pared 10% palladium-on-carbon catalyst. Hydrogen uptake was complete in 10 hr. The catalyst was removed by filtration and the solvent removed *in vacuo* leaving a semicrystalline residue (2.5 g.).

A solution of 2.3 g. of the residue in 5 ml. of dry pyridine was treated with 1.28 g. of diphenyl phosphorochloridate. The reaction was kept 25° for 10 hr. and then worked up in the usual fashion to give 3.5 g. of a colorless sirup. The phenyl groups were removed by hydrogenation of the sirup in absolute ethanol solution over 0.7 g. of platinum oxide. When the uptake of hydrogen ceased (2.5 hr.) the catalyst was removed by filtration and 20 ml. of 1.02 *N* sodium hydroxide was added to tne filtrate. The saponification was complete in 4 hr.; the ethyl alcohol was removed *in vacuo* at 40°; and the aqueous residue was extracted with ether to remove the triphenylmethane. Sodium ions were removed on Dowex 50 (H+) and the majority of the benzoic acid by filtration. The clear aqueous solution was adjusted to pH 9.0 with cyclohexylamine and then concentrated to a small volume. Upon addition of acetone crystallization occurred and after 8 hr. a small crop of crystals was collected and identified as cyclohexylammonium benzoate. Addition of more acetone gave 1.15 g. of a crude crystalline product which on being fractionally crystallized from water–acetone gave 0.7 g. of material which gave a positive periodate test and a negative test for inorganic phosphate. The chromatographically pure material [R_f (*n*-butyl alcohol–acetic acid–water, 3:1:2), 0.23; R_f (methanol–ammonia–water, 6:1:3), 0.87; R_f (Methyl Cellosolve–pyridine–acetic acid–water, 8:4:1:1), 0.3; R_f (isobutyric acid–ammonia–water, 66:10:20), 041] had $[\alpha]^{25}D$ −20.0° (*c* 1.0, water) and analyzed as a dihydrate.

Anal. Calcd. for $C_{22}H_{45}N_3O_8 2H_2O$ (549) C, 48.1; H, 9.49; N, 7.65; P, 5.66. Found: C, 48.5; H, 9.70 N, 7.17; P, 5.65.

The Reactions of 4-Phenyl-2-butanone and 5-Phenyl-2-pentanone with Phosphorus Pentachloride[1]

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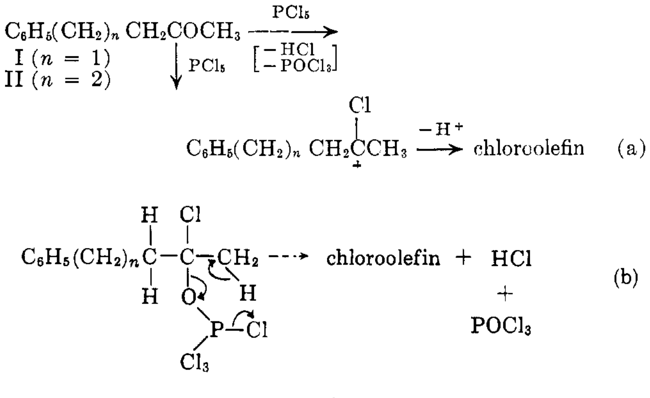
On treatment with phosphorus pentachloride at 25° in methylene chloride, 4-phenyl-2-butanone gave mixtures of 2-chloro-4-phenyl-1-butene (53%), *cis*-2-chloro-4-phenyl-2-butene (12%), and *trans*-2-chloro-4-phenyl-2-butene (35%). Similarly 5-phenyl-2-pentanone gave mixtures of 2-chloro-5-phenyl-1-pentene (43%), *cis*-2-chloro-5-phenyl-2-pentene (14%), and *trans*-2-chloro-5-phenyl-2-pentene (43%). These results indicate that chlorocarbonium ions are not involved in these reactions.

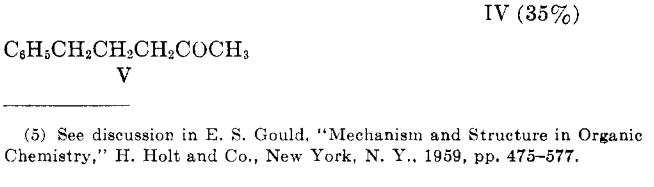
In a previous discussion of the mechanism of the reaction of ketones with phosphorus pentachloride two paths for the formation of chloroolefin were outlined: (a) loss of a proton from a chlorocarbonium ion; and (b) direct elimination of hydrogen chloride and phosphorus oxychloride from the addition product of the ketone and phosphorus pentachloride.[3] The work herein presented was done in order to shed light on the processes involved.



The two ketones chosen for study were 4-phenyl-2-butanone, I, and 5-phenyl-2-pentanone, V, since, if chlorocarbonium ions were involved in the reaction with phosphorus pentachloride (scheme a above), cyclization to 1-chloro-1-methylindane and 1-chloro-1-methyl-1,2,3,4-tetrahydronaphthalene would be expected.[4] Since no trace of either of these cyclic products (or of their dehydrochlorination products) was found, we believe that chlorocarbonium ions are not involved in these reactions with phosphorus pentachloride.

The main products, formed in well over 90% yield in each case, consisted of mixtures of chloroolefins (see Tables II and II). The large amounts of terminal olefins, 2-chloro-4-phenyl-1-butene, II (*ca.* 53% of total), and 2-chloro-5-phenyl-1-pentene, VI (*ca.* 43% of total), obtained provide another argument against the involvement of chlorocarbonium ions. If the latter were involved, much smaller amounts of terminal olefins would be expected in analogy with elimination of protons from ordinary carbonium ions.[5]

The remaining olefins consisted of *cis*-2-chloro-4-phenyl-2-butene, III (*ca.* 12%), and *trans*-2-chloro-4-phenyl-2-butene, IV (*ca.* 35%), in the case of I and of *cis*-2-chloro-5-phenyl-2-pentene, VIII (*ca.* 44%), and *trans*-2-chloro-5-phenyl-2-pentene, VIII (*ca.* 14%), in the case of V. These olefins were separated as described in Experimental.



I

II (53%)

III (12%)

IV (35%)

V

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[1] This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research.

[2] This work formed part of the M.S. thesis of W. N. K. presented to the Ohio State University in June, 1962.

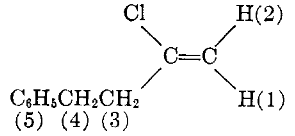
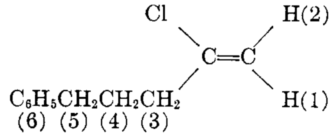
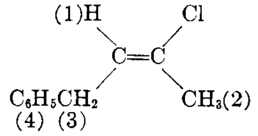
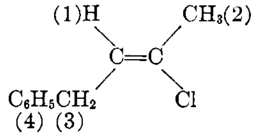
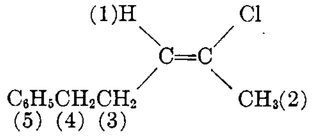
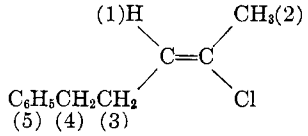
[3] M. S. Newman and L. L. Wood, Jr., *J. Am. Chem. Soc.*, **81**, 4300 (1959).

[4] Cyclization of ordinary carbonium ions to form five- and six-membered rings are known to occur readily, *e.g.*, D. Perlman, D. Davidson, and M. T. Bogart, *J. Org. Chem.*, **1**, 288 (1936).

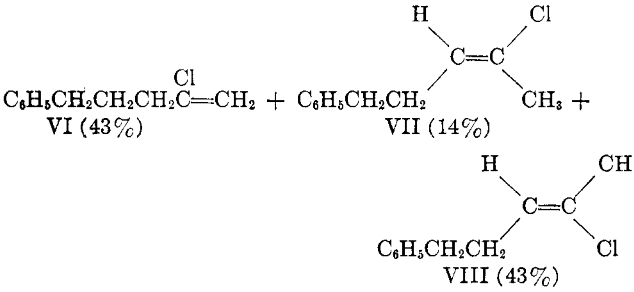
[5] See discussion in E. S. Gould, "Mechanism and Structure in Organic Chemistry," H. Holt and Co., New York, N. Y., 1959, pp. 475–577.

TABLE I

N.M.R. DATA FOR CHLOROOLEFINS

Compound	Chemical shifts, τ scale						Coupling constants, c.p.s.		
	δ_1	δ_2	δ_3	δ_4	δ_5	δ_6	$J_{1,2}$	$J_{1,3}$	$J_{2,3}$
	4.95	5.03	7.3[a]	7.3[a]	2.89			−1.06	−1.20
	4.73	4.91	8.00[a]	8.00	8.00[a]	2.91		−1.41	−0.94
	4.41	7.91	6.54	2.88			−1.37	+7.20	+1.53
	4.27	7.92	6.71	2.90			−1.46	+7.95	+0.70
	4.44	7.99	7.4[a]	7.4[a]	2.90		−1.07	6.40	
	4.46	8.10	7.5[a]	7.5[a]	2.89		−1.50	7.20	

[a] Approximate region for δ.



The structures of these olefins were established by the methods of n.m.r. spectroscopy.[6] The types and relative numbers of hydrogens in each compound were obtained from the positions and relative integrated intensities of the different bands in each spectrum. Chemical shift and coupling parameters are listed in Table I.

The chemical shift for terminal olefinic hydrogens occurs in the region of 4.9 ± 0.2 p.p.m. Thus compounds II and IV are identified as terminal olefins. For the other compounds the vinyl hydrogen resonance pattern consisted in each case of a triplet of quartets. The large triplet splitting yields the value for $J_{CH_2, CH}$ and the smaller quartet structure arises form $J_{CH_3, CH}$. Bothnerby[7] has reported that for propene $J_{CH, CH_3\, cis} = -1.75$ c.p.s. while $J_{CH, CH_3\, trans} = -1.33$ c.p.s. By analogy to this result we assign the structure in which the vinyl hydrogen and methyl group are oriented *cis* to the isomer with the *larger negative coupling constant* in each pair of *cis, trans* isomers, see Table I.

Interestingly, we were unable to find any of the dichlorides which would result from replacement of the carbonyl oxygen with two chlorine atoms. This result may be contrasted with that for pinacolone in which case considerable dichloride is produced.[8]

Results described previously were those obtained when the ketones were treated with a small excess of phosphorus pentachloride in methylene chloride at about 25°. In a brief study of solvent effects it was found that in methylene chloride, V, reacted completely in three hours whereas, in nitroethane, after twenty-five hours only 43% had reacted and, in acetonitrile, only 32% had reacted after forty-eight hours. Similar results were obtained with I. In the reactions in methylene chloride the effect of added anhydrous aluminum chloride was studied briefly. When one equivalent of the 1:1 complex of phosphorus pentachloride–aluminum chloride[9] was used in methylene chloride solution, the ketones, I and V, were recovered essentially unchanged. The dark color of the reaction mixtures suggested that the $PCl_4^+AlCl_4^-$ complex dissociated and that the ketones then complexed with aluminum chloride. The latter complex is evidently stable toward phosphorus pentachloride.

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[6] All spectra were determined with the Varian HR 60 n.m.r. spectrometer at 33°. The solvent was carbon tetrachloride and the internal standard was tetramethylsilane. Calibrations were accomplished by the methods of audio-side-band modulation.

[7] A. A. Bothnerby and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961).

[8] M. P. Ivitsky, *Bull. soc. chim.*, [4] **35**, 357 (1924). We have confirmed this in our laboratory.

[9] See footnote 6 in ref. 3. We are indebted to S. Shore and V. Petro for a gift of this complex, $PCl_4^+AlCl_4^-$.

Experimental[10]

Phenylbutyric Acid.—This acid was obtained in 95% yield by the modified Wolff–Kishner reduction.[11]

5-Phenyl-2-pentanone, V.—This compound was prepared by adding a solution of 0.98 mole of methyllithium in 400 ml. of ether to a solution of 72 g. of δ-phenylbutyric acid in 150 ml. of dry ether at gentle reflux. After an additional 1 hr. at reflux, V was isolated by a conventional procedure and distilled to give pure V, b.p. 89–91° at 2 mm.,[12] in 67% yield. The semicarbazone melted at 128–129°. In addition 23% of starting acid was recovered. The ketone was pure by v.p.c. analysis over Carbowax 4000 on firebrick.

4-Phenyl-2-butanone was purchased from the Aldrich Chemical Co., and found pure by similar v.p.c. analysis.

Reactions of Ketones with Phosphorus Pentachloride.—In a typical run a solution of 29.6 g. (0.2 mole) of 4-phenyl-2-butanone, I, in 100 ml. of methylene chloride was added to a suspension of 45.7 g. (0.22 mole) of phosphorus pentachloride in 200 ml. of dry methylene chloride in a three-necked 500-ml. flask fitted with a reflux condenser and stirrer. The reaction mixture was held at reflux for 30 hr., cooled, and treated with ice. The organic products were taken into benzene–ether and washed well with water, 10% sodium carbonate solution, water, and saturated sodium chloride solution. The organic layer was then filtered through a magnesium sulfate layer and the solvent removed by distillation. On vacuum distillation the residue yielded a mixture of II, III, and IV, boiling in the range 84–94° at 7 mm., in 93–98% yield. The entire distillate in the above run was analyzed.

Anal. Calcd. for $C_{10}H_{11}Cl$: C, 72.0; H, 6.7; Cl, 21.3. Found[13]: C, 72.1; H, 6.6; Cl, 21.3.

In a similar run using 5-phenyl-2-pentanone, V, chloroolefins were obtained in about 95% yield and boiled in the range 105–115° at 11 mm.

Anal. Calcd. for $C_{11}H_{13}Cl$: C, 73.1; H, 7.2; Cl, 19.8. Found[13]: C, 73.0; H, 7.3; Cl, 19.6.

TABLE II

(All runs were at 25° in methylene chloride unless otherwise indicated)

	Reactants (moles × 10)				Products,[a] %			
Expt.	Ketone	PCl_5	$AlCl_3$	Time, hr.	I	II	III	IV
1[a]	0.14	0.15	0	96	0	52	12	36
2[b]	2.0	2.2	0	40	0	54	12	34
3[c]	2.0	2.2	0	30	0	53	12	35
4	1.0	1.0	1.0	80	87	7	1	5
5	0.8	0.8	0.008	5	16	41	10	33
6	0.8	0.8	0.008	20	14	40	12	34
7[d]	0.2	0.2	0	48	69	15	1	15
8[e]	0.8	0.9	0	4	39	20	8	33
9[e]	0.8	0.9	0	20	32	23	6	39
10[f]	0.19	0.19	0.19	44	80	10	2	8

[a] The per cents listed are those determined by v.p.c. analysis of a representative sample of the reaction mixture. [b] Run at 0°. [c] Run at 40°. [d] Solvent was acetonitrile. [e] Solvent was nitroethane. [f] The complex, $PCl_4^+AlCl_4^-$, was used as supplied by S. Shore and Victor Petro.

A number of other runs were carried out and the results are listed in Tables I and II. The analyses of the reaction mixtures were carried out as described.

Gas Chromatographic Analyses.—The chloroolefins obtained as described earlier were analyzed on a 6 ft. × $^1/_4$ in. copper column packed with Carbowax 4000[14] on 42–60-mesh firebrick using a Model 500 unit manufactured by the F. and M. Scientific Corp. equipped with an integrating unit manufactured by Minneapolis-Honeywell Corp. Quantitative determination of the composition of runs was done by integration of the area under each peak. Addition of synthetic 1-methylindene,[15] b.p. 70–72° at 10 mm., prepared in 90% yield from 1-indanone and methyllithium, to the reaction mixture of phosphorus pentachloride and 4-phenyl-2-butanone proved that no methylindene was present. Similarly, addition of 1-methyl-3,4-dihydronaphthalene,[16] b.p. 90–93° at 8 mm., prepared in 80% yield from 1-tetralone and methylmagnesium bromide in ether, proved that none of this material was formed in the reactions of 5-phenyl-2-pentanone.

In the case of results reported in Table II three separate peaks were obtained in addition to a peak corresponding to starting ketone in certain runs. A representative sample was put through the column on a preparative scale and the fractions were identified by n.m.r. and infrared analyses.

In the case of the results reported in Table III only two peaks were obtained other than starting ketone. The larger of these peaks was analyzed by n.m.r. and found to consist of about equal amounts of VI and VIII. This result was confirmed by analysis on a 100-ft. squalene capillary column.[17]

TABLE III

(All runs were at 25° in methylene chloride unless otherwise noted)

	Reactants (moles × 10)				Products,[a] %		
Expt.	Ketone	PCl_5	$AlCl_3$	Time, hr.	V	VI and VIII	VII
1[b]	1.2	1.2	0	96	6	77	17
2	3.7	1.2	0	3	6	77	17
3	3.7	4.3	0	3	2	84	14
4	3.7	4.3	0	18	2	85	13
5[c]	1.6	1.7	0	34	0	85	15
6	1.2	1.2	1.2	15	100	0	0
7	6.0	6.0	6.0	80	100	0	0
8[d]	1.8	1.9	1.9	44	76	19	5
9[e]	1.2	1.3	0	48	68	25	7
10[f]	1.2	1.3	0	25	57	36	7

[a] The per cents listed are those determined by v.p.c. analysis of a representative sample of the reaction mixture. The column headed by VI and VIII represents the total per cent of VI and VIII. These were not separated on the v.p.c. column used. N.m.r. and infrared[15] studies on the mixture showed that this fraction was very nearly a 1:1 mixture of VI and VIII in each of the cases examined. It is assumed that all of these are 1:1 mixtures of VI and VIII. [b] Run at 0°. [c] Run at 40°. [d] The complex, $PCl_4^+AlCl_4^-$, was used as supplied by S. Shore and Victor Petro. [e] Solvent was acetonitrile. [f] Solvent was nitroethane.

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(10) All melting points uncorrected.

(11) Compare Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).

(12) J. Levy and M. Sfiras, *Compt. rend.*, **184**, 1337 (1927), give b.p. 132–135° at 17 mm., m.p. of semicarbazone, 127–128°.

(13) Microanalyses by J. Galbraith Co., Knoxville, Tenn.

(14) Carbowax 4000 is a polyethylene glycol of molecular weight about 4000, having a melting range of 50–55° and made by the Union Carbide Co.

(15) Our material agreed well with that reported by W. E. Parham, H. E. Reiff, and P. Swartzen, *J. Am. Chem. Soc.*, **78**, 1437 (1956).

(16) K. von Auwers, *Ber.*, **58**, 154 (1925) gives b.p. 238–239° at 760 mm.

(17) We thank J. Wiley for this analysis.