Table I. Substituents and Product Data[j] for RR'CHCN → RC(O)R'

category	compd	R	R'	base[a]	mp[b] (found), °C	% yield
A	1	Ph	Ph	K	57-48.5	95
	2	Ph	Ph-*p*-NO_2	K	138-139	100[c]
	3	Ph	Ph-*p*-OCH_3	K	61-61.5	90[c]
	4	Ph	Ph-*p*-Cl	K	73.5-75	90
	5	Ph	Ph-*p*-Br	K	81-82.5	93
	6	Ph	Ph-*p*-CH_3	K	57-58	90
	7	Ph-*p*-Cl	Ph-*p*-Cl	K	146-147	95
	8	Ph	Ph-*p*-NH_2	K	121.5-123	94
	9	Ph	Ph-2-Cl,4-NH_2	K	143.5-144.5	90
	10	Ph	Ph-*p*-F	K	230-233[d]	90
	11	Ph	2-C_5H_4N	K	39.5-41	48
B	12	Ph	$CH(Ph)_2$	L[e]		96
	13	Ph	CH_2Ph	L	57-59	50
	14	Ph-*p*-Cl	CH_2Ph-*p*-Cl	L	110-110.5	40[e]
	15	Ph-*p*-Cl	CH_2Ph	L		12
	16	Ph-*p*-Cl	CH_2Ph-*p*-OCH_3	K		*f*
C	17	Ph	c-C_6H_{11}	L[e]		97
	18	Ph	C_2H_5	L[e]		92
	19	Ph	$CH_2CH(CH_3)_2$	L		20[g]
	20	Ph-*p*-Br	H	L		26[g]
	21	Ph-2,4-Cl_2	H	L		13[h]
	22	Ph-*p*-F	CH_3	K		44[i]
	23	Ph	$CH(CH_3)_2$	K		26[g]
	24	CH_3	CH_3	L		60[g]

[a] K = K_2CO_3; L = LICA. [b] Found melting points agreed satisfactorily with reported values. For other compounds the spectral data were consistent with reported and expected absorptions. [c] See ref 1. 2-Chloro-4-aminobenzophenone. Anal. Calcd for $C_{13}H_{10}ClNO$: C, 67.39; H, 4.32; Cl, 15.33; N, 6.05. Found: C, 67.31; H, 4.49; Cl, 15.37; N, 5.95. [d] Melting point of 2,4-dinitrophenylhydrazone. [e] Very poor yield with K_2CO_3. [f] Hydrolysis to amide; see text and Experimental Section. [g] Additional products formed: i.e., acid, polymer, aldol. Yield estimated by spectral absorption. [h] With KH as the base and *t*-buOH as the solvent the product was the dimer 2,4-bis(2,4-dichlorophenyl)-3-amino-2-butenenitrile, mp 139.5-140.5 °C. Anal. Calcd for $C_{16}H_{10}N_2Cl_4$: C, 51.61; H, 2.69; N, 7.53; Cl, 38.15. Found: C, 51.74; H, 2.74; N, 7.57; Cl, 36.60. [i] Reaction temperature of 110 °C for 72 h; the oily product was converted to the 2,4-dinitrophenylhydrazone. [j] Satisfactory analytical data were reported for all new compounds listed in the table.

magnetically stirred overnight at room temperature, the mixture was added to 100 mL of ice–water. Three extractions with ether (3 × 30 mL) were combined. The extract was washed with water, dried overnight (Na_2SO_4), filtered, and allowed to concentrate. The residual clear oil was triturated with petroleum ether (30–60 °C) to give white crystals: 0.80 g (95%); mp 44–46 °C. After recrystallization from methanol the benzophenone melted at 47–48.5 °C (lit. mp 49 °C). The infrared spectrum matched that of an authentic sample.

Me_2SO/LICA Method. To 50 mL of Me_2SO was added 1.41 g (10 mmol) of isopropylcyclohexylamine, and then 5.5 mL of 1.8 M (9.9 mmol) butyllithium solution was slowly injected into the solution. A solution of 2.83 g (10 mmol) of phenylbenzhydrylacetonitrile in 50 mL of Me_2SO was then added over 2 min. After the mixture was stirred 16 h at room temperature, the reaction workup was as above, but an acid wash to remove amine was added.

2-(4-Chlorophenyl)-3-(4-methoxyphenyl)propanamide. The Me_2SO/K_2CO_3 method above gave poor results; however, the reaction time and temperature were increased to 96 h and 100 °C with K_2CO_3 as the base. The workup as above gave light yellow crystals: mp 166.5–167.5 °C; 78% yield (from methanol). The infrared spectrum did not show CN absorption but had peaks at 1680 (C=O) and at 3410 and 3530 (NH_2) cm^{-1}. Anal. Calcd for $C_{16}H_{16}ClNO_2$: C, 66.32; H, 5.57; Cl, 12.23; N, 4.83. Found: C, 66.30; H, 5.72; Cl, 12.45; N, 4.79.

Kinetic Data. The reactions were run as in the general procedure for the preparation of benzophenone with the Me_2SO/K_2CO_3 method. At regular time intervals, a 3-mL aliquot was removed from the reaction mixture and added to 10 mL of distilled water. Extraction with portions of methylene chloride (3 × 10 mL) followed by overnight drying (Na_2SO_4), filtration, and concentration left a residue. This was dissolved in deuterated chloroform, and an NMR tracing, with integration, was obtained. The disappearance of the hydrogen on the α-carbon of the substrate nitrile at 5 ppm vs. time was noted. For each aliquot the ratio of aromatic hydrogens to methinyl hydrogen was plotted vs. reaction time by drawing the best straight line. In order to determine the half-life for a specific substrate, we prepared a 1:1 mixture of authentic nitrile/authentic ketone. The NMR integration ratio for the standard solution was used to read the half-life from the aliquots plot. The $t_{1/2}$ values for entries 7, 4, 5, 1, and 6 were 0.3, 1.8, 2.0, and 2.6 h, respectively.

Registry No. 1, 86-29-3; 1 (ketone), 119-61-9; 2, 7599-05-5; 2 (ketone), 1144-74-7; 3, 4578-79-4; 3 (ketone), 611-94-9; 4, 4578-80-7; 4 (ketone), 134-85-0; 5, 33268-46-1; 5 (ketone), 90-90-4; 6, 6974-49-8; 6 (ketone), 134-84-9; 7, 20968-04-1; 7 (ketone), 90-98-2; 8, 28694-90-8; 8 (ketone), 1137-41-3; 9, 4760-53-6; 9 (ketone), 61747-12-4; 10, 719-82-4; 10 (ketone), 345-83-5; 10 (ketone DNP hydrazone), 87184-37-0; 11, 5005-36-7; 11 (ketone), 91-02-1; 12, 5350-66-3; 12 (ketone), 1733-63-7; 13, 3333-14-0; 13 (ketone), 451-40-1; 14, 36770-81-7; 14 (ketone), 51490-05-2; 15, 5681-31-2; 15 (ketone), 1889-71-0; 16, 5422-48-0; 16 (amide), 87184-36-9; 17, 3893-23-0; 17 (ketone), 712-50-5; 18, 769-68-6; 18 (ketone), 93-55-0; 19, 5558-31-6; 19 (ketone), 582-62-7; 20, 16532-79-9; 20 (aldehyde), 1122-91-4; 21, 6306-60-1; 21 (aldehyde), 874-42-0; 22, 51965-61-8; 22 (ketone), 403-42-9; 23, 5558-29-2; 23 (ketone), 611-70-1; 24, 78-82-0; 24 (ketone), 67-64-1.

Countercation Effects on the Palladium-Catalyzed Allylation of Enolates[1]

Ei-ichi Negishi* and Robert A. John

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Received February 8, 1983

Our recent finding[2] that allylation of potassium enoxyborates, that are obtainable by the reaction of ketones with either KH or $KN(SiMe_3)_2$ followed by treatment with BEt_3,[3] can be markedly catalyzed by Pd–phosphine com-

(1) Selective Carbon–Carbon Bond Formation via Transition-Metal Catalysis. 34. Part 33: Negishi, E.; Luo, F. T. *J. Org. Chem.* **1983**, *48*, 1560.

(2) (a) Negishi, E.; Matsushita, H.; Chatterjee, S.; John R. A. *J. Org. Chem.* **1982**, *47*, 3188. (b) Negishi, E.; Luo, F. T.; Pecora, A. J.; Silveira, A., Jr. *J. Org. Chem.* **1983**, *48*, 2427.

0022-3263/83/1948-4098$01.50/0

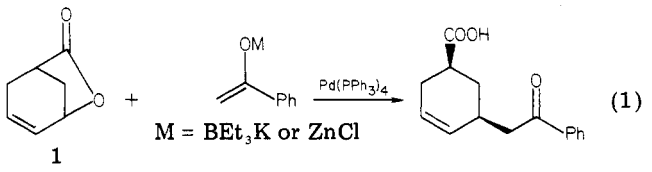
Table I. Reaction of Metal 6-Methylcyclohexenolates (2) with Neryl Acetate in the Presence of $Pd(PPh_3)_4$[a]

entry	M in 2	reaction time, h	yield of 3, % GLC	yield of 3, % isolated	6-Me/2-Me ratio	retention of the neryl identity, %
1	BEt_3K[b]	12	84	73	95/5	≥98
2	Li	24	0			
3	Li + $2BEt_3$[c]	12	78	62	91/9	≥98
4	MgCl[d]	24	17			
5	ZnCl[e]	12		64	96/4	≥98
6	$AlMe_2$[f]	24	0			
7	$AlMe_3Li$[g]	24	0			
8	$AlMe_3K$[h]	24	0			
9	$SiMe_3$[i]	24	0			
10	$Sn(Bu\text{-}n)_3$[j]	72	35			
11	$Ti(C_5H_5\text{-}\eta^5)_2Cl$[k]	24	0			

[a] All reactions were run in THF at room temperature. [b] These data are taken from ref 2a for comparison. [c] The reaction was run in the same manner as in entry 2 in the presence of 2 equiv of BEt_3. [d] 2b + $MgCl_2$. [e] 2b + $ZnCl_2$. [f] 2b + $ClAlMe_2$. [g] 2b + $AlMe_3$. [h] 2a + $AlMe_3$. [i] 2b + $ClSiMe_3$. [j] 2b + $ClSn(Bu\text{-}n)_3$. [k] 2b + $Ti(C_5H_5\text{-}\eta^5)_2Cl_2$.

plexes, e.g., $Pd(PPh_3)_4$, has added a new dimension to the Pd-catalyzed allylation of enolates.[4] Three noteworthy features of the reaction are as follows. First, allylation of metal enolates of "ordinary" ketones, e.g., cyclohexanone, can be achieved with various allylic electrophiles containing halogens and OAc. Second, the regioselectivity observed with both the "kinetic" and the "thermodynamic" enolates of 2-methylcyclohexanone is in the range 90–95%. Third, in the allylation with geranyl or neryl derivatives, the stereo- and regiospecificities with respect to the allylic moiety are ≥98%. Although a few papers[5] describing similar results obtained with enolates of Li and Sn have also appeared, the above-described features collectively appear to be unique to our reaction.

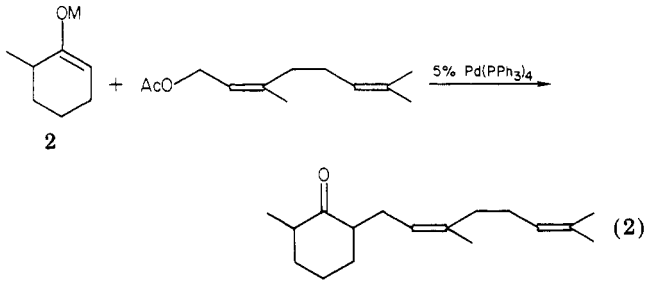
Since lithium enolates are much more commonly employed than the corresponding potassium enolates, we hoped to be able to use either lithium enolates or others readily derived from them and examined the effects of countercations on the Pd-catalyzed allylation of enolates. We now present the following generalizations as a set of synthetically useful guides, which should also clarify some confusions and puzzles with respect to the Pd-catalyzed allylation of enolates. (1) The scope of the reaction with a given metal cation is very much dependent on the leaving group and other hetero substituents in the allylic electrophiles as well as on the nature of the Pd catalysts, as detailed below. (2) In addition to the potassium enoxyborates reported earlier,[2] zinc enolates, readily obtainable by treating lithium enolates with dry $ZnCl_2$, permit a high regioselectivity (≥90%) with respect to 2-methylcyclohexanone and/or high stereo- and regiospecificities (≥98%) with respect to geranyl or neryl derivatives. Lithium enolates themselves are relatively unreactive and do not permit high regiospecificity with respect to 2-methylcyclohexanone. However, the corresponding reaction run in the presence of BEt_3 does provide results comparable with those realized with potassium enoxyborates or zinc enolates despite the fact that the extent of ate complexation between lithium enolates and BEt_3 is minimal[3b] (vide infra). All other countercations tested so far suffer from low product yields, e.g., MgCl, $AlMe_2$, $LiAlMe_3$, $KAlMe_3$, $SiMe_3$, and $Ti(C_5H_5\text{-}\eta^5)_2Cl$, and/or low regio- or stereospecificity, e.g., Li and $Sn(Bu\text{-}n)_3$.[5] (3) The overall retention with respect to the allylic carbon center of 1 has been observed in its reaction with either the potassium enoxyborate or zinc enolate of acetophenone (eq 1). Taken



1 (1)

together with previous stereochemical findings,[5,6] we may now generalize that, in sharp contrast with the Pd-catalyzed allylation of aryl- or alkenylmetals,[6,7] the corresponding reaction of metal enolates generally involves net retention at the allylic carbon center.

For exploration of the scope of the Pd-catalyzed allylation of metal enolates, the reaction of the "kinetic" enolates **2** containing various countercations with neryl acetate (eq 2) was chosen as a test system. Potassium



2 3 (2)

a, M = K; b, M = Li; c, BEt_3K; d, M = Li (+ BEt_3); e, MgCl; f, ZnCl; g, $AlMe_2$; h, $AlMe_3Li$; i, $AlMe_3K$; j, $SiMe_3$; k, $Sn(Bu\text{-}n)_3$; l, $Ti(C_5H_5\text{-}\eta^5)_2Cl$

enoxyborates and potassium enoxyalanates were prepared via **2a**, while the others were prepared via **2b**. The experimental results are summarized in Table I, and these results support the second generalization presented above.

Although allylic acetates do not react readily with enolates in the absence of Pd catalysts, allylic halides are known to react readily with enolates, e.g., lithium enolates. We therefore made a critical comparison of the conventional lithium enolate methodology with that reported herein. The pertinent experimental results are summarized in Table II, and these results indicate the following. First, although the conventional reactions of lithium

(3) (a) Negishi, E.; Idacavage, M. J.; DiPasquale, F.; Silveira, A., Jr. *Tetrahedron Lett.* **1979**, 845. (b) Idacavage, M. J.; Negishi, E.; Brown, C. A. *J. Organomet. Chem.* **1980**, *186*, C55. (c) Negishi, E.; Chatterjee, S. *Tetrahedron Lett.* **1983**, *24*, 1341.

(4) For a review, see: Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385.

(5) (a) Trost, B. M.; Keinan, E. *Tetrahedron Lett.* **1980**, *21*, 2591. (b) Fiaud, J. C.; Malleron, J. L. *J. Chem. Soc., Chem. Commun.* **1981**, 1159.

(6) Dunkerton, L. V.; Serino, A. J. *J. Org. Chem.* **1982**, *47*, 2812.

(7) Matsushita, H.; Negishi, E. *J. Chem. Soc., Chem. Commun.* **1982**, 160.

(8) For a review, see: Negishi, E. "Organometallics in Organic Synthesis"; Wiley-Interscience: New York, 1980; Vol. 1, Section 4.3.4.

Table II. Allylation of Lithium and Zinc Enolates[a]

entry	enolate	metal cation	allylic electrophile	catalyst[b]	other reagents	product	yield, %	regioselectivity or others, %
1	LCH[c]	Li	2,3-DCP[d]			4	⩽2	
2	LCH	Li	2,3-DCP		HMPA[e]	4	20	20 (diallylation)
3	LCH	Li	2,3-DCP		LiI (1 equiv)	4	45	13 (diallylation)
4	LCH	Li	2,3-DCP	I (5%)		4	92	⩽2 (diallylation)
5	2b	Li	2,3-DCP	I (5%)		5	90	98
6	2b	Li	IPC[f]			6	45	39[g]
7	2b	Li	IPC	I (5%)		6	77	77
8	2f	ZnCl	IPC			6	40	79
9	2f	ZnCl	IPC	I (5%)		6	92	95
10	LCH	Li	GA[h]	I (5%)		7	0	
11	LCH	Li	GA	II (1%)		7	78	
12	LCH	Li	GA	I (5%)	BEt_3[i]	7	80	
13	2b	Li	NA[k]	I (5%)	BEt_3[i]	3	62	91[l]

[a] Unless otherwise mentioned the reaction was run in THF at room temperature for up to 24 h. [b] I = $Pd(PPh_3)_4$. II = $Pd(dba)_2$ + $(Ph_2PCH_2-)_2$. [c] LCH = lithium cyclohexenolate. [d] 2,3-DCP = 2,3-dichloropropene. [e] The reaction was run in a 1:1 mixture of THF and HMPA. [f] IPC = isoprenyl chloride. [g] The major product was the 2,2-isomer. [h] GA = geranyl acetate. [i] The reaction was run in the presence of 2 equiv of BEt_3. [j] The stereoselectivity was ⩾98% *E*. [k] NA = neryl acetate. [l] The stereoselectivity was ⩾98% *Z*.

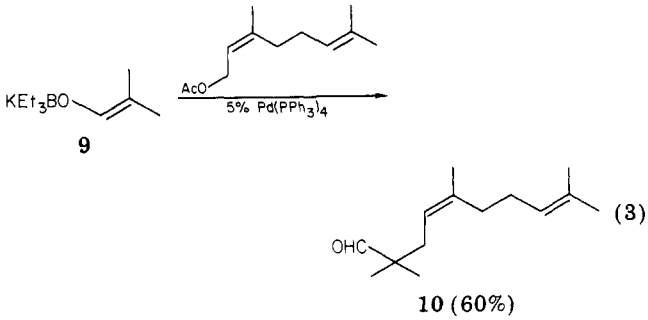
Chart I

enolate **2b** with isoprenyl chloride and 2,3-dichloropropene give the desired monoallylated ketones, these reactions are plagued by low regiospecificity and/or low product yields (entries 1–3 and 6). Second, in light of recent results by others[5] on the Pd-catalyzed allylation of lithium enolates with allylic acetates vis-à-vis our failure to achieve the same, we reexamined the scope of the Pd-catalyzed reaction of lithium enolates with allylic electrophiles. Whereas the reaction of lithium enolates with relatively unreactive allylic electrophiles, e.g., geranyl acetate, in the presence of $Pd(PPh_3)_4$ failed (entry 10), the corresponding reaction run under Fiaud's conditions[5b] with 1 mol % each of bis(dibenzylideneacetone)palladium [$Pd(dba)_2$] and bis(diphenylphosphino)ethane (DIPHOS) did give the desired product in good yield (entry 11). Catalysis by Pd–phosphine complexes can significantly improve regiospecificity and/or product yields even in cases where uncatalyzed allylation occurs (entries 4, 5, and 7). However, even the Pd-catalyzed allylation of lithium enolates is not highly regiospecific[9] except in very rapid reactions (entries 5 and 6). Fortunately, zinc enolates (entry 9) and lithium enolates used in conjunction with 2–3 equiv of BEt_3 (entry 13), as well as potassium enoxyborates reported previously,[2] permit both high regiospecificity (≥90%) and high product yields in all cases examined to date. The reaction of lithium enolates in the presence of BEt_3, however, poses an intriguing puzzle, since we earlier found that lithium enolates of ketones do not form ate complexes with organoboranes to significant extents. Lithium cyclohexenolate generated by treating cyclohexanone with lithium diisopropylamide (LDA) in THF in the presence of 1–3 equiv of BEt_3 displays a broad ^{11}B NMR signal at ca. 82 ppm relative to BF_3·OEt_2 along with a very minor signal (≤5% of the area of the major signal for the 1:3 mixture) at -3.3 ppm assignable to an ate complex.[10] Signals for BEt_3 and a 1:1 mixture of BEt_3 and $HN(Pr\text{-}i)_2$ in THF appear at 79.3 and 79.7 ppm, respectively. We therefore judge that the extent of formation of lithium (cyclohexenyloxy)triethylborate is ≤5%, even though some weak interaction between the lithium enolate and BEt_3 cannot be ruled out.

Finally, the following preliminary results are also worth noting. The reaction of the zinc enolate of 3-pentanone with 2,3-dichloropropene in the presence of 2 mol % of a chiral catalyst generated by treating Cl_2Pd[DIOP-(+)] with 2 equiv of $HAl(Bu\text{-}i)_2$ gave **8** (70% yield; Chart I), which was only 34% ee by ^1H NMR in the presence of $Eu(hfc)_3$. Potassium enoxyborate **9**, obtained by reacting isobutyraldehyde with KH followed by addition of BEt_3, reacted with neryl acetate in the presence of 5 mol % of $Pd(PPh_3)_4$ to give **10** in 60% yield (eq 3). However, the corre-

(9) Dr. J. C. Fiaud of Universite de Paris-Sud has informed us that the Pd-catalyzed reaction of **2b** with 2-cyclohexenyl pivalate produced a 6:4 mixture of the 2,2- and 2,6-isomers in a 40% combined yield.

(10) Potassium enoxyborates show a signal at ca. -2 ppm.[3b] The signs used in ref 3b are opposite those used in this paper.



(3)

sponding reaction of heptanal gave a mixture of more than several unidentified products. Application of the new allylation procedure to the aldehyde cases may therefore be limited to those cases where α-branched or hindered aldehydes are involved.

Experimental Section

All metal enolate and organometallic reactions were run under an atmosphere of nitrogen. Tetrakis(triphenylphosphine)palladium,[11] bis(dibenzylideneacetone)palladium,[12] and dichlorobis(benzonitrile)palladium[13] were prepared as described in the literature. The preparation of Cl_2Pd[DIOP-(+)] involves addition of 1.5 equiv of (+)-DIOP [(+)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane] to 1.0 equiv of $Cl_2Pd(C_6H_5CN)_2$ in dry benzene. Geranyl acetate[14a] and neryl acetate[14b] were prepared by treating the corresponding alcohols with acetic anhydride in pyridine. 7-Oxabicyclo[3.2.1]oct-2-en-6-one prepared by a literature method[15] was available in our laboratory. Chlorodimethylalane was prepared by mixing 2 equiv of Me_3Al with 1 equiv of $AlCl_3$. Zinc chloride was dried in a reaction flask at ca. 50 °C (≤1 mm). Removal of mineral oil from KH was done as described in the literature.[16] Tetrahydrofuran was purified by its distillation from Na and benzophenone. All other reagents were purchased from commercial sources and used without purification.

Generation of Metal Enolates. (a) Potassium Enolates. The potassium enolates of cyclohexanone, acetophenone, 3-pentanone, isobutanal, and heptanal were prepared as described in the literature[16] by dropwise addition of a carbonyl compound to a suspension of 1–1.2 equiv of KH in THF (1 mL/mmol) at room temperature. Conversion of 2-methylcyclohexanone into **2a** was carried out, as described previously,[2a,16] by sequential addition of bis(trimethylsilyl)amine (1.2 equiv, 22–25 °C) and 2-methylcyclohexanone (1 equiv, −78 °C) to 1.1 equiv of KH suspended in THF.

(b) Lithium Enolates. All lithium enolates used in this study were prepared by adding a ketone to a solution of LDA in THF according to the literature.[17]

(c) Other Metal Enolates. Potassium enoxytriethylborates were prepared by adding 1.2–1.3 equiv of a 1 M solution of BEt_3 in THF to potassium enolates.[3] Potassium enoxytrimethylalanates were prepared similarly by using $AlMe_3$. Metal enolates containing Mg, Zn, $AlMe_2$, $AlMe_3Li$, Si, Sn, and Ti were prepared by treating lithium enolates with $MgCl_2$, $ZnCl_2$, $ClAlMe_2$, $AlMe_3$, Me_3SiCl, n-Bu_3SnCl, and $Cl_2Ti(C_5H_5\text{-}\eta^5)_2$, respectively. The structures of the products in these cases were not established.

Palladium-Catalyzed Allylation of Metal Enolates Other than Potassium Enoxyborates. The following procedure for the reaction of the zinc enolate derived from lithium 6-methyl-2-cyclohexenolate with neryl acetate in the presence of $Pd(PPh_3)_4$ is representative. The preparation of the "kinetic" zinc enolate of 2-methylcyclohexanone (**2f**) was carried out as described above by using n-BuLi (2.2 M in hexane, 13.6 mL, 30 mmol), diisopropylamine (3.18 g, 31.5 mmol), 2-methylcyclohexanone (3.36 g, 30 mmol), THF (30 mL), and a solution of $ZnCl_2$ (4.08 g, 30 mmol) in THF (30 mL). To the above-prepared solution of **2f** was added at −78 °C a solution of neryl acetate (5.88 g, 30 mmol) and $Pd(PPh_3)_4$ (1.74 g, 1.5 mmol) in 30 mL of THF. The reaction mixture was warmed to room temperature over a few hours, stirred overnight, quenched with 3 N HCl, and extracted with ether. The organic layer was washed with aqueous $NaHCO_3$ and water, dried over $MgSO_4$, concentrated, and passed through a short Florisil column (10% ether–hexane). After evaporation of the solvents, distillation gave **3**: 4.76 g (64% yield); bp 145–149 °C (0.5 mm); IR(neat) 1710(s) cm^{-1}; ^1H NMR (470 MHz, $CDCl_3$, Me_4Si) δ 1.015 and 1.075 (2 sets of doublets, J = 8 Hz, 3 H), 1.5–2.5 (m, 23 H), 4.9–5.2 (m, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.15, 15.19, 17.20, 20.14, 22.99, 25.26, 26.17, 27.15, 28.37, 31.42, 31.56, 31.64, 34.47, 34.75, 37.09, 42.40, 45.17, 48.88, 50.96, 121.92, 122.48, 122.84, 123.82, 123.95, 131.07, 135.83, 136.52, 212.54, 215.37. In addition to these signals for the cis and trans 2,6-isomers, minor signals for the 2,2-isomer were also present. The regioselectivity determined by ^1H NMR (470 MHz) is 96% (the areas for peaks at 1.01 and 1.07 ppm/the total area for the α-Me signals including a singlet at 1.045 ppm). The regio- and stereospecificities of the reaction are ≥98% by ^1H and ^{13}C NMR.

The procedure represented by that described above has been applied to the synthesis of **4–7**.

2-(2-Chloro-2-propenyl)cyclohexanone[2b] (4). This compound was obtained in 92% yield by the palladium-catalyzed reaction of lithium cyclohexenolate with 2,3-dichloropropene. The extent of diallylation was ≤2%. The product **4** yielded the following spectral data: IR (neat) 1710 (s), 1635 (s), 1130 (s), 880 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.1–3.05 (m, 11 H), 5.20 (br s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 25.19, 27.99, 33.10, 39.11, 42.11, 47.77, 113.98, 140.81, 210.88.

When the reaction was carried out in the absence of $Pd(PPh_3)_4$, under otherwise the same conditions as those used above, the yield of **4** observed after 6 h (also after 3 h) was ≤2%, with essentially 100% of 2,3-dichloropropene remaining unreacted. When a 1:1 mixture of THF and HMPA was used as a solvent, the uncatalyzed reaction yielded 20% of **4** in 6 h, with only 10% of 2,3-dichloropropene remaining unreacted. The extent of diallylation was ca. 20%. When the uncatalyzed reaction in THF was run in the presence of 1 equiv of LiI, the yield of **4** after 6 h was 45%, with 25% of 2,3-dichloropropene remaining. The extent of diallylation was 13%. These results are summarized in Table II (entries 1–4).

2-Methyl-6-(2-chloro-2-propenyl)cyclohexanone[2b] (5; Table II, Entry 5). The compound yielded the following spectral data: IR (neat) 1710 (s), 1630 (m), 875 (m) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.01 (d, J = 7 Hz, 3 H), 1.1–3.1 (m, 10 H), 5.18 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.50, 25.33, 34.15, 37.29, 39.06, 45.65, 47.78, 113.99, 140.85, 212.57.

6-Methyl-2-(3-methyl-2-butenyl)cyclohexanone (6; Table II, Entries 6–9). This compound, obtained in 92% yield by the reaction of **2f** with isoprenyl chloride in the presence of $Pd(PPh_3)_4$, was a 95:5 mixture of the 2,6- and 2,2-isomer: IR (neat) 1705 (s), 1445 (m), 1375 (m), 905 (s), 725 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.00 and 1.05 (2 sets of doublets, J = 7 Hz, 3 H), 1.2–2.6 (m with singlets at 1.60 and 1.68 ppm, 16 H), 4.8–5.2 (m, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.01, 15.00, 17.16, 20.00, 25.17, 27.33, 28.55, 31.19, 34.25, 34.62, 36.96, 42.21, 44.98, 48.68, 50.70, 121.16, 122.06, 131.76, 132.49, 212.79, 215.07. In addition to these signals for the cis and trans 2,6-isomers, some minor signals assignable to the 2,2-isomer are also present. The regioselectivity of the reaction is estimated to be 95%.

The results of three other experiments producing **6** are summarized in Table II.

2-Geranylcyclohexanone (7; Table II, Entries 10–12). The reaction of lithium cyclohexenolate with geranyl acetate in the presence of 5 mol % of $Pd(PPh_3)_4$ by using the representative procedure described above did not produce **7** over 24 h. However, when 1 mol % of a Pd catalyst prepared by treating bis(dibenzylideneacetone)palladium with bis(1,2-diphenylphosphino)ethane[5b] was used in place of $Pd(PPh_3)_4$, **7** was obtained

(11) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.
(12) Takakashi, Y.; Ito, T.; Sakai, S.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1970**, 1065.
(13) Doyle, J. R.; Slade, P. E.; Jonassen, H. B. *Inorg. Synth.* **1960**, *6*, 216.
(14) (a) Knights, J.; Waight, E. S. *J. Chem. Soc.* **1955**, 2830. (b) Sornet, R. *Rev. Quim. Ind. (Rio de Janeiro)* **1930**, *204*, 98.
(15) Trost, B. M.; Verhoeven, T. R. *J. Org. Chem.* **1976**, *41*, 3215.
(16) Brown, C. A. *J. Org. Chem.* **1974**, *39*, 3913.
(17) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324.

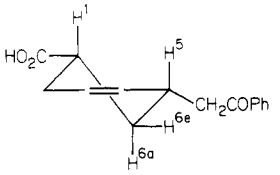
in 78% yield: IR (neat) 1710 (s), 1450 (m), 1130 (m), 830 (m) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.0–2.6 (m with peaks at 1.60, 1.67, and 2.00 ppm, 24 H), 4.9–5.25 (m, 2 H).

Palladium-Catalyzed Allylation of Lithium Enolates in the Presence of Triethylborane (Table II, Entries 12 and 13). These reactions were carried out in a manner similar to those described above, the use of 2–3 equiv of triethylborane being the only difference. The yields of **7** obtained by the reaction of lithium cyclohexenolate with geranyl acetate catalyzed by 5 mol % of $Pd(PPh_3)_4$ and run in the presence of 1, 2, and 3 equiv of BEt_3 were 55%, 78%, and 78%, respectively.

The yield of **3** obtained by this procedure was 62%, and the regioselectivity determined by ^{13}C NMR was 91%.

Palladium-Catalyzed Allylation of Potassium Enoxyborates. The Pd-catalyzed allylation of potassium enoxyborates was carried out as described previously.[2a] Although BEt_3 is, in principle, recoverable by distillation, it was destroyed by oxidation with 3 M NaOH and 30% H_2O_2. This oxidation makes the subsequent workup free from any complication due to the presence of BEt_3.

(*Z*)-5-(2-Oxo-2-phenylethyl)-3-cyclohexenecarboxylic Acid. The potassium enoxytriethylborate of acetophenone was prepared from 2.40 g (20 mmol) of acetophenone, KH (0.8 g, 20 mmol), 20 mL of THF, and 22 mL of 1 M solution of BEt_3 in THF, as described above. Its reaction with 7-oxabicyclo[3.2.1]oct-2-en-6-one (2.48 g, 20 mmol) in the presence of $Pd(PPh_3)_4$ (1.16 g, 1 mmol) was carried out overnight at room temperature according to the procedure reported previously.[2a] After oxidation with 3 M NaOH and 30% H_2O_2, the mixture was acidified to pH 3 by adding HCl and was extracted with ether. The organic extract was washed with saturated aqueous $NaHCO_3$, dried over $MgSO_4$, and evaporated to give an oil, which solidified later. The solid product was recrystallized from methanol–water to give the title compound: 4.05 g (83% yield); mp 103–105 °C; IR (Nujol) 1705, 1685 cm^{-1}; ^1H NMR (470 MHz, $CDCl_3$, Me_4Si) δ 1.15–1.25 (m, H-6a, 1 H), 2.0–2.25 (m, H-2a, H-2e, and H-6e, 3 H), 2.5–2.6 (m, H-1, 1 H), 2.75–2.95 (m, H-5, H-α, 3 H), 5.5–5.9 (H-3 and H-4, 2 H), 7.3–8.1 (m, 5 H), 10.4 (br s, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 27.52, 31.86, 32.94, 39.49, 44.50, 125.60, 128.06, 128.62, 130.66, 133.66 137.12, 181.75 198.90. The ^{13}C NMR spectrum indicates that the compound is stereochemically ≥95% pure. Selectively ^1H-decoupled ^1H NMR spectra (470 MHz) with $CDCl_3$ or benzene-d_6 as a solvent not only permit the peak assignments shown above but also provide the following coupling information indicating the cis stereochemistry for the compound.



$J_{H^1\text{-}H^{6a}} \simeq J_{H^5\text{-}H^{6a}} = 10.5$ Hz

The corresponding reaction of the zinc enolate **2f** gave a product which yielded ^1H and ^{13}C NMR spectra that are virtually the same as those described above. Thus this product must also be the cis isomer.

Asymmetric Reaction of the Zinc Enolate of 3-Pentanone with 2,3-Dichloropropene in the Presence of Chiral Palladium–Phosphine Complexes. The zinc enolate of 3-pentanone was generated, and it was reacted with 2,3-dichloropropane in the presence of a catalyst generated in situ by treating Cl_2Pd-[(+)-DIOP] (2 mol %) with DIBAH (4 mol %), following the representative procedures described above. 6-Chloro-4-methyl-6-hepten-3-one (**8**) was obtained in 56% yield (62% by GLC): IR (neat, 1715 (s), 1630 (s), 1455 (s), 1375 (s), 1150 (s), 970 (m), 880 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.9–1.2 [m consisting of a triplet at 1.04 (J = 7 Hz) and a doublet at 1.08 (J = 7 Hz, 6 H)], 2.1–3.1 (m, 5 H), 5.1–5.2 (m, 2 H).

The product obtained above was further examined by ^1H NMR by using tris[3-[(heptafluoropropyl)hydroxymethylene]-*d*-camphorato]europium [Eu(hfc)$_3$] as a chiral shift reagent. To a 0.2 M solution of the ketone product in benzene were added 10 mol % portions of solid Eu(hfc)$_3$. Integrations of the diastereomeric 1-Me and 4-Me proton signals, shifted down to the 3–4-ppm range in the presence of ca. 50 mol % of Eu(hfc)$_3$, indicate that the product is 34% ee.

(4*E*)-2,2,5,9-Tetramethyl-4,8-decadien-1-al (10). The preparation of the potassium triethylenoxyborate of 2-methylpropanal (**9**) and its reaction with neryl acetate in the presence of 5 mol % of $Pd(PPh_3)_4$ were carried out according to the representative procedures described above. The yield of **10** by isolation was 60%: IR (neat) 2700 (m), 1720 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.00 (s, 6 H), 1.60 (s, 3 H), 1.67 (s, 6 H), 1.9–2.3 (m, 6 H), 4.9–5.2 (m, 2 H), 9.45 (s, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 17.12, 20.75, 23.07, 25.21, 26.06, 31.54, 34.85, 45.72, 60.54, 118.96, 123.72, 131.04, 137.76, 205.19. The ^{13}C NMR spectrum indicates that the product is ca. 95% pure and that the byproduct probably is the stereoisomer. The ^1H NMR indicates the *Z* stereochemistry of **10**.

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health for support of this work. Dr. J. C. Fiaud has kindly informed us of some unpublished results related to those reported here. The high-field NMR study was supported by the Purdue University Biochemical Magnetic Resonance Laboratory (Grant NIH RR 01077). We also thank Professor H. C. Brown for allowing us to use their ^{11}B NMR facilities. Dr. R. G. Naik, Dr. E. John, and S. Chatterjee kindly provided technical assistance in obtaining spectra.

Registry No. **2c**, 82167-45-1; **2b**, 86901-70-4; **2e**, 43131-80-2; **2f**, 86901-71-5; **2g**, 86901-72-6; **2h**, 86901-65-7; **2i**, 86901-66-8; **2j**, 19980-33-7; **2k**, 41294-51-3; **2l**, 86901-67-9; **3**, 86941-23-3; **4**, 17392-07-3; **5**, 72009-04-2; **6**, 78461-63-9; **7**, 74016-20-9; **8**, 86901-75-9; **9**, 86901-69-1; **10**, 58558-37-5; acetophenone potassium enoxytriethylborate, 86901-68-0; lithium cyclohexenolate, 56528-89-3; 7-oxabicyclo[3.2.1]oct-2-en-6-one, 4720-83-6; (*Z*)-5-(2-oxo-2-phenylethyl)-3-cyclohexenecarboxylic acid, 86901-73-7; 3-pentanone zinc enolate, 86901-74-8; BEt_3, 97-94-9; $Pd(PPh_3)_4$, 14221-01-3; neryl acetate, 141-12-8; 2,3-dichloropropene, 78-88-6; isoprenyl chloride, 503-60-6; geranyl acetate, 105-87-3; acetophenone, 98-86-2.

Photoadducts of 1-Cyclohexene-1,2-dicarboxylic Anhydride

T. S. Nimry and E. K. Fields*

Research and Development Department, Amoco Chemicals Corporation, Naperville, Illinois 60566

Seymour Meyerson

Research Department, Standard Oil Company (Indiana), Naperville, Illinois 60566

M. E. Wright and H. K. Hall, Jr.

Department of Chemistry, University of Arizona, Tucson, Arizona 85721

Received February 14, 1983

1-Cyclohexene-1,2-dicarboxylic anhydride (I) reacts with butadiene, isoprene, and dimethylbutadiene only under vigorous conditions (12 hours at 175 °C) to give 50–60% yields of thermal [2 + 4] adducts.[1,2] It does not react even at 175 °C with furan, chloroprene, or cyclopentadiene.[2]

We have found that, in contrast to its reluctance to undergo thermal cycloaddition, I reacts readily with a variety of olefins under irradiation with weak ultraviolet light at 25–80 °C to give [2 + 2] cycloadducts.[3] The lower

(1) Alder, K.; Backendorf, K. H. *Ber.* **1938**, *71B*, 2199. Brigl, P.; Herrmann, R. *Ibid.* **1938**, *71B*, 2280.
(2) Buckles, R. E.; Deets, M. L. *J. Org. Chem.* **1958**, *23*, 485.

0022-3263/83/1948-4102$01.50/0