generalizations can be drawn. The method is most successful for primary alcohols. The approximate rates of oxidation suggest that the process is sensitive to steric factors and relatively insensitive to electronic features such as an allylic double bond. Secondary alcohols are driven to completion in a reasonable time (12–18 h) only with a full equivalent of **1**. The diol in entry 8 is oxidized preferentially at the primary hydroxyl and is subsequently converted to the lactone, presumably via the cyclic hemiacetal. At the same time, the presence of 10 mol equiv of water in the electrolysis medium does not lead to further oxidation of aldehydes to acids. Benzylic primary alcohols react particularly fast, producing turnover numbers in excess of 40 (e.g., entry 4, 0.05 mol equiv of **1**). At least 0.2 mol equiv of **1** (10 turnovers) is needed for complete conversion of typical aliphatic alcohols.

The compatibility of the electrochemical system with other functional groups should be high,[9] but little is known about the functional group compatibility of **2**. We find that a 1:1 mixture of *n*-dodecanol and thioanisole under the conditions of entry 1 in Table I produces *n*-dodecanal (90%) and recovered thioanisole (>90%). However, entries 7 and 9 suggest *intra*molecular selectivity is less efficient.

An equimolar mixture of 1-dodecanol and 5-dodecanol under the conditions of entry 1 of Table I leads to complete conversion of the primary alcohol (83% yield of *n*-dodecanal) and <3% yield of the ketone (93% recovery of the secondary alcohol). This selectivity for primary over secondary alcohols is also easily demonstrated in the intramolecular test cases, **4**–**7**.[20] Table II displays results with diol substrates that were chosen to test for the steric effect of α- and β-methyl substituents and the allylic double bond.[21] In the competition of simple primary vs. secondary (**4**, **5**) selectivity for the primary site is nearly quantitative. In the more difficult test of primary vs. secondary allylic (**6**, **7**), catalytic electrooxidation at 25 °C shows a good preference for the primary hydroxyl, but oxidation of both hydroxyls is significant even at just 90% conversion for **6** and 75% conversion for **7**. At −40 °C with preformed **2** in equivalent amount, better selectivity is observed, allowing isolation of (*E*)-8-hydroxy-2-methylnon-6-enal in 58% yield (63% when corrected for **7** not reacted). We are unaware of other methods that produce comparable selectivity.[22,23] Work is in progress to devise nitroxyl catalysts with better turnover numbers and to further define the scope and origins of the selectivity.

Acknowledgment. Financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowled. We thank Professor Andrew Bocarsly (Princeton) for technical suggestions.

Registry No. 4, 61448-29-1; **4A**, 85926-51-8; **5**, 85926-47-2; **5A**, 85926-52-9; **5B**, 85926-53-0; **6**, 85926-48-3; **6A**, 85926-54-1; **6B**, 85926-55-2; **6C**, 85926-56-3; **7**, 85926-49-4; **7A**, 85926-57-4; **7C**, 79971-12-3; benzenepropanol, 122-97-4; 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanemethanol, 5617-92-5; 4-methoxybenzenemethanol, 105-13-5; 2-hexen-1-ol, 2305-21-7; 4-*tert*-butylbenzenemethanol, 877-65-6; 3-(phenylthio)propanol, 24536-40-1; 2-hydroxycyclohexaneethanol, 24682-42-6; 1,5-dithiaspiro[5.5]undecane-7-ethanol, 85926-46-1; TEMPO, 2564-83-2; benzenepropanol, 104-53-0; 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxaldehyde, 7427-85-2; 4-methoxybenzaldehyde, 123-11-5; 2-hexenal, 505-57-7; 4-*tert*-butylbenzaldehyde, 939-97-9; 3-(phenylthio)propanal, 27098-65-3; octahydrobenzofuran-2-one, 6051-03-2; 1,5-dithiaspiro[5.5]undecane-7-ethanal, 85926-50-7; dodecanol, 112-53-8; dodecanal, 112-54-9.

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[20] The synthesis of diols **4–7** follows that previously reported: Stork, G.; Shiner, C. S.; Winkler, J. D. *J. Am. Chem. Soc.* **1982**, *104*, 310.

[21] A pure sample of each of the products A–C from each of the diols **4–7** was prepared, fully characterized, and used for calibration of GLPC analysis of the electrooxidation procedure. The electrooxidations were carried out according to the typical procedure.[15]

[22] Catalytic oxidation using PtO_2 and oxygen is an effective method for oxidation of primary alcohols in the presence of secondary. However, the process is not generally effective at producing simple aldehydes. Further oxidation to carboxylic acids or lactones is the most effective application. (a) Heyns, K.; Paulsen, H. In "Newer Methods of Preparative Organic Chemistry"; Academic Press: New York, 1963; Vol. 2, pp 303 ff. For specific recent applications in lactone synthesis, see: (b) Lansbury, P. T. Hangauer, D. G.; Vacca, J. P. *J. Am. Chem. Soc.* **1980**, *102*, 3964. (c) Kretchmer, A.; Thompson, W. J. *Ibid.* **1976**, *98*, 3379. (d) Fried, J.; Sih, J. C. *Tetrahedron Lett.* **1973**, 3899.

[23] A recent report describes an oxidation procedure that is effective for primary alcohols in the presence of secondary. A test of primary vs. allylic secondary was not included. the system requires stoichiometric amounts of the oxidizing agent tris(triphenylphosphine)trichlororuthenium(II). Tomioka, N.; Takai, K.; Oshima, K.; Nozak, H. *Tetrahedron Lett.* **1981**, *22*, 1605–1608.

Tris(trimethylsilyl)aluminum and Transition-Metal Catalysts. Silylation of Allyl Acetates

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Received February 25, 1983

The burgeoning use of allylsilanes as synthetic intermediates[1] opens the question of their methods of preparation.[2–4] In attempting to synthesize new conjunctive reagents, we sought a method to effect an "umpolung" of allyl acetates, i.e., to convert these electrophilic partners into nucleophilic ones by transforming them into allylsilanes. Limitations associated with generating trimethylsilylcuprates[3] led us to examine tris(trimethylsilyl)aluminum (**1**)[5] as an alternative. Unfortunately, direct reaction of allyl acetates with **1** normally proceeded very slowly, if at all, at room temperature and was accompanied by substantial elimination at elevated temperature. We report that palladium[6] and molybdenum[7] catalysts facilitate the transfer of the trimethylsilyl residue from aluminum to carbon with surprising regioselectivity and the first example of the use of "hard" nucleophiles in molybdenum-catalyzed coupling.

The reactions were very simple to perform. In a palladium-catalyzed reaction, an aliquot of a standardized pentane solution of $(Me_3Si)_3Al$·etherate[8] (0.5 mol) was added to a solution of 1.0 mol of allyl acetate and 4–6 mol % of the palladium catalyst in benzene or THF. After being stirred at room temperatue or below

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[1] For reviews see: Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761. Sakurai, H. *Pure Appl. Chem.* **1982**, *54*, 1. Fleming, I. *Comp. Org. Chem.* **1979**, *3*, 539. Magnus, P. D.; Sarkar, T.; Djuric, S. *Comp. Organom. Chem.* **1982**, *7*, 515.

[2] Hayashi, T.; Konishi, M.; Ito, H.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 4962. Hosomi, A.; Iguchi, H.; Sakurai, H. *Chem. Lett.* **1982**, 223. Negishi, E.; Luo, F.-T.; Rand, C. L. *Tetrahedron, Lett.* **1982**, *23*, 27. Tzeng, D.; Weber, W. P. *J. Org. Chem.* **1981**, *46*, 265. Nishiyama, H.; Narimatsu, S.; Itoh, K. *Tetrahedron Lett.* **1981**, *22*, 5289. Hosomi, A.; Sakurai, H. *Ibid.* **1978**, 2589. Pillot, J.-P.; Dunogues, J.; Calas, R. *Ibid.* **1976**, 1871. Biran, C.; Duffaut, N.; Dunogues, J.; Calas, R. *J. Organomet. Chem.* **1975**, *91*, 279. Also see: Fleming, I.; Paterson, I. *Synthesis* **1979**, 446.

[3] Ager, D. J.; Fleming, I.; Patel, S. K. *J. Chem. Soc., Perkin, Trans. 1* **1981**, 2520. Fleming, I.; Newton, T. W.; Roessler, F. *Ibid.* **1981**, 2527. Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1982**, *104*, 3733.

[4] For a Pd-catalyzed coupling of allyl chloride with a disilane see: Matsumoto, H.; Yako, T.; Nagashima, S.; Motegi, T.; Nagai, Y. *J. Organomet. Chem.* **1978**, *148*, 97. Attempts to extend this reaction to allyl acetates or substituted allyl halides has thus far failed in our hands.

[5] Roesch, L.; Altnau, G. *J. Organomet. Chem.* **1980**, *195*, 47. Roesch, L. *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 480. Roesch, L. Altnau, G.; Otto, W. H. *Ibid.* **1981**, *20*, 581. Altnau, G.; Roesch, L.; Bohlmann, F.; Lonitz, M. *Tetrahedron Lett.* **1980**, *21*, 4069.

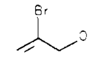
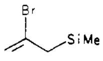
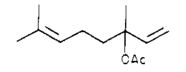
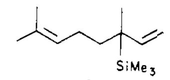
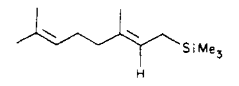
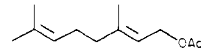
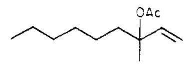
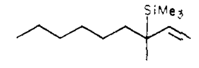
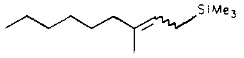
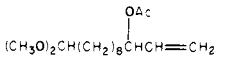
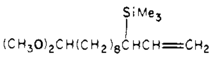
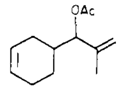
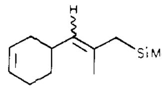
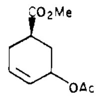
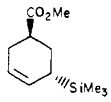
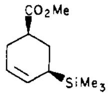
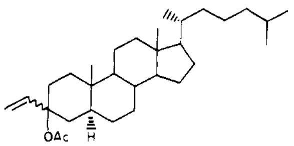
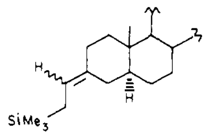
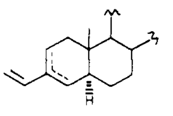
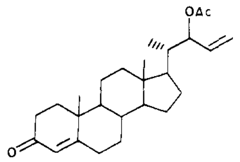
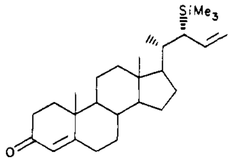
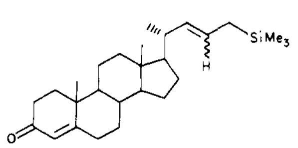
[6] Trost, B. M. *Pure Appl. Chem.* **1981**, *53*, 2357. Trost, B. M.; Verhoeven, T. R. *Comp. Organomet. Chem.* **1982**, *8*, 799. Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385. Tsuji, J. "Organic Synthesis with Palladium Compounds"; Springer-Verlag: Berlin, 1980. Tsuji, J. *Adv. Organomet. Chem.* **1979**, *17*, 141.

[7] Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1982**, *104*, 5543.

[8] Prepared according to ref 5 from aluminum powder and granular aluminum activated by adding iodine in ether and then adding mercury and trimethylchlorosilane. After completion, filtration, and removal of ether, the solid residue was stirred with pentane and filtered to form the stored solutions. These solutions were conveniently titrated by adding an aliquot to a known excess of iodine in toluene and back-titrating the excess iodine with sodium thiosulfate.

0002-7863/83/1505-4494$01.50/0

Table I. Metal-Catalyzed Coupling of 1 and Allyl Acetates

entry	allyl acetate	catalyst	solvent	temp, °C, time, h	product(s)[a]		yield,[j] %
1		$(Ph_3P)_4Pd$	THF	0, 0.5			87[k]
2					 2	 3	
		(a) $(Ph_3P)_4Pd$	THF	rt,[m] 2	61	39[b]	86
		(b) $2Ph_3P$, $Pd(OAc)_2$	PhH	rt, 4.5	19	81[c]	70
		(c) $Mo(CO)_6$	$PhCH_3$	reflux, 2		100[d]	72
3		(a) $(Ph_3P)_4Pd$	THF	rt, 20	55	45[e]	69
		(b) $2Ph_3P$, $Pd(OAc)_2$	PhH	rt, 24	29	71[f]	58
4	 4				 5	 6	
		(a) $(Ph_3P)_4Pd$	THF	rt, 3	64	36[g]	73-83
		(b) $2Ph_3P$, $Pd(OAc)_2$	PhH	rt, 2	18	82[g]	78
		(c) $Mo(CO)_6$	$PhCH_3$	reflux, 2.5		100[h]	65
5	 $(CH_3O)_2CH(CH_2)_8\overset{OAc}{CH}CH{=}CH_2$				 $(CH_3O)_2CH(CH_2)_8\overset{SiMe_3}{C}HCH{=}CH_2$	$(CH_3O)_2CH(CH_2)_8CH{=}CHCH_2SiMe_3$	
		(a) $(Ph_3P)_4Pd$	THF	rt, 2	76	24	65
		(b) $2Ph_3P$, $Pd(OAc)_2$	PhH	rt, 3	45	55	63
6		$Mo(CO)_6$	$PhCH_3$	reflux, 20			66
7					 7	 8	
		(a) $(Ph_3P)_4Pd$	THF	rt, 20	72	28	42
		(b) $(Ph_3P)_4Pd$	PhH	rt, 2	75	25	56
		(c) $Mo(CO)_6$	$PhCH_3$	reflux, 8	30	70	42
8							
		$Mo(CO)_6$	$PhCH_3$	reflux, 0.6	78	22	83[l]
9	 9				 10	 11	
		$(Ph_3P)_4Pd$	THF	−78, 0.2 0, 1 rt, 3	82	18	76

[a] All products have been fully characterized by spectral means and elemental compositions determined by high-resolution mass spectroscopy. [b] $E:Z = 1:1$. [c] $E:Z = 3:2$. [d] $E:Z = 2:1$. [e] $E:Z = 4:1$. [f] >95% E. [g] $E:Z = 3:2$. [h] $E:Z = 2:1$. [i] $E:Z = 2.5:1$. [j] All yields are for isolated pure product unless otherwise noted. [k] Yield determined by VPC. [l] The yield corresponds to the unseparable mixture of diene and allyl silane. [m] Room temperature.

for 0.5–24 h, the reaction was quenched with water, extracted with ether, and purified. In a molybdenum-catalyzed reaction, 1 mol of allyl acetate was added to a solution of 0.75 mol of $(Me_3Si)_3Al$·etherate in toluene. After addition of 10 mol % of $Mo(CO)_6$, the reaction was refluxed for 0.6–20 h and worked up as above. Table I summarizes the results.

The most striking aspect of the results is the dependence of the regiochemistry on the nature of the catalyst and solvent. The molybdenum catalyst invariably introduces the silyl group at the less hindered end of the allyl group (entries 2c, 4c, and 6).[9] To demonstrate the role of the molybdenum catalyst, subjection of **4** to the aluminum reagent **1** in the absence of catalyst led mostly

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(9) The regiochemistry and stereochemistry is readily assigned on the basis of the NMR spectral data. Ratios are verified by VPC analysis using a 2.13 m × 0.16 cm SE-30 column. For example, **5** shows characteristic NMR absorptons at δ 0.95 (s, 3 H), 4.67 (dd, J = 17, 2 Hz, 1 H), 4.90 (dd, J = 11, 2 Hz, 1 H), and 5.76 (dd, J = 17, 11 Hz, 1 H), and **6** shows the vinyl methyl groups at δ 1.52 (E isomer) and 1.65 (Z isomer). In the case of **10** it shows δ −0.03 (s, 9 H), 0.69 (s, 3 H), 0.98 (d, J = 7 Hz, 3 H), 1.15 (s, 3 H), 4.85 (m, 2 H), 5.73 (m, 1 H), 5.70 (s, 1 H).

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

entry	catalyst	solvent	time, h	5:6 ratio	yield, %
1	$(Ph_3P)_4Pd$	THF	3	64:36	78
2	$(Ph_3P)_4Pd$	CH_3CN	20	42:58	58
3	$(Ph_3P)_4Pd$	DME	2	35:65	85
4	$(Ph_3P)_4Pd$	PhH	2	35:65	78
5	$(Ph_3P)_4Pd$	ether	2	9:91	86
6	$(Ph_3P)_4Pd$	C_2H_5OAc	2	8:92	83
7	$2Ph_3P + Pd(OAc)_2$	THF	3	34:66	68
8	$2Ph_3P + Pd(OAc)_2$	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 Me_3Si 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 $2Ph_3P + Pd(OAc)_2$ in PhH for the silylation reaction; (2) use of $Mo(CO)_6$ in $PhCH_3$ for the silylation reaction; (3) fluoride-initiated isomerization of a regioisomeric mixture according to eq 1.[11]

$$\mathbf{5} + \mathbf{6} \xrightarrow[100\ °\mathrm{C},\ 84\%]{(C_4H_9)_4NF} \mathbf{6} \qquad (1)$$

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 Me_3Si group first undergoes transmetalation from Al to Pd and then transfer to carbon[12] but directly transfers to carbon with the Mo catalyst. The stereochemistry of **7** and **8** rests on the ^{13}C NMR data since it has been observed that the methyl carbon of an axial Me_3Si group resonates at lower field than an equatorial Me_3Si 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 Me_3Si group into organic molecules.

Acknowledgment. We thank the National Science Foundation for their generous support of our programs and NSERC of Canada for a predoctoral fellowship for M.L. We gratefully acknowledge generous supplies of palladium salts from Johnson Matthey and Englehardt Industries and of molybdenum hexacarbonyl from Pressure Chemical Co. and Climax Molybdenum Co. of MI.

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; $(CH_3O)_2CH(CH_2)_8CH(TMS)CH{=}CH_2$, 85956-65-6; $(CH_3O)_2CH(CH_2)_8CH{=}CHCH_2TMS$, 85956-66-7; $CH_2{=}C(Br)CH_2OAc$, 63915-88-8; $(CH_3)_2C{=}CHCH_2CH_2C(CH_3)(OAc)CH{=}CH_2$, 115-95-7; $(CH_3)_2C{=}CHCH_2CH_2C(CH_3){=}CHCH_2OAc$, 16409-44-2; **4**, 22616-16-6; $(CH_3O)_2CH(CH_2)_8CH(OAc)CH{=}CH_2$, 85956-69-0; $(Ph_3P)_4Pd$, 14221-01-3; $Pd(OAc)_2$, 3375-31-3; $Mo(CO)_6$, 13939-06-5; THF, 109-99-9; CH_3CN, 75-05-8; DME, 110-71-4; PhH, 71-43-2; C_2H_5OAc, 141-78-6; $CH_2C(Br)CH_2TMS$, 81790-10-5; [3-(1-cyclohexen-4-yl)-2-methyl-2-propenyl]trimethylsilane, 85956-62-3; 5-α-3-[2-(trimethylsilyl)ethylidene]cholestane, 85956-67-8; 5-α-3-ethenylcholest-2-ene, 77192-26-8; 5-α-3-ethenylcholest-3-ene, 85956-68-9; α-(1-methylethenyl)-3-cyclohexene-1-methanol acetate, 85390-70-1; methyl *cis*-5-(acetoxy)-3-cyclohexen-1-carboxylate, 60729-55-7; 5-α-3-(acetoxy)-3-ethenylcholestane, 85390-73-4; ether, 60-29-7.

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

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Received February 14, 1983

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 ^{13}C spins. The present communication describes an alternative technique that utilizes correlated motion of ^{13}CH spin pairs.[3,4]

The new pulse sequence is depicted in Figure 1. It combines polarization transfer[5] 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 $\pi/2(y)$ pulse for ^1H spins and at the beginning of data acquisition for ^{13}C 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 $t_1 + 2\tau$ 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 $\pi/2(x)$ pulse turns equilibrium proton magnetization of CH groups from the z to y direction of the rotating reference frame. Due to coupling with ^{13}C nuclei in the up ($\vec{C}^0{}_a$) or down ($\vec{C}^0{}_b$) state proton spins are divided into two groups ($\vec{H}^0{}_a$ and $\vec{H}^0{}_b$), which start to precess in opposite directions. During the time $\tau = 1/(2\,^1J_{CH})$ magnetization is split into $\vec{M}^0{}_{H_a}$ and $\vec{M}^0{}_{H_b}$ along $\pm x$. At this moment ^{13}C $\pi/2(x)$ pulse is applied, and the attached ^{13}C spins are also brought into the xy plane of the rotating frame.

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