compounds (X = Cl and Br). The methyl derivative (X = CH_3) was obtained by treating a sample of the chloro compound with trimethylaluminium as previously described.[55] A solution of 1-*tert*-butyl-4-phenylbicyclo[2.2.2]octane[55] (**2b**, X = C_6H_5) (0.283 g, 0.0012 mol) in acetic anhydride (3 mL) was nitrated as above for the preparation of **2c** (X = p-$NO_2C_6H_4$). Recrystallization from methanol afforded 1-*tert*-butyl-4-(*p*-nitrophenyl)bicyclo[2.2.2]octane (**2b**, X = p-$NO_2C_6H_4$) as fine colorless needles (0.21 g, 62%). Physical and elemental analytical data for these systems (**2b**) are given in Table IX.

Acknowledgment. We thank Dr. A. N. Abeywickrema, Dr. H. A. Olszowy, and Ms. Inge Schott for synthetic contributions.

Registry No. **2a** (X = CN), 84010-79-7; **2a** (X = CF_3), 105253-17-6; **2a** (X = $COCH_3$), 105253-18-7; **2a** (X = $COOCH_3$), 105253-19-8; **2a** (X = $CON(CH_3)_2$), 105253-20-1; **2a** (X = F), 78385-88-3; **2a** (X = Cl), 84010-80-0; **2a** (X = Br), 84010-81-1; **2a** (X = I), 84010-82-2; **2a** (X = OCH_3), 84010-84-4; **2a** (X = $OCOCH_3$), 105253-21-2; **2a** (X = $N(CH_3)_2$), 84010-83-3; **2a** (X = C_6H_5), 68756-27-4; **2a** (X = p-FC_6H_4), 68756-25-2; **2a** (X = p-$CH_3OC_6H_4$), 105253-22-3; **2a** (X = $C{\equiv}CSi(CH_3)_3$), 105253-23-4; **2a** (X = CH_3), 84010-85-5; **2a** (X = $C(CH_3)_3$), 84010-86-6; **2a** (X = $Sn(CH_3)_3$), 84010-87-7; **2a** (X = H), 73075-71-5; **2b** (X = COOH), 5605-13-0; **2b** (X = F), 81687-86-7; **2b** (X = Cl), 105253-35-8; **2b** (X = Br), 105253-36-9; **2b** (X = I), 94994-05-5; **2b** (X = OCH_3), 81687-94-7; **2b** (X = C_6H_5), 64872-46-4; **2b** (X = p-$NO_2C_6H_4$), 105253-37-0; **2b** (X = CH_3), 105253-38-1; **2b** (X = H), 49576-45-6; **2c** (X = F), 95552-61-7; **2c** (X = I), 99631-74-0; **2c** (X = C_6H_5), 76889-41-3; **2c** (X = p-FC_6H_4), 76889-50-4; **2c** (X = P-$NO_2C_6H_4$), 105253-33-6; **2c** (X = CH_3), 105176-60-1; **2c** (X = H), 105253-32-5; **2d** (X = F), 95552-63-9; **2d** (X = C_6H_5), 76889-43-5; **2d** (X = p-FC_6H_4), 76889-52-6; **2d** (X = CH_3), 105176-62-3; **2d** (X = H), 105253-34-7; **3a** (X = CN), 105253-40-5; **3a** (X = $COCH_3$), 105253-24-5; **3a** (X = $CON(CH_3)_3$), 105253-25-6; **3a** (X = F), 84010-89-9; **3a** (X = Cl), 105253-26-7; **3a** (X = Br), 105253-27-8; **3a** (X = I), 84010-90-2; **3a** (X = OCH_3), 84010-88-8; **3a** (X = $N(CH_3)_2$), 105253-28-9; **3a** (X = C_6H_5), 105253-29-0; **3a** (X = CH_3), 105253-30-3; **3a** (X = $C(CH_3)_3$), 105253-31-4; **3a** (X = $Sn(CH_3)_3$), 84010-91-3; **3a** (X = H), 42204-95-5; 1-iodobicyclo[2.2.2]octane, 931-98-6; 1-methoxybicyclo[2.2.2]octane, 7697-14-5; 4-iodobicyclo[2.2.2]octane-1-carboxylic acid, 80745-61-5; (trimethylstannyl)lithium, 17946-71-3; 1-iodo-4-methylbicyclo[2.2.2]octane, 55044-63-8; trimethyllead chloride, 1520-78-1; 1-iodo-4-(*p*-fluorophenyl)bicyclo[2.2.2]octane, 61541-35-3; tin-119, 14314-35-3; lead-207, 14119-29-0.

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$PdCl_2$–$NaHCO_3$ Catalyzed Phenylation of Acyclic Allylic Alcohols. 3.[1] 1,2-Chirality Transfer in a Heck Reaction via a Wacker-Type Intermediate

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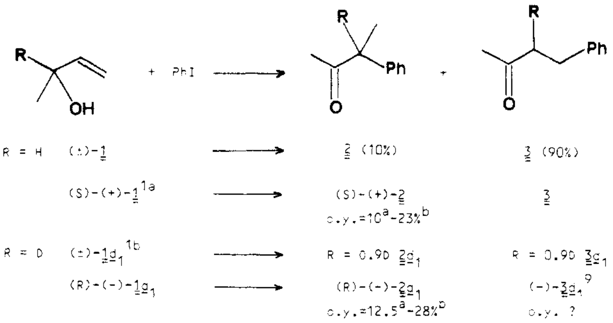
$PdCl_2$–$NaHCO_3$ catalyzed γ-phenylation of chiral 3-methylbut-3-en-2-ol with aryl iodides, a Heck-type reaction, affords chiral 3-benzylbutanone with up to 27% optical yield. The configuration of this ketone is clearly related to that of the unstable (β-hydroxyalkyl)palladium σ-complex, which is a key feature in the Wacker process. Different stereoselectivities were observed for *cis*- and *trans*-pent-3-en-2-ols.

Introduction

Stereoselective transition-metal-catalyzed formation of carbon–carbon bonds in acyclic molecules is a challenging objective. In previous work,[1a] we have shown that a measure of stereocontrol could be achieved in applying the Heck reaction[2] to chiral but-3-en-2-ol (eq 1). Although the observed chirality transfer was only moderate, we decided that our usual mechanistic probes,[3] namely, the use of chiral acyclic allylic alcohols, could be valuable for the further stereochemical study of this reaction.



(1)

[a] Optical yield calculated from the maximum specific rotation $[\alpha]_D^{20}$ 866° (cyclohexane).[1] [b] Calculated from $[\alpha]_D^{20}$ 368° (*c* 1.6, cyclohexane).[11] o.y. = optical yield.

We report here our results on the stereochemistry of the phenylation of several such substrates under catalytic conditions[1] similar to those previously reported[4-7] ($PdCl_2$; $NaHCO_3$; DMF).

Results and Discussion

Since the phenylation of chiral butenol **1**[1a] affords the achiral **3** as a major product, we decided to extend our

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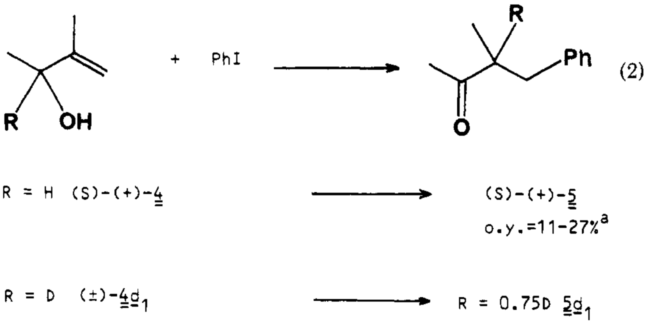
Table I. $PdCl_2$-$NaHCO_3$-Catalyzed Stereospecific γ-Phenylation of 4 (See Eq 2)

	starting alcohol 4		conditns		3-benzylbutanone (5)			
entry	structure	op,[h] %	temp, °C	time, h	structure	op,[h] %	chem yield, %	optical yield, %
1	(*S*)-(+)	68.5	130	2	(*S*)-(+)	7.8	38	11.4[a]
2	ibid.		130	2	ibid.	12.0	40	17.5[b]
3	ibid.		120	6.5	ibid.	12.5	50	22.7[b,c]
4	(*R*)-(−)	52.5	120	27	(*R*)-(−)	14.4	37	27.5[b,d]
5	ibid.		130	3	ibid.	8.9	45	15.4[b]
6	ibid.		120	7	ibid.	9.8		18.7[e]
7	ibid.		120	23	ibid.	6.0	37.5	11.5[e]
8	ibid.		120	72	ibid.	1.0		2.0[e,f]
9	ibid.		120	19	ibid.	8.2		15.6[b,g]

[a] Workup by steam distillation. [b] Workup by extraction with ether. [c] 0.1 molar equiv of $PdCl_2$. [d] Sixfold excess of PhI. [e] Nonaqueous workup followed by dilution with ether, filtration, distillation (90 °C (0.1 torr)), and separation by VPC. [f] Including gradual overheating to 180 °C. [g] $PdCl_2$ was replaced by palladium on charcoal. [h] op = optical purity.

study to the case of 3-methylbut-3-en-2-ol (4), which bears a *prochiral* methyl substituent at carbon C-3. A preliminary study[8] has already established that arylation of (±)-4 provides predominantly the desired β-arylated ketone 5 (eq 2).



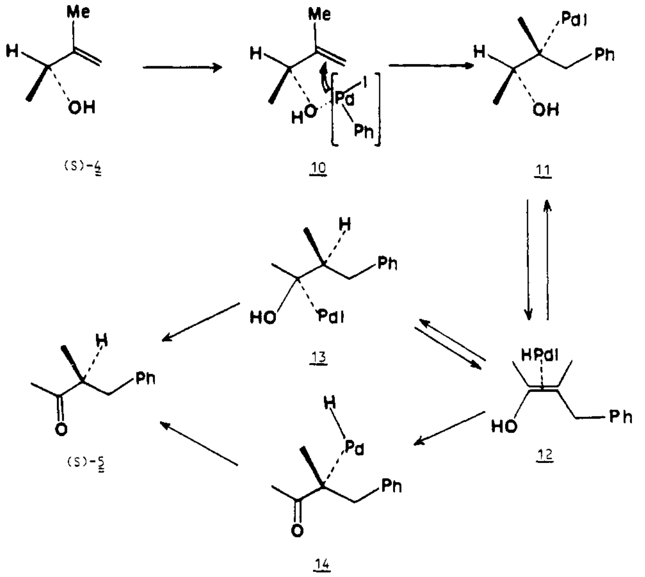
(2)

[a] Calculated from optically pure 5 with $[\alpha]^{20}{}_D$ 45.5° (*c* 3, EtOH).[12] o.y. = optical yield.

The results obtained with optically active 3-methylbut-3-en-2-ol (4) are summarized in Table I and eq 2. Palladium-catalyzed γ-phenylation of 4 afforded optically active ketone 5 with up to 27.5% stereospecificity (entry 4 of Table I). It must be pointed out that the use of an excess of $PdCl_2$, workup by steam distillation, and long heating resulted in increasing additional racemization of 5 (compare entries 3 with 4, 1 with 2, and 6 with 7 and 8).

It appears necessary then to determine to which extent the limited stereospecificity could be due to racemization of optically active ketones 2 and 5 under the reaction conditions employed. As a matter of fact, we have shown in previous work[1a] that no chirality transfer occurred using triethylamine as a base with (*S*)-(+)-1. However, we have also shown[1d] that under the title reaction conditions, deuteriated alcohol 1-d_1 afforded ketone 2-d_1 and alcohol 4-d_1 afforded 5-d_1 with respectively 90% and 75% deuterium transfer to carbon-3 (eq 1 and 2). Furthermore, (R)-(−)-1-d_1 gave rise to optically active 2-d_1 with 28% chirality transfer, which is comparable to the 23% optical yield obtained for (*S*)-(+)-2 (eq 1), if one assumes that the specific rotations of the hydro and the deuterio congeners of the alcohols 1 and 1-d_1 and of the ketones 2 and 2-d_1 are respectively very similar.

Scheme I



Finally, the racemization being caused undoubtedly by proton or deuterium exchange with the medium, possibly through enolization, the deuterium loss at the asymmetric center from 2-d_1 and 5-d_1 should correspond to the amount of racemization,[12] i.e., 10% for 2-d_1 and consequently for 2 and 25% for 5-d_1 and 5.

It is to be noted that the same degree of stereospecificity could be attained when phenylation was performed by using palladium-on-charcoal as a catalyst[4,13] (compare entries 5 and 9).

The diastereofacial selection[14,15] observed is qualitatively predictable by Cram's rule[16] and can be rationalized by assuming that derived models[17-19] using a perpendicular

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(8) (a) Regioselectivity with racemic alcohol 1 was studied by analytical VPC and found to be as follows: 3/2 = 91/9 (Ar = Ph), 88/12 (Ar = *p*-$MeOC_6H_4$), and 90/10 (nAr = *p*-ClC_6H_4). Since no significant differences were observed and optical rotations of chiral ketones 2 and 5 were known, this study was limited to phenylation. Cavallaro, J., unpublished results. (b) Besides ketone 5, a very small amount (2%) of an unknown compound was detected by VPC. It was not possible to purify it, and, therefore, its structure was not elucidated. Nevertheless, the absence of a CH_3CO group was ascertained by ^{1}H NMR.

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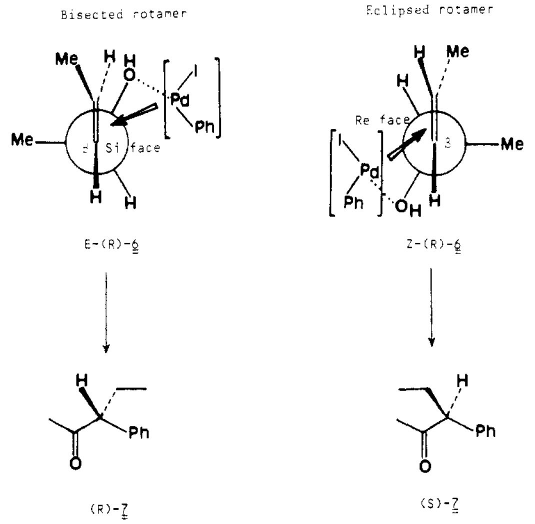
Scheme II. 1,2-Chirality Transfer and Conformational Analysis



rotamer[17] are operative during the reaction. A very similar model has been proposed for diversely catalyzed epoxidation reactions[20,21] in which a strong directing effect of a hydroxy group[22] predominated over those of bulky substituents.

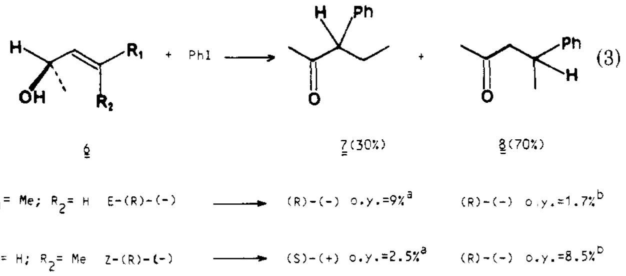
The observed diastereoselection[23] could be due to the preferential attack of palladium on the *re* face of the *β-prochiral* trigonal carbon atom C-3 in the perpendicular conformer of the corresponding alcohols (*S*)-**1** and (*S*)-**4**, leading to a π-complex in which the hydroxy group is in a syn relationship with the palladium atom (Scheme I).

Experiments conducted in this laboratory with deuteriated allylic butenols established that the phenylation reaction was highly regioselective (eq 1)[1c,24] in agreement with a multistep mechanism involving successive additions and eliminations of HPdI as proposed by several authors[5,25] and with a cis transfer of the phenyl group[26] and the PdI species from the π-palladium complex **10** (Scheme I).

To comply with the results of the 1,2 transfer of chirality, the vinyl alcohol **12** must not be completely dissociated before hydride addition occurs[1c] leading to the σ-complex **13**. In other words, hydride readdition to the newly formed π-complex **12** must be considerably faster than either alkene dissociation or exchange. Release of chiral ketone **5** from **13** takes place by an irreversible β-elimination of HPdI. An alternative route[27] might be a rearrangement of **12** to a (β-oxoalkyl)palladium hydride **14** followed by a reductive elimination (Scheme I).

These results seem pertinent in regard to the stereochemistry of the penultimate step in the Wacker process.[28] More precisely, the stereochemistry of **5** is related to that of **11** by a transformation leading to an overall retention, hydrogen replacing palladium at the carbon atom β to the hydroxy group in **11**.

This important role of conformations in distinguishing the two diastereo faces of the double bond by a transition metal finds good support in the study with *cis*- and *trans*-pent-3-en-2-ols **6** (eq 3). It is clear that the *trans*-(*R*) enantiomer affords ketone **7** with the *R* configuration, whereas the *cis*-(*R*)-**6** leads to a ketone with the opposite configuration.



ᵃCalculated from optically pure **7** with $[\alpha]^{20}{}_{D}$ 662° (cyclohexane).[10] ᵇCalculated from $[\alpha]_D{}^{20}$ 74.5° (*c* 1, benzene).[29] o.y. = optical yield.

Such reversal of stereoselectivity was already observed in the epoxidation of allylic alcohols[21a,23a] and may be attributed to the intervention of the *eclipsed* conformer of the sterically hindered alcohol *cis*-(*R*)-**6** whereas alcohols **1**, **4**, and *trans*-(*R*)-**6** react as the *bisected* forms (Scheme II). Moreover, no cis–trans isomerization of **6** occurred during the reaction. Therefore, the differences in the optical yields observed from cis and trans alcohols should be directly related to the configuration of the double bond, although the factors determining the yield of chirality transfer are not yet fully understood.

The lower chirality transfer obtained with pentenols compared to butenols could be due to the higher flexibility of the conformers.

Conclusion

Although the amount of chirality transfer was limited under the reaction conditions employed (high temperature, presence of base), to the best of our knowledge it is the first example of such a transfer for the Heck reaction. These results shed some new light on the reactivity of organopalladium intermediate and bring information on the stereochemical course of the last step of the Wacker reaction.

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Experimental Section

General Methods. Analytical chromatography was carried out on a Girdel 75 FD 2 instrument equipped with flame ionization detectors and fitted with a 10% SE 30 on 80–100 Mesh Chromosorb Q-DMCS-AW (3.5 m × 0.125 in.) at 150 °C, using N_2 as carrier gas.

Preparative chromatography was carried out on an Aerograph A 700 instrument fitted with 30% Carbowax 20M on 45–50 mesh Chromosorb W-NAW columns. Column A was 1.8 m × 0.375 in. and was used for the separation of ketones at 195 °C and column B was 5 m × 0.375 in. and was used for the purification of alcohols at 140 °C. A Jobin-Yvon chromatospac 100 HPLC system equipped with a refractometric detector and packed with silica gel H60 (5-40nm), operating isocratically with 20:80 ether–pentane was also used for the purification of the ketones. Infrared spectra were recorded on a Unicam SP-300 spectrophotometer and calibrated to the 1601.4 and 906.7 cm^{-1} absorptions of a polystyrene film. Only the most characteristic or prominent peaks are quoted.

^1H NMR spectra were recorded at 60 MHz on a Varian EM 360 instrument and at 420 MHz on a Brucker apparatus operating in the FT mode. ^{13}C NMR spectra were recorded at 62.89 MHz on a Brucker WM 250 apparatus. $CDCl_3$ was used as a solvent, and chemical shifts are reported relative to tetramethylsilane as internal standard. Deuterium isotope effect ($\Delta\delta_j$) of labeled **5**-d_1 was also measured for ^{13}C and ^1H chemical shifts, in which j is the number of bonds between deuterium and the atom studied.

Optical rotations were measured on a Perkin-Elmer 141 polarimeter at 589 nm. The structures of all the described compounds were confirmed by comparison with published data for the known ones and supported by fitting IR spectra and the requisite substituent resonances displayed in the ^1H NMR.

Aryl iodides (Aldrich) were used as supplied after simple distillation.

But-3-en-2-ol (1) (Aldrich) was distilled from CaH_2. Deuteriated **1**-d_1 was prepared by reduction of butenone using $LiAlD_4/Et_2O/H_2O$ technique:[30] ^1H NMR δ 6.15–5.80 (dd, 1 H, H-3, $J_{3,4}$ = 10 Hz, $J_{3,4'}$ = 18 Hz), 5.33–4.90 (m, 2 H, H-4, 4′), 4.57 (s, 1 H, OH), 3.60 (m, 0.02 H, H-2), 1.17 (s, 3 H, H-1); IR (neat) 3350, 3090, 2980, 2925, 2120, 1640, 1440, 1410, 1360, 1210, 1125, 990, 915 cm^{-1}. Both alcohols were resolved according to a literature procedure.[31]

3-Methylbut-3-en-2-ol (4) was prepared by reduction of the corresponding enone (EGA) by $LiAlH_4/Et_2O/H_2O$ technique.[30] Its resolution was carried out by means of the brucine salt of the acid phthalic ester: (±)-alcohol (43 g, 0.5 mol), phthalic anhydride (74 g, 0.5 mol), and pyridine (100 mL) were heated on a steam bath for 2 h. The cold homogeneous reaction mixture, when poured into dilute hydrochloric acid, afforded the acid ester as an oil in 91% yield (106 g). Anhydrous brucine (374.5 g, 0.45 mol) was dissolved in a warm solution of the racemic hydrogen phthalic ester (106 g, 0.45 mol) in 800 mL of 1:9 water–acetone. Hydrolysis[31] and treatment with 5 N NaOH solution of the crystals which separated on cooling (135 g) gave 11 g (25% yield) of dextrorotatory alcohol $\alpha^{20}{}_D$ 1.58° (neat, l = 1). Hydrogenation of a sample (Raney nickel) afforded (*S*)-(+)-3-methyl-2-butanol, $\alpha^{20}{}_D$ 2.78° (neat, l = 1) which was 68.5% optically pure.[32] Consequently, the maximum rotation of **4** may be calculated as 2.31°, and its absolute configuration is also (*S*)-(+).

Deuteriated **4**-d_1 was prepared by reduction of 3-methylbut-3-en-2-one using $LiAlD_4/Et_2O/H_2O$ technique:[30] ^1H NMR δ 4.93 (m, 1 H, H-4, $J_{4\text{-}4'}$ = 1.8 Hz, $J_{4\text{-}3'}$ = 1.5 Hz), 4.75 (m, 1 H, H-4′, $J_{4'\text{-}3'}$ = 0.7 Hz), 1.70 (m, 3 H, H-3′), 1.55 (s, 1 H, OH), 1.20 (t, 3 H, H-1, $J_{H\text{-}D}$ = 1 Hz); IR (neat) 3350, 3080, 2980, 2940, 2880, 2130, 2070, 1650, 1450, 1370, 1290, 1135, 1070, 1040, 950, 930, 900 cm^{-1}.

***trans*-(*R*)- and *cis*-(*R*)-(−)-Pent-3-en-2-ols (6)** were synthesized from the corresponding chiral acetylenic alcohol (*R*)-(+) pent-3-yn-2-ol, $\alpha^{20}{}_D$ 3.30° (neat, l = 1), 61% optically pure.[33] Chemical reduction of this alcohol by the $LiAlH_4/THF/H_2O$ technique[34] afforded *trans*-(*R*)-**6** which is known to have a low and variable specific rotation,[35] and catalytic reduction in the presence of Lindlar catalyst in ether gave, after purification by VPC, *cis*-(*R*)-(−)-**6** with $\alpha^{20}{}_D$ −11.0° (neat, l = 1). Both isomers were assumed to have the optical purity of the starting acetylenic alcohol. The maximum calculated specific rotation of *cis*-**6** is $[\alpha]^{20}{}_D$ 21.97° (neat, l = 1) since $d_4{}^{20}$ = 0.835.

Typical Procedure of Arylation. A magnetically stirred mixture of 20 mmol of starting alcohol, 1 molar equiv of aryl iodide, 1.7 g of $NaHCO_3$ (1 molar equiv), and 35 mg of $PdCl_2$ (0.01 molar equiv) in 16 mL of dimethylformamide (DMF) was heated in a thermoregulated bath. The reaction was followed by analytical VPC, and the resulting ketones were isolated either by HPLC or by preparative VPC (column A). In the last case no racemization was observed.

Phenylation of [2-$^2H_1$]But-3-en-2-ol (**1**-d_1) with $[\alpha]^{20}{}_D$ −11.6° (neat, l = 1), 34.4% optically pure,[31] afforded a 10% yield of (*R*)-(−) **2**-d_1 with $[\alpha]^{20}{}_D$ = −35° (c 1.8, ether) which is 9.5% optically pure according to ref. 11 and only 4.0% according to ref. 10. The calculated corresponding optical yields, were, respectively, 28% and 12%. The major ketone **3**-d_1 (90%) also was found to be chiral with $[\alpha]^{20}{}_D$ = −0.46° (c 3, cyclohexane) and 99.97% pure by VPC. The absolute configuration and the specific rotation of **3**-d_1 are unknown and the use of a chiral shift reagent such as $Eu(tfc)_3$ did not provide any further information about the e.e. of the chiral ketone. It is important to note that a direct determination of the ee of a ketone in which the optical activity is only due to deuterium has never been realized.[9]

Phenylation of 3-Methylbut-3-en-2-ol (4). The results are summarized in Table I. Optical activity of ketone **5** was well-established. From a sample with $[\alpha]^{20}{}_D$ 4.86° (c 5.2, EtOH) the ee was determined based on the methyl singlet splitting at 2.0 ppm by using ^1H NMR and a chiral shift reagent such as $Eu(hfc)_3$. It was found to be 12% for an optical purity of 10.7%. The first crop of the tosylhydrazone derivative (mp 129.5–130 °C) of chiral **5** was also shown to be optically active with $[\alpha]^{20}{}_D$ 28° (c 1.9, benzene).

Phenylation of [2-$^2H_1$]3-Methylbut-3-en-2-ol (**4**-d_1) afforded ketone **5**-d_1 with 75% deuterium transfer to carbon-3: ^1H NMR δ 7.33–7.10 (m, 5 H, C_6H_5), 3.0 (m, 1 H, H-4, $J_{4\text{-}4'}$ = 14 Hz, $\Delta\delta_3$ = −0.020), 2.82 (m, 0.25 H, H-3), 2.55 (m, 1 H, H-4′, $\Delta\delta_3$ = −0.014), 2.09 (s, 3 H, H-1, $\Delta\delta_4$ = −0.004), 1.08 (s, 3 H, CH_3-CD, $\Delta\delta_3$ = −0.016); ^{13}C NMR δ 211.4 (s, C-2), 139.6, 128.8, 128.3, 126.1 (s, C_6H_5), 48.7 (s, C-3), 48.2 (t, C-3, $J_{C\text{-}D}$ = 20.2 Hz, $\Delta\delta_1$ = −0.46), 38.9 (s, C-1), 28.5 (s, C-4, $\Delta\delta_2$ = −0.066), 16.1 (s, CH_3-CD, $\Delta\delta_2$ = −0.078).

Phenylation of *trans*-Pent-3-en-2-ol. (*E*)-(*R*)-**6**, 60.1% optically pure, afforded (*R*)-(−)-**7** with $[\alpha]^{20}{}_D$ 36.05° (c 2.8, cyclohexane), 5.45% optically pure,[10] and (*R*)-(−)-**8** with $[\alpha]^{20}{}_D$ 0.78° (c 9, cyclohexane), 1.05% optically pure.[29] The optical yields were respectively 9% and 1.7%.

Phenylation of *cis*-Pent-3-en-2-ol. (*Z*)-(*R*)-(−)-**6**, 60.1% optically pure, gave (*S*)-(+)-**7** with $[\alpha]^{20}{}_D$ 10.06° (c 3, cyclohexane), 1.5% optically pure,[10] and (*R*)-(−)-**8** with $[\alpha]^{20}{}_D$ 3.80° (c 5, cyclohexane), 5.1% optically pure.[29] The optical yields were respectively 2.5% and 8.5%.

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Registry No. (±)-**1**-d_1, 105228-57-7; (*R*)-**1**-d_1, 105183-77-5; (±)-**2**-d_1, 105228-59-9; (*R*)-**2**-d_1, 105183-80-0; (±)-**3**-d_1, 105183-85-5; (−)-**3**-d_1, 105205-37-6; (±)-**4**, 60041-32-9; (±)-**4** (acid ester), 105183-78-6; **4** (enone), 78-94-4; (*R*)-**4**, 105228-58-8; (*S*)-**4**, 88376-46-9; (±)-**4**-d_1, 105183-79-7; (*R*)-**5**, 29393-17-7; (*S*)-**5**, 21869-55-6; (*S*)-**5** (tosylhydrazone), 105183-81-1; (±)-**5**-d_1, 105183-82-2; *trans* (*R*)-**6**, 35666-69-4; *cis* (*R*)-**6**, 79646-46-1; (*R*)-**7**, 105183-83-3; (*S*)-**7**, 105183-84-4; (*R*)-**8**, 67110-72-9; PhI, 591-50-4; phthalic anhydride, 85-44-9; (*S*)-3-methyl-2-butanol, 1517-66-4; 3-methyl 3-buten-2-one, 814-78-8; (*R*)-3-pentyn-2-ol, 57984-70-0.

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