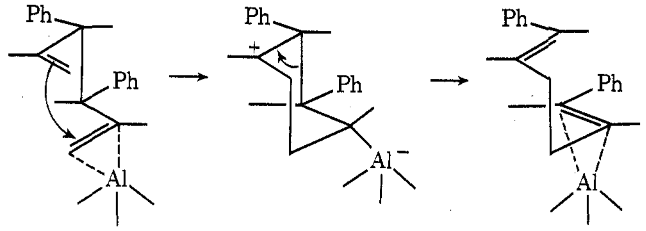
Scheme I



A few examples of catalyzed Cope rearrangements have been previously reported, each involving a transition metal complex.[4] The oxa-Cope (Claisen) rearrangement is catalyzed by more or less ordinary Lewis acids.[5]

Experimental Section

Melting points are uncorrected and were obtained in capillary tubes. Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. VPC analysis of the systems under study has already been described.[2] TLC analyses were on silica gel (Merck, HF$_{254}$) impregnated with about 20% silver nitrate, with sample components directly visible under short-wavelength uv light or upon spraying with 2,7-dichlorofluorescein followed by long-wavelength uv. Except where noted, alumina (Woelm 200, neutral, grade super I, approximately 200 m^2/g BET surface area) was activated at 650–700 °C for 4 h prior to use. Weighings of alumina were carried out in a drybox. *n*-Heptane (Mallinckrodt spectrophotometric grade) was dried over molecular sieves.

Rearrangement of *dl*-3,4-Diphenylhexa-1,5-diene on Aluminum Oxide. Approximately 1 g of alumina was weighed into each of four 5-ml Pyrex ampules; into each ampule was injected a solution of *dl* diene (mp 34.7–35.6 °C) in *n*-heptane (20 mg/ml) in such quantity that the diene:alumina ratio was 1:50. The ampules were closed with serum caps and left at room temperature with frequent manual shaking for 15, 30, 45, and 60 min, respectively. Crude products were isolated by vacuum evaporation of solvent after filtration and rinsing of the pale yellow alumina with a small amount of methanol. The ir spectra of all samples were virtually identical with that of authentic *trans,trans*-1,6-diphenylhexa-1,5-diene. VPC confirmed that this was the major component, with only traces of other materials; isomeric 1,6-diphenylhexa-1,5-dienes were absent in amounts greater than 0.1%. Melting points and percent material recovery for the crude samples follow: 15 min (84%), mp 74.0–77.2 °C; 30 min (94%), 73.5–76.7 °C; 45 min (87%), 75.5–77.5 °C; 60 min (84%), 73.5–76.0 °C; lit.[2] 79.0–79.5 °C.

Another run used 20 mg of *dl* diene in 2 ml of *n*-heptane with 2 g of Woelm alumina taken directly from its container without further heating. Rearrangement was monitored by TLC (development in 1:1 carbon tetrachloride–acetone); the reaction appeared complete after 70 h. The crude product, mp 73.5–76.0 °C, analyzed by VPC as *trans,trans*-1,6-diphenylhexa-1,5-diene with only traces of other components.

A similar run was carried out at 60 °C with 40 mg of *dl* diene in 2 ml of *n*-heptane and 2 g of Woelm alumina taken directly from its container. VPC analysis of the crude product (mp 76.0–77.5 °C) after 1.5 h showed no significant components other than the trans,trans diene.

Rearrangement of *meso*-3,4-Diphenylhexa-1,5-diene on Aluminum Oxide. Run 1. Into each of four ampules containing approximately 1 g of alumina was injected a solution of meso diene (mp 85.6–86.5 °C) in *n*-heptane (25 mg/ml) in such quantity that the diene:alumina ratio was 1:50. Crude products were isolated after 15, 30, 45, and 60 min at room temperature. The ir spectrum of each was determined quantitatively, following which unreacted meso diene was removed by preparative TLC (70:30 carbon tetrachloride–acetone). The faster moving unresolved 1,6-diphenylhexa-1,5-dienes were eluted from the silica gel with dichloromethane. VPC analysis identified *cis,trans*- and *trans,trans*-1,6-diphenylhexa-1,5-diene as the only products present in other than trace amount, with their relative ratios determined by integration. The percent conversion for each sample was determined from the intensity of the 10.4-μ ir band common to the two dienes, employing an average extinction coefficient calculated from the VPC data and the extinction coefficients for the pure cis,trans diene (0.67 ml mg^{-1} cm^{-1}) and the trans,trans diene (1.97 ml mg^{-1} cm^{-1}). Results are shown in Table I.

Run 2. In a second run ampules were kept at room temperature for 1, 2, 3, and 4 h, respectively. Results are given in Table I. Characteristics of this run were similar to those of the earlier one, except that the later samples showed a slight unidentified shoulder on the downward slope of the VPC trace of the trans,trans diene.

A third run was carried out at 60 °C, with crude products isolated at 15, 30, 45, and 60 min. Results are given in Table II. A trace component with a retention time corresponding to that of *cis,cis*-1,6-diphenylhexa-1,5-diene could also be observed in the VPC traces. The "110%" conversion in 60 min probably reflects inability to isolate product absorption at 10.4 μ from background ir absorption, since pure trans,trans diene showed linearity in the concentration range employed. Visual inspection of the ir spectrum actually suggested approximately 5% unreacted meso diene after 60 min. No attempt was made to improve the ir analysis in view of the inherent lack of reproducibility encountered and expected in a heterogeneous system involving a highly activated alumina.

Stability of *trans*-1,4-Diphenylhexa-1,5-diene on Alumina. Two ampules prepared as above using *trans*-1,4-diphenylhexa-1,5-diene in *n*-heptane were maintained, respectively, at room temperature for 4 h and at 60 °C for 1 h. Isolation of the diene followed by ir and VPC examination showed that the trans 1,4-diene had undergone no change.

Registry No.—**1**, 33788-15-7; **2**, 58463-02-8; **3**, 33788-14-6; **4**, 33788-20-4; alumina, 1344-28-1.

References and Notes

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(2) R. P. Lutz, S. Bernal, R. J. Boggio, R. O. Harris, and M. W. McNicholas, *J. Am. Chem. Soc.*, **93**, 3985 (1971).
(3) H. Pines and W. O. Haag, *J. Am. Chem. Soc.*, **82**, 2471 (1960).
(4) (a) J. C. Trebellas, J. R. Olechowski, and H. B. Jonassen, *J. Organomet. Chem.*, **6**, 412 (1966); (b) P. Heimbach and W. Brenner, *Angew. Chem., Int. Ed. Engl.*, **6**, 800 (1967).
(5) J. Borgulya, R. Madeja, P. Fahrni, H. J. Hansen, H. Schmid, and R. Barner, *Helv. Chim. Acta*, **56**, 14 (1973).

Carboxylation of Aromatic Compounds by Palladium(II) Carboxylates

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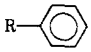
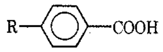
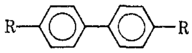
Benzenoid compounds react with palladium(II) salts in a variety of ways, depending on the reaction conditions used. The products resulting from chlorination,[1] acetoxylation,[2] nitration,[3] carbonylation,[4] and oxidative dimerization[5] are known. The authors have already communicated a newer type of reaction by palladium(II) chloride and sodium acetate, i.e., aromatic carboxylation.[6] However, the yields of aromatic acids therein produced were relatively poor.

The present paper describes that the use of palladium(II) carboxylates improves the yields of aromatic acids and that the olefinic hydrogen of styrene is also substituted by carboxyl group, although in a low yield.

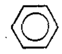
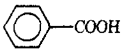
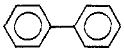
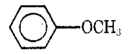
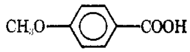
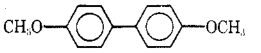
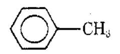
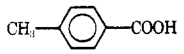
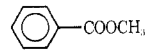
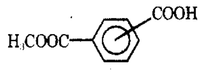
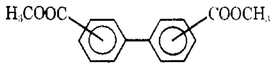
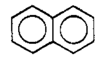
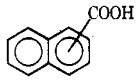
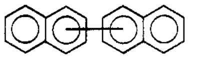
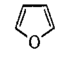
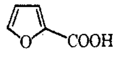
The reaction of aromatic compounds with sodium palladium(II) malonate (A)[7] in a mixed solvent of acetic acids and acetic anhydride or carbon tetrachloride gave aromatic acids in good yields, together with lower yields of aromatic dimers. The results are shown in Table I. It can be seen that sodium palladium(II) malonate (A) is much more efficient for aromatic carboxylation than the palladium(II) chloride–sodium acetate system.[6]

Table I. Carboxylation of Aromatic Compounds by Sodium Palladium(II) Malonate (A)

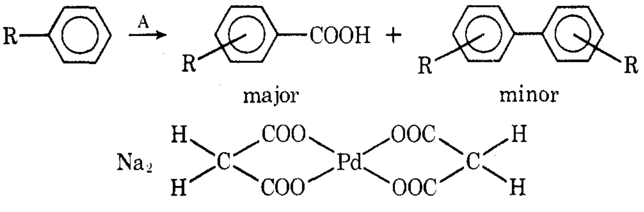
Reactants[a]			Products, %[b]	
 (0.1 mol)	A, mmol	Solvents (ratio) (100 ml)		
R = H	1.4	AcOH–Ac_2O (1:1)	98	None
H	2.8	AcOH–Ac_2O (1:1)	70	Trace
H	2.8	AcOH–CCl_4 (5:1)	66	20
OCH_3	2.8	AcOH–CCl_4 (5:1)	55.4	Small

[a] Reactants were heated at 100 °C or reflux for 10 h. [b] Yields are based on A used.

Table II. Carboxylation of Aromatic Compounds by Palladium(II) Malonate Complex (A) in the Presence of Silver Acetate

Registry no.	Reactants[a] aromatic compd (mmol)	Products (%)[b] Aromatic acids	Aromatic dimers
71-43-2	 (113)	 (72)	 (20)
100-66-3	 (92)	 (111)[c]	 (20)
108-88-3	 (94)	 (51)[c]	ND[d]
93-58-3	 (81)	 (30)[e]	 (5)
91-20-3	 (90)	 (90)[f]	 (15)
110-00-9	 (138)	 (101)[c]	ND[d]

[a] The complex A (2.8 mmol), AgOAc (12 mmol), and aromatic compound (10 ml)[11] were allowed to react in the mixed solvent (96 ml) of acetic acid and carbon tetrachloride (5:1). [b] Yields are based on the complex A used. [c] Exclusively formed. [d] Not determined. [e] The meta isomer (80%) and para isomer (20%) were formed. [f] The formation ratio of α and β isomer was 2:1.



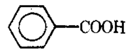
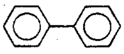
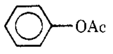
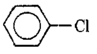
A

When silver acetate was used in addition to the salt (A), the best yield of aromatic acid was raised to 111%, based on palladium(II) salt used. The results for various aromatic compounds are summarized in Table II. The addition of reoxidation agent for metallic palladium(0) may make palladium-catalyzed carboxylation possible. Even though reoxidation of palladium(0) during the present reaction may produce palladium(II) acetate rather than regenerate sodium palladium(II) malonate (A), it is emphasized that the catalytic reaction is possible, as palladium(II) acetate also introduces the carboxyl group into aromatic rings. The attempted reactions of palladium(II) acetate with benzene under similar conditions gave benzoic acid in yields of 18–21%.

The difference in yields between A and palladium(II) acetate suggests that carboxylate ions around the palladium atom have an important role upon the aromatic carboxylation.[8] Furthermore, the carboxylation of benzene by palladium(II) acetate occurred in other solvents, such as acetic anhydride (in a yield of 21%), isobutyric anhydride (64%), or tetrachloroethylene (10%), showing that the carbon atom introduced into the aromatic ring should not be derived from solvent molecules. Further supporting evidence for this inference may be the result of reactions of phenylmercury compounds with palladium(II) salts in the mixed solvent of acetic acid and acetic anhydride (Table III). The substitution of mercury atom with carboxyl group was successful only in the presence of acetate ion. Consequently, these observations elucidate that the carbon atom of the carboxyl group introduced should be derived from carboxylate ions (e.g., malonate or acetate ions) which may be bonded to palladium atom.

The reaction of styrene with palladium(II) salt was further investigated, in order to know the scope of the carboxylation. The result showed that the olefinic hydrogen of styrene was

Table III. Reaction of Phenylmercury Compounds with Palladium(II) Salts

Reactants[a]			Products, %[b]			
Pd Salt (5 mmol)	PhHg salt (5 mmol)	Na salt (50 mmol)				
$PdCl_2$	PhHgCl	NaCl	Trace	45	None	52
$PdCl_2$	PhHgCl	NaOAc	11	48	Trace	ND[c]
$Pd(OAc)_2$	PhHgOAc	NaOAc	60	1.0	2.0	

[a] Reactants were heated in the mixed solvent of acetic acid (100 ml) and acetic anhydride (50 ml) at 100 °C for 5 hr. [b] Yields are based on phenylmercury compounds used. [c] Not determined

substituted by carboxyl group to give olefinic acid, although in a low yield. In a typical experiment, styrene was allowed to react with palladium(II) chloride and sodium acetate in a mixed solvent of acetic acid and acetic anhydride, to give cinnamic acid (trace) and 3-phenylallylic acid (2.6%), together with 1,4-diphenylbutadiene (2.4%) and β-acetoxystyrene (23.3%). Furthermore, the reaction of styrene with palladium(II) chloride and sodium propionate in a mixed solvent of propionic acid and propionic anhydride gave cinnamic acid (5.0%), in addition to 1,4-diphenylbutadiene (9.0%) and β-propioxystyrene (44.0%).

Experimental Section

Materials. Commercially available palladium(II) chloride (a guaranteed reagent by Tokyo Kasei Kogyo Co. Ltd.) was powdered and used without further purification. Palladium(II) acetate was prepared according to the method of Stephenson et al.[9] Thiophene-free benzenes were used after drying by Na wire. Sodium acetate was dried by heating in solid state before use. Malonic acid and the sodium salt were commercially available. All solvents were distilled and dried by sodium sulfate. All authentic aromatic acids and dimers were commercially available and compared with isolated products in melting point, ir, NMR, and GLC retention time.

Sodium Palladium(II) Malonate (A). A mixture of palladium(II) chloride (3.6 g, 0.02 mol) and sodium malonate (6.0 g, 0.04 mol) in water (60 ml) was stirred on a boiling water bath. The brown mixture was gradually changed to a yellow precipitate. After 1 h, the yellow precipitate was filtered out (60% yield). The addition of acetone to the concentrated mother liquid gave further precipitate. The collected solids were recrystallized from water: yellow needles, mp 198–200 °C dec; ir data was identical with that of potassium palladium(II) malonate, prepared by Schmerz et al.[10]

Anal. Calcd for $C_6H_4O_8Na_2Pd$: C, 20.20; H, 1.12. Found: C, 20.31; H, 1.04.

A was also synthesized from the reaction in nonaqueous system. Namely, the reaction of palladium(II) chloride and sodium malonate (1:2) in a mixed solvent of acetic acid and carbon tetrachloride (1:1) under reflux for 5 h gave a yellow palladium(II) compound in a yield of 90%. The isolated compound was identical with A from the preceding reaction in all spectral data.

Carboxylation of Benzene by Palladium(II) Acetate. A stirred solution of palladium(II) acetate (4.5 g, 0.02 mol), sodium acetate (8.2 g, 0.1 mol), and benzene (15.6 g, 0.2 mol) in a mixed solvent of acetic acid (100 ml) and acetic anhydride (100 ml) was heated at 100 °C for 6 h under nitrogen. The initial clear brown solution gradually turned black, showing precipitation of metallic palladium. After 6 h, gas evolution almost ceased, whose total amount was 71 ml and consisted of carbon dioxide, confirmed by GLC analysis, using a 3-m, 20% acetonylacetone on Neopac 1A column (0 °C, He carrier). Metallic palladium (2.1 g, 95%) was removed by filtration. Distillation of the filtrate gave a low-boiling fraction I (40–80 °C) and a high-boiling fraction II (80–136 °C). Fraction I contained methyl acetate, benzene, and acetic acid, by GLC analysis using a 1.5-m, silicon DC 550 on Celite 545 column (50 °C, H_2 carrier) and a 1.5-m, polyethylene glycol 20M on Celite 545 column (30 °C, H_2 carrier). Redistillation of fraction I gave a small amount of almost pure methyl acetate, which was identical with authentic material in ir spectrum. Fraction II consisted of benzene, acetic acid, and acetic anhydride. Further distillation of the residue under a reduced pressure removed residual solvents. The residual mixture was basified by aqueous sodium carbonate (15%) and extracted several times by diethyl ether. Then the aqueous layer was acidified by concentrated hydrogen chloride and similarly extracted. The ether extracts were dried over anhydrous sodium sulfate. The acidic ether extract gave 526 mg of benzoic acid (21%): needles from water, mp 121–122 °C (lit. mp 122°C). The neutral ether extract gave 118 mg of acetophenone (5%), 44 mg of phenyl acetate (1.5%), and a trace of biphenyl, which were identified with authentic materials by GLC and ir.

The reactions under other conditions were similarly treated. However, other products, except benzoic acid and biphenyl, were not identified.

Carboxylation of Benzene by A. A mixture of aromatic compounds (0.1 mol) and A (1.4 or 2.8 mmol) was heated under nitrogen for 19 h at 100 °C in a mixed solvent (100 ml) of acetic acid and acetic anhydride (1:1) or under reflux in a mixed solvent (100 ml) of acetic acid and carbon tetrachloride (5:1). The reaction mixtures were similarly treated as described in the above reaction.

Carboxylation of Aromatic Compounds by A in the Presence of Silver Acetate. A mixture of aromatic compounds (ca. 10 ml),[11] A (1.0 g, 2.8 mmol), and silver acetate (3.0 g, 12 mmol) was heated in a mixed solvent of acetic acid (80 ml) and carbon tetrachloride (16 ml) under reflux for 10 h. The reaction mixtures were similarly treated as described above. The isolated aromatic products were identified with the authentic materials by ir, NMR, and mass spectra. The isomer distribution of aromatic acids was determined by GLC analysis, after the esterification with diazomethane.

Reaction of Phenylmercury Compounds with Palladium(II) Salts. Palladium(II) acetate (1.1 g, 5 mmol) was allowed to react with phenylmercuric acetate (1.7 g, 5 mmol) in the presence of sodium acetate (4.1 g, 50 mmol) in a mixed solvent of acetic acid (100 ml) and acetic anhydride (50 ml) at 100 °C for 5 h. The reaction mixture was treated as described above. An acidic part (367 mg) of products contained benzoic acid (350 mg, 3 mmol). Biphenyl and phenyl acetate were identified by GLC analysis of the neutral part (70 mg).

Competitive Carboxylation of Benzene and Hexadeuteriobenzene by Palladium(II) Acetate. A mixture of benzene (49.4 mmol) and hexadeuteriobenzene (44.5 mmol) was carboxylated by palladium(II) acetate (2.2 g, 0.01 mol) and sodium acetate (8.2 g, 0.1 mol) in a mixed solvent of acetic acid (50 ml) and acetic anhydride (50 ml) at 100 °C for 5 h. After the filtration of precipitated metallic palladium and then evaporation of solvents and unreacted benzenes, the residual mixture was basified by aqueous sodium carbonate and washed several times by ethyl ether. Then the aqueous solution was acidified by concentrated hydrochloric acid and extracted by 100 ml of ethyl ether. The ether extract was dried over anhydrous sodium sulfate. After evaporation of ether, the residual mixture of aromatic acids (277 mg) was analyzed by mass spectra, which showed two peaks at the mass number of 127 and 122 with relative peak height of 1.00 and 4.38, respectively.

Competitive Carboxylation of Benzene and Hexadeuteriobenzene by A. A mixture of benzene (4.23 g, 54.2 mmol) and hexadeuteriobenzene (4.57 g, 54.4 mmol) was allowed to react with A (1.0 g, 6.8 mmol) in a mixed solvent of acetic acid (80 ml) and carbon tetrachloride (16 ml) under reflux (92 °C) for 5 h. After the treatment described in the reaction with palladium(II) acetate, both the acidic products (58.5 mg) and the neutral products (small amount) were analyzed by mass spectra. The acidic part had two peaks at the mass number of 127 and 122 with relative peak height of 1.00 and 3.90, respectively, corresponding to pentadeuteriobenzoic acid and benzoic acid. The neutral part had three peaks at the mass number 164, 159, and 154 with relative intensity of 1.00, 6.08, and 12.9, respectively, corresponding to decadeuteriodiphenyl, pentadeuteriodiphenyl, and diphenyl. Thus the relative number of phenyl group and pentadeuteriophenyl group in the produced aromatic dimers was 3.9 and 1.0, respectively.

Reaction of Styrene with Palladium(II) Chloride and Sodium Acetate. A stirred mixture of styrene (52.1 g, 0.5 mol), palladium(II) chloride (7.2 g, 0.04 mol), and sodium acetate (16.4 g, 0.2 mol) was heated in a mixed solvent of acetic acid (600 ml) and acetic anhydride (300 ml) at 105 °C for 7 h under nitrogen. The acidic products and the neutral products were separated by a similar treatment of the reaction mixture as described in the reaction of palladium(II) acetate. The distillation of the acidic part under a reduced pressure (1–2 mmHg) gave white sublimate (5 mg): mp 131–132 °C (lit. mp 133 °C); the ir identical with that of a specimen of cinnamic acid. The distillation residue (630 mg) was dissolved into water. Water-soluble substances were recovered and recrystallized from water. 3-Phenylallylic acid (167 mg) was isolated and further purified by sublimation: mp 85–86 °C; ir (KBr disk) 2750–2450, 1700, 1410, 1222 (–COOH), 3040, 748, 695 (–Ph), 972 cm^{-1} (trans HC═CH); NMR (CCl_4) τ 6.80 (d, 2 H), 2.85–4.10 (m, 2 H), 2.79 (s, 5 H), −1.76 (s, 1 H).

Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.07; H, 6.17. Found: C, 74.10; H, 6.19.

The neutral part was filtered after evaporation of ethyl ether and cooling of the oily liquid to give 1,4-diphenylbutadiene (200 mg): pale yellow leaflets from benzene, mp 152–153 °C (lit. mp 153 °C); NMR (CCl_4) τ 2.65–3.70 (m); ir (KBr disk) 3060, 1603, 1580, 1500, 1450, 1073, 992, 988, 912, 745, 736, 687 cm^{-1}. The filtrate was distilled under a reduced pressure (2 mmHg) to collect a fraction I (30–93 °C, 2 mmHg). Redistillation of fraction I gave 1.5 g of β-acetoxystyrene: bp 88–91 °C (2 mmHg); n^{18}D 1.5491 [lit.[12] bp 119–121 °C (10 mmHg), n^{20}D 1.5483]; ir 1758, 1220, 1103 (–OAc), 3060, 1655, 940 (–HC═CH–), 1600, 758, 700 cm^{-1} (–Ph); NMR (CCl_4) τ 2.25 (d, 1 H), 2.82 (s, 5 H), 3.74 (d, 1 H), 7.91 (s, 3 H). The residual oily liquid is considered to contain saturated acetate compounds and oligomers of styrene from the spectral data.

Reaction of Styrene with Palladium(II) Chloride and Sodium Acetate. A stirred mixture of styrene (52.1 g, 0.5 mol), palladium(II) chloride (3.6 g, 0.02 mol), and sodium propionate (9.6 g, 0.1 mol) was heated in a mixed solvent of propionic acid (98.4 g) and propionic anhydride (91.0 g) at 103 °C for 7.5 h under nitrogen. After the treatment described above, cinnamic acid (324 mg, 5.0%), 1,4-diphenylbutadiene (380 mg, 9.0%), and β-propioxystyrene (1.5 g, 44%) were isolated.

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Registry No.—A, 31168-61-3; palladium(II) chloride, 7647-10-1; sodium malonate, 23549-97-5; palladium(II) acetate, 3375-31-3; styrene, 100-42-5; sodium acetate, 127-09-3; phenylallylic acid, 2243-53-0; 1,4-diphenylbutadiene, 886-65-7; β-acetoxystyrene, 10521-96-7; PhHgCl, 100-56-1; PhHgOAc, 62-38-4.

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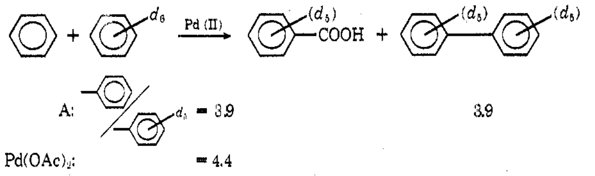

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Synthesis of 4-Lithio-2-methyl-2-pentene. A New Type of Allylic Organometallic Compound[1]

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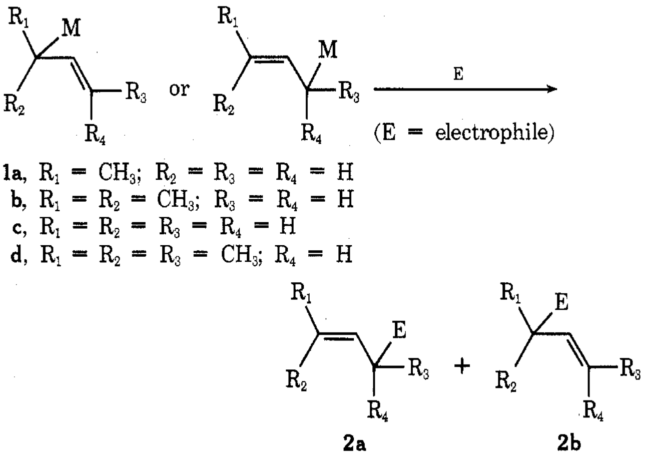
Allylic organometallics have long been the subject of intensive investigation.[2] In particular, the ability of unsymmetrical allylic organometallics (1) to attach themselves to electrophiles by either end of the allylic system (**2a** and **2b**) (Scheme I) has interested many workers. The nature of some electrophiles (alkyl halide, mineral acid, carbon dioxide) can greatly affect the ratio of these two possible product types.[3] It is, therefore, difficult to say anything about the point of attachment of the metal in the organometallic species unless some physical method such as NMR is used as a probe.

Fortunately, much NMR work has been done and compounds such as 2-butenyl (crotyl)[4] (**1a**), 2-methyl-2-butenyl[5] (**1b**), and propenyl (allyl)[6] (**1c**) Grignard reagents have been investigated. In each of the above cases where the allylic system is unsymmetrical (**1a** and **1b**), the organometallic compound has been shown to be a rapidly interconverting mixture of isomeric compounds (Scheme II). The predominant isomer is always the isomer in which the metal is attached to the *least* substituted end of the allylic system (herein termed the α carbon).[4,5] The isomer with metal attached to the most substituted carbon (herein termed the γ carbon) is presumably present in only small quantities at room temperature.[5]

Scheme I



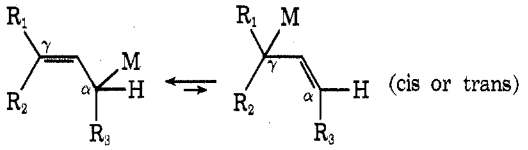
(E = electrophile)

1a, $R_1 = CH_3$; $R_2 = R_3 = R_4 = H$
b, $R_1 = R_2 = CH_3$; $R_3 = R_4 = H$
c, $R_1 = R_2 = R_3 = R_4 = H$
d, $R_1 = R_2 = R_3 = CH_3$; $R_4 = H$

2a **2b**

M = metal (Li) or metal halide (MgBr)

Scheme II



(cis or trans)

To date, all investigation concerning unsymmetrical allylic organometallics where all the nonhydrogen substituents on the α and γ carbons are alkyl has been with systems where the point of metal attachment may be either on a primary or secondary allylic carbon (crotyl and related systems) or a primary or tertiary allylic carbon (2-methyl-2-butenyl and related systems). No simple allylic organometallic in which the position of attachment of the metal atom may be on either a secondary and tertiary allylic carbon has been synthesized and studied. We now wish to report the synthesis of such a system, namely 4-lithio-2-methyl-2-pentene (**1d**), and the results of several reactions of this new organometallic with several carbonyl compounds.

Generally, the synthesis of allylic organometallics can easily be effected from the corresponding bromide or chloride. With this in mind, we attempted to synthesize 4-bromo-2-methyl-2-pentene (**4**) from 2-methyl-2-penten-4-ol (**3**) using phosphorus tribromide in ether (Scheme III), a method reported by Roberts and co-workers for the synthesis of 4.[7a] The results of this attempt were disappointing as the bromide spontaneously decomposed to give HBr and what NMR studies indicated to be 4,4-dimethyl-1,3-butadiene (**5**). The report by Roberts is, it should be noted, the only reference in the chemical literature to the synthesis of 4.[7b] Similar results were obtained when the synthesis of 4-chloro-2-methyl-2-pentene (**6**) was attempted using **3** and a mixture of triphenylphosphine and carbon tetrachloride, a method reported to be suitable for the synthesis of allylic chlorides which are prone to rearrangement.[8] Presumably, the extreme difficulty of obtaining these halides in pure form under normal conditions accounts for the fact that the corresponding allylic anion (**1d**) and related systems have not been prepared.

Mesitoate esters of allylic alcohols, however, have been