TABLE II

DOUBLE-BOND STRETCHING ABSORPTION OF ALLYL–X COMPOUNDS

X	ν, cm⁻¹ Ether	Tetrahydrofuran	
HgC_3H_5			1620[a]
MgC_3H_5	1577[b,c]	1568[b,c]	
MgBr[d]	1588	1570	
MgCl[d]	1580	1565	
Li[e]	1540[f]	*f*	1542[g]
Na[h]			1535[g]

[a] Perkin-Elmer 237, 0.1-mm NaCl cells in CCl_4 solution. [b] Beckman IR-7, 0.1-mm IRTRAN-2 cells. [c] G. Wilke and P. Heimbach [*Angew. Chem. Intern. Ed. Engl.*, **5**, 151 (1966)] cite an unpublished value of 1575 cm⁻¹. [d] C. Prevost and B. Grosse, *C. R. Acad. Sci., Paris*, **252**, 1023 (1961). [e] D. Seyferth and M. Weiner, *J. Org. Chem.*, **26**, 4797 (1961). [f] Reported as 1525–1540 cm⁻¹ in ref 3a. [g] Nujol mull. [h] E. J. Lanpher, *J. Amer. Chem. Soc.*, **79**, 5578 (9957).

the values for covalent diallylmercury and ionic allyllithium (see Table II). In any case, it should be clear that rotation around all of the C—C and C=C bonds of the species which comprise diallylmagnesium is extremely facile.

Experimental Section

Diallylmercury, bp 59–60.5° (0.75 mm), was prepared in 61% yield from allylmagnesium bromide (75–90%)[9] following literature directions.[10]

Diallylmagnesium.—Equivalent quantities of triply sublimed magnesium (0.0106 mol) and diallylmercury (0.010 mol) were stirred in 25 ml of dry ether in a nitrogen atmosphere at room temperature. A white precipitate of insoluble diallylmagnesium and metallic mercury began to form at once. After 2 hr, the reaction appeared to be complete and the colorless supernatant showed the presence of diallylmagnesium from its infrared spectrum but was too dilute to give satisfactory proton nmr spectra.

Diallylmercury (0.01 mol) reacted with magnesium (0.0106 g atom) in dry tetrahydrofuran (10.0 ml) to give a solution of diallylmagnesium. The reaction was not complete after 3.0 hr, therefore an excess of magnesium was added and the mixture was stirred overnight. Several samples of the resulting solution were placed in thick-walled nmr tubes, diluted with freshly distilled dry tetrahydrofuran and sealed. Concentrations ranged from 0.28 to 1.00 *M* and the chemical shifts were concentration invariant over this range.

Registry No.—Diallylmagnesium, 6928-75-2.

(9) O. Grummitt, E. P. Budewitz, and C. C. Chudd in "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, pp 749–750.

(10) A. E. Borisov, I. S. Saveljeva, and S. R. Serdyuk, *Izv. Akad. Nauk SSSR, Ser. Khim*, **5**, 924 (1965). An English translation appears in *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 896 (1965)

Reductions with Organosilicon Hydrides. II. Preparation of Aldehydes from Acyl Chlorides[1a]

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In the preceding paper,[1a] the palladium-catalyzed cleavages of carbon–halogen bonds of halocarbons by organosilicon hydrides were reported. In this Note the analogous reaction with acyl chlorides performed *via* a simple procedure that may prove useful for the preparation of aldehydes is described (eq 1).

$$R_3SiH + RCOCl \xrightarrow{Pd} R_3SiCl + RCHO \qquad (1)$$

TABLE I

10% PALLADIUM–CHARCOAL-CATALYZED REACTIONS OF TRIETHYLSILANE WITH ACYL CHLORIDES

Acyl halide	Procedure[a]	Yield of 2,4-DNPH, % Crude	Recrystallized
CH_3COCl	A	Reacts[b]	
CH_3CH_2COCl	C	0	
n-C_3H_7COCl	A	65	59
$(CH_3)_2CHCOCl$	E	0	
$CH_3CH_2CH(CH_3)COCl$	D	0	
$(CH_3)_2CHCOBr$	A	71	65
$(CH_3)_3CCOCl$	E	9	5
n-$C_7H_{15}COCl$	B		46
C_6H_5COCl	C	70	60
o-$CH_3C_6H_4COCl$	D	28	15
o-$CH_3OC_6H_4COCl$	C	42	38
o-$CH_3OC_6H_4COCl$	E	35	30
p-$CH_3OC_6H_4COCl$	A	43	39
m-$C_6H_4(COCl)_2$[c]	E	75[d]	
$CH_3CHCHCOCl$	C	33	18
PhCHCHCOCl	D		9

[a] See Experimental Section. [b] The reaction was so violent that all of the acetaldehyde distilled. [c] An excess of Et_3SiH (15 mmol) was used for the amount of isophthaloyl chloride (5 mmol) used. [d] Isolated as the bisphenylhydrazone derivative.

Jenkins and Post[2] have reported the uncatalyzed reaction of aroyl halides with tribenzylsilane in refluxing ether, and with triethylsilane when catalyzed by $AlCl_3$, to give the corresponding halosilane and the aldehyde, the latter in 30–50% yields. However, a later study by Eaborn and Baines[3] showed that in the uncatalyzed reactions the transformations actually took place not at ether reflux, but at a much higher temperature, probably during distillation. However, the yields of aldehyde obtained by the latter workers were always less than 15%, and this was attributed to decomposition of the aldehyde in the reaction mixture at the temperatures required for the reaction (≫100°). Very high yields of the halosilanes were obtained, thus indicating that substantial amounts of the aldehyde had formed initially.

We have found that a palladium catalyst apparently drastically alters the course of the reaction, since in many cases the reaction proceeds at room temperature. The results of the palladium-catalyzed reactions of triethylsilane with various acyl chlorides are given in Table I. The aldehydes were isolated as their 2,4-dinitrophenylhydrazone derivatives (2,4-DNPH), after the catalyst was filtered. The yields for the unbranched aliphatic acyl chlorides are in the range 50–70%, which is higher than that reported for the corresponding reductions by $Li(t\text{-}BuO)_3AlH$[4] and comparable or slightly less than that obtained with the

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[1] (a) For the preceding paper, see J. D. Citron, J. E. Lyons, and L. H Sommer, *J. Org. Chem.*, **34**, 638 (1969). (b) To whom correspondence should be addressed: Elastomer Chemicals Department, Experimental Station, E. I. du Pont de Nemours and Co., Wilmington, Del. 19898.

[2] J. W. Jenkins and H. W. Post, *ibid.*, **15**, 556 (1950).

[3] C. E. Baines, Ph.D. Dissertation, University of Leicester, 1957. The author is indebted to Professor C. Eaborn for supplying a copy of this dissertation.

[4] H. C. Brown and B. C. Subba Rao, *J. Amer. Chem. Soc.*, **80**, 5377 (1958).

Rosenmund reaction.[5] While the low reactivity of pivaloyl chloride, $(CH_3)_3CCOCl$, isobutyryl chloride, and α-methylbutyryl chloride could be explained on steric grounds, the complete inertness of propionyl chloride was unexpected. A subtle change in steric requirements may cause a specific poisoning effect, but other factors such as traces of foreign catalyst poisons cannot be ruled out. Use of acyl bromides as illustrated by isobutyryl bromide may permit isolation of α-branched aldehydes.

The aroyl chlorides gave yields in the 40–70% range, which is slightly lower than either the lithium alkoxyaluminum hydride[4] or Rosenmund reductions.[5] However, it should be emphasized that the reactions are extremely easy and convenient to perform, a factor which may compensate for lower yields, especially when only small amounts of aldehyde are needed. Some care is necessary to ensure that groups which react catalytically with organosilicon hydrides such as α-halo[6] and polyhalo[1a] are not present.

Table II

10% Palladium–Charcoal-Catalyzed Reactions of Octanoyl Chloride with Organosilicon Hydrides

Silane	Procedure[a]	—Yield of 2,4-DNPH, %—	
		Crude	Recrystallized
$MeCl_2SiH$	C	0	
Me_2ClSiH	B	0	
Et_3SiH	B		46
Me_2PhSiH	E	0	
$MePh_2SiH$[b]	E	40	21[c]
Ph_2SiH_2	E	0	
$MePhClSiH$	E	24	16

[a] See Experimental Section. [b] n-C_3H_7COCl was used. [c] The melting point, 94–103.5°, indicated that this derivative was very impure.

Attempts were made to improve the yields by varying the silane (Table II), the molar ratio of the reactants (Table III), and the temperature (Table IV). It is quite apparent from Table II that Et_3SiH is the most effective reducing agent. Relatively small changes in the steric and/or electronic properties of the silane cause large, and as yet unexplained, differences in reactivity at the catalyst surface. Table III illustrates that varying the molar ratio of the reactants has little effect upon the yield of aldehyde. A small excess of either Et_3SiH or octanoyl chloride gives a slightly higher yield.

Table III

10% Palladium–Charcoal-Catalyzed Reactions of Triethylsilane with Octanoyl Chloride[a]

Molar ratio of Et_3SiH/n-$C_7H_{15}COCl$	Yield, % recrystallized 2,4-DNPH[b]
3.0:1.0	43
1.25:1.0	55
1.0:1.0	46
1.0:1.25	55
1.0:3.0	56

[a] Using procedure B. [b] Based upon deficient constituent of the reaction.

Table IV

Low Temperature 10% Palladium–Charcoal-Catalyzed Reactions of Triethylsilane with Acyl Chlorides

Acyl chloride	—Yield of 2,4 DNPH, %—	
	Crude	Recrystallized
n-C_3H_7COCl	80	74
n-$C_7H_{15}COCl$	83	75
C_6H_5COCl	46	45
o-$CH_3OC_6H_4COCl$	4	2
p-$CH_3OC_6H_4COCl$[a]	23	7

[a] Reacted at +10–15° for 2 hr.

Use of low temperatures (~−70°) at the start of the reaction appreciably increased the yield of the unbranched aliphatic aldehydes by 19–29%. However, the yields from aroyl chlorides which reacted at low temperature were decreased. This may be due to lower inherent reactivity. However, difficulty was experienced at low temperatures with these acid chlorides because they solidified. Even when p-methoxybenzoyl chloride was allowed to react at +10–15°, a lower yield was obtained.

Isolation of the aldehyde by distillation at atmospheric pressure of the filtered reaction mixture confirmed the observation[3] that little or no aldehyde could survive in this medium at higher temperatures. However, as indicated in eq 2 and 3, good yields of Et_3SiCl were obtained. In order to circumvent the decomposition, a reaction mixture was washed with water until neutral, thus hydrolyzing the chlorosilane and any residual acyl chloride. Upon vacuum distillation a yield of octanal comparable with the 55% yield of 2,4-DNPH was obtained (eq 4). Thus removal of the possible hydrogen chloride sources in the reaction mixture allows isolation of the free aldehyde.

$$Et_3SiH + PhCOCl \xrightarrow[\text{2. atm distillation}]{\text{1. 10\% Pd–C}} \underset{66\%}{Et_3SiCl} + \underset{31\%}{PhCHO} \qquad (2)$$

$$Et_3SiH + n\text{-}C_3H_7COCl \xrightarrow[\text{2. atm distillation}]{\text{1. 10\% Pd–C}} \underset{88\%}{Et_3SiCl} + \underset{<3\%}{n\text{-}C_3H_7CHO} \qquad (3)$$

$$Et_3SiH + n\text{-}C_7H_{15}COCl \xrightarrow[\substack{\text{2. H}_2\text{O wash} \\ \text{3. vacuum distillation}}]{\text{1. 10\% Pd–C}} \underset{51\%}{n\text{-}C_7H_{15}CHO} \qquad (4)$$

Experimental Section

All of the acyl chlorides were the best commerical grades and were distilled just before use. The organochlorosilanes were obtained from the Dow Corning Corp. and redistilled. Triethylsilane, dimethylphenylsilane, and methyldiphenylsilane were prepared by $LiAlH_4$ reduction of the corresponding chlorosilanes. The catalyst (10% Pd–C) was used as purchased from Matheson Coleman and Bell. All reactions were performed in a nitrogen atmosphere.

Preparation of 2,4-Dinitrophenylhydrazone Derivatives.—To 45–55 mg of 10% Pd–C was added 10 mmol of the freshly distilled acyl chlorides. The organosilicon hydride (10 mmol) was then added, and the reaction was allowed to proceed (cooling in a water bath if the temperature exceeded ~80°). In the various procedures referred to in Tables I, II, and III, the following times of reaction were used: A, 5 min; B, 15 min; C, 16–24 hr; D, 5 min (on steam bath); E, 16–24 hr (on steam bath). After the appropriate period had elapsed, 5 ml of pentane (benzene in the case of aroyl chlorides) was added, and the mixture

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[5] E. Mosettig and R. Mozingo, *Org. Reactions*, **4**, Chapter 7, 362 (1948).

[6] N. F. Orlov, R. A. Bogatkin, Z. I. Sergeeva, and M. G. Voronkov, *Zh. Obshch. Khim.*, **33**, 1934 (1963); N. F. Orlov and L. N. Slezar, *ibid.*, **36**, 1078 (1966).

was filtered into either an H_3PO_4–EtOH or HCl–EtOH solution of 10 mmol of 2,4-dinitrophenylhydrazine. The derivative was filtered, dried, weighed, and recrystallized from an appropriate solvent. Yields are given in Tables I, II, and III.

Reaction of Et_3SiH with Benzoyl Chloride.—Into a 25-ml erlenmeyer flask containing 100 mg of 10% Pd–C and 6.0 ml (50 mmol) of PhCOCl was added 8.0 ml (50 mmol) of Et_3SiH. The mixture heated to 60° and some gas was evolved. After standing overnight (18 hr), the mixture was filtered and then distilled at atmospheric pressure on a $\frac{3}{8} \times 24$ in. spinning-band column. The first fraction was pure Et_3SiCl, and a total of 5.0 g (66%) of the chlorosilane, bp 142.5–147°, was isolated. The mixture was then distilled at reduced pressure to give 1.6 g (31%) of PhCHO, bp 60.5–65° (16 mm).

Reaction of Et_3SiH with Butyryl Chloride.—The procedure is similar to the preceding reaction except that the reaction mixture was filtered after 15 min. Upon distillation the first fractions, bp 89–135°, were mixtures of n-C_3H_7COCl (0.6 g), Et_3SiH (1.0 g), and n-C_3H_7CHO (0.1 g) [all estimated by infrared (ir) spectrum]. The next fractions were 5.4 g (88%, correcting for recovered Et_3SiH) of Et_3SiCl, bp 143–147°. No other material except a trace of butyric acid distilled up to a pot temperature of 205°.

Reaction of Et_3SiH with Octanoyl Chloride.—Into a 25-ml erlenmeyer flask were placed 100 mg of 10% Pd–C, 4.25 ml (25 mmol) of octanoyl chloride, and 4.8 ml (30 mmol) of Et_3SiH. After some bubbling, the temperature of the flask rose to ~100° (2 min), and it was cooled in a water bath. After 1 hr, the reaction mixture was filtered into a separatory funnel containing 20 ml of ether, 20 ml of water, and 0.21 g of $NaHCO_3$. The contents were shaken, and then the ether layer was washed with water several times over the course of 2 hr until neutral. The organic layer was dried over anhy Na_2SO_4 and then distilled under vacuum. The first fraction isolated was n-octanal, 1.63 g (51%), bp 31° (0.6 mm), $n^{23.5}D$ 1.4234.

Low Temperature Reactions.—Into a flask containing 50 mg 10% Pd–C was added 10 mmol of acid chloride. While stirring (magnetic) the mixture was cooled to $\sim -70°$ with a Dry Ice–acetone bath. Ten millimoles of Et_3SiH (in the case of aroyl chlorides the Et_3SiH was added first, owing to solidification of the acid chloride) was then added and the system was stirred for 1 hr. At the end of this time, the mixture was allowed to warm slowly (1 hr) to +10° in the acetone bath. It was allowed to stir for 15 min at room temperature and then worked up with 2,4-DNPH as above. The results are given in Table IV.

Registry No.—Triethylsilane, 617-86-7; benzoyl chloride, 98-88-4; butyryl chloride, 141-75-3; octanoyl chloride, 111-64-8.

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Activation of Manganese Dioxide by Azeotropic Removal of Water

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Manganese dioxide, once known as a relatively selective oxidant of allylic alcohols, is now viewed as a less discriminate, condition-dependent oxidizing agent. Numerous functionalities can be oxidized by various types of manganese dioxide used over a wide range of time, temperature, and solvent polarity.[1] Whereas oxidations with manganese dioxide are generally simple to perform, the reproducible preparation of the activated reagent is often difficult and time consuming. The preparation and properties of manganese dioxide activated by an expeditious and reproducible procedure are reported herein.

Precipitated manganese dioxide was prepared from solutions of manganous sulfate, sodium hydroxide, and potassium permanganate according to a modified Attenburrow procedure.[2] Following the filtration and washing steps, the wet filter cake, containing about 40–60% water, was stored in a closed bottle. Portions of the wet material were activated conveniently, as needed, by the simple expedient of azeotropic distillation of the excess water with benzene, thereby circumventing the lengthy drying and grinding procedures usually employed for activation of precipitated manganese dioxide. With adequate rates of stirring (to break up lumps) and heating, the azeotropic activation is complete in about 1 hr, leaving a dense, brownish black, rapidly sedimenting precipitate having the appearance of irregular agglomerates under the microscope. In the presence of substrate, however, the agglomerates are quickly dispersed in benzene to a blackish brown suspension of fine, slowly sedimenting particles. Reagent activated by the azeotropic method can be used directly or stored under benzene; the benzene may be replaced with another solvent by successive decantations and washings; or the reagent may be collected by filtration for storage and/or use in other solvents. Both wet filter cake and the activated reagent under benzene have been stored unchanged for more than 1 year.

Inspection of the data in Table I shows that the reagent prepared by the azeotropic method is a typical activated manganese dioxide. No effort was made to optimize yields and conditions, or to evaluate activity and substrate specificity in comparison with activated manganese dioxide prepared *via* standard procedures.[3]

Azeotropic procedures have been employed by Pratt[2,4] as a useful device for following the rates of manganese dioxide oxidations in which the by-product water is distilled into a Dean–Stark trap. The reagent used for these studies, however, had already been activated in the conventional way in a prior step.[5]

The structure of activated manganese dioxide remains an enigma.[3,6,7] Gritter, *et al.*,[3] have noted an important role for cationic impurities, and Evans[6] and Henbest[8] have pointed to the critical role for water of hydration. In the present procedure, the azeotroping serves to remove occluded (not firmly bound) water and, presumably, water adsorbed to oxidatively active

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[1] (1) For leading references, see L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," 1st ed, John Wiley & Sons, Inc., New York, N. Y., 1967, p 637.

[2] (2) E. F. Pratt and S. P. Suskind, *J. Org. Chem.*, **28**, 638 (1963).

[3] (3) Some differences in activity for various preparations of activated manganese dioxide have been demonstrated in the study of R. J. Gritter, G. D. Dupre, and T. J. Wallace, *Nature*, **202**, 179 (1964).

[4] (4) E. F. Pratt and J. F. Van de Castle, *J. Org. Chem.*, **26**, 2973 (1961); E. F. Pratt and T. P. McGovern, *ibid.*, **29**, 1540 (1964).

[5] (5) The activation procedures employed in the studies of Pratt[2,4] included a combination of some of the following steps prior to azeotroping: drying at 125° for various periods of time, grinding to pass a 60-mesh screen, redrying at 125°, equilibration with atmospheric moisture, and storing at −20° in closed containers.

[6] (6) R. M. Evans, *Quart. Rev.* (London), **13**, 61 (1959), and references cited therein.

[7] (7) W. F. Pickering, *Rev. Pure Appl. Chem.*, **16**, 185 (1966), and references cited therein.

[8] (8) H. B. Henbest, E. R. H. Jones, and T. C. Owen, *J. Chem. Soc.*, 4909 (1957); and H. B. Henbest and A. Thomas, *ibid.*, 3032 (1957).