Aluminum Chloride Catalyzed Reaction between *t*-Butylbenzene and Phosphorus Trichloride[1]

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The reaction of *t*-butylbenzene with phosphorus trichloride in the presence of aluminum chloride gives *p*-*t*-butylphenyl-*t*-butylphosphinic acid after hydrolysis of the phosphinyl chloride, which is a reaction intermediate. Small amounts of phenyl-*t*-butylphosphinic acid were isolated in some of the reactions. The mass spectra of these compounds were examined.

The reaction between *t*-butylbenzene and phosphorus trichloride in the presence of aluminum chloride, followed by treatment with chlorine, and then with ethanol, and then with aqueous hydrochloric acid, is reported to give a mixture of *p*-*t*-butylphenylphosphonic acid (I) and di-*p*-*t*-butylphenylphosphinic acid (II).[3] The overall yields were low because of isolation and purification problems.

We attempted to follow the original procedure given by Kosolapoff but were unable to isolate either I or II and obtained *p*-*t*-butylphenyl-*t*-butylphosphinic acid (III) in *ca.* 20% yield (based on *t*-butylbenzene) which we assume was formed by reactions between an aryl group, a *t*-butyl cation or isobutene, and a trivalent phosphorus compound. A possible reaction scheme is shown in Scheme I. (In Schemes I and II possible addition complexes between *t*-butylbenzene and aluminum and phosphorus chloride are not shown, and these schemes therefore represent oversimplified minimum descriptions.)

In addition to III a small amount of phenyl-*t*-butylphosphinic acid (IV) was sometimes formed, either by dealkylation of one of the precursors of III or by a reaction of benzene, generated for example by dealkylation of *t*-butylbenzene. The maximum amount found was *ca.* 5% of that of III. A possible reaction sequence is shown in Scheme II. The particular sequences of reactions shown in Schemes I and II are assumed; *e.g.*, the dealkylation could follow an initial reaction with PCl_3.

Reactions between trivalent phosphorus and electrophiles[4] and dealkylations of alkylbenzenes by Lewis acids[5] are well known. There appeared to be no role for chlorine in these reactions and therefore we repeated the experiments omitting the addition of chlorine, followed by ethanol and acid hydrolysis, as in Kosolapoff's original procedure,[3] and we isolated the phosphinyl chloride (V) which was subsequently hydrolyzed in alkali to the acid III.

The reaction which we observe provides a simple single-step procedure for the synthesis of alkylarylphosphinic acids,[3,6,7] although the scope of the reaction needs to be explored. It seems that the original procedure using phosphorus trichloride and aluminum chloride is not always satisfactory for the synthesis of phosphonic acids.[3]

Experimental Section

Materials.—Phosphorus trichloride (B and A) was redistilled and aluminum chloride (B and A) was sublimed *in vacuo*. *t*-Butylbenzene (MCB) was shown by glc to contain <0.1% benzene.

Reaction Conditions.—The first experiment was done following the original procedure of Kosolapoff,[3] with PCl_3 (270 g), $AlCl_3$ (45 g), and *t*-butylbenzene (67 g). The materials were refluxed for 4 hr and the volatiles, including PCl_3, were distilled off. 1,1,2,2-Tetrachloroethane (200 ml) was then added and the solution was saturated with chlorine. Ethanol (146 ml) was added dropwise at 15° giving amounts of HCl gas. The mixture was treated with ice and then concentrated HCl. The organic layer was washed with water and saturated salt solution and dried over anhydrous $MgSO_4$. The solvent was then evaporated to give an oil which solidified on standing. According to the original procedure, the esters of the phosphonic and phosphinic acids should have been sufficiently volatile to be distilled *in vacuo*, but we obtained no distillate and therefore refluxed the nonvolatile material with concentrated HCl, as described.[3] A white solid, sparingly soluble in cold H_2O, was obtained. Extraction of this solid with hot water and subsequent evaporation of water gave a white crystalline solid which after several recrystallizations from 50:50 H_2O–EtOH had mp 154–156°. This solid was shown to be phenyl-*t*-butylphosphinic acid (IV).

The bulk of the material was not extracted into hot water but was recrystallized several times from a 50:50 H_2O–EtOH solution giving solid white crystalline needles, mp 208–209°. This solid was shown to be *p*-*t*-butylphenyl-*t*-butylphosphinic acid (III), obtained in 20% yield. Considerable amounts of material were probably lost in the recrystallizations.

Neither of these acids had the properties of *p*-*t*-butylphenylphosphonic acid (mp 199–200°) or di-*p*-*t*-butylphenylphosphinic acid (mp 211–212°).[3]

The reaction was repeated on half the original scale omitting the addition of chlorine and the refluxing with concentrated HCl. The initial product formed after removal of the volatile materials was an oil which solidified on standing, yielding the white solid V, 14 g (23% yield). Recrystallization from petroleum ether gave *p*-*t*-butylphenyl-*t*-butylphosphinyl chloride (mp 116–118°). It was identified by comparison of its 60-MHz nmr spectrum with that of material prepared from the phosphinic acid and thionyl chloride,[7] and by chloride analysis. Hydrolysis of the crude chloride in alkali gave much less phenyl-*t*-butylphosphinic acid (IV) than in the original experiment, and the major product was *p*-*t*-butylphenyl-*t*-butylphosphinic acid (III). In another preparation, $AlCl_3$ was used without sublimation and the same phosphinic acids were formed. The isolation of the chloride V depends on the extent of hydrolysis during isolation, and the formation of the acid IV depends fortuitously upon the reaction conditions, *e.g.*, upon the extent to which the $AlCl_3$ catalyzes the dealkylation relative to the Friedel–Crafts reaction.

In order to determine the possibility that phenyl-*t*-butylphosphinic acid (IV) was formed by a loss of a *t*-butyl group from a *p*-*t*-butylphenyl-*t*-butylphosphinyl derivative, we heated 5 g of III with $AlCl_3$ (8 g) and PCl_3 (50 ml) for 2 hr under reflux, but found none of the acid IV. This experiment suggests that alkyl cleavage precedes formation of the acid III.

Evidence for Structure.—*p*-*t*-Butylphenyl-*t*-butylphosphinic

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[1] Support of this work by the National Institute of Arthritis and Metabolic Diseases of the USPHS is gratefully acknowledged.

[2] To whom inquiries should be addressed.

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[5] E. H. Rodd, "Chemistry of Carbon Compounds," Vol. IIIA, Elsevier, New York, N. Y., 1954, p 96.

[6] G. O. Doak and L. D. Freedman, *J. Amer. Chem. Soc.*, **73**, 5658 (1951).

[7] T. H. Siddall and C. A. Prohaska, *ibid.*, **84**, 2502 (1962).

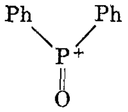
acid (III), mp 208–209°, is a monobasic acid (molecular weight by neutralization 252). *Anal.* Calcd for $C_{14}H_{23}O_2P$: C, 66.1; H, 9.1; P, 12.2. Found: C, 66.6; H, 8.6; P, 12.3.

The mass spectrum has a parent peak P = 254, and the nmr spectrum in $CDCl_3$ (60 MHz) gave a doublet, δ 0.90 and 1.16 (9, J = 16 Hz), 1.31 (9), a multiplet, δ 7.58 (9), and a singlet, δ 12.10 (1). (The relative areas are shown in parentheses.) The latter peak is that of the ionizable hydrogen and disappears on treatment with D_2O in CH_3CN. The infrared spectrum (Nujol mull or KBr pellet) showed peaks at 9.0, 11.5–12.5 μ which are characteristic of 1,4-disubstituted phenyl compounds.[8]

Phenyl-*t*-butylphosphinic acid (IV), mp 154–156°, is a monobasic acid. *Anal.* Calcd for $C_{10}H_{15}O_2P$: C, 60.6; H, 7.7; P, 15.7. Found: C, 60.6; H, 7.8; P, 15.9. The nmr spectrum in $CDCl_3$ (60 MHz) gave a doublet, δ 0.90 and 1.17 (9), multiplet, δ 7.57 (5), and a singlet, δ 11.6 (1). (The relative areas are shown in parentheses.) The latter peak is that of the ionizable hydrogen and disappears after treatment with D_2O. The proton phosphorus nmr coupling is well established from work on compounds containing alkyl groups attached to phosphorus.[7,9] Siddall and Prohaska have studied the nmr of IV and its chloride and report a coupling constant J = 15.7 Hz for the acid and J = 17.7 Hz for the chloride.[7] (They reported no other physical properties for these compounds.)

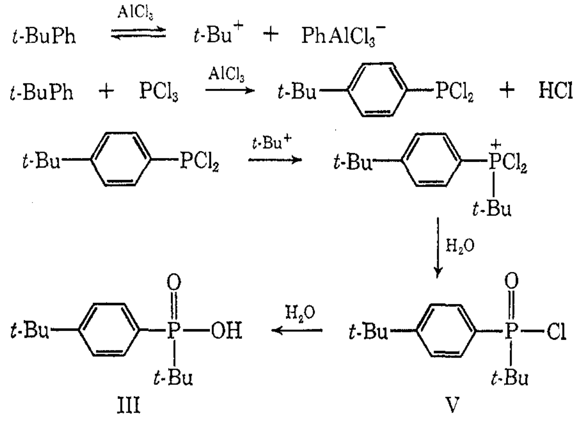
The phosphinyl chloride V had mp 116–118° (found Cl, 12.9% by Ag titration; calcd Cl, 13.0%). The mass spectrum has parent peaks P = 272 (^{35}Cl) and P = 274 (^{37}Cl). The nmr spectrum (60 MHz in CCl_4) is very similar to that of III and the peaks were a doublet δ 1.06 and 1.36 (9), 1.35 (9), and a multiplet, δ 7.5 (4). A coupling constant J = 17 Hz was found in agreement with the results of Siddall and Prohaska.[7]

The mass spectra (MS 902, 70 eV) of these compounds are quite different from the spectra observed by Haake and his coworkers for diarylphosphinic acids[10] and related compounds, in that there is no evidence for VI or ions derived from it.

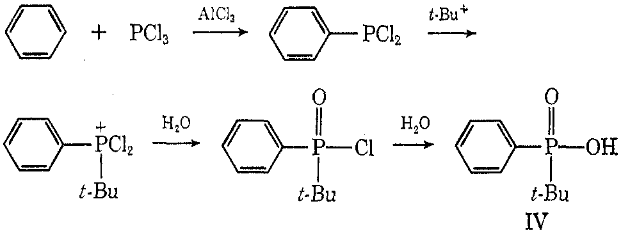


VI

SCHEME I



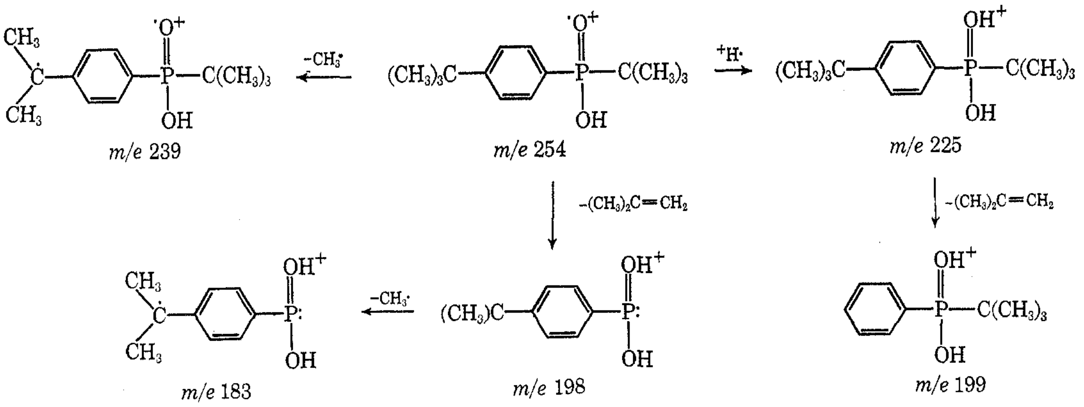
SCHEME II



Results

Mass Spectra.—The principal peaks of the mass spectrum of *p*-*t*-butylphenyl-*t*-butylphosphinic acid, with their sizes relative to the base peak 198 are 256 (2), 255 (21), 254 (33), 239 (9), 199 (19), 198 (100), 197 (8), and 183 (40%). There are metastable ions at 169 and 154 which correspond to the transition 198 → 183 and 254 → 198, respectively. In agreement with the results of Haake and coworkers,[10] we find a large M + 1 peak and a large peak which could be formed by loss of isobutene from the molecular ion. Existing evidence suggests that isobutene is lost from the *t*-butyl group attached to phosphorus; a *t*-butyl cation could also be lost from the P + 1 ion. This reaction is also observed with phenyl-*t*-butylphosphinic acid. These reactions in the ion source are analogous to the reverse reaction of attack of the *t*-butyl cation upon a trivalent phosphorus compound in the synthesis of these phosphinic acids. Scheme III accounts for the mass spectrum.

SCHEME III



The principal peaks of the mass spectrum of phenyl-*t*-butylphosphinic acid with their sizes relative to the base peak 142 are 200 (0.3), 199 (3), 198 (13), 183 (1.2), 143 (6), and 141 (3%). The metastable ion at 101.8 corresponds to the transition 198 → 142. Scheme IV accounts for the observed spectrum.

The nmr spectra and these mass spectra, together with the results of Haake and his coworkers on the mass

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[8] R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," 2nd ed, Wiley, New York, N. Y., 1967, p 73.

[9] D. Fiat, M. Halmann, L. Kugel, and J. Reuben, *J. Chem. Soc.*, 3837 (1962).

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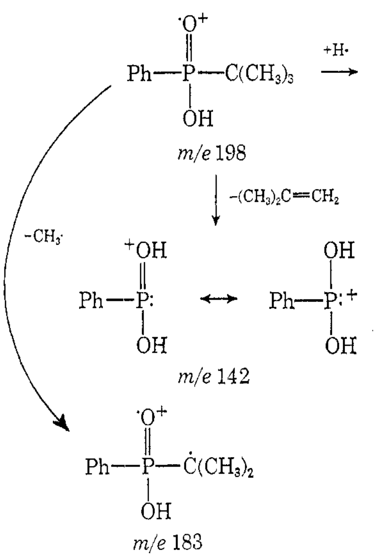
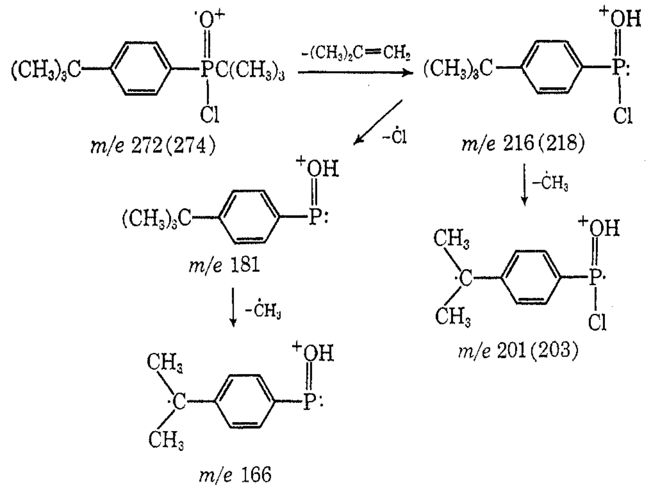
SCHEME IV



SCHEME V[a]



[a] The mass numbers in parenthesis denote the ion containing ^{37}Cl.

spectra of diarylphosphinic acids,[10] confirm that we isolated arylalkylphosphinic acids and not the compounds originally reported.[3]

The principal peaks of the mass spectrum of *p*-*t*-butylphenyl-*t*-butylphosphinyl chloride with sizes relative to the base peak 216 are 274 (11), 272 (30), 218 (43), 203 (24), 201 (83), 181 (6), and 166 (4%). Metastable ions are observed at 189, 187 with a broad peak at 171.8, and correspond to the transitions 218 → 203, 216 → 201 and 272 → 216, and 274 → 218, respectively. Scheme V illustrates this pattern.

Registry No.—III, 25097-42-1; IV, 4923-86-8; V, 25097-44-3; aluminum chloride, 7446-70-0; *t*-butylbenzene, 98-06-5; phosphorus trichloride, 7719-12-2.

Conformation of the Sodium Salts of 4-Phenylbutyric Acid and ω-Phenyloctanoic Acid in Aqueous Solution

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The conformations of the sodium salts listed in the title have been investigated in deuterium oxide by nuclear magnetic resonance spectroscopy. The conformation of 4-phenylbutyric acid sodium salt has been found to exist in the *anti* form with respect to the β,γ carbon–carbon bond. The data do not permit the establishment of a unique conformation for sodium ω-phenyloctanoate, but possible conformations are delineated.

The nature and extent of the intermolecular and the intramolecular interaction of two or more apolar moieties in water continues to be a subject of extensive and lively investigation.[2-11] The elucidation of these interactions is crucial to an understanding of molecular conformations and reaction mechanisms in aqueous solution.

Over the past few years many investigators have examined the nature, structure, and the effect on reactivity of micelles.[5,7,12-15] However, the conformations of the molecular constituents of micelles have received relatively little attention. It has been fairly well established in a number of cases that at concentrations below the critical micelle concentration (cmc), intermolecular association can occur.[6,16] We have initiated a study of ω-phenylalkylcarboxylic acid salts in aqueous solution with the goal of obtaining information regarding the conformations of the anions at concentrations below the cmc. Our approach makes use of the phenyl ring as a conformational probe. The magnetic anisotropy arising from the ring current of the phenyl ring will affect the chemical shifts of any protons located in the

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