Divergent Reaction Pathways between Rhodium(II)-Stabilized Vinylcarbenoids and Benzenes

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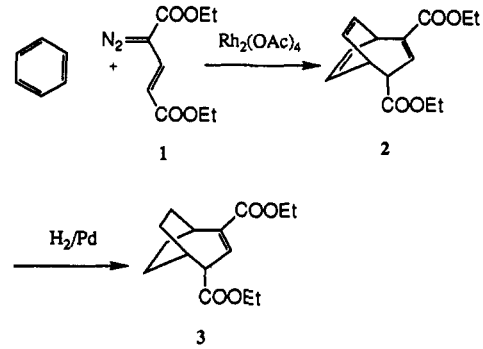
Rhodium(II) carboxylate stabilized vinylcarbenoids reacted intermolecularly with benzenoid compounds by two distinct modes. With benzene, alkylbenzenes, and 1-methoxynaphthalene, 3 + 4 annulations were observed, presumably arising through initial cyclopropanation followed by a Cope rearrangement. In contrast, alkylation products were formed with methoxy-substituted benzenes. In an intramolecular reaction a delicate balance existed between norcaradiene formation, 3 + 4 annulation, and 3 + 2 annulation.

Decomposition of α-diazo carbonyl compounds in the presence of benzene and its derivatives has been extensively used in organic synthesis.[1] The reaction is considered to proceed through norcaradiene intermediates which rapidly rearrange to cycloheptatrienes, although occasionally an equilibrating mixture of both is formed.[2] The initially formed cycloheptatrienes may also be labile and isomerize to more stable cycloheptatrienes or convert to alkylation products.[3] Intramolecular versions of this reaction have been used to prepare a variety of structures[4] including azulenes[4a] and pseudoguaianes.[4b] When the aromatic system is too constrained to form cycloheptatrienes[5] or dipolar intermediates are favored,[6] substitution products are generated.

For some time, we have been examining the chemistry of rhodium(II)-stabilized vinylcarbenoids.[7] We have shown that their reaction with dienes, including pyrroles[7a] and furans,[7b] is a general method for the synthesis of seven-membered rings by means of a tandem cyclopropanation/Cope rearrangement. In this paper, examples of reactions between vinylcarbenoids and benzenes leading to 3 + 4 annulation, as well as alkylation, norcaradiene formation and 3 + 2 annulation, will be described.

Rhodium(II) acetate catalyzed decomposition of the vinyldiazo ester 1 in the presence of benzene gave a rather unstable product whose NMR spectrum was consistent with the bicyclo[3.2.2]nonatriene structure 2. The structural assignment was confirmed by partial catalytic reduction of 2 which gave the bicyclo[3.2.2]nonene 3 in 24% overall yield. A slight improvement in yield (29%) was possible using rhodium(II) trifluoroacetate as catalyst. When similar reactions were carried out with alkylbenzenes such as toluene, 1,2-xylene, or *tert*-butylbenzene, the NMR spectra of the crude reaction mixtures revealed the presence of mixtures of 3 + 4 annulation products. However, due to their lack of stability and the fact that complex isomeric mixtures were formed on catalytic hydrogenation, purification and full characterization of these compounds was not possible.



1 2 (1)

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The reaction with methoxy-substituted benzenes led to a different reaction pathway. Instead of the formal 3 + 4 cycloadducts, electrophilic substitution products 4a–c were formed as mixtures of geometrical isomers. In each case, alkylation occurred at the favored position for electrophilic attack. The reaction is sensitive to substitution pattern because with 1,4-dimethoxybenzene the vinyldiazo ester 1 was recovered unchanged which was indicative of catalyst poisoning. In contrast, rhodium(II) octanoate catalyzed decomposition of 1 in the presence of 1-methoxynaphthalene proceeded smoothly to the 3 + 4 annulation product 5, which was unstable to silica gel chromatography, but could be isolated in 39% yield by crystallization from hexane/ether. Only one stereoisomer of the cycloadduct was formed, and based on our earlier studies with dienes,[7] this was expected to be 5.

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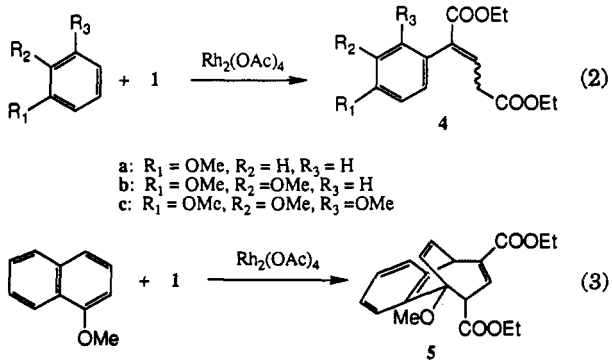


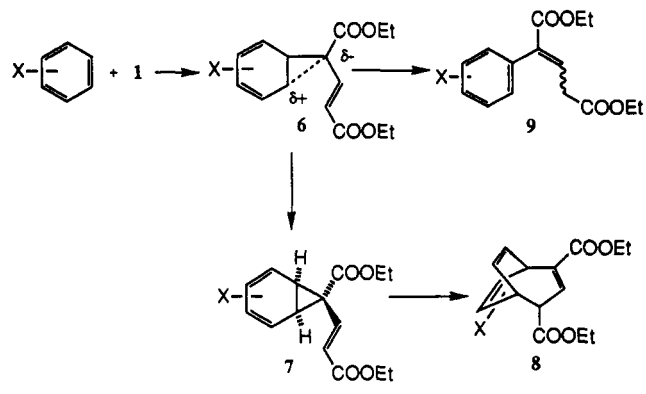
The formation of either 3 + 4 annulation or alkylation products can be rationalized by assuming that the initial interaction between the vinylcarbenoid and the aromatic compound proceeded in a nonsynchronous manner. A similar rationalization has been made by us to explain the side products observed in the reactions of vinylcarbenoids with furans,[7a] pyrroles,[7b] and oxygenated dienes.[7c] The extent of dipolar character in **6** would depend on the functionality present. With benzene and alkylbenzenes as substrates the stabilization of dipolar structures would be limited. Consequently, cyclopropanation proceeded normally, presumably to give a *cis*-divinylcyclopropane intermediate **7**,[8] which then underwent a Cope rearrangement to generate **8**. With the methoxy-substituted benzenes, a highly dipolar structure would be more favorable because of greater stabilization of the positive charge by the methoxy groups. Thus, an alternative pathway occurred involving aromatization and double-bond isomerization,[9] which produced the alkylation product **9**. With 1-methoxynaphthalene, a highly dipolar structure again would be well stabilized, but as there would be less driving force for rearomatization, the formal 3 + 4 annulation still occurred.

Reactions between **1** and aromatic compounds were far cleaner than parallel reactions with other vinylcarbenoid precursors. For example, decomposition of methyl (*E*)-2-diazo-4-phenylbutenoate in the presence of benzene failed to generate any product derived from capture of the vinylcarbenoid with benzene, while the reaction with veratrole led to an uncharacterized mixture of products. An intramolecular reaction with 2-diazo-4-phenylbutenoate (**10**), however, did result in the effective capture of the carbenoid but the isolable product was very dependent on reaction conditions. The resulting solid that was obtained in 48% yield from reaction of **10** with rhodium(II) octanoate at 0 °C followed by recrystallization of the crude material from hexane/CH_2Cl_2 was shown to be the norcaradiene **11**. Particularly diagnostic in the structural assignment were the NMR signals for the vinyl protons (δ 7.04, 5.51 ppm, both d, J = 16.4 Hz; δ 5.14 ppm, d, J = 5.5 Hz; and δ 4.99 ppm, s). The norcaradiene structural assignment **11**, rather than the isomeric cycloheptatriene, was supported by the distinctive chemical shift for H_a (δ 2.65 ppm).[10]

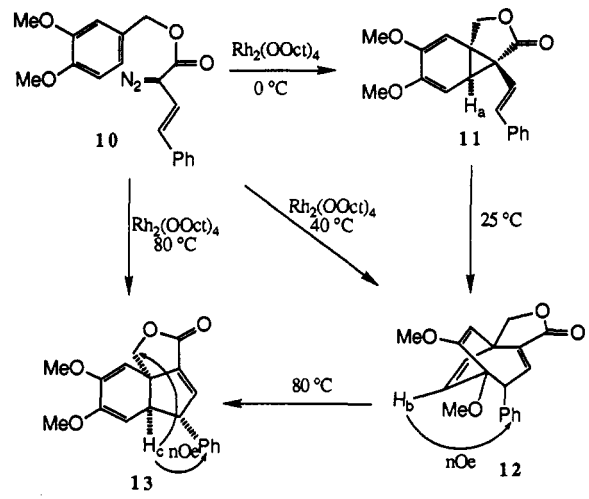
Although the norcaradiene **11** is reasonably stable in the crystalline form, on standing in $CDCl_3$ for 3 days, **11** rearranged to the 3 + 4 annulation product **12**. Indeed, rhodium(II) octanoate catalyzed decomposition of **10** in refluxing dichloromethane resulted in the clean formation of **12**, which though thermally and chromatographically unstable was isolable by crystallization from hexane/CH_2Cl_2 in 72% yield. Distinctive features of the NMR which supported the structural assignment were the signals for the vinyl protons (δ 6.61, 5.88 ppm, both d, J = 8.8 Hz; δ 6.43 ppm, d, J = 3.7 Hz; and δ 5.39 ppm, s) as well as for the methoxy groups (δ 3.70, 3.24 ppm), which clearly show that one of the methoxy groups is not bound to a vinyl group. The stereochemistry of **12** was assigned based on NOE difference analysis which showed an enhancement of the phenyl group on irradiation of H_b.

The 3 + 4 annulation product **12** also had limited stability in solution at room temperature and, on heating in refluxing benzene for 24 h, rearranged to **13**, the product of a formal 3 + 2 annulation. The 3 + 2 annulation product **13** could also be formed directly from the rhodium(II) octanoate catalyzed decomposition of the vinyldiazomethane **10** in refluxing 1,2-dichloroethane. Presumably, the formation of **13** occurred either by reversal of the Cope rearrangement of **12** to generate the norcaradiene **11**, which then underwent a vinylcyclopropane rearrangement, or by a 1,3-sigmatropic rearrangement of **12**. The NMR signals for the vinyl protons (δ 6.78 ppm, d, J = 1.7 Hz; δ 4.91 ppm, s; and δ 4.72 ppm, d, J = 6.6 Hz) were characteristic for **13** and could be used to rule out the product from a 3,5-sigmatropic rearrangement of the norcaradiene **11**.[11] The stereochemical assignment of

Scheme I



Scheme II



(8) One of the distinctive features of vinylcarbenoid cyclopropanations is that they are highly stereoselective. See ref 7.

(9) The detailed mechanism for the formation of the alkylation product is uncertain because there are several viable alternatives. For a summary of the mechanistic ambiguities associated with the reaction of ketocarbenoid intermediates with benzene derivatives, see ref 1b.

(10) Typically, equilibration between the norcaradiene and the cycloheptatriene systems is very rapid at room temperature and the chemical shift for Ha occurs between the typical values observed for this proton in norcaradienes (2–3 ppm) and cycloheptatrienes (5–6 ppm). See ref 2a,b.

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13 was based on the occurrence of strong NOE enhancements of one of the methylene protons and the *o*-phenyl protons on irradiation of H_c.

In summary, formal 3 + 4 annulation products are derived from the reactions of rhodium(II) stabilized vinylcarbenoids with benzene derivatives. Competing alkylation products may be formed in intermolecular reactions if a dipolar intermediate is strongly favored. In the intramolecular example, a delicate balance exists between the 3 + 4 annulation product and other isomeric structures.

Experimental Section

General. ^1H and ^{13}C NMR spectra were recorded at 200 and 50.3 MHz, respectively. Mass spectral determinations were carried out at 70 eV. CH_2Cl_2 was freshly distilled from CaH_2. Column chromatography was carried out on silica gel 60 (230–400 mesh).

General Procedure for the Rhodium(II) Acetate Catalyzed Decomposition of 1 in the Presence of Aromatics. A solution of 1[7b] (1 equiv) in CH_2Cl_2 (10 mL) was added over 10 min to a stirred mixture of $Rh_2(OAc)_4$ (0.01 equiv) and the aromatic system (5 equiv) in CH_2Cl_2 (30 mL) heated at reflux under Ar. After being heated for a further 10 min, the solvent was evaporated and the product was purified.

Diethyl Bicyclo[3.2.2]non-1-ene-1,3-dicarboxylate (3). The general procedure was modified by using 0.53 g (2.5 mmol) of 1, rhodium(II) trifluoroacetate as catalyst, and benzene as solvent. The crude product 2 was unstable to chromatography and was hydrogenated (45 psi) with platinum on activated carbon (5%, 0.07 g) in ethanol (75 mL) for 12 h. The solution was then filtered, the solvent was evaporated under reduced pressure, and the residue was purified by chromatography on silica with ether/pentane (20:80) as solvent to give 3 as a gum: 0.14 g (29% yield); IR (neat) 1735, 1710, 1650, 1460 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.83 (dd, 1 H, J = 3.5, 1.4 Hz), 4.14 (q, 2 H, J = 7.2 Hz), 4.08 (q, 2 H, J = 7.2 Hz), 3.39 (t, 1 H, J = 3.5 Hz), 2.95 (m, 1 H), 2.33 (m, 1 H), 1.84–1.50 (m, 8 H), 1.24 (t, 3 H, J = 7.2 Hz), 1.22 (t, 3 H, J = 7.2 Hz). Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.59; H, 8.33. Found: C, 67.73; H, 8.35.

Diethyl 2-(4-Methoxyphenyl)pent-2-enedioate (4a). The reaction was carried out using 1.07 g (5.05 mmol) of 1, and the crude product was purified by chromatography on silica with ether/petroleum ether (10:90–20:80) as solvent gradient to give 4a as a gum: 1.03 g (70% yield), E/Z ratio 1:10; IR (neat) 1730, 1715, 1645, 1620, 1475, 1460 cm^{-1}; ^1H NMR ($CDCl_3$) Z isomer δ 7.12 (t, 1 H, J = 7.2 Hz), 7.11 (d, 2 H, J = 8.7 Hz), 6.88 (d, 2 H, J = 8.7 Hz), 4.19 (q, 2 H, J = 7.5 Hz), 4.12 (q, 2 H, J = 7.5 Hz), 3.79 (s, 3 H), 3.12 (d, 2 H, J = 7.2 Hz), 1.25 (t, 3 H, J = 7.5 Hz), 1.23 (t, 3 H, J = 7.5 Hz). Anal. Calcd for $C_{16}H_{20}O_5$: C, 65.74; H, 6.89. Found: C, 65.62; H, 6.91.

Diethyl 2-(3,4-Dimethoxyphenyl)pent-2-enedioate (4b). The reaction was carried out using 1.08 g (5.09 mmol) of 1, and the crude product was purified by chromatography on silica with ether/pentane (10:90–50:50) as solvent gradient to give 4b as a gum: 1.03 g (63% yield), E/Z ratio 1:7; IR (neat) 1720, 1705, 1600, 1580, 1500, 1460, 1440, 1410 cm^{-1}; ^1H NMR ($CDCl_3$) Z isomer δ 7.12 (t, 1 H, J = 7.6 Hz), 6.85 (d, 1 H, J = 8.8 Hz), 6.73 (m, 2 H), 4.22 (q, 2 H, J = 7.6 Hz), 4.14 (q, 2 H, J = 7.6 Hz), 3.88 (s, 3 H), 3.85 (s, 3 H), 3.14 (d, 2 H, J = 7.6 Hz), 1.28 (t, 3 H, J = 7.6 Hz), 1.24 (t, 3 H, J = 7.6 Hz). Anal. Calcd for $C_{17}H_{22}O_6$: C, 63.34; H, 6.88. Found: C, 63.15; H, 6.92.

Diethyl 2-(2,3,4-Trimethoxyphenyl)pent-2-enedioate (4c). The reaction was carried out using 1.08 g (5.09 mmol) of 1. The reaction mixture was heated for an extended period of 3h, and the crude product was purified by chromatography on silica with ether/pentane (20:80–50:50) as solvent gradient to give 4c as a gum: 0.86 g (49% yield), E/Z ratio 0:1; IR (neat) 1730, 1640, 1570, 1470, 1455 cm^{-1}; ^1H NMR ($CDCl_3$) Z isomer δ 7.13 (t, 1 H, J = 7.7 Hz), 6.78 (d, 1 H, J = 8.8 Hz), 6.66 (d, 1 H, J = 8.8 Hz), 4.22 (q, 2 H, J = 7.3 Hz), 4.14 (q, 2 H, J = 7.3 Hz), 3.86 (s, 6 H), 3.75 (s, 3 H), 3.11 (d, 2 H, J = 7.7 Hz), 1.26 (t, 3 H, J = 7.3 Hz), 1.24 (t, 3 H, J = 7.3 Hz). Anal. Calcd for $C_{18}H_{24}O_7$: C, 61.35; H, 6.86. Found: C, 61.44; H, 6.91.

Diethyl 8-Methoxytricyclo[6.3.2.0^{2,7}]trideca-2,3,5,10,12-pentaene-9,11-dicarboxylate (5). The reaction was carried out using 1.06 g (5 mmol) of 1. The crude product was purified by chromatography on neutral alumina using ether/petroleum ether (10:90) to ether as solvent gradient followed by recrystallization from ether/hexane to give 5 as a colorless solid: 0.67 g (39% yield); mp 98–100 °C; IR (Nujol) 1740, 1705, 1470, cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.50 (d, 1 H, J = 7.1 Hz), 7.31–7.18 (m, 3 H), 6.80 (dd, 1 H, J = 9.2, 6.8 Hz), 6.53 (d, 1 H, J = 9.2 Hz), 6.33 (dd, 1 H, J = 3.4, 2.6 Hz), 4.65 (d, 1 H, J = 6.8 Hz), 4.23 (q, 2 H, J = 7.3 Hz), 4.18 (q, 2 H, J = 7.3 Hz), 3.42 (s, 3 H), 3.39 (d, 1 H, J = 3.4 Hz), 1.31 (t, 3 H, J = 7.3 Hz), 1.27 (t, 3 H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ 169.5, 166.0, 142.7, 139.5, 137.1, 135.4, 134.8, 132.9, 127.0, 126.2, 124.3, 123.0, 78.7, 61.2, 53.5, 52.2, 39.1, 14.2. Anal. Calcd for $C_{20}H_{22}O_5$: C, 70.16; H, 6.48. Found: C, 70.11; H, 6.51.

3,4-Dimethoxybenzyl 4-Phenyl-3-butenoate. A solution of 4-phenylbutenoyl chloride (1.31 g, 7.28 mmol) in CH_2Cl_2 was added to a stirred mixture of the 3,4-dimethoxybenzyl alcohol (1.20 g, 7.14 mmol) and pyridine (0.65 g, 8.23 mmol) in CH_2Cl_2 at 0 °C. After warming to rt and stirring for a further 12 h, the mixture was washed with saturated NH_4Cl solution and dried ($MgSO_4$), and then the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica with ether/petroleum ether (20:80) as solvent to give the title compound as a colorless solid: 1.76 g (79% yield); mp 47–49 °C; IR ($CDCl_3$) 1734, 1595 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40–7.21 (m, 5 H), 6.93 (dd, 1 H, J = 8.2, 1.8 Hz), 6.89 (d, 1 H, J = 1.8 Hz), 6.84 (d, 1 H, J = 8.2 Hz), 6.49 (d, 1 H, J = 15.9 Hz), 6.30 (dt, 1 H, J = 15.9, 6.7 Hz), 5.09 (s, 2 H), 3.87 (s, 3 H), 3.85 (s, 3 H), 3.28 (d, 2 H, J = 6.7 Hz); ^{13}C NMR ($CDCl_3$) δ 171.3, 149.0, 148.9, 136.7, 133.4, 128.4, 128.2, 127.5, 126.1, 121.5, 121.2, 111.7, 111.0, 66.5, 55.8, 55.7, 38.3. Anal. Calcd for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 73.18; H, 6.49.

3,4-Dimethoxybenzyl 2-Diazo-4-phenyl-3-butenoate (10). DBU (1.41 g, 9.28 mmol) was added to a stirred solution of 3,4-dimethoxybenzyl 4-phenyl-3-butenoate (1.72 g, 5.51 mmol) and *p*-acetamidobenzenesulfonyl azide (1.40 g, 5.83 mmol) in acetonitrile (100 mL) at 0 °C. After the resulting solution was stirred for 4 h at 0 °C, saturated NH_4Cl solution was added and the mixture was extracted with ether. The organic layer was then dried (Na_2SO_4), the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica with ether/petroleum ether (20:80) as solvent to give 10 as a red gum: 1.21 g (65% yield); IR (neat) 2100, 1695, 1630, 1602, 1520 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.36–7.18 (m, 5 H), 6.96 (dd, 1 H, J = 8.1, 1.7 Hz), 6.92 (d, 1 H, J = 1.7 Hz), 6.85 (d, 1 H, J = 8.1 Hz), 6.48 (d, 1 H, J = 16.4 Hz), 6.19 (d, 1 H, J = 16.4 Hz), 5.22 (s, 2 H), 3.89 (s, 3 H), 3.88 (s, 3 H). Due to lack of stability, 10 was used immediately in subsequent reactions.

7-(2-Phenylethenyl)-3,4-dimethoxy-9-oxatricyclo-[5.3.0.0^{1,6}]deca-2,4-dien-8-one (11). A solution of 10 (0.30 g, 0.89 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a stirred solution of rhodium(II) octanoate (0.069 g, 0.009 mmol) in CH_2Cl_2 (5 mL) under argon at 0 °C. After being stirred for an additional 10 min, the solvent was removed under reduced pressure at 0 °C and the residue was recrystallized from hexane/CH_2Cl_2 to give 11 as a colorless solid: 0.13 g (48% yield); mp = 93–95 °C; IR (CCl_4) 1755, 1585 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.26–7.17 (m, 5 H), 7.04 (d, 1 H, J = 16.4 Hz), 5.51 (d, 1 H, J = 16.4 Hz), 5.14 (d, 1 H, J = 5.5 Hz), 4.99 (s, 1 H), 4.33 (d, 1 H, J = 9.1 Hz), 4.25 (d, 1 H, J = 9.1 Hz), 3.70 (s, 3 H), 3.69 (s, 3 H), 2.65 (d, 1 H, J = 5.5 Hz). Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 73.29; H, 5.92. On standing in $CDCl_3$ at rt for 3 days, 11 had rearranged mainly to 12.

8,9-Dimethoxy-7-phenyl-3-oxatricyclo[8.2.0.0^{1,5}]dodeca-5,9,11-trien-4-one (12). A solution of 10 (1.18 g, 3.5 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a stirred mixture of rhodium(II) octanoate (0.027 g, 0.035 mmol) in CH_2Cl_2 (20 mL) heated under reflux in Ar. After the mixture was heated for an additional 10 min, the solvent was removed under reduced pressure, and the residue was recrystallized from hexane/CH_2Cl_2 to give 12 as a colorless solid: 0.78 g, 72% yield; mp 130–131 °C; IR ($CDCl_3$) 1750, 1666, 1614 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.27–7.15 (m, 5 H), 6.61 (d, 1 H, J = 8.8 Hz), 6.43 (d, 1 H, J = 3.7 Hz), 5.88 (d, 1 H, J = 8.8 Hz), 5.39 (s, 1 H), 4.65 (d, 1 H, J = 9.8 Hz), 4.53 (d, 1 H, J = 9.8 Hz), 3.77 (d, 1 H, J = 3.7 Hz), 3.69 (s, 3 H), 3.24 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 169.0, 160.9, 140.2, 139.0, 135.4, 135.1, 132.1, 130.2, 127.8, 127.5, 107.4, 79.4, 76.1, 56.2, 53.0, 46.2, 43.5; MS $m/$ (relative intensity) 310 (40), 280 (100), 265 (32), 252 (25),

237 (35), 207 (25), 191 (22), 178 (32), 165 (45), 115 (40), 91 (35), 77 (28), 63 (25), 39 (20); HRMS calcd for $C_{19}H_{18}O_4$ 310.1205, found 310.1232. Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 73.54; H, 5.81.

3,4-Dimethoxy-7-phenyl-11-oxatricyclo[7.3.0.0^{1,6}]dodeca-2,4,8-trien-10-one (13). A solution of **10** (1.59 g, 4.7 mmol) in dichloroethane (25 mL) was added dropwise to a stirred solution of rhodium(II) octanoate (0.035 g, 0.047 mmol) in dichloroethane (25 mL) heated under reflux in an argon atmosphere. After being heated for an additional 12 h, the solvent was removed under reduced pressure and the residue was recrystallized from hexane to give **13** as a colorless solid: 0.35 g, 17% yield; mp 126–130 °C; IR (CCl_4) 1765, 1605 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.37–7.15 (m, 5 H), 6.78 (d, 1 H, J = 1.7 Hz), 4.91 (s, 1 H), 4.72 (d, 1 H, J = 6.7 Hz), 4.34 (d, 1 H, J = 8.7 Hz), 4.29 (dd, 1 H, J = 9.3, 1.7 Hz), 4.14 (d, 1 H, J = 8.7 Hz), 3.69 (s, 3 H), 3.59 (s, 3 H), 2.93 (dd, 1 H, J = 9.3, 6.7 Hz); ^{13}C NMR ($CDCl_3$) δ 165.3, 149.2, 149.1, 141.9, 141.7, 140.4, 128.9, 127.5, 127.4, 95.0, 94.1, 82.0, 66.7, 65.8, 57.0, 55.2, 54.6. Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 73.90; H, 6.02. Refluxing of **12** in benzene under argon for 24 h resulted in the formation of **13** in 78% yield.

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Reactivity of Allylic Dimetallic Zinc Reagents. 1

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Allylic 1,1-dimetallic species **2**, prepared in situ from the propargylic ether **1**, are multicoupling reagents. They were allowed to react in a one-pot reaction, with a large variety of electrophiles E_1—carbonyl compounds (acyl chlorides, aldehydes, ketones, phenyl isocyanate, methyl chloroformate), alkyl bromides, and an amino ether—and then E_2—acidic water, iodine, aryl or vinyl iodide in the presence of palladium(0). The isolated yields, based on **1** (5 steps), are fair to good in most cases. The first attack (E_1) always occurs on the carbon atom α to the oxygen; the second attack (E_2) is regio- and stereoselective on the carbon atom α to the TMS moiety.

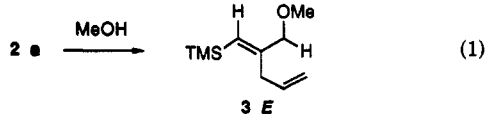
Introduction

Allylic 1,1-dimetallic reagents **2** are potential dicoupling nucleophiles, easily available from 1-(trimethylsilyl)-3-alkoxyprop-1-yne **1** which is first metallated with *n*-butyllithium and then reacted with allylzinc bromide[1] (Scheme I). m_1 and m_2 are not yet clearly defined but may represent two zinc atoms, the species being a dimer.

In a previous paper,[1] we reported the reactivity of the dimetallic species **2a** with benzaldehyde, isobutyraldehyde, acetophenone, and ethyl benzoate as first electrophiles (E_1) and proton as the second one (E_2). We describe herein the extension of this reaction to **1b** with a large variety of carbonyl compounds, with alkyl halides, and with an amino ether. The second electrophile is either acidic water (H_3O^+), iodine, or aryl or vinyl iodide in the presence of palladium(0). In all cases, the reaction is regio- and stereoselective as shown below.

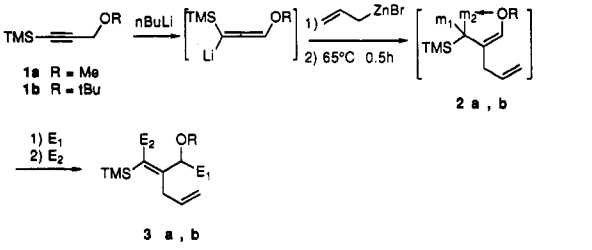
Results and Discussion

(a) Regio- and Stereoselectivity of the Reaction. First, the treatment of **2a** with excess methanol[1] led to a single isomer (**3*E***) (eq 1). Compound **3*E*** has been compared to both ***E*** and ***Z*** authentic samples prepared by other routes[2] described in Scheme II. Concerning the preparation of isomer **3*Z***, it is important to notice that

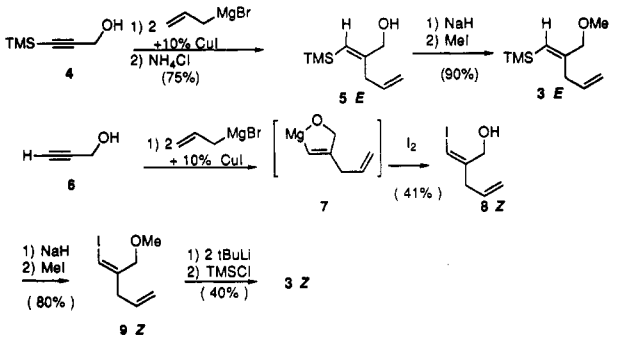


(1)

Scheme I. Synthesis and General Reactivity of Dimetallic Reagents 2



Scheme II. Synthesis of *E* and *Z* Isomers of 3



the supposed intermediate **7** did not react with chlortrimethylsilane to give **5*Z*** in acceptable yield, as previously observed by Jousseaume.[3] Indeed, in compound **7**, the strong chelation of magnesium with the oxygen atom

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