is converted very easily to the corresponding azine, just by standing.

The (unhindered) ketones that were conjugated (camphorquinone 12; acetophenones 14, 17, 19) gave hydrazones with either no azines, or just small amounts of azines. In the cases where azines were formed (14, 19), their amount increases upon standing, faster if the hydrazone is a liquid (14), slower where it is a solid (19).

In cases of unconjugated ketones (1–3, 6), the ketones that have a phenol moiety gave hydrazones with no azines, or just a very small amount of azines. The azine amount increased upon standing, but extremely slowly (over a period of over a year). In contrast, the ketone 6, which does not have the phenol moiety, gave a mixture of hydrazone (minor) and azine (major), which was converted upon standing in the solid state to azine after a couple of months.

In summary, the few ketones that we have studied indicate that the mechanisms of formation of azines is neither simple nor straightforward and deserves further study. Instead of a nucleophilic addition–elimination, an electron-transfer process could be operating. Such processes are usually not sensitive to steric hindrance and also show a different electronic demand than simple nucleophilic substitutions.

Synthesis and Iron Carbonyl Promoted Coupling Reactions of 7-(Aryloxy)norbornadienes

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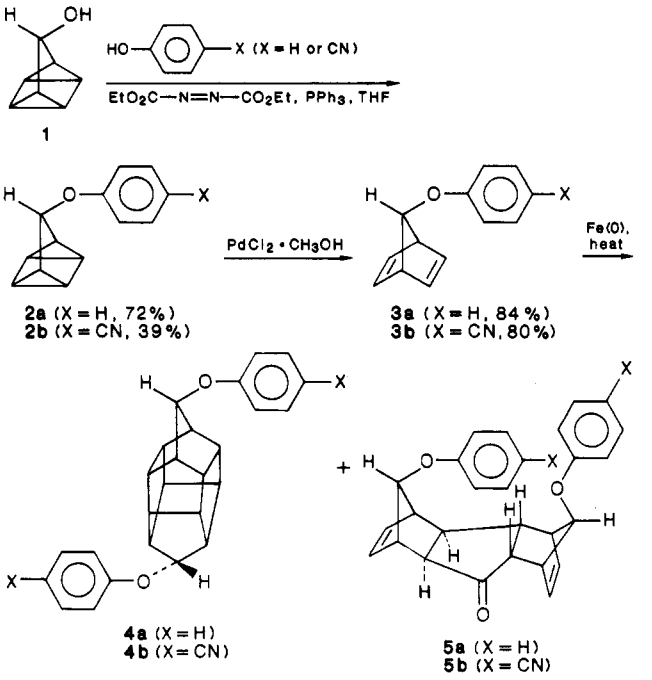
Thermal reactions of 7-substituted norbornadienes with iron carbonyls provide a convenient method for synthesizing a variety of unusual polycyclic compounds.[1,2] In this connection, we desired to study the corresponding reactions by employing 7-(aryloxy)norbornadienes as substrates. However, to our knowledge, no prior syntheses of 7-(aryloxy)norbornadienes have been reported. Accordingly, it was necessary to devise a method by which this class of compounds could be synthesized. The route summarized in Scheme I has been found to be useful for this purpose. The key synthetic step involves application of the Mitsunobu reaction[3] for converting 3-hydroxyquadricyclane (1) into 3-(aryloxy)quadriclanes **2a** and **2b**.

Scheme I



Thus, a tetrahydrofuran solution of 3-hydroxyquadricyclane (1)[4] was reacted with phenol in the presence of diethyl azodicarboxylate and triphenylphosphine in tetrahydrofuran solvent. This reaction afforded the corresponding 3-phenoxyquadricyclane (**2a**, Scheme I) in 72% yield. Valence isomerization of **2a** to the corresponding norbornadiene derivative, **3a**, was performed by treating **2a** with methanolic $PdCl_2$.[5] Similarly, Mitsunobu reaction[3] of 1 with *p*-cyanophenol afforded 3-(*p*-cyanophenoxy)quadricyclane (**2b**) in good yield. Treatment of **2b** with methanolic $PdCl_2$ promoted its valence isomerization to **3b**. We conclude that the route shown in Scheme I is useful for synthesing 3-(aryloxy)quadricyclanes and 7-(aryloxy)norbornadienes from the readily available[4] 3-hydroxyquadricyclane.

Next, the thermal reactions of **3a** and of **3b** with $Fe(CO)_5$ (di-*n*-butyl ether solvent, reflux 72 h) and with Fe_2CO_9 (dry benzene solvent, reflux 72 h) were studied. In all cases, oxidative workup was performed by stirring the reaction mixture with an acetone solution of excess ferric chloride heptahydrate for one week to decompose unreacted iron carbonyl and/or Fe(0) complexes that might be present.[6] The organic products were separated by column chromatography on silica gel by using a gradient elution scheme (see the Experimental Section).

Reactions of **3a** and **3b** with Fe(0) each afforded a cage dimer (**4a** and **4b**, respectively) and a dimer ketone (**5a** and **5b**, respectively) in low to moderate yields (Table I). The syn,exo,trans,endo,syn configuration of each dimer ketone, **5a**[1k] and **5b**,[8] was established by X-ray structural analysis. Surprisingly, the reaction of **3b** with $Fe(CO)_5$ afforded only

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Table I. Products Formed from Reactions of 3a and 3b with Iron Carbonyls

substrate	Fe(0) reagent	conditions	products
3a	$Fe(CO)_5$	$(n\text{-}Bu)_2O$, reflux 72 h under N_2	3a (8%) + 4a (19%) + 5a (11%)
	$Fe_2(CO)_9$	dry benzene, reflux 72 h under N_2	4a (13%) + 5a (31%)
3b	$Fe(CO)_5$	$(n\text{-}Bu)_2O$, reflux 72 h under N_2	4b (1.3%) + *p*-cyanophenol (36%)
	$Fe_2(CO)_9$	dry benzene, reflux 72 h under N_2	3b (56%) + 4b (2.9%) + 5b (6.2%)

traces of cage dimer **4b** and no dimer ketone; instead, the major product of this reaction was *p*-cyanophenol (36%).

It was of interest to determine the origin of the *p*-cyanophenol in this reaction, i.e., to determine whether ether cleavage took place during the reaction of **3b** with Fe(0) (an occurence which, to our knowledge, is unprecedented),[9] or if it happened instead during oxidative workup with ferric chloride (a moderately strong Lewis acid). Accordingly, a control study was performed by stirring **3b** with an acetone solution of ferric chloride heptahydrate at room temperature for one week. During this time, cleavage of the ether linkage gradually occurred, thereby affording material that was identical in all respects with authentic *p*-cyanophenol.

Some years ago, we observed that another 7-(Lewis base substituted) norbornadiene, i.e., 7-*tert*-butoxynorbornadiene, also afforded exclusively the corresponding syn,exo,trans,endo,syn dimer ketone.[1d] Since we now find that **3a** behaves similarly in its thermal reaction with either $(Fe(CO)_5$ or $Fe_2(CO)_9$, we considered **3a** to be a model for a 7-(aryloxy)norbornadiene in which the OPh group functions as an electron donor.[1h] For comparison, **3b** was chosen as substrate with the expectation that the presence of the *p*-cyano substituent in the OAr group would exert an electron-withdrawing effect, thereby reducing the availability of lone electron pairs on the OAr oxygen for coordination with Fe(0).[1h] However, our results indicate that, even if this is true, the influence of the distant *p*-cyano substituent in the OAr group is not sufficient to alter the stereochemistry of iron carbonyl promoted coupling of **3b** to carbon monoxide vis-à-vis the corresponding reaction that involves **3a** as substrate.

Experimental Section

Melting points are uncorrected. High-resolution mass spectra were obtained by personnel at the Midwest Center for Mass Spectrometry, Department of Chemistry, University of Nebraska—Lincoln, Lincoln, NE 68588-0362.

3-Phenoxyquadricyclane (2a). A modification of the procedure described by Manhas and co-workers[3e] was employed to synthesize **2a**. Thus, a solution of 3-hydroxyquadricyclane[4] (108 mg, 1.0 mmol), phenol (94 mg, 1.0 mmol), triphenylphosphine (262 mg, 1.0 mmol), and diethyl azodicarboxylate (174 mg, 1.0 mmol) in dry tetrahydrofuran (THF, 25 mL) was stirred under nitrogen at room temperature for 4 days. The reaction mixture then was concentrated in vacuo, and the residue was purified via column chromatography on silica gel by eluting with 1:6 ethyl acetate–hexane mixed solvent. One of the chromatographic fractions was further purified via column chromatography on silica gel by using 1:30 ethyl acetate–hexane mixed solvent as eluent. A colorless oil was thereby obtained (129 mg, 72%); distillation at reduced pressure afforded pure **2a** as a colorless oil, bp 101 °C (0.1 mmHg), that solidified upon standing. Recrystallization from aqueous ethanol afforded colorless needles: mp 47.5–48.0 °C; IR (KBr) 3040 (w), 2900 (w), 1570 (s), 1470 (s), 1225 cm^{-1} (vs); ^1H NMR ($CDCl_3$) δ 1.4–2.05 (m, 6 H), 5.4, (s, 1 H), 6.6–7.8 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 14.44 (d), 16.19 (d), 25.95 (d), 84.67 (d), 115.50 (d), 120.44 (d), 129.28 (d), 158.94 (s); mass spectrum (70 eV), *m/e* (relative intensity) 184.0 (molecular ion, 1.0), 91.0 (100).

Anal. Calcd for $C_{13}H_{12}O$: C, 84.77; H, 6.55. Found: C, 84.79; H, 6.62.

(9) (a) Bhatt, M. V.; Kulkarni, S. U. *Synthesis* **1983**, 249. (b) Tiecco, M. *Synthesis* **1988**, 749.

7-Phenoxynorbornadiene (3a).[5] To a solution of **2a** (5.0 g, 27 mmol) in dry methanol (200 mL) was added $PdCl_2$ (100 mg), and the resulting mixture was stirred under nitrogen at room temperature for 48 h. The reaction mixture was then filtered to remove catalyst, and the residue was washed with methanol (10 mL). The combined filtrates were concentrated in vacuo, thereby affording a brown oil. The crude product was purified via column chromatography on silica gel by using 1:9 ethyl acetate–hexane as eluent, thereby affording **3a** as a colorless oil (4.2 g, 84%). Distillation at reduced pressure afforded pure **3a** as a colorless oil: bp 93 °C (0.8 mmHg); IR (KBR) 3020 (w), 2970 (w), 1540 (m), 1470 (m), 1220 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 3.76 (m, 2 H), 4.36 (m, 1 H), 6.7–7.3 (complex m, total 9 H); ^{13}C NMR ($CDCl_3$) δ 52.93 (d), 104.31 (d), 115.34 (d), 120.90 (d), 129.22 (d), 137.30 (d), 139.80 (d), 157.35 (s); mass spectrum (70 eV), *m/e* (relative intensity) 184.0 (molecular ion, 5.1), 91.0, (100.0).

Anal. Calcd for $C_{13}H_{12}O$: M_r 184.0840. Found (high-resolution mass spectrometry): M_r 184.0835.

3-(*p*-Cyanophenoxy)quadricyclane (2b). The same procedure used for the synthesis of **2a**, above, was employed to synthesize **2b**. The product was purified via column chromatography on silica gel by using 1:9 ethyl acetate–hexane mixed solvent as eluent. Pure **2b** was thereby obtained (39%) as colorless cubes: mp 131.5 °C; IR (KBr) 2190 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.5–1.7 (m, 4 H), 1.8–2.0 (m, 2 H), 5.35 (s, 1 H), 7.1 (d, 2 H), 7.6 (d, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.92 (d), 16.46 (d), 26.01 (d), 85.37 (d), 103.60 (s), 115.97 (d), 119.32 (s), 133.90 (d), 162.37 (s); mass spectrum (70 eV), *m/e* (relative intensity) 209 (molecular ion, 1.1), 91 (100.0).

Anal. Calcd for $C_{14}H_{11}NO$: C, 80.36; H, 5.30. Found: C, 80.64; H, 5.56.

7-(*p*-Cyanophenoxy)norbornadiene (3b).[5] A suspension of **2b** (20 mg, 0.095 mmmol) and $PdCl_2$ (5 mg) in methanol (20 mL) was stirred under nitrogen at room temperature for 48 h. The reaction mixture then was filtered to remove catalyst, and the residue was washed with methanol (5 mL). The combined filtrates were concentrated in vacuo, and the residue was purified by column chromatography on silica gel by using 10% ethyl acetate–hexane mixed solvent as eluent. Recrystallization of the material thereby obtained from ethanol afforded pure **3b** (16 mg, 80%) as a colorless microcrystalline solid: mp 83.0–83.5 °C; IR (KBr) 2205 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 3.44–3.66 (m, 2 H), 4.16–4.32 (br s, 1 H), 6.48–6.96 (m, 6 H), 7.36–7.60 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 52.58 (d), 103.12 (d), 104.18 (s), 115.88 (d), 119.12 (s), 133.96 (d), 137.47 (d), 140.03 (d), 161.03 (s).

Anal. Calcd for $C_{14}H_{11}NO$: C, 80.36; H, 5.30. Found: C, 80.18; H, 5.40.

Reaction of 3a with $Fe(CO)_5$. To a solution of **3a** (7.50 g, 40.7 mmol) in freshly distilled di-*n*-butyl ether (50 mL) under nitrogen was added a solution of $Fe(CO)_5$ (16.0 g, 82.1 mmol) in freshly distilled di-*n*-butyl ether (10 mL). The reaction mixture was refluxed under nitrogen with stirring for 72 h and then was cooled to room temperature. A solution of ferric chloride hexahydrate (50 g, excess) in acetone (200 mL) was added, and the resulting mixture was stirred at room temperature for 7 days to decompose unreacted iron pentacarbonyl and Fe(0) complexes that might be present.[6] Distilled water (300 mL) was added, and the mixture was extracted with ethyl acetate (7 × 100 mL). The combined extracts were washed with water, dried (anhydrous magnesium sulfate), and filtered, and the filtrate was concentrated in vacuo. The residue was purified via elution chromatography on Florisil by using a 3%–15% ethyl acetate–hexane gradient elution scheme. After a forerun of unreacted **3a** (600 mg, 8%), cage dimer **4a** was collected (1.43 g, 19%) as a colorless microcrystalline solid: mp 220–221 °C; IR (KBr) 1580 (m), 1475 (m), 1240 (s), 1035 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 2.5–3.1 (m, 6 H), 2.73 (br s, 2 H), 2.9 (br s, 4 H), 4.93 (s, 2 H), 6.83–6.87 (m, 6 H), 7.2–7.3 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 48.66 (d), 49.30 (d), 51.20 (d), 51.29

(d), 51.93 (d), 53.41 (d), 90.49 (d), 115.42 (d), 120.48 (d), 129.30 (d), 158.10 (s); mass spectrum (70 eV), m/e (relative intensity) 368 (molecular ion, 23.9), 275 (100.0).

Anal. Calcd for $C_{26}H_{24}O_2$: M_r 368.1776. Found (high-resolution mass spectrometry): M_r 368.1771.

Further elution of the chromatography column afforded dimer ketone **5a** as a colorless microcrystalline solid. Repeated recrystallization from hexane afforded pure **5a** (885 mg, 11%) as a colorless microcrystalline solid: mp 138 °C; IR (KBr) 1714 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 2.0–2.2 (m, 2 H), 2.8–3.6 (m, 6 H), 4.1 (s, 1 H), 4.2 (s, 1 H), 6.0–6.3 (m, 4 H), 6.7–7.4 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 42.44 (d), 45.13 (d), 48.29 (d), 49.29 (d), 49.95 (d), 50.93 (d), 57.35 (d), 58.51 (d), 86.00 (d), 89.32 (d), 114.66 (d), 115.43 (d), 121.15 (d), 121.29 (d), 129.37 (d), 129.55 (d), 133.20 (d), 133.91 (d), 134.19 (d), 136.28 (d), 156.29 (d), 156.73 (d), 220.29 (s); mass spectrum (70 eV), m/e (relative intensity) 396 (molecular ion, 1.6), 303 (18.8), 275 (3.0), 91.0 (100.0).

Anal. Calcd for $C_{27}H_{24}O_3$: M_r 396.1726. Found (high-resolution mass spectrometry): M_r 396.1711.

Reaction of 3a with $Fe_2(CO)_9$. To a solution of **3a** (3.5 g, 19 mmol) in dry benzene (100 mL) under nitrogen was added iron enneacarbonyl (6.9 g, 19 mmol). The resulting mixture was refluxed under nitrogen with stirring for 72 h and then was cooled to room temperature, and a solution of ferric chloride hexahydrate (10.5 g, 39 mmol) in acetone (75 mL) was added. The resulting mixture was stirred under nitrogen at room temperature for 7 days and then was concentrated in vacuo. The residue was partitioned between ether (100 mL) and water (100 mL). The aqueous layer was extracted sequentially with ether (3 × 100 mL) and ethyl acetate (3 × 100 mL). The combined extracts were dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo. The residue was purified via elution chromatography on Florosil by using a 3%–30% ethyl acetate–hexane gradient elution scheme. Cage dimer **4a** (44 mg, 13%) and dimer ketone **5a** (1.10 g, 31%) were thereby obtained.

Reaction of 3b with $Fe_2(CO)_9$. To a solution of **3b** (1.7 g, 8 mmol) in dry benzene (50 mL) under nitrogen was added iron enneacarbonyl (2.9 g, 8 mmol). The resulting mixture was refluxed under nitrogen with stirring for 72 h and then was cooled to room temperature, and a solution of ferric chloride hexahydrate (4.6 g, 17 mmol) in acetone (30 mL) was added. The resulting mixture was stirred under nitrogen at room temperature for 7 days and then was concentrated in vacuo. Workup was performed in the manner described above for the corresponding reaction of **3a** with $Fe_2(CO)_9$. The crude product was purified via elution chromatography on Florisil by using a 3%–30% ethyl acetate–hexane gradient elution scheme. After a forerun of unreacted **3b** (950 mg, 56%), cage dimer **4b** (50 mg, 2.9%) was collected as a colorless microcrystalline solid: mp 246–248 °C; IR (KBr) 2210 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 2.60 (br s, 6 H), 2.73 (s, 2 H), 2.87 (br s, 4 H), 4.96 (s, 2 H), 6.90–6.95 (m, 6 H), 7.57–7.65 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 48.45 (d), 49.12 (d), 50.88 (d), 51.12 (d), 51.77 (d), 53.11 (d), 90.63 (d), 103.62 (s), 115.79 (d), 119.30 (s), 133.91 (d), 161.74 (s).

Anal. Calcd for $C_{26}H_{24}O_2$: M_r 418.1681. Found (high-resolution mass spectrometry): M_r 418.1666.

Further elution of the chromatography column afforded dimer ketone **5b** (105 mg, 6.2%) as a colorless microcrystalline solid. Repeated recrystallization from ethyl acetate–hexane afforded pure **5b** as a colorless microcrystalline solid: mp 197–199 °C; IR (KBr) 2200 (m), 1710 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 2.05–2.25 (m, 2 H), 2.73–2.80 (m, 1 H), 3.05–3.14 (m, 2 H), 3.23–3.32 (m, 2 H), 3.38–3.45 (m, 1 H), 4.15 (s, 1 H), 4.20 (s, 1 H), 6.06–6.30 (m, 4 H), 6.70–7.60 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 42.15 (d), 44.90 (d), 48.05 (d), 48.99 (d), 49.76 (d), 50.43 (d), 56.84 (d), 58.10 (d), 86.10 (d), 89.20 (d), 104.71 (s), 104.98 (s), 115.43 (d), 115.65 (d), 118.82 (s), 118.88 (s), 131.34 (d), 133.15 (d), 133.84 (d), 134.09 (d), 134.16 (d), 136.18 (d), 159.54 (s), 160.19 (s), 219.09 (s).

Anal. Calcd for $C_{27}H_{24}O_3$: M_r 446.1631. Found (high-resolution mass spectrometry): M_r 446.1653.

Reaction of 3b with $Fe(CO)_5$. To a solution of **3b** (3.0 g, 14 mmol) in freshly distilled di-*n*-butyl ether (30 mL) under nitrogen was added $Fe(CO)_5$ (5.6 g, 28 mmol), and the mixture was refluxed under nitrogen with stirring for 72 h. The reaction mixture was cooled to room temperature, and a solution of ferric chloride hexahydrate (15 g, excess) in acetone (75 mL) was added. The resulting mixture was stirred at room temperature for 7 days. Distilled water (100 mL) was added, and the mixture was extracted with ethyl acetate (7 × 100 mL). The combined extracts were washed with water (100 mL), dried (anhydrous magnesium sulfate), and filtered, and the filtrate was concentrated in vacuo. The residue was purified via elution chromatography on Florisil by using a 3%–30% ethyl acetate–hexane gradient elution scheme. The only products thereby obtained were *p*-cyanophenol (mp 110–112 °C, undepressed upon admixture with authentic *p*-cyanophenol, 600 mg, 36%) and a small amount of cage dimer **4b** (40 mg, 1.3%).

Control Experiment. Reaction of 2b with $FeCl_3$–Acetone. To a solution of **2b** (60 mg, 0.28 mmol) in acetone (20 mL) was added ferric chloride hexahydrate (300 mg, excess), and the resulting mixture was stirred at room temperature for 7 days. The progress of the reaction was monitored periodically by thin-layer chromatographic (TLC) analysis. The reaction mixture was concentrated in vacuo, and the residue was partitioned between ethyl acetate (25 mL) and water (25 mL). The layers were separated, and the organic layer was extracted with 10% aqueous sodium hydroxide solution (25 mL). The aqueous layer then was extracted with ethyl acetate (25 mL), and the organic layer was discarded. The aqueous layer was acidified by gradual addition of concentrated hydrochloric acid solution and then was extracted with ethyl acetate (25 mL). The organic layer was dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo. The residue was purified by passage through a short silica gel column and eluted with 20% ethyl acetate–hexane mixed solvent. Pure *p*-cyanophenol (8 mg, 24%), identical in all respects with a sample of authentic material, was thereby obtained as colorless needles: mp 108–109 °C.

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Improved Synthesis of 3,4-Disubstituted Furans: Use of Phase-Transfer Conditions

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In the course of work toward the total synthesis of a natural product containing a 3,4-disubstituted furan, we have realized the utility of a new reagent and reaction conditions for the preparation of this type of compound. This methodology advances the general method for the preparation of 3,4-disubstituted furans reported by Garst in 1973.[1] The methodology described herein is cheaper, does not necessitate the use of anhydrous solvents and strong organic bases, and does not require low reaction temperatures.

The central step in the Garst sequence (Scheme I) is formation of a vinyl oxirane from treatment of an *S*-butyl-α-thiomethylene ketone with a nonstabilized sulfur ylide prepared from trimethylsulfonium fluoroborate[2] and *n*-butyllithium in dimethoxyethane at −78 °C. Trimethylsulfonium iodide under similar conditions was described as unsuitable; this was found to be the case in our hands as well.[3] However, formation of simple oxiranes

(1) Garst, M. E.; Spencer, T. A. *J. Am. Chem. Soc.* **1973**, *95*, 250.
(2) The fluoroborate salt is not commercially available and requires expensive precursors for its preparation.

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