Reactivity of a Nickel Acylate Complex with Acetylenes under an Ar and a CO Atmosphere

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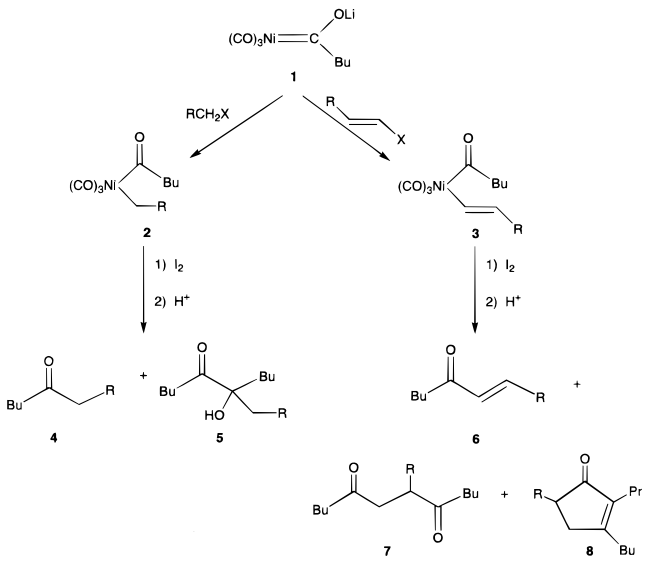
The reaction of an alkyl nickel acylate complex with a variety of mono- and disubstituted acetylene derivatives was investigated. Depending upon the substitution pattern and the reaction time, the reaction product can be a 1,4-diketone, a cyclopentenone, or a γ-lactone, but only when the reaction is performed under an Ar atmosphere. When a CO atmosphere is used, no reaction occurs. The mechanism for formation of each of these compounds is discussed.

As we have shown previously (Scheme 1),[2] nickel acylate complex **1** reacts with alkyl and vinyl halides to generate a variety of products. Although these reactions initially appear quite different, there are many commonalties. First of all, in each case, when THF is used as the solvent, the initially formed intermediate is a 1:1 adduct (complex **2** or **3**) of the acylate complex and the electrophile. Second, when the reaction is relatively fast ($t_{1/2}$ of less than 10 min at −40 °C or below), the product is a 1:1 adduct of the acyl group and the alkyl or vinyl group (product **4** or **6**). In contrast, when the reaction is relatively slow ($t_{1/2}$ of greater than an hour at room temperature), the product is a 2:1 adduct of the acyl group and the alkyl or vinyl group (product **5**, **7**, or **8**). As usual, the reaction rate is determined by the nature of the organic portion of the electrophile, as well as the leaving group. Third, in all cases, the final organic product is obtained only after an oxidative workup. In other words, all intermediates in the formation of these products are metal complexes. Therefore, it is a metal complex precursor to compound **7** that, given enough time, cyclizes to a precursor of **8**, *prior* to the oxidation and protonation steps in workup, rather than **7** giving **8** directly.[2]

With the alkyl halides, the initial intermediate **2** could be formed by an S_N2-type reaction;[3] however, with the vinyl halides, this is not possible. (Complex **1** undergoes substitution only with primary alkyl halides. With secondary and tertiary halides, an E2 reaction is observed.) Thus the question remains, is the initial interaction of the acylate complex and the vinyl halide through the carbon−halide bond or through the π system? The obvious way to test this idea is to study the reactivity of complex **1** with an alkene such as styrene or propene; however, nickel acylate complexes react only with electron-deficient double bonds.[4] As an alternative, we decided to study the reaction of complex **1** with acetylenes, because, in general, the reaction between a nucleophile and an alkyne is more facile than between a nucleophile and an alkene.[5]

Scheme 1



Known Reactions of Acylate Complexes with Acetylenes. In contrast to the large number of papers that deal with the reactions of Fischer-type carbene complexes and related systems with acetylenes,[6] the number of publications dealing with the reactions of acylate complexes with acetylenes is limited. Approximately thirty years ago, the reaction of a variety of nickel acylate complexes with monosubstituted acetylenes in Et_2O (Scheme 2) was first reported.[7,8] When

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(2) (a) Simunic, J. L.; Pinhas, A. R. *Inorg. Chem.* **1989**, *28*, 2400. (b) Hermanson, J. R.; Hershberger, J. W.; Pinhas, A. R. *Organometallics* **1995**, *14*, 5426.

(3) Chamchaang, W.; Pinhas, A. R. *J. Org. Chem.* **1990**, *55*, 2943.

(4) (a) Corey, E. J.; Hegedus, L. S. *J. Am. Chem. Soc.* **1969**, *91*, 4926. (b) Hegedus, L. S. Ph.D. Dissertation; Harvard University: Cambridge, MA, 1970. (c) Hermanson, J. R. Dissertation; University of Cincinnati: Cincinnati, OH, 1994.

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(6) For some leading references see: (a) Dotz, K. H. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, Germany, 1983. (b) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 2nd ed.; Wiley-Interscience: New York, 1994. (c) Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Books: Mill Valley, CA, 1994.

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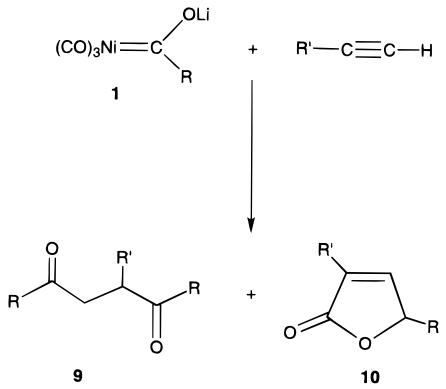
Scheme 2



the reaction was kept at −70 °C, the sole product was a 1,4-diketone (**9**), the same type of product we have obtained from the reactions of **1** with vinyl halides (**7**).[2b] In contrast, when the reaction was allowed to run at −30 °C, in addition to the 1,4-diketone, a lactone (**10**) was generated. (No mention was made in ref 7 about what happens with disubstituted acetylenes.)

On the basis of the product composition, the authors made the very reasonable suggestion that 1,4-diketone **9** was generated from a dimeric acylate complex at −70 °C and lactone **10** from a monomeric acylate complex at −30 °C. This is just the opposite of what we would have expected. We have shown spectroscopically that the structure of the acylate complex in Et_2O below −50 °C is monomeric complex **1** and that complex **1** dimerizes when the reaction temperature is raised to about −20 °C.[9]

Another point of interest, recently, it was shown that the reaction of chromium and manganese acylate complexes with terminal acetylenes generates only lactones similar to compound **10**.[10] The authors observed none of the 1,4-diketone product analogous to **9**. (The only mention of an internal acetylene is a footnote in the paper dealing with chromium acylate complexes.) In contrast, an iron acylate complex was found to react with mono- and disubstituted acetylenes to generate lactones similar to **10**.[11] A side product in each of these reactions was a cyclobutenedione.

Thus, in addition to learning about the first step in the reaction of nickel acylate complex **1** with a vinyl halide, we decided to investigate the reactivity of **1** with acetylenes in order to understand in more detail how the 1,4-diketone and the lactone are generated and to compare the chemistry of the nickel complex with the chemistry of analogous chromium, manganese, and iron complexes.

Results and Discussion

The specific acetylenes chosen for this study are phenyl acetylene, diphenyl acetylene, phenyl methyl acetylene, 1-hexyne, and 3-hexyne. We felt that this was a good mixture of phenyl and alkyl, mono- and disubstituted compounds. As in our previous work,[2,9] THF was chosen as the solvent because nickel acylate complexes are more stable upon warming to room temperature and because the acylate complex and other intermediate nickel complexes are more soluble in THF as compared with Et_2O. The results for these reactions are generalized in Scheme 3. Yields for each of the products under a standard set of reaction conditions (3 mmol of each reactant, 25 mL of solvent, and 15 h reaction time) and two different sets of workup conditions (reaction products oxidized with I_2 and reaction mixture first neutralized with NH_4Cl and then oxidized with I_2) are given in Table 1.

Table 1. Product Yields for the Reactions of Complex 1 with Various Alkynes at 15 h Reaction Time

	workup conditions	
alkyne	I_2[a]	(1) NH_4Cl; (2) I_2[b]
phenyl acetylene	**11** none[c]	**11** none
	12 1.15 mmol, 77%	**12** 0.78 mmol, 52%
	13 trace[d]	**13** trace
1-hexyne (butyl acetylene)	**11** none	**11** none
	12 0.65 mmol, 43%	**12** 0.86 mmol, 58%
	13 trace	**13** trace
3-hexyne (diethyl acetylene)	**11** none	**11** none
	12 0.08 mmol, 6%	**12** 0.20 mmol, 13%
	13 trace	**13** trace
diphenyl acetylene	**11** 0.12 mmol, 7%	**11** 0.14 mmol, 9%
	12 0.86 mmol, 58%	**12** 1.08 mmol, 72%
	13 trace	**13** trace
phenyl methyl acetylene	**11** none	**11** none
	12 0.83 mmol, 55%	**12** 1.13 mmol, 75%
	13 trace	**13** trace

[a] The reaction mixture was added directly to solid I_2. [b] The reaction mixture was quenched with a saturated NH_4Cl solution before being added to solid I_2. [c] No distinguishable peak could be observed by GC, and thus, less than 1% of this product was generated. [d] A small peak could be observed by GC corresponding to a yield of 2−3%.

Reaction of Acylate Complex 1 with Terminal Acetylenes. The first example is the reaction of acylate complex **1** with phenyl acetylene. The major product from this reaction is cyclopentenone **12** (R = Ph, R′ = H is the major isomer and R = H, R′ = Ph is the minor isomer). Shorter reaction times give a lower yield of **12** and a correspondingly higher yield of **11**. Longer reaction times, not only for this reaction but for all reactions discussed below, give a lower yield of **12** and a great deal of intractable material.

As has been determined for reactions of acylate complex **1**, the precursor to compound **11** isomerizes to the precursor to compound **12** when a reaction stands for an extended period of time. In other words, the organic product(s) is (are) obtained only after an oxidative workup.[2] Therefore, it is not surprising that compound **11** was observed at shorter reaction times and that none of compound **11** was observed at 15 h.

The reaction of complex **1** with 1-hexyne (butyl acetylene) generates compound **12** (R = Bu, R′ = H is the major isomer and R = H, R′ = Bu is the minor isomer) as the major product, again with only a trace amount of lactone **13** (R = Bu, R′ = H). The behavior of this reaction with respect to time is very similar to that observed with phenyl acetylene. Both the reaction of

(8) For other reactions of acylate complexes, see: (a) Myeong, S. K.; Sawa, Y.; Ryang, M.; Tsutsumi, S. *Bull. Chem. Soc.* **1965**, *38*, 330. (b) Ryang, M.; Myeong, S. K.; Sawa, Y.; Tsutsumi, S. *J. Organometal. Chem.* **1966**, *5*, 305. (c) Fukuoka, S.; Ryang, M.; Tsutsumi, S. *J. Org. Chem.* **1968**, *33*, 2973; **1970**, *35*, 3184; **1971**, *36*, 2721. (d) Sawa, Y.; Ryang, M.; Tsutsumi, S. *J. Org. Chem.* **1970**, *35*, 4183.

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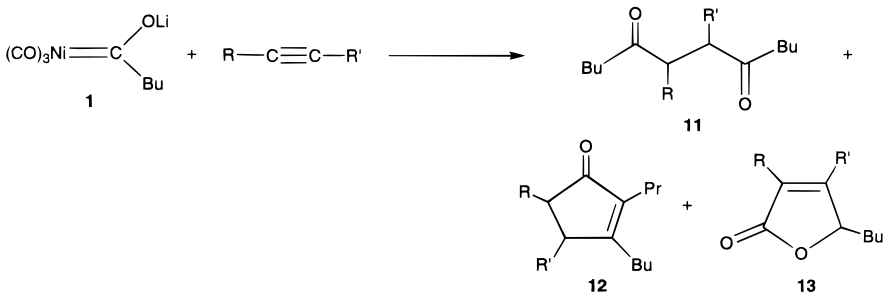
(11) Radhakrishnan, U.; Periasamy, M. *Organometallics* **1997**, *16*, 1800.

Scheme 3



phenyl acetylene and butyl acetylene are much slower than the reactions of the corresponding vinyl halide. Thus in the vinyl halide chemistry, a reaction mechanism in which the vinyl halide eliminates HX to form the acetylene (and it is the acetylene which generates compounds **6**, **7**, or **8**) is inconsistent with these results.

Reaction of Acylate Complex 1 with Internal Acetylenes. As above, the reaction of 3-hexyne (diethyl acetylene) with acylate complex **1** generates mainly cyclopentenone **12** (R = R′ = Et), but in low yield, and only a trace amount of lactone **13** (R = R′ = Et). For the reaction of **1** with diethyl acetylene at all reaction times tried, there is a great deal of intractable material.

Running the acylate reaction with diphenyl acetylene generates compounds **11** and **12**, with again only a trace amount of **13** (R = R′ = Ph). When the diphenyl acetylene reaction is run for a short time period, which should maximize the formation of compound **11**, but is quenched with a very large excess of I_2 rather than with the usual 1.5 equiv, the major product is the α,β-unsaturated analogue of compound **11**, i.e., 6,7-diphenyl-6-dodecen-5,8-dione, **14**, with again only a trace of **13**. This suggests that the precursor to compound **11** is an anionic nickel complex which is adding the equivalent of I^+ and then eliminating HI.

Consistent with the above, under our standard 15 h reaction time, using phenyl methyl acetylene, the major product is cyclopentenone **12** (R = Ph and R′ = Me). However, in contrast to all the chemistry discussed thus far in which compound **13** is formed in only trace amounts, with phenyl methyl acetylene as the reactant, when the reaction is run for a shorter time, usually about 4 h, the major products are both compounds **12** and **13** (R = Ph, R′ = Me), the latter being formed in a 33% yield.

Reactions of Acylate Complex 1 with Acetylenes, Bromostyrene, and Allyl Bromide under a CO Atmosphere. Next the reaction of acylate complex **1** with acetylenes was run under an atmosphere of carbon monoxide rather than argon. If the first step is a precoordination of the triple bond to the nickel, then the reaction should generate no product. On the other hand, if some other mechanism is taking place, then the CO atmosphere should greatly increase the amount of lactone.

When the reaction of phenyl acetylene, diethyl acetylene, diphenyl acetylene, or phenyl methyl acetylene is run under a CO atmosphere and monitored by IR spectroscopy, the peaks for complex **1** remain unchanged. When the reaction is worked up, the only organic compounds observed are the starting acetylene and those from the direct oxidation of **1**, i.e., the same results as if the acetylene were never added.

To ensure that there were no other factors affecting product formation, the reaction of each acetylene was run under a CO atmosphere as above. After 2 days, the CO was removed by blowing Ar into the reaction flask. The color of the solution immediately changed, and the IR spectrum indicated that a reaction was occurring. When any of these reactions were worked up after 15 h, compound **12** was observed as usual.

It was next decided to repeat two reactions under a CO atmosphere that we had run previously under an argon atmosphere.[2] When bromostyrene and acylate complex **1** were mixed under CO, as with the acetylenes, no reaction occurred. However, when allyl bromide and **1** were mixed under CO, the reaction proceeded in high yield just as it did under Ar. These results suggest that the acetylene and styrene reactions proceed by initial coordination of the double or triple bond to the nickel, whereas the allyl bromide reaction proceeds by an S_N2- or S_N2'-type mechanism.

Mechanism. Taking into account all the data we have, we would like to propose the mechanism shown in Scheme 4 for the acetylene reactions. This mechanism is based on the investigations of others[6,11−13] dealing with the reactions of metal complexes, especially carbene complexes, with alkynes, and our work dealing with the reactions of acylate complex **1** with vinyl halides.[2] The first step is a precoordination of the acetylene to the metal (**15**), as is required by the CO inhibition study, followed by a 2 + 2 type reaction (**16**), and then a ring opening of the metallacyclobutene to give **17**. A Michael-type addition gives complex **18**. Upon an oxidatively induced reductive-elimination reaction and protonation, straight chain compound **11** is formed. If a proton transfer occurs, **19** is formed. Upon cyclization (**20**), an oxidatively induced reductive-elimination reaction, and protonation, cyclopentenone **12** is generated. This part of the mechanism is similar to that proposed previously.[2]

If complex **17** undergoes a CO insertion reaction, complex **21** is formed. This CO insertion reaction must be reversible because the lactone product was observed at only short reaction times and for only one acetylene. As in the formation of the other final products, upon

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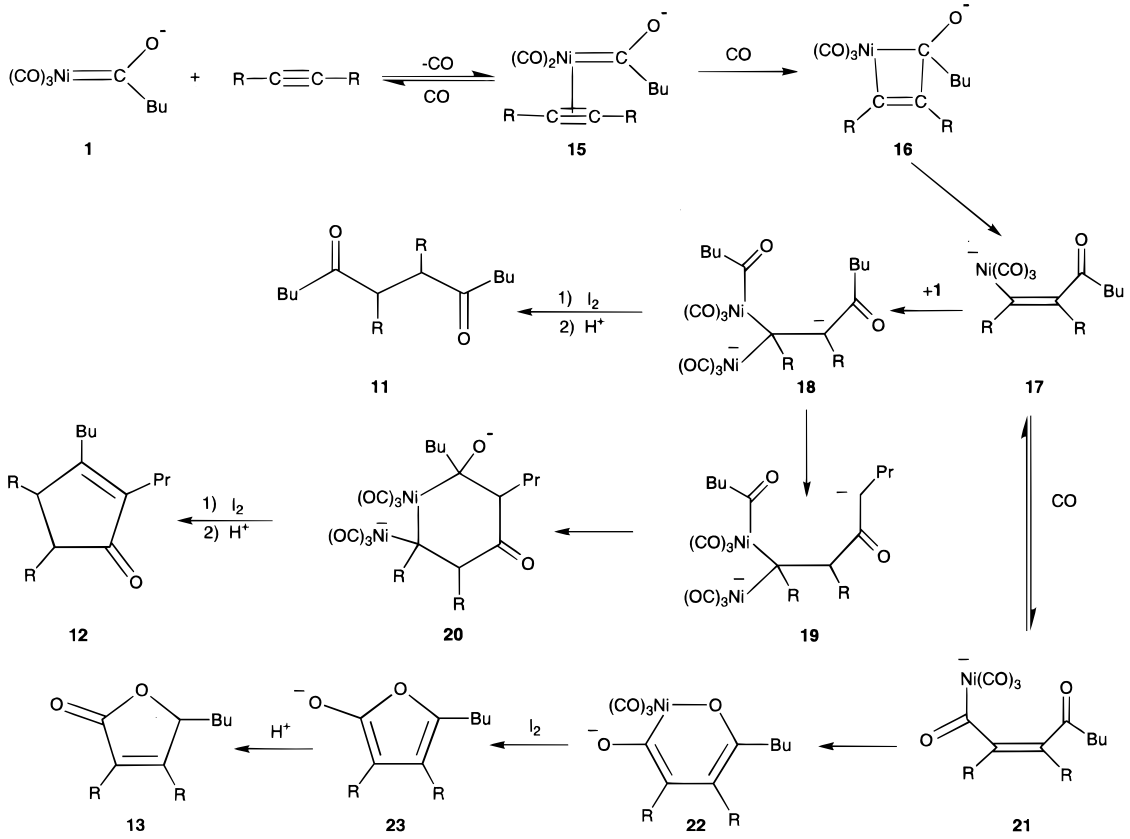
(13) Vicente, J.; Saura-Llamas, I.; Turpin, J.; Ramirez de Arellano, M. C.; Jones, P. G. *Organometallics* **1999**, *18*, 2683.

Scheme 4



cyclization (**22**), an oxidatively induced reductive-elimination reaction, and protonation, lactone **13** is generated.

Experimental Section

General Comments. All reactions were carried out using glassware dried in a 110 °C oven and cooled under an argon atmosphere or in a desiccator. All reactions, except where indicated, were run under an argon atmosphere. Tetrahydrofuran was freshly distilled from potassium benzophenone ketyl. Nickel tetracarbonyl was transferred from a 1 lb lecture bottle and filtered through Celite into a 10 mL sidearm flask, maintaining a strong argon flow, and stored under argon until used. Transfers were made via syringe, and excess $Ni(CO)_4$ was quenched in an iodine/$CHCl_3$ bath. ($Ni(CO)_4$ is toxic and flammable when exposed to air. All work should be conducted in a well-ventilated hood, maintaining an argon atmosphere during all transfers and using nonflammable solvents in the iodine bath to reduce the probability of fire.) Spectroscopic data for compounds **11** (R = Ph, R′ = H), **12** (R = Ph, R′ = H), and **12** (R = H, R′ = Ph) have been reported previously.[2]

Instrumentation. Gas chromatographic analyses were done using a Hewlett-Packard model 6890 gas chromatograph/mass spectrometer with a 15 m × 250 μm × 0.25 μm fused silica capillary SPB1 column and temperature programming. All infrared spectra were recorded on a Perkin-Elmer model 1600 series FTIR spectrophotometer using KBr cells. All NMR spectra were recorded on a Bruker 250 MHz spectrometer and referenced to tetramethylsilane at 0.00 ppm. The substitution pattern on each carbon was determined by the DEPT method. High-resolution mass spectra were done on a Kratos model mass spectrometer. Chromatotron separations were performed on a Harrison Research model 7924T preparative centrifugally accelerated radial thin layer chromatotron. Samples were loaded onto a rotor packed with 2 mm × 7.5 cm of silica gel 60 PF_{254} containing gypsum.

Nickel Acylate Complex 1. This was done in a manner similar to our published procedure.[2] To a three-neck round-bottom flask, under an inert atmosphere and equipped with a glass stopper, a rubber septum, a stir bar, and a gas inlet adapter, was added approximately 25 mL of degassed THF. The solvent was cooled to −78 °C, and 0.36 mL (3.0 mmol) of nickel tetracarbonyl was added. To this was added 1.8 mL of 1.6 M butyllithium (3.0 mmol) over a 15 min period. (It has been found that near the end of the addition there is a significant darkening of the color of the reaction mixture. Cleaner reactions result when the addition is stopped at this point.) The reaction was kept at −78 °C for an additional 15 min and then allowed to warm to room temperature for 1 h.

General Procedure. After stirring at room temperature, nickel acylate complex **1** again was cooled to −78 °C. Then, the acetylene was added dropwise over a period of about 5 min. The mixture was allowed to warm to room temperature slowly and allowed to stir for the appropriate time. Then, the reaction solution either was poured directly onto 1.14 g (4.50 mmol) of I_2 and allowed to react for 30 min or was quenched with 5 mL of a saturated NH_4Cl solution and then added to the I_2. In either case, a 10% $NaHSO_3$ solution was added to remove excess I_2, and the entire mixture was extracted with 75 mL of Et_2O. The organic layer was washed with additional bisulfite until the water layer was colorless. The organic layer then was washed with water, followed by a saturated NaCl solution, and dried with K_2CO_3. The solvent was removed under vacuum.

Acetylenes: phenyl acetylene (0.34 mL, 3.0 mmol), 1-hexyne (0.35 mL, 3.0 mmol), 3-hexyne (0.35 mL, 3.0 mmol), 1-phenyl-1-propyne (0.38 mL, 3.0 mmol), diphenyl acetylene (0.53 g, 3.0 mmol).

Procedure to Generate Compound 14. Everything was done the same as discussed above except for the I_2 quench. Here, 9.0 g (35 mmol) of solid I_2 was carefully added to the solution through an opened sidearm to the flask. Note: the argon gas supply was increased to avoid introducing oxygen

or water into the system. The reaction was stirred for 2 h, at which time it was worked up as in the general procedure above.

3,5-Dibutyl-2-propyl-2-cyclopentenone, 12 (R = Bu, R′ = H): GC ret time 8.03 min; ^{1}H NMR ($CDCl_3$) δ 2.68 (dd, J = 18.0, 6.5 Hz, 1 H), 2.41 (t, J = 7.5 Hz, 1 H), 2.35−2.25 (m, 1 H), 2.15 (dd, J = 14.4, 6.4 Hz, 2 H), 1.90−1.75 (m, 2 H), 1.62−1.15 (m, 12 H), 1.00−0.80 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 211.888 (C), 172.356 (C), 139.486 (C), 44.974 (CH), 36.031 (CH_2), 31.433 (CH_2), 30.760 (CH_2), 29.662 (CH_2), 29.453 (CH_2), 25.063 (CH_2), 22.787 (CH_2), 22.702 (CH_2), 21.768 (CH_2), 14.007 (CH_3), 13.923 (CH_3), 13.838 (CH_3); IR ($CHCl_3$) 2962 (vs), 2933 (vs), 2874 (s), 2863 (s), 2253 (vs), 1743 (w), 1684 (vs), 1636 (s), 1564 (vw), 1467 (s), 1367 (sh), 1095 (m), 902 (vs,b) cm^{-1}; MS (EI) *m/e* 237 (0.7%), 236 (4%), 207 (12%), 193 (18%), 180 (29%), 151 (12%), 139 (10%), 138 (100%), 137 (15%), 123 (29%) 110 (23%), 109 (10%), 95 (16%), 91 (11%), 81 (12%), 79 (15%), 77 (12%), 67 (17%) 55 (25%), 53 (8%); HRMS exptl 236.2139, calcd for $C_{16}H_{28}O$ 236.2140.

3,4-Dibutyl-2-propyl-2-cyclopentenone, 12 (R = H, R′ = Bu): GC ret time 8.08 min; ^{1}H NMR ($CDCl_3$) δ 2.80−2.70 (m, 1 H), 2.48 (dd, J = 13,4.6 Hz, 2 H), 2.35−2.25 (m, 1 H), 2.20−2.05 (m, 2 H), 1.9−1.75 (m, 1 H), 1.60−1.10 (m, 12 H), 1.0−1.85 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 209.142 (C), 176.909 (C), 140.323 (C), 40.628 (CH_2), 39.827 (CH), 32.658 (CH_2), 29.699 (CH_2), 29.198 (CH_2), 28.312 (CH_2), 25.105 (CH_2), 22.912 (CH_2), 22.742 (CH_2), 21.858 (CH_2), 14.006 (CH_3), 13.916 (CH_3), 13.841 (CH_3); IR ($CHCl_3$) 2959 (s), 2933 (s), 2874 (w) 2865 (sh), 2253 (vs), 1744 (w), 1685 (s), 1633 (w), 1564 (vw), 1466 (s), 1380 (s), 1268 (vw, b), 1168 (w), 1095 (s), 904 (vs) cm^{-1}; MS (EI) *m/e* 237 (4%), 236 (19%), 208 (9%), 207 (54%), 193 (25%), 179 (18%), 151 (13%), 139 (11%), 138 (100%), 123 (18%), 110 (17%), 109 (18%), 107 (8%), 95 (27%), 93 (10%), 91 (17%), 81 (18%), 79 (21%), 77 (17%), 67 (21%), 55 (22%), 53 (9%); HRMS exptl 236.2147, calcd for $C_{16}H_{28}O$ 236.2140.

3,5-Dibutyl-2-oxa-4-cyclopentenone, 13 (R = Bu, R′ = H): GC ret time 7.36 min; ^{1}H NMR ($CDCl_3$) δ 5.8 (s, 1 H), 4.90−4.85 (m, 1 H), 2.50−2.15 (m, 4 H), 1.95−1.80 (m, 2 H), 1.75−1.20 (m, 6 H), 1.0−0.75 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 173.407 (C), 115.512 (CH), 84.001 (CH), 65.839 (C), 31.928 (CH_2), 29.104 (CH_2), 27.877 (CH_2), 26.574 (CH_2), 22.402 (CH_2), 15.248 (CH_2), 13.873 (CH_3), 13.746 (CH_3); IR (neat oil) 3456 (w), 2973 (s), 2947 (s), 2908 (vs), 2880 (vs), 2860 (vs), 2819 (w), 1753 (vs), 1637 (m), 1467 (m), 1420 (vs), 1380 (w), 1329 (w), 1274 (w), 1234 (w), 1203 (vw), 1171 (m), 1112 (w), 1072 (vw), 1005 (vw) cm^{-1}; MS (EI) *m/e* 197 (0.1%), 196 (0. 5%), 167 (10%), 139 (14%), 112 (12%), 111 (100%), 98 (36%), 97 (16%), 93 (15%), 85 (12%), 83 (9%), 67 (15%), 57 (13%), 55 (52%), 53 (13%), HRMS: exptl 196.1450, calcd for $C_{12}H_{20}O_2$ 196.1463.

3-Butyl-4,5-diethyl-2-propyl-2-cyclopentenone, 12 (R = R′ = Et): GC ret time 7.92 min; ^{1}H NMR ($CDCl_3$) δ 2.60−2.40 (m, 2 H), 2.30−2.21 (m, 1 H), 2.19−2.18 (m, 2 H), 2.02−1.91 (m, 1 H), 1.90−1.62 (m, 2 H), 1.61−1.49 (m, 2 H), 1.48−1.25 (m, 6 H), 1.12−0.75 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 211.548 (C), 175.477 (C), 139.992 (C), 51.056 (CH), 46.902 (CH), 29.659 (CH_2), 28.225 (CH_2), 25.150 (CH_2), 25.000 (CH_2), 22.907 (CH_2), 21.896 (CH_2), 13.965 (CH_3), 13.879 (CH_3), 11.139 (CH_3), 10.674 (CH_3), one peak in this spectrum is missing; IR (neat oil) 2956 (vs), 2932 (vs), 2875 (s), 2735 (w), 2249 (w), 1699 (vs), 1637 (s), 1458 (s), 1379 (m), 1364 (m), 1339 (m), 1319 (w), 1233 (w), 1174 (w), 1109 (w), 1063 (w) cm^{-1}; MS (EI) *m/e* 237 (5%), 236 (28%), 208 (30%), 207 (100%), 193 (16%), 179 (19%), 166 (16%), 165 (16%), 151 (10%), 138 (21%), 123 (11%), 109 (10%), 107 (9%), 95 (13%), 91 (16%), 81 (18%), 79 (18%), 77 (16%), 69 (11%), 67 (17%), 57 (11%), 55 (37%), 53 (12%); HRMS exptl 236.2138, calcd for $C_{16}H_{28}O$ 236.2140.

3-Butyl-4,5-diethyl-2-oxa-4-cyclopentenone, 13 (R = R′ = Et): GC ret time 6.90 min; ^{1}H NMR ($CDCl_3$) δ 4.82 (d, J = 6.8 Hz, 1 H), 2.51 (d, q, J = 14.0, 6.8 Hz, 1 H), 2.31−2.16 (m, 3 H), 1.80−1.95 (m, 1 H), 1.51−1.22 (m, 5 H), 1.65−1.06 (m, 6 H), 0.90 (t, J = 6.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 174.461 (C), 164.071 (C), 128.423 (C), 81.512 (CH), 31.904 (CH_2), 26.637 (CH_2), 22.439 (CH_2), 19.640 (CH_2), 16.876 (CH_2), 13.878 (CH_3), 13.172 (CH_3), 12.701 (CH_3); IR (neat oil) 2968 (m), 2938 (m), 2875 (w), 2255 (w), 1740 (vs), 1699 (w), 1464 (m), 1382 (w) cm^{-1}; MS (EI) *m/e* 197 (3%), 196 (20%), 167 (12%), 153 (14%), 140 (18%), 139 (24%), 125 (13%), 112 (10%), 111 (100%), 93 (7%), 83 (10%), 67 (19%), 55 (40%); HRMS exptl 196.1462, calcd for $C_{12}H_{20}O_2$ 196.1463.

6-Methyl-7-phenyl-5,8-dodecadione, 11 (R = Ph, R′ = Me): GC ret time 20.46 min; ^{1}H NMR ($CDCl_3$) δ 7.40−7.16 (m, 5 H), 3.97 (d, J = 10.8 Hz, 1 H), 3.30−3.23 (m, 1 H), 2.61 (dt, J = 2.0, 7.4 Hz, 2 H), 2.47−2.22 (m, 2 H), 1.70−1.10 (m, 11 H), 0.92 (t, J = 7.3 Hz, 3 H), 0.80 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 214.688 (C), 210.496 (C), 136.823 (C), 129.098 (CH), 128.980 (CH), 127.663 (CH), 61.460 (CH), 48.301 (CH), 41.585 (CH_2), 25.772 (CH_2), 22.480 (CH_2), 22.144 (CH_2), 15.047 (CH_3), 14.015 (CH_3), 13.825 (CH_3); IR (neat oil) 3061(m), 3027 (m), 2982 (s), 2963 (s), 2934 (s), 2875 (s), 1952 (vw), 1885 (vw), 1807 (vw), 1712 (vs) 1671 (m),1600 (m), 1584 (w), 1494 (s), 1454 (vs), 1408 (m), 1376 (s), 1299 (w), 1265 (m), 1229 (w), 1187 (m), 1125 (s), 1041 (s), 998 (m), 968 (w) cm^{-1}; MS (EI) *m/e* 288.05 (2%), 246.05 (3%), 231.00 (2%), 205.00 (2%), 204.00 (10%), 203.00 (5%), 187.05 (2%), 186.05 (9%), 161.95 (5%), 160.95 (2%), 148.00 (4%), 147.00 (16%), 144.90 (2%), 144.00 (3%), 143.00 (2%), 128.95 (2%), 127.95 (2%), 118.90 (5%), 117.90 (16%), 116.90 (18%), 114.90 (8%),102.95 (3%), 90.95 (15%), 88.90 (2%), 85.90 (6%), 85.00 (100%), 77.90 (2%), 77.00 (3%), 64.95 (2%), 58.00 (3%), 57.05 (5%), 57.00 (68%), 54.90 (5%); HRMS exptl 288.2052, calcd for $C_{19}H_{28}O_2$ 288.2089.

3-Butyl-4-methyl-5-phenyl-2-propyl-2-cyclopentenone, 12 (R = Ph, R′ = Me): GC ret time 20.8 min; ^{1}H NMR ($CDCl_3$) δ 7.51−7.26 (m, 5 H), 3.41 (broad singlet, 1 H), 2.44−2.39 (m, 1 H), 2.28−2.19 (m, 2 H), 2.02−1.89 (m, 1 H), 1.61−1.38 (m, 4 H), 1.22 (d, J = 7.3 Hz, 3 H), 0.94 (t, J = 7.3 Hz, 3 H), 0.84 (d, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 211.307 (C), 173.494 (C), 142.007 (C), 140.176 (CH) 129.014 (CH), 127.745 (CH), 127.078 (CH), 57.867 (CH), 50.961 (CH), 29.735 (CH2), 28.644 (CH_2), 25.516 (CH_2), 22.853 (CH_2), 22.137 (CH_2), 15.673 (CH_3), 14.263 (CH_3), 13.962 (CH_3); IR (neat oil) 3067 (w), 3025 (vw), 2960 (s), 2931 (s), 2872 (m), 1701 (vs), 1636 (m), 1601 (w), 1494 (m), 1454 (s), 1370 (w), 1358 (w), 1340 (vw), 1229 (vw), 1168 (vw) cm^{-1}; MS (EI) *m/e* 272.10 (1%), 271.10 (8%), 270.10 (39%), 255.15 (2%), 243.10 (2%), 242.10 (18%), 241.10 (100%), 228.05 (2%), 227.05 (4%), 214.10 (3%), 213.10 (15%), 211.00 (1%), 200.05 (4%), 199.05 (3%), 186.05 (2%), 185.00 (9%), 183.00 (2%), 181.00 (3%), 179.10 (3%), 171.00 (4%), 169.05 (3%), 166.95 (3%), 166.05 (2%), 165.05 (5%), 157.05 (5%), 156.05 (2%), 155.05 (7%), 153.00 (6%), 152.00 (6%), 151.00 (8%), 145.00 (2%), 143.00 (9%), 142.00 (5%), 141.00 (11%), 139.00 (2%), 131.05 (2%), 130.05 (2%), 129.05 (15%), 128.05 (16%), 127.05 (5%), 123.05 (2%), 119.00 (2%), 118.00 (3%), 117.00 (13%), 116.00 (4%), 115.00 (19%), 109.00 (3%), 107.05 (3%), 106.05 (2%), 104.95 (13%), 103.05 (4%), 102.05 (2%), 95.05 (4%), 93.05 (3%), 92.05 (4%), 91.00 (39%), 89.00 (3%), 85.00 (4%), 83.00 (2%), 81.00 (4%), 79.00 (8%), 78.00 (6%), 77.00 (13%), 74.05 (3%), 71.05 (2%), 69.05 (4%), 67.05 (6%), 65.05 (5%), 63.05 (2%), 59.00 (4%), 57.00 (8%), 55.00 (11%), 53.00 (6%), 52.10 (2%), 51.00 (4%); HRMS exptl 270.2002, calcd for $C_{19}H_{26}O$ 270.1984.

3-Butyl-4-methyl-5-phenyl-2-oxa-4-cyclopentenone, 13 (R = Ph, R′ = Me): GC ret time 22.77 min; ^{1}H NMR ($CDCl_3$) δ 7.49−7.31 (m, 5 H), 4.86 (dd, J = 3.4, 7.6 Hz, 1 H), 2.12 (s, 3 H), 2.00−1.97 (m, 1 H), 1.87−1.82 (m, 1 H), 1.62−1.34 (m, 4 H), 0.92 (t, J = 4.7 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 172.684 (C), 160.831 (C), 130.153 (C), 128.963 (CH), 128.465 (CH), 128.384 (CH), 126.988 (C), 82.977 (CH), 31.924 (CH_2), 26.537 (CH_2), 22.484 (CH_2), 13.917 (CH_3), 13.118 (CH_3); IR (neat oil): 3060 (m), 3025 (m), 2961 (s), 2933 (s), 2870 (m), 2856 (m), 1950 (vw), 1887 (vw), 1820 (vw), 1749 (vs),1661 (s), 1602 (w), 1577 (vw), 1496 (m), 1466 (m), 1446 (m), 1383 (s), 1330 (s), 1283(w), 1223 (m), 1148 (s), 1107 (w), 1083 (m), 956 (s) cm^{-1}; MS (EI) *m/e*

231.05 (4%), 230.05 (2%), 187.05 (4%), 173.00 (12%), 146 (17%), 145.00 (67%), 129.05 (2%), 128.05 (3%), 118.10 (9%), 117.10 (100%), 116.10 (10%), 115.00 (36%), 91.00 (13%), 89.00 (3%), 77.10 (3%), 65.05 (3%), 63.05 (3%), 57.10 (3%), 51.10 (3%); HRMS exptl 230.1306, calcd for $C_{19}H_{27}O$ 230.1307.

6,7-Diphenyl-5,8-dodecadione, 11 (R = R′ = Ph): 3:2 mixture of two isomers; GC ret time 23.3 min; ^{1}H NMR ($CDCl_3$) δ 7.33−6.83 (m, 12 H), 4.54 (s, 1 H), 4.32 (s, 1 H), 4.21 (s, 3 H), 3.60 (s, 6 H), 2.51−1.91 (m, 7 H), 1.59−1.31 (m, 5 H), 1.26−1.02 (m, 5.5 H), 0.91−0.69 (m, 6 H), 0.57 (t, 2 H); ^{13}C NMR ($CDCl_3$) δ 210.358 (C), 208.679 (C), 136.771 (C), 135.979 (C), 129.060 (CH), 128.878 (CH), 128.659 (CH), 127.663 (CH), 127.301 (CH), 61.639 (CH), 60.748 (CH), 43.197 (CH_2), 41.804 (CH_2), 25.854 (CH_2), 25.360 (CH_2), 22.227 (CH_2), 21.881 (CH_2), 13.873 (CH_3), 13.707 (CH_3); IR ($CHCl_3$) 3086 (vw), 3064 (w), 3030 (m), 3011 (m), 2960 (s), 2933 (s), 2874 (m), 1950 (vw), 1881 (vw), 1807 (vw), 1707 (vs),1599 (w), 1584 (w), 1494 (m), 1465 (m), 1454 (m), 1404 (m), 1380 (w), 1366 (w), 1264 (m), 1234(w), 1124 (m), 1032 (w), 909 (m) cm^{-1}; MS (EI) *m/e* (early retention isomer) 350.00 (<1%), 332.2 (2%), 290.05 (2%), 289.05 (7%), 266.05 (6%), 265.05 (3%), 248.00 (4%), 208.95 (5%), 204.95 (3%), 181.95 (2%), 180.95 (7%), 179.95 (12%), 178.95 (7%), 177.95 (1%), 164.90 (4%), 114.95 (2%), 104.9 (2%), 102.9 (2%), 90.95 (6%), 85.95(6%), 84.95 (100%), 76.90 (3%), 58.05 (2%),57.05 (55%), 54.90 (3%); (EI) *m/e* (late retention isomer) 350.00 (<1%), 332.2 (6%), 290.05 (6%), 289.05 (24%), 266.05 (4%), 265.05 (2%), 248.10 (3%), 215.00 (3%), 208.95 (3%), 204.95 (3%), 202.95 (3%), 201.95 (5%), 180.95 (5%), 179.95 (10%), 178.95 (7%), 177.95 (7%), 175.95 (2%), 164.90 (4%), 151.95 (2%), 114.95 (4%), 104.9 (5%), 102.9 (3%), 101.90 (2%), 90.95 (9%), 88.95 (2%), 85.95(6%), 84.95 (100%), 76.90 (5%), 59.95 (2%),56.05 (65%), 54.90 (6%); HRMS exptl 350.2213, calcd for $C_{24}H_{30}O_2$ 350.2232.

3-Butyl-4,5-diphenyl-2-propyl-2-cyclopentenone, 12 (R = R′ = Ph): GC ret time 24.1 min; ^{1}H NMR ($CDCl_3$) δ 7.34−7.02 (m, 10 H), 3.92 (br singlet, 1 H), 3.43 (d, J = 2.45 Hz, 1 H), 2.57−2.48 (m, 1 H), 2.33 (t, J = 15.3 Hz, 2 H), 2.08−1.97 (m, 1 H), 1.64−1.17 (m, 6 H), 0.97 (t, J = 14.7 Hz, 3H), 0.86 (t, J = 14.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 208.332 (C), 174.747 (C), 141.730 (C), 141.105 (C), 140.025 (C), 129.193 (CH), 129.013 (CH), 128.081 (CH), 127.832 (CH), 127.751 (CH), 127.334 (CH), 127.061 (CH), 62.120 (CH), 57.493 (CH), 29.840 (CH_2), 28.980 (CH_2), 25.738 (CH_2), 22.996 (CH_2), 22.211 (CH_2), 14.377 (CH_3), 14.010 (CH_3); IR (neat oil) 3083 (w), 3060 (w), 3026 (w), 2938 (vs), 2868 (vs), 2667 (m), 1947 (m), 1871 (m), 1802 (m), 1704 (vs), 1639 (vs),1601 (s), 1584 (w), 1495 (s), 1453 (s), 1379(m), 1358 (m), 1377 (w), 1317 (w), 1297 (w), 1231 (w), 1217 (w), 1165 (m), 1118 (m), 1093 (m), 1075 (m), 1031 (w), 1001 (w), 930 (w), 891 (w) cm^{-1}; MS (EI) *m/e* 333.20 (19%), 332.20 (72%), 304.20 (24%), 303.2 (100%), 290.15 (9%), 289.15 (14%), 276.10 (17%), 275.10 (77%), 255.15 (7%), 247.10 (9%), 241.10 (5%), 215.10 (10%), 213.10 (16%), 205.05 (12%), 204.05 (6%), 203.05 (8%), 202.05 (10%), 199.05 (7%), 179.05 (21%), 178.05 (27%), 171.05 (6%), 167.00 (11%), 165 (22%), 157 (7%), 155.00 (10%), 152.95 (10%), 151.95 (12%), 151.05 (10%), 141.05 (21%), 129.00 (24%), 128.00 (23%), 127.00 (9%), 117.95 (6%), 117.05 (9%), 115.05 (29%), 105.00 (28%), 103.00 (8%), 102.00 (7%), 91.95 (7%), 91.05 (81%), 88.95 (6%), 79.00 (7%), 78.00 (7%), 77.00 (16%), 66.95 (6%), 64.95 (6%), 55.00 (9%); HRMS exptl 332.2153, calcd for $C_{14}H_{18}O$ 332.2150.

6,7-Diphenyl-6-dodecen-5,8-dione, 14 (R = R′ = Ph): GC ret time 25.0 min; ^{1}H NMR ($CDCl_3$) δ 7.41−7.34 (m, 10 H), 2.16 (t, J = 14.5 Hz, 4 H), 1.35−1.23 (q, J = 7.3 Hz, 4 H), 1.05−0.90 (sextet, J = 7.3 Hz, 4 H), 0.66 (t, J = 7.27 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 207.033 (C), 142.719 (C), 134.592 (C), 128.946 (CH), 128.804 (CH), 42.985 (CH2), 25.597 (CH_2), 21.958 (CH_2), 13.734 (CH_3); IR ($CHCl_3$) 3025 (m), 2961 (s), 3026 (w), 2933 (s), 2874 (m), 1956 (vw), 1894 (vw), 1812 (vw), 1767 (m), 1697 (vs),1599 (w), 1493 (m), 1445 (m), 1363 (m), 1260 (m), 1140 (m), 1086 (w), 1031 (w), 909 (m) cm^{-1}; MS (EI) *m/e* 348.10 (1%), 332.15 (2%), 292.05 (5%), 291.05 (21%), 290.10 (2%), 289.00 (7%), 287.00 (3%), 266.05 (2%), 263.05 (4%), 249.00 (2%), 248.10 (2%), 234.95 (2%), 221.00 (2%), 214.95 (2%), 208.95 (2%), 206.95 (2%), 205.95 (2%), 202.95 (2%), 201.90 (3%), 180.95 (3%), 179.95 (5%), 178.95 (10%), 177.95 (18%), 176.95 (3%), 175.95 (5%), 165.00 (3%), 151.95 (4%), 150.95 (3%), 128.95 (2%), 127.95 (2%), 125.95 (2%), 114.9 (4%), 104.90 (6%), 103.00 (2%), 102.00 (2%), 90.95 (7%), 85.95 (6%), 85.00 (100%), 77.00 (5%), 58.05 (4%), 57.05 (86%), 54.90 (6%), 51.00(2%); HRMS exptl 348.2093, calcd for $C_{24}H_{28}O_2$ 348.2094.

Reaction of Complex 1 with Bromostyrene and Allyl Bromide. These reactions were performed as in ref 2, except after the acylate complex was formed and before the bromostyrene or allyl bromide was added, the reaction was placed under a CO atmosphere rather than remaining under an argon atmosphere.

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