

Department of Chemistry, University of Pittsburgh

Alkaline Degradation of Tri-2-thienylphosphine Oxide

K. R. Martin (1) and C. E. Griffin

Carbon-phosphorus bonds in arylphosphine oxides are generally extremely resistant to hydrolysis (2). Fusion of diphenylmethylphosphine oxide with sodium hydroxide at 200-300° was required to effect cleavage to benzene and sodium methylphenylphosphinate (3). Triphenylphosphine oxide (I) undergoes a modest degree (18%) of cleavage to yield benzene and inorganic sodium metaphosphate under milder conditions, *i.e.* treatment with refluxing ethanolic 2 N sodium hydroxide for forty-eight hours (4). In contrast, tri-2-pyrrylphosphine oxide (II) undergoes cleavage with the formation of pyrrole (87%) upon treatment with refluxing 10% aqueous sodium hydroxide for twenty-four hours (5). This cleavage was postulated to occur by protonative dephosphonation of the anion of II.

In order to determine if the hydrolytic lability of the carbon-phosphorus bonds of II and other pyrrylphosphorus derivatives (5) is a property common to heteroarylphosphorus structures, the alkaline hydrolysis of tri-2-thienylphosphine oxide (III) has been examined. Treatment of a solution of III (6) in 10% aqueous sodium hydroxide at 100° for twenty-four hours led to the isolation of thiophene (65%) and a 12% recovery of III. Acidification of the reaction mixture gave a sodium metaphosphate similar to that reported in the hydrolysis of I (4). Acidification also gave a minor product which was identified as di-2-thienylphosphinic acid (IV) on the basis of its PMR, ultraviolet and infrared spectra. In the basic hydrolysis of I, the analogous diphenylphosphinic acid was not isolated (4). Forty-eight hour reaction periods gave a quantitative decomposition of III; thiophene (73%), IV (28%) and sodium metaphosphate were isolated. After five weeks at room temperature in this basic medium, a 70% recovery of III was achieved; neither IV nor inorganic salts could be isolated.

The high degree of reactivity observed for III indicates that the heteroarylphosphorus compounds most probably constitute a special class with regard to carbon-phosphorus bond stability. The greater degree of cleavage observed for III as compared to I is probably a reflection of the greater stability of the 2-thienyl anion (7) as compared to the phenyl anion. In the mechanisms postulated (3-5) for this type of carbon-phosphorus bond cleavage, the expulsion of the aryl group as an anion is required.

EXPERIMENTAL (8)

Alkaline Hydrolysis of Tri-2-thienylphosphine Oxide (III).

The following procedure is typical. A solution of 0.50 g. (1.69

mmole) of III in 25 ml. of 10% aqueous sodium hydroxide containing a small amount of ethanol to ensure homogeneity was selected in a Pyrex tube and held at 100° in an oil bath for twenty-four hours. The tube was cooled to 25° and the reaction mixture was extracted thoroughly with ether-pentane. The extract was made up to a standard volume and analyzed by gas-liquid chromatography for thiophene (65%). Standardized samples of thiophene in ether-pentane were used for calibration. Evaporation of these extracts to dryness under reduced pressure gave unreacted III (0.06 g., 12%). The aqueous solution was acidified with 10% hydrochloric acid, concentrated to a volume of 25 ml. and cooled to 15°. After three hours at this temperature, precipitation of a colorless solid was complete. The solid was removed by filtration and extracted (Soxhlet) with 95% ethanol until no further material was extracted. Evaporation of the ethanolic extracts gave, after drying, 85.8 mg. (22%) of IV, m.p. 189-190°. The unextracted material was dried over phosphorus pentoxide at 75° (10 mm.) to give 0.4 g. of inorganic material which was shown to be very similar to the sodium metaphosphate prepared by the method of Akaes and Songstad (4, 9).

Identification of Di-2-thienylphosphinic Acid (IV).

A sample of IV from a number of hydrolyses of the above type was recrystallized from ethanol-hexane, m.p. 192-193°.

Anal. Calcd. for $C_8H_7O_2PS_2$: C, 41.73; H, 3.07; P, 13.46; Neut. Equiv., 230.2. Found: C, 41.60, 41.49; H, 2.87, 2.93; P, 13.31; Neut. Equiv., 221.8, 231.5, 233.9.

The ultraviolet spectrum of IV (λ max = 239, 254 sh) in 95% ethanol was almost identical to that of III (λ max = 238, 250 sh) (6) and the infrared spectrum of IV showed all of the bands reported for III (6). The PMR spectrum of IV in acetone showed two proton multiplets at τ = 2.76, 2.47 and 2.06 p.p.m. assignable as H-4, H-3 and H-5 of the thienyl rings; in deuteriochloroform, a broad one proton singlet (exchangeable with deuterium oxide) due to the acidic proton was observed at τ = -1.75 p.p.m. Comparable multiplets due to the ring protons (H-4, H-3, H-5) are observed at τ = 2.80, 2.51 and 2.08 p.p.m. for III and at τ = 2.73, 2.36 and 2.06 p.p.m. for dimethyl 2-thienylphosphonate (10).

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- (8) Ultraviolet spectra were determined on a Cary Model 14 spectrophotometer. Gas-liquid-chromatographic analyses were performed on an F and M Model 500 chromatograph using a column of 17% tricresyl phosphate on Celite 545. PMR spectra were determined with a Varian Associates A-60 spectrometer at a probe temperature of 35°. Microanalyses were performed by Galbraith Laboratories; melting points are uncorrected.
- (9) In a reaction carried out in refluxing aqueous sodium hydroxide in an open system at atmospheric pressure, thiophene could not be detected. The other products were obtained in yields comparable to those of sealed tube reactions.
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Pittsburgh, Pennsylvania 15213