4 protons, $=CCH_2$), 1.58 (doublet, 3 protons, CH_3); all signals showed some fine structure. Although it was possible to separate the *cis*- and *trans*-4-ethylidenecyclohexanes using a 150-ft capillary column coated with UCON 550-X, the packed column used for collecting pure *cis*- and *trans*-3-ethylidenecyclohexene was not efficient enough for collection of the pure isomers of 4-ethylidenecyclohexene. Stereochemical assignment was made by inspection of the kinetic curve of the $PtCl_2(Ph_3P)_2$–$SnCl_2$-catalyzed isomerization. It was assumed that the isomer formed in higher yield was the precursor to *trans*-3-ethylidenecyclohexene and the isomer formed in lower yield was the precursor to *cis*-3-ethylidenecyclohexene. This assumption was consistent with an experiment which showed that geometrical isomerization of the *cis*- and *trans*-4-ethylidenecyclohexenes obtained from the Ru(II)-catalyzed isomerizations was very slow relative to double bond isomerization to the 3-ethylidenecyclohexenes.

Registry No.—$RuCl_2(Ph_3P)_3$, 15529-49-4; 4-vinylcyclohexene, 100-40-3; $RuCl_2(CO)(Ph_3P_2)_2(C_4H_{12})$, 12521-89-0; allylcyclopentane, 3524-75-2; $IrCl(CO)(Ph_3P)_2$, 14871-41-1; $PtCl_2(Ph_3P)_2$, 10199-34-5; *cis*-4-ethylidenecyclohexene, 30318-84-4; *trans*-4-ethylidenecyclohexene, 30319-25-6; 5-vinylnorbornene, 3048-64-4; vinylcyclohexane, 695-12-5; vinylcyclopentane, 3742-34-5.

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The Condensation of α Olefins with Paraformaldehyde, Acetylating Agents, and Hydrogen Chloride[1]

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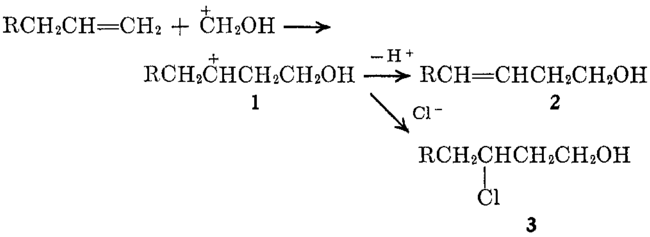
Reaction of 1-hexene, paraformaldehyde, and either acetonitrile, acetic anhydride, or acetyl chloride, with hydrogen chloride at −60 to −70° gave principally acyclic materials. The major component (30–50% yield) was identified as a *cis*- and *trans*-3-heptenyl acetate (**8**) mixture, and smaller quantities of *cis*- and *trans*-4-chloro-3-propyltetrahydropyran (**9**) and 3-chloro-1-heptyl acetate (**11**) were found. In addition, 20–40% yields of 2-chlorohexane (**4**) were obtained and minor amounts of 2-methyl-3-hexen-1-yl acetate (**7**) and 3-chloro-2-methyl-1-hexyl acetate (**10**) were separated and identified. Similar product mixtures were obtained from propylene. This procedure provides a convenient one-step synthesis of homoallylic acetates from readily available 1 olefins.

Recent articles[2-5] have described a modification of the Prins reaction in which various types of olefins were condensed with paraformaldehyde and hydrogen halides at low temperatures. The nature of the product was dependent on the structure of the starting olefin, but in each case it appeared that it was derived from initial electrophilic attack of protonated formaldehyde upon the double bond. Cyclic deprotonation[2] of the adduct **1** led to the homoallylic alcohol **2**, a precursor to other observed products, while chloride ion capture gave the corresponding 3-chloro-1-alkanol (**3**).



$$RCH_2CH{=}CH_2 + \overset{+}{C}H_2OH \longrightarrow$$

$$\underset{\mathbf{1}}{RCH_2\overset{+}{C}HCH_2CH_2OH} \xrightarrow{-H^+} \underset{\mathbf{2}}{RCH{=}CHCH_2CH_2OH}$$

$$\xrightarrow{Cl^-} \underset{\mathbf{3}}{RCH_2\underset{Cl}{C}HCH_2CH_2OH}$$

During the study of extensions of the modified Prins reaction it has been observed that, if the reaction is carried out in the presence of acetylating agents, predominantly linear materials are produced. In the initial experiment it was found that 1-hexene, paraformaldehyde, and acetonitrile reacted smoothly with hydrogen chloride in methylene chloride at −60 to −70°. Glpc analysis of the reaction mixture after an aqueous work-up showed that, in addition to low yields of a mixture of *cis*- and *trans*-4-chloro-3-propyltetrahydropyran (**9**), 3-chloro-1-heptyl acetate (**11**), and 40% of 2-chlorohexane (**4**), a rather substantial quantity of still another compound was formed (40% yield). This was purified by fractionation and identified as 3-heptenyl acetate (**8**) by elemental analysis and infrared, nmr, and mass spectra. Analogous experiments substituting acetyl chloride or acetic anhydride for the acetonitrile gave similar reaction mixtures. Treatment of a solution of acetonitrile in methylene chloride with hydrogen chloride, followed by addition of the other reactants and again introducing hydrogen chloride, gave a product mixture indistinguishable from that obtained using free acetonitrile. Similar experiments with propylene gave mixtures containing 3-butenyl acetate, 4-chlorotetrahydropyran, and 3-chloro-1-butyl acetate in somewhat lower yields, presumably due to losses because of greater water solubility during the aqueous work-up. Although the yields of unsaturated esters are moderate by this procedure, it does represent a simple one-step synthesis of homoallylic acetates from readily available starting materials.

In the condensations with 1-hexene, several minor components were consistently present in varying amounts depending on the reaction conditions. These were separated by preparative glpc and identified by nmr, infrared, and mass spectra. Scheme I summarizes the compounds observed in a typical experiment and Table I shows typical product distributions under identical conditions with the different acetylating agents.

A single sharp peak (on both UCON and Carbowax glpc columns) appeared to be a mixture of chloromethyl acetate (**5**) and 2-hexyl acetate (**6**), in approximately

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[1] Presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 29–April 2, 1971.

[2] P. R. Stapp, *J. Org. Chem.*, **34**, 479 (1969).

[3] P. R. Stapp, *ibid.*, **34**, 1143 (1969).

[4] P. R. Stapp and D. S. Weinberg, *ibid.*, **34**, 3592 (1969).

[5] P. R. Stapp and J. C. Randall, *ibid.*, **35**, 2948 (1970).

SCHEME I

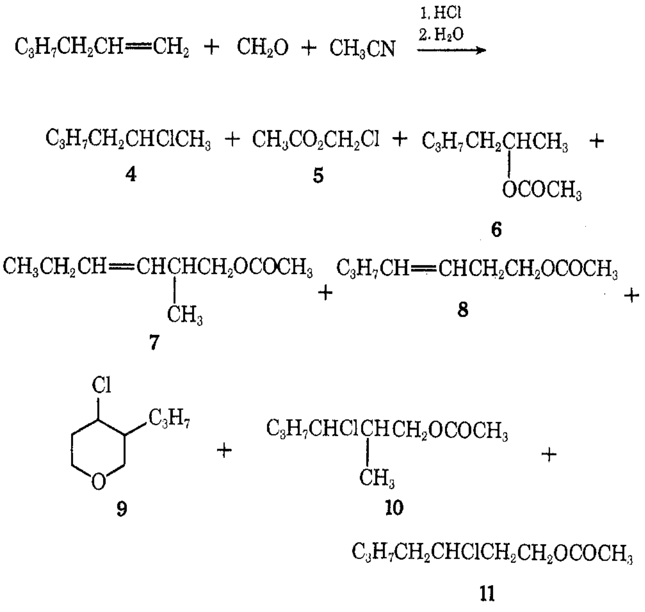


TABLE I

REACTION OF 1-HEXENE, PARAFORMALDEHYDE, ACETYLATING AGENTS, AND HYDROGEN CHLORIDE AT −65°

$$C_3H_7CH_2CH{=}CH_2 + CH_2O + CH_3Z \xrightarrow{HCl^a} \text{product}$$

	Z = -COCl		Z = $-CO_2CO-$		Z = -CN	
Product	Yield,[b] %	Yield,[c] %	Yield,[b] %	Yield,[c] %	Yield,[b] %	Yield,[c] %
4	41		41		24	
5 + 6	Trace	Trace	Trace	Trace	Trace	Trace
7	5	7	4	6	3	4
8	21[d]	32	31[e]	47	34[f]	51
9	10	30	8	23	6	18
10	2	3	1	2	2	3
11	6	9	7	10	10	15
	85	81	92	88	79	91

[a] Reactions were run using 3.0 mol of 1-hexene, 2.0 mol of 97% paraformaldehyde, and 2.0 mol of acetylating agent. [b] Based on olefin. [c] Based on paraformaldehyde. [d] Contained 66% trans and 34% cis. [e] 61% trans. [f] 60% trans.

equal proportions, by a combination of infrared and nmr spectra. 2-Methyl-3-hexen-1-yl acetate (**7**) and 3-chloro-2-methyl-1-hexyl acetate (**10**) were separated and the structures assigned by spectroscopic methods (see Experimental Section) and their mode of formation. In this system, as in the earlier modification,[2] low temperatures favored the reaction; very little reaction was observed upon treatment of a mixture of acetic anhydride, 1-hexene, and paraformaldehyde with hydrogen chloride at 0–10°.

In this set of runs very little heavier material was produced and material balances are reasonably good. Neither methylene diacetate[6] nor 4-butyl-1,3-dioxane[7] were present in detectable amounts by glpc (each was resolved on spiking the reaction mixtures with authentic samples). It is of particular interest that the yield of 4-chloro-3-propyltetrahydropyran (**9**) is relatively low under these conditions. In the earlier work[2] yields of 80–90% were found in the absence of acetylating agent. In Table II, however, which shows the effect of variation in olefin/acetylating agent ratio, higher concentrations of acetylating agent appear to increase the rate of formation of tetrahydropyran relative to acyclic product. The rather high proportion of **4** in the system using an excess of acetylating agent is also rather surprising.

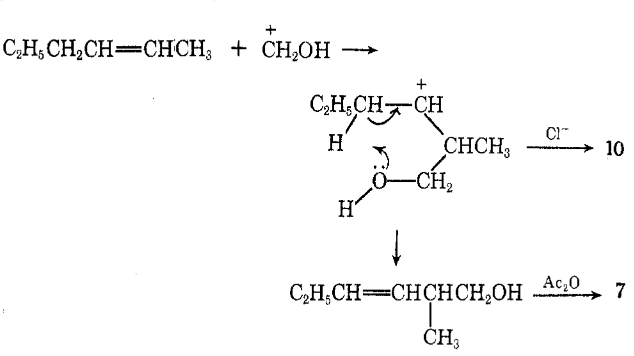
TABLE II

VARIATION OF OLEFIN/ACETIC ANHYDRIDE RATIO[a]

	3.0 mol of 1-hexene, 2.0 mol of acetic anhydride		2.08 mol of 1-hexene, 2.0 mol of acetic anhydride		2.0 mol of 1-hexene, 3.0 mol of acetic anhydride	
Product	Yield,[b] %	Yield,[c] %	Yield,[b] %	Yield,[c] %	Yield,[b] %	Yield,[c] %
4	41		39		39	
7	4	6	4	4	3	3
8	31	47	29	30	22	22
9	8	23	14	30	20	40
10	1	2	2	2		
11	7	10	8	9	13	13

[a] Reactions were run using 2.0 mol of 97% paraformaldehyde. [b] Based on olefin. [c] Based on paraformaldehyde.

Mechanism.—We have previously proposed[2] a mechanism to account for the production of **9** and 3-chloro-1-heptanol in the low temperature modification of the Prins reaction and have established that 3-chloro-1-alkanol formation from *cis*- and *trans*-2-butene is about 80% stereoselective.[4] Superficially, it appears tempting to extrapolate the same line of reasoning to the present system. Thus, formation of 4-chlorotetrahydropyrans occurs *via* cyclization of an unstable chloromethyl ether of the intermediate homoallylic alcohol **2**.[2,8] In the present case, the homoallylic alcohol is acetylated by either acetyl chloride, acetic anhydride, or an acetonitrile/hydrogen chloride complex,[9] giving **8** in competition with chloromethyl ether formation. Similarly, chloride ion capture before deprotonation would give 3-chloro-1-heptanol, which is acetylated to give **11**. Formation of the methyl-branched compounds **7** and **10** is more difficult to explain. It may be that 1-hexene is slowly isomerized to 2-hexene in the reaction medium and a similar process occurs as in the production of the open chain materials.



No evidence was found for the production of branched chain materials in the earlier work[2] nor was 3-chlorohexane (from competitive HCl addition to 2-hexene) detected in this study. It is possible that the present system, presumably of higher dielectric constant, would tend to increase the rate of isomerization

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(6) M. Descudé, *Bull. Soc. Chim. Fr.*, **27**, 867 (1902).

(7) P. R. Stapp, *J. Org. Chem.*, **35**, 2419 (1970).

(8) J. Colonge and P. Boisde, *Bull. Soc. Chim. Fr.*, **23**, 824 (1956).

(9) The structure of the reaction product of acetonitrile with 2 mol of hydrogen chloride has been formulated as either acetimidoyl chloride hydrochloride, $CH_3CCl{=}NH_2^+Cl^-$, or a nitrillium salt, $CH_3C{\equiv}NH^+HCl_2^-$. A literature survey as well as evidence favoring the latter structure is discussed by G. J. Janz and S. S. Danyluk, *J. Amer. Chem. Soc.*, **81**, 3850 (1959).

of the starting 1-hexene but that the concentration of 3-chlorohexane produced, if any, might still be so low as to escape detection. Alternatively, the rate of attack of protonated formaldehyde upon the internal olefin may be sufficiently fast that competitive HCl addition is not observed. The observation that the ratio of trans to cis olefin in **8** is approximately constant (and near the thermodynamic ratio) is not unexpected since the cyclic deprotonation would not be stereospecific. This supports the earlier assumption[4] that stereoselective chloride ion capture must involve either an associated charged intermediate or a concerted reaction.

Although all of the observed products can be rationalized from the above scheme, two puzzling aspects remain. Very little HCl addition to the starting olefin was observed in the earlier work and the relatively high yield of **4** is surprising. In addition, the effect of higher concentrations of acetic anhydride in producing more 4-chloro-3-propyltetrahydropyran (**9**) (Table II) is not easy to explain. If the acetylation reaction is relatively slow at these temperatures, it may be that the increase in rate of formation of **9** in more polar solvents[2] might become a dominant factor and override the expected increase in rate of acetylation.

Although a small amount of chloromethyl acetate (**5**) was observed in each of these runs, no methylene diacetate could ever be detected. It appeared possible that hydrogen chloride might promote ionization of methylene diacetate to the acetoxymethyl cation which would give electrophilic attack upon the starting olefin and give rise to the observed products.

$$CH_2(OCOCH_3)_2 \xrightarrow{HCl} CH_3CO_2H + \overset{+}{C}H_2OCOCH_3 + Cl^-$$

Treatment of 1-hexene and methylene diacetate with hydrogen chloride at −65° gave no detectable condensation products and confirmed that the initial step in the process is formaldehyde protonation.

Experimental Section[10]

Reaction of 1-Hexene, Paraformaldehyde, Acetonitrile, and Hydrogen Chloride.—Only a typical procedure is given. Hydrogen chloride was passed into a mixture of 62 g (2.0 mol) of 97% paraformaldehyde, 252 g (3.0 mol) of 1-hexene, 82 g (2.0 mol) of dry acetonitrile, and 300 ml of methylene chloride at −60 to −70° (Dry Ice–acetone bath) for 2.5 hr, and the mixture was stirred an additional 1 hr and allowed to warm to room temperature overnight. The mixture was treated with 500 ml of water and stirred for 1 hr at room temperature. The layers were separated, the organic layer was washed with sodium carbonate solution and dried ($MgSO_4$), the solvent was removed, and the residue was distilled through a short column under reduced pressure to give 363.2 g of colorless oil, bp 35–130° (12 mm), and 7.3 g of residue. Fractionation through a 4-ft helices packed column gave 120 g (38.5%) of 3-heptenyl acetate, bp 90–93° (30 mm), containing 60% of the trans isomer.

Anal. Calcd for $C_9H_{10}O_2$: C, 69.4; H, 10.3. Found: C, 69.2; H, 10.4.

Glpc analysis of a duplicate run gave the distribution shown in Table I with the following order of elution from the 5-ft UCON column at 200°: **4**, **5** + **6**, **7**, **8**, **9**, **10**, and **11**. Preparative glpc on a 20 ft × 0.75 in. Carbowax 20M column gave the same elution order and furnished **5** + **6** as a mixture and the rest of the compounds as pure materials. Compounds **4**, **8**, **9**, and **11** were identified by comparison of infrared and nmr spectra with authentic samples in addition to their retention times. The nmr spectrum of **7** was in agreement with the assigned structure with 2 vinyl protons centered at −325 Hz, 2 protons at −234 Hz as the AB portion of an ABX system [$C(=O)OCH_2—CH<$], a 3-proton singlet at −120 Hz (CH_3CO_2) overlapping a complex 3-proton allylic resonance from −90 to −160 Hz, and 6 methyl protons consisting of a doublet overlapping a triplet centered at −60 Hz (CH_3CH_2 and CH_3CH). The infrared spectrum showed a strong trans adsorption at 970 cm^{-1} and the mass spectrum was in full agreement with the assigned structure. The nmr spectrum of **10** was in general agreement with the indicated structure with a 3-proton signal from −210 to −260 Hz consisting of an AB portion of an ABX system [$C(O)OCH_2CH$] overlapping a complex resonance of the methine proton α to the chlorine atom, a 3-proton singlet at −222 Hz (CH_3CO_2), a 5-proton complex resonance centered at −93 Hz representing the methylene protons, and 6 methyl protons (doublet overlapping a triplet) at −60 Hz. Mass and infrared spectra were in agreement with the assigned structure.

Registry No.—**4**, 638-28-8; **7**, 1708-86-7; *cis*-**8**, 1576-78-9; *trans*-**8**, 1576-77-8; *cis*-**9**, 18755-78-7; *trans*-**9**, 18755-79-8; **10**, 30275-71-9; **11**, 30316-05-3.

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[10] All melting and boiling points are uncorrected. Nmr spectra were obtained on a Varian A-60 spectrometer in chloroform-*d* with tetramethylsilane as internal standard. Glpc analyses were carried out on a Perkin-Elmer Model 720 gas chromatograph using a 5 ft × 0.25 in. column of 20% UCON LB-550-X on Chromosorb P for the complete analysis and a 5 ft × 0.25 in. 20% tris(cyanoethoxy)propane on Chromosorb P column to separate *cis-* and *trans*-3-heptenyl acetate. Olefins used were Phillips Petroleum Co. pure grade materials. Pure *trans*-3-hepten-1-ol was obtained from Chemical Samples Co., and a cis/trans mixture was obtained from K & K Laboratories. 3-Chloro-1-heptanol was obtained as previously described[2] and all were converted to the acetates by standard techniques.