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Insertion of Fischer Carbene Complexes into the Carbon−Carbon Bond of 1,2-Diphenylcyclopropenone: Formation of Cyclobutenones and *o*- and *p*-Methoxyphenol Derivatives

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Summary: The reaction between 1,2-diphenylcyclopropenone and Fischer carbene complexes has been investigated. The reaction produced a mixture of diphenylacetylene and cyclobutenones. When α,β-unsaturated carbene complexes were employed, benzannulation products and diphenylacetylene were produced. A mechanism involving metallacyclobutenone formation, followed by either carbene insertion and reductive elimination or fragmentation has been proposed.

Recently, we reported that carbon−carbon bond insertion is the major reaction pathway when Fischer carbene complexes react with 1,2-cyclobutenediones,[1] affording 4-cyclopentene-1,3-diones and/or 5-alkylidenefuranones. Other strained rings might lead to insertion products as well. A variety of additional ring systems were tested in this reaction, including cyclobutenones, cyclobutenes, cyclopropanes, cyclopentadienones, and cyclopropenones. Of these, only the cyclopropenone ring system afforded carbon−carbon bond insertion products when treated with Fischer carbene complexes. Herein we report the reaction between 1,2-diphenylcyclopropenone and Fisher carbene complexes.

Results

Reaction of 1,2-diphenylcyclopropenone (**1**) and methylcarbene complex **2A** afforded cyclobutenone **3A** (35%), accompanied by diphenylacetylene (20%) (Scheme 1). Similarly, reaction of diphenylcyclopropenone and cyclopropylcarbene complex **2B** afforded the corresponding cyclobutenone **3B** (32%) and diphenylacetylene (18%). Reaction of diphenylcyclopropenone and phenylcarbene complex **2C** led to diphenylacetylene (5%) and benzannulation products **4** (39%) and **5** (16%) (Scheme 2). Similarly, the reaction of diphenylcyclopropenone and alkenylcarbene complex **2D** afforded diphenylacetylene (4%) and benzannulation products **6** (48%) and **7** (8%).

Discussion

For the reaction in Scheme 1, a mechanism involving CO dissociation followed by oxidative addition into the cyclopropenone carbon−carbon σ-bond[2] can be invoked to explain formation of all the observed products (Scheme 3). Oxidative addition affords metallacyclobutene **8**,[3] which undergoes either retro [2 + 2] cycloaddition[4] to afford the starting carbene complex and diphenylacetylene or vinyl or acyl migration[5] to provide either metallacyclopentenone **9** or **10**, respectively. Simple reductive elimination from the metallacyclopentenones provides the observed cyclobutenones. Alternatively, the cyclobutenones might arise from direct reaction of the starting carbene complexes with diphenylacetylene.[6]

A more complex situation arises from the reaction of unsaturated carbene complexes **2C** and **2D** with diphenylcyclopropenone. The direct reaction of the starting carbene complexes with diphenylacetylene can afford only benzannulation products **4** or **6**.[7] Similarly, thermal rearrangement of unobserved cyclobutenones **3C** or **3D** can afford only benzannulation products **4** or **6**.[8] These processes cannot account for the formation of compounds **5** and **7**; *o*-methoxyphenols have been prepared from dienylcarbene complexes,[9] but have never been reported in the reaction of simple alkynes and α,β-unsaturated carbene complexes.

The mechanism for formation of benzannulation products **5** and **7** is presented in Scheme 4. Here, metallacyclopentenone **10C** (**10D**) undergoes a 1,3-shift of chromium. The resulting metallacycloheptadienone **11** then undergoes reductive elimination and enolization, affording the benzannulation products. Although an earlier mechanistic proposal involves metallacycloheptadienone intermediates (e.g. **11**),[10] the 1,3-shift step is without precedent. As noted previously, benzannulation products **4** and **6** could arise from a variety of

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[2] For reviews of cyclopropenone chemistry, see: (a) Billups, W. E.; Moorehead, A. W. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: New York, 1987; Chapter 24. (b) Eicher, T.; Weber, J. L. *Top. Curr. Chem.* **1975**, *57*, 1−109. (c) Potts, K. T.; Baum, J. S. *Chem. Rev.* **1974**, *74*, 189−213.

[3] A similar chromacyclobutenone intermediate has been proposed in a different reaction process. (a) Xu, Y.-C.; Challener, C. A.; Dragisch, V.; Brandvold, T. A.; Peterson, G. A.; Wulff, W. D.; Williard, P. G. *J. Am. Chem. Soc.* **1989**, *111*, 7269−7271. (b) For a possible related reaction, see: Semmelhack, M. F.; Ho, S.; Steigerwald, M.; Lee, M. C. *J. Am. Chem. Soc.* **1987**, *109*, 4397−4399.

[4] For other examples of metal carbonyl-induced conversion of diphenylcyclopropenone to diphenylacetylene, see: (a) Baba, A.; Ohshiro, Y.; Agawa, T. *J. Organomet. Chem.* **1976**, *110*, 121−127. (b) Bird, C. W.; Briggs, E. M.; Hudec, J. *J. Chem. Soc. C* **1967**, 1862−1864. (c) Wang, S. L. B.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 4550−4552.

[5] (a) Chong, K. S.; Green, M. L. H. *Organometallics* **1982**, *1*, 1586−1590. (b) Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984−5986. (c) Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650−2659.

[6] (a) Dötz, K. H.; Dietz, R. E. *J. Organomet. Chem.* **1978**, *157*, C55−C57. (b) Chan, K. S.; Peterson, G. A.; Brandvold, T. A.; Faron, K. L.; Challener, C. A.; Hyldahl, C.; Wulff, W. D. *J. Organomet. Chem.* **1987**, *334*, 9−56.

[7] For a recent review of the benzannulation reaction between carbene complexes and alkynes, see: Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon: Oxford, U.K., 1991; Vol. 5, pp 1065−1113.

[8] Moore, H. W.; Yerxa, B. R. *Chemtracts: Org. Chem.* **1992**, *5*, 273−313.

[9] Merlic, C. A.; Xu, D. *J. Am. Chem. Soc.* **1991**, *113*, 7418−7420.

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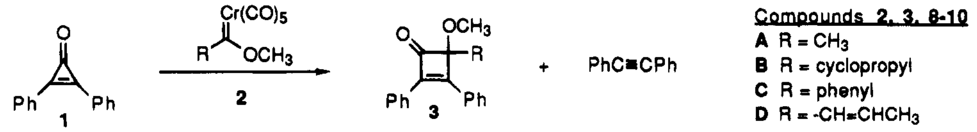
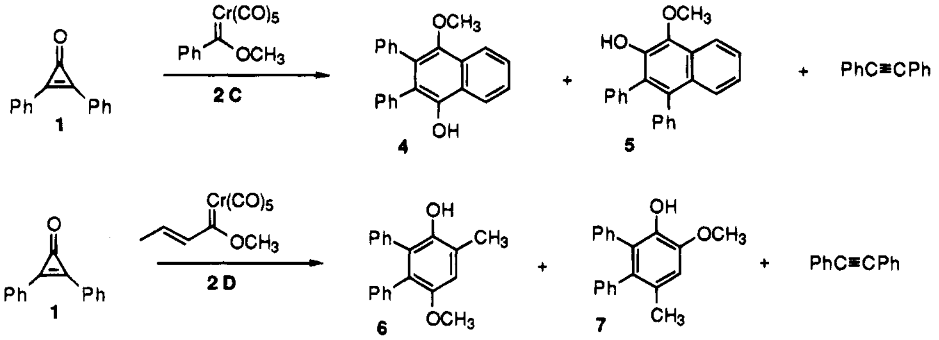
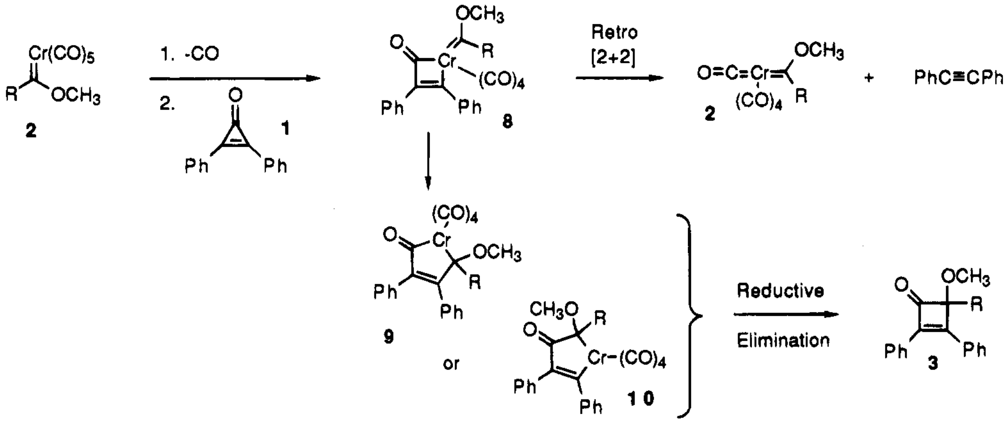
Scheme 1



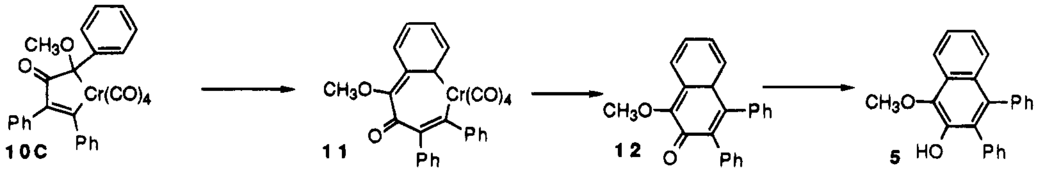
Scheme 2



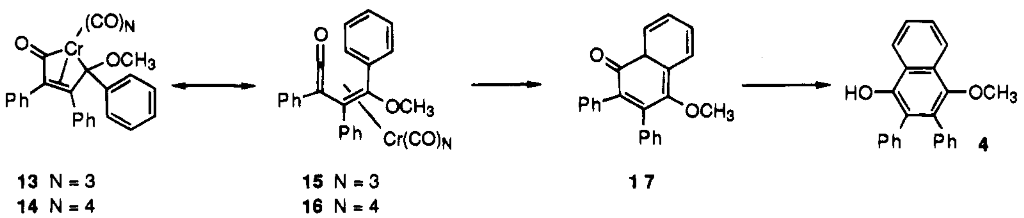
Scheme 3



Scheme 4



Scheme 5



well-precedented reaction pathways. These compounds might also arise from intermediate metallacyclopentenone **9C** (Scheme 5). Coordination of the double bond in compound **9C** provides compound **14**, which is a resonance form of coordinatively saturated vinylketene complex **16**; the analog of **16** having one less CO ligand (**15**) is a key intermediate in the carbene–alkyne benzanulation reaction.[11] Given the thermal instability of chromium–diene complexes,[12] loss of a CO ligand from complex **14** (**16**) is predicted to be facile at the reaction temperature.

Conversion of carbene complex **8** into complex **9** involves migration of a vinyl group, while conversion to complex **10** involves an acyl migration. If it is assumed that all of the benzannulation products in

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(10) (a) Casey, C. P. In *Reactive Intermediates;* Jones, M., Jr., Moss, R. A., Eds.; Wiley-Intersience: New York, 1981; Vol. 2, Chapter 4, pp 135–174. (b) Casey, C. P. In *Reactive Intermediates;* Jones, M., Jr., Moss, R. A., Eds.; Wiley-Intersience: New York, 1985; Vol. 3, Chapter 4, pp 109–150.

(11) Bos, M. E.; Wulff, W. D.; Miller, R. A.; Chamberlin, S.; Brandvold, T. A. *J. Am. Chem. Soc.* **1991**, *113*, 9293–9319.

(12) Kreiter, C. G. *Adv. Organomet. Chem.* **1986**, *26*, 297–375.

Scheme 2 arise from metallacyclopentenone intermediates **9** and **10**, then the ratios of **4**:**5** (71:29) and **6**:**7** (86:14) suggest that vinyl migration is favored over acyl migration in complex **8**. A strong preference for vinyl migration over acyl migration was previously reported for carbon monoxide insertions involving metallacyclobutenones;[13] however in pinacol-type ring expansions of cyclobutenone derivatives, strong preferences for acyl migration have been noted.[14]

In summary, chromium carbene complexes insert into the carbon–carbon σ-bond of diphenylcyclopropenone and ultimately afford products that would have been produced from the reaction of the carbene complex with the corresponding alkyne, diphenylacetylene. The intermediates of the reaction resemble the intermediates derived from the reaction of carbene complexes and alkynes,[11] but have an extra CO ligand. To some extent benzannulation reactions appear to proceed via allylic rearrangement (1,3-shift) of intermediate metal complexes rather than through electrocyclization of vinylketene intermediates. Although the involvement of chromacycloheptadienones in the reaction between arylcarbene complexes and alkynes has largely been ruled out, the formation of phenols **5** and **7** demonstrates that chromacycloheptadienones are potential precursors to benzannulation products.

Experimental Section

General. Nuclear magnetic resonance (^{1}H and ^{13}C) spectra were recorded on a Bruker AF200 (200 MHz) or Bruker AF400 (400 MHz) spectrometer. Chemical shifts are reported in parts per million (δ) downfield from an internal tetramethylsilane reference. Coupling constants (*J* values) are reported in hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Infrared spectra were recorded on a Nicolet 5DXC FT-IR spectrometer. Band positions are reported in reciprocal centimeters (cm^{-1}). Band intensities are reported relative to the most intense band and are listed as br (broad), vs (very strong), s (strong), m (medium), and w (weak). Mass spectra (MS) were obtained on a VG 7070E spectrometer using electron impact (EI) or chemical ionization (CI) or on a Hewlett-Packard GC-Mass Spec 5970B with a mass selection detector; *m/e* values are reported, followed by the relative intensity in parentheses. Flash column chromatography was performed using thick-walled glass columns and "flash grade" silica (Bodmann 230–400 mesh). Routine thin layer chromatography (TLC) was effected by using precoated 0.25-mm silica gel plates purchased from Whatman. The relative proportion of solvents in mixed chromatography solvents refers to the volume:volume ratio.

Diphenylcyclopropenone was purchased from Aldrich Chemical Co. and used without further purification. Carbene complexes **2A**–**2D** were prepared from the corresponding organolithium reagent according to a literature procedure.[15] Dioxane was distilled from sodium–benzophenone ketyl prior to use. All reactions were performed in an inert atmosphere created by a slight positive pressure (ca. 0.1 psi) of nitrogen.

General Procedure. Reaction of Carbene Complexes with Diphenylcyclopropenone. A solution of diphenylcyclopropenone (1.00 mmol) and carbene complex (1.30 mmol) in dioxane (5 mL) was heated to reflux under nitrogen for a period of 6 h. The mixture was allowed to cool to room temperature, and the solvent was removed on a rotary evaporator. The residue was dissolved in 9:1 hexane–ethyl acetate (25 mL) and filtered through Celite. After removal of solvent on a rotary evaporator, final purification was achieved by flash chromatography on silica gel using 19:1 hexane–ethyl acetate as the eluent.

Reaction of Carbene Complex 2A with Diphenylcyclopropenone. The General Procedure was followed using diphenylcyclopropenone (**1**) (0.206 g, 1.00 mmol) and carbene complex **2A** (0.325 g, 1.30 mmol). After chromatographic purification, two fractions were isolated. The first fraction (R_f = 0.80 in 9:1 hexane–ethyl acetate) yielded diphenylacetylene (0.056 g, 20%). The product in the second fraction (R_f = 0.33 in 9:1 hexane–ethyl acetate) was assigned as 4-methoxy-4-methyl-2,3-diphenylcyclobutenone (**3A**) (0.093 g, 35%). ^{1}H NMR (CDCl$_3$): δ 7.85 (m, 2 H), 7.74 (m, 2 H), 7.48–7.38 (m, 6 H), 3.36 (s, 3 H), 1.68 (s, 3 H). ^{13}C NMR (CDCl$_3$): δ 195.0, 171.5, 144.4, 131.9, 130.9, 129.6, 129.2, 129.0, 128.8, 128.2, 128.0, 97.1, 52.9, 19.6. IR (CDCl$_3$): 3067 (w), 2981 (w), 2935 (w), 2832 (w), 1750 (vs), 1622 (w), 1444 (w), 1348 (m), 1145 (m), 1063 (w) cm^{-1}. Mass spec (EI): *m/e* 264 (M$^+$, 100), 249 (65), 235 (15), 221 (21), 205 (38), 193 (39), 178 (90), 176 (36), 165 (16), 159 (18), 152 (22), 129 (11), 115 (38), 91 (12), 77 (19), 51 (13). HRMS: calcd for $C_{18}H_{16}O_2$, 264.1150; found, 264.1129.

Reaction of Carbene Complex 2B with Diphenylcyclopropenone. The General Procedure was followed using diphenylcyclopropenone (**1**) (0.206 g, 1.00 mmol) and carbene complex **2B** (0.359 g, 1.30 mmol). After chromatographic purification, two fractions were isolated. The first fraction (R_f = 0.80 in 9:1 hexane–ethyl acetate) yielded diphenylacetylene (0.050 g, 18%). The product in the second fraction (R_f = 0.38 in 9:1 hexane–ethyl acetate) was assigned as 4-cyclopropyl-4-methoxy-2,3-diphenylcyclobutenone (**3B**) (0.093 g, 32%). ^{1}H NMR (CDCl$_3$): δ 7.93 (m, 2 H), 7.82 (m, 2 H), 7.40–7.55 (m, 6 H), 3.42 (s, 3 H), 1.45 (tt, 1 H, *J* = 8.3, 5.3 Hz), 0.82 (m, 1 H), 0.60 (m, 2 H), 0.42 (m, 1 H). ^{13}C NMR (CDCl$_3$): δ 193.2, 170.8, 145.3, 131.7, 131.2, 129.6, 129.1, 128.8, 128.3, 128.0, 100.1, 53.1, 14.6, 3.4, 2.6. IR (CDCl$_3$): 3080 (w), 3010 (w), 2940 (m), 2825 (w), 1753 (s), 1625 (w), 1600 (w), 1485 (w), 1450 (m), 1355 (m), 1100 (s), 1095 (m), 1030 (w) cm^{-1}. MS (EI): *m/e* 290 (M$^+$), 262 (100), 247, 234, 191, 152, 115, 69. The spectral data for compound **3B** were in agreement with those previously reported for this compound.[15]

Reaction of Carbene Complex 2C with Diphenylcyclopropenone. The General Procedure was followed using diphenylcyclopropenone (**1**) (0.206 g, 1.00 mmol) and carbene complex **2C** (0.406 g, 1.30 mmol). After chromatographic purification, three fractions were isolated. The first fraction (R_f = 0.80 in 9:1 hexane–ethyl acetate) yielded diphenylacetylene (0.014 g, 5%). The product in the second fraction (R_f = 0.40 in 9:1 hexane–ethyl acetate) was assigned as 4-methoxy-2,3-diphenyl-1-naphthol (**4**) (0.128 g, 39%). ^{1}H NMR (CDCl$_3$): δ 8.22 (dd, 1 H, *J* = 7.9, 1.6 Hz), 8.10 (dd, 1 H, *J* = 9.0, 1.3 Hz), 7.49 (m, 2 H), 7.24–7.04 (m, 10 H), 5.36 (s, 1 H), 3.41 (s, 3 H). ^{13}C NMR (CDCl$_3$): δ 146.8, 144.6, 136.9, 135.1, 131.1, 130.8, 128.9, 128.3, 127.7, 127.4, 126.7, 126.4, 125.8, 124.4, 122.8, 122.2, 121.7, 61.3. IR (CCl$_4$): 3552 (vs), 3062 (w), 2931 (w), 2843 (w), 1602 (w), 1589 (m), 1495 (m), 1456 (m), 1386 (s), 1367 (vs), 1304 (vs), 1288 (m), 1212 (m), 1142 (m), 1078 (vs), 1060 (m), 987 (s) cm^{-1}. Mass spec (EI): *m/e* 326 (M+, 100), 311, 293, 283, 265, 252, 233, 205, 178, 121, 105, 77. The spectral data are in agreement with those previously reported for this compound.[16] This compound afforded the expected naphthoquinone derivative upon oxidation with ceric ammonium nitrate.[17] The product in the third fraction (R_f = 0.18 in 9:1 hexane–ethyl acetate) was assigned as 1-methoxy-3,4-

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[16] Dötz, K. H. *J. Organomet. Chem.* **1977**, *140*, 177–186.

[17] Wulff, W. D.; Tang, P.-C.; McCallum, J. S. *J. Am. Chem. Soc.* **1981**, *103*, 7677–7678.

diphenyl-2-naphthol (**5**) (0.530 g, 16%). ^{1}H NMR ($CDCl_3$): δ 8.00 (ddd, 1 H, J = 8.5, 1.2, 0.7 Hz), 7.44 (m, 2 H), 7.20–7.03 (m, 11 H), 5.61 (s, 1 H), 4.00 (s, 3 H). ^{13}C NMR (CDCl3): δ 143.0, 139.2, 138.5, 136.0, 135.9, 131.4, 131.3, 130.8, 128.4, 127.9, 127.6, 127.4, 127.1, 126.6, 126.2, 123.8, 120.4, 61.5. IR (CCl_4): 3544 (s), 3063 (m), 3028 (w), 2960 (m), 2931 (m), 1713 (m), 1604 (s), 1494 (m), 1446 (s), 1372 (vs), 1286 (s), 1214 (s), 1133 (s), 1091 (s) cm^{-1}. Mass spec (EI): *m*/*e* 326 (M^+, 100), 311 (54), 283 (27), 265 (16), 252 (8), 239 (8), 208 (16), 178 (11), 162 (8), 133 (8), 121 (59), 105 (19), 97 (11), 91 (8), 83 (8), 77 (22), 69 (19), 57 (54). HRMS: calcd for $C_{23}H_{18}O_2$, 326.1307; found, 326.1310. The extensive downfield shift for the methoxy protons in naphthol **5** was also noted for a similar compound, 1-methoxy-3-phenyl-2-naphthol.[9] Attempted oxidation by ceric ammonium nitrate failed to produce a stable naphthoquinone derivative.[17]

Reaction of Carbene Complex 2D with Diphenylcyclopropenone. The General Procedure was followed using diphenylcyclopropenone (**1**) (0.206 g, 1.00 mmol) and carbene complex **2D** (0.406 g, 1.30 mmol). After chromatographic purification, three fractions were isolated. The first fraction (R_f = 0.80 in 9:1 hexane–ethyl acetate) yielded diphenylacetylene (0.011 g, 4%). The product in the second fraction (R_f = 0.40 in 9:1 hexane–ethyl acetate) was assigned as 4-methoxy-6-methyl-2,3-diphenylphenol (**6**) (0.140 g, 48%). ^{1}H NMR ($CDCl_3$): δ 7.25–7.05 (m, 8 H), 7.01 (m, 2 H), 6.83 (s, 1 H), 4.72 (s, 1 H), 3.69 (s, 3 H), 2.35 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 150.3, 145.0, 136.8, 135.3, 131.0, 130.8, 128.8, 128.2, 127.5, 127.2, 126.1, 123.8, 114.2, 56.6, 16.6. IR ($CDCl_3$): 3553 (m), 3563 (w), 3028 (w), 2955 (w), 2936 (w), 2839 (w), 1605 (w), 1466 (vs), 1443 (m), 1408 (vs), 1342 (m), 1292 (m), 1253 (w), 1215 (vs), 1192 (s), 1165 (s), 1118 (vs), 1061 (s), 1030 (w) cm^{-1}. Mass spec (EI): *m*/*e* 290 (M^+, 100), 275 (19), 260 (11), 257 (6), 229 (5), 202 (5), 178 (3), 176 (2), 152 (2), 115 (3), 101 (2). HRMS: calcd for $C_{20}H_{18}O_2$, 290.1307; found, 290.1320. Oxidation of this compound with aqueous ceric ammonium nitrate produced a stable quinone derivative.[17] The product in the second fraction (R_f = 0.35 in 9:1 hexane–ethyl acetate) was assigned as 6-methoxy-4-methyl-2,3-diphenylphenol (**7**) (0.024 g, 8%). ^{1}H NMR ($CDCl_3$): δ 7.45–7.26 (m, 10 H), 6.51 (s, 1 H), 4.88 (s, 1 H), 3.75 (s, 3 H), 2.13 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 156.4, 150.7, 137.1, 136.3, 133.3, 130.9, 130.6, 128.9, 128.5, 127.5, 127.4, 127.2, 104.9, 55.8, 20.9. IR ($CDCl_3$): 3544 (m), 2962 (m), 2931 (m), 2856 (w), 1618 (m), 1465 (m), 1407 (m), 1322 (m), 1262 (vs), 1193 (m), 1158 (s), 1094 (vs), 1013 (s) cm^{-1}. Mass spec (EI): *m*/*e* 290 (M^+, 100), 275 (7), 260 (7), 257 (3), 229 (4), 228 (3), 202 (4), 115 (3), 77 (2). HRMS: calcd for $C_{20}H_{18}O_2$, 290.1307; found, 290.1306. Attempted oxidation to the quinone using ceric ammonium nitrate afforded a complex reaction mixture.[17]

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