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THE SYNTHESIS AND REACTIONS OF POTASSIUM BENZOYLPHOSPHIDE, BENZOYLPHOSPHINE, AND BENZOYLMETHYLPHOSPHINE.

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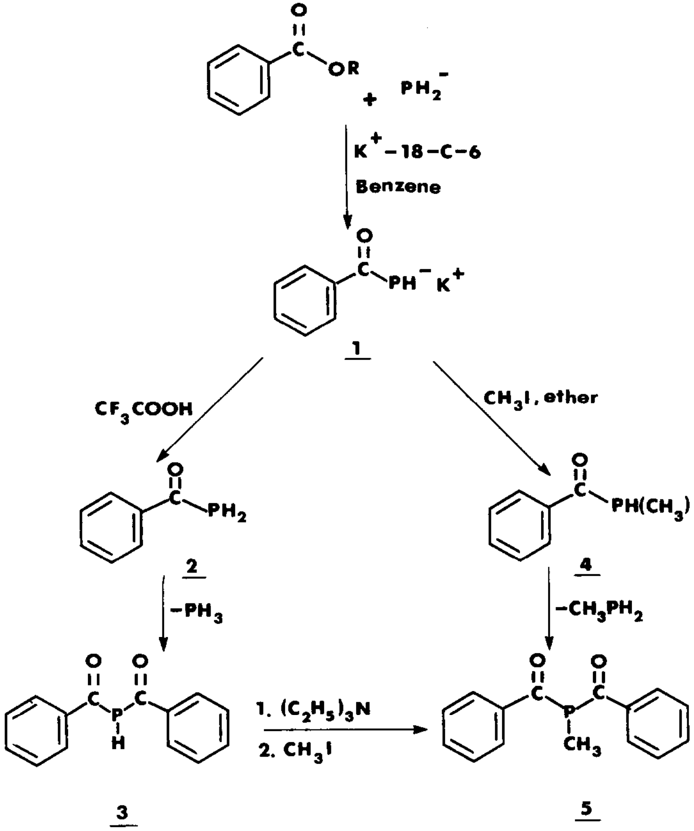
Abstract: Reaction of potassium dihydrogenphosphide with aromatic esters produces potassium benzoylphosphide (1). Protonation of 1 produces benzoylphosphine 2. The physical and chemical properties of 1 and 2 are discussed.

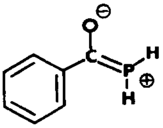
Potassium dihydrogenphosphide (KPH_2) is an off-white solid prepared from the reaction of phosphine with potassium dissolved in liquid ammonia.[1,2] While KPH_2 has been known for decades, very little new chemistry has been performed with this species owing to its poor solubility in most organic solvents, its reactivity with protic solvents and its great susceptability toward oxidative degradation by air. With the advent of crown ethers, simple means have become available for the solubilization of KPH_2 in non-polar, aprotic solvents such as benzene and toluene. Using catalytic quantities of 18-crown-6 under solid-liquid phase transfer catalytic conditions, sufficient quantities of PH_2^- can be transferred into solution for reaction with a variety of substrates. This Communication reports the reactions of PH_2^- with simple aromatic esters and the subsequent reactions of the resulting phosphide derivatives with a variety of electrophilic reagents. The results are outlined in Scheme 1.

Reaction of an alkyl or aryl benzoate (CH_3, C_2H_5, $i\text{-}C_3H_7$, $t\text{-}C_4H_9$, or C_6H_5) with KPH_2 in benzene for 72 hours in the presence of 10 mole % 18-crown-6 under an inert atmosphere (N_2) produced potassium benzoylphosphide (1) as an orange-yellow precipitate in 80 % yield.[3] The material prepared in this manner was analytically pure after filtration and subsequent drying.[4] Reaction of 1 suspended in $DCCl_3$ with less than an equivalent of anhydrous trifluoroacetic acid (or other strong acids such as anhydrous HCl and HBr) produced benzoylphosphine (2). ^1H analysis of the filtered reaction mixture at ambient temperatures and at -60°C revealed a well-ressolved doublet (4.20 ppm, d, J_{PH} = 218 Hz) for the two protons attached to phosphorus. This indicated that the protons in question remained magnetically equivalent over this temperature range. The reported chemical shift and coupling constant are consistent with those recently reported by Becker et. al.[5] for pivaloylphosphine and acetylphosphine (^1H, 3.77; J_{PH} = 214 Hz and ^1H, 3.87; J_{PH} = 217 Hz, respectively). The lack of significant restricted rotation in 2 may be attributed to poor overlap between the atomic orbital containing the phosphorus lone pair and the adjacent pi-carbonyl system.



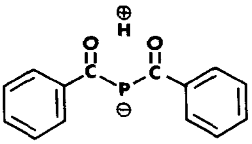
SCHEME 1.

Thus, resonance structures of the type illustrated in 2a appear to make little contribution to the bonding in 2. Similar observations have been made from the study of the temperature dependence of the ^{13}C NMR spectrum of tribenzoylphosphine. In that case, no evidence for restricted rotation about the carbonyl carbon-phorphorus bond was found.[6]



2a

Neat 2 is a greenish-yellow oil. Unfortunately, complete characterization was difficult since the molecule was unstable at room temperature and decomposed withing a period of six hours to dibenzoylphosphine (69 % yield), 3[7], and phosphine. In solution, the decomposition was slower but observable even at -78°C (20 % decomposition within 3 days). Both the ^{1}H and ^{31}P NMR spectra showed no phosphorus-hydrogen coupling and the IR spectrum showed no absorbance in the range normally found for a P-H stretching vibration (2300 - 2350 cm^{-1}). These observations are consistent with the results of a single crystal X-ray analysis reported by Becker and Beck[8] on dipivaloylphosphine in which the hydrogen was found to be more closely associated with the carbonyl oxygens than the phosphorus. In ^1H NMR studies on diacetylphosphine and dipivaloylphosphine reported by Becker et. al.[5], it was found that as the dielectric constant of the solvent decreases, the keto-enol equilibrium favored the enol form. The ^1H NMR spectrum of dibenzoylphosphine was conducted in deuteroacetonitrile (a solvent of relatively high dielectric constant) and found to be essentially completely in the enolic from. Thus, 3a appears to be a reasonable structural representation of the dibenzoylphosphine molecule in solution.



3a

Reaction of 1, suspended in ether, with CH_3I in the presence of catalytic quantities (1 mole %) of 18-crown-6 for 18 hours under an inert (N_2) atmosphere produced benzoylmethylphosphine (63 % yield), 4. An IR spectrum of 4 revealed an absorption of medium intensity at 2315 cm^{-1}. This was attributed to the P-H stretching vibration. A well-resolved ^1H NMR spectrum showed only one type of hydrogen attached to phosphorus (4.55, d of q, J_{PH} = 217 Hz) and only one type of methyl attached to phosphorus (1.27, d of d, J_{PCH3} = 1 Hz, J_{PHCH3} = 7 Hz). 4 was found to be substantially more stable than 3, however, over a four day period at room temperature 4 decomposed to dibenzoylmethylphosphine, 5[9], and methyl phosphine. The decomposition was quickly driven to completion by applying a vacuum to eliminate the volitile methyl phosphine. In fact, unless methyl phosphine was removed by continuous evacuation, the reaction stopped. 5 was also prepared by reaction of 4 with triethylamine and methyl iodide in ether. The ease with which 2 and 4 decompose to 3 and 5, respectively, again suggests poor overlap between the pi-bond of the carbonyl group and the lone pair on phosphorus.

In conclusion, the results presented in this Communication are (1) that KPH_2, solubilized by catalytic quantities of 18-crown-6 under solid-liquid phase transfer conditions, reacts quickly and efficiently with aromatic esters to produce potassium benzoylphosphide (1), (2) that ^1H NMR analyses of benzoylphosphine (2) and benzoylmethylphosphine (4) indicate that delocalization of a phosphorus lone pair onto an adjacent carbonyl group is not significant, and (3) benzoylphosphine (2) and benzoylmethylphosphine (4) readily undergo bimolecular decompostion with the formation of dibenzoylphosphine (3) and dibenzoylmethylphosphine (5), respectively.

References

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(3) The IR spectrum (P-H stretching vibration at 2340 cm^{-1}), the elemental analysis (calculated for C_7H_6KOP: C, 47.72 %; H, 3.43 %; found: C, 47.56 %; H, 3.48 %), and analysis of the products of subsequent reactions of 1 were consistent with the assigned structure. As a result of the insolubility of 1 in a wide variety of solvents, ^{1}H and ^{13}C NMR spectra could not be obtained.

(4) In preliminary reactions, the crude reaction product was found to be impure by combustion analysis. Since the salt was insoluble in all common, non-reactive organic solvents, further purification by recrystallization was not possible. It was discovered, however, that very efficient stirring and prolonged reaction times consistently gave analytically pure material from the reaction mixture. These conditions apparently allowed the catalytic 18-crown-6 to repeatedly solubilize very small quantities of product as the crown complex and reprecipitate a purer material.

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(6) D. Kost, F. Cozzi and K. Mislow, *Tet. Lett.*, 1983 (1979).

(7) Elemental Analysis: calculated for $C_{14}H_{11}O_2P$: C, 69.42 %; H, 4.54 %; found: C, 69.27 %; H, 4.74 %; m.p. (sealed capillary under N_2): 97.0 - 99.0°C; ^{1}H NMR (CD_3CN; ppm): 8.40 - 7.80 and 7.79 7.17 (complex, 10H), 5.73 (broad, 1H); ^{13}C NMR ^{1}H decoupled (CD_3CN; ppm) 150.7 (d, J_{CP} = 863.7 Hz), 129.8 (d, J_{CP} = 21.4 Hz), 129.4 (d, J_{CP} = 25.9 Hz), 126.2 (d, J_{CP} = 16.8 Hz), 117.6 (s); ^{31}P NMR ^{1}H coupled (C_6D_6; ppm) 56.25 (s); MS (M/e, relative intensity) (selected peaks): 243 (1), 242 (M^+, 9), 105 (100).

(8) V. G. Becker and H. P. Beck, *Z. anorg. allg. Chem.*, *430*, 77 (1977).

(9) ^{1}H NMR (C_6D_6; ppm) 1.55 (d, J_{PCH} = 6 Hz); 6.9 - 7.3 (m); ^{31}P NMR ^{1}H decoupled ($DCCl_3$; ppm) 17 (s); MS (M/e, relative intensity) (selected peaks): 257 (1), 256 (M^+, 3; calculated 256.0653, found 256.0689), 105 (100).

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