δ 2.13–2.26 (m, 1 H), 2.33–2.46 (m, 2 H), 3.04–3.16 (m, 1 H), 3.44–3.50 (m, 1 H), 4.05–4.12 (m, 1 H), 6.68 (d, J = 5.0 Hz, 1 H), 7.12–7.16 (m, 2 H), 7.40–7.50 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 2.92 (q, J_{C-C-F} = 30.1 Hz), 33.1 (q, J_{C-C-F} = 27.8 Hz), 39.21, 43.40, 123.6 (q, J_{C-F} = 53.1 Hz), 125.8 (q, J_{C-F} = 52.2 Hz), 127.3, 128.0, 128.3, 133.2, 151.4, 166.7; ^{19}F NMR (acetone-d_6) δ 99.12 (t, J = 11.5 Hz), 99.50 (t, J = 11.5 Hz). Anal. Calcd for $C_{14}H_{12}N_2O_2F_6$: C, 47.47; H, 3.41; N, 7.91. Found: C, 47.49; H, 3.28; N, 8.06.

5,6-Bis(2,2,2-trifluoroethyl)-5,6-dihydro-2,4(1*H*,3*H*)-pyrimidinedione (20). A mixture of **14** (50 mg, 0.16 mmol) and polyphosphoric acid (3 g) was stirred at 100 °C for 17 h. The above-mentioned workup and chromatography (SiO_2, hexane–AcOEt) gave **20** (34 mg, 76%) as colorless crystals: IR (Nujol) 3240, 3100, 1730, 1254, 1152 cm^{-1}; ^1H NMR (acetone-d_6) δ 2.44–2.97 (m, 4 H), 2.97–3.09 (m, 1 H), 3.38–3.46 (m, 1 H), 3.94–4.00 (m, 1 H), 4.07–4.14 (m, 1 H), 7.13 (s, 1 H), 7.41 (s, 1 H), 9.40 (s, 1 H); ^{19}F NMR (acetone-d_6) δ 99.50 (t, J = 22.6 Hz), 99.80 (t, J = 21.6 Hz), 100.32 (t, J = 22.1 Hz), 100.54 (t, J = 20.7 Hz). Anal. Calcd for $C_8H_8N_2O_2F_6$: C, 34.54; H, 2.90; N, 10.07. Found: C, 34.59; H, 3.23; N, 9.96.

3,4-Bis(2,2,2-trifluoroethyl)-1,2-bis(trimethylsiloxy)-cyclobutene (21). Under a nitrogen atmosphere, a mixture of **2** (501 mg, 1.6 mmol), sodium (200 mg, 8.7 mmol), trimethylchlorosilane (1.1 mL, 8.3 mmol), and toluene (5 mL) was stirred at 100 °C for 4 h. After cooling, the mixture was filtered with a glass filter. The filtrate was fractionally distilled (130 °C/6 mmHg) to give **21** (319 mg, 50%) as a colorless liquid: IR (neat) 2968, 1730, 1312, 1256 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.20 (s, 18 H), 2.00–2.20 (m, 4 H), 2.34–2.38 (m, 2 H), 2.88–2.92 (m, 2 H); ^{19}F NMR ($CDCl_3$) δ 96.81 (t, J = 10.2 Hz), 97.67 (t, J = 11.0 Hz); MS, m/e (relative intensity) 394 (M^+, 25), 297 (7), 147 (20), 115 (6), 73 (100). Anal. Calcd for $C_{14}H_{24}O_2F_6Si_2$: C, 42.62; H, 6.13. Found: C, 42.46; H, 6.26.

Acknowledgment. We are grateful to The Mazda Foundation, The Japan Securities Scholarship, The Asahi Glass Foundation, and the Ministry of Education, Culture and Science of Japan (a Grant-in-Aid for Scientific Research on Priority Area. NO. 63607521) for financial support and the SC-NMR Laboratory of Okayama University for 500-MHz NMR analysis.

Importance of Structure of α,β-Ethylenic Ketones during Their Reductive Coupling Promoted by the $TiCl_4$–Mg Reagent

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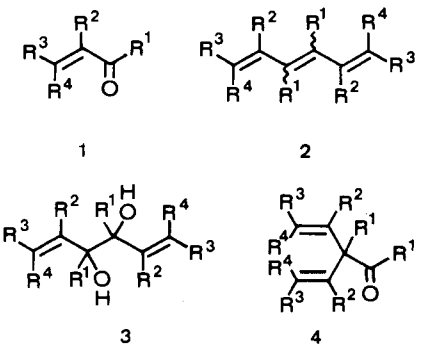
Received January 25, 1988

In most cases, the reductive coupling of α,β-ethylenic ketones by the $TiCl_4$–Mg reagent leads to 1,3,5-trienes and bisallylic pinacols. Some α,β-enones of *s*-cis configuration, such as (+)-pulegone, show a particular reactivity: formation of dihydro ketones in the presence of *tert*-butyl alcohol and reductive alkylation with allylic halides or benzyl bromide. Results are in accordance with a polymeric structure for the native low-valent titanium species, and in the case of some *s-cis*-enones, they can be explained by the intervention of a oxametallacyclopentene.

The reductive coupling of carbonyl compounds by a low-valent transition metal has been the subject of many studies.[1] Most of these are of practical value for the synthesis of diols or alkenes.[2] In order to extend the scope of the reaction, reductive dimerization of α,β-enones has been investigated.[3] In this paper, we emphasize the mechanistic aspects and stereochemical implications. Only those studies on Ti(0) reagents, resulting from the reduction of $TiCl_3$ by $LiAlH_4$ (McMurry's reagent), K, or Mg on saturated or aromatic ketones have been reported.[1,2,4] Surprisingly, few investigations have been reported involving the coupling of enones and the cross-coupling between enones and an excess of acetone.[1a,4b,5]

Mechanistic studies are intricate because most of the reagents used are of unknown structure. For Ti(0) reagents, the metal surface has been proposed as the active coupling species.[4b,c] Many low-valent transition metal complexes have been described,[6] but, to our knowledge,

Chart I[a]



[a] **a**, $R^1 = R^2 = R^4 = H$, $R^3 = CH_3$; **b**, $R^1 = R^3 = R^4 = CH_3$, $R^2 = H$; **c**, $R^1 = CH_3$, R^2–$R^3 = -(CH_2)_3-$, $R^4 = CH_3$.

(1) (a) McMurry, J. E. *Acc. Chem. Res.* **1974**, *7*, 281. (b) Finocchiaro, P.; Libertini, E.; Recca, A. *Chim. Ind. (Milan)* **1982**, *64*, 644. (c) McMurry, J. E. *Acc. Chem. Res.* **1983**, *16*, 405.

(2) Pons, J. M.; Santelli, M. *Tetrahedron* **1988**, *44*, 4295.

(3) (a) Pons, J. M.; Zahra, J. P.; Santelli, M. *Tetrahedron Lett.* **1981**, *22*, 3965. (b) Pons, J. M.; Santelli, M. *Tetrahedron Lett.* **1982**, *23*, 4937. (c) Pons, J. M.; Santelli, *Tetrahedron Lett.* **1986**, *27*, 4153.

(4) (a) McMurry, J. E.; Krespi, L. R. *J. Org. Chem.* **1976**, *41*, 3929. (b) McMurry, J. E.; Fleming, M. P.; Kees, K. L.; Krespi, L. R. *J. Org. Chem.* **1978**, *43*, 3255. (c) Dams, R.; Malinowski, M.; Westdorp, I.; Geise, H. Y. *J. Org. Chem.* **1982**, *47*, 248. (d) Coutts, R. S. P.; Wailes, P. C.; Martin, R. L. *J. Organomet. Chem.* **1973**, *50*, 145.

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(6) For examples, see: (a) Allmann, R.; Batzel, V.; Pfeil, R.; Schmid, G. *Z. Naturforsch. B.* **1976**, *31*, 1329. (b) Guggenberger, L. J.; Tebbe, F. N. *J. Am. Chem. Soc.* **1976**, *98*, 4137. (c) Huffman, J. C.; Moloy, K. G.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 3009. (d) Kool, L. B.; Rausch. M. D.; Alt, H. G.; Herberhold, M.; Thewalt, U.; Wolf, B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 394. (e) Folting, K.; Huffman, J. C.; Bansemer, R. L.; Caulton, K. G. *Inorg. Chem.* **1984**, *23*, 3289. (f) Girolami, G. S.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc. Dalton Trans.* **1984**, 2347. (g) Smith, P. D.; Martin, J. L.; Huffman, J. C.; Bansemer, R. L.; Caulton, K. G. *Inorg. Chem.* **1985**, *24*, 2997. (h) Durfee, L. D.; Fanwick, P. E.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 4720.

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Table I. Reductive Coupling of the Ketones 1, 9, 11, 13, 15, 22, 26, 29, and 31

entry	ketone	reagents (ratio)	temp, °C	time, h	1,3,5-triene		pinacol		ketone 4 (%)	dihydro ketone (%)	other product (%)
					E (%)	*Z* (%)	*meso* (%)	*dl* (%)			
1	**1a**	$TiCl_4$-Mg/*t*-BuOH	20	72			**3a** (45)[36b]				
2	**1b**	4($TiCl_4$-Mg)	reflux	10	**2b** (60)	**2b** (25)					
3	**1b**	$TiCl_4$-Mg/*t*-BuOH[a]	20	4			**3b** (40)	**3b** (25)			7 (15), 8 (5)
4	**1b**	$TiCl_4$-Mg/*t*-BuOH	20	48	**2b** (10)	**2b** (5.5)	**3b** (14.5)	**3b** (8.5)	**4b** (37)		6 (5), 7 (20)
5	**1c**	2($TiCl_4$-Mg)	reflux	12	**2c** (65)	**2c** (15)					
6	**1c**	$TiCl_4$-Mg/*t*-BuOH	reflux	12	**2c** (30)	**2c** (6)			**4c** (42.5)		
7	**9**	2($TiCl_4$-Mg)	20	12	**10** (33)	**10** (33)					
8	**11**	2($TiCl_4$-Mg/*t*-BuOH)	reflux	10	12 (60)						
9	**13**	2($TiCl_4$-Mg/*t*-BuOH)	reflux	3	**14** (40)	**14** (35)					
10	**15**	2($TiCl_4$-Mg/*t*-BuOH)	20	14			**16** (60)				
11	**1b** + **1c**	4($TiCl_4$-Mg)	reflux	15	**2b** (13)	**2b** (5.5)					
					2c (21)	**2c** (5.2)					
					17 (22.5)	**17** (22.5)					
12	**22a**	2($TiCl_4$-Mg)/4*t*-BuOH	20	24						**23a** (60)	
13	**22b**	2($TiCl_4$-Mg)4*t*-BuOH	20	3						**23b** (70)	
14	**22b**	$TiCl_4$-Mg	20	36						**23b** (18)	**24a-e** (58), **25a,b** (13)
15	**26**	2($TiCl_4$-Mg)/4*t*-BuOH	20	24				**27** (55)		**28** (10)	
16	**29**	4($TiCl_4$-Mg)/2*t*-BuOH	20	8				**30** (50)			
17	**31**	2($TiCl_4$-Mg)/4*t*-BuOH	20	10				**32** (55)		**33** (5)	

[a] Solvent: tetrahydrofuran–pentane (4:1).

none of them has been used for reductive duplication of ketones (except the Vohwinkel's complex and titanocene).[7,8]

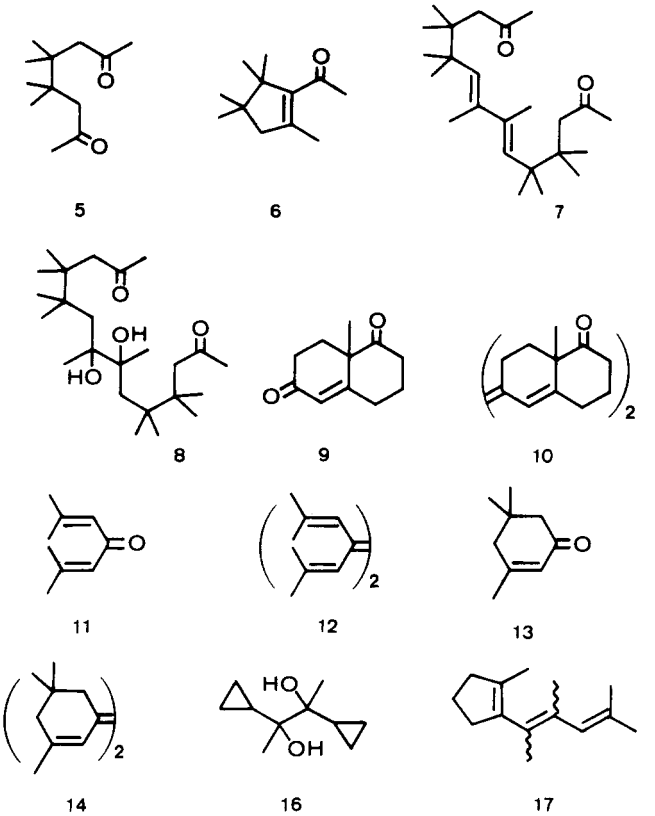
Our present investigations concern the reduction of enones by Ti(II) species in tetrahydrofuran, resulting from the reduction of $TiCl_4$ by magnesium (1:1).

Results

The reductive coupling of enones **1a–c**, **9**,[9] **11**, **13**, and acetylcyclopropane **15** (Charts I and II) by $TiCl_4$–Mg mainly yields bisallylic pinacols **3a,b**, **16**, or 1,3,5-trienes **2b,c**, **10**, **12**, **14**, depending on the structure of the ketone and the reagent–enone ratio. Byproducts **4b,c** result from the pinacol rearrangement of diols.[7,10,11] All these results are summarized in Table I.

As already mentioned,[3a] the presence of *tert*-butyl alcohol does not modify the reactivity of the reagent. Moreover, it diminishes the proportion of pinacolic ketone **4** and prevents the formation of large quantities of 1,3,5-trienes, when the reaction is carried out at room temperature. Thus, a clean reaction leading to pinacol **3b** was observed when using *tert*-butyl alcohol (entry 3).[12,13] Nevertheless, the formation of the minor product **7** (probably coming from the dehydration of **8**), resulting from a dimerization of the nonisolated diketone **5** (a tetramerization of the mesityl oxide) (entries 3 and 4), could be noted. The cross-coupling between **1b** and **1c** (carbonyl

Chart II



compounds of similar reduction potential values)[14] leads to a nearly statistical distribution of 1,3,5-trienes **2b** (21%), **2c** (29%), and **17** (50%) (entry 11).

The diol **19** (mp 172 °C) (70% yield) was obtained by reduction of (*R*)-(−)-carvone (*p*-mentha-6,8-dien-2-one) (**18**).[15] ^{13}C NMR data (10 lines) were consistent with a diol possessing a C_2 axis of symmetry, that is a threo isomer; **19** was subjected to single-crystal X-ray analysis, which revealed it to be the 1*S*,5*R*,1′*S*,5′*R* isomer.[16,17] The

(7) Corey, E. J.; Danheiser, R. L.; Chandrasekaran, S. *J. Org. Chem.* **1976**, *41*, 260.

(8) The structure of the complex $|(THF)Cl_2Mg_2Ti|_2$ used for the reductive duplication of (−)-*cis*-caran-4-one was not really established, see: Sobota, P.; Jezowska-Trzebiatowska, B. *Coord. Chem. Rev.* **1978**, *26*, 71.

(9) Mandell, L.; Hamilton, H.; Day, R. A., Jr. *J. Org. Chem.* **1980**, *45*, 1710.

(10) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 963.

(11) Rearrangements of bisallylic pinacols are very easy, see: Calas, R.; Bolourtchian, M.; Dunogues, J.; Duffaut, N. *J. Organomet. Chem.* **1972**, *34*, 269.

(12) We have found that the results were easier to reproduce when the titanium species was generated by addition of a solution of $TiCl_4$ in pentane (and not neat) on the magnesium turnings in tetrahydrofuran (pentane–THF, 1:4).

(13) Electrochemical or chemical reductive coupling of mesityl oxide led to a mixture of **6** and other coupling products. The pinacol **3b** seems to have never been isolated, see: (a) Wiemann, J.; Bouguerra, M. L. *Ann. Chim. (Paris)* **1967**, *2*, 35; **1968**, *3*, 215. (b) Kolobielski, M.; Wiemann, J. C. *R. Seances Acad. Sci.* **1951**, *233*, 691; **1953**, *237*, 909; **1954**, *238*, 1039. (c) Calas, R.; Dunogues, J.; Bolourtchian, M. *J. Organomet. Chem.* **1971**, *26*, 195. (d) Simonet, J. *C. R. Seances Acad. Sci. Ser. C* **1968**, *267*, 1548.

(14) House, H. O.; Huber, L. E.; Umen, M. J. *J. Am. Chem. Soc.* **1972**, *94*, 8471.

(15) Electrochemical reduction of (+)-carvone is known to give two ϵ-diketonic hydrodimers, see: Grimshaw, J.; Trocha-Grimshaw, J. *J. Chem. Soc. Perkin Trans. 1* **1973**, 2584.

Table II. Reductive Alkylation of the Enones 22b, 26, and 18

entry	ketone	halide (ratio)	reagent (ratio)	temp °C	time, h	hydrocarbons (%)	ketone (%)	alcohol (%)
1	**22b**	2(allyl bromide)	2($TiCl_4$–Mg)	20	48	**34a** (65), **36** (10)	**35** (5)	
2	**22b**	2(crotyl chloride)	2($TiCl_4$–Mg)	20	48	**34b** (60)		
3	**22b**	benzyl bromide	2($TiCl_4$–Mg)	reflux	2.5	**38** (10)	**37** (45)[a]	
4	**26**	2(allyl bromide)	2($TiCl_4$–Mg)	20	72		**39** (15),	**40** (30)[a]
5	18	3(allyl bromide)	2($TiCl_4$–Mg)	reflux	4		**41** (15)[a]	

[a] Other products are of indetermined structure.

other threo isomer (1*R*,5*R*,1′*R*,5′*R*) (mp 78–79 °C), **20**, was formed as intermediate (Chart III).

We managed to increase its proportion by adding pentane (or mesitylene) to the reaction mixture. In this case, a third component, the ketol **21**, was also obtained. The infrared spectrum (CCl_4) of the ketol **21** contained a relatively narrow band due to the free hydroxy group, and a broader band at a lower frequency was attributed to the intramolecular hydrogen bond (concentration-independent band). The CD curve of **21** in hexane showed a very weak positive Cotton effect (the amplitude decreases with lower temperature) (see the Experimental Section) consistent as expected from the octant rule[18] and the presence of an intramolecular hydrogen bond.

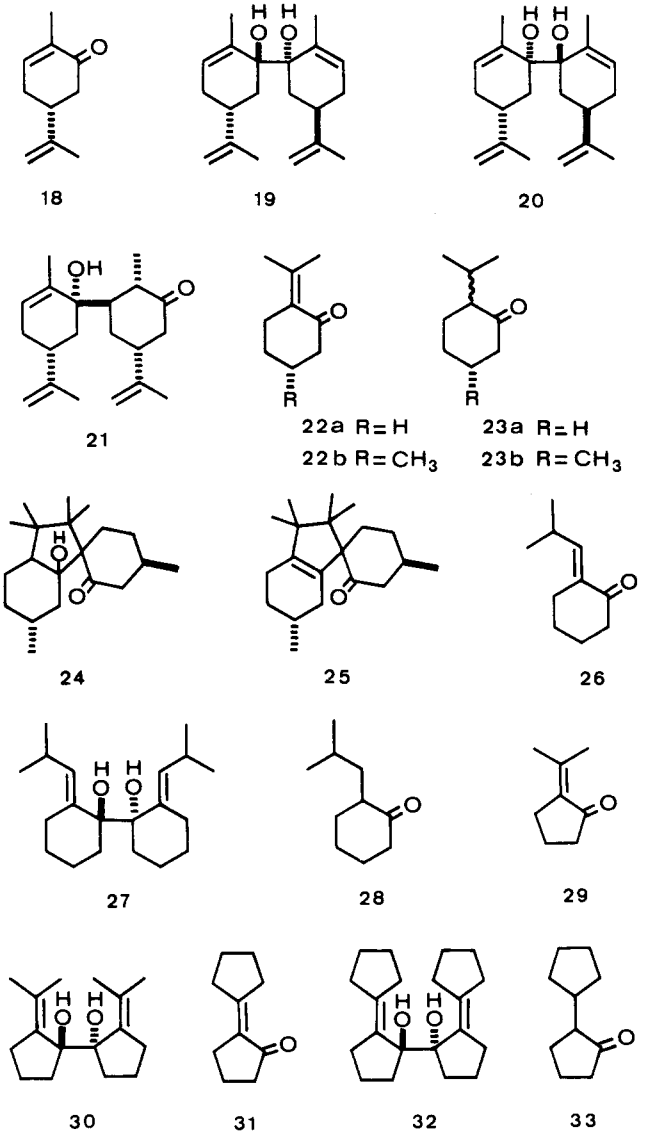
The action of $TiCl_4$–Mg to cyclic enones of cis configuration is a complex reaction. In particular, bisallylic pinacols were not systematically obtained as the main products, and the formation of 1,3,5-trienes were not observed. The reduction of **22a** and (*R*)-(+)-pulegone (**22b**), in the presence of *tert*-butyl alcohol, gave, respectively, the dihydro ketones **23a** and **23b**. In the absence of alcohol, the reaction with pulegone was slower and the major products were ketols **24** (five isomers formed and isolated)[19] and unsaturated ketones **25** (two isomers).

An experiment with *tert*-butyl alcohol-d_1 (2 equiv), followed by protic hydrolysis, led to labeled menthone **23b**. NMR analysis has shown that each of its C_4 and C_8 carbon atoms bear 0.6 deuterium. A similar result was observed when a mixture of pulegone **22b** and deuterium oxide (1:2) was added to the reagent.

In contrast to these results, ketones **26**, **29**, and **31** are reduced, in the presence of *tert*-butyl alcohol, into pinacols **27**, **30**, and **32** and sometimes into dihydro ketones **28** and **33** (see Table I). For each pinacol, only one isomer has been isolated. The infrared spectra (CCl_4) of pinacols **27**, **30**, and **32** contained a relatively narrow band due to the free hydroxyl group. A broader band at a lower frequency was assigned to the intramolecular hydroxy interaction (concentration-independent bands). The relative importance of these bands and the high $\Delta\nu$ values are consistent with racemate (*dl*) structures.[20]

Interestingly enough, reduction of alkylidenecycloalkanones in the presence of allylic halides or benzyl bromide (1–2 equiv) gives rise to an alkylation.[21] Thus, (+)-pulegone affords a mixture of **34a** (65%), **35** (5%),[22] and **36** (10%)[23] with allyl bromide and a mixture of ketone **37** (45%) and hydrocarbon **38** (10%) with benzyl bromide. Moreover, the alkylation reaction is stereoselective; condensation with crotyl chloride gives rise to **34b** (60%). The *R* configuration of the chiral center of the methylallyl substituent has been determined by comparison with the dehydration product of alcohol **43** of known structure.[24] With 2-isobutylidenecyclohexanone (**26**), the use of allyl

Chart III



(16) Details on crystallographic measurements of this compound will be published elsewhere (Pierrot, M.; Pons, J. M.; Santelli, M. *Tetrahedron Lett.*, in press).

(17) Structure of **19** has been revised to account for the results of X-ray analysis; see: ref 3c.

(18) Moffit, W.; Woodward, R. B.; Moscowitz, A.; Klyne, W.; Djerassi, C. *J. Am. Chem. Soc.* **1961**, *83*, 4013.

(19) The reductive coupling of (+)-pulegone has been carried out by [Al–Hg] method. See: (a) Bartual, J.; Font, J. M.; Forne, E.; Pascual, J.; Roque, J. *Anal. Quim.* **1972**, *68*, 483. (b) Font-Cistero, J. M.; Pascual, J. *Anal. Quim.* **1974**, *70*, 90. (c) Camps, P.; Pascual, J. *Anal. Quim.* **1976**, *72*, 1032. (d) Munoz-Madrid, F.; Pascual, J. *Anal. Quim.* **1978**, *74*, 1270.

(20) In pinacols, nonbonded repulsion results in larger $\Delta\nu$'s for *dl* than for meso isomers; for **30** and **32**, the $\Delta\nu$ values are higher (respectively 50 and 51 cm^{-1}) than for pinacol–cyclopentanone ($\Delta\nu$ = 40 cm^{-1}). One can expect that substitution on the cycle should decrease the azimuthal angle between vicinal OH groups, see: (a) Kuhn, L. P. *J. Am. Chem. Soc.* **1958**, *80*, 5950. (b) Kuhn, L. P.; Schleyer, P. v. R.; Baitinger, W. F., Jr.; Eberson, L. *J. Am. Chem. Soc.* **1964**, *86*, 650.

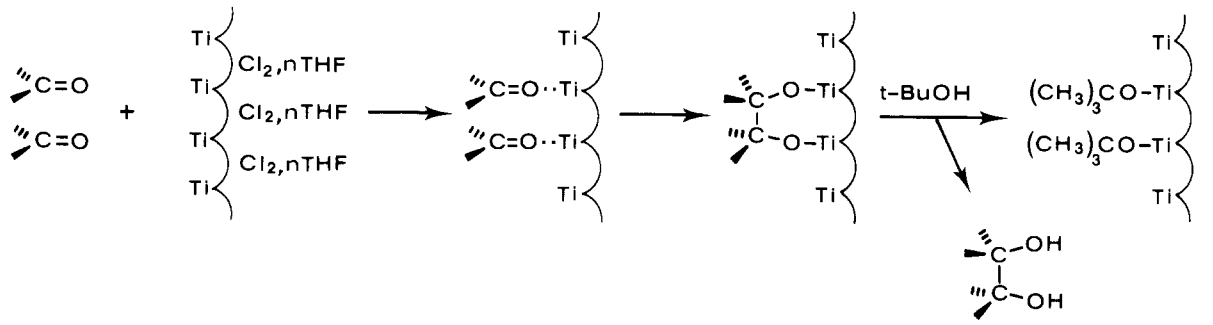
(21) Reductive coupling of allylic halides did not occur in the reaction conditions, and we have not been able to detect any reductive alkylation of mesityl oxide when using allyl bromide.

(22) Pardo, R.; Zahra, J. P.; Santelli, M. *Tetrahedron Lett.* **1979**, 4557.

(23) This minor compound was characterized only by GC/MS.

(24) El Idrissi, M.; Santelli, M. *J. Org. Chem.* **1988**, *53*, 1010.

Scheme I



bromide leads to the formation of the ketone **39** (15%) and the alcohol **40** (30%) resulting respectively from a 1,4- and a 1,2-addition. These reductive alkylations occur only with *s-cis*-enones, the (−)-carvone excepted, leads to allyldihydrocarvone **41** in low yield (15%) (mixture of four isomers) (Chart IV).

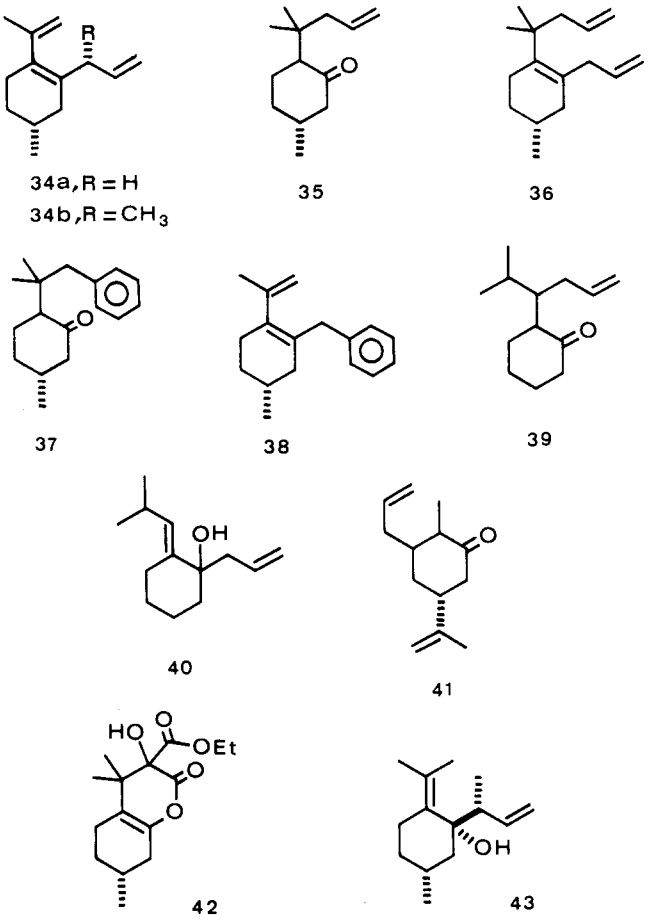
All attempts at the condensation of (+)-pulegone with various electrophilic reagents[25] failed, except with the diethyl mesoxalate, which led to the β-lactone **42** (mixture of two isomers).[26] All the results concerning the reductive alkylation of enones are summarized in Table II.

Discussion

Let us consider the physical structure of the reagent $TiCl_4$–Mg/THF. Our experiments on mesityl oxide led us to the following conclusions: (1) The reagent, resulting from the reduction of $TiCl_4$–2THF[8] by magnesium turnings, is a black slurry. Left standing, it turns into a gel. (2) The presence of tetrahydrofuran is necessary to obtain the dissolution of magnesium; thus, with other solvents (benzene, toluene, dimethyl sulfide), it is necessary to add at least 4 equiv of tetrahydrofuran to complete the reaction. The usual reagent is about 0.8–1.0 M.[27] (3) In an experiment, the black slurry was submitted to moderate centrifugation (4000 rpm for 20 min). The resulting black solution was unreactive toward mesityl oxide or pulegone. The sediment slurry proved to have some reducing power but only when tetrahydrofuran was added (giving a 0.4–0.6 M solution); the sediment can be dissolved in a large amount of tetrahydrofuran, and the resulting black solution is no longer reactive. Lastly, after a slow concentration in vacuo at room temperature of the latter diluted solution, a precipitate was recovered and proved to be *unreactive* after addition of tetrahydrofuran.

These various experiments enable us to propose that the efficiency of the reagent is correlated to the *insoluble phase and to its preparation.* In particular, the unreactivity of the soluble reagent can be explained by a strong solvation of the Ti(II) species by tetrahydrofuran, which impedes the association of the enone with the metal.[27] On the other hand, the fact that only the *native unsoluble reagent* is reactive appeared to be relevant with a polymeric structure, which can be irreversibly destroyed by dissolution.[28] A dimeric or a polymeric structure has been

Chart IV



proposed for the complex resulting from the $TiCl_4$–3Mg system.[8] Such an organized structure is also consistent with the tetramerization of mesityl oxide leading to **7**.

Concerning the mechanism of pinacol formation, all the titanium-mediated reactions have been readily rationalized by metal-bound ketyls.[4] Meanwhile, a radical intermediate is inconsistent with the coupling of cyclopropyl ketones (as, for example, **15**)[29] since it is well known that the cyclopropylhydroxycarbinyl radical derivatives isomerize into 4-hydroxy-but-3-enyl radical derivatives with a large con-

(25) Condensation of (+)-pulegone with 1 equiv of chlorotrimethylsilane, acetyl chloride, methyl vinyl ketone, ethyl chloroformiate, phenylisocyanate, or crotonyl chloride gave rise mainly to a mixture of **23b** and **24**. With acetyl chloride and crotonyl chloride, 4-acetoxy-1-chlorobutane and 4-crotonyl-1-chlorobutane were isolated; for a review on ether cleavage, see: Bhatt, M. V.; Kulkarni, S. U. *Synthesis* **1983**, 249.

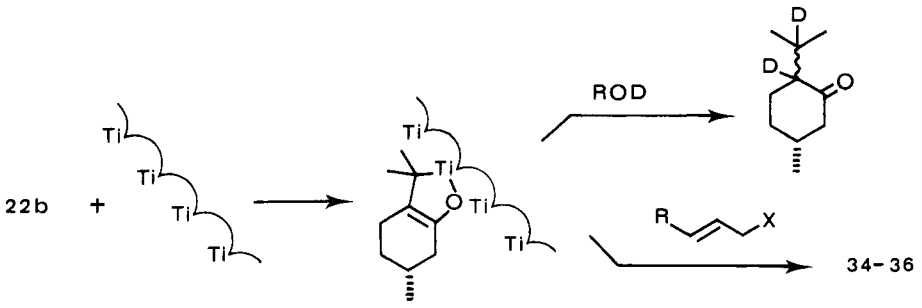
(26) No reaction occurred between (−)-carvone or mesityl oxide and diethyl mesoxalate. In the last case, diethyl hydroxymalonate was formed.

(27) When the concentration of the reagent is below 0.2 M, no reaction occurs. The addition of pyridine, triethylamine, HMPA, or methanol cancels the reducing power of the reagent.

(28) Concerning the structural parameters of $TiCl_2$, see: Vlaic, G.; Bart, J. C. J.; Caviglio, W.; Mobilio, S.; Navarra, G. *Chem. Phys.* **1982**, *64*, 115.

(29) For examples, see: **4b**, (a) Nishida, S.; Kataoka, F. *J. Org. Chem.* **1978**, *43*, 1612. (b) Paquette, L. A.; Wells, G. J.; Wickham, G. *J. Org. Chem.* **1984**, *49*, 3618. (c) Bohrer, G.; Knorr, R. *Tetrahedron Lett.* **1984**, *25*, 3675. (d) McMurry, J. E.; Bosch, G. K.; Kocovsky, P. *Tetrahedron Lett.* **1985**, *26*, 2167. (e) Bruch, M.; Jun, Y. M.; Luedtke, A. E.; Schneider, M.; Timberlake, J. W. *J. Org. Chem.* **1986**, *51*, 2969. (f) Wenck, H.; De Meijere, A.; Gerson, F.; Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 335. (g) Schwager, H.; Wilke, G. *Chem. Ber.* **1987**, *120*, 79.

Scheme II



stant rate at room temperature.[30] We suggest a vicinal association of two carbonyl compounds on the polymeric chain and then a concerted electron transfer from the metal to the carbonyl groups (avoiding the formation of discrete ketyl radicals).[31] An alternative hypothesis would involve the formation of a dianion and its addition on a neutral molecule, but we have not observed any difference of reactivity between the enones of various reduction potentials.

The striking behavior of some *s-cis*-enones is difficult to rationalize. In particular, with pulegone, the incorporation of deuterium in C_4 and C_8 carbon atoms from *tert*-butyl alcohol-d_1 suggests a slow protonation of an organometallic species,[32] especially since 3-heptanol and diphenylcarbinol were recovered intact when used instead of *tert*-butyl alcohol. Since secondary alcohols are known to be good hydrogen atom donors,[33] we can rule out a transfer of hydrogen atom. Instead, we propose the formation of a metallacycle intermediate (oxametallacyclopentene) resulting from the association of one molecule of pulegone with a titanium atom of the polymeric chain.[34] The formation of the metallacycle intermediate could result from the *s*-cis configuration of the enone. A two-electron transfer, promoted by the polymeric structure, is necessary. The protolysis and the alkylation of such an intermediate could explain the formation of the corresponding dihydro ketones, alkylated products, and lactone **42**. These alkylations constitute an example of *umpolung* of the enones.[35] The different reactivities of the isopropylidenecyclohexanone **22a** and -cyclopentanone **29** could result from the more strained structure of the bicyclic metallacycle in the latter.

Conclusion

In comparison to the classic method (Mg–MgI_2,[36] Zn–AcOH,[37] Al(Hg)[19,38]), the reductive coupling of α,β-ethylenic ketones promoted by a low-valent transition metal is certainly a complex reaction. Nevertheless, its use in organic synthesis can be recommended. The organized polymeric structure of the reagent could explain the high selectivity observed in tetramerization of mesityl oxide and in bicyclic pinacol formation.

Experimental Section

General Methods. ^1H NMR spectra were determined on Varian EM 360 or Varian XL 200 spectrometers. ^{13}C NMR spectra of $CDCl_3$ solutions were recorded on a Varian XL 200 (50.309 MHz) spectrometer with Me_4Si as the internal standard. Assignments were confirmed by *J*-modulated spin echo. Mass spectra were obtained on a Varian MAT 311 mass spectrometer. Melting points were uncorrected. All reactions were carried out in an argon atmosphere.

General Procedure for Reductive Coupling of Enones Using $TiCl_4$–Mg. In a dry two-necked reaction flask equipped with a magnetic stirrer, a reflux condenser, and a dropping funnel was placed magnesium (Grignard turnings) (0.1 g-atom, 2.43 g) in anhydrous THF (100 mL). After the reaction flask was cooled to −60 °C, $TiCl_4$ (0.1 mol, 18.97 g) was added dropwise. The reaction mixture was then allowed to warm up to room temperature in about 3 or 4 h; the resulting black slurry was stirred for an additional 20 h. A solution of enone (0.10, 0.05, or 0.025 mol as indicated) with possibly *tert*-butyl alcohol or alkyl halide in 20 mL of tetrahydrofuran was then added dropwise, and the reaction mixture was stirred (time and temperature will be indicated in Table I or II) until it was poured onto ice–ammonium chloride. After the usual extractive workup procedure (with diethyl ether), the organic layers were washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure (on the rotary evaporator). The resulting crude product was either chromatographed on silica gel or distilled.

Reductive Coupling of Crotonaldehyde (1a). 2,6-Octadiene-4,5-diol (3a):[37b] Table I, entry 1; 0.1 mol (7.01 g) of **1a** and 0.1 mol (7.41 g) of *t*-BuOH were used; a 45% yield of **3a** was obtained by distillation, bp 90 °C (0.15 Torr).

Reductive Coupling of Mesityl Oxide (1b). 2,4,5,7-Tetramethyl-2,4,6-octatriene (2b): Table I, entry 2; 0.025 mol (9.82 g) of **1b** was used; a 85% yield of **2b** was obtained by distillation; bp 52 °C (0.6 Torr). **2b**: IR (CCl_4) 1650, 1250, 1190, 1050, 980 cm^{-1}. The *Z* and *E* isomers were separated by preparative GLC. **2b** (*Z*): ^1H NMR (200 MHz, $CDCl_3$) δ 5.66 (2, br s), 1.73 (6, s),

(30) When the [(cyclopropylstannyl)oxy]methyl or cyclopropylhydroxymethyl radicals were generated in the esr cavity at −100 °C, only the opened radicals were observed, see: Davies, A. G.; Muggleton, B.; Godet, J. Y.; Pereyre, M.; Pommier, J. C. *J. Chem. Soc., Perkin Trans. 2* **1976**, *1719*. For other examples, see: (a) Itzel, H.; Fischer, H. *Tetrahedron Lett.* **1975**, 563. (b) Beckwith, A. L. J.; Moad, G. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1473. (c) Mariano, P. S.; Bay, E. *J. Org. Chem.* **1980**, *45*, 1763. (d) MacInnes, I.; Nonhebel, D. C.; Orszulik, S. T.; Suckling, C. J. *J. Chem. Soc., Chem. Commun.* **1982**, 121. (e) Hwu, J. R. *J. Chem. Soc., Chem. Commun.* **1985**, 452. (f) Mathew, L.; Warkentin, J. *J. Am. Chem. Soc.* **1986**, *108*, 7981.

(31) The oxidative cleavage of 1,2-diols with periodate can be considered as the formal reverse reaction of reductive coupling. The requirement for the mechanism of periodate oxidation is the formation of a bidentate complex as an intermediate, which then breaks down into the products via a two-electrons process, see: Fatiadi, A. J. *Synthesis* **1974**, 229.

(32) The formation of a dianion is unlikely and does not explain the particular reactivity of some *s-cis*-enones.[33] Thus, the polarographic half-wave potential values of a *s-trans*-enone **18** and a *s-cis*-enone **22b** are as expected.[14] **18**: $E_{1/2}$ = −2.19 V. **22b**: $E_{1/2}$ = −2.30 V vs sce (this work, in the same experimental conditions as in ref 14).

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(34) Titanacycles of similar structure have already been isolated and X-ray characterized, see: (a) Kolomnikov, I. S.; Lobeeva, T. S.; Gorbachevskaya, V. V.; Aleksandrov, G. G.; Struchkov, Y. T.; Vol'pin, M. E. *J. Chem. Soc., Chem. Commun.* **1971**, 972. (b) Shur, V. B.; Burlakov, V. V.; Yanovski, A. I.; Petrovsky, P. V.; Struchkov, Y. T.; Vol'pin, M. E. *J. Organomet. Chem.* **1985**, *297*, 51.

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(38) Mundy, B. P.; Srinivasa, R.; Kim, Y.; Dolph, T.; Warnet, R. J. *J. Org. Chem.* **1982**, *47*, 1657.

1.59 (6, s), 1.56 (6, s); ^{13}C NMR δ 131.74 (s), 129.69 (s), 127.90 (d), 26.13 (q), 19.80 (q), 19.03 (q). **2b** (*E*): ^1H NMR δ 5.66 (2, br s), 1.77 (6, s), 1.59 (6, s), 1.58 (6, s); ^{13}C NMR δ 132.75 (s), 129.14 (s), 126.98 (d), 25.42 (q), 20.09 (q), 19.62 (q).

2,4,5,7-Tetramethyl-2,6-octadiene-4,5-diol (3b) (Table I, entry 3). $TiCl_4$ was added in a pentane solution (25 mL); 0.1 mol (9.81 g) of **1b** and 0.1 mol (7.41 g) of *t*-BuOH were used. Compound **3b** was obtained by distillation: bp 70–80 °C (0.6 Torr) (mp ca. 30 °C); IR (CCl_4) 3450, 1370, 1215, 830 cm^{-1}. **3b** (meso): ^1H NMR (200 MHz, $CDCl_3$) δ 5.29 (2, br s), 1.90 (6, s), 1.73 (6, s), 1.32 (6, s); ^{13}C NMR δ 135.42 (s), 126.89 (d), 78.77 (s), 27.93 (q), 24.30 (q), 19.81 (q). **3b** (*dl*): ^1H NMR δ 5.39 (2, br s), 1.90 (6, s), 1.73 (6, s), 1.30 (6, s); ^{13}C NMR δ 136.00 (s), 127.38 (d), 78.64 (s), 27.91 (q), 22.18 (q), 18.96 (q).

Synthesis of 4b, 6, and 7 (Table I, entry 4). A 0.1-mol (9.82 g) portion of **1b** and 0.1 mol (7.41 g) of *t*-BuOH were used. Compounds **2b** (15.5%), **3b** (23%), **4b** (37%), **6** (5%), and **7** (20%) were isolated by distillation and chromatographed on silica gel with Et_2O–pentane.

4-Acetyl-2,4,6-trimethyl-2,5-heptadiene (4b): bp 62 °C (0.15 Torr); IR (CCl_4) 1700, 1360, 1345, 830 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.35 (2, br s), 1.98 (3 s), 1.70 (6, s), 1.47 (6, s), 1.26 (3, s); ^{13}C NMR δ 209.71 (s), 134.27 (s) (2 C), 129.38 (d) (2 C), 53.36 (s), 26.58 (q) (2 C), 24.56 (q) (2 C), 18.83 (q).

1-Acetyl-2,4,4,5,5-pentamethylcyclopentene (6):[13d] IR (neat) 1675–1660 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 2.15 (3, s), 1.86 (3, s), 0.95 (6, s), 0.85 (6, s); HRMS, *m/e* calcd for $C_{12}H_{20}O$ 180.1514, found 180.1520.

4,4,5,5,7,8,10,10,11,11-Decamethyl-6,8-tetradecadiene-2,13-dione (7): bp 145 °C (0.6 Torr) (mp 43–44 °C (Et_2O–pentane)); IR (CCl_4) 1705 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.31 (2, br s), 2.56 (4, s), 2.06 (6, s), 1.78 (6, s), 1.11 (18, s), 1.09 (6, s); ^{13}C NMR δ 208.36 (s), 138.26 (s), 131.58 (d), 54.00 (t), 43.51 (s), 40.52 (s), 31.79 (q), 28.07 (q) (2 C), 24.55 (q) (2 C), 14.25 (q); HRMS, *m/e* calcd for $C_{12}H_{21}O$ ($M^+/2$) 181.1592, found 181.1589.

Reductive Coupling of 1c. Synthesis of 2c (Table I, entry 5). A 0.05-mol (6.20 g) sample of **1c** was used. Triene **2c** (80%) was isolated by distillation: bp 85 °C (0.05 Torr); IR (CCl_4) 1250, 860 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 2.80 (8, m), 1.75 (6, s), 1.55 (3, s), 1.45 (3, s); HRMS, *m/e* calcd for $C_{16}H_{24}$ 216.1879, found 216.1881.

Synthesis of 2c and 4c (Table I, entry 6). A 0.1-mol (12.40 g) sample of **1c** and 0.1 mol (7.41 g) of *t*-BuOH were used; **2c** (36%) and **4c** (48%) (purification by preparative GLC showed the presence of 10% of a nonconjugated ketone) were obtained by distillation. **4c**: bp 103 °C (0.05 Torr); IR (CCl_4) 1705, 1210, 1175 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 2.05 (3, s), 1.65 (6, br s), 1.30 (3, s); ^{13}C NMR δ 204.35 (s), 135.35 (s), 134.74 (s), 56.71 (s), 40.37 (t), 35.64 (t), 27.28 (q), 22.63 (q), 21.63 (t), 15.82 (t); HRMS, *m/e* calcd for $C_{16}H_{24}O$ 232.1827, found 232.1821.

Reductive Coupling of Miescher–Wieland Ketone (9). Synthesis of 10 (Table I, entry 7). For the synthesis of **10** 0.05 mol (8.91 g) of **9** was used; the crude product was chromatographed on silica gel with Et_2O–pentane (1:3) to afford a mixture of **10** (*Z* and *E*, 1/1) (66%): mp 199 °C ($CHCl_3$–pentane); IR (CCl_4) 1700, 1260, 1235, 1080, 1020 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 6.31 (2, br s), 1.27 (6, s); ^{13}C NMR δ 214.28 and 214.12 (s), 142.85 and 142.74 (s), 127.39 and 127.18 (s), 122.32 and 122.27 (d), 50.57 and 50.42 (s), 38.54 (t) (2 C), 32.01 (t) (2 C), 30.53 and 30.39 (t), 25.07 and 24.91 (t), 21.64 and 21.57 (t), 24.26 and 24.19 (q); HRMS, *m/e* calcd for $C_{22}H_{28}O_2$ 324.2089, found 324.2097.

Reductive Coupling of Phorone (11). Synthesis of 12 (Table I, entry 8). A 0.05-mol (6.91 g) portion of phorone and 0.1 mol (7.41 g) of *t*-BuOH were used; **12** (60%) was isolated from the crude product by crystallization (pentane): mp 95 °C (CCl_4); IR 1675, 1625, 1370 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 5.81 (4, br s), 1.72 (12, s), 1.41 (12, s); ^{13}C NMR δ 154.25 (s) (4 C), 129.73 (s) (2 C), 126.19 (d) (4 C), 27.75 (q) (4 C), 20.54 (q) (4 C).

Reductive Coupling of Isophorone (13). Synthesis of 14 (Table I, entry 9). A 0.05-mol (6.91 g) portion of isophorone and 0.1 mol (7.41 g) of *t*-BuOH were used; **14** (75%) was purified by preparative GLC: IR (CCl_4) 1680, 1380, 1375, 1130, 995 cm^{-1}. **14** (*Z*): ^1H NMR (200 MHz, $CDCl_3$) δ 6.44 (2, br s), 2.06 (4, s), 1.86 (10, br s), 0.89 (12, s); ^{13}C NMR δ 133.95 (s), 127.79 (s), 119.80 (d), 45.05 (t), 39.83 (t), 30.53 (s), 28.67 (q) (2 C), 24.48 (q). **14** (*E*): ^1H NMR δ 6.24 (2, br s), 2.12 (4, s), 1.78 (10, br s), 0.89 (12, s); ^{13}C NMR δ 134.84 (s), 127.68 (s), 120.96 (d), 45.22 (t), 39.00 (t), 30.67 (s), 28.58 (q) (2 C), 24.59 (q).

Reductive Coupling of Acetylcyclopropane (15). 2,3-Dicyclopropyl-2,3-butanediol (16) (Table I, entry 10). A 0.05-mol (4.21 g) sample of **15** and 0.1 mol (7.41 g) of *t*-BuOH were used. The crude product was chromatographed on silica gel (elution with Et_2O–pentane, 1:9) to give **16** (60%). **16**: IR (neat) 3450, 3090, 1100, 1020 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 1.10 (6, s), 0.36 (4, m), 0.26 (4, m); ^{13}C NMR (resp major and minor isomer) δ 76.24 and 76.03 (s), 21.38 and 21.55 (q), 16.95 and 16.90 (d), 1.20 and 1.35 (t) (2 C).

Reductive Cross-Coupling of 1b and 1c. Synthesis of 2b, 2c, and 17 (Table I, entry 11). A 0.025-mol (2.45 g) portion of **1b** and 0.025 mol (3.10 g) of **1c** were used. A distillation of the crude product led to a fraction with bp 50–85 °C (0.05 Torr) (90%), which was then purified by preparative GLC to give **2b** (21%), **2c** (29%), and **17** (50%). **17** (*Z* and *E* isomers 1:1): IR (CCl_4) 2960, 1440, 1375 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 5.61 (1, br s), 2.35 (4, m), 1.80 (3, s), 1.70 (3, s), 1.57 (6, s), 1.50 (3, s); ^{13}C NMR δ (isomers *E* and *Z*) 138.46 and 136.69 (s), 133.03 and 133.38 (s), 130.87 and 132.91 (s), 129.84 and 130.46 (s), 128.96 and 129.44 (s), 127.21 and 128.63 (d), 38.48 and 38.25 (t), 35.95 and 35.71 (t), 25.46 and 26.40 (q), 22.57 (t) (2 C), 19.60 and 19.79 (q), 18.48 and 19.02 (q), 15.04 and 15.38 (q); HRMS, *m/e* calcd for $C_{14}H_{22}$ 190.1721, found 190.1723.

Reductive Coupling of (−)-Carvone (18). (+)-(1*S*,5*R*,1′*S*,5′*R*)-1-(1′-Hydroxy-5′-isopropenyl-2′-methyl-2′-cyclohexenyl)-5-isopropenyl-2-methyl-2-cyclohexenol (19). Reaction conditions: 48 h at room temperature; 0.05 mol (7.51 g) of **18** and 0.1 mol (7.41 g) of *t*-BuOH were used. The solution was evaporated to dryness, and the residue was recrystallized from $CHCl_3$–pentane to give **19** (70%): mp 172 °C; $[\alpha]^{22}_{578}$ +19° (*c* 0.9, ethanol); IR (CCl_4, 1.6×10^{-3} M) 3626 (35%), 3580 (65%), 1645, 1160, 1070, 960 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.77 (2, d, J = 6.5 Hz, quint, J = 1.5 Hz), 4.72 (2, q, J = 1.5 Hz), 4.68 (2, q, J = 0.8 Hz), 1.88 (6, s), 1.71 (6, s); ^{13}C NMR δ 149.01 (s), 136.01 (s), 128.05 (d), 108.82 (t), 77.42 (s), 37.94 (t), 37.78 (d), 30.67 (t), 20.95 (q), 20.83 (q); HRMS, *m/e* calcd for $C_{20}H_{28}O$ 284.2140, found 284.2144.

Reductive Coupling of (*R*)-(−)-Carvone in the Presence of Mesitylene. Synthesis of 20 and 21. Mesitylene (1.8 g) was added with carvone (0.05 mol, 7.51 g) and *t*-BuOH (0.1 mol, 7.41 g). Reaction conditions: 100 h at room temperature. The crude product was chromatographed on silica gel (Et_2O–pentane) to afford **19** (15%), **20** (50%), and **21** (10%).

(−)-(1*R*,5*R*,1′*R*,5′*R*)-1-(1′-Hydroxy-5′-isopropenyl-2′-methyl-2′-cyclohexenyl)-5-isopropenyl-2-methyl-2-cyclohexenol (20): mp 78–79 °C (hexane); $[\alpha]^{22}_{578}$ −70° (*c* 0.55, ethanol); IR (CCl_4, 3.3×10^{-3} M) 3620 (6%), 3555 (94%), 1645, 1035 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.64 (2, m), 4.78 (4, d, J = 4 Hz), 1.87 (6, q, J = 1.4 Hz), 1.77 (6, s); ^{13}C NMR δ 149.14 (s), 136.35 (s), 126.17 (d), 109.92 (t), 76.98 (s), 38.69 (d), 38.32 (t), 29.74 (t), 21.36 (q), 2055 (q); HRMS, *m/e* calcd for $C_{10}H_{15}O$ 151.1122, found 151.1122.

21: mp 135 °C (hexane); $[\alpha]^{22}_{578}$ 46° (*c* 1.4, ethanol); IR (CCl_4, 4×10^{-2} M) 3628 (32%), 3577 (68%), 1710, 1645, 1225, 1145 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.72 (1, d, J = 6.6 Hz), 4.79 (1, m), 4.76 (1, s), 4.72 (1, s), 4.68 (1, s), 1.76 (6, s), 1.73 (3, s), 0.97 (3, d, J = 6.2 Hz); ^{13}C NMR δ 211.98 (s), 149.17 (s), 147.33 (s), 136.20 (s), 128.15 (d), 110.09 (t), 108.98 (t), 77.54 (s), 47.03 (d), 46.60 (t), 45.20 (d), 44.25 (d), 38.09 (d), 37.92 (t), 30.84 (t), 29.64 (t), 21.13 (q), 21.03 (q), 20.51 (q), 11.00 (q); HRMS, *m/e* calcd for $C_{20}H_{30}O_2$ 302.2245, found 302.2239; CD, hexane, 25 °C, λ_{max} 296 nm, $|\Theta|$ 630; λ_{max} 305 nm, $|\Theta|$ 530; ethanol, 25 °C, λ_{max} 282 nm, $|\Theta|$ 300; −60 °C, λ_{max} 310 nm, $|\Theta|$ 250, nm, $|\Theta|$ 250, λ_{max} 287 nm, $|\Theta|$ −200, λ_{max} 276, $|\Theta|$ 280.

Reductive Coupling of (+)-Pulegone (22b). Synthesis of 24a–e and 25a,b (Table I, entry 14). A 0.1-mol (15.22 g) sample of pulegone was used. The crude product was chromatographed on silica gel (Et_2O–pentane) to give **23b** (18%), **25** (13%), and **24** (58%). **24a**: mp 114–115 °C (hexane); $[\alpha]^{20}_{578}$ +51° (*c* 2.3, $CHCl_3$); IR (CCl_4, 5.9×10^{-2} M) 3580 cm^{-1}; ^1H NMR (200 MHz, CDL_3) δ 1.11 (3, s), 1.02 (3, d, J = 6.0 Hz), 0.98 (3, s), 0.92 (3, s), 0.90 (3, s), 0.88 (3, d, J = 6.0 Hz); ^{13}C NMR δ 219.15 (s), 82.35 (s), 65.45 (s), 45.83 (s), 44.11 (s), 52.80 (t), 52.02 (d), 39.49 (t), 31.24 (t), 31.02 (d), 29.90 (d), 29.46 (t), 28.61 (q), 27.53 (t), 26.70 (q),

26.50 (q), 24.71 (q), 23.15 (q), 22.54 (q), 21.97 (t); HRMS, *m/e* calcd for $C_{20}H_{34}O_2$ 306.2558, found 306.2573. **24b**: mp 127 °C; $[\alpha]^{20}_{578}$ +43° (*c* 0.5, $CHCl_3$); IR (CCl_4, 3.3 × 10^{-2} M) 3625 cm^{-1}; ^1H NMR δ 1.09 (3, s), 1.03 (3, d, *J* = 6.0 Hz), 1.00 (3, s), 0.89 (3, d, *J* = 6.0 Hz), 0.89 (3, s), 0.87 (3, s); ^{13}C NMR δ 215.61 (s), 83.50 (s), 67.37 (s), 52.54 (d), 51.34 (t), 49.80 (s), 43.98 (t), 42.97 (s), 34.86 (t), 28.69 (t), 28.47 (d) (2 C), 27.21 (q), 26.66 (q), 26.08 (q), 24.85 (t), 23.63 (q), 22.78 (q), 22.34 (q), 21.83 (t). **24c**: mp 156–157 °C; $[\alpha]^{20}_{578}$ +58° (*c* 1.3, $CHCl_3$); IR (CCl_4, 4.2 × 10^{-2} M) 3630 cm^{-1}; ^1H NMR δ 0.98 (3, s), 0.97 (3, d, *J* = 6.0 Hz), 0.94 (3, s), 0.89 (3, s), 0.86 (3, d, *J* = 6.0 Hz), 0.83 (3, s); ^{13}C NMR δ 213.55 (s), 83.25 (s), 67.32 (s), 54.20 (t), 54.11 (d), 50.65 (s), 44.83 (t), 44.63 (s), 31.28 (d), 31.22 (t) (2 C), 30.89 (t), 27.09 (d), 26.63 (q), 25.86 (q), 22.71 (q), 22.60 (q), 22.39 (q), 21.56 (q), 21.44 (t). **24d**: oil; IR (CCl_4, 6.1 × 10^{-2} M) 3480 cm^{-1}; ^{13}C NMR δ 219.72 (s), 84.88 (s), 64.45 (s), 53.85 (d), 52.17 (t), 49.08 (s), 44.62 (s), 43.12 (t), 35.35 (t), 34.37 (d), 32.18 (t), 32.04 (t), 30.39 (d), 27.91 (q), 27.76 (q), 26.55 (q), 22.73 (q), 22.47 (q), 22.38 (q), 21.45 (t). **24e**: mp 138–139 °C; $[\alpha]^{20}_{578}$ +73° (*c* 3.9, $CHCl_3$); IR (CCl_4, 3.3 × 10^{-2} M) 3640 cm^{-1}; ^1H NMR δ 1.14 (3, s), 1.12 (3, d, *J* = 6.0 Hz), 0.98 (3, d, *J* = 6.0 Hz), 0.91 (3, s), 0.87 (6, s); ^{13}C NMR δ 215.71 (s), 85.25 (s), 66.64 (s), 53.38 (d), 52.41 (t), 48.94 (s), 44.21 (s), 39.26 (t), 31.94 (t), 30.57 (d), 29.67 (t), 27.93 (d), 27.75 (q), 27.68 (q), 26.68 (t), 26.36 (q), 23.34 (q), 22.59 (q), 22.15 (q), 17.75 (t). **25a,b** (mixture of two spiro isomers): oil; IR (neat) 1690, 910 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.20 (3, s), 1.11 (3, s), 1.02 (3, d, *J* = 6.0 Hz), 1.00 (3, d, *J* = 6.0 Hz), 0.98 (3, d, *J* = 7.0 Hz), 0.97 (3, s), 0.93 (3, d, *J* = 7.0 Hz), 0.90 (3, s), 0.83 (3, s), 0.79 (3, s), 0.77 (3, s), 0.73 (3, s); ^{13}C NMR δ 213.55 (s), 213.41 (s), 141.48 (s), 140.87 (s), 134.72 (s), 133.64 (s), 68.33 (s), 67.43 (s), 51.87 (t), 50.48 (s), 50.27 (s), 49.43 (t), 47.16 (s), 47.05 (s), 34.21 (d), 32.04 (t), 31.96 (t), 31.90 (t), 31.29 (t) (2 C), 31.12 (t), 30.92 (d), 30.22 (d), 29.11 (d), 28.84 (t), 27.90 (t), 25.48 (q), 25.07 (q) (2 C), 24.10 (q), 22.56 (q) (3 C), 22.21 (q), 21.84 (t), 21.76 (t), 21.60 (q) (2 C), 21.37 (q), 19.15 (q).

Reductive Coupling of 2-Isobutylenecyclohexanone (26). Synthesis of 27 and 28 (Table I, entry 15). A 0.05-mol (7.61 g) sample of **26** and 0.2 mol (14.82 g) of *t*-BuOH were used; **27** (55%) was isolated from the crude product by crystallization (CCl_4) and **28** (10%) by distillation. **27**: mp 129–130 °C (CCl_4); IR (CCl_4, 3.6 × 10^{-3} M) 3617 (51%), 3594 (49%), 1210 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.53 (2, d, *J* = 9.0 Hz), 0.98 (12, d, *J* = 6.0 Hz); ^{13}C NMR δ 139.24 (s), 133.70 (d), 79.49 (s), 35.76 (t), 26.80 (d), 25.59 (t), 25.39 (t), 23.78 (q), 23.28 (q), 20.94 (t); HRMS, *m/e* calcd for $C_{20}H_{34}O_2$ 306.2558, found 306.2544. **28**: bp 42–43 °C (0.1 Torr).

Reductive Coupling of 2-Isopropylidenecyclopentanone (29). Synthesis of 30 (Table I, entry 16). A 0.025-mol (3.1 g) portion of **29** and 0.05 mol (3.71 g) of *t*-BuOH were used; **30** (50%) was isolated from the crude product by crystallization. **30**: mp 115–116 °C (Et_2O–pentane); IR (CCl_4, 2.2 × 10^{-3} M) 3626 (43%), 3576 (57%), 1065, 975 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.96 (6, s), 1.70 (6, s); ^{13}C NMR δ 140.49 (s), 127.30 (s), 85.44 (s), 41.37 (t), 33.72 (t), 23.76 (q), 22.26 (t), 21.77 (q); HRMS, *m/e* calcd for $C_{16}H_{24}O$ 232.1827, found 232.1822.

Reductive Coupling of 2-Cyclopentylidenecyclopentanone (31). Synthesis of 32 and 33 (Table I, entry 17). A 0.05-mol (7.50 g) portion of **31** and 0.2 mol (14.82 g) of *t*-BuOH were used; **32** (55%) was isolated from the crude product by crystallization (Et_2O) and **33** (5%) by distillation. **32**: mp 138–139 °C (Et_2O); IR (CCl_4, 5 × 10^{-3} M) 3623 (36%), 3572 (64%), 1160, 975 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 2.81 (4, s), 2.51 (4, s), 2.18 (4, s); ^{13}C NMR δ 137.89 (s), 127.24 (s), 85.23 (s), 40.18 (t), 34.73 (t), 33.90 (t), 31.60 (t), 27.79 (t), 25.81 (t), 22.73 (t); HRMS, *m/e* calcd for $C_{20}H_{28}O$ 284.2140, found 284.2144. **33**: bp 50 °C (0.1 Torr).

Reductive Alkylation of (+)-Pulegone Using Allyl Bromide. Synthesis of 3-Allyl-*p*-mentha-3,8-diene (34a), 35, and 36 (Table II, entry 1). A 0.05-mol (7.61 g) sample of pulegone and 0.1 mol (12.10 g) **of** allyl bromide were used. Compounds **34a** (65%) and **35** (5%) were isolated by distillation; **36** (10%) was identified by GC/MS only. **34a**: bp 55 °C (0.15 Torr); IR (CCl_4) 3080, 1630, 1240, 990, 910, 895 cm^{-1}; ^1H NMR (200 MHz, CCl_4) δ 5.65 (1, d, *J* = 17.0 Hz, d, *J* = 10.0 Hz, t, *J* = 6.5 Hz), 4.96 (1, d, *J* = 17 Hz, m), 4.94 (1, d, *J* = 10 Hz, m), 4.80 (1, m), 4.60 (1, m), 2.72 (2, d, *J* = 6.5 Hz), 1.78 (3, d, *J* = 1.0 Hz), 0.96 (3, d, *J* = 5.0 Hz); ^{13}C NMR δ 147.09 (s), 137.78 (d), 135.41 (s), 127.58 (s), 114.88 (t), 111.91 (t), 38.75 (t), 37.15 (t), 31.44 (t), 29.62 (t), 29.04 (d), 22.52 (q), 21.84 (q). **35** (mixture of isomers): bp 70–75 °C (4.5 Torr); IR (neat) 1715, 1645, 1215, 1005, 920 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 6.03–5.37 (1, m), 5.07 (1, m), 4.87 (1, m), 1.07 (3, s), 1.00 (3, s). **36**: mass spectrum (GC/MS), *m/e* 218 (16), 204 (18), 203 (100), 161 (34), 147 (18), 105 (26), 91 (22), 55 (23), 41 (32).

Reductive Alkylation of (+)-Pulegone Using Crotyl Chloride. 3-((1*R*)-1-Methyl-2-propen-1-yl)-*p*-mentha-3,8-diene (34b) (Table II, entry 2). A 0.05-mol (7.61 g) sample of pulegone and 0.1 mol (9.06 g) of crotyl chloride were used; **34b** (60%) was isolated by distillation. **34b**: bp 50 °C (0.1 Torr); $[\alpha]^{20}_{578}$ +183° (*c* 2.3, $CHCl_3$); IR (neat) 3080, 1630, 1265, 1000, 910, 895 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.81 (1, d, *J* = 16.8 Hz, d, *J* = 10.8 Hz, d, *J* = 5.1 Hz), 4.98–4.82 (3, m), 4.63 (1, m), 1.77 (3, br s), 1.02 (3, d, *J* = 7.0 Hz), 0.93 (3, d, *J* = 7.0 Hz); ^{13}C NMR δ 147.56 (s), 143.04 (d), 134.50 (s), 131.75 (s), 112.66 (t), 111.56 (t), 39.29 (d), 31.89 (t), 31.46 (t), 29.97 (t), 28.92 (d), 22.81 (q), 22.04 (q), 17.07 (q); HRMS, *m/e* calcd for $C_{14}H_{22}$ 190.1721, found 190.1724.

Reductive Alkylation of (+)-Pulegone Using Benzyl Bromide. Synthesis of 37 and 38 (Table II, entry 3). A 0.05-mol (7.61 g) portion of pulegone and 0.05 mol (8.55 g) of benzyl bromide were used; **37** (45%) and **38** (10%) were isolated by distillation. **37**: bp 110 °C (0.05 Torr); IR (neat) 1700, 1210 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.25 (3, m), 7.10 (2, m), 3 (1, $^1/_2$AB, *J* = 12.0 Hz), 2.58 (1, $^1/_2$AB), 1.05 (3, s), 1.00 (3, d, *J* = 6.0 Hz), 0.94 (3, s); ^{13}C NMR δ 212.53 (s), 139.31 (s), 130.58 (d) (2 C), 127.73 (d) (2 C), 125.83 (d), 56.60 (d), 52.62 (t), 50.56 (s), 45.75 (t), 36.54 (d), 34.72 (t), 28.43 (t), 25.80 (q), 24.11 (q), 22.34 (q); HRMS, *m/e* calcd for $C_{10}H_{17}O$ 153.1279, found 153.1274. **38**: bp 75 °C (0.05 Torr); IR (neat) 1600, 895 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.24 (5, m), 4.92 (1, m), 4.74 (1, m), 3.42 (2, br s), 1.86 (3, br s), 0.90 (3, d, *J* = 7.0 Hz); ^{13}C NMR δ 147.21 (s), 141.19 (s), 136.08 (s), 127.93 (s), 128.62 (d) (2 C), 128.16 (d) (2 C), 125.55 (d), 112.14 (t), 39.83 (t), 36.94 (t), 31.36 (t), 29.75 (t), 28.98 (d), 22.81 (q), 21.79 (q); HRMS, *m/e* calcd for $C_{17}H_{22}$ 226.1721, found 226.1727.

Reductive Alkylation of 2-Isobutylidenecycohexanone (26) Using Allyl Bromide. Synthesis of 39 and 40 (Table II, entry 4). A 0.05-mol (7.61 g) sample of **26** and 0.1 mol (12.10 g) of allyl bromide were used; **28** (15%), **39** (15%), and **40** (30%) were isolated from the crude product by distillation. **39** (mixture of isomers): bp 90 °C (0.1 Torr); IR (neat) 1700, 1120, 910 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.98–5.64 (1, m), 5.10–4.92 (2, m), 0.88 (3, d, *J* = 7.0 Hz), 0.87 (3, d, *J* = 7.0 Hz); ^{13}C NMR δ 213.05 (s), 139.65 and 139.16 (d), 115.46 and 114.85 (t), 53.01 and 52.30 (d), 42.09 and 41.98 (t), 41.43 and 40.55 (d), 33.70 and 33.23 (t), 29.84 and 28.43 (d), 29.01 (t), 27.35 (t), 27.28 (t), 24.72 (t), 22.55 (q), 20.51 (q), 19.97 (q), 19.03 (q); HRMS, *m/e* calcd for $C_{13}H_{22}O$ 194.1670, found 194.1660. **40**: bp 65 °C (0.1 Torr); IR (neat) 3450, 910 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 6.2–4.93 (4, m), 0.98 (3, d, *J* = 7 Hz), 0.96 (3, d, *J* = 7 Hz); ^{13}C NMR δ 140.06 (s), 133.95 (d), 128.66 (d), 118.32 (t), 73.94 (s), 42.48 (t), 40.66 (t), 27.56 (t), 26.41 (t), 23.70 (d), 23.60 (q), 23.54 (q), 23.45 (t).

Synthesis of the δ-Lactone 42. For the synthesis of **42**, 0.01 mol (1.52 g) of pulegone, 0.01 mol (1.74 g) of diethyl mesoxalate, and 0.02 mol of $TiCl_4$–Mg reagent were used (8 h at room temperature). The crude product was chromatographed on silica gel with Et_2O–pentane (1:20) to give **42** (60%) (two isomers, 1.1:1): $[\alpha]^{20}_{578}$ +46° (*c* 2.6, $CHCl_3$); IR (neat) 3500, 1750,1175, 1100, 1040 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 4.20 (2, q, *J* = 7 Hz), 1.27 (3, t, *J* = 7 Hz), 1.11 (3, s), 1.07 (3, s); ^{13}C NMR δ 168.65 and 168.60 (s), 168.56 and 168.50 (s), 143.57 and 143.38 (s), 116.32 and 116.20 (s), 79.79 and 79.65 (s), 62.54 and 62.48 (t), 40.02 and 39.93 (s), 34.09 and 33.90 (t), 30.78 and 30.01 (t), 28.92 and 28.13 (d), 23.17 and 21.82 (t), 22.82 and 22.52 (q), 21.33 ands 20.53 (q), 19.06 and 18.29 (q), 14.06 (q) (2 C); HRMS, *m/e* calcd for $C_{15}H_{22}O_5$ 282.1467, found 282.1466.

Acknowledgment. We are indebted to M. Guénot (Université de Rennes, France) for high-resolution mass spectra. We also thank Dr. Gronchi for measurements of polarographic half-wave potentials.

Registry No. **1a**, 4170-30-3; **1b**, 141-79-7; **1c**, 3168-90-9; (*E*)-**2b**, 80885-64-9; (*Z*)-**2b**, 80885-63-8; (*E*)-**2c**, 117712-85-3; (*Z*)-**2c**, 117734-21-1; *meso*-**3a**, 102517-71-5; *meso*-**3b**, 80885-65-0; *dl*-**3b**, 80885-66-1; **4b**, 80885-62-7; **4c**, 117712-88-6; **6**, 13144-88-2; **7**,

117712-65-9; **8**, 117712-66-0; *dl*-**9**, 20007-99-2; **10**, 117712-67-1; **11**, 504-20-1; **12**, 117712-68-2; **13**, 78-59-1; (*E*)-**14**, 117712-69-3; (*Z*)-**14**, 117712-86-4; **15**, 765-43-5; *meso*-**16**, 117712-70-6; *dl*-**16**, 117712-90-0; (*E*)-**17**, 117712-71-7; (*Z*)-**17**, 117712-87-5; **18**, 6485-40-1; **19**, 117712-72-8; **20**, 117773-77-0; **21**, 117712-73-9; **22a**, 13747-73-4; **22b**, 89-82-7; *dl*-**23a**, 64870-43-5; **23b**, 117773-78-1; **24**, 20489-87-6; **25** (isomer 1), 40285-80-1; **25** (isomer 2), 40285-62-9; **26**, 43108-69-6; *dl*-**27**, 117712-74-0; *dl*-**28**, 117712-75-1; **29**, 2758-17-0; *dl*-**30**, 117712-76-2; **31**, 825-25-2; *dl*-**32**, 117712-77-3; *dl*-**33**, 3063-68-1; **34a**, 108762-96-5; **34b**, 117712-89-7; *cis*-**35**, 74310-83-1; *trans*-**35**, 74272-01-8; **36**, 117712-78-4; **37**, 117712-79-5; **38**, 117712-80-8; *dl*-**39** (isomer 1), 117712-81-9; *dl*-**39** (isomer 2), 117712-92-2; *dl*-**40**, 117712-82-0; **41** (isomer 1), 117712-83-1; **41** (isomer 2), 117712-93-3; **41** (isomer 3), 117712-94-4; **41** (isomer 4), 117712-95-5; *cis*-**42**, 117712-91-1; *trans*-**42**, 117712-84-2; $TiCl_4$, 7550-45-0; Mg, 7439-95-4; *t*-BuOH, 75-65-0; CH_2=$CHCH_2Br$, 106-95-6; CH_3CH=$CHCH_2Cl$, 591-97-9; $C_6H_5CH_2Br$, 100-39-0; mesitylene, 108-67-8; diethyl mesoxalate, 609-09-6.

Acetoxyselenenylation of Olefins for the Preparation of Vinylic and Allylic Acetates

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Received August 30, 1988

Terminal and 1,2-disubstituted olefins were irreversibly acetoxyselenenylated by treatment with PhSeBr in an acetate buffer solution. Styrene derivatives yielded only Markovnikov adducts whereas simple terminal olefins and olefins containing an allylic oxygen substituent (acyloxy or aryloxy group) afforded significant amounts (50–85%) of the anti-Markovnikov isomer. The product mixtures were isomerized to contain 90–97% of the Markovnikov product by treatment with a catalytic amount (6–41%) of BF_3·OEt_2 in chloroform. Oxidation (SO_2Cl_2/hydrolysis or MCPBA) of the isomerized products and selenoxide elimination at elevated temperature toward the acetoxy group afforded enol acetates in fair yields. The selenoxides of the anti-Markovnikov isomers (unisomerized mixtures) spontaneously eliminated, in the presence of the selenoxides of the Markovnikov isomer, to give allylic acetates in good yields at ambient temperature.

Introduction

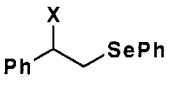
The oxyselenenylation reaction is a very useful procedure for the anti-1,2-addition of an organylseleno group and an oxygen substituent (HO, RO, RCO_2) to an olefin.[1] In general, Markovnikov addition to the olefin predominates (trisubstituted olefins, styrene derivatives), but anti-Markovnikov products are sometimes formed in substantial amounts (monosubstituted olefins). Since the adducts undergo facile selenoxide elimination regiospecifically *away* from the oxygen substituent, they have proven very useful for the preparation of allylic alcohols, ethers, and esters.

Much less attention has been directed to reactions where the selenoxide elimination occurs *toward* an oxygen substituent. Oxyselenenylation/selenoxide elimination would in this case convert olefins to ketones, enol ethers, or enol esters. This type of reaction would occur only if no other β-hydrogens are available for elimination, or, for steric reasons, the selenoxide function is unable to orient itself *syn* to the other β-hydrogens in the molecule. The first example of an elimination reaction toward oxygen was reported by Ho and Hall[2] in a deprotection procedure for alcohols protected as 2-(phenylseleno)ethyl ethers (enol ether involved). More recently the reaction was applied to the preparation of ketene acetals,[3] enol ethers,[4] enol acetates,[5,6] ketones,[6] an enol carbonate,[7] and an enol phosphate.[8]

In this paper we report the acetoxyselenenylation of terminal and 1,2-disubstituted olefins and, after proper manipulations, the conversion of the products into synthetically useful[9] vinylic or allylic acetates.

Results

Initially, in order to study the influence of the β-substituent in a selenoxide elimination reaction toward oxygen, we prepared the hydroxy-, methoxy-, and acetoxyselenenylation products **1a–c** from styrene. After SO_2Cl_2



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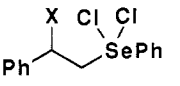
c X=OAc



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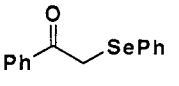

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