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Nickel(0)-Catalyzed Dimerization of Ethyl Cyclopropylideneacetates

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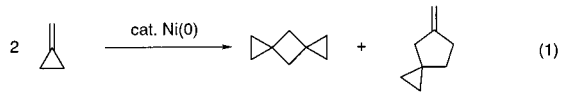
The dimerization of ethyl cyclopropylideneacetates proceeded in the presence of Ni(0) catalysts, and cyclic compounds or linear compounds were formed in selective manners. The structures of products were highly dependent on the structure of the substrate and the ligands bound to the catalyst. The mechanism of the reactions was discussed in detail.

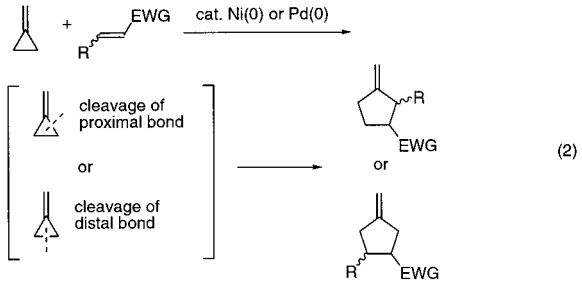
Introduction

Alkylidenecyclopropanes are strained reactive molecules, and many transition-metal catalyzed reactions have been reported.[1] For example, unsubstituted methylenecyclopropane cyclodimerized in the presence of Ni or Pd catalyst and the formation of cyclobutane and cyclopentane derivatives have been reported (eq 1).[2] In



(1)

the presence of similar catalysts, methylenecyclopropane also reacted with unsaturated hydrocarbons and cyclopentane derivatives were isolated (eq 2).[3] The cleavage



(2)

of the distal bond and proximal bond was observed, depending on various factors such as the reaction condition and the structure of the substrate.[4]

Compared to that of the unsubstituted methylenecyclopropane, the reactivity of substituted methylenecyclopropanes is lower. Though a large number of the codimerizations of substituted methylenecyclopropanes with olefins have been reported in the literature,[1] fewer examples of homodimerization reactions have been reported.[1,5]

We have recently examined the reactivities of unsaturated hydrocarbons such as conjugated enynes[6] and allenes[7] in the presence of nickel(0) catalysts and discovered that the reactivities of these compounds changed dramatically by the introduction of an electron-withdrawing group to the hydrocarbons. These studies led us to examine the reactivities of electron-deficient alkylidenecyclopropanes in the presence of nickel catalysts. In this paper, we report the dimerization reactions of ethyl cyclopropylideneacetates in the presence of nickel catalysts.

Results

Ethyl cyclopropylideneacetate (**1**) dimerized in the presence of Ni(0) catalysts at room temperature. The distribution of the products was highly dependent on the ligand bound to the Ni catalyst, and the results were summarized in Table 1. Thus, the formation of cyclopentane derivatives such as **2** and **3** was observed when the reaction was carried out in the presence of Ni−PPh_3 complexes, which were prepared in situ from $Ni(cod)_2$ and PPh_3 (entries 1−2). Higher selectivity was observed when the reaction was carried out at 80 °C (entry 3). On the other hand, the formation of cyclohexane derivatives (**4** and **5**) was observed when the reaction was carried out in the presence of $Ni(cod)_2$ alone or in the presence of the Ni−P(*o*-tol)$_3$ complex (entries 4−5).

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(1) Reviews: (a) Binger, P.; Büch, H. M. *Top. Curr. Chem.* **1987**, *135*, 77−151. (b) Dzhemilev, U. M.; Khusnutdinov, R. I.; Tolstikov, G. A. *J. Organomet. Chem.* **1991**, *409*, 15−65. (c) Binger, P.; Schmidt, T. Metal-Catalyzed Cycloadditions of Methylenecyclopropanes. In *Carbocyclic Three- and Four-Membered Ring Compounds*; Houben-Weyl, de Meijere, A., Eds.; Thieme: Stuttgart, 1997; Vol. E 17b, pp 2217−2294.

(2) Binger, P. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 309−310.

(3) Noyori, R.; Odagi, T.; Furukawa, J. *J. Am. Chem. Soc.* **1970**, *92*, 5780−5781.

(4) Binger, P.; Wedemann, P. *Tetrahedron Lett.* **1985**, *26*, 1045−1048.

(5) Binger, P.; Germer, A. *Chem. Ber.* **1981**, *114*, 3325−3335.

(6) (a) Saito, S.; Tanaka, T.; Koizumi, T.; Tsuboya, N.; Itagaki, H.; Kawasaki, T.; Endo, S.; Yamamoto, Y. *J. Am. Chem. Soc.* **2000**, *122*, 1810−1811. (b) Saito, S.; Kawasaki, T.; Tsuboya, N.; Yamamoto, Y. *J. Org. Chem.* **2001**, *66*, 796−802.

(7) Saito, S.; Hirayama, K.; Kabuto, C.; Yamamoto, Y. *J. Am. Chem. Soc.* **2000**, *122*, 10776−10780.

10.1021/jo0255678 CCC: $22.00
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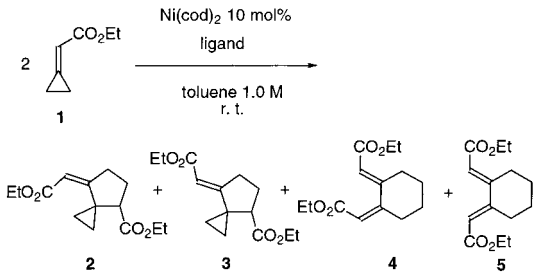
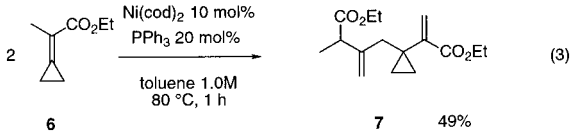
TABLE 1. Nickel-Catalyzed Dimerization of Ethyl Cyclopropylideneacetate (1)



			yield (%)			
entry	ligand (mol %)	time[a] (h)	**2**	**3**	**4**	**5**
1	PPh_3 (40)	4	39	22		
2	PPh_3 (20)	2	52	28		
3	PPh_3 (20)	1[b]	0	74		
4[c]		42	2	6	21	2
5[c]	P(*o*-tol)$_3$ (20)	0.25	8	32	20	9

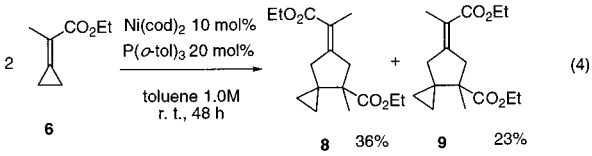
[a] The progress of the reaction was monitored by TLC until compound **1** disappeared. [b] The reaction was carried out at 80 °C. A similar result was obtained when the reaction was carried out at 100 °C. [c] NMR yields (%).

We next examined the reaction of ethyl cyclopropylidenepropanoate (**6**) in the presence of Ni catalysts. Though the rate of the reaction of **6** was very slow at room temperature and at 50 °C, the formation of a linear dimer **7** was observed when the reaction was carried out at 80 °C in the presence of the Ni−PPh_3 complex (eq 3).



(3)

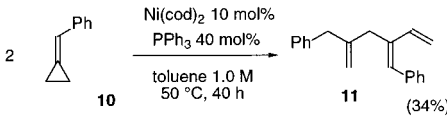
When the catalyst was switched to the Ni−P(*o*-tol)$_3$ complex, a drastic change was observed and cyclopentane derivatives **8** and **9** were isolated as the products at room temperature (eq 4). On the other hand, the formation of



(4)

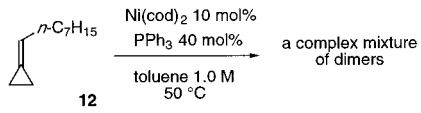
a complex mixture was observed when **6** was treated with $Ni(cod)_2$ (result not shown). It is noteworthy that the products observed in the reaction of **6** were quite different from those observed in the reaction of **1**.

Though the reactivity of unsubstituted methylenecyclopropane is comparable to the reactivities of **1** and **6** and many examples for the codimerization of the substituted methylenecyclopropanes with olefins have been reported, the reactivity of substituted methylenecyclopropanes in the homodimerization reactions has been scarcely reported in the literature.[1,5] We carried out the reactions of non-electron-deficient methylenecyclopropanes such as **10** and **12** and compared the reactivities of **10** and **12** with those of **1** and **6** (eqs 5 and 6). The reactivity of **10** was lower, and no reaction took place at room temperature. However, the formation of a dimerized product **11** was observed after prolonged heating at 50 °C (eq 5). The reaction of **12** also proceeded at 50 °C, but



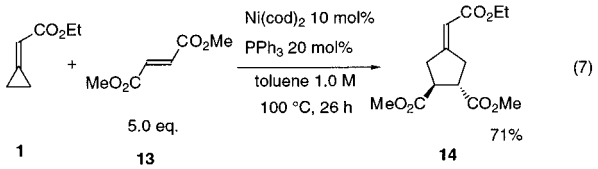
(5)

the product turned out to be a complex mixture of dimerized compounds (eq 6).[8]

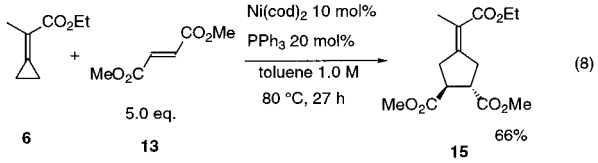


(6)

Finally, we examined the [3 + 2] cycloaddition reactions of **1** and **6** with methyl fumarate **13** to compare the reactivities of the compounds. Unlike the results produced by dimerization reactions, similar products were isolated in these reactions. Thus, cyclopentane derivatives **14** and **15** were isolated respectively in the reactions of **1** and **6** with **13** in the presence of the Ni−PPh_3 complex (eqs 7 and 8). In both reactions, the cleavage of



(7)



(8)

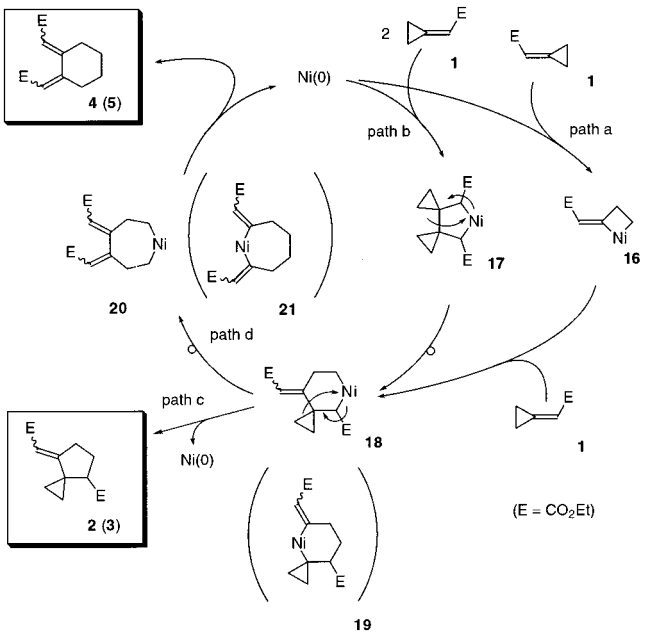
the distal bond was observed. It is noteworthy that these reactions did not proceed at room temparature.

Discussion

Though it has been reported that unsubstituted methylenecyclpropane cyclodimerized in the presence of nickel catalyst, the homodimerization reactions of substituted methylenecyclopropanes have been scarcely reported. To the best of our knowledge, the reactions of a few methylenecyclopropanes such as 1-methylene-2-vinylcyclopropane,[5] 2-methyl-1-methylenecyclopropane, and 2,2-dimethyl-1-methylenecyclopropane[1] are the only transition metal-catalyzed cyclodimerization reactions reported to date. We have shown that the dimerization of some electron-deficient ethoxycarbonyl methylenecyclopropanes proceeded under mild conditions, while the reactivity of alkyl- or arylmethylenecyclopropanes is considerably lower. Since the Ni-catalyzed reaction of alkylmethylenecyclopropanes with olefins proceeded

(8) Similar results were obtained when the reactions were carried out at 80 °C and/or in the presence of a smaller amount (20 mol %) of PPh_3. The result of the reaction which gave the best isolated yield was shown.

SCHEME 1



under milder conditions when an electron-withdrawing group was introduced to the olefin,[1,9] the enhanced reactivities of electron-deficient methylenecyclopropanes could be explained in terms of the enhanced reactivity of the carbon−carbon double bond of the methylenecyclopropane. The reactivity of this bond was further enhanced by the strain induced by the cyclopropyl ring.

It is noteworthy that the structures of products in the dimerization reactions of **1** and **6** were quite different, depending on several factors such as the structure of the starting material and the ligand. In the reaction of **1**, cyclopentane derivatives **2** and **3** were isolated when the Ni-catalyzed reaction was carried out in the presence of PPh_3, while cyclohexanes **4** and **5** were also isolated in the presence of P(*o*-tol)$_3$ or in the absence of the phosphine ligand. The formation of these products could be explained by proposing Scheme 1 as the mechanism of this reaction. Thus, compound **1** was activated by the coordination of Ni catalyst, and a nickelacyclobutane **16** (path a) or a nickelacyclopentane **17** (path b) would be generated. The nickelacyclohexane **18** would be formed by the addition of nickelacyclobutane **16** to **1** or by the cyclopropenyl−butenyl rearrangement[10] of **17**.[11] The reductive elimination of the nickel catalyst will follow, and the cyclopentane derivative **2** (**3**) will be formed in the presence of PPh_3 ligand (path c). Though we did not confirm that the isomerization of **2** to **3** took place under the reaction condition, the observed high selectivity of this reaction at high temperature strongly indicates that the isomerization of **2** proceeds under the reaction condition. In the presence of P(*o*-tol)$_3$ or in the absence of the ligand, however, another rearrangement might take place, and a nickelacycloheptane **20** (or **21**) might be formed (path d). Cyclohexane **4** (or **5**) would be formed by the reductive elimination of the Ni complex. In the reactions of **1**, the cleavage of the proximal bond of the cyclopropane ring always took place.

On the other hand, the cleavage of the distal bond of the cyclopropane ring took place in the reactions of **6**, and the proposed mechanisms of the reactions were summarized in Scheme 2. In contrast to the reactions of **1**, the cleavage of the proximal bond would be suppressed by the strong steric hindrance of the substituents, and the less sterically hindered nickelacyclobutane **22** or the isomers such as **23** and **24** would be formed by the cleavage of the distal bond. These complexes will further react with the double bond of **6** to yield a π-allyl intermediate **25** (or **26**). In the presence of the P(*o*-tol)$_3$ ligand, the formation of the nickelacyclohexane **27** and the reductive elimination of the nickel catalyst will follow, and the cyclopentane **8** (or **9**) would be formed (path a). However, in the presence of Ni−PPh_3 catalyst, a more sterically hindered nickelacyclohexane **29** would be generated because the ligand (PPh_3) bound to the Ni atom is less bulky (path b). The β-elimination of the nickel hydride would follow, and the linear dimer **7** would be isolated as the product.

While the reaction of **6** with methyl fumarate (**13**) proceeded as we expected and the formation of the cyclopentane **15** was observed by the cleavage of the distal bond, the result of the reaction of **1** with **13** was unexpected. In this reaction, the distal bond was cleaved, and the cyclopentane derivative **14** was isolated. This result is in sharp contrast to the result of the cyclodimerization of **1**, where the cleavage of the proximal bond was observed (Table 1). Since the coordination ability of **13** is very strong[12] and an excess of **13** was present in the reaction mixture, it is likely that **13** strongly interacts with the Ni catalyst and the formation of **16** was suppressed (Scheme 3). Instead, the generated fumarate complex **31** would further react with **1** and complex **34** would be generated. The cleavage of the distal bond would occur probably because of the steric and/or electronic effect of **13** bound to the Ni atom. A similar result has been reported by Binger and Wedemann in the reaction of unsubstituted methylenecyclopropane with acrylates and fumarates. While the cleavage of the proximal bond occurred in the reactions of acrylates with methylenecyclopropane, the cleavage of the distal bond was observed in the reactions of fumarates.[4]

Conclusion

We examined the Ni-catalyzed dimerization of ethyl cyclopropylideneacetates for the first time and found that the [3 + 2] cyclodimerizations and linear dimerizations proceeded in the presence of Ni catalysts under mild

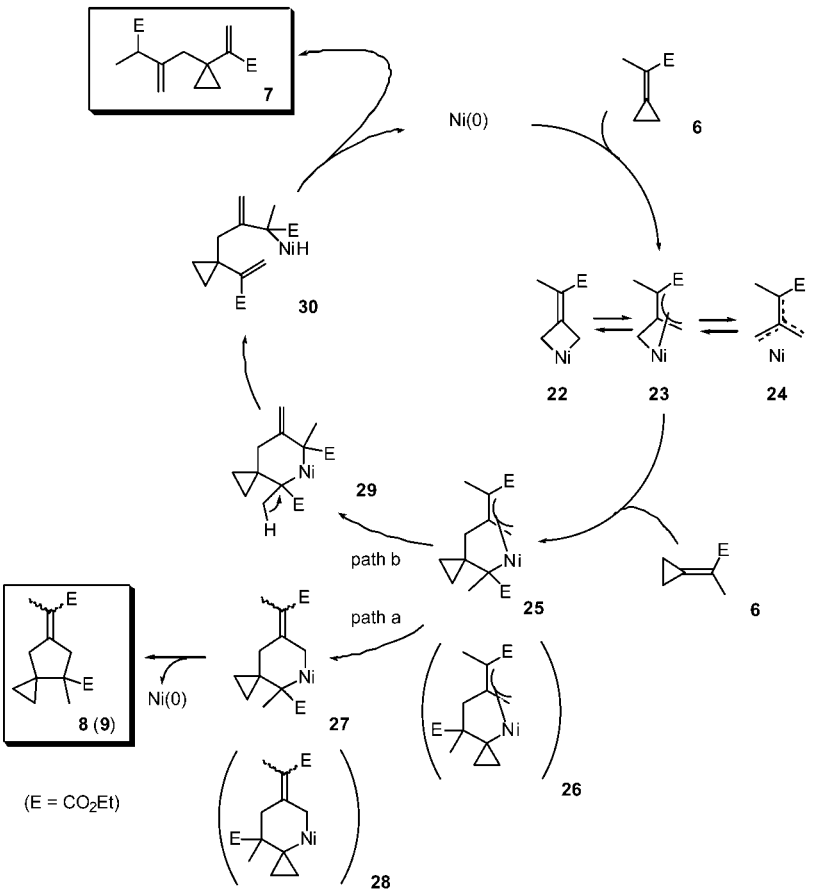
(9) Other examples: (a) Binger, P. *Synthesis* **1973**, 427−428. (b) Noyori, R.; Odagi, T.; Furukawa, J. *J. Am. Chem. Soc.* **1972**, *94*, 4018−4020. (c) Binger, P.; Brinkmann, A.; Wedemann, P. *Chem. Ber.* **1983**, *116*, 2920−2930.

(10) The structures of some intermediates proposed in Scheme 1 have been isolated or characterized spectroscopically. The cyclopropenyl−butenyl rearrangement has also been observed. See: Binger, P.; Doyle, M. J.; Benn, R. *Chem. Ber.* **1983**, *116*, 1−10.

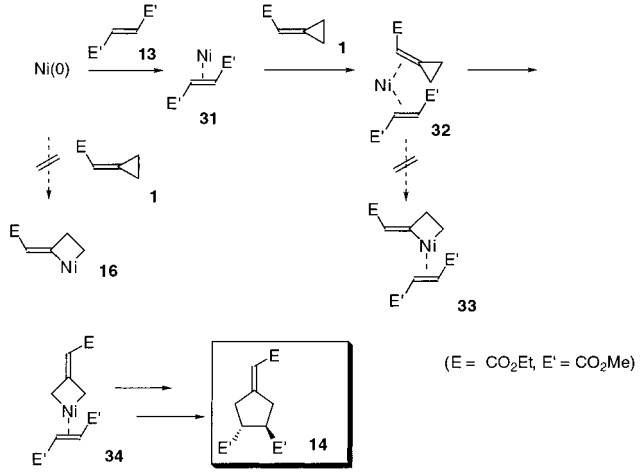
(11) A reviewer has pointed out the possibility of the formation of a nickelaspiroheptane as an intermediate, which might be generated by the oxidative addition of **16** to **1**.

(12) Closely related Ni, Pd, and Pt species formed more stable π-complexes with olefins having substituents of greater electron-withdrawing abilities. See: Chatt, J.; Rowe, G. A.; Williams, A. A. *Proc. Chem. Soc.* **1957**, 208. Greaves, E. O.; Lock, C. J. L.; Maitlis, P. M. *Can. J. Chem.* **1968**, *46*, 3879−3891. Takahashi, S.; Hagihara, N. *Nippon Kagaku Zasshi* **1967**, *88*, 1306−1310. Yamamoto, T.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* **1971**, *93*, 3360−3364.

SCHEME 2



SCHEME 3



conditions. The reactivities of the methylenecyclopropanes were enhanced by the introduction of an electron-withdrawing ethoxycarbonyl group. The mode of the reactions was significantly affected by the structure of substrates and the ligand bound to the Ni catalyst, and the mechanisms of the reactions were proposed. This study provided a new synthetic method for the preparation of functionalized spiro compounds containing cyclopropyl rings, some of which are known as antitumor agents.[13]

(13) McMorris, T. C. *Bioorg. Med. Chem.* **1999**, *7*, 881−886.

Experimental Section

Methylenecyclopropanes **1**,[4,14] **6**,[15] **10**,[16,17] and **12**[17,18] were prepared as reported. Other reagents were commercially available and used without further purification. The nickel-catalyzed reactions were carried out under Ar. The structures of **2**, **3**, **7**, **8**, and **9** were further confirmed by carrying out NOE experiments (see Supporting Information).

Nickel(0)-Catalyzed Reaction of Electron-Deficient Methylenecyclopropanes. A Representative Procedure. To a dark red mixture of $Ni(cod)_2$ (13.8 mg, 0.05 mmol) and PPh_3 (27 mg, 0.1 mmol) in dry toluene (0.25 mL) was added a solution of **1** (63 mg, 0.5 mmol) in dry toluene (0.25 mL) at room temperature. The progress of the reaction was monitored by TLC, and the mixture was stirred until the starting material disappeared (2 h). The mixture was passed through a short silica gel column (hexane and ether) and evaporated. The residue was further purified by MPLC (hexane/AcOEt 15:1) to give **2** (33 mg, 52%) and **3** (18 mg, 28%). Other reactions were carried out under the same conditions except for the time and temperature, which have already been described (vide supra).

***(Z)*-4-Ethoxycarbonyl-7-(ethoxycarbonylmethylene)-spiro[2.4]heptane (2):** colorless oil; ^1H NMR (300 MHz, $CDCl_3$) 5.62 (dd, J = 1.8, 1.8 Hz, 1H), 4.14−4.00 (m, 4H), 3.01−2.90 (m, 1H), 2.65−2.55 (m, 2H), 2.18−1.92 (m, 3H), 1.85−

(14) Miller, S. A.; Gadwood, R. C. *Organic Syntheses;* Wiley & Sons: New York, 1993; Collect. Vol. VIII, pp 556−562.
(15) Kortmann, I.; Westermann, B. *Synthesis* **1995**, 931−933.
(16) Schweizer, E. E.; Berninger, C. J.; Thompson, J. G. *J. Org. Chem.* **1968**, *33*, 336−339.
(17) Utimoto, K.; Tamura, M.; Sisido, K. *Tetrahedron* **1973**, *29*, 1169−1171.
(18) Nemoto, H.; Miyata, J.; Hakamata, H.; Nagamochi, M.; Fukumoto, K. *Tetrahedron* **1995**, *51*, 5511−5522.

1.77 (m, 1H), 1.23 (dd, J = 7.2, 7.2 Hz, 3H), 1.21 (dd, J = 7.1, 7.1 Hz, 3H), 1.01−0.92 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 174.2, 168.4, 165.2, 108.9, 60.4, 59.5, 54.6, 38.3, 29.3, 27.3, 20.1, 14.4, 14.3, 14.2; IR (neat) 2980, 2905, 1736, 1719, 1639, 1560, 1460, 1448, 1425, 1383, 1346, 1269, 1180, 1096, 1040 cm^{-1}. HRMS Calcd for $C_{14}H_{20}O_4$: 252.1360. Found: 252.1368. Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.71; H, 7.99.

(*E*)-4-Ethoxycarbonyl-7-(ethoxycarbonylmethylene)-spiro[2.4]heptane (3): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) 5.11 (dd, J = 2.4, 2.4 Hz, 1H), 4.15−4.04 (m, 4H), 3.21−3.01 (m, 2H), 2.65 (dd, J = 7.2, 5.2 Hz, 1H), 2.22−2.00 (m, 2H), 1.24 (dd, J = 7.2, 7.2 Hz, 3H), 1.22 (dd, J = 7.1, 7.1 Hz, 3H), 1.11−1.05 (m, 2H), 0.97−0.84 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 173.9, 172.1, 167.0, 105.1, 60.4, 59.5, 50.4, 32.8, 30.5, 27.8, 21.3, 15.6, 14.3, 14.2; IR (neat) 3078, 2980, 2937, 2907, 2874, 1736, 1713, 1647, 1458, 1448, 1369, 1348, 1327, 1261, 1177, 1161, 1096, 1078, 1040 cm^{-1}. HRMS Calcd for $C_{14}H_{20}O_4$: 252.1360. Found: 252.1350. Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.60; H, 8.16.

(1*E*,2*Z*)-Di(ethoxycarbonylmethylene)cyclohexane (4): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) 5.64 (s, 1H), 5.59 (s, 1H), 4.13 (ddd, J = 7.2, 7.2, 7.2 Hz, 2H), 4.10 (ddd, J = 7.1, 7.1, 7.1 Hz, 2H), 3.01−3.00 (m, 2H), 2.33−2.31 (m, 2H), 1.75 (dd, J = 3.2, 3.1 Hz, 4H), 1.25 (dd, J = 7.3, 7.3 Hz, 3H), 1.20 (dd, J = 7.2, 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 166.2, 165.9, 158.1, 157.9, 115.2, 114.6, 60.1, 59.8, 39.1, 30.9, 28.0, 27.5, 14.2, 14.0; IR (neat) 2982, 2937, 2860, 1715, 1639, 1445, 1371, 1304, 1269, 1225, 1190, 1161, 1134, 1096, 1061, 1036 cm^{-1}. HRMS Calcd for $C_{14}H_{20}O_4$: 252.1360. Found: 252.1333. Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.80; H, 8.15.

(1*E*,2*E*)-Di(ethoxycarbonylmethylene)cyclohexane (5). The charactarization of this compound was based on the spectral data of (1*E*,2*E*)-di(methoxycarbonylmethylene)cyclohexane.[19] **5:** colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) 5.81 (dd, J = 1.4, 1.4 Hz, 2H), 4.15 (ddd, J = 7.1, 7.1, 7.1 Hz, 4H), 2.96−2.95 (m, 4H), 1.71 (dddd, J = 3.3, 3.3, 3.3, 3.3 Hz, 4H), 1.26 (dd, J = 7.2, 7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 166.3, 160.3, 115.0, 60.0, 30.0, 25.7, 14.2; IR (neat) 2980, 2937, 2860, 1715, 1634, 1445, 1371, 1329, 1286, 1236, 1177, 1134, 1096, 1074, 1036 cm^{-1}. HRMS Calcd for $C_{14}H_{20}O_4$: 252.1360. Found: 252.1366.

Ethyl 4-[1-(1-Ethoxycarbonylvinyl)cyclopropyl]-2-methyl-3-methylenebutanoate (7): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) 6.14 (d, J = 1.3 Hz, 1H), 5.50 (d, J = 1.5 Hz, 1H), 4.90 (s, 1H), 4.88 (d, J = 0.9 Hz, 1H), 4.19 (ddd, J = 7.1, 7.1, 7.1 Hz, 2H), 4.09 (ddd, J = 7.1, 7.1, 7.1 Hz, 2H), 3.17 (ddd, J = 7.3, 7.3, 7.3 Hz, 1H), 2.47 (d, J = 15.4 Hz, 1H), 2.16 (d, J = 15.2 Hz, 1H), 1.29 (dd, J = 7.1, 7.1 Hz, 3H), 1.211 (dd, J = 7.2, 7.2 Hz, 3H), 1.206 (d, J = 7.0 Hz, 3H), 0.77−0.57 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) 174.5, 166.7, 146.1, 143.3, 126.1, 112.9, 60.4, 44.5, 42.6, 22.1, 15.9, 14.2, 14.1, 12.8, 12.5; IR (neat) 3082, 2982, 2939, 2907, 2876, 1720, 1645, 1626, 1553, 1447, 1425, 1371, 1339, 1302, 1273, 1246, 1184, 1121, 1096, 1028 cm^{-1}. HRMS Calcd for $C_{16}H_{24}O_4$: 280.1673. Found: 280.1690. Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.54; H, 8.63. Found: C, 68.41; H, 8.82.

(*E*)-4-Ethoxycarbonyl-6-(1-ethoxycarbonyl-1-methylmethylene)spiro[2.4]heptane (8): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) 4.17−4.04 (m, 4H), 3.20 (d, J = 18.2 Hz, 1H), 2.85 (dd, J = 21.6, 21.6 Hz, 2 H), 2.40 (d, J = 18.0 Hz, 1H), 1.85 (s, 3H), 1.25 (dd, J = 7.2, 7.2 Hz, 3 H), 1.21 (dd, J = 7.1, 7.1 Hz, 3H), 1.09 (s, 3H), 0.77−0.70 (m, 1H), 0.52−0.42 (m, 2H), 0.37−0.31 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 175.5, 168.0, 155.9, 119.1, 60.5, 59.9, 49.5, 45.3, 43.2, 28.9, 20.6, 15.6, 14.4, 14.2, 9.9, 8.5; IR (neat) 3078, 2982, 2936, 2905, 1726, 1709, 1647, 1460, 1418, 1366, 1308, 1283, 1259, 1196, 1157, 1109, 1057, 1022 cm^{-1}. HRMS Calcd for $C_{16}H_{24}O_4$: 280.1673. Found: 280.1678. Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.54; H, 8.63. Found: C, 68.35; H, 8.84.

(19) Piers, E.; McEachern, E. J.; Romero, M. A. *J. Org. Chem*. **1997**, *62*, 6034−6040.

(*Z*)-4-Ethoxycarbony-6-(1-ethoxycarbonyl-1-methylmethylene)spiro[2.4]heptane (9): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) 4.16 (ddd, J = 7.1, 7.1, 7.1 Hz, 2H), 4.07 (ddd, J = 7.1, 7.1, 7.1 Hz, 2H), 3.52 (ddd, J = 18.7, 2.0, 2.0 Hz, 1H), 2.77 (ddd, J = 18.7, 2.2, 2.2 Hz, 1H), 2.61 (d, J = 17.9 Hz, 1H), 2.38 (d, J = 18.4 Hz, 1H), 1.78 (s, 3H), 1.28 (dd, J = 7.2, 7.2 Hz, 3H), 1.20 (dd, J = 7.1, 7.1 Hz, 3H), 1.04 (s, 3H), 0.80−0.73 (m, 1H), 0.57−0.46 (m, 2H), 0.35−0.28 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 175.8, 168.1, 155.7, 119.1, 60.3, 59.9, 50.6, 45.7, 43.3, 27.4, 20.3, 15.7, 14.4, 14.2, 9.5, 9.1; IR (neat) 3078, 2982, 2936, 2905, 2827, 1726, 1708, 1647, 1462, 1421, 1366, 1319, 1283, 1240, 1204, 1173, 1153, 1096, 1057, 1024 cm^{-1}. HRMS Calcd for $C_{16}H_{24}O_4$: 280.1673. Found: 280.1661. Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.54; H, 8.63. Found: C, 68.46; H, 8.72.

(*Z*)-5-Benzyl-3-phenylmethylene-1,5-hexadiene (11): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) 7.35−7.18 (m, 10H), 6.79 (ddd, J = 17.5, 11.1, 0.9 Hz, 1H), 6.41 (s, 1H), 5.26 (d, J = 17.6 Hz, 1H), 5.11 (ddd, J = 11.0, 1.5, 1.5 Hz, 1H), 4.95 (s, 1H), 4.88 (s, 1H), 3.38 (s, 2H), 3.03 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 147.0, 139.6, 137.3, 136.1, 133.9, 131.5, 129.4, 129.1, 128.3, 128.1, 126.7, 126.1, 115.9, 113.4, 42.8, 40.3; IR (neat) 3082, 3061, 3026, 2905, 1749, 1734, 1717, 1699, 1684, 1670, 1647, 1601, 1576, 1558, 1541, 1522, 1508, 1493, 1474, 1456, 1437, 1394, 1339, 1074, 1030, 1003 cm^{-1}. HRMS Calcd for $C_{20}H_{20}$: 260.1564. Found: 260.1562.

Nickel(0)-Catalyzed Coupling Reaction between Methylenecyclopropanes and Fumarate. A Representative Procedure. To a dark red mixture of $Ni(cod)_2$ (13.8 mg, 0.05 mmol), PPh_3 (27 mg, 0.1 mmol), and dimethyl fumarate (360 mg, 2.5 mmol) in dry toluene (0.25 mL) was added a solution of **1** (63 mg, 0.5 mmol) in dry toluene (0.25 mL) at room temperature. The mixture was stirred at 100 °C, and the progress of the reaction was monitored by TLC until the starting material disappeared (26 h). The mixture was passed through a short silica gel column (hexane and ether) and evaporated. The residue was further purified by silica gel column chromatography (hexane/AcOEt 10:1) to give **14** (96 mg, 71%). Other reactions were carried out under the same conditions except for the time and temperature, which have already been described.

***trans*-1-(1-Ethoxycarbonylmethylene)-3,4-dimethoxycarbonylcyclopentane (14):** colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) 5.79 (dddd, J = 2.2, 2.2, 2.2, 2.2 Hz, 1H), 4.13 (ddd, J = 7.1, 7.1, 7.1 Hz, 2H), 3.70 (s, 3H), 3.69 (s, 3H), 3.47−3.33 (m, 1H), 3.26−3.12 (m, 2H), 2.98−2.84 (m, 2H), 2.78−2.69 (m, 1H), 1.25 (dd, J = 7.2, 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 173.7, 173.5, 166.1, 161.3, 113.6, 59.7, 52.11, 52.06, 46.8, 45.7, 38.1, 35.6, 14.2; IR (neat) 2982, 2955, 2907, 2845, 1738, 1713, 1661, 1437, 1373, 1348, 1269, 1209, 1128, 1096, 1034 cm^{-1}. Anal. Calcd for $C_{13}H_{18}O_6$: C, 57.77; H, 6.71. Found: C, 57.72; H, 6.82.

***trans*-1-(1-Ethoxycarbonyl-1-methylmethylene)-3,4-dimethoxycarbonylcyclopentane (15):** colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) 4.16 (ddd, J = 7.1, 7.1, 7.1 Hz, 2H), 3.70 (s, 3H), 3.69 (s, 3H), 3.38−3.29 (m, 1H), 3.20−3.13 (m, 2H), 2.90−2.83 (m, 2H), 2.66−2.57 (m, 1H), 1.83 (s, 3H), 1.27 (dd, J = 7.2, 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 174.0, 173.9, 167.6, 152.8, 120.8, 60.2, 52.2, 52.1, 47.4, 45.8, 37.2, 36.7, 15.9, 14.3; IR (neat) 2984, 2955, 2907, 2851, 1738, 1735, 1705, 1647, 1437, 1367, 1340, 1312, 1285, 1267, 1200, 1101, 1026 cm^{-1}. Anal. Calcd for $C_{14}H_{20}O_6$: C, 59.14; H, 7.09. Found: C, 59.09; H, 7.26.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for compounds **2**−**5**, **7**−**9**, **11**, **14**, and **15** and the summary of the NOE experiments (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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