where m_1 and m_2 are successive values of molalities, T_1 and T_2 are corrected freezing points at the corresponding molalities, θ_2 is the freezing-point depression (10.625° − T_2), pue $m^s(HOSO_3^-)$ is the concentration of produced bisulfate assuming 2 moles of $HOSO_3^-$ generated per mole of substrate added. A solution of 20% *N,N*-dimethyldiphenylphosphinamide in stock sulfuric acid was used to add the substrate to the cryoscope. The first two measurements were made within 3 hr of preparation of this solution; the remaining five measurements were done between 6 and 8 hr after preparation.

The ν values which we determined for sodium bisulfate, mesitoic acid, and benzoic acid are in good agreement with published values.[11] A sample set of data is in Table V.

The phosphorus compounds were prepared by methods previously published[9,13] except for the following. Methylphenylphosphinic acid was prepared by the method of Harwood and Grisley.[27] Di-*tert*-butylphosphinic acid was prepared by addition of 2 moles of *tert*-butyllithium in pentane to PCl_3 in hexane, using Dry Ice-acetone to cool the reaction mixture. After stirring overnight at room temperature, $CHCl_3$ was added and Cl_2 was bubbled through the solution to oxidize R_2PCl to R_2PCl_3. Water was added to hydrolyze the phosphorane, the layers were separated, and the organic solvents were removed. The resultant yellow oil was refluxed overnight with dilute sodium hydroxide. Acidification with HCl followed by extraction with chloroform gave a small yield of white crystals: mp 201-205° (lit.[28] 208-210°); nmr (CH_2Cl_2) τ 8.80 (doublet), J_{PCCH} = 17 Hz; ir (KBr) 2970 m, 2960 m, 2900 m, 2870 m, 1610 broad m, 1470 s, 1390 m, 1365 m, 1350 m, 1240 m, 1140 s, 935 s, 820 m, 810 m, 675 m, 590 m.

Table V. Freezing Point Depression of Solutions of Methyl Dimethylphosphinate

$m^{s\,a}$	Fp,^{a} °C	$m^{s\,b}$	Fp,^{b} °C	θ,^{c} °C	ν^d
0.00000		0.005	10.320	0.295	2.10
0.00319	10.345	0.010	10.288	0.337	2.09
0.00845	10.300	0.015	10.246	0.379	2.05
0.01379	10.257	0.020	10.187	0.428	2.07
0.01883	10.210	0.030	10.089	0.536	2.08
0.02647	10.125	0.040	9.971	0.644	2.06
0.03385	10.050	0.050	9.862	0.763	2.06
0.04300	9.948				
0.05112	9.848				

[a] Experimentally determined molalities and freezing points. Freezing points have been corrected for supercooling. [b] Molalities for which values of m^d have been determined. Freezing points obtained by linear interpolation. [c] Freezing point depression (10.625° − fp). [d] Average value for ν = 2.07 ± 0.02.

N,N-Dimethyldiphenylphosphinamide (**9**) was prepared by addition of dimethylamine to diphenylphosphinyl chloride. The amide was extracted with CCl_4, the solution was dried, and solvent was removed by evaporation. Recrystallization from acetone-hexane and sublimation gave white crystals: mp 104-105° (lit.[29] 103-105°).

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(28) P. C. Crofts and G. M. Kosolapoff, *ibid.*, **75**, 3379 (1953).

(29) I. N. Zhmurova, I. Yu. Voitsekhovskaya, and A. V. Kirsanov, *Zh. Obshch. Khim.*, **33**, 1015 (1963).

SN1 Mechanisms in Displacement at Phosphorus. Solvolysis of Phosphinyl Chlorides[1-3]

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Contribution from the Department of Chemistry, University of California, Los Angeles, California 90024, and the Department of Chemistry, Wesleyan University, Middletown, Connecticut 06457. *Received October 26, 1970*

Abstract: The solvolysis reactions of phosphinyl chlorides have been investigated in order to define the tendency of phosphorus to undergo substitution by dissociative reactions. In the case of di-*tert*-butylphosphinyl chloride, $[(CH_3)_3C]_2P(O)Cl$ there is clear evidence for a dissociative, or SN1(P), reaction. Since this is an exceedingly hindered compound, it is a dramatic indication of the great preference for associative, SN2(P), displacement at phosphorus. This is the mechanism found for diisopropylphosphinyl chloride. Conjugative effects do not lead to SN1(P) mechanisms. Angle strain does not appear to have the inhibitory effect on SN1(P) reactions that it has on SN1(C) reactions. The *m* values from log *k*/*Y* plots are lower for solvolysis of phosphinyl halides than for solvolysis of alkyl halides.

Displacement at tetrahedral carbon by an SN1 dissociative mechanism is one of the most extensively studied fields of chemistry, and the factors which predispose to this mechanism in any particular reaction are well understood.[5,6] Although displacement at tetrahedral phosphorus apparently can proceed by a dissociative pathway, reliably authentic examples are few[7-10] and largely confined to phosphate derivatives[11] where the intermediate of reduced coordination number can be stabilized by delocalization as in the generation of metaphosphate (**2**) from aryl phosphates (eq 1).[12]

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(1) This research was supported by Grants GP-8142 and GP-13453 from the National Science Foundation and by Grant AM-12743 from the National Institute of Arthritis and Metabolic Diseases.

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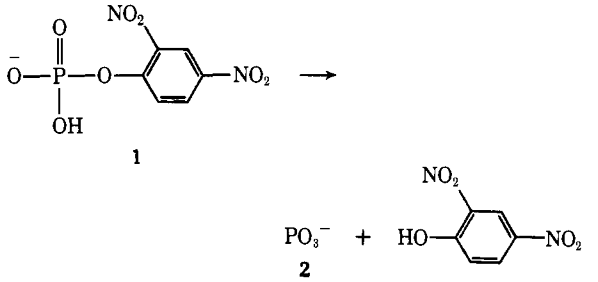

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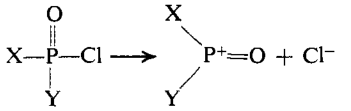
(1)

It is of considerable interest to understand the mechanism of solvolysis of phosphacyl[13] chlorides and particularly those cases which may undergo reaction by a dissociative mechanism.



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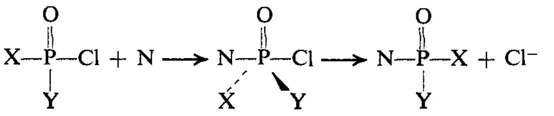
(2)

Previous studies demonstrate that the rates of solvolysis increase as alkyl groups replace alkoxy groups bonded to phosphorus in the series phosphoryl,[13] phosphonyl,[13] and phosphinyl[13] chlorides.[14,15] This indicates an associative mechanism, since conjugation between alkoxy groups and phosphorus appears to stabilize the ground state more than the transition state. No ^{18}O is incorporated when the solvolysis of $(C_2H_5O)_2P(O)Cl$ is carried out in $[^{18}O]H_2O$,[16] but this may not rule out some involvement of a pentacoordinate intermediate.[17]

Rate comparisons in isosolvolytic[18] media also indicate the predominance of associative mechanisms. Solvolysis of phosphoryl and phosphonyl chlorides are 10^3 slower in formic acid than in the isosolvolytic but more nucleophilic aqueous ethanol.[14,19] Also, m values from the Winstein–Grunwald equation,[20] $\log k/k_0 = mY$, were 0.43 for solvolysis of $(n\text{-PrO})_2P(O)Cl$ and 0.33 for solvolysis of $(i\text{-octyl-O})(CH_3)P(O)Cl$.[19] These are typical values for bimolecular, associative substitutions.

Additional evidence for associative displacement in phosphacyl chlorides (eq 3) includes: (1) rate enhancement on addition of nucleophilic reagents,[14] (2) rate dependence on size of nucleophile,[21] (3) steric retardation by large substituents at phosphorus,[15,22] and (4) rate inhibition due to angle strain at phosphorus.[23]

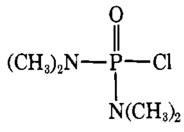


3

5

(3)

However, dissociative substitution may be possible in amido halides. In the hydrolysis of 6, addition of ^-OH, *m*-cresoxide, and pyrrolidine failed to increase the rate markedly; addition of mercurous perchlorate, on the other hand, a reagent which promotes ionization, was observed to enhance the rate. However, the compound did react bimolecularly with azide ion.[24] Evidence for bimolecular substitution includes a decrease in rate as the basicity (and consequently the electron-donating ability) of the amino groups increase,[19] rate enhancements ranging from 30 to 200 for aqueous solvents isosolvolytic to formic acid,[19] and m values ranging from 0.36 to 0.58,[25] considerably below the value of 1.0 for the solvolysis of *tert*-butyl chloride. The presence of an NH, as in **7**, may promote a base-catalyzed dissociative mechanism involving proton removal and cleavage of the P–Cl bond (**8** or in two steps).[26] However, it has been impossible to trap an intermediate.



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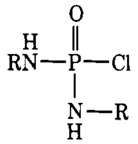

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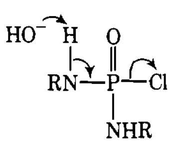
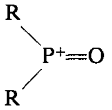


8

Therefore, there is little evidence for dissociative substitution at phosphorus of the type found in displacement reactions of tertiary halides in carbon chemistry. The results reported in this paper quite clearly *demonstrate* such *a dissociative displacement at phosphorus.* Our data define some factors that predispose to S_N1-like displacement at phosphorus and clearly demonstrate the predominance of associative mechanisms. We have already shown that phosphinylium ions (**9**) are not formed in the equilibria occurring in very strong acids starting from **10**. However, this does not preclude **9** functioning as a reaction intermediate,[11] and in this study we define the conditions under which **11** may solvolyze through **9**.



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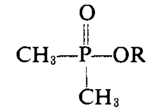
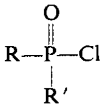


10 ($R = H, CH_3$)



11

Results

Y Value for CF_3CO_2H. The rate of solvolysis of *tert*-butyl chloride in trifluoroacetic acid was measured at 25.0° in order to determine the solvolytic power of the solvent. Addition of water and/or sodium trifluoroacetate was necessary to advance the reaction sufficiently so that a rate could be determined, but in each case the reaction followed first-order kinetics for 35–40% reaction. The titrimetric rate constants from these determinations as well as similar measurements

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(12) A. J. Kirby and A. G. Varvoglis, *J. Amer. Chem. Soc.*, **89**, 415 (1967).

(13) By phosphacyl we mean any X(Y)P(=O) grouping. Therefore, a phosphacyl chloride is X(Y)P(=O)Cl. The term phosphacyl therefore includes phosphoryl, RO(OR′)P(=O), phosphonyl, RO(R′)P(=O), and phosphinyl, R(R′)P(=O).

(14) I. Dostrovsky and M. Halmann, *J. Chem. Soc.*, 502 (1953).

(15) A. A. Neimyscheva and I. L. Knunyants, *Zh. Obshch. Khim.*, **36**, 1090 (1966).

(16) I. Dostrovsky and M. Halmann, *J. Chem. Soc.*, 1004 (1956).

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(18) The term isosolvolytic describes media of equal solvolyzing power for the solvolysis of *tert*-butyl chloride: A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2770 (1956).

(19) R. F. Hudson and L. Keay, *J. Chem. Soc.*, 1865 (1960).

(20) S. Winstein, E. Grunwald, and H. W. Jones, *J. Amer. Chem. Soc.*, **70**, 846 (1948).

(21) I. Dostrovsky and M. Halmann, *J. Chem. Soc.*, 511 (1953).

(22) R. F. Hudson and L. Keay, *ibid.*, 1859 (1960).

(23) P. Haake, R. D. Cook, T. Koizumi, P. S. Ossip, W. Schwarz, and D. A. Tyssee, *J. Amer. Chem. Soc.*, **92**, 3828 (1970).

(24) H. K. Hall, Jr., *J. Org. Chem.*, **21**, 248 (1956); H. K. Hall, Jr., and C. H. Lueck, *ibid.*, **28**, 2818 (1962).

(25) E. W. Crunden and R. F. Hudson, *J. Chem. Soc.*, 3591 (1962).

(26) P. S. Traylor and F. H. Westheimer, *J. Amer. Chem. Soc.*, **87**, 553 (1965).

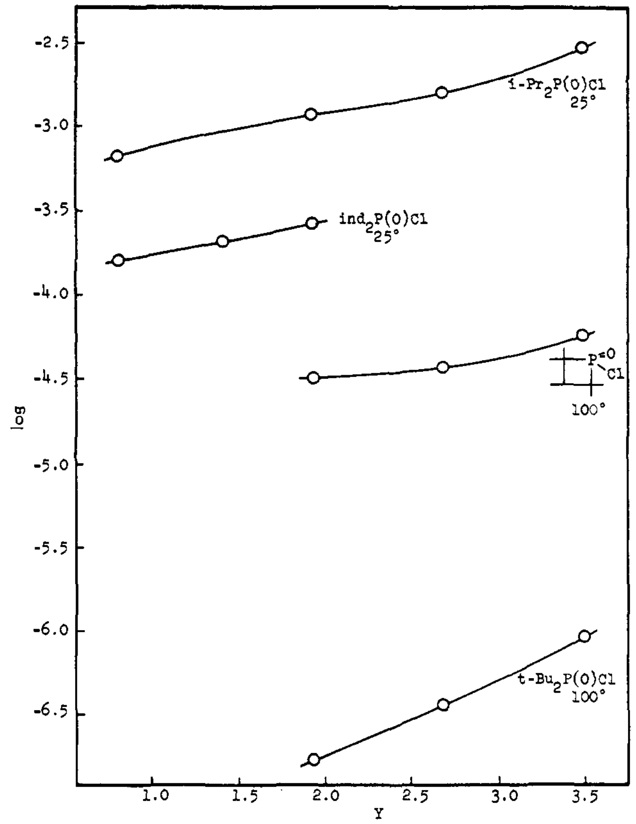


Figure 1. Log *k vs. Y* for solvolysis of phosphinyl chlorides in aqueous acetone.

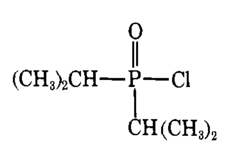
in two solvents of known[18] solvolytic power are given in Table I. The *Y* value we observe for CF_3CO_2H is 1.84.[27]

Table I. Kinetic Data for Solvolysis of *tert*-Butyl Chloride at 25.0°

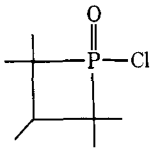
Solvent	% reaction[a]	10^3k sec^{-1} [b]
CF_3CO_2H + 0.33 *M* H_2O	30	0.48 ± 0.02
CF_3CO_2H + 0.50 *M* H_2O	51	0.75 ± 0.04
CF_3CO_2H + 1.0 *M* H_2O	35	0.72 ± 0.09
CF_3CO_2H + 0.04 *M* $NaOCOCF_3$ + 0.02 *M* H_2O	35	0.72 ± 0.04
CF_3CO_2H + 0.05 *M* $NaOCOCF_3$	47	0.62 ± 0.05
CF_3CO_2H + 0.05 *M* $NaOCOCF_3$	45	0.57 ± 0.05
HCO_2H + 0.036 *M* H_2O	60	1.19 ± 0.01[c]
38.5% aqueous acetone[d]	74	1.00 ± 0.01[c]

[a] For the solvolyses in trifluoroacetic acid this represents the limit of linear first-order kinetics. For the other two solvents this value represents the last point taken other than the experimental infinity point. [b] Deviation is the std deviation by least-squares analysis. Average value for $k_{CF_3CO_2H}$ = $(0.64 \pm 0.10) \times 10^{-3}$ sec^{-1}; $Y_{CF_3CO_2H}$ = 1.84. [c] Reported value is 1.05×10^{-3} sec^{-1} for both solvents.[18] [d] 38.5% acetone, 61.5% water by volume at 25°.

Solvolysis of Phosphinyl Halides. Rates of solvolysis were determined for diisopropylphosphinyl chloride (**12**), 2,2,3,4,4-pentamethyltrimethylenephosphinyl chloride (**13**), di-*tert*-butylphosphinyl chloride (**14**), and di-3-indolylphosphinyl chloride (**15**) in various


$(CH_3)_2CH-\underset{CH(CH_3)_2}{\overset{\overset{O}{\|}}{P}}-Cl$

12



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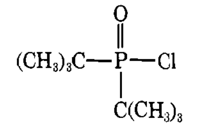
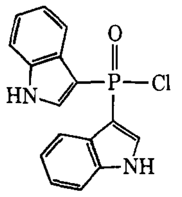

$(CH_3)_3C-\underset{C(CH_3)_3}{\overset{\overset{O}{\|}}{P}}-Cl$

14



15

concentrations of aqueous acetone, in trifluoroacetic acid with sodium trifluoroacetate present, and in formic acid with sodium formate or water added (Table II). An attempt was also made to measure the solvolysis rate of diethylphosphinyl chloride, but the reaction was too rapid; a minimum rate constant is given in Table II. All correlation coefficients were greater than 0.99 except for the two rates for **15** in CF_3CO_2H where the standard deviations can be seen to be large. Despite the small standard deviations and the generally high correlation coefficients, the rate constants in Table II are probably not accurate to better than ±10%. The main source of uncertainty in the conductometric rates and in the *tert*-butyl chloride solvolyses (Table I) is in the experimental determination of the infinity point. The chief error in all titrimetric rates was the uncertainty inherent in the chloride analyses, particularly for the slow reactions and for those which did not progress very far before approaching equilibrium. Despite the uncertainties in these rate constants, they should be more than adequate for the conclusions in this paper (see Discussion).

Figure 1 illustrates the dependence of reaction rates on solvolyzing power of the solvent. By plotting log *k vs. Y*, the slopes, *m*, of the lines are obtained. Table III presents this data for the four phosphinyl halides studied. Because the plots were curved (Figure 1), tangential values are given.

Rate ratios for solvolysis in isosolvolytic media are given in Table IV. They are calculated from rate constants in acids containing 0.05 *M* salt. The formic acid ratios are from interpolated rates for 38.5% acetone. Although the rate ratios are somewhat inaccurate because of the inaccuracy of the rates in CF_3CO_2H, the accuracy is more than adequate for the conclusions in this paper. Relative rates as a function of substrate structure are in Table V. Since the solvolysis of **12** was studied at 25 and 45° in 41% aqueous acetone, it is possible to calculate an activation energy, E_a = 11 kcal/mole.

Crude kinetic results were obtained from nmr measurements of solvolysis of di-*tert*-butylphosphinyl bromide in water and in water 1.1 *M* in silver ion. The rates were followed by disappearance of the doublet resonance signal for the $PCCH_3$ groups of the chloride and appearance of a similar signal for the $PCCH_3$ groups of the acid. A rate enhancement on **13** by silver ion was observed at 70°. These experiments also demonstrated no observable rearrangement of the substrate during solvolysis.

(27) Our results on CF_3CO_2H are supported by the results of A. Diaz, I. L. Reich, and S. Winstein, *J. Amer. Chem. Soc.*, 91, 5637 (1969).

Table II. Kinetic Data for Solvolysis of Phosphinyl Chlorides

Compd	Solvent[a]	Temp, °C[a]	Method[d]	% reaction[b]	k, sec^{-1}
12	H_2O	25	C	100	$(2.897 \pm 0.009) \times 10^{-3}$
	25% acetone	25	C	100	$(1.558 \pm 0.004) \times 10^{-3}$
	41% acetone	25	C	100	$(1.157 \pm 0.002) \times 10^{-3}$
	41% acetone	25	T	100	$(1.04 \pm 0.04) \times 10^{-3}$
	41% acetone	45	C	100	$(4.48 \pm 0.03) \times 10^{-3}$
	60% acetone	25	C	100	$(0.649 \pm 0.002) \times 10^{-3}$
	$CF_3CO_2H + 0.05\ M\ NaOCOCF_3$	25	T	33^b	$(5.69 \pm 0.25) \times 10^{-7}$
	$CF_3CO_2H + 0.50\ M\ NaOCOCF_3$	25	T	48^c	$(4.27 \pm 0.22) \times 10^{-7}$
	$HCO_2H + 0.05\ M\ NaO_2CH$	25	T	100	$(2.66 \pm 0.03) \times 10^{-5}$
	$HCO_2H + 0.50\ M\ NaO_2CH$	25	T	100	$(7.58 \pm 0.32) \times 10^{-5}$
	$HCO_2H + 0.06\ M\ H_2O$	25	T	95^b	$(1.75 \pm 0.04) \times 10^{-5}$
14	H_2O	100	T	81^c	$(9.10 \pm 0.09) \times 10^{-7}$
	25% acetone	100	T	50^c	$(3.47 \pm 0.10) \times 10^{-7}$
	41% acetone	100	T	31^c	$(1.70 \pm 0.05) \times 10^{-7}$
	$CF_3CO_2H + 0.05\ M\ NaOCOCF_3$	100	T	15^b	$(8.47 \pm 0.46) \times 10^{-8}$
	$CF_3OC_2H + 0.50\ M\ NaOCOCF_3$	100	T	14^c	$(5.78 \pm 0.34) \times 10^{-8}$
13	H_2O	100	T	100	$(5.64 \pm 0.05) \times 10^{-5}$
	25% acetone	100	T	100	$(3.60 \pm 0.04) \times 10^{-6}$
	41% acetone	100	T	100	$(3.13 \pm 0.09) \times 10^{-5}$
	$CF_3CO_2H + 0.05\ M\ NaOCOCF_3$	100	T	80^c	$(3.06 \pm 0.10) \times 10^{-6}$
	$CF_3CO_2H + 0.50\ M\ NaOCOCF_3$	100	T	66^b	$(2.63 \pm 0.14) \times 10^{-6}$
15	41% acetone	25	C	100	$(2.571 \pm 0.007) \times 10^{-4}$
	50% acetone	25	C	100	$(2.037 \pm 0.106) \times 10^{-4}$
	60% acetone	25	C	100	$(1.579 \pm 0.003) \times 10^{-4}$
	$CF_3CO_2H + 0.05\ M\ NaOCOCF_3$	25	T	8^b	$(4.29 \pm 0.71) \times 10^{-8}$
	$CF_3CO_2H + 0.50\ M\ NaOCOCF_3$	25	T	11^c	$(5.51 \pm 0.45) \times 10^{-8}$
	$HCO_2H + 0.05\ M\ NaO_2CH$	25	T	60^c	$(8.60 \pm 0.16) \times 10^{-7}$
$(C_2H_5)_2P(O)Cl$	41% acetone	25	C	100	3×10^{-1} or greater

[a] Temperatures are accurate to ±0.1°. [b] Limit of linear first-order kinetics. [c] Reaction was too slow to be followed further. [d] C = conductometric; T = titrimetric.

Table III. m Values for Solvolysis of Phosphinyl Halides (R_2POCl) in Aqueous Acetone

% acetone	12	15	13	14
60	0.22	0.18		
50		0.19		
41	0.20	0.19	0.08	0.40
25	0.25		0.17	0.45
0	0.33		0.24	0.52

Table IV. Comparison of Relative Rates of Solvolysis of Phosphinyl Halides in Isosolvolytic Media

Substrate	Temp, °C	k(38.5% acetone)/k(HCO_2H)[a]	k(41% acetone)/k(CF_3CO_2H)[a]
12	25	46	2000
15	25	310	6000
13	100		10
14	100		2

[a] Rate ratios in isosolvolytic media.

Table V. Relative Rates of Solvolysis of Phosphinyl Halides

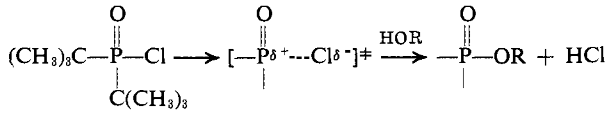
	In 41% aqueous acetone		In CF_3CO_3H[a]
	k_{rel}(25.0°)	k_{rel}(100.0°)	k_{rel}(100°)
$(C_2H_5)_2P(O)Cl$	>250		
12	1	1^b	1
13		6.5×10^{-4}	0.13
14		3.6×10^{-6}	3.6×10^{-3}
15	0.23		

[a] Calculated from relative rates in aqueous acetone and the rate ratios in Table IV. [b] Extrapolated values.

Discussion

Mechanisms of Solvolysis. We believe that the most important data diagnostic of mechanism are in Table IV—the ratios of rates in isosolvolytic solvents. The large rate ratios in Table IV for compounds **12** and **15** indicate that they must solvolyze by associative pathways[23] as concluded for other compounds in previous studies.[21–26]

It is particularly important to note the much larger rate ratios for **12** and **15** with 41% aqueous acetone–CF_3CO_2H than with 38.5% aqueous acetone–HCO_2H. These ratios demonstrate the very low nucleophilicity of CF_3CO_2H. Since the two aqueous acetone mixtures must be similar in nucleophilicity, the data for **12** indicate that CF_3CO_2H is about 40 times less nucleophilic than HCO_2H for displacement at phosphorus. This suggests that the rate ratio for solvolysis in 41% aqueous acetone and in CF_3CO_2H is a very good test for dissociative pathways of solvolysis. Therefore, the small rate ratios for **13** and **14** (Table IV) indicate a major contribution of dissociation in the transition state for solvolysis



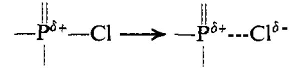
$$(CH_3)_3C-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle C(CH_3)_3}{|}}{P}}-Cl \longrightarrow [-\overset{\overset{\displaystyle O}{\|}}{\underset{|}{P}}{}^{\delta+}\text{---}Cl^{\delta-}]^{\ddagger} \xrightarrow{HOR} -\overset{\overset{\displaystyle O}{\|}}{\underset{|}{P}}-OR + HCl$$

Since there was no change of nmr spectrum during solvolysis of **14** there is apparently no rearrangement, as there is in similar reactions at carbon centers similar to the phosphorus center in **14**. Even Br^- as the leaving group and Ag^+-assisted solvolysis do not lead to rearrangement.

The data for **12** and **15** would lead one to expect very low ratios—near 1—for **13** and **14** in 38.5% acetone–HCO_2H. In comparison, SN1-type solvolyses of alkyl halides give ratios of 1 for *tert*-butyl chloride, 4 for α-phenylethyl chloride,[28] and 9 for CH_3OCH_2Cl.[29]

The SN2 solvolysis of methyl bromide yields a ratio of 200.[19] Previously investigated phosphorus compounds appear to fall in the same SN2-type class as **12**: ratios of 77 were found for **7** (R = C_2H_5)[25] and 2000 for $(CH_3CH_2CH_2O)_2P(O)Cl$[19]—a phosphoryl chloride.[30]

The *m* values (Table III) present an apparent contradiction. In the solvolysis of alkyl halides, unimolecular, dissociative pathways yield m = 0.76–1.2, and bimolecular, associative mechanisms yield m = 0.2–0.5.[6] This would appear to provide evidence for associative pathways for all the phosphinyl chlorides. However, the conclusions from isosolvolytic rate ratios seem incontrovertible and there is a reasonable explanation of the *m* values. Unlike solvolysis of alkyl halides, in the solvolysis of phosphinyl halides the ground state is quite polar due to the P–O bond. In the transition state for dissociative reaction, the π bonding in the P–O bond will be strengthened as the P–Cl bond breaks (see below). There will therefore be much less increase in polarity in the transition state than with alkyl halides. To emphasize this picture, we depict the ground state in the polarized form.



$$-\overset{O^{\delta-}}{\overset{\|}{P}}{}^{\delta+}-Cl \longrightarrow -\overset{O}{\overset{\|}{P}}{}^{\delta+}\text{---}Cl^{\delta-}$$

ground state transition state

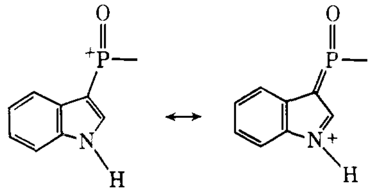
This expected difference in charge separation in phosphinyl chlorides compared to alkyl halides should affect the *m* value. Less charge separation should cause a smaller dependence on change in *Y* value of the solvent. This is, in fact, observed in the solvolysis of the phosphinyl halides; the *m* values for **14** indicate that, as expected, there is less charge separation than in the solvolysis of alkyl halides.

The very low *m* values for **13** are surprising, but **13** may be an example involving some merging of mechanism and the extent of nucleophilic participation may change as *Y* changes causing a variation in *m*. The ground state–transition state change in charge separation may also be unusual due to the strained structure of **13**.

The associative reaction of **12** results in an *m* value of 0.2, which is on the lower border of *m* values for solvolyses of alkyl halides. This also suggests that charge separation in the ground state causes a different range of *m* values for phosphacyl halides than the *m* values observed for alkyl halides. These considerations suggest that previous conclusions from *m* values (see introductory paragraphs) may be suspect unless supported by other evidence.

Structural Effects. The data in Tables IV and V enable some conclusions about structural effects on dissociative reactions at phosphorus. First, it is clear that *large steric effects* are necessary to observe SN1(P) mechanisms. Both **13** and **14** have highly hindered P atoms. The P atom in **14** has a doubled neopentyl effect,[6] and it is not surprising that nucleophilic attack is difficult. This is a particularly striking demonstration of the *preference for associative reactions in nucleophilic displacement at phosphorus*. Even the steric hindrance of two isopropyls in **12** does not slow nucleophilic attack enough to observe the SN1(P) mechanism. And when **14** does react by dissociation, the rate is nearly a million times slower than the associative displacement in **12** (Table V) in water.

The di-3-indolylphosphinyl chloride (**15**) is a critical test of the possibility of enhancing the rate of an SN1(P) mechanism by delocalization of positive charge.



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It may be true that the SN1(P) reaction is faster in **15** than in $(C_2H_5)_2P(O)Cl$, for example. But in both cases the associative reaction is so much faster that the SN1(P) mechanism cannot be observed. This supports the view that solvolyses of amidophosphoryl halides (**7**) and $(C_6H_5)_2P(O)Cl$[31] proceed by an associative mechanism.

The effect of angle strain has been evaluated using the four-membered ring, **13**.[23] There has recently been great interest in derivatives of **13**.[32] This ring system has a twofold effect. (1) The four α-methyl groups provide considerable steric hindrance (see above). (2) The C–P–C angle is approximately 83°.[32a] This provides a considerable driving force in associative reactions because in the formation of pentacoordinate intermediates strain can be released. These effects appear in the esters of **13** which undergo alkaline hydrolysis with displacement at phosphorus at a rate which is comparable to much less hindered phosphinates,[32b,c] and 10^5 faster than the similarly substituted (but probably more hindered) di-*tert*-butylphosphinate ester.[32d] Retention of configuration in displacement by hydroxide on certain phosphonium ions (**2**)[32e,f] is consistent with formation of a pentacoordinate intermediate and pseudorotation.

The very slow rate of solvolysis of **13** in aqueous acetone is therefore significant.[23] If one compares **13** to $(C_2H_5)_2P(O)Cl$ (Table V), **13** hydrolyzes at least

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(28) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 1602 (1957).

(29) T. C. Jones and E. R. Thornton, *ibid.*, **89**, 4863 (1967).

(30) There appear to be two possible problems in these conclusions. First, the ratios are related to the solvolysis of *tert*-butyl chloride. This reaction is the basis for deciding which composition of aqueous acetone is isosolvolytic with CF_3CO_2H. Both solvents are protic and can therefore stabilize, by hydrogen bonding, the Cl^- which is being generated in the transition state. However, aqueous acetone has a much greater dielectric constant and will stabilize a charge-separated transition state better than a carboxylic acid. Therefore, the results could be somewhat misleading if charge separation (transition state *vs.* ground state) is different in the solvolysis of *tert*-butyl chloride than in the solvolysis of phosphinyl chlorides. Second, because of the slow rates for **13** and **14**, it was necessary to carry out the reactions at 100°. At that temperature the solvents could have sufficiently different properties so that 41% aqueous acetone and CF_3CO_2H are not isosolvolytic. Both of these considerations would be expected to cause small effects compared to the enormous effect if there is a nucleophilic, associative factor in the mechanism of solvolysis. Again, the very low nucleophilicity of CF_3CO_2H makes the 41% aqueous acetone–CF_3CO_2H pair a sensitive method for detecting nucleophilic participation. We therefore believe that the low ratios for **13** and **14** must indicate little or no nucleophilic participation despite the above problems.

(31) I. Dostrovsky and M. Halmann, *J. Chem. Soc.*, 516 (1953).

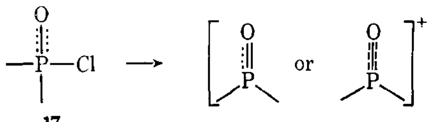
(32) (a) D. D. Swank and C. N. Caughlan, *Chem. Commun.*, 105 (1968); (b) P. Haake, R. D. Cook, W. Schwarz, and D. R. McCoy, *Tetrahedron Lett.*, 5251 (1968); (c) P. Haake, C. E. Diebert, and R. S. Marmor, *ibid.*, 5247 (1968); (d) W. Hawes and S. Trippett, *Chem. Commun.*, 577 (1968); (e) W. Hawes and S. Trippett, *ibid.*, 295 (1968); (f) K. E. DeBruin, G. Zon, K. Naumann, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 7027 (1969).

4×10^5 times slower. Yet, in the alkaline hydrolysis of esters, it has been observed that $(C_2H_5)_2PO_2CH_3$ hydrolyzes at about the same rate as the methyl ester of the four-membered ring (as in **13**).[32b] Furthermore, as discussed above, **13** solvolyzes even in aqueous acetone by a mechanism which must have considerable dissociative character. The rate ratio of 10 (Table IV) indicates some nucleophilic participation but the rate ratio certainly demonstrates that the solvolysis is mainly dissociative and quite different from the associative solvolysis of **12** or $(C_2H_5)_2P(O)Cl$. The rate comparison in Table V is therefore limiting. True associative solvolysis of **13** (that is, the same mechanism as for **12** or $(C_2H_5)_2P(O)Cl$) must be considerably slower than the observed rate for **13** and the ratio of rates of associative solvolysis of $(C_2H_5)_2P(O)Cl$ and **13** must be greater than 10^6. This large rate inhibition due to the four-membered ring indicates increased strain in the transition state which must therefore have a preferred geometry with entering and leaving groups colinear with the phosphorus atom. A reasonable conclusion is that the normal mechanism of solvolysis of phosphinyl halides involves a direct displacement, similar to an SN2 reaction. Is an intermediate involved? Basic to considerations of displacements at phosphorus are the factors favoring intermediates. The transition states for all but a few reactions at phosphorus (such as solvolysis of **13** and **14**) appear to have considerable associative character. Since phosphorus is known to form many stable pentacoordinate compounds, transition states in associative reactions would be expected to be stabilized to at least a small extent by pentacoordinate character and intermediates generally should be involved. Whether one can detect an intermediate is then a matter of stability, geometry, rates of pseudorotation, and proton transfer, etc. Our rates demonstrate that in the associative solvolysis of phosphinyl chlorides any intermediate must have entering and leaving groups colinear with phosphorus. This mechanism is therefore a type of direct displacement although the activated complex should have some stabilization through pentacoordinate character and another view could involve slow pseudorotation.

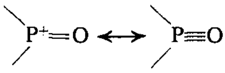
Structure of Phosphinylium Ions. The existence of dissociative mechanisms for solvolysis of **13** and **14** raises the question of the preferred bonding and geometry in phosphinylium ions (**4**). In this regard it is particularly useful to compare **13** and **14** since they have the same substitution at the α-carbon atoms. The angle effect will decrease the steric hindrance in **13** compared to **14**,[32] but the P atom in both is shielded from nucleophilic attack. In SN1(C) solvolyses, a four-membered ring has a large inhibitory effect on the rate because the angle strain increases in the transition state due to the preferred trigonal geometry of carbonium ions. Why then does **13** solvolyze 40 times faster than **14** in CF_3CO_2H? If both react by SN1(P) mechanisms, **14** should have the driving force of release of nonbonded interactions in the transition state and the angle effect would be expected, by analogy to carbonium ions, to slow **13**. Both effects are the reverse of what we observe (Tables II and V).

There appear to be two possible explanations. First, the solvolysis of **13** could involve nucleophilic participation that is absent in the solvolysis of **14**. The curved *mY* plot (Figure 1) supports that view. However, the isosolvolytic rate ratio of 10 appears too small for this to be correct.

Second, the extent of π bonding should be very important in the stabilization of an SN1(P) transition state. The P–O bond in a phosphinyl derivative, although written as a double bond, must really involve two partial π bonds[33] if π bonding is at all important energetically (**17**).[34] As a dissociative reaction proceeds, one of the σ orbitals can begin to be used for stronger π bonding (**18**). Alternatively the extra orbital might be hybridized to enable two equally strong π bonds (**19**). It is known that π-bond energies depend sharply on interatomic distances. Any factor which could shorten the P–O bond would stabilize the transition state by increasing the P–O π-bond energy. If the two P–C bonds have predominant $p_\sigma(P)$ character in the transition state from **13**, the P–O bond would have predominant $s_\sigma(P)$ character which should cause an unusually short P–O bond and therefore considerably more π-bond energy than in **14** where nonbonded interactions should widen the C–P–C angle in the transition state and cause a decrease in π-bond energy of the P–O bond. Therefore, it cannot be assumed that the preferred geometry of **18** would be symmetrical trigonal. Rather, the preferred C–P–C angle may be considerably less than 120° to enable stronger P–O π bonding. This then may explain the relative rates of **13** and **14** (Table V) in CF_3CO_2H.



17 **18** **19**



18a **18b**

Predominance of Associative Reactions at Phosphorus. The difficulty of generating phosphinylium ions from phosphinyl halides is probably a matter of bond energies. The P–Cl bond has been assigned an approximate bond energy of 76 kcal/mole from measurements on PCl_3.[35] Although the P–Cl bond in phosphinyl chlorides may be somewhat weaker, it is clear that a dissociative reaction will involve a considerable loss of P–Cl bond energy in the transition state. The compensating increase in P–O bond energy (**18** *vs.* **17**) would be expected to be small because only one strong P–O π bond can be formed from valence shell orbitals at P in **18**. In contrast, acylium ions, RCO^+, have valence orbitals for CO triple bonding. Also, it seems clear that PO multiple bonding involving outer orbitals requires a partial negative charge at oxygen.[34] This will inhibit the multiple bonding indicated in **18** and prevent the large increase in PO bond energy required for a dissociative reaction.

In contrast the transition state for associative reactions would involve a large increase in σ bond energy.

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[33] Sulfoxides would also be expected to have two partial π bonds. Chemical shifts in sulfoxides support this view of SO and PO bonding: K. W. Buck, A. B. Foster, W. D. Pardoe, M. H. Qadir, and J. M. Webber, *Chem. Commun.*, 759 (1966).

[34] K. A. R. Mitchell, *Chem. Rev.*, **69**, 157 (1969).

[35] S. B. Hartley, W. S. Holmes, J. K. Jacques, M. F. Mole, and J. C. McCoubrey, *Quart. Rev., Chem. Soc.*, 17, 204 (1963).

Since the transition state would be expected to be near a pentacoordinate intermediate on the reaction coordinate,[17] the bonds to entering and leaving groups should be nearly completely formed. This increase in σ bond energy should compensate effectively for loss in P–O bond energy. Therefore, *changes in bond energies appear to explain the predominance of associative mechanisms in displacement at phosphorus.*

Experimental Section

Mixed solvents were prepared on a v/v basis at 25°; for example, 41% H_2O-59% acetone (v/v). Water used both in solvolyses and in titrations was deionized by passage through an ion-exchange column. Acetone was Baker's AnalaR Reagent and was distilled from Drierite before use in solvolyses but not before use in titrations. Formic acid (Allied Chemical Company) was purified according to the directions of Winstein and Marshall.[36] Trifluoroacetic acid and *tert*-butyl chloride (both Matheson Coleman and Bell) were distilled through a 3-ft column packed with glass helices. Solutions of sodium trifluoroacetate and sodium formate were prepared by adding weighed amounts of sodium carbonate to the acids and adding the stoichiometric amount of the respective anhydride to react with the water produced.

All solutions were immersed in constant-temperature baths during reaction. Temperatures were controlled to ±0.1°, as indicated by standard thermometers calibrated by the National Bureau of Standards. Kinetic data were analyzed by the least-squares method and the standard deviation $= [\Sigma d_i^2/(N - 2)]^{1/2}$ where d_i = individual deviations and N = the number of points.

Conductometric rates were measured using a Phillips PR 9501 meter and solutions 0.02–0.07 M in substrate. **Titrimetric rates** were measured by potentiometric titration of aliquots for chloride ion using $AgNO_3$ as titrant and glass and Ag wire electrodes. Concentrated HNO_3 (5 drops) was added to the acetone–water solutions before titration except when the solvent was HCO_2H or CF_3CO_2H. A small amount of dextrin was added to help disperse the AgCl precipitate and prevent adsorption of Cl^-. In these rates substrate concentration was approximately 0.01 M. Experimental infinity points agreed with theoretical to ±10%. In the *tert*-butyl chloride solvolyses, infinity points were determined experimentally by pipetting a 4-ml aliquot into 20 ml of water and allowing time for complete reaction.

In the solvolysis of **13** and **14**, solutions were sealed in glass ampoules and, after quenching the reaction by cooling, aliquots (4 ml) were pipetted into 20 ml of water plus 10 ml of acetone and titrated. In the solvolysis of **15**, aliquots were pipetted into 20 ml of diethyl ether and extracted rapidly with two 10-ml portions of H_2O. Acetone (10 ml) was added to the aqueous extracts, and the solution was titrated. In the solvolysis of **12** its solubility in water necessitated the following procedure. Aliquots (4 ml) were added to 20 ml of $CHCl_3$ and extracted by 10 ml of H_2O. This aqueous extract was washed with 10 ml of $CHCl_3$, and, after being added to 10 ml of H_2O plus 10 ml of acetone, it was titrated. It was demonstrated by controls that Cl^- was not lost in this procedure. Aliquots (4 ml) of *tert*-butyl chloride solutions were pipetted into 20 ml of hexane and extracted with two 10-ml portions of water. Acetone (10 ml) was added, and the solution was titrated.

Tetraethylbiphosphine disulfide was prepared from ethyl magnesium bromide and thiophosphoryl chloride.[37] Crystallization from aqueous ethanol gave brownish crystals, mp 75–76° (lit.[38] 76–77°). Sublimation gave white crystals: mp 75.5–77°; 53% yield; nmr (CCl_4), τ 7.86 (overlapping doublet of triplets, area $\propto$ 2), $J_{\mathrm{PCH}} = 7$–8 cps, τ 8.7 (overlapping doublet of triplets, area $\propto$ 3), $J_{\mathrm{PCCH}} = 18$–21 cps. *Anal.* Calcd for $C_8H_{20}P_2S_2$: C, 39.65; H, 8.32. Found: C, 39.80; H, 8.10.

Diethylphosphinyl chloride was prepared from tetraethylbiphosphine disulfide using SO_2Cl_2. The crude product was vacuum distilled to give a slightly pink liquid: bp 54° (0.25 mm); nmr (CH_2Cl_2), τ 7.98 (overlapping doublet of quartets, area $\propto$ 2), τ 8.79 (doublet of triplets, area $\propto$ 3), $J_{\mathrm{PCCH}} = 22$ cps. The mass spectrum revealed parent peaks at 142 and 140, a base peak at 112 ($-C_2H_4$), and a $(C_2H_5)_2PO^+$ fragment at 105 in agreement with the structure.[11]

Diisopropylphosphinyl chloride (12) was prepared by the method of Christen and van der Linde.[39] Vacuum distillation gave a yellow liquid, bp 83–84° (3 mm) (lit.[39] 50° (0.2 mm)). The product was redistilled through a Teflon spinning band column under vacuum. Yield was 48% of theoretical: nmr (neat), τ 7.75 (septet, area $\propto$ 1), τ 8.78 (doublet of doublets, area $\propto$ 6), $J_{\mathrm{PCCH}} = 19$ cps. The mass spectrum had a parent peak at 168 and a base peak at 126 ($-C_3H_6$) in agreement with the structure.[11]

Di-*tert*-butylphosphinyl chloride (14) was prepared in a manner analogous to the procedure described for synthesis of di-*tert*-butylphosphinic acid.[27] Following hydrolysis of the di-*tert*-butyltrichlorophosphorane, the yellow oil obtained from the organic extracts was distilled under reduced pressure to give an unidentified yellow liquid followed by moist, transparent crystals of di-*tert*-butylphosphinyl chloride. The product could be recrystallized from either water or hexane to give fluffy white crystals: mp 79–81° (lit.[40] 80.1–80.9°); nmr (CH_2Cl_2), τ 8.65 (doublet), $J_{\mathrm{PCCH}} = 17$ cps. The mass spectrum had a parent peak at *m/e* 196 and a base peak at 57. *Anal.* Calcd for $C_8H_{18}ClOP$: C, 48.86; H, 9.23. Found: C, 49.01; H, 9.25.

The butane-1,3-phosphinyl chloride (**13**) was prepared by the usual method.[41] The product was recrystallized from hexane to give fluffy white, extremely hygroscopic crystals: mp 73–74° (lit.[41] 72–74°); nmr (CH_2Cl_2), τ 8.2 (multiplet, area $\propto$ 1), τ 8.60 (doublet, area $\propto$ 12), $J_{\mathrm{PCCH}} = 23$ cps, τ 9.07 (doublet of doublets, area $\propto$ 3), $J_{\mathrm{PCCCH}} = 1$–2 cps. *Anal.* Calcd for $C_8H_{16}ClOP$: C, 49.37; H, 8.28. Found: C, 49.54; H, 8.32.

Di-3-indolylphosphinyl Chloride. Indole (0.85 mole) was added to ethyl magnesium iodide (1 mole) in anhydrous ether. Phosphorus oxychloride (1 mole) in ether was added slowly with ice cooling. After warming to room temperature, the mixture was poured into ice and neutralized with sodium bicarbonate. The layers were separated, the aqueous layer was extracted with water, and the combined organic layers were concentrated to a dark red oil. Chromatography through silica gel using hexane–ether gave lavender crystals. Recrystallization from hexane–ether gave slightly brownish crystals, mp 75–76°. The compound was observed to decompose slowly in air and rapidly at elevated temperatures: nmr (CCl_4), τ 2.5 (multiplet, area $\propto$ 2), τ 2.8 (multiplet, area $\propto$ 3), τ 3.6 (multiplet, area $\propto$ 1); infrared (KBr), 1440 s, 1295 s, 1255 s, 1150 m, 1135 s, 1005 m, 750 s, 725 s, 665 and 655 doublet m, 600 m, 560 m; mass spectrum (direct insertion) (*m/e*, % of base): 317, 7; 316, 33; 315, 31; 314, 100; 313, 45; 277, 15; 242, 27; 241, 17; 163, 9; 117, 49; 116, 76; 90, 15; 89, 48; 63, 17. *Anal.* Calcd for $C_{16}H_{12}ClN_2OP$: C, 61.06; H, 3.84. Found: C, 60.53; H, 3.84.

Di-*tert*-butylphosphinyl Bromide. The preparation of di-*tert*-butylphosphinyl chloride was modified; phosphorus tribromide was used in place of phosphorus trichloride and bromine was used for the oxidation. Recrystallization from water and from ethanol gave fluffy white needles: mp 94–95° (lit.[40] 98–99°); nmr (CH_2Cl_2), τ 8.64 (doublet), $J_{\mathrm{PCCH}} = 17$ cps; infrared (KBr), 2980 m, 2960 s, 2920 m, 2900 m, 2880 m, 1470 s, 1460 sh, 1365 m, 1360 m, 1220 s, 1015 m, 810 m, 650 m, 580 m; mass spectrum (*m/e*, % of base): 186, 7; 184, 7; 161, 5; 105, 6; 63, 4; 58, 6; 57, 100; 56, 6; 55, 4; 47, 5.

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