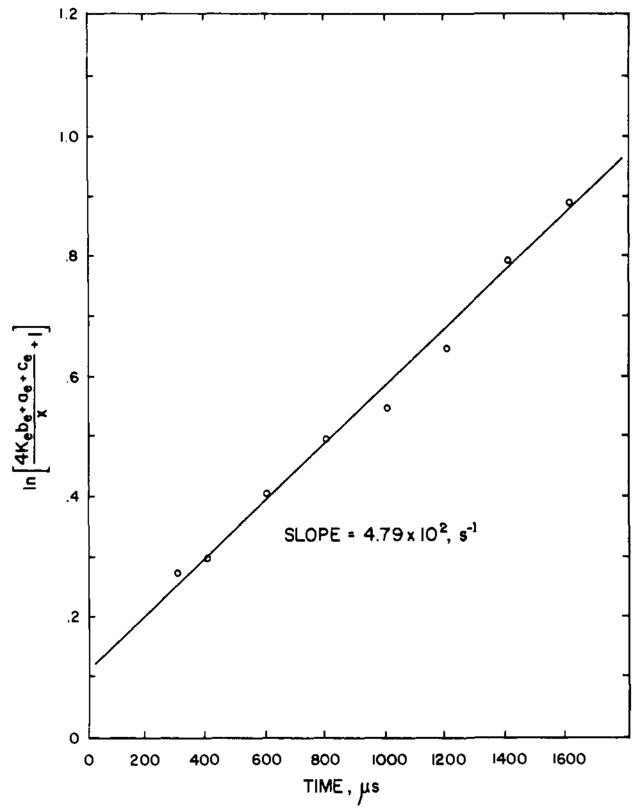

Figure 4. Kinetic of the disproportionation reaction: λ 409 nm, 1-cm cell.

found to be 479 s^{-1}. In the same way the slope was found to be 2680 s^{-1} for expt 2. Using the slopes and the equilibrium constant the forward and backward rate constants were calculated. The summary of this calculation is found in Table II.

It is worthwhile to mention, before we conclude, that, according to our assumptions, the equilibrium between the radical cation and the dimeric radical cation is also disturbed owing to the disappearance of the dimer. However, if we assume that the rate constant of dimerization is similar to the one obtained by Führhop,[14] i.e., $k_d = 1.0 \times 10^8\ M^{-1}\ s^{-1}$, then the return to the equilibrium will be in the range of 4 μs and the complication resulting from the two simultaneous reactions is avoided.

Acknowledgment. We gratefully acknowledge the support of the North Atlantic Treaty Organization the Scientific Affairs Division, Grant No. 1777, and the continued support of the National Science Foundation. Also, one of the authors (G.L.) thanks Professor Moshe Levy for valuable discussions during his sabbatic leave at the Weizmann Institute.

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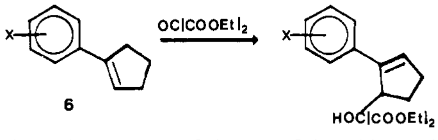
Synthesis of Allylcarboxylic Acids from Olefins with Diethyl Oxomalonate, an Enophilic Equivalent of Carbon Dioxide

Sir:

Control of the sites of C—C bond formation and C—H bond cleavage is important for synthetic exploitation of allylic activation in carbon skeletal construction. Ene reactions[1] of diethyl oxomalonate[2] (**2**), constrained by a pericyclic mechanism to occur with allylic transposition of the C=C bond, substitute an α-hydroxymalonyl group for allylic hydrogen (**1** → **3**). Conversion of this group into carboxyl allows olefin functionalization equivalent to an ene reaction of carbon dioxide (Scheme I).

We now show that **2** is indeed a synthetically valuable enophilic equivalent of carbon dioxide. Catalysis not only allows ene reactions of **2** under mild conditions, but also modifies the relative reactivities of olefins. Moreover, cerium(IV) oxidatively bisdecarboxylates α-hydroxymalonic (tartronic) acid intermediates (**4** → **5**).

Mono-, di-, and trisubstituted olefins listed in Table I afforded ene adducts with diethyl oxomalonate upon heating at 145-180 °C for 1-3 days. In each case only a single isomer was isolated by simple short-path distillation from the ene reaction mixture.[3] The selectivity of these ene reactions is primarily steric in origin, although small electronic effects are also operative. Thus, C—C bond formation occurs exclusively at the least substituted terminus of the C=C bond in arylcyclopentenes (**6**) and electron-donating substituents enhance reactivity moderately[4] ($\rho = -1.2 \pm 0.2$). However, steric effects readily overbalance this electronic bias since monosubstituted olefin reacts more readily than trisubstituted (entry 9). Both steric and electronic factors favor C—C bond formation at the less substituted terminus of a trialkyl olefin (entry 4), whereas the selective reaction of a monosubstituted C=C bond in the presence of a disubstituted C=C bond (entry 8) is sterically determined.



Synthetic methods which achieve stepwise substitution of a carboxyl group for allylic hydrogen by oxidation or metalation followed by C—C bond formation can result in retention or migration of the C=C bond (Scheme II). Our interest in ene reactions of **2** was sparked by the prospect that a regio-

Scheme I

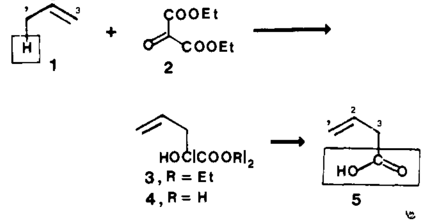
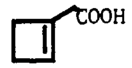
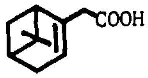
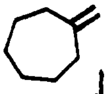
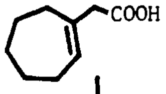
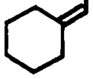
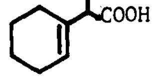
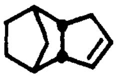
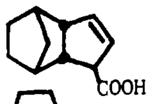
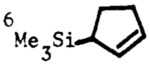
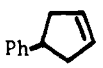
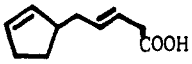
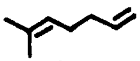
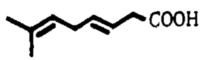
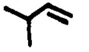
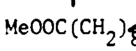
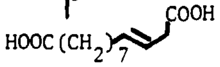
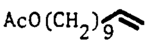
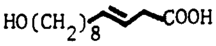
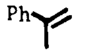
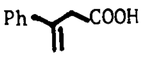
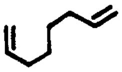
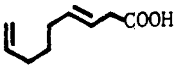
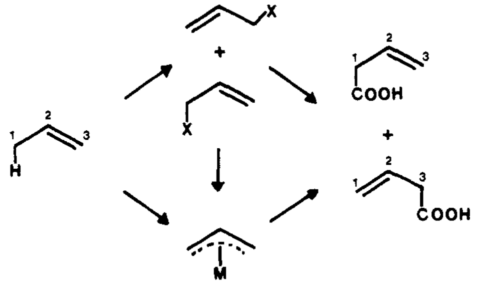


Table I. Allylcarboxylic Acids from Olefins via Thermal Ene Reactions of Diethyl Oxomalonate

Entry	Olefin	Ene Adduct Yield[a] (%)	Allylcarboxylic Acid	Yield (%) IO_4^-	Yield (%) Ce^{+4}
1		63		96	98
2		96		65	-
3		87		65	45
4		49		43	-
5		93		65	33
6		49		76	84
7		19		97	81
8		77		<5	68
9		75		57	-
10		47		49	-
11		63		<5	82
12		94		<5	60
13		80		62	83
14		86		94	64
15		60		<5	87

[a] >90% pure products isolated by distillation.

Scheme II



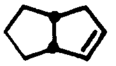
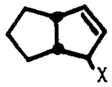
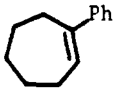
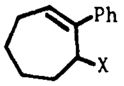
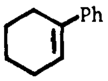
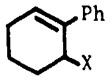
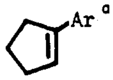
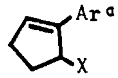
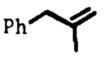
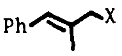
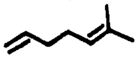
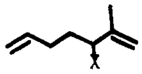
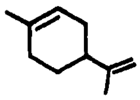
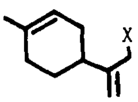
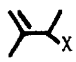
controlled alternative approach for allylic carboxylation could be achieved by oxidative bisdecarboxylation of the derived α-hydroxymalonic acids (Scheme I). In fact, the diacids **4** from saponification[5] of the ene adducts **3** are converted into allylcarboxylic acids **5** by treatment with sodium periodate and a trace of pyridine.[6] However, this reagent was unsatisfactory in some cases, especially for α-hydroxymalonic acids **4** derived from monosubstituted alkenes (Table I, entries 8, 11, 12, 15). Fortunately, we discovered an alternative reagent for these bisdecarboxylations, ceric ammonium nitrate,[7] which complements periodate (see Table I).

Allylic carboxylation of methylenecyclobutane provides a noteworthy contrast between the ene approach and a metalation-carboxylation procedure.[8] The overall conversion via ene reaction of diethyl oxomalonate provides transposed allylcarboxylic acid regiospecifically (Scheme III).

Additional control of relative olefin reactivities, as well as lower reaction temperatures, is possible by catalysis. Various Lewis acids promote ene reactions of diethyl oxomalonate at or below room temperature (Table II). Electronic effects strongly influence the selectivity of these catalyzed reactions. Electron donating substituents markedly enhance the relative reactivity of arylcyclopentenes (**6**) ($\rho = -3.9 \pm 0.3$).

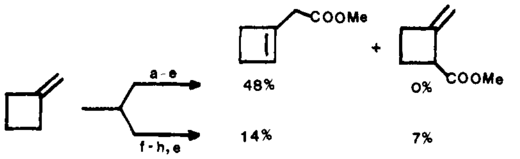
Entry 6 of Table II provides a striking contrast with entry

Table II. Lewis Acid Catalyzed Ene Reactions of Diethyl Oxomalonate

Entry	Olefin	Reaction Conditions	Ene Adduct $X = \underset{OH}{C}(COOEt)_2$	Yield (%) b.p. (°C)/Torr
1		1.0eq $SnCl_4$ 23°C/12h/bz		86 130-133/0.15
2		1.0eq $SnCl_4$ 23°C/12h/bz		72 183-185/0.4
3		1.0eq $SnCl_4$ 23°C/12h/bz		50 177-180/0.5
4		1.0eq $SnCl_4$ 23°C/12h/bz		52-88 a
5		1.0eq $SnCl_4$ 23°C/12h/bz		75 147-153/0.25
6		0.2eq $SnCl_4$ 0°C/5min/bz		40 170-174/15
7		0.2eq $ZnCl_2$ 23°C/1week Et_2O		67 145-160/0.2
8		0.2eq $Hg(OCOCF_3)_2$ 23°/5h/bz		90 115-120/0.1
9		0.2eq $SnCl_4$ 0°C/5min/bz		50 96-100/2

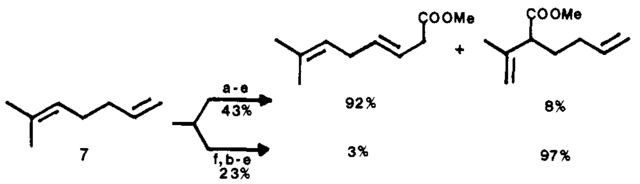
[a] Products [Ar (bp/Torr or mp, °C)]: Ph (160-165/0.1), *p*-MeOPh (113-115), *p*-ClPh (121-123), *p*-CF_3Ph (129-131), *p*-MePh (95-96), *m*-MePh (190-195/0.3), *m*-ClPh (79-80).

Scheme III[a]



[a] (a) $OC(COOEt)_2$, 80 °C, 6 days; (b) KOH, H_2O; (c), HCl; (d) $NaIO_4$, H_2O, pyridine; (e) CH_2N_2, Et_2O; (f) BuLi, TMEDA, −78 °C, (g) CO_2; (h) H_3O^+.

Scheme IV[a]



[a] (a) 180 °C, 48 h; (b) KOH, H_2O; (c) HCl; (d) $NaIO_4$, H_2O, pyridine; (e) CH_2N_2, ether; (f) 0.2 equiv of $SnCl_4$, benzene, 5 min, 0 °C.

9 of Table I. The strong electronic bias in the catalyzed reaction is sufficient to overcome the steric bias which dominates relative olefin reactivities in the thermal reaction. The excellent control which characterizes our method for allylic carboxylation is epitomized by the two different structurally specific functionalizations possible with diene **7** (Scheme IV).

Acknowledgment. We thank the National Science Foundation for financial support.

References and Notes

(1) For reviews see: (a) Hoffman, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 556. (b) Conia, J. M.; LePerchee, P. *Synthesis* **1975**, 1.

(2) Achmatowicz, O.; Achmatowicz, O., Jr.; *Rocz. Chem.* **1962**, *36*, 1791; *Chem. Abstr.* **1963**, *59*, 8610b.

(3) The structures of all new compounds were corroborated by ^{1}H NMR spectra and elemental analysis.

(4) For a pertinent recent study on substituent effects in pericyclic reactions, see Gajewski, J. J. *J. Am. Chem. Soc.* **1979**, *101*, 4393.

(5) Ene adduct (1 g) is stirred vigorously with 10% aqueous KOH (15 mL) for 18 h to afford the α-hydroxymalonic acid **4** in nearly quantitative yield after acidification to pH 3 with HCl, extraction into ether, and evaporation of solvent.

(6) Cf. Corey, E. J.; Wollenberg, R. H. *Tetrahedron Lett.* **1976**, 4705. The α-hydroxymalonic acid **4** (1.0 mmol) is added to aqueous $NaIO_4$ (10 mL of 0.25 M) containing pyridine (15 μL). After vigorous stirring for 1 h, acid **5** is isolated, after acidification to pH 3 with HCl, by extraction into ether (2 × 20mL). For water-soluble products, the acidified reaction mixture is saturated with NaCl prior to extraction with ether. The acids **5** are methylated with diazomethane. Samples of the esters were purified for analysis by gas-liquid phase chromatography.

(7) The α-hydroxymalonic acid **4** (1.0 mmol) is stirred vigorously for 1 h with a solution of aqueous cerric ammonium nitrate (5 mL of 1.0 M) in acetonitrile (15 mL). The acid **5** is isolated, after dilution with water (100 mL), by extraction into ether (2 × 100 mL).

(8) Wilson, S. R.; Phillips, L. R. *Tetrahedron Lett.* **1975**, 3047.

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trans-Bromo(2-, 3-, and 4-pyridyl)bis(triethylphosphine)palladium(II) Complexes

Sir:

Oxidative addition reactions of 2- and 3-bromopyridines to tetrakis(triphenylphosphine)nickel(0) occurred in toluene at room temperature to afford the dinuclear nickel(II) complexes containing the carbon-bonded 2- and 3-pyridyl ligands, respectively.[1] The former complex is quite stable, but the latter is less stable and the corresponding 4-pyridylnickel(II) complex has not been obtained. On the other hand, tetrakis(triphenylphosphine)palladium(0) reacted with 2-, 3-, and 4-bromopyridines in toluene at 90 °C to produce stable complexes, $[PdBr(C_5H_4N\text{-}C^2)(PPh_3)]_2$ (**1a**), *trans*-$PdBr(C_5H_4N\text{-}C^3)(PPh_3)_2$ (**2a**), and *trans*-$PdBr(C_5H_4N\text{-}C^4)(PPh_3)_2$ (**3a**) in 55, 90, and 73% yields, respectively. These are the first examples of the carbon-bonded pyridyl complexes with palladium(II), although several pyridyl complexes with cobalt(III),[2] gold(I),[3] titanium(III),[4] and some other metals[5] as well as nickel(II)[1] have been reported so far.

Treatment of compounds **1a**–**3a** with triethylphosphine in diethyl ether at room temperature resulted in the *trans*-$PdBr(C_5H_4N\text{-}C^2$, $\text{-}C^3$, and $\text{-}C^4)(PEt_3)_2$ complexes (**1b**, **2b**, and **3b**, respectively). They are all mononuclear[6] and trans since the methyl protons of triethylphosphine resonate as a 1:4:6:4:1 quintet and the proton-decoupled methylene carbons as a triplet with J(P-C) = 13 Hz. The trans structure is also supported by the existence of single ν(Pd-P) bands in the 330–320-cm^{-1} region. Thus these compounds are isomers.[7]

X-ray crystallographic studies[9] of the crystals of **1b**, **2b**, and **3b** showed similar square-planar geometry around the palladium atom (Table I): the only significant difference in the bond lengths appears as the longer Pd-Br length of **3b** than those of **1b** and **2b**, although a reasonable rationalization is difficult. The substituents of the phosphorus atoms are staggered about the P-Pd-P sequence in **1b**, whereas they are almost eclipsed in **2b** and **3b**.

Table I. Some Results of Structure Analyses Including Bond Distances and Bond Angles around Pd[a]

	1b	**2b**	**3b**
crystal system	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/c$	$Pn2_1a$
bond distances, Å			
Pd-C	1.993 (6)	1.998 (6)	2.030 (17)
Pd-Br	2.524 (1)	2.522 (1)	2.563 (3)
Pd-P	2.313 (3)	2.322 (2)	2.328 (5)
	2.314 (2)	2.323 (2)	2.325 (4)
bond angles, deg			
P-Pd-P	175.88 (8)	176.71 (7)	171.1 (2)
Br-Pd-C	178.2 (2)	178.2 (2)	178.1 (5)
P-Pd-Br	88.36 (6)	89.77 (5)	89.0 (2)
	95.55 (6)	90.37 (5)	92.8 (1)
P-Pd-C	89.9 (2)	90.1 (1)	89.8 (5)
	86.2 (2)	89.8 (2)	88.6 (5)

[a] Esd's are given in parentheses.

To compare basicities of these complexes, titration with perchloric acid was performed in dioxane-water (1:1 by volume) at 25 °C and μ = 0.1 ($NaClO_4$), and the pK_a values for the conjugate acids of **1b** and **2b** were determined to be 8.04 and 5.47, respectively. Basicity of **1b** is astonishingly stronger than that of uncoordinated pyridine (pK_a = 4.47). Unfortunately the solubility of **3b** in the mixed solvent was not enough in the presence of added sodium perchlorate to give an accurate pK_a value. For the sake of comparison, acid titration was carried out in the absence of sodium perchlorate in the same mixed solvent and the pK_a values obtained were 7.44, 5.01, and 5.38 for **1b**, **2b**, and **3b**, respectively, indicating that **3b** is a stronger base than **2b**.

^{1}H and ^{13}C NMR chemical shifts were determined and assigned as is shown in Figure 1 on the basis of the C-H and C-P coupling patterns and of the selected decoupling data. In each case the carbon atom bonded to palladium resonates at remarkably lower field compared with the corresponding carbon in uncoordinated pyridine. The ortho (adjacent) carbons also show 5.6–10.2-ppm downfield shifts, but the para carbons in **1b** and **2b** show ~6-ppm upfield shifts, while the meta carbons show smaller change. The change of the shieldings of the pyridine-ring carbons on σ bonding to palladium is quite similar to that observed for the phenyl-ring carbons in some phenylplatinum(II) complexes.[10]

With the aim of gaining some insight into the nature of chemical bonds in these complexes, we carried out MO calculations based on the CNDO/2 method of the simplified model complexes, *trans*-$PdCl(2\text{-}, 3\text{-}, \text{and } 4\text{-pyridyl})(PH_3)_2$. Standard values[11] were used for CNDO/2 parameters asso-

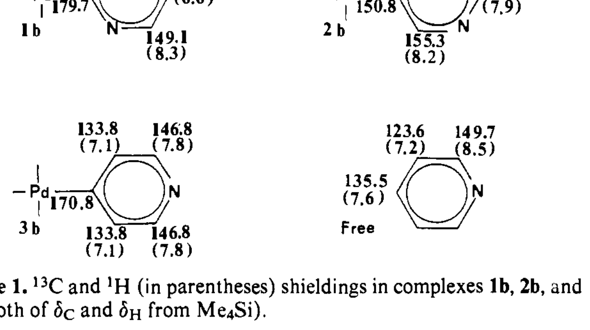

Figure 1. ^{13}C and ^{1}H (in parentheses) shieldings in complexes **1b**, **2b**, and **3b** (both of δ_C and δ_H from Me_4Si).

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