A reaction was run using an alternate sequence of mixing the components. To 5 mmol of chromous perchlorate reagent in 20 mL of DMF was added 1.5 mL (23 mmol) of ethylenediamine. To this reagent was added 100 mg (1 mmol) of **1a**. Analysis after 24 h indicated only 4% conversion to **2a**.

***trans*-1-Phenylpropene (3a)**.[6] To 1.0 g of $LiAlH_4$ suspended in 30 mL of THF was added 1.0 g of **1a**. The mixture was refluxed for 60 h, cooled, and quenched with 5 mL of saturated Na_2SO_4 solution. The organic layer was dried, filtered, and concentrated to yield a 23:7:70 mixture of **1a**/**2a**/**3a**. Isolation by preparative GLC yielded 600 mg (60%) of **3a**.

Reduction of 2-Butyn-1-ol (4a). A. To 10 mmol of Cr^{II}en reagent was added 140 mg (2 mmol) of **4a**. Analysis after 24 h showed a 3:90:7 mixture of **4a**/**5a**/**6a**. *trans*-Crotyl alcohol (**5a**) shows: NMR δ 5.65–5.25 (m, 2), 3.90 (m, 2), 3.25 (s, 1), 1.68 (d of d, 3, J = 3.5, 1.5 Hz). *cis*-Crotyl alcohol (**6a**) shows: NMR δ 5.65–5.25 (m, 2), 4.04 (d, 2, J = 5 Hz), 3.62 (s, 1), 1.63 (d, 3, J = 5 Hz).

The stability of the products was examined by subjecting a 59:41 mixture of **5a**/**6a** to the Cr^{II}en reagent. After 24 h the ratio was 58:42.

Phenylacetylene-*2-d* (1g).[12] To 30 mL of 1.6 M *n*-butyllithium in 50 mL of THF was added 4.0 g of **1f**. The mixture was refluxed for 1 h followed by the addition of 5 mL of D_2O (98% D). The THF layer was dried and concentrated to yield 3.7 g (93%) of **1g**. The IR and NMR showed no absorptions for the acetylenic hydrogen; the mass spectrum indicated ~98% isotopic purity: *m/e* (relative intensity) 104 (7.4), 103 (100.0), 102 (4.0), 77 (14.2), 76 (9.9).

Registry No. **1a**, 673-32-5; **1b**, 622-76-4; **1c**, 4250-81-1; **1d**, 501-65-5; **1e**, 693-02-7; **1f**, 536-74-3; **1g**, 3240-11-7; **1h**, 928-49-4; **2a**, 766-90-5; **2b**, 1560-09-4; **2c**, 7642-18-4; **2e**, 592-41-6; **2f**, 100-42-5; **2g**, 21370-59-2; **3a**, 873-66-5; **3d**, 103-30-0; **3g**, 6911-81-5; **4a**, 764-01-2; **4b**, 6261-22-9; **4c**, 764-60-3; **4d**, 1002-36-4; **4e**, 1504-58-1; **4f**, 27301-54-8; **4g**, 590-38-5; **5a**, 504-61-0; **5b**, 1576-96-1; **5c**, 928-95-0; **5d**, 33467-76-4; **5f**, 3899-34-1; **5g**, 71195-14-7; **6a**, 4088-60-2; **6b**, 1576-95-0; **6c**, 928-94-9; **6d**, 55454-22-3; **6e**, 71195-15-8; **6f**, 24652-50-4; **6g**, 71195-16-9; chromous perchlorate, 13931-95-8.

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[12] J. M. Lalancette, Y. Beauregand, and M. Bhereur, *Can. J. Chem.*, 48, 1093 (1970).

Palladium(II)-Catalyzed Carboxylation Reactions of Olefins: Scope and Utility

J. K. Stille* and R. Divakaruni

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

Received April 20, 1979

The palladium-catalyzed carbomethoxylation reaction of olefins, which takes place with methanol, carbon monoxide, stoichiometric amounts of cupric chloride as a reoxidant, and a sodium butyrate buffer, usually adds two carbomethoxy functions to the double bond. Thus, dimethyl succinate is obtained from ethylene. The product of the reaction of 1,5-hexadiene, however, depends on the carbon monoxide pressure. At 6 atm of carbon monoxide, dimethyl 2-(3-buten-1-yl)succinate was obtained while at 1-3 atm of carbon monoxide dimethyl 3,6-bis(carbomethoxy)octane-1,8-dioate was formed exclusively. The utility and the synthetic versatility of the carboxylation reaction was studied by using conjugated and nonconjugated, cyclic and acyclic diolefins. The carboxylation of various functionally substituted olefins such as unsaturated ketones, alcohols, and esters was carried out to determine the versatility of the dicarboxylation reaction. Generally the olefin function could be dicarboxylated in high yields.

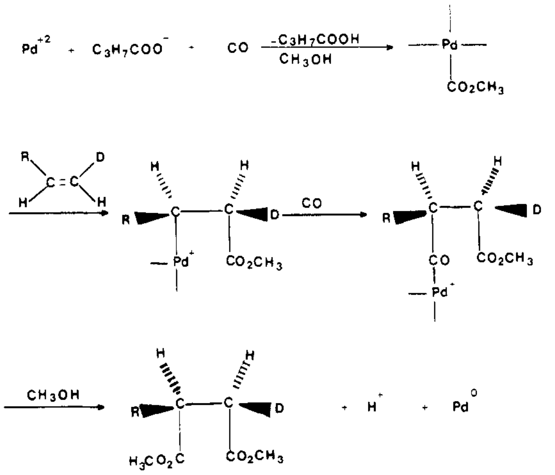
The reaction of olefins with carbon monoxide in methanol to form esters can be effected in the presence of palladium(II) chloride (eq 1).[1] When a weak base such as sodium butyrate is present, a diester is formed under mild conditions (25 °C, 3 atm of CO). The reaction can be made catalytic with respect to palladium chloride by using stoichiometric amounts of cupric chloride as a reoxidant.[2]

$$PdCl_2 + RCH{=}CH_2 + 2CO + 2CH_3OH \xrightarrow{C_3H_7CO_2Na} R(CO_2CH_3)CHCH_2CO_2CH_3 + Pd^0 + 2HCl \quad (1)$$

$$Pd^0 + 2CuCl_2 \rightarrow PdCl_2 + 2CuCl \quad (2)$$

The stereochemistry of the dicarboxylation reaction is cis and proceeds with the direct transfer of the carbomethoxyl group from the palladium to an olefinic carbon atom in a regiospecific anti-Markownikoff direction[2,3] (Scheme I). In the absence of a base a β-methoxy ester is obtained instead.

Scheme I



A palladium(II)-catalyzed reaction which produces diesters from olefins, carbon monoxide and alcohol under mild reaction conditions offers considerable synthetic potential. In order to determine the versatility of this reaction, we have studied the carboxylation of representative monoolefins, diolefins, and functionally substituted olefins.

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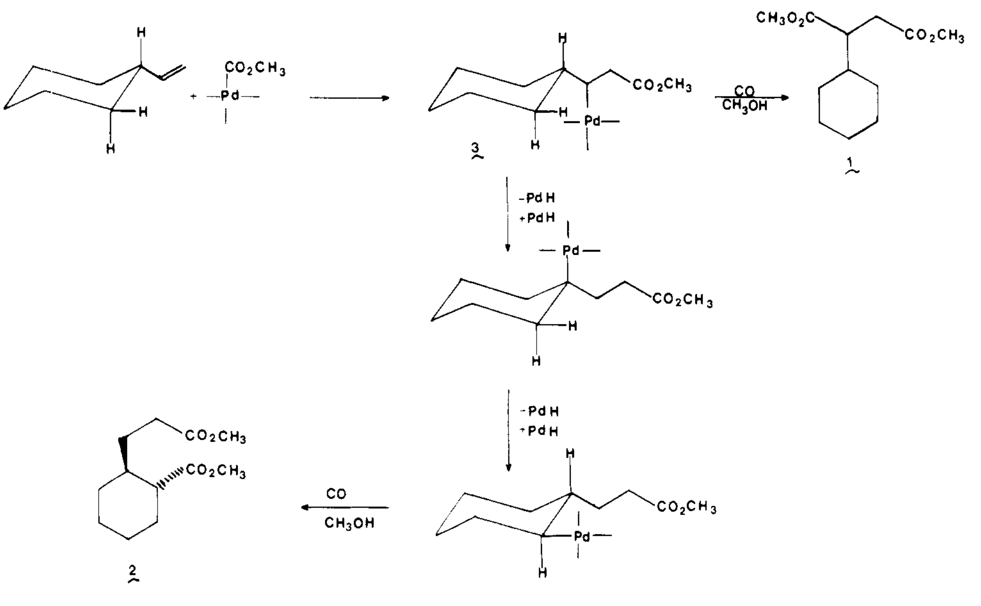
[1] J. K. Stille and D. E. James, "Transition Metal Catalyzed Carbonylation of Olefins. The Chemistry of Functional Groups, Supplement A. Double Bonded Functional Groups", S. Patai, Ed., Wiley, London, 1976, p 1099.

[2] D. E. James and J. K. Stille, *J. Am. Chem. Soc.*, 98, 1810 (1976).

[3] D. E. James, L. F. Hines, and J. K. Stille, *J. Am. Chem. Soc.*, 98, 1806 (1976).

0022-3263/79/1944-3474$01.00/0

Scheme II



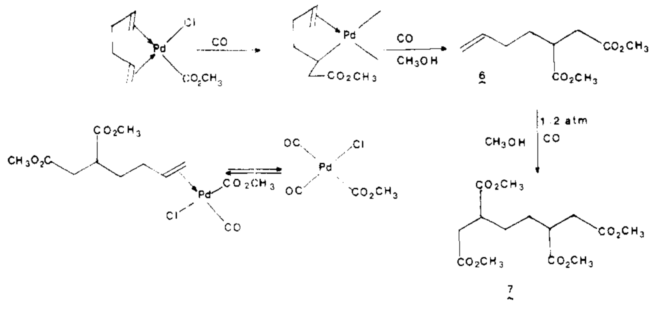
Results and Discussion

Carboxylation of Monoolefins. The reaction of ethylene and propylene, for example, with carbon monoxide in methanol in the presence of base, catalytic amounts of palladium(II) chloride, and stoichiometric amounts of cupric chloride as a reoxidant afforded dimethyl succinate and dimethyl α-methylsuccinate, respectively. The catalytic carboxylation of vinylcyclohexane gave two esters, **1** and **2**, in 32 and 67% yields, respectively, as a result of a β-hydride elimination readdition mechanism[2] (Scheme II). Since the carbon bearing the palladium in the intermediate complex **3** is attached to a secondary carbon, the rates of hydride abstraction of a tertiary hydrogen and carbonylation are competitive, leading to the two diesters. Carboxylation of 3-phenylpropene gave both dimethyl 2-benzylsuccinate (**4**) (70%) and the β-methoxy ester **5** (30%) (eq 4).

$$\mathrm{RCH{=}CH_2 + CO + CH_3OH \xrightarrow[C_3H_7CO_2Na]{} R(CO_2CH_3)CHCH_2CO_2CH_3} \quad (3)$$
$$\mathrm{R = H, CH_3}$$

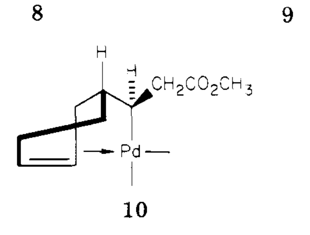
$$\mathrm{C_6H_5CH_2CH{=}CH_2 \xrightarrow{C_3H_7CO_2Na} \underset{\mathbf{4}}{C_6H_5CH_2(CO_2CH_3)CH\ CH_2CO_2CH_3} + \underset{\mathbf{5}}{C_6H_5CH_2(OCH_3)CHCH_2CO_2CH_3}} \quad (4)$$

Carboxylation of Nonconjugated Diolefins. The reaction of 1,5-hexadiene gave different products depending on the pressure of the reaction. At pressures greater than 5 atm, dimethyl 2-(3-buten-1-yl)succinate (**6**) was formed in 70% conversion, while at pressures of 1–3 atm of carbon monoxide, dimethyl 3,6-bis(carbomethoxy)octane-1,8-dioate (**7**) was obtained in 60% conversion.



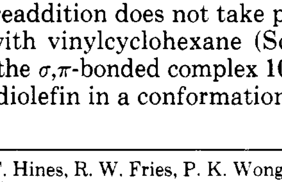
These results are consistent with a pressure-dependent competition by olefin and carbon monoxide for coordination sites on palladium. Since 1,5-hexadiene is a chelating diolefin it is not easily displaced by carbon monoxide even at high pressures and the carboxylation of one double bond is ensured. Competition of the resulting monoolefinic diester with carbon monoxide for a coordination site is determined by the carbon monoxide pressure. At high pressures, carbon monoxide coordinates to palladium displacing the monoolefin, while at low pressures the monoolefin coordinates and is carboxylated. In separate experiments it was shown that both **6** and 1-hexene can be carboxylated at 1–3 atm of carbon monoxide while both remain unchanged at pressures greater than 5 atm.

Carboxylation of 4-vinylcyclohexene yields the β-methoxy ester **8** (15%) and the diester **9** (85%). The selectivity for the vinyl group as compared to that for the internal double bond is not surprising since the carboxylation of cyclohexene proceeds 100 times slower than the carboxylation of 1-olefins.[2,4] Rearrangement by β-hydride elimination and readdition does not take place as readily in this case as with vinylcyclohexane (Scheme II), apparently because the σ,π-bonded complex **10** is rigidly held by the chelating diolefin in a conformation that does not



(5)

8 9



10

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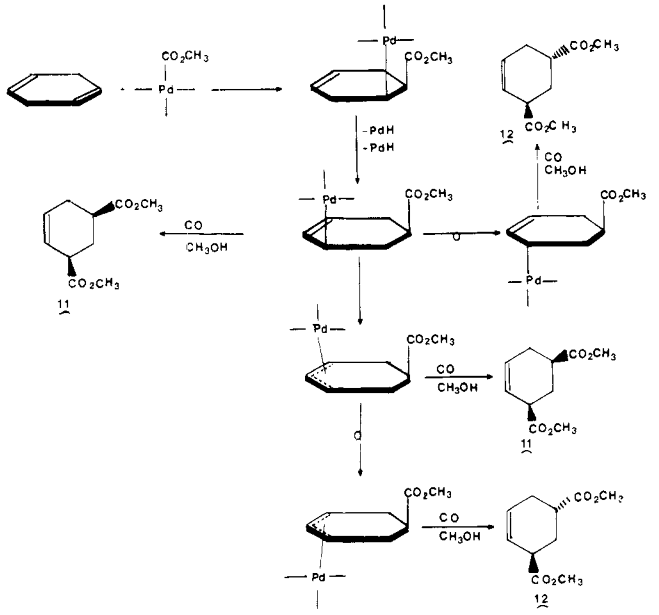
[4] J. K. Stille, L. F. Hines, R. W. Fries, P. K. Wong, D. E. James, and K. Lau, *Adv. Chem. Ser.*, No. 132, 90 (1974).

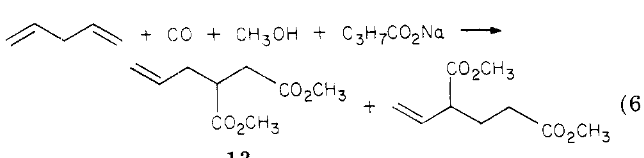
Scheme III



allow cis β-hydride elimination.

The carboxylation of 1,4-cyclohexadiene afforded the *cis*- and *trans*-cyclohex-4-ene-1,3-dicarboxylates **11** and **12** in 87 and 13% yields, respectively. Under the reaction conditions **11** and **12** are not interconvertible. While the formation of the cis diester can take place by a palladium hydride elimination–readdition mechanism, the formation of minor amounts of the trans diester could not be expected to take place readily (Scheme III). Formation of the trans diester requires that the palladium hydride addition must take place from the opposite side of the ring. Alternatively the π-allyl–palladium complex can rearrange by flipping the ring ligand. The rearrangement process may be aided by the increased stability of the 1,3-disubstituted complex compared to that of the 1,2-disubstituted complex (steric) and by the presence of the allylic hydrogen.

The open-chain analogue 1,4-pentadiene gave predominantly (78%) the 1,2-dicarboxylation product dimethyl 2-allylsuccinate (**13**), as well as 22% of the rearranged product dimethyl 2-vinylglutarate (**14**) (eq 6).



(6)

13 14

Carboxylation of Conjugated Diolefins. The palladium(II)-catalyzed carboxylation of 1,3-butadiene affords different products depending on the reaction conditions and the ligands present (eq 7). Hydrocarboxylation with a palladium(II)–phosphine complex (100 °C, 100 atm) gave 3-pentenoates.[5] The suggested mechanism of this reaction[5] requires prior formation of a palladium hydride complex followed by its conversion to a π,σ-palladium complex, which rearranges to an unsymmetrical π-allyl complex. Thus, the carbomethoxy–palladium species should react by a similar mechanism, affording the diester products. The product distribution in the carboxylation of 1,3-butadiene depends on both the concentration of base and the temperature of the reaction mixture (Table I).

$$+ CO + CH_3CH + C_3H_7CO_2Na \longrightarrow$$

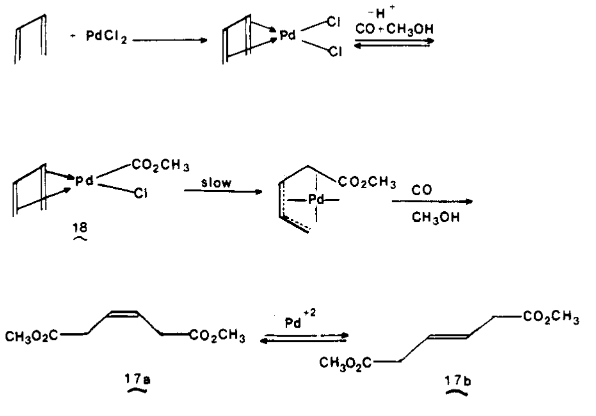
$$\underset{\mathbf{15}}{ClCH_2CH{=}CHCH_2CO_2CH_3} + \underset{\mathbf{16}}{CH_3OCH_2CH{=}CHCO_2CH_3} + \underset{\mathbf{17a},\ cis;\ \mathbf{b},\ trans}{CH_3OCOCH_2CH{=}CHCH_2CO_2CH_3} \quad (7)$$

Table I. Carboxylation of 1,3-Butadiene[a]

mmol of C_3H_7-COONa	temp, °C	% convrsn	products, %		
			15	16	17a,b
100	25	37	45	43[b]	12[c]
200	25	52	0	0	100
300	70	75	0	0	100

[a] 25 mmol of butadiene and 100 mmol of cupric chloride were used; the total pressure was 3 atm for 144 h.
[b] Cis-trans ratio was determined to be 56:44 by ¹H NMR.
[c] Cis-trans ratio was determined to be 32:68 by ¹H NMR.

Scheme IV



The attack of methanol on the carbonyl ligand to generate the carbomethoxyl complex **18** and a proton may be equilibrium controlled, accounting for the dependence of the reaction products on the concentration of base. At lower base concentration, chloro palladation and methoxy palladation were observed. Under the reaction conditions the equilibrium mixture of the diester **17** consisted of 68% trans (**17b**) and 32% cis isomer (**17a**) (Scheme IV). The carboxylation of 1,3-butadiene in benzyl alcohol afforded dibenzyl *trans*-hex-3-ene-1,6-dioate exclusively, in 90% conversion.

Carboxylation of 1,3-cyclohexadiene resulted in the formation of the four cyclohexenedicarboxylates **19**, **20**, **11**, and **12** (in 46, 11, 28, and 15% yields, respectively). The mechanism of formation of the trans diesters **12** and **20** requires that the palladium hydride addition must take place from the opposite side of the ring (Scheme V).

Catalytic Carboxylation of α,β-Unsaturated Ketones, Unsaturated Alcohols, and Esters. The carboxylation of functionalized monoolefins such as unsaturated ketones, alcohols, and esters was carried out in an attempt to determine the kind of functional groups that could be introduced in the olefinic system and their effect on the carboxylation reaction.

Carboxylation of methyl vinyl ketone under the standard conditions yielded dimethyl α-acetylsuccinate (**21**). In general, the conversions were low (5–30%) but the remaining methyl vinyl ketone could be recovered unchanged. The diester **21** was easily converted to the butenolide[6] (**22**) by a decarboxylation followed by

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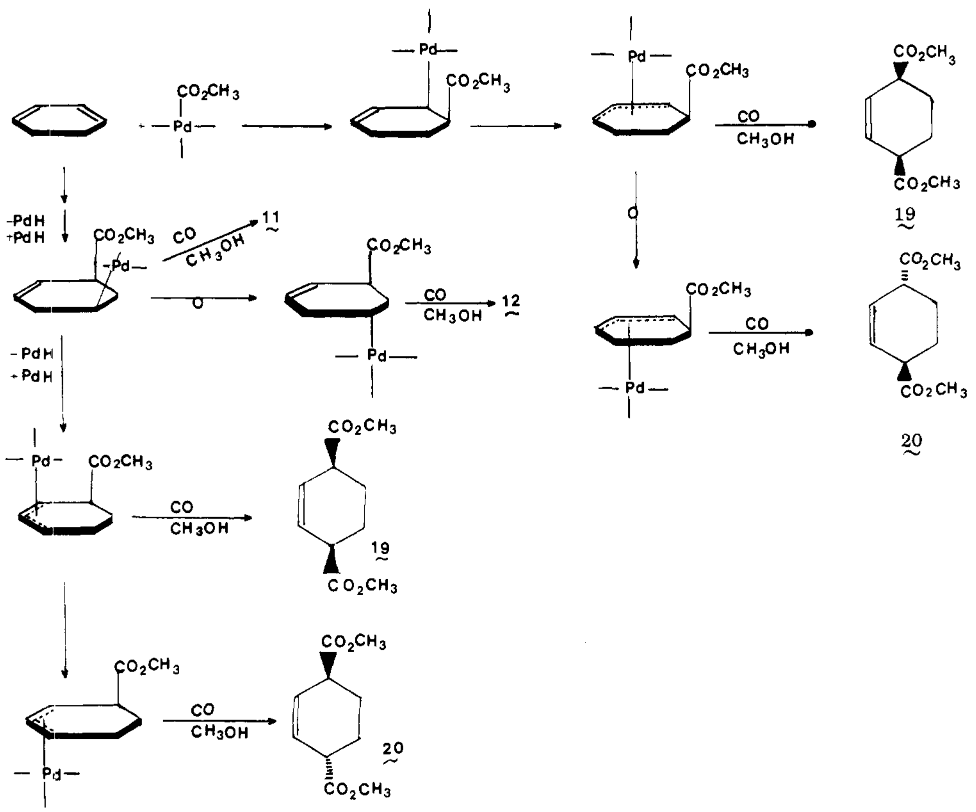
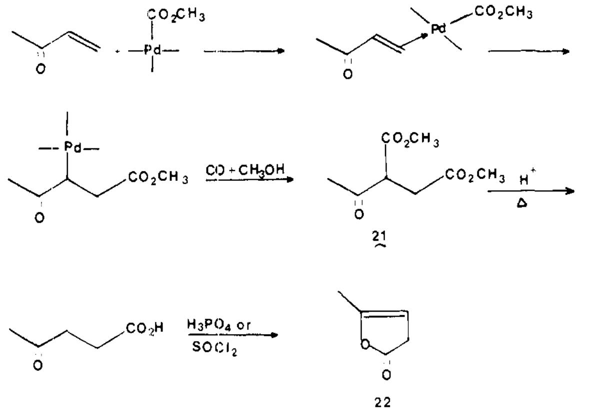
[5] J. Tsuji, Y. Mori, and M. Hara, *Tetrahedron*, **28**, 3721 (1972).

[6] R. Lukeš and J. Jarý, *Chem. Listy*, **49**, 1808 (1955).

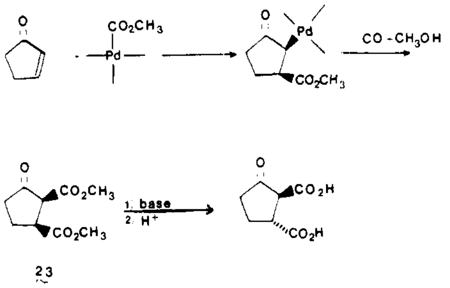
Scheme V



Scheme VI



Scheme VII



cyclization[7] of the keto acid (Scheme VI).

Cyclopent-2-en-1-one was carboxylated to dimethyl 3-oxo-cyclopentane-1,2-dicarboxylate (**23**) in 60% conversion; 28% of cyclopent-2-en-1-one could be recovered unchanged. The structure of **23** was determined by an independent synthesis from trimethylbutane-1,2,4-tricarboxylate.[8]

The absence of any products formed by a palladium hydride elimination–readdition mechanism indicated that the carbonyl function probably directs the addition of the palladium–carboxylate species regiospecifically (electronic control). The intermediate complex that results from such an addition cannot undergo β-hydride elimination (Scheme VII).

The ^{1}H NMR spectrum of **23** was inconclusive in defining the stereochemistry of the diester. Base hydrolysis resulted in the formation of a diacid which could not be cyclized in the presence of acetic anhydride. Since this is a known method for the preparation of dicarboxylic acid anhydrides[9] without decarboxylation of a β-keto acid, the geometry of the diacid and hence that of the diester is probably trans. Although the cis diester is undoubtedly formed, initially rapid isomerization could take place under the reaction conditions.

The reaction of allyl alcohol with carbon monoxide in methanol yielded methyl α-methoxybutyrate (**24**) and isopropyl alcohol in yields depending on the concentration of base. When the ratio of olefinic alcohol to base was 1:4, yields of **24** and isopropyl alcohol were 33 and 58%, respectively. No isopropyl alcohol was generated when the molar ratio of olefinic alcohol to base was 1:8, and **24** was obtained in a 93% yield. The carboxylation reaction is probably preceded by the formation of the intermediate allyl methyl ether as evidenced by the fact that careful distillation of the reaction mixture produced 7% of this ether. Palladium hydride addition followed by rearrangement and carbonylation could afford the observed ester (Scheme VIII).

Under the standard conditions, carboxylation of 3-buten-1-ol gave the three diesters **25**–**27**. The formation

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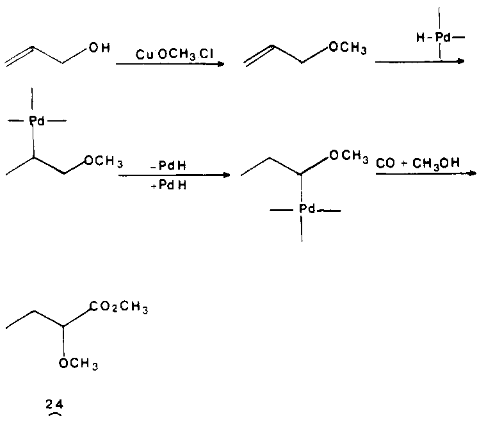
[7] J. H. Helberger, S. Ulubay, and H. Civelekoglu, *Justus Liebigs Ann. Chem.*, **561**, 215 (1949).

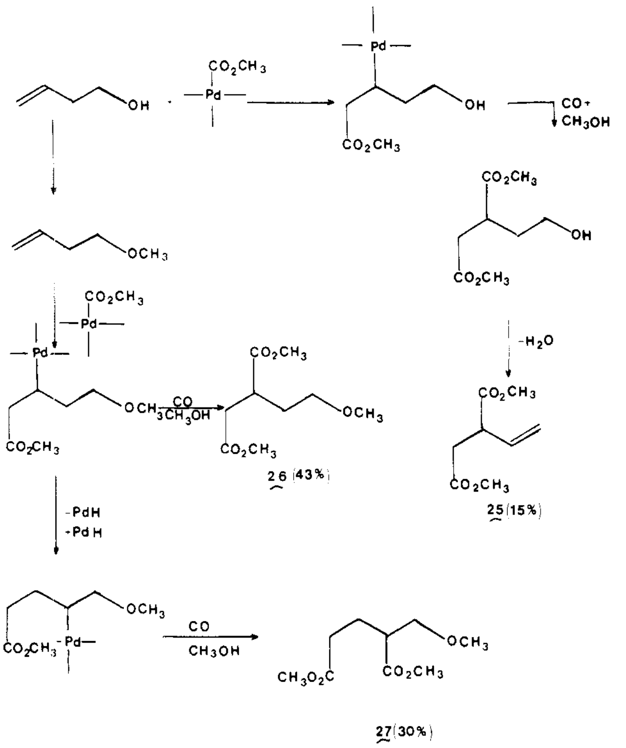
[8] P. C. Mukharji, J. C. Sircar, and V. V. Devasthale, *Indian J. Chem.*, **9**, 515 (1971).

[9] S. P. Findlay, *J. Org. Chem.*, **22**, 1385 (1957).

Scheme VIII



Scheme IX



of the three products can be explained in terms of various competing reactions taking place simultaneously through a hydride abstraction readdition mechanism[2] (Scheme IX).

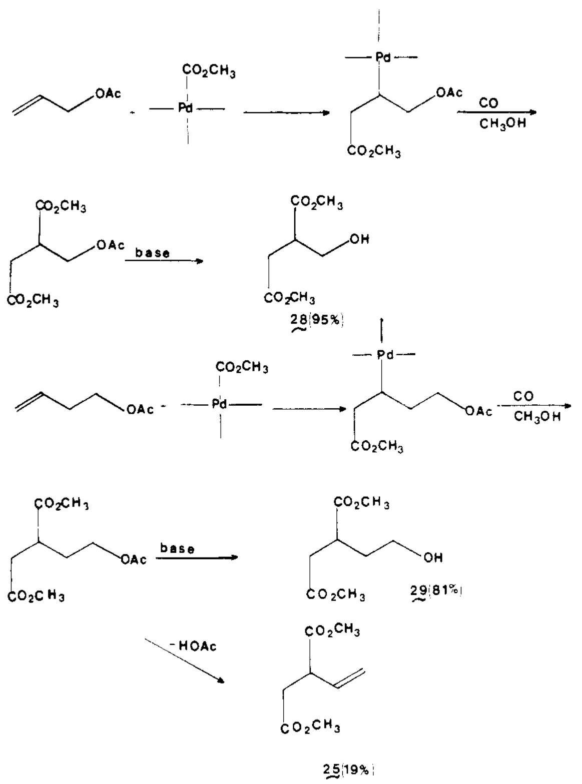
The reaction of allyl acetate with carbon monoxide under the standard conditions gave dimethyl 2-(hydroxyethyl)succinate (**28**), while the reaction of 3-buten-1-yl acetate afforded the two diesters **25** and **29** (Scheme X).

Experimental Section

Separation, quantitative analysis, and product identification were achieved on a gas chromatograph by using one or a sequential combination of the following three columns: a 10 × $^3/_8$ in. 20% FFAP/Chromosorb W (160/80 mesh) column, a 10 × $^3/_8$ in. 30% DEGS/Chromosorb W (30/60 mesh) column, and a 10 × $^3/_8$ in. Carbowax/Chromosorb W (30/60 mesh) column. The FFAP column gave the best product separation while the DEGS column was used in the separation of isomeric diesters.

Catalytic Carboxylation of Olefins. A solution of 13.44 g (100.0 mmol) or 26.88 g (200.0 mmol) of cupric chloride in 75–100 mL of methanol was treated sequentially with 11.00 g (100.0 mmol) or 22.00 g (200.0 mmol) of sodium butyrate, 25.0 mmol of olefin, 3.00 g (28.3 mmol) of trimethyl orthoformate, and 0.10–0.50 g (0.5–2.8 mmol) of palladium(II) chloride. The mixture was quickly pressurized with 1–6 atm of carbon monoxide, and the reaction was allowed to proceed until the carbon monoxide uptake had

Scheme X



ceased (144 h). Upon completion of the reaction, the reaction mixture was concentrated under reduced pressure. The residue was stirred with several portions of pentane. The pentane extracts were combined, filtered, and concentrated under reduced pressure until all of the solvent was removed.

Carboxylation of Ethylene. Formation of Dimethyl Succinate. A mixture of 13.44 g (100.0 mmol) of cupric chloride and 11.00 g (100.0 mmol) of sodium butyrate in 75 mL of methanol was treated with 0.50 g (2.8 mmol) of palladium(II) chloride and 3.00 g (28.3 mmol) of trimethyl orthoformate. The reaction vessel was subjected to 1 atm of ethylene, and the total pressure was increased to 3 atm with carbon monoxide. The reaction was allowed to proceed for 36 h, after which no further carbon monoxide uptake was observed. The usual workup procedure yielded dimethyl succinate in 92% yield, the identity of which was established by VPC analysis and comparison of its ^{1}H NMR spectrum with that of a known sample. The diester was also hydrolyzed to succinic acid. The melting point of the diacid was identical with that of an authentic sample.

Carboxylation of Propylene. Formation of Dimethyl 2-Methylsuccinate. The catalytic carboxylation of propylene was effected exactly as for ethylene. The usual workup procedure revealed the presence of one diester in 90% conversion, identified to be dimethyl 2-methylsuccinate by comparison of its ^{1}H NMR spectrum with that of a known sample and also by its hydrolysis to 2-methylsuccinic acid. The melting point of the diacid was the same as that of an authentic sample of 2-methylsuccinic acid.

Carboxylation of Vinylcyclohexane. Formation of Dimethyl α-Cyclohexylsuccinate (1) and *trans*-Methyl 3-[2-(Carbomethoxy)cyclohexyl]propanoate (2). A solution of 2.75 g (25.0 mmol) of vinylcyclohexane in 75 mL of methanol was subjected to carboxylation under the usual conditions. The reaction was allowed to proceed with stirring for 72 h. Workup of the black reaction mixture indicated the presence of two diester products. The minor component (32%) was identified as diester **1** by its hydrolysis to α-cyclohexylsuccinic acid, mp 144–146 °C (lit.[10] mp 144–145 °C): ^{1}H NMR (CDCl$_3$) δ 3.8 (s, 3 H, carboxylate methyl), 2.4–2.8 (m, 3 H, C-3 methine, C-2 methylene), 0.9–1.7 (m, 11 H, cyclohexyl); ^{13}C NMR (neat) δ 175.46, 174.23 (carbonyl), 51.13, 51.01 (carboxylate methyl), 40.31 (C-3 methine), 33.23 (C-2

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[10] J. Blanc and B. Gastambide, *Bull. Chim. Soc. Fr.*, 2055 (1962).

methylene), 30.79, 26.73, 20.62, 20.17 (cyclohexyl carbons). Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83. Found: C, 63.56; H, 8.96.

The major component (67%) was identified as the trans diester (2) by analysis and hydrolysis to *trans*-3-(2-carboxycyclohexyl)propanoic acid, mp 138–139 °C (lit.[11] mp 142–143 °C): ^1H NMR ($CDCl_3$) δ 3.9 (s, 3 H, carboxylate methyl), 2.4–2.7 (m, 3 H, C-2′ methine, C-2 methylene), 0.9–1.6 (m, 11 H, C-1′ methine, C-3, C-3′, C-4′, C-5′, C-6′ methylenes); ^{13}C NMR (neat) δ 173.25, 172.38 (carbonyl), 51.82, 51.01 (carboxylate methyl), 38.23 (C-2′ methine), 31.87 (C-2 methylene), 28.50 (C-1′ methine, C-3′, C-4′, C-5′, C-6′, C-3 methylenes); mass spectrum (relative intensity) *m/e* 228 (M^+, 12), 197 (100), 169 (33), 155 (42). Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83. Found: C, 63.22; H, 8.79.

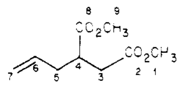
Carbonylation of 3-Phenyl-1-propene. Formation of Methyl 3-Methoxy-4-phenylbutanoate (5) and Dimethyl α-Benzylsuccinate (4). A solution of 2.95 g (25.0 mmol) of 3-phenyl-1-propene in 75 mL of methanol was subjected to carboxylation under the usual conditions. The reaction was allowed to take place for 48 h, after which no further carbon monoxide uptake was observed. The usual workup procedure yielded two ester products in 71% conversion. The minor component (30%) was identified as the β-methoxy ester 5: IR (neat) 1735 (carbonyl), 1585 (aromatic) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.2–7.4 (m, 5 H, aromatic), 3.8 (s, 3 H, carboxylate methyl), 3.45 (s, 3 H, methoxyl), 2.2–2.6 (m, 5 H, methine, methylenes); ^{13}C NMR (neat) δ 178.46 (carbonyl), 138.32, 136.01, 133.62, 129.20 (aromatic), 51.02, (carboxylate methyl), 48.64 (methoxyl), 38.61 (methine), 37.21, 32.41 (methylenes); mass spectrum (relative intensity) *m/e* 208 (M^+, 54), 177 (100), 162 (21), 77 (62), 46 (14). Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 68.98; H, 8.06.

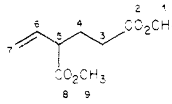
The major component (70%) was identified as the diester dimethyl α-benzylsuccinate (4) by comparison of its ^1H NMR spectrum with that of a known sample and also by its hydrolysis to α-benzylsuccinic acid, mp 160–163 °C (lit.[12] mp 160–163 °C): ^1H NMR ($CDCl_3$) δ 7.3–7.45 (m, 5 H, aromatic), 3.8 (s, 6 H, carboxylate methyl), 2.3–2.5 (m, 5 H, methine, methylenes); ^{13}C NMR δ 176.21, 175.03 (carbonyl), 137.24, 136.04, 133.18, 129.22 (aromatic), 52.21, 51.63 (carboxylate methyl), 38.68 (methine), 30.24 (methylene adjacent to carboxyl), 25.74 (methylene adjacent to aromatic ring). Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83. Found: C, 66.46; H, 6.67.

Carboxylation of 1,5-Hexadiene. Formation of Dimethyl 2-(3-Buten-1-yl)succinate (6). A solution of 2.10 g (25.6 mmol) of 1,5-hexadiene in 75 mL of methanol was catalytically carboxylated under the standard conditions at 6 atm of carbon monoxide for 72 h. No more carbon monoxide uptake was observed after this time. Product workup indicated one diester component on GC, identified as dimethyl 2-(3-buten-1-yl)succinate (6) (70% conversion): IR (neat) 1735 (carbonyl), 1640 (olefin) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.5–5.8 (m, 1 H, vinylic methine), 4.8–5.2 (m, 2 H, vinylic methylene), 3.8 (s, 6 H, methoxyl), 2.4–2.8 (m, 3 H, C-2 methylene, C-3 methine), 1.4–2.0 (m, 4 H, C-4 methine, C-5 methylene); ^{13}C NMR (neat) δ 174.95, 172.15 (carbonyl), 138.11, 115.48 (olefinic), 51.96, 51.60 (methoxyl), 40.87 (C-3 methine), 35.80 (C-2 methylene), 31.45 (allylic methylene), 27.62 (C-4 methylene). Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 59.60; H, 8.20.

Carboxylation of Dimethyl 2-(3-Butenyl)succinate (6). Formation of Dimethyl 3,6-Bis(carbomethoxy)octane-1,8-dioate (7). To a slurry of 1.00 g (5.0 mmol) of diester 6, 2.68 g (20.0 mmol) of cupric chloride, and 2.20 g (20.0 mmol) of sodium butyrate in 25 mL of methanol were added 0.10 g (0.5 mmol) of palladium(II) chloride and 1.00 g (10.0 mmol) of trimethyl orthoformate. The mixture was subjected to 1–2 atm of carbon monoxide for 90 h. At the end of this time, no further carbon monoxide uptake was observed. Workup of the reaction mixture yielded one product, in 51% conversion based on the olefinic diester. Hydrolysis of 7 gave the known 3,6-dicarboxyoctane-1,8-dioic acid, mp 170–172 °C (lit.[13] mp 170–174 °C).

Table II. ^1H and ^{13}C Chemical Shifts for 13 and 14 (ppm)





	^1H	^{13}C		^{13}C
1	3.75	51.33	3.65	51.64
2		171.86		173.34
3	2.3-3.2	32.26	2.3-3.2	31.77
4		38.59	1.8-1.9	22.62
5		30.12	4.2-4.3	62.21
6	5.3-5.9	115.67	5.3-5.9	117.98
7	4.8-5.2	105.11	4.8-5.2	106.42
8		174.29		176.26
9	3.75	50.93	3.65	50.02

Carboxylation of 1,5-Hexadiene. Formation of Dimethyl 3,6-Bis(carbomethoxy)octane-1,8-dioate (7). A solution of 2.10 g (25.6 mmol) of 1,5-hexadiene in 75 mL of methanol was treated with 1–2 atm of carbon monoxide under the standard conditions. The reaction was allowed to proceed for 144 h, after which no further carbon monoxide uptake was observed. Product workup revealed 7 in 62% conversion based on diolefin, and 38% of unreacted 1,5-hexadiene could be recovered on GC.

High-Pressure Catalytic Carboxylation of 1-Hexene. A solution of 4.22 g (50.2 mmol) of 1-hexene in 75 mL of methanol was subjected to carboxylation under standard conditions, except that the pressure of the system was maintained at 6 atm. No further carbon monoxide uptake was observed after 72 h. VPC analysis of the green reaction mixture indicated 92% unchanged 1-hexene.

Carboxylation of 4-Vinylcyclohexene. Formation of Methyl 3-(4-Cyclohexen-1-yl)-3-methoxypropanoate (8) and Dimethyl 2-(4-Cyclohexen-1-yl)succinate (9). A stirred solution of 2.45 g (22.6 mmol) of 4-vinylcyclohexene in 75 mL of methanol was carboxylated under the standard conditions at 3 atm of carbon monoxide for 72 h. At the end of this time, the black reaction mixture was worked up as usual. VPC analysis revealed two ester products, and no unreacted starting material was observed.

The minor component (15%) was identified as the β-methoxy ester 8: IR (neat) 1740 (carbonyl), 1655 (olefinic), 795 (cis olefin) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.85 (s, 3 H, carboxylate methyl), 3.4–3.5 (m, 1 H, methine adjacent to methoxyl), 3.3 (s, 3 H, methoxyl), 1.9–2.45 (m, 6 H, methylenes adjacent to olefin and carbonyl), 1.2–1.4 (m, 3 H, methine, methylene); ^{13}C NMR (neat) δ 174.82 (carbonyl), 126.99, 125.82 (olefinic), 52.78 (carboxylate methyl), 50.08 (methine adjacent to methoxyl), 48.12 (methoxyl), 36.08, 33.80, 30.82 (methylenes adjacent to olefin and carbonyl), 26.30, 24.91 (methine, methylene); mass spectrum (relative intensity) *m/e* 198 (M^+, 9), 167 (100), 144 (92), 125 (32), 54 (12). Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.42; H, 9.56.

The major component (85%) was identified as the diester 9: ^1H NMR ($CDCl_3$) 5.7–5.8 (br, 2 H, vinylic), 3.8 (s, 6 H, carboxylate methyl), 2.2–2.8 (m, 7 H, methine, methylenes adjacent to olefin and carbonyl), 1.6–2.0 (methine, methylene); ^{13}C NMR (neat) δ 174.01, 172.84 (carbonyl), 126.87, 125.72 (olefinic), 51.66, 50.03 (carboxylate methyl), 42.17 (methine adjacent to carbonyl), 35.30, 32.83 (methylenes adjacent to olefin), 26.30 (methine), 24.91 (methylene). Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.29; H, 7.91.

Carboxylation of 1,4-Pentadiene. Formation of Dimethyl Allylsuccinate (13) and Dimethyl 2-Vinylglutarate (14). A solution of 13.44 g (100.0 mmol) of cupric chloride in 75 mL of methanol was treated with 11.00 g (100.0 mmol) of sodium butyrate, 3.00 g (28.3 mmol) of trimethyl orthoformate, and 0.50 g (2.8 mmol) of palladium(II) chloride. The mixture was cooled well in an ice bath, and 1.70 g (25.0 mmol) of 1,4-pentadiene was added. The reaction vessel was subjected to 3 atm of carbon monoxide for 72 h at the end of which time the carbon monoxide uptake ceased and the reaction mixture was green. The usual workup yielded 4.02 g of a mixture of products. VPC analysis indicated that no unreacted 1,4-pentadiene was present. The mixture of diesters eluted on the FFAP column was identified

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as a mixture of the two diesters **13** (78%) and **14** (22%) on the basis that the mixture could not be separated by GC, TLC, or column chromatography. The ^{1}H and ^{13}C NMR assignments for the two compounds are given in Table II.[14]

Irradiation of the δ 5.3–5.5 region caused the complex signal in the δ 4.2–4.3 region to collapse to a triplet (J = −7 Hz). Irradiation of the peaks at δ 1.8–1.9 caused the signal in the δ 4.2–4.3 region to collapse to a doublet (J = −10 Hz). The ratio of the two esters was based on the integration ratios of the methoxyl peaks.

Carboxylation of 1,4-Cyclohexadiene. Formation of *cis*- and *trans*-Dimethyl Cyclohex-4-ene-1,3-dicarboxylate (11 and 12). The catalytic carboxylation of 2.01 g (25.1 mmol) of 1,4-cyclohexadiene was effected under the usual conditions at 3 atm of carbon monoxide. After 72 h no more carbon monoxide uptake was observed. Workup of the green reaction mixture and VPC analysis indicated the presence of two diester products.

The major component (89%) was identified to be the cis diester **11**: ^{1}H NMR ($CDCl_3$) δ 5.6–5.7 (m, 2 H, olefinic), 3.9 (s, 6 H, carboxylate methyl), 3.4–3.5 (m, 1 H, C-3 methine), 2.0–2.4 (m, 3 H, C-1 methine, C-6 methylene), 1.4–1.6 (m, 2 H, C-2 methylene); ^{13}C NMR (neat) δ 180.31, 175.21 (carbonyl), 127.90, 126.96 (olefinic), 51.42, 50.92 (carboxylate methyl), 46.71 (C-3 methine), 32.12 (C-1 methine), 29.32 (C-6 methylene), 21.67 (C-2 methylene); mass spectrum (relative intensity) m/e 198 (M^+, 7), 167 (32), 152 (100), 139 (21), 46 (19), 28 (11). Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.02; H, 7.12.

Diester **11** was also hydrolyzed to the *cis*-cyclohex-4-ene-1,3-dicarboxylic acid, mp 128–129 °C (lit.[15] mp 161 °C). It was further hydrogenated to *cis*-dimethyl cyclohexane-1,3-dicarboxylate followed by its hydrolysis to the known *cis*-cyclohexane-1,3-dicarboxylic acid, mp 161 °C (lit. mp 167 °C,[16a] 161 °C[16b]).

The minor component (11%) was identified as trans diester **12**: ^{1}H NMR ($CDCl_3$) δ 5.5–5.65 (m, 2 H, olefinic), 3.85 (s, 6 H, carboxylate methyl), 3.4–3.45 (m, 1 H, C-3 methine), 2.1–2.35 (m, 3 H, C-1 methine, C-6 methylene), 1.3–1.5 (m, 2 H, C-2 methylene); ^{13}C NMR (neat) δ 176.29, 173.21 (carbonyl), 129.98, 127.32 (olefinic), 51.68, 51.42 (carboxylate methyl), 46.29 (C-3 methine), 29.32 (C-1 methine), 25.21 (C-6 methylene), 20.20 (C-2 methylene), mass spectrum (relative intensity) m/e 198 (M^+, 7), 167 (44), 139 (100), 59 (54). Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.54; H, 7.56.

Diester **12** was also hydrolyzed to *trans*-cyclohex-4-ene-1,3-dicarboxylic acid, mp 248–249 °C (lit.[15] mp 225–227 °C). It was further hydrogenated to *trans*-dimethyl cyclohexane-1,3-dicarboxylate, followed by its hydrolysis to *trans*-cyclohexane-1,3-dicarboxylic acid, mp 148 °C (lit.[17] mp 149–150.5 °C).

Carboxylation of 1,3-Butadiene. Formation of *cis*- and *trans*-Dimethyl Hex-3-ene-1,6-dioate (17). A green slurry of 13.44 g (100.0 mmol) or 26.88 g (200.0 mmol) of cupric chloride and 11.00 g (100.0 mmol) or 22.00 g (200.0 mmol) of sodium butyrate in 75 mL of methanol was treated with 3.00 g (28.3 mmol) of trimethyl orthoformate and 0.50 g (2.8 mmol) of palladium(II) chloride. The mixture was cooled in a dry ice–2-propanol slush for 0.5 h. The pressure bottle was weighed and then evacuated. In a separate apparatus 1,3-butadiene was condensed in a Schlenk tube cooled in a dry ice–2-propanol bath. The Schlenk tube was then connected to the pressure bottle (which was under reduced pressure) and allowed to warm to room temperature. The butadiene was condensed into the pressure bottle until approximately 1.35 g (25.0 mmol) of butadiene had condensed into the reaction vessel. The pressure was brought to 1 atm by introducing nitrogen, and the bottle was then weighed again to determine the exact amount of butadiene that had condensed. The reaction vessel was then pressurized with 3 atm of carbon monoxide and kept at the appropriate temperature (either at room temperature or in an oil bath heated at 70 °C). The reaction was allowed to proceed until the carbon monoxide uptake had ceased (144 h). The product was worked up as for the formation of unsaturated dicarboxylates from diolefins. The separation of the two reaction products was effected on the DEGS column in conjunction with the FFAP column. The major component (62%) was identified as the trans diester **17b** by VPC and comparison of the ^{1}H NMR spectrum of the product with that of an authentic sample prepared by the methylation of *trans*-hex-3-ene-1,6-dioic acid and also by its hydrolysis to the above acid, mp 197–198 °C. The melting point of a mixture of this product and an authentic sample was not depressed. The identity of **17b** was further established by its hydrogenation to dimethyl adipate, followed by its hydrolysis to adipic acid, as proven by comparison with an authentic sample: ^{1}H NMR of **17b** ($CDCl_3$) δ 5.4–5.7 (m, 1 H, olefinic), 3.65 (s, 3 H, carboxylate methyl), 2.6–3.0 (m, 2 H, methylene); ^{13}C NMR (neat) δ 178.84 (carbonyl), 120.17 (olefinic), 51.92 (carboxylate methylene), 46.81 (methylene). Anal. Calcd for $C_8H_{12}O_4$: C, 55.84; H, 6.97. Found: C, 55.99; H, 7.42.

The minor component (38%) was identified to be the cis diester **17a** by hydrolysis to *cis*-hex-3-ene-1,6-dioic acid, mp 124 °C (lit.[18] mp 122–123 °C): ^{1}H NMR ($CDCl_3$) δ 6.0–6.3 (m, 1 H, olefinic), 3.9 (s, 3 H, carboxylate methyl), 2.4–2.6 (m, 2 H, methylene); ^{13}C NMR (neat) δ 175.54 (carbonyl), 114.65 (olefin), 58.23 (carboxylate methyl), 36.73 (methylene); mass spectrum (relative intensity) m/e 172 (M^+, 6), 141 (44), 126 (100), 113 (22), 46 (17). Anal. Calcd for $C_8H_{12}O_4$: C, 55.80; H, 7.03. Found: C, 56.23; H, 7.51.

Isomerization of 17a or 17b. Formation of an Equilibrium Mixture of 17a and 17b. A solution of 0.95 g (5.5 mmol) of either **17a** or **17b** in 35 mL of methanol was treated with 6.72 g (50.0 mmol) of cupric chloride, 5.20 g (47.2 mmol) of sodium butyrate, 1.50 g (14.1 mmol) of trimethyl orthoformate, and 0.25 g (1.4 mmol) of palladium(II) chloride. The mixture was pressurized with carbon monoxide and either maintained room temperature or heated to 70 °C in an oil bath. Analysis indicated 38% of **17a** and 62% of **17b** on the basis of VPC peak ratios.

Carboxylation of 1,3-Butadiene. Formation of *trans*-Dibenzyl Hex-3-ene-1,6-dioate. To a suspension of 20.22 g (150.4 mmol) of copper(II) chloride and 16.50 g (150.0 mmol) of sodium butyrate in 75 mL of freshly distilled benzyl alcohol were added 3.00 g (28.3 mmol) of trimethyl orthoformate and 0.20 g (1.1 mmol) of palladium(II) chloride. As before, 1.01 g (19.0 mmol) of butadiene was transferred into the pressure bottle. The mixture was pressurized with 3 atm of carbon monoxide and heated to 70 °C in an oil bath for 144 h. The black reaction mixture was worked up as usual. Analysis of the product on the DEGS column indicated the presence of one diester component identified to be the trans diester by comparison of the ^{1}H NMR spectrum with that of an authentic sample prepared by the esterification of the diacid: ^{1}H NMR ($CDCl_3$) δ 7.2–7.4 (m, 5 H, aromatic), 6.4–6.8 (m, 1 H, olefinic), 3.9 (s, 2 H, methylene adjacent to oxygen), 2.0 (m, 1 H, methylene); ^{13}C NMR (neat) δ 171.61 (carbonyl), 138.89, 126.60, 125.27, 124.96, 124.08 (aromatic and olefinic), 53.54 (methylene adjacent to oxygen), 38.84 (methylene). Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.09; H, 6.17. Found: C, 73.76; H, 7.06.

The identity of the diester was further established by its hydrolysis to *trans*-hex-3-ene-1,6-dioic acid and hydrogenation to adipic acid. The melting points of the two diacids were identical with those of authentic samples.

Carboxylation of 1,3-Cyclohexadiene. Formation of *cis*- and *trans*-Dimethyl Cyclohex-2-ene-1,4-dicarboxylate (19 and 20). A solution of 2.00 g (25.0 mmol) of 1,3-cyclohexadiene in 75 mL of methanol was subjected to carboxylation under the usual conditions at 3 atm of carbon monoxide. The reaction was allowed to proceed for 72 h, after which time no further carbon monoxide uptake was observed. Workup and VPC analysis revealed the presence of four products. The relative peak areas in order of increasing retention times on the DEGS column were 46, 11, 28, and 14%.

The 46% component was identified as *cis*-dimethyl cyclohex-2-ene-1,4-dicarboxylate (**19**): ^{1}H NMR ($CDCl_3$) δ 5.7–5.8 (m, 1 H, olefinic), 3.8 (s, 3 H, carboxylate methyl), 3.4–3.55 (m, 1 H, C-1, C-4 methines), 1.6–1.8 (m, 2 H, C-6 methylene); ^{13}C NMR (neat) δ 173.51 (carbonyl), 130.63 (olefinic), 51.81 (carboxylate methyl), 48.10 (C-1, C-4 methines), 24.62 (C-5, C-6 methylenes);

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mass spectrum (relative intensity) *m/e* 198 (M^+, 14), 170 (9), 167 (100), 139 (68), 28 (44). Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.63; H, 7.06. Found: C, 60.52; H, 7.68.

Hydrolysis of the diester resulted in formation of *cis*-cyclohex-2-ene-1,4-dicarboxylic acid, mp 161 °C (lit.[19] mp 161 °C). The diester was also hydrogenated to *cis*-dimethyl cyclohexane-1,4-dicarboxylate, followed by its hydrolysis to *cis*-cyclohexane-1,4-dicarboxylic acid, mp 173–174 °C (lit.[20] mp 169–170 °C).

The 11% component was determined to be *trans*-dimethyl cyclohex-2-ene-1,4-dicarboxylate (**20**): ^1H NMR ($CDCl_3$) δ 5.5–5.7 (m, 1 H, olefinic), 3.85 (s, 3 H, carboxylate methyl), 3.45–3.55 (m, 1 H, C-1, C-4 methines), 1.45–1.6 (m, 2 H, C-5, C-6 methylenes); mass spectrum (relative intensity) *m/e* 198 (M^+), 167 (100), 139 (74). Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.63; H, 7.06. Found: C, 60.46; H, 7.28.

The product was also hydrolyzed to *trans*-cyclohex-2-ene-1,4-dicarboxylic acid, mp 225 °C (lit.[21] mp 228 °C). The identity was further proved by its hydrogenation to dimethyl *trans*-cyclohexane-1,4-dicarboxylate, followed by its hydrolysis to *trans*-cyclohexane-1,4-dicarboxylic acid (from methanol), mp 285 °C dec (lit.[22] mp 309 °C (from water)).

The other two products (28% and 14%) were identical with **11** and **12** obtained from the carboxylation of 1,4-cyclohexadiene.

Carboxylation of But-3-en-2-one (Methyl Vinyl Ketone). Formation of Dimethyl α-Acetylsuccinate (21). To 75 mL of methanol was added 1.75 g (25.0 mmol) of methyl vinyl ketone, and the solution was treated with 20.16 g (150.0 mmol) of cupric chloride and 22.00 g (200.0 mmol) of sodium butyrate. The above mixture was subjected to carboxylation under the usual conditions at 3 atm for 72 h, after which time no further carbon monoxide uptake was observed. The green reaction mixture was worked up to yield dimethyl 2-acetylsuccinate in 29% conversion: IR 1735 (ester carbonyl), 1680 (ketone carbonyl) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.9 (s, 6 H, carboxylate methyl), 3.6 (t, 1 H, $J = -7$ Hz, methine), 2.4 (d, 2 H, $J = -7$ Hz, methylene), 2.3 (s, 3 H, methyl); ^{13}C NMR (neat) δ 208.41 (ketone carbonyl), 173.54, 172.62 (ester carbonyl), 51.62, 50.23 (carboxylate methyl), 44.62 (methine), 36.21 (methylene), 31.02 (methyl). Anal. Calcd for $C_8H_{12}O_5$: C, 51.06; H, 6.43. Found: C, 51.42; H, 6.70.

The product diester was hydrolyzed, followed by decarboxylation to β-acetylpropionic acid, mp 37–38 °C (lit.[23] mp 38 °C), which was further converted to the butenolide 4-hydroxy-3-pentenoic acid γ-lactone[6] **22** by refluxing with either thionyl chloride or phosphoric acid.[7]

Carboxylation of Cyclopent-2-en-1-one. Formation of *trans*-Dimethyl 3-Oxocyclopentane-1,2-dicarboxylate (23). A solution of 2.05 g (25.0 mmol) of cyclopent-2-en-1-one in 75 mL of methanol was subjected to carboxylation at 3 atm of carbon monoxide under the usual conditions for 90 h. At the end of this time, workup of the green reaction mixture indicated the formation of the diester **23** in 59% conversion. The structure of **23** was verified by an independent synthesis from dimethyl succinate and β-chloropropionate:[8] IR 1735 (ester carbonyl), 1640 (ketonic carbonyl) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.7–3.8 (m, 1 H, C-2 methylene), 3.6 (s, 6 H, carboxylate methyl), 2.2–2.8 (m, 3 H, C-4 methylene, C-1 methine), 1.6–2.0 (m, 2 H, C-5 methylene); ^{13}C NMR (neat) δ 208.19 (ketone carbonyl), 173.83, 171.42 (ester carbonyl), 54.85 (C-2 methine), 51.40, 51.12 (carboxylate methyl), 30.35, 26.91 (C-4 methylene, C-1 methine), 19.81 (C-5 methylene). Anal. Calcd for $C_9H_{12}O_5$: C, 53.99; H, 6.04. Found: C, 54.30; H, 6.41.

The structure of **23** was also verified by its hydrolysis followed by decarboxylation to 3-oxocyclopentanecarboxylic acid, mp 66 °C (lit.[24] mp 65–66 °C), followed by its conversion to the 2,4-dinitrophenylhydrazone, mp 158 °C (lit.[25] mp 149–50 °C).

The base hydrolysis of **23** resulted in the formation of a diacid, which is probably a trans isomer of 3-oxocyclopentane-1,2-dicarboxylic acid, mp 242–243 °C: ^1H NMR ($CDCl_3$) δ 11.00–11.30 (br, 2 H, disappears after D_2O exchange), 3.65–3.8 (m, 1 H, C-2 methine), 2.2–2.8 (m, 3 H, C-4 methylene, C-1 methine), 1.6–2.0 (m, 2 H, C-5 methylene). An attempt to form the anhydride was carried out as follows: A suspension of 0.65 g (4.1 mmol) of 3-oxocyclopentane-1,2-dicarboxylic acid in 7 mL of acetic anhydride was heated at reflux for 7 h. At the end of this time, the acetic anhydride was cautiously distilled from the reaction mixture (42 °C (10 mm)). The resulting oil was then subjected to VPC and ^1H NMR analysis, which indicated no anhydride formation.

Isomerization of 23 under the Reaction Conditions. A solution of 2.00 g (10.0 mmol) of **23** in 75 mL of methanol was treated with 6.72 g (50.0 mmol) of cupric chloride, 5.50 (50.0 mmol) of sodium butyrate, 1.50 g (14.1 mmol) of trimethyl orthoformate, and 0.25 g (1.4 mmol) of palladium(II) chloride. The reaction mixture was subjected to 3 atm of carbon monoxide for 72 h.

The product was worked up as in the carboxylation reaction of cyclopent-2-en-1-one. VPC and ^1H and ^{13}C NMR analysis indicated 99% of unchanged **23**.

Carboxylation of Prop-2-en-1-ol. Formation of Methyl 2-Methoxybutanoate (24). A mixture of 1.45 g (25.0 mmol) of freshly distilled prop-2-en-1-ol, 13.44 g (100.0 mmol) of cupric chloride, and 22.00 g (200.0 mmol) of sodium butyrate in 75 mL of methanol was subjected to 3 atm of carbon monoxide under the regular carboxylation conditions. No further carbon monoxide uptake was observed after 24 h.

The usual workup procedure yielded **24** in 90% yield. The identity of **24** was established by comparison of its ^1H NMR spectrum with that of an authentic sample: ^1H NMR ($CDCl_3$) δ 4.9 (t, 1 H, $J = -6$ Hz, C-2 methine), 3.65 (s, 3 H, carboxylate methyl), 3.2 (s, 3 H, methoxyl), 1.3–1.8 (m, 2 H, C-3 methylene), 0.9 (t, 3 H, $J = -5$ Hz, C-4 methyl); ^{13}C NMR (neat) δ 173.14 (carbonyl), 69.02 (C-2 methine), 51.04 (carboxylate methyl), 49.80 (methoxyl), 22.63 (C-3 methylene), 19.43 (C-4 methyl). Anal. Calcd for $C_6H_{12}O_3$: C, 54.56; H, 9.09. Found: C, 54.24; H, 9.28.

Further analysis by VPC indicated the presence of allyl methyl ether in 7% yield.

Carboxylation of Prop-2-en-1-yl Acetate. Formation of Dimethyl 2-(Hydroxymethyl)succinate (28). A solution of 2.50 g (25.0 mmol) of prop-2-en-1-yl acetate in 70 mL of methanol was subjected to carboxylation under the usual conditions for 72 h. The black reaction mixture was worked up as usual. VPC analysis indicated the presence of one diester product **28** in 95% yield: IR (neat) 3450–3550 (hydroxyl), 1730 (carbonyl) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.8 (s, 6 H, carboxylate methyl), 3.6 (d, $J = -8$ Hz, 2 H, hydroxymethyl), 3.0 (s, 1 H, disappears after D_2O exchange), 2.4–2.9 (m, 3 H, C-2 methylene, C-3 methine); ^{13}C NMR (neat) δ 176.63, 173.86 (carbonyl), 52.75, 51.59 (carboxylate methyl), 49.92 (hydroxymethyl), 36.74 (C-3 methine), 29.62 (C-2 methylene); mass spectrum (relative intensity) *m/e* 176 (M^+, 2), 175 (M^+, 100), 158 (55), 145 (82), 144 (77), 130 (18), 117 (12). Anal. Calcd for $C_7H_{12}O_5$: C, 47.72; H, 6.87. Found: C, 47.97; H, 7.28.

Carboxylation of But-3-en-1-ol. Formation of Dimethyl 2-Vinylsuccinate (25), Methyl 3-(Carbomethoxy)-5-methoxypentanoate (26), and Methyl 4-(Carbomethoxy)-5-methoxypentanoate (27). A bright green slurry of 1.75 g (24.2 mmol) of but-3-en-1-ol in 75 mL of methanol under the usual conditions was subjected to carboxylation at 3 atm of carbon monoxide for 100 h. The green reaction mixture was worked up as usual. VPC analysis indicated the presence of three product diesters.

The minor component (15%) was identified as the diester **25**: IR (neat) 1730 (carbonyl), 1610 (olefinic) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.7–5.9 (m, 1 H, vinylic methine), 5.5–5.6 (m, 2 H, vinylic methylene), 3.8 (s, 6 H, carboxylate methyl), 3.4 (m, 1 H, methine), 2.4 (br, 2 H, methylene); ^{13}C NMR (neat) δ 175.10, 172.38 (carbonyl), 120.11, 114.20 (olefinic), 50.41, 50.12 (carboxylate methyl), 40.39 (methine), 31.96 (methylene); mass spectrum (relative intensity) *m/e* 172 (M^+, 8), 144 (24), 141 (100), 126 (52), 46 (6). Anal. Calcd for $C_8H_{12}O_4$: C, 55.80; H, 7.02. Found: C, 56.17; H, 7.18.

The second product was identified as the diester **26** (43%): ^1H NMR ($CDCl_3$) δ 3.85 (s, 6 H, carboxylate methyl), 3.4–3.5 (br, 2 H, C-5 methylene), 3.35 (s, 3 H, methoxyl), 2.4–2.8 (m, 3 H, C-3

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methine, C-2 methylene), 1.4–1.7 (m, 2 H, C-4 methylene); ^{13}C NMR (neat) δ 171.79, 171.30 (carbonyl), 52.84, 52.43 (carboxylate methyl), 51.29 (C-5 methylene), 50.12 (methoxyl), 39.70 (C-3 methine), 34.59 (C-2 methylene), 25.69 (C-4 methylene); mass spectrum *m/e* 204 (M^+, 4), 173 (92), 158 (74), 145 (100). Anal. Calcd for $C_9H_{16}O_5$: C, 52.93; H, 7.90. Found: C, 53.12; H, 7.82.

The third product was identified as the diester **27** (30%): ^1H NMR ($CDCl_3$) δ 3.9 (s, 6 H, carboxylate methyl), 3.45 (d, J = 7 Hz, C-5 methylene), 3.3 (s, 3 H, methoxyl), 2.4–2.75 (m, 5 H, C-2 methylene, C-4 methine), 1.4–1.7 (m, 2 H, C-3 methylene); ^{13}C NMR (neat) δ 175.10, 172.38 (carbonyl), 52.91, 52.64 (carboxylate methyl), 51.28 (C-5 methylene), 50.59 (methoxyl), 34.92 (C-4 methine), 30.96 (C-2 methylene), 23.33 (C-3 methylene); mass spectrum (relative intensity) *m/e* 204 (M^+, 11), 173 (67), 159 (100), 158 (88), 131 (28). Anal. Calcd for $C_9H_{16}O_5$: C, 52.93; H, 7.90. Found: C, 53.28; H, 7.64.

About 10% of unreacted 3-butenol could be recovered by GC.

Carboxylation of But-3-en-1-yl Acetate. Formation of 25 and Methyl 3-(Carbomethoxy)-5-hydroxypentanoate (29). A solution of 2.85 g (25.0 mmol) of 3-buten-1-yl acetate in 75 mL of methanol was subjected to carboxylation under the standard conditions. The product workup was effected after 60 h when no further carbon monoxide uptake was observed. VPC analysis indicated the presence of two products. The minor component (19%) was identified as **25** by VPC and ^1H NMR analysis.

The second product (81%) was identified as the diester **29**: IR (neat) 3400–3500 (br, hydroxyl), 1735 (carbonyl) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.2 (br, 1 H, disappears after D_2O exchange), 3.85 (s, 6 H, carboxylate methyl), 3.4–3.5 (br, 2 H, C-5 methylene), 2.4–2.8 (m, 3 H, C-3 methine, C-2 methylene), 1.9 (m, 2 H, C-4 methylene); ^{13}C NMR (neat) δ 174.10, 172.31 (carbonyl), 52.40, 52.11 (carboxylate methyl), 50.92 (C-5 methylene), 34.92 (C-3 methine), 30.93 (C-2 methylene), 24.48 (C-4 methylene); mass spectrum (relative intensity) *m/e* 189 (M^+ – H, 100), 172 (66), 159 (91), 146 (34), 145. Anal. Calcd for $C_8H_{14}O_5$: C, 50.52; H, 7.42. Found: C, 50.24; H, 7.82.

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Registry No. **1**, 40745-20-8; **2**, 71195-17-0; **4**, 35262-43-2; **5**, 71195-18-1; **6**, 71195-19-2; **7**, 71195-20-5; **8**, 71195-21-6; **9**, 71195-22-7; **11**, 71195-23-8; **12**, 71195-24-9; **13**, 1069-40-5; **14**, 71195-25-0; **15**, 71195-26-1; (*E*)-**16**, 13168-99-5; (*Z*)-**16**, 25665-54-7; **17a**, 70354-00-6; **17b**, 25126-93-6; **19**, 71195-27-2; **20**, 71195-28-3; **21**, 10420-33-4; **22**, 591-12-8; **23**, 69285-43-4; **24**, 18797-18-7; **25**, 50782-87-1; **26**, 71195-29-4; **27**, 16096-26-7; **28**, 50782-89-3; **29**, 71195-30-7; $PdCl_2$, 7647-10-1; ethylene, 74-85-1; dimethyl succinate, 106-65-0; succinic acid, 110-15-6; propylene, 115-07-1; dimethyl 2-methylsuccinate, 1604-11-1; 2-methylsuccinic acid, 498-21-5; vinylcyclohexane, 695-12-5; α-cyclohexylsuccinic acid, 1489-63-0; *trans*-3-(2-carboxycyclohexyl)propanoic acid, 71195-31-8; 3-phenyl-1-propene, 300-57-2; α-benzylsuccinic acid, 884-33-3; 1,5-hexadiene, 592-42-7; 3,6-dicarboxyoctane-1,8-dioic acid, 4388-94-7; 1-hexene, 592-41-6; 4-vinylcyclohexene, 100-40-3; 1,4-pentadiene, 591-93-5; 1,4-cyclohexadiene, 628-41-1; *cis*-cyclohex-4-ene-1,3-dicarboxylic acid, 71195-32-9; dimethyl *cis*-cyclohexane-1,3-dicarboxylate, 6998-82-9; *cis*-cyclohexane-1,3-dicarboxylic acid, 2305-31-9; *trans*-cyclohex-4-ene-1,3-dicarboxylic acid, 71195-33-0; dimethyl *trans*-cyclohexane-1,3-dicarboxylate, 10021-92-8; *trans*-cyclohexane-1,3-dicarboxylic acid, 2305-30-8; *trans*-hex-3-ene-1,6-dioic acid, 29311-53-3; dimethyl adipate, 627-93-0; adipic acid, 124-04-9; *cis*-hex-3-ene-1,6-dioic acid, 26472-26-4; dibenzyl *trans*-hex-3-ene-1,6-dioate, 71195-34-1; 1,3-butadiene, 106-99-0; 1,3-cyclohexadiene, 592-57-4; *cis*-cyclohex-2-ene-1,4-dicarboxylic acid, 3919-11-7; dimethyl *cis*-cyclohexane-1,4-dicarboxylate, 3399-21-1; *cis*-cyclohexane-1,4-dicarboxylic acid, 619-81-8; *trans*-cyclohex-2-ene-1,4-dicarboxylic acid, 3919-12-8; dimethyl *trans*-cyclohexane-1,4-dicarboxylate, 3399-22-2; *trans*-cyclohexane-1,4-dicarboxylic acid, 619-82-9; but-3-en-2-one, 78-94-4; β-acetylpropionic acid, 123-76-2; cyclopent-2-en-1-one, 930-30-3; methyl β-chloropropionate, 6001-87-2; 3-oxocyclopentanecarboxylic acid, 98-78-2; 3-oxocyclopentanecarboxylic acid DNP, 71195-35-2; *trans*-3-oxocyclopentane-1,2-dicarboxylic acid, 71195-36-3; prop-2-en-1-ol, 107-18-6; allyl methyl ether, 627-40-7; prop-2-en-1-yl acetate, 591-87-7; but-3-en-1-ol, 627-27-0; but-3-en-1-yl acetate, 1576-84-7.

Metalation of Polymethylnaphthalenes

Ezra Dunkelblum and Harold Hart*

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

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The reaction of several polymethylnaphthalenes with excess *n*-BuLi–TMEDA in THF–hexane resulted mainly in monometalation of a methyl substituent. In contrast with what might be expected from simple molecular orbital calculations, metalation of a C_2 methyl group was preferred over that of a C_1 methyl group.

Polyamine-chelated alkali-metal compounds such as *n*-butyllithium–*N*,*N*,*N'*,*N'*-tetramethylethylenediamine (BuLi–TMEDA)[1,2] are useful metalating agents for aromatic hydrocarbons.[3] Mono- or polymetalation is possible, depending on the particular substrate and reaction conditions, and metalation may occur on the ring or in benzylic positions. For example, toluene can be polylithiated to give mainly the α,α,*p*, α,*p*, and α,*o* derivatives,[4] and mesitylene can be converted mainly to 1,3,5-tris(lithiomethylene)benzene.[5a] The metalation of other tri- and tetramethylbenzenes has been described.[5b] Metalated hydrocarbons prepared in this way can be useful synthetic intermediates through reaction with carbon dioxide, alkyl halides, and a variety of other electrophiles.

The metalation of methylnaphthalenes has been examined briefly. 1,8-Dimethylnaphthalene gave only the α-lithio derivative, even when it was treated for prolonged periods with a large excess of BuLi,[6] whereas with *n*-amylsodium–TMEDA the α,α'-disodio derivative was produced quantitatively.[7] Other isomers, such as 1,2-, 1,3- and 1,6-dimethylnaphthalene (and *o*- and *m*-xylene), also formed α,α'-disodio derivatives, but 1,4-dimethylnaphthalene (and *p*-xylene) was only monometalated. A reasonable explanation for the relative reactivities of the

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