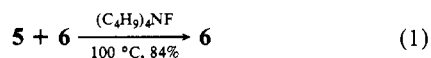


Table II. Solvent Dependence of Pd-Catalyzed Silylation of 4

entry	catalyst	solvent	time, h	5:6 ratio	yield, %
1	(Ph ₃ P) ₄ Pd	THF	3	64:36	78
2	(Ph ₃ P) ₄ Pd	CH ₃ CN	20	42:58	58
3	(Ph ₃ P) ₄ Pd	DME	2	35:65	85
4	(Ph ₃ P) ₄ Pd	PhH	2	35:65	78
5	(Ph ₃ P) ₄ Pd	ether	2	9:91	86
6	(Ph ₃ P) ₄ Pd	C ₂ H ₅ OAc	2	8:92	83
7	2Ph ₃ P + Pd(OAc) ₂	THF	3	34:66	68
8	2Ph ₃ P + Pd(OAc) ₂	PhH	2	18:82	78
9	none	THF	20		0
10	none	PhH	72	0:100	57

to elimination product.

In contrast to the Mo reactions, the regioselectivity of the Pd-catalyzed reactions proved sensitive to reaction conditions. As Table II shows, the regiochemistry depended upon solvent although no discernible trend is obvious. That the nature of the ligands on palladium plays a major role is readily seen by comparing entries 1 and 7 (Table II), where by changing the type of palladium catalyst, opposite regioselectivity is obtained.¹⁰ That the introduction of the Me₃Si group into the more hindered position can be synthetically useful is especially demonstrated in the case of allyl acetate **9** (Table I, entry 9).⁹ Obtention of the silane at the less substituted carbon can be accomplished in one of three ways: (1) use of 2Ph₃P + Pd(OAc)₂ in PhH for the silylation reaction; (2) use of Mo(CO)₆ in PhCH₃ for the silylation reaction; (3) fluoride-initiated isomerization of a regioisomeric mixture according to eq 1.¹¹



The two catalysts give stereochemically complementary results (Table I, entry 7); in particular the Pd catalyst gives net inversion, but the Mo catalyst gives net retention—a most unusual result considering their similarity in stereochemical course with carbon nucleophiles. If it is assumed that the initial ionization proceeds with inversion,^{6,7} then the Me₃Si group first undergoes transmetalation from Al to Pd and then transfer to carbon¹² but directly transfers to carbon with the Mo catalyst. The stereochemistry of **7** and **8** rests on the ¹³C NMR data since it has been observed that the methyl carbon of an axial Me₃Si group resonates at lower field than an equatorial Me₃Si group.¹³ High diastereoselectivity was also noted with **9**, which, being essentially a single diastereomer, translates into a single diastereomer of **10** (mp 159–161 °C, unrecrystallized).

The chemoselectivity of this method is particularly noteworthy.¹⁴ In Table I, entries 1–3, 5–7, and 9 show that acetals, esters, enones, and isolated double bonds are unreactive. To our knowledge, none of the current methods for converting allyl derivatives to allylsilanes possesses this range of chemoselectivity. The results also illustrate that great flexibility exists in modifying the nature of the coupling process by choice of catalyst. Considering the possible complications such as the transition-metal-catalyzed coupling of allylsilanes with allyl acetates,¹⁵ the efficiency and selectivity of this process is especially noteworthy. Thus, the simply available tris(trimethylsilyl)aluminum combined with transition metals offers a valuable approach for introduction of a Me₃Si group into organic molecules.

Acknowledgment. We thank the National Science Foundation for their generous support of our programs and NSERC of Canada

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Registry No. **1**, 65343-66-0; **2**, 85956-58-7; (*E*)-**3**, 78055-70-6; (*Z*)-**3**, 78055-72-8; **5**, 85956-59-8; (*E*)-**6**, 71442-90-5; (*Z*)-**6**, 71443-03-3; **7**, 85956-60-1; **8**, 85956-61-2; **9**, 85994-21-4; **10**, 85956-63-4; **11**, 85956-64-5; (CH₃O)₂CH(CH₂)₈CH(TMS)CH=CH₂, 85956-65-6; (CH₃O)₂CH(CH₂)₈CH=CHCH₂TMS, 85956-66-7; CH₂=C(Br)CH₂OAc, 63915-88-8; (CH₃)₂C=CHCH₂CH₂C(CH₃)(OAc)CH=CH₂, 115-95-7; (CH₃)₂C=CHCH₂CH₂C(CH₃)=CHCH₂OAc, 16409-44-2; **4**, 22616-16-6; (CH₃O)₂CH(CH₂)₈CH(OAc)CH=CH₂, 85956-69-0; (Ph₃P)₄Pd, 14221-01-3; Pd(OAc)₂, 3375-31-3; Mo(CO)₆, 13939-06-5; THF, 109-99-9; CH₃CN, 75-05-8; DME, 110-71-4; PhH, 71-43-2; C₂H₅OAc, 141-78-6; CH₂C(Br)CH₂TMS, 81790-10-5; [3-(1-cyclohexen-4-yl)-2-methyl-2-propenyl]trimethylsilane, 85956-62-3; 5-α-3-[2-(trimethylsilyl)ethylidene]cholestanol, 85956-67-8; 5-α-3-ethenylcholestan-2-ene, 77192-26-8; 5-α-3-ethenylcholestan-3-ene, 85956-68-9; α-(1-methylethenyl)-3-cyclohexene-1-methanol acetate, 85390-70-1; methyl *cis*-5-(acetoxyl)-3-cyclohexen-1-carboxylate, 60729-55-7; 5-α-3-(acetoxyl)-3-ethenylcholestanol, 85390-73-4; ether, 60-29-7.

Indirect Measurement of Scalar Spin-Spin Coupling between Chemically Equivalent Hydrogen Nuclei

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Accurate measurements of all scalar (*J*) coupling constants between nuclear spins are very important for studies of molecular conformations. Since coupling between chemically (and magnetically) equivalent hydrogen nuclei does not appear in ¹H NMR spectra, a special measuring procedure was developed.^{1,2} It is based on the fact that isotopic labeling removes magnetic equivalence and the *J* coupling shows up in the fine splitting of satellite lines arising from natural abundance ¹³C spins. The present communication describes an alternative technique that utilizes correlated motion of ¹³CH spin pairs.^{3,4}

The new pulse sequence is depicted in Figure 1. It combines polarization transfer⁵ with evolution of the spin system in the doubly rotating frame. Since precession resulting from the chemical shift has to be refocused at the last π/2(*y*) pulse for ¹H spins and at the beginning of data acquisition for ¹³C spins, refocusing π pulses cannot be applied simultaneously. Evolution from *J* coupling becomes opposite between the π pulses, and the total evolution period is not *t*₁ + 2τ but only *t*₁. This technical detail has no significant influence on the behavior of the spin system. Description is simplified by assuming that precession resulting from chemical shift is suitably refocused and that only *J* coupling has to be considered.

The initial ¹H π/2(*x*) pulse turns equilibrium proton magnetization of CH groups from the *z* to *y* direction of the rotating reference frame. Due to coupling with ¹³C nuclei in the up (\bar{C}_a^0) or down (\bar{C}_b^0) state proton spins are divided into two groups (\bar{H}_a^0 and \bar{H}_b^0), which start to precess in opposite directions. During the time τ = 1/(2¹J_{CH}) magnetization is split into $\bar{M}_{H_a}^0$ and $\bar{M}_{H_b}^0$ along ±*x*. At this moment ¹³C π/2(*x*) pulse is applied, and the attached ¹³C spins are also brought into the *xy* plane of the rotating frame.

[†] On leave of absence from J. Stefan Institute, Ljubljana, Yugoslavia.

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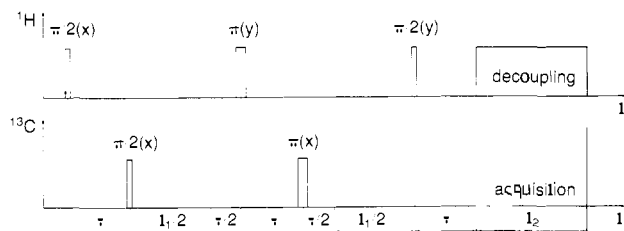


Figure 1. Schematic representation of the pulse sequence that utilizes correlated motion of ^{13}CH spin pairs for indirect detection of long-range J coupling constants.

Subsequent motion of ^{13}CH spin pairs becomes correlated.³ If one of H_a spins flips over, the attached carbon C_a must also have flipped over and the proton spin starts to behave exactly as a H_b spin. Because of this mutual flipping, the net magnetization vectors should not change during the evolution period t_1 .

The above conclusion holds only for "isolated" spin pairs which experience one-bond coupling $^1J_{\text{CH}}$ used to establish correlated motion.³ In most real molecules long-range couplings are present, and they have a small but steady influence on both ^1H and ^{13}C spins.⁴ The effect becomes apparent when the $\pi/2(y)$ pulse turns protons back into the $\pm z$ directions. The correlated motion is quenched and ^{13}C components establish phase coherence during the last period.⁶ Signals are detected if (i) ^{13}C magnetization is present (\bar{M}_{C_a} and \bar{M}_{C_b}) and (ii) attached protons are found with suitable orientations (\bar{M}_{H_a} and \bar{M}_{H_b}).

As an illustration *cis*-dichloroethylene is described. It contains two chemically equivalent hydrogens that give rise to a single sharp peak in the ordinary ^1H NMR spectrum. Equivalence is removed in ^{13}C spectroscopy, which detects signals from $\text{ClH}^{13}\text{C}=\text{CHCl}$ molecules, and the ^{13}CH spin pairs are coupled to the proton spin in the ^{12}CH group.

During the evolution period t_1 magnetization of ^1H spins oscillates along $\pm x$ as

$$M_{\text{H}_a} = M^0_{\text{H}_a} \cos(\pi^3 J_{\text{HH}} t_1) \quad (1)$$

$$M_{\text{H}_b} = M^0_{\text{H}_b} \cos(\pi^3 J_{\text{HH}} t_1) \quad (2)$$

where $^3J_{\text{HH}}$ denotes coupling between ^1H spins and t_1 is the effective evolution period in the pulse sequence (Figure 1). ^{13}C spins also experience two-bond coupling $^2J_{\text{CH}}$ and

$$M_{\text{C}_a} = M^0_{\text{C}_a} \cos(\pi^2 J_{\text{CH}} t_1) \quad (3)$$

$$M_{\text{C}_b} = M^0_{\text{C}_b} \cos(\pi^2 J_{\text{CH}} t_1) \quad (4)$$

therefore, the signal $s(t_1)$ is proportional to

$$s(t_1) = s_0 \cos(\pi^2 J_{\text{CH}} t_1) \cos(\pi^3 J_{\text{HH}} t_1) \quad (5)$$

where $s_0 = s(t_1 = 0)$ denotes signal amplitude. After rearrangement

$$s(t_1) = \frac{1}{2} s_0 \{ \cos[\pi(2J_{\text{CH}} + ^3J_{\text{HH}})t_1] + \cos[\pi(2J_{\text{CH}} - ^3J_{\text{HH}})t_1] \} \quad (6)$$

it becomes evident that Fourier transformation with respect to t_1 reveals resonances at frequencies $\pm \frac{1}{2}(2J_{\text{CH}} + ^3J_{\text{HH}})$ and $\pm \frac{1}{2}(2J_{\text{CH}} - ^3J_{\text{HH}})$, while $^1J_{\text{CH}}$ has been eliminated by the correlated motion.³

Equation 6 was used to calculate $^2J_{\text{CH}} = 15.8 \pm 0.1$ Hz and $^3J_{\text{HH}} = 5.2 \pm 0.1$ Hz from Figure 2. The same experiment on *trans*-dichloroethylene gave $^3J_{\text{HH}} = 12.1 \pm 0.1$ Hz and $^2J_{\text{CH}} < 0.2$ Hz. The results are in agreement with previous measurements via ^{13}C satellites in ^1H NMR spectra.^{1,7,8}

The new method has serious disadvantages, because it needs detection of weaker ^{13}C signals, two-dimensional data processing,

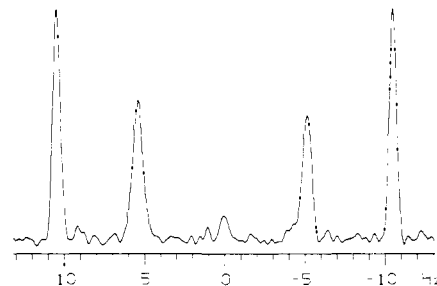


Figure 2. Cross section of the NMR spectrum of *cis*-dichloroethylene as obtained by the pulse sequence from Figure 1 and after the Fourier transformation with respect to the evolution time t_1 which has been incremented in steps of 38 ms. Presaturation⁹ of the ^{13}C spin system and phase alternations¹⁰ of the last proton pulse [$\pi/2(y)$ add and $\pi/2(-y)$ subtract] ensured that all signals were due to polarization transfer.

and ^{13}CH spin pairs as "probes"; therefore, it can not become a universal way for measuring J coupling between chemically equivalent hydrogen nuclei. On the other hand two very important advantages must be pointed out:

(i) π pulses refocus precession resulting from inhomogeneous magnetic field, and resolution of the experiment is limited only by natural line widths.

(ii) Overlap of satellite and main peaks occurs very often in complex ^1H NMR spectra, and determination of the J coupling becomes impossible. The new pulse sequence solves this problem.

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Photocatalytic Formylation of Primary and Secondary Amines on Irradiated Semiconductor Powders

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Although amines have been often used as sacrificial single-electron donors in many photoinduced redox studies, little is known of the chemical fate of the oxidized species so generated. We report here the identity of products formed by photocatalytic oxidation of a primary and a secondary aliphatic amine on irradiated TiO_2 powders suspended in oxygenated acetonitrile. These experiments represent the first characterizations of solution-phase aliphatic amine photooxidations sensitized by a heterogeneous metal oxide catalyst.

By use of previously described procedures,¹ *N*-methyl-4-phenylbutylamine (**1a**) and its demethylated analogue **1b** were catalytically photooxidized. The major products obtained were the respective *N*-formylation (**2**) and α -C-N oxidative cleavage (**3**) products (eq 1 and 2). Smaller amounts of other cleavage products were also formed.² The relative amounts of the two

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