0 (2C), and 187.4. IR ν: 3250 and 1620 cm^{-1}. UV λ_{max}^{MeOH}: 227 nm (ε=27800) and 306 (8900).

3c: Colorless plates, mp 144—145 °C, 75%. Found: C, 75.95; H, 4.70; N, 5.98%. Calcd for $C_{15}H_{11}O_2N$: C, 75.93; H, 4.67; N, 5.90%. ^1H NMR δ=5.24 (2H, s), 6.6—7.1 (3H, m), 7.1—7.3 (2H, m), 7.53 (2H, d, J=8.5 Hz), and 7.66 (2H, d, J=8.5 Hz). ^{13}C NMR δ=69.8, 112.1, 115.4, 118.7, 127.7 (2C), 129.1, 132.5, 132.7 (2C), 136.7, 137.9, 141.1, 164.1, and 180.7. IR ν: 2225, 1615, 1595, 1565, 1490, 1465, and 1400 cm^{-1}. UV λ_{max}^{MeOH}: 237 nm (ε=40000), 320 (8900), and 345 (6900).

Base-Promoted Rearrangement of 3a. An anhydrous HMPA solution (2 cm^3) of **3a** (49 mg) was treated with NaH (4 mg) at room temperature for 5 min. Silica-gel column chromatography of the mixture gave **5a**, 35.3 mg (72%), which was identical with the sample prepared as described above.

Thermolysis of 3a. A DCB solution (17.5 cm^3) of **3a** (202 mg) was heated in a sealed tube at 180 °C for 12 h. Column chromatography of the mixture afforded **4a**, 161 mg (80%), which was identical with the sample described above.

Preparation of 6 and 7 from 2-(4-Nitrobenzylsulfonyl)-tropone (8) by Thermolysis.[6] A decalin solution (20 cm^3) of **8** (157 mg) [colorless crystals, mp 162—163.5 °C. Found: m/z, 305.0365. Calcd for $C_{14}H_{11}O_4NS$: M, 305.0358. ^1H NMR δ=4.94 (2H, s), 6.8—7.3 (4H, m), 7.52 (2H, m), 7.86 (1H, dd, J=8, 1 Hz), and 8.14 (2H, m). ^{13}C NMR δ=60.5, 123.6 (2C), 131.3, 131.6 (2C), 134.8, 135.8, 139.5, 140.3, 143.9, 145.9, 160.1, and 182.3], prepared from an oxidation of the corresponding sulfinyl derivative by m-chloroperbenzoic acid,[5] was heated at 205 °C for 2 h. The mixture was then chromatographed on a silica-gel column to give a colorless oil, **6**, 28 mg (23%) [Found: m/z, 241.0740. Calcd for $C_{14}H_{11}O_3N$: M, 241.0740. ^1H NMR δ=4.03 (2H, s), 6.9—7.3 (5H, m), 7.40 (2H, d, J=9 Hz), and 8.09 (2H, d, J=9 Hz). ^{13}C NMR δ=40.9, 123.6 (2C), 129.9 (2C), 133.4, 133.6, 135.7 (2C), 136.1, 141.0, 147.0, 152.7, and 186.1], and a colorless oil, **7**, 7 mg (6%) [Found: m/z, 241.0739. ^1H NMR δ=3.93 (2H, s), 6.8—7.1 (5H, m), 7.30 (2H, m), and 8.16 (2H, m)].

PDC-Oxidation of 5a. Formation of 9a. To a CH_2Cl_2 suspension (10 cm^3) of PDC (440 mg) and Celite (1.5 g), a CH_2Cl_2 solution of **5a** (100.4 mg) was added and stirred at room temperature for 5 h. The mixture was then purified by chromatography with Florisil column to give pale yellow crystals, mp 174—176 °C, 72 mg (72%), **9a** [Found: C, 65.77; H, 3.63; N, 5.64%. Calcd for $C_{14}H_9O_4N$: C, 65.88; H, 3.55; N, 5.49%. ^1H NMR δ=7.0—7.5 (5H, m), 7.91 (2H, d, J=9 Hz), and 8.23 (2H, d, J=9 Hz). ^{13}C NMR δ=124.1 (2C), 130.0 (2C), 134.2, 136.8, 137.0, 137.5, 141.0, 143.9, 150.1, 150.5, 186.2, and 195.1. IR ν: 1675, 1625, and 1603 cm^{-1}. UV λ_{max}^{MeOH}: 228 nm (ε=20000), 265 (16000), and 305 (9400)].

Thermolysis of 3b. Similarly, a DCB solution (2 cm^3) of **3b** (100 mg) was heated in a sealed tube at 180 °C for 13 h. The chromatography of the mixture afforded **4b**, 14.3 mg (44%) [Found: m/z, 257.0663. Calcd for $C_{14}H_{11}O_4N$: M, 257.0686. ^1H NMR δ=4.41 (2H, s), 7.2—7.5 (7H, m), and 7.94 (1H, dd, J=9, 2 Hz)], along with unchanged **3b** (67.6 mg; 68%).

Base-Promoted Rearrangement of 3b. An anhydrous HMPA solution (1.5 cm^3) of **3b** (150 mg) was treated with NaH (12.5 mg) at room temperature to give **5b**, 142 mg (95%).

Base-Promoted Rearrangement of 3c. An anhydrous HMPA solution (2.5 cm^3) of **3c** (121.8 mg) was treated with NaH (55%, 6 mg) at 0 °C for 5 min. The mixture was then diluted with water, and extracted with AcOEt. Silica-gel column chromatography of the extract yielded yellow brown crystals, mp 131—133 °C, **5c**, 40.4 mg (62%) [Found: C, 76.00; H, 4.74; N, 5.96%. Calcd for $C_{15}H_{11}O_2N$: C, 75.93; H, 4.67; N, 5.90%. ^1H NMR δ=5.83 (1H, s), 6.9—7.3 (4H, m), 7.45 (1H, d, J=5 Hz), and 7.51 (4H, s). ^{13}C NMR δ=74.9, 111.3, 127.2

(2C), 132.1 (2C), 134.2, 135.1, 135.7, 136.8, 142.0 (2C), 147.4, 153.3, and 187.2. IR ν: 3350, 2240, 1630, 1605, 1575, and 1400 cm^{-1}. UV λ_{max}^{MeOH}: 235 nm (ε=31000) and 314 (7800)], and the recovered **3c** (56.7 mg; 47%).

Thermolysis of 3c. A DCB solution (1.5 cm^3) of **3c** (55.7 mg) was heated at 180 °C for 9 h. Silica-gel column chromatography of the resultant mixture afforded colorless needles, mp 116—118 °C, **4c**, 21.5 mg (55%) [Found: C, 75.76; H, 4.61; N, 5.88%. Calcd for $C_{15}H_{11}O_2N$: C, 75.93; H, 4.67; N, 5.90%. ^1H NMR δ=4.18 (2H, s) and 6.8—7.6 (8H, m), ^{13}C NMR δ=41.4, 110.7, 119.1, 120.7, 127.6, 129.9 (2C), 132.5 (2C), 136.8, 139.5, 140.0, 145.1, 168.1, and 173.5. IR ν: 3200, 2240, 1605, 1550, 1485, 1415, and 1385 cm^{-1}. UV λ_{max}^{MeOH}: 236 nm (ε=30300), 324 (7400), 372 (5500), and 400 (2500)], and **3c** (16.9 mg; 30%).

PDC-Oxidation of 5b. Formation of 9b. To a CH_2Cl_2 suspension (10 cm^3) of PDC (133 mg) and Celite (500 mg), a CH_2Cl_2 solution (10 cm^3) of **5b** (30.1 mg) was added and stirred at room temperature for 5 h. The mixture was worked up in a manner similar to the case of **5a** and afforded yellow crystals, mp 131—133 °C, 15 mg (50%), **9b** [Found: C, 65.72; H, 3.67; N, 5.78%. Calcd for $C_{14}H_9O_4N$: C, 65.88; H, 3.55; N, 5.49%. ^1H NMR δ=6.9—7.3 (4H, m), 7.4—7.8 (3H, m), and 8.0—8.2 (2H, m). ^{13}C NMR δ=123.9, 124.8, 129.0, 130.3, 133.4, 134.1, 135.6, 137.8, 138.5, 140.1, 144.3, 146.5, 185.6, and 193.7. IR ν: 1670, 1620, 1570, 1515, and 1340 cm^{-1}. UV λ_{max}^{MeOH}: 237 nm (ε=28600), 319 (9800), 347 (7300), and 362 (4400, sh)].

PDC-Oxidation of 5c. Formation of 9c. To a CH_2Cl_2 suspension (5 cm^3) of PDC (122.6 mg) and Celite (500 mg), a CH_2Cl_2 solution (5 cm^3) of **5c** (25.1 mg) was added and similarly oxidized to give a light yellow crystals, mp 166—168 °C, 18.5 mg (74%), **9c** [Found: C, 76.44; H, 3.91; N, 5.97%. Calcd for $C_{15}H_9O_2N$: C, 76.58; H, 3.86; N, 5.96%. ^1H NMR δ=7.0—7.5 (5H, m), 7.67 (2H, d, J=8.5 Hz), and 7.87 (2H, d, J=8.5 Hz). ^{13}C NMR δ=116.6, 127.4, 129.5 (2C), 132.7 (2C), 134.2, 136.6, 136.9, 137.3, 139.4, 143.8, 150.2, 186.1, and 195.2. IR ν: 3050, 2220, 1670, 1620, 1560, 1460, and 1395 cm^{-1}. UV λ_{max}^{MeOH}: 233 nm (ε=24500) and 313 (7200)].

Condensation of 1 with 11. Formation of 10 and 12. An anhydrous HMPA solution (3 cm^3) of **1** (300.6 mg) and **11** (305 mg) was stirred at 50 °C for 2.5 h. The mixture was then acidified with dil HCl and extracted with AcOEt. The AcOEt extract was, after drying on $MgSO_4$, chromatographed on a silica-gel column to afford **10** [light brown crystals, mp 132—133 °C, 63.5 mg; 17%. Found: C, 74.97; H, 5.04%. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03%. ^1H NMR δ=5.52 (2H, s) and 6.7—8.1 (10H, m). ^{13}C NMR δ=71.7, 117.8, 128.4 (2C), 129.1 (3C), 129.7, 132.7, 134.3, 136.8, 138.4 (2C), 164.3, and 193.6. IR ν: 1685, 1625, 1590, 1565, 1495, 1470, 1450, 1430, 1405, 1395, 1375, and 1300 cm^{-1}. λ_{max}^{MeOH}: 241 nm (ε=31000), 321 (8800), 346 (7300, sh), and 361 (4700, sh)], **12** [colorless crystals, mp 118—120 °C, 222 mg; 59%. Found: C, 75.15; H, 5.08%. ^1H NMR δ=4.4—4.8 (1H, br), 6.19 (1H, s), 6.8—7.2 (4H, m), 7.2—7.6 (4H, m), and 7.8—8.1 (2H, m). ^{13}C NMR δ=73.9, 128.9 (2C), 129.0 (3C), 134.1 (2C), 135.4, 136.4, 137.2, 142.4, 151.4, 185.7, and 199.1. IR ν: 3300, 1670, 1620, 1590, 1535, 1515, 1465, 1445, 1405, and 1330 cm^{-1}. λ_{max}^{MeOH}: 233 nm (ε=25000) and 307 (7900)], and unreacted tropolone [36.8 mg; 16%].

Conversion of 10 to 12. An HMPA solution (1 cm^3) of NaH (trace) and **10** (25.1 mg) was stirred at room temperature for 10 min. After acidification with dil HCl, the mixture was extracted with AcOEt and chromatographed on a silica-gel column to give **12**, 11.1 mg (44%).

Attempted Base-Treatment of 2-Benzyloxytropone (3d). An anhydrous HMPA solution (1.5 cm^3) of NaH (6.8 mg) and **3d**[2] (60 mg) was kept at room temperature for 1.5 h. Thin-layer chromatograms of the mixture gave the recovered **3d** [44 mg; 74%] as the sole identifiable compound.

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References

1) T. Nozoe, K. Takase, and H. Matsumura, "Non-Benzenoid Aromatic Compounds," Vol. 13 of "Dai Yuki Kagaku (Comprehensive Organic Chemistry) (ed. M. Kotake)," Asakura Shoten, Tokyo (1960), pp. 181—191.

2) H. Takeshita, H. Mametsuka, A. Chisaka, and N. Matsuo, *Chem. Lett.*, **1981**, 73.

3) H. Takeshita and H. Mametsuka, *Heterocycles*, **22**, 663 (1984).

4) H. Takeshita, H. Mametsuka, and H. Motomura, *J. Heterocyclic Chem.*, **23**, 1211 (1986).

5) H. Takeshita, N. Matsuo, and H. Mametsuka, *Bull. Chem. Soc. Jpn.*, **57**, 2321 (1984).

6) We thank Mr. Norihide Matsuo, M. Eng., for this experiment.

7) On the basis of a mechanistic ground, a formation of 3-substituted tropone derivatives via a less-strained oxetane intermediate than the oxirane intermediate, **B**, as depicted in Scheme 2 may be equally probable.

8) T. Nozoe, T. Mukai, and J. Minegishi, *Proc. Jpn. Acad.*, **27**, 419 (1951); W. von E. Doering and C. F. Haskey, *J. Am. Chem. Soc.*, **74**, 5688 (1952).

9) T. Nozoe, T. Mukai, J. Minegishi, and T. Fujisawa, *Sci. Repts. Tohoku Univ., Ser. I*, **37**, 388 (1953); T. Mukai, *Bull. Chem. Soc. Jpn.*, **31**, 852 (1958).

10) Benzenoid analogs, salicylaldehyde or other phenolic compounds carrying electron-attractive substituents, seem to be worth trying, but at least to date every attempt was unsuccessful.