will now be briefly discussed in terms of the four reaction states displayed on the composition-time plots:

A short initial phase, possibly of several minutes, is encountered, during which hydrogen uptake proceeds at a very low rate. As the reaction pressure is decreased, one experiences an extension of this initial phase, indicating that the initial reaction is one of penetration through a surface film, which is slower as the pressure of the reaction is decreased.

Following this period of relative stagnancy, the reaction enters an autoacceleration phase. Again, except for 250° and 500° C., elevated temperatures and pressures generally shorten the length of this segment of the reaction.

The predominant fraction of the total hydrogen absorbed by the specimen occurs, by far, in the linear segment of the plot.

In its final stage, the reaction rate decreases constantly until finally becoming zero, indicating that the sample has reached its highest saturation value at the given temperature. Inspection of the shape of the composition *vs.* time plot during this terminal phase of the reaction suggests a parabolic rate behavior and a possible diffusion-controlled reaction.

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Reaction of Alpha-Olefins with Formaldehyde and Hydrogen Halides

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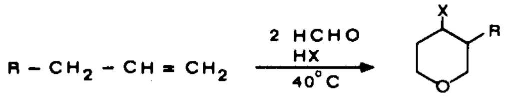
The reaction of alpha-olefins, 1-butene, 1-pentene, 1-hexene, and 1-dodecene, with formaldehyde and hydrogen halides is described. The novel product of the reaction is the *cis*- and *trans*-4-halo-3-alkyltetrahydropyran in 45 to 55% yield, based on formaldehyde consumed. Some of the major products are 4-chloro-3-methyltetrahydropyran, 4-chloro-3-ethyltetrahydropyran, 4-chloro-3-propyltetrahydropyran, 4-bromo-3-propyltetrahydropyran, and 4-chloro-3-nonyltetrahydropyran.

THE MINERAL ACID–CATALYZED condensation of formaldehyde with olefins, known as the Prins reaction (*4*), was reviewed in 1952 (*1*). Most of the material reviewed was taken from the patent literature, which describes the synthesis of 1,3-dioxanes, the corresponding glycols, glycol esters, and diolefins. The reacting olefins were ethylene, propylene, and the butenes. Recently, a modification of the original Prins reaction was reported. One group (*2*) studied the reaction of propylene with formaldehyde in concentrated hydrochloric acid and obtained the formal of 3-chloro-1-butanol as the major product. Another group (*5*) treated cyclohexene with formaldehyde under similar conditions and obtained *trans*-2-chlorocyclohexyl carbinol as the major product.

We investigated the reaction of alpha-olefins, 1-butene, 1-pentene, 1-hexene, and 1-dodecene, with formaldehyde and hydrogen chloride (hydrogen bromide). Our work has shown that not only the corresponding chlorohydrin and/or its formal is obtained, but that the major and novel product of the reaction (45 to 55% yield, based on formaldehyde consumed) is the 3,4-disubstituted tetrahydropyran as a ca. 50 to 50 mixture of the cis and trans isomers.



The products (I to V) were worked up by vacuum distillation (Table I). The cis and trans stereoisomers could not be separated, even by gas chromatography, although their composition was readily apparent from the NMR spectrum. The NMR spectra of I to V were in accord with the published spectra for each of the geometrical isomers of VI (R = C_9H_{19}, X = OAc) (*3*). Consequently, we synthesized VII (R = C_3H_7, X = OAc) and VIII (R = C_3H_7, X = OH) to have a standard for comparison. The most helpful feature in the NMR spectrum for determining the ratio of geometrical isomers is the position of proton bound to C_4. This proton in the cis isomer of VI is coupled to three protons on C_3 and C_5 and appears as a quartet (two overlapping triplets) at 5.07δ. In the trans isomer, it is coupled to two axial protons on C_3 and C_5, and one equatorial proton on C_5, and appears as a sextet (triplet of doublets) centered at 4.56δ. The characteristic positions of proton bound to C_4 as a function of substituent X are given in Table II.

In the cis and trans isomers of I, the CH_3 groups are sufficiently different in their environment to appear as superimposed doublets centered at 0.97δ and 0.94δ.

The mass spectra for I to V consisted of the respective parent ions and the peaks corresponding to the loss of X· and/or HX, and HCHO—for example, the following peaks were observed for I: 134 (*P*) (15%), 99 (*P*—Cl) (11%), 98 (*P*—HCl) (11%), 69 (*P*—Cl—HCHO)

Table I. Major Products from Reaction of Alpha-Olefin, HCHO, and HCl (HBr)

Alpha-Olefin	Product	Yield, %	B.P., ° C., (Mm. Hg)	n_D^{20}	Mol. Wt. (*m/e*)	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
1-Butene	(I) 4-Chloro-3-methyltetrahydropyran	45	40 (1.5)	1.4570	134	53.58	53.80	8.24	8.30
1-Pentene	(II) 4-Chloro-3-ethyltetrahydropyran	50	50 (1.0)	1.4625	148	56.56	56.51	8.82	8.83
1-Hexene	(III) 4-Chloro-3-propyltetrahydropyran	55	27 (ca. 0.5)	1.4620	162	59.10	59.05	9.29	9.14
1-Hexene	(IV) 4-Bromo-3-propyltetrahydropyran	48	65–70 (ca. 1.5)	...	207	46.37	46.27	7.30	7.21
1-Dodecene	(V) 4-Chloro-3-nonyltetrahydropyran	46	125 (ca. 1.5)	...	246	68.13	68.35	11.03	11.27

(47%), and 68 (*P*—HCl—HCHO) (100%). Thus, the fragmentation patterns of I to V are dominated by the dehydrohalogenation and the reverse Diels-Alder reactions, followed by a typical fragmentation pattern of the dienes formed.

EXPERIMENTAL

The NMR spectra were determined on Varian HA 60-EL spectrometer in carbon tetrachloride solvent as a 10 to 20% solution with tetramethylsilane as an internal standard. The chemical shifts are quoted in δ units (parts per million). The mass spectra were obtained with CEC, Model 21-110 high resolution, or Model 21-103C low resolution spectrometers. The infrared spectra were recorded either on Perkin-Elmer Infracord or Perkin-Elmer Model 237B spectrometers. A 4-foot, 20% silicone gum (GE XE 60) on a Diatoport S column at 50° to 260° was used for all chromatographic work.

COMPOUND I. About 100 grams of formaldehyde solution (37%) was mixed with 60 grams of concentrated hydrochloric acid in a 500-ml., three-necked, round-bottomed flask equipped with a condenser, mechanical stirrer, and two gas inlet tubes. In a typical run, 1-butene and anhydrous HCl were simultaneously passed through the HCHO solution for 2 hours at 20° C.

The crude product, about 109 grams, was taken up in ether, washed with water, neutralized (aqueous $NaHCO_3$), and dried ($CaSO_4$). Compound I was obtained by distillation, b.p. 40° (1.5 mm.), n_D^{20} 1.4570, 38 grams (47%). Infrared (cm.$^{-1}$): 1050 to 1150 (*S*) (cyclic ether), 710 to 740 (*M*) (—Cl). NMR (δ): 0.97 and 0.94 (*d,d*,3, $J \cong 6.5$ *c/s*, CH_3—), 1.2 to 2.7 (*m*, 3, —CH_2— and =CH—), 3.4 to 3.7 (*d*, 2, —O—CH_2—CH—CH_3), 2.7 to 4.2 (*m*, 2 3/8. —O—CH_2—CHCl— and =CHCl of trans), 4.33 (*q*, 5/8, =CHCl of cis). As the temperature of the sample was raised, the two methyl doublets began to coalesce into a single doublet, indicative of equilibration. Mass spectrum (*m/e*): 134 (*P*), 99 (*P*—Cl), 98 (*P*—HCl), 69 (*P*—Cl—HCHO), 68 (*P*—HCl—HCHO).

Table II. Positions of C_4 Proton as a Function of Substituent X

	R = C_9H_{19}, X = OAc	R = C_3H_7, X = Cl	R = C_3H_7, X = Br	R = C_3H_7, X = OH
cis	5.07	4.38	4.8	4.3
trans	ca. 4.56	2.8 to 4.2[a]	3.0 to 4.5	2.7 to 4.1

[a] Range given since 4-alpha protons on C_6 and C_2 of cis and trans I to V appear together with C_4 proton of trans isomer.

COMPOUND III. To 200 ml. of 1-hexene in a 500-ml., three-necked, round-bottomed flask, equipped with a mechanical stirrer, a condenser, an addition funnel, and a gas inlet tube, was added 33.5 grams of 35% HCHO solution in 45 ml. of concentrated hydrochloric acid while a steady stream of HCl gas was passed through the reaction mixture. (In an alternative procedure, paraformaldehyde was dissolved in HCl and then added to 1-hexene with similar results.) Once the addition of HCHO was completed, the mixture was stirred for 1 to 2 hours at 40°.

After separation of the organic layer, the aqueous layer was extracted with ether. The combined organic layers were washed two times with cold water, neutralized (aqueous $NaHCO_3$), washed with water, and dried ($CaSO_4$). The unreacted olefin and the ether were removed under vacuum and the remaining portion, about 72 grams of crude product, was fractionated. Compound III was isolated as a mixture of cis and trans isomers, 27.5 grams (55%), b.p. 27° (ca. 0.5 mm.), n_D^{20} 1.4620. Infrared (cm.$^{-1}$): 1050 to 1150 (*S*) (cyclic ether), 710 to 750 (*M*) (C—Cl). NMR (δ): 0.96 (*t*, 3, CH_3—), 1.3 and 1.94 (*m,m*, 7, —CH_2—, and =CH—C_3), 3.52 (*m*, 4 1/2, —CH_2—O—CH_2— and =CHCl of trans), 4.38 (*q*, 1/2, =CHCl of cis). Mass spectrum (*m/e*): 162.080041 (*P*), 96 (*P*—HCl—HCHO).

COMPOUND II. Compound II was made by reaction of 1-pentene with HCHO in HCl by a procedure used for III, 24.5 grams (50%), b.p. 50° (1.0 mm.), n_D^{20} 1.4625. Infrared (cm.$^{-1}$): 1050 to 1150 (*S*) (cyclic ether). Mass spectrum (*m/e*): 148 (*P*), 82 (*P*—HCl—HCHO).

COMPOUND IV. According to the procedure used for III, compound IV was isolated from the reaction of 1-hexene with HCHO in concentrated HBr, 21 grams (48%), b.p. 65° to 70° (ca. 1.5 mm.). Infrared (cm.$^{-1}$): 1050 to 1150 (*S*) (cyclic ether), 685 to 705 (*M*) (C—Br). NMR (δ): 1.08, 1.38, 2.2 (*m,m,m*, 10, C_3H_7—, —CH_2—CHBr, =CH—C_3H_7), 3 to 4.5 (*m*, 4 3/8, —CH_2—O—CH_2— and =CHBr of trans), 4.8 (*q*, 5/8, =CHBr of cis). Mass spectrum (*m/e*): 207 (*P*), 96 (*P*—HBr—HCHO).

COMPOUND V. Compound V, 14.7 grams (46%), b.p. 125° (ca. 1.5 mm.), was obtained from the reaction of 1-dodecene with HCHO in HCl as described for III. Infrared (cm.$^{-1}$): 1088 (*S*), 1145 (*S*) (ether), 710 (*M*) (C—Cl). NMR (δ): 0.8 to 2.3 (*m*, 22, —CH_2—CHCl—,

$=CH—C_9H_{19}$), 3 to 4.3 (*m*, 4 1/3, $—CH_2—O—CH_2—$, =CHCl of trans), 4.7 (*q*, 2/3, =CHCl of cis). Mass spectrum (*m/e*) : 246 (*P*), 180 (*P*—HCl—HCHO).

COMPOUND VII. According to a procedure described (*3*), a mixture of 270 grams of acetic acid, 45 grams of sulfuric acid, and 81 grams of paraformaldehyde was heated to 100° to dissolve the aldehyde, cooled to 40°, and added gradually to 95 grams of 1-hexene. After stirring for 21 hours at 55°, the mixture was worked up by distillation to give VII, b.p. 56 to 58° (0.6 mm.), 89 grams (45%). Infrared ($cm.^{-1}$): 1241 (*S*) and 1730 (*S*) (acetate group), 1085 to 1160 (*S*) (cyclic ether). Mass spectrum (*m/e*) : 186 (*P*), 143 ($P—C_3H_7$), 126 (*P*—HOAc), 96 (*P*—HOAc—HCHO).

COMPOUND VIII. The acetate, VII, 63 grams, was heated under reflux for 6 hours in a mixture of 60 grams of KOH, 100 ml. of water, and 250 ml. of ethanol. Distillation afforded 39 grams (81%) of VIII, b.p. 63 to 65° (2 mm.), n_D^{20} 1.4623. Infrared ($cm.^{-1}$) : 3500 (*S*), 3570 (*S*) (—OH), 1050 to 1160 (*S*) (cyclic ether). NMR (δ): 0.95, 1.28, 1.6 (*m,m,m*, 10, $=CH—C_3H_7$ and $—CH_2—CHOH$), 2.7 to 4.12 (*m*, 5 1/2, $—CH_2—O—CH_2—$, =CHOH of trans), 4.3 (*q*, 1/2, =CHOH of cis). Mass spectrum (*m/e*) : 144 (*P*), 101 ($P—C_3H_7$), 96 ($P—H_2O—HCHO$).

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Kinetics of Methanolysis of Benzoyl Chloride in Methanol-Dioxane Mixtures

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The rates of methanolysis of benzoyl chloride have been determined conductometrically for the reaction in mixtures of methanol and p-dioxane containing 50 to 100 weight % methanol. The first-order rate constants and activation parameters for the reaction in each solvent mixture are reported.

THE HYDROLYSIS and ethanolysis of acid chlorides, particularly benzoyl chloride and substituted benzoyl chlorides, have been the subject of a large number of investigations (*4*). The analogous reaction in methanol and mixed solvents containing methanol have received relatively little attention (*5, 7*). Because of the considerable interest in obtaining sufficient data to formulate a generally acceptable mechanism of solvolysis of acid chlorides and in understanding the nature of the solvent effect in these reactions, the results of a limited investigation of the methanolysis of benzoyl chloride in MeOH-*p*-dioxane mixtures are reported.

Table I gives illustrative data for each composition at one temperature. The expected error in the conductivity, κ, is of the order of 1%.

Table II lists the pseudo-first-order rate constants for three mixed solvents and pure methanol at three temperatures. The values listed are the mean of two to four runs at each composition and temperature. For convenience, the dielectric constant (*3*) for the mixtures at 25° C. is listed. Table III contains the activation parameters derived for the reactions, the entropies having been calculated using the first-order rate constants.

Plots of log k_1 *vs.* log $[CH_3OH]$ show slight but definite curvature, the slope increasing from ~1.1 in the range 52 to 66% MeOH to 1.65 at 81 to 100% MeOH at each temperature.

The observed increase in k_1 at 25° C. with increasing methanol content of the solvent mixture does not correlate linearly with the functions of dielectric constant suggested by either the Laidler and Eyring equation or that of Amis (*1*).

EXPERIMENTAL

Chemicals. Fisher reagent grade methanol was dried by refluxing over magnesium oxide, then fractionated in a 50-cm. column packed with glass helices. The fraction collected at 63.90–4.05° C./741 mm. had a refractive index, n_D^{22}, of 1.3282.

Fisher reagent grade benzoyl chloride was distilled through an ordinary fractionating head; the middle portion recovered at 195.0–7.2° C./740 mm. had n_D^{22} = 1.5525.

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