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Reaction of Hydrogen with Praseodymium at Various Temperatures

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The reaction of praseodymium with hydrogen was investigated in the temperature region 100° to 800° C. The predominant portion of the hydrogen is taken up at a constant rate. The final saturation with hydrogen is diffusion-controlled and obeys the parabolic laws. A reaction mechanism is proposed in terms of the various phases of reaction displayed by plots of average composition vs. time.

THE LITERATURE of rare-earth hydrides is somewhat clouded by conflicting results, especially with regard to rates of reaction. Thus, while the thermodynamics and structures of the various hydrides have been adequately investigated (*1, 2*), little attention has been paid to the times required to reach equilibrium. The object of this investigation is therefore to elucidate some of the variables that govern the rate of hydrogen uptake of praseodymium, hopefully gaining some insight into the various steps involved in the reaction. Because of their great "storage" capacity for hydrogen per unit volume, rare-earth metal hydrides have been the subject of frequent investigations by workers in such diverse fields as electronics, preparative chemistry, vacuum technology, and others. The greatest incentive for studying rare-earth hydrides lies, however, in their contribution to the over-all understanding of the complex field of solid-gas reactions.

EXPERIMENTAL

Preparation of Metal Samples. The praseodymium used in this study was obtained from Lindsay Rare-Earth Chemicals, American Potash and Chemical Corp., West Chicago, Ill. Analyses were as follows:

Praseodymium:	99.9%, Lot LU06044	
Impurities:	Tantalum	0.001%
	Calcium	0.0015
	Magnesium	0.001
	Aluminum	0.0005
	Oxygen	0.005
	Nitrogen	0.005
	Molybdenum	0.005
	Other rare-earths	<0.1

Samples 4 × 6 × 2 mm. cut from ingots using a fine-tooth saw were filed smooth and then abraded under light mineral oil, with silicon carbide paper. They were then washed under acetone, weighed, and placed under vacuum in a reaction vessel that had previously been purged three times with hydrogen. All samples were annealed at 700° C. for 3 hours.

Hydrogen. Matheson Ultra Pure hydrogen (Analysis: oxygen 0.5 p.p.m., nitrogen less than 5.0 p.p.m., total hydrocarbons as CH_4 less than 0.3 p.p.m.) was passed through a trap of equal molar concentrations of sodium and potassium to remove trace impurities. Electrolytic grade hydrogen was used for Run 7 (Analysis: oxygen 20 p.p.m., nitrogen 50 p.p.m., carbon dioxide 5 p.p.m., CH_4 and CO "trace").

Apparatus. The reaction was carried out in a high-vacuum system of conventional design (pressure, 10^{-5} mm. of Hg). The 20-mm.-diameter quartz reaction tube was heated by means of a Hevi-Duty furnace. Temperature control was achieved with a Type 500 Temcometer. A chromel-alumel thermocouple placed against the outer wall of the quartz tube served as a sensing element. The Temcometer was calibrated against a platinum-platinum 10% rhodium thermocouple. The specimen in a porcelain boat was positioned in the approximate center of the quartz tube.

Procedure. With the annealed metal sample in position under vacuum, the reaction chamber was brought up to temperature. Hydrogen was then admitted to give the desired pressure and the timer actuated simultaneously. Manometer readings were made with a Gaertner cathetometer. A run was considered completed when no pressure change occurred over at least a 15-minute period. At the conclusion of a run, the furnace was turned off, and, in some cases, hydrogen uptake was allowed to proceed overnight at ambient temperature, thus yielding the room-temperature ratio of hydrogen

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Table I. Summary of Data

Run No.	Temp., ° C.	Grams Pr	Moles Pr × 10⁻³	Hydrogen Press., Mm. Hg. Initial	Hydrogen Press., Mm. Hg. Final	Press. Change, Mm. Hg	Gram-Atoms H_2 Abs. × 10⁻³	H/Pr at Equil.	Time to Reach Equil., Mins.	Induction Time, Mins.	Room Temp. Equil. Press., Mm. Hg	Press. Change, Mm. Hg, Room Temp.	Gram-Atoms H_2 Abs. Room Temp. × 10⁻³	H/Pr, Room Temp.	Rate Constant $\left(\frac{\text{G.-Atoms H.}}{\text{G.-Atoms Pr}}\right) \times$ minutes for Rect. Part of Curves
1	100	0.3133	2.233	455.6	377.6	78.0	6.349	2.86	14	0	. . .	. . .	. . .	. . .	0.378
2	100	0.2920	2.072	460.4	388.0	72.4	5.893	2.85	16	0	. . .	. . .	. . .	. . .	0.377
3	100	0.3382	2.400	253.2	171.6	81.6	6.642	2.77	18	0	. . .	. . .	. . .	. . .	0.377
4	100	0.3049	2.164	99.4	26.0	73.4	5.975	2.76	38	1	22.2	77.2	6.284	2.90	0.163
5	250	0.2088	1.482	467.6	419.6	48.0	3.907	2.64	9	0	. . .	. . .	. . .	. . .	0.80
6	250	0.2553	1.812	459.8	400.6	59.2	4.820	2.66	6	0	. . .	. . .	. . .	. . .	0.55
7[a]	350	0.1886	1.339	476.8	426.8	41.0	3.340	2.49	14	3	. . .	. . .	. . .	. . .	0.32
8	350	0.2490	1.767	460.8	407.2	53.6	4.363	2.47	6	0	. . .	. . .	. . .	. . .	0.70
9	350	0.3001	2.130	270.0	205.2	64.8	5.275	2.45	7	0	127.2	78.0	6.349	2.98	0.55
10	350	0.3464	2.458	103.2	34.2	69.0	5.617	2.29	25	5	. . .	. . .	. . .	. . .	0.19
11	500	0.3186	2.261	482.6	419.4	63.2	5.144	2.28	10	2	397.8	84.8	6.903	3.03	0.57
12	500	0.3380	2.369	471.6	405.4	66.2	5.389	2.27	8	0	387.0	84.6	6.886	. . .	0.53
13	650	0.3622	2.571	458.3	391.2	67.2	5.503	2.14	6	0	. . .	. . .	. . .	. . .	0.42
14	650	0.3014	2.139	249.6	193.0	56.6	4.607	2.15	11	0	. . .	. . .	. . .	. . .	0.24
15	650	0.2967	2.106	97.2	43.0	54.2	4.412	2.09	35	1	. . .	. . .	. . .	. . .	0.12
16	800	0.3186	2.260	455.0	398.0	57.0	4.640	2.05	6	0	. . .	. . .	. . .	. . .	1.05

[a] This run was made with electrolytic grade hydrogen.

over metal. The hydrogen uptake as a function of time was calculated from the pressure drop, using the perfect gas law.

DISCUSSION OF RESULTS

Table I summarizes the data obtained. The equilibrium H/Pr ratios decrease steadily from a value of about 2.85 at 100° C. to approximately 2.0 at 800° C. Samples that were allowed to react with hydrogen at room temperature, following a run at elevated temperature, all converge toward a composition H/Pr of 2.9 to 3.0 after an overnight exposure of about 12 hours.

Table II compares equilibrium values of H/Pr obtained in this work with those reported by Ellinger *et al.* (*1*). Agreement is fair, with the literature ratios being somewhat higher and possibly closer to true equilibrium because of much longer equilibration times.

Figures 1 through 5 represent plots of average composition as a function of time, at different temperatures. In Figure 1, plots 2 and 3 show good reproducibility in the linear portion of the reaction, even though run 2 shows a more extended autoacceleration period, the period where the reaction rate increases to a constant value. Comparison of runs 1, 2, and 3 indicates that a pressure decrease from 455 to 253 mm. of Hg has no effect on rate at 100° C. There is, however, an appreciable drop in the over-all rate of reaction at 99 mm. of Hg. In addition, the linear portion for this run extends only over 0.9 gram-atom of hydrogen whereas, at the same temperature, linear uptake prevails over at least 1.5 gram-atom of hydrogen per mole of praseodymium for runs at more elevated pressures.

At 250° C., Figure 2, one notes the absence of an induction period and only a very slight autoacceleration phase. The higher rate is obtained with the run whose initial hydrogen uptake deviates the least from the linear rate. This would indicate that difference in rate of surface penetration is a factor which can persist through the entire linear portion of the reaction. Indeed, the equilibrium ratio is the same for both runs; the difference is in the linear rate.

At 350° C., Figure 3, runs 8 and 9 were performed with "ultra pure" hydrogen, while run 7 was done with

Table II. Comparison of Equilibrium Values

Temp., ° C.	Ellinger *et al.* (*1*) H/Pr	Ellinger *et al.* (*1*) Pressure, mm. Hg	Gayer and Grunwald H/Pr	Gayer and Grunwald Pressure, mm. Hg
200	2.90	400	. . .	. . .
200	2.81	200	. . .	. . .
250	. . .	. . .	2.66	400
250	. . .	. . .	. . .	. . .
300	2.75	400	. . .	. . .
300	2.64	200	. . .	. . .
350	. . .	. . .	2.47	407
350	. . .	. . .	2.45	205
400	2.62	400	. . .	. . .
400	2.49	200	. . .	. . .
500	2.50	400	2.28	419
500	2.37	200	. . .	. . .
600	2.43	400	. . .	. . .
600	2.28	200	. . .	. . .
650	. . .	. . .	2.14	391
650	. . .	. . .	2.15	193
700	2.35	400	. . .	. . .
700	2.22	200	. . .	. . .
800	. . .	. . .	2.05	398

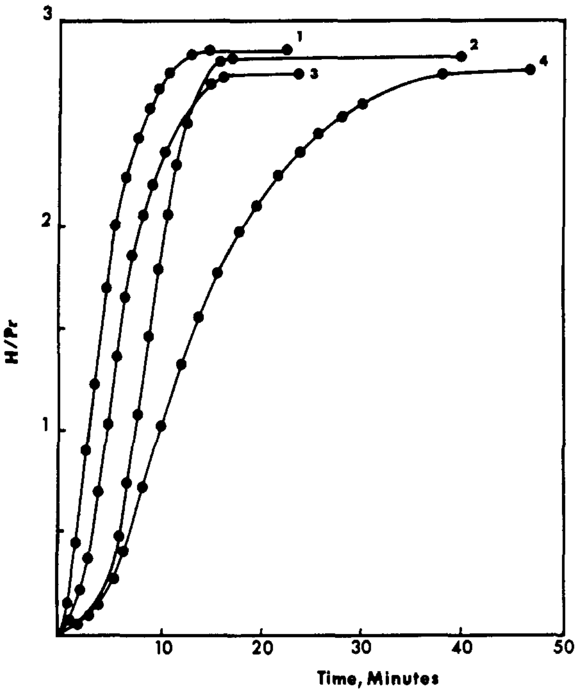

Figure 1. Variation of average composition of H/Pr as a function of time at 100° C.

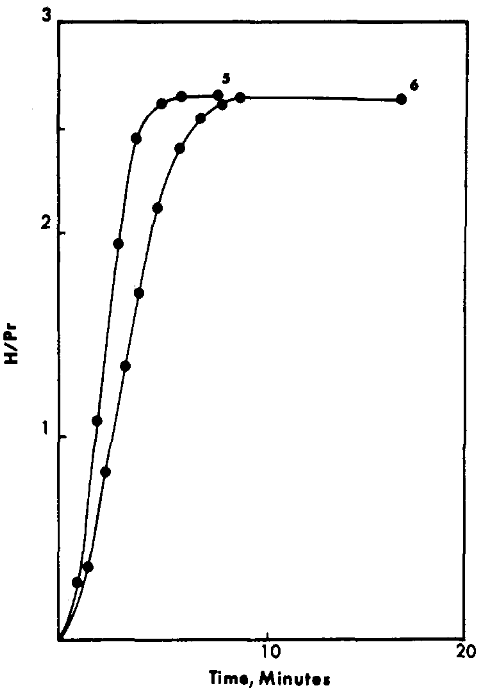

Figure 2. Variation of average composition of H/Pr as a function of time at 250° C.

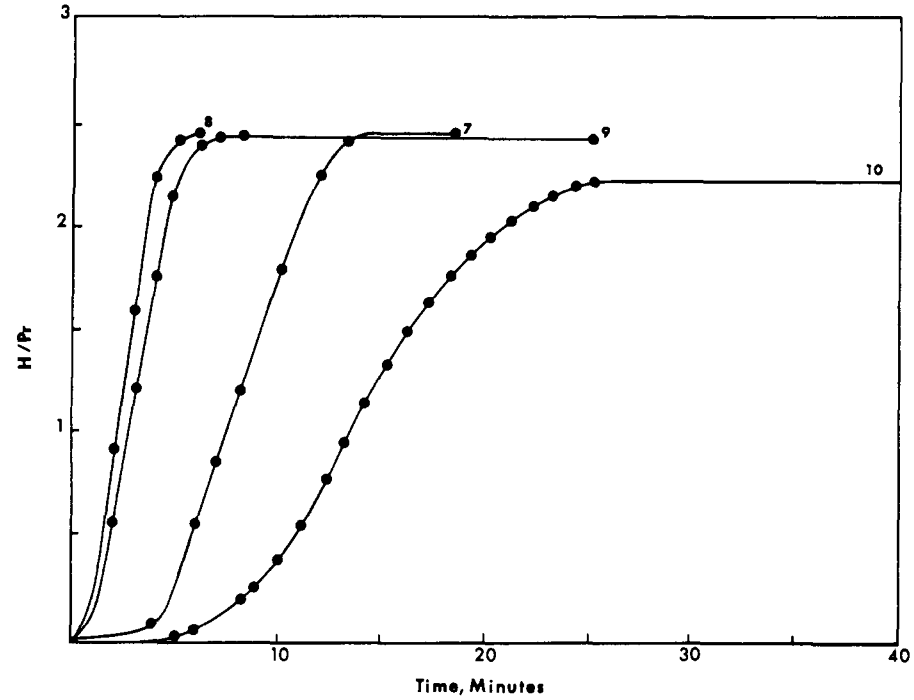

Figure 3. Variation of average composition of H/Pr as a function of time at 350° C.

electrolytic grade hydrogen. In the latter, hydrogen uptake is negligible during the first 4 minutes; the slope of the linear portion of the curve is also lower. Further comparison of runs 7, 8, and 9 indicates that the equilibrium H/Pr ratio is the same, even though the time required to achieve equilibrium varies and is longest for run 9. Run 10 denotes the effect of lower pressure on both the linear rate and the initial stages of the hydrogenation reaction. Interestingly, the induction period for this run is the longest at this temperature, despite the fact that "ultra pure" hydrogen was used. The linear portion of the curve has been greatly reduced in run 10, extending only over the absorption of 0.95 gram-atom of hydrogen.

At 500° C., Figure 4, the slopes and the equilibrium ratio H/Pr are in good agreement with one another.

Figure 5 represents experimental runs at 650° C. and a single run at 800° C. Run 13 shows a complete absence of both induction and autoacceleration periods and displays no initial deviation from linearity. Run 14 undergoes an appreciable autoacceleration period, which also coincides with a lower linear rate. Both effects can be reasonably attributed to the lower pressure of this run. Run 15, at 97.2 mm. of Hg, displays a curve composed of two portions; one, at the beginning of the reaction, has an average slope of 0.035, and lasts for 10 minutes, whereas the other extends over a portion of 1.2 gram-atoms of absorbed hydrogen and lasts for 12 minutes, giving a slope of 0.1 gram-atom of hydrogen per gram-atom of praseodymium × minutes. The induction period, even at this low pressure, is less than two minutes.

A single run at 800° C. is represented in plot 16. The reaction shows very rapid kinetics with 2 gram-atoms of hydrogen absorbed in 5 minutes, giving an average rate of 0.40 gram-atom of hydrogen per gram-atom of praseodymium × minutes. Based on the first minute of the reaction, one gets a rate of 1.05 gram-atom of H per gram-atom of Pr × minutes. There is complete absence of induction as well as autoacceleration periods.

Figure 6 represents a series of typical pressure *vs.* time plots at various temperatures. The short induction and autoacceleration stages and good reproducibility of linear rates at a given temperature indicate that any possible oxide-nitride films are porous.

The influence of temperature on the reaction rates is illustrated by the following average linear slopes in gram-atoms of hydrogen per gram-atoms of metal times minutes at different temperatures and comparable pressures of 400 to 500 mm. of Hg:

T°, C.	100	250	350	500	650	800
Linear rate	0.37	0.67	0.70	0.53	0.42	1.05

A rise in linear rate between 100° and 350° C. and a drop at 500° and 650° C. followed by an increase in rate at 800° C. possibly indicates an increasing porosity of any surface film with temperature.

The rate behavior at various temperatures provides some insight on the mechanism of hydrogen uptake and

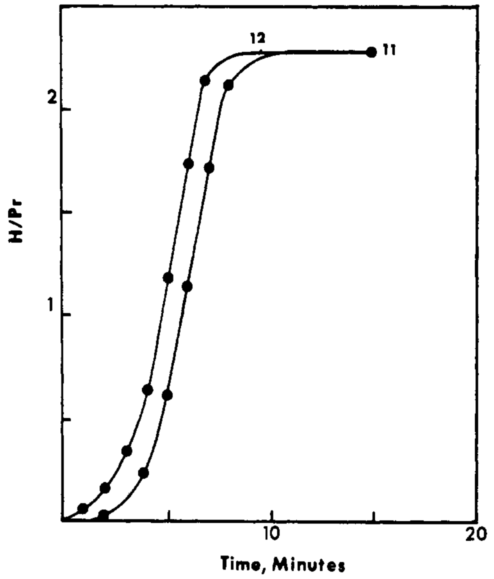

Figure 4. Variation of average composition of H/Pr as a function of time at 500° C.

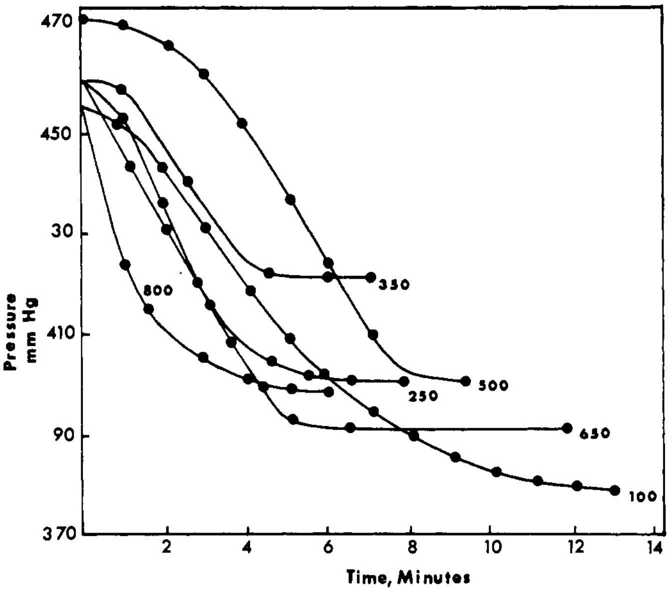

Figure 6. Typical pressure vs. time at various temperatures

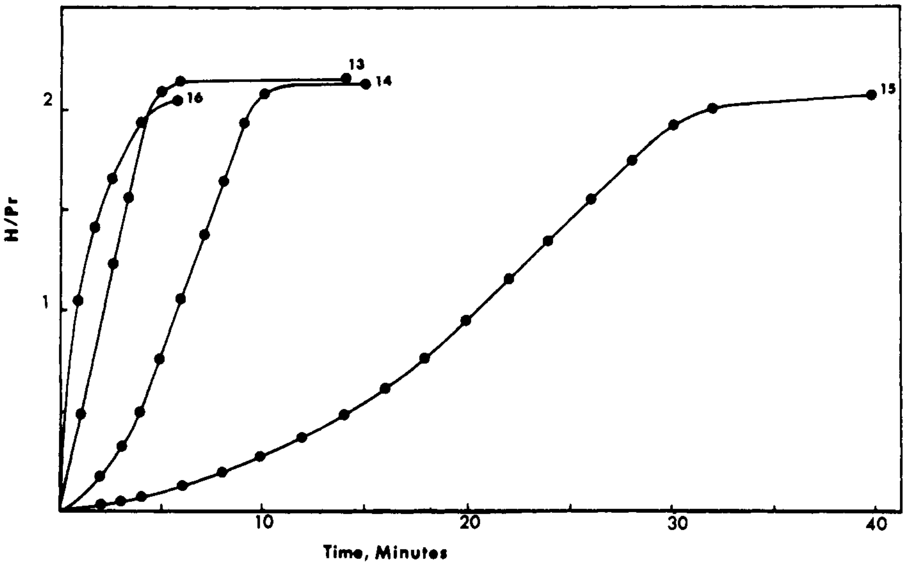

Figure 5. Variation of average composition of H/Pr as a function of time at 650° and 800° C.

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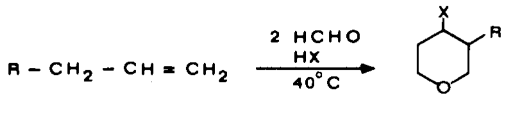
The reaction of alpha-olefins, 1-butene, 1-pentene, 1-hexene, and 1-dodecene, with formaldehyde and hydrogen halides is described. The novel product of the reaction is the *cis-* and *trans-*4-halo-3-alkyltetrahydropyran in 45 to 55% yield, based on formaldehyde consumed. Some of the major products are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