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THE BARRIER TO CARBON-PHOSPHORUS BOND ROTATION IN TRIBENZOYLPHOSPHINE. AN EXPERIMENTAL REINVESTIGATION

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Summary: An examination of the ^{13}C NMR spectrum of tribenzoylphosphine over the temperature range -75 to +70°C fails to disclose any evidence for hindered rotation about the P-C bonds, contrary to a previous claim.

It was recently reported[1] that tribenzoylphosphine (TBP) exhibits two carbonyl signals in its ^{13}C NMR spectrum, that at low temperature the relative ratio of intensities of the downfield (ca 206 ppm) to upfield (ca 199 ppm) signals is about 2:1, and that these signals coalesce at 49.5°C. From these observations, it was concluded[1] that there is hindered rotation about the P-C bonds in TBP, and it was proposed[1] that the P-C double bond character resulting from the delocalization of the electron pair on phosphorus into one of the carbonyl groups was responsible for the calculated barrier ($\Delta G^{\ddagger}$) of 15 kcal/mol at 49.5°C and for the 2:1 intensity ratio.

However, it is difficult to understand why this barrier should be appreciably higher than a similar barrier in a triacylamine;[2] also baffling is the apparent isochrony of the two downfield resonances which together constitute the more intense signal, since under conditions of slow rotation about one P-C partial double bond the other two benzoyl groups are diastereotopic. We therefore undertook a reinvestigation of this system. TBP was prepared as previously described,[3] with minor variations. Pyridine and benzoyl chloride were carefully dried and redistilled prior to use, phosphine was purified by the procedure of Pospelov et al.,[4] and nitrogen was used as a carrier gas. The product, a bright yellow solid, was washed with and recrystallized from absolute ethanol. Despite these precautions, the ^{31}P spectra of various preparations of the product typically indicated the presence of a major, and previously unreported, contaminant of unknown composition, δ ca 22 ppm (Table 1), in addition to the expected[1] signal for TBP at ca 54 ppm. This was the case even for twice recrystallized, analytically pure samples FC 4 (mp 147-149°C. Anal. calcd. for $C_{21}H_{15}O_3P$: C, 72.83; H, 4.37; P, 8.94. Found: C, 72.41; H, 4.41; P, 8.65) and FC 9 (mp 147-149°C. Anal. found: C, 72.26, H, 4.27; P, 8.98). This, and the further observation that the NMR samples suffer extensive deterioration on standing (as monitored by ^{31}P NMR), points to the need for rigorous exclusion of air once the product is in solution; thus, a sample (FC 11) worked up and stored under nitrogen contained only 10% of the contaminant. In short, solutions of TBP (and presumably of other triaroylphosphines[1] as well) are extremely air sensitive and difficult to obtain free of a major, phosphorus-containing contaminant.

Table 1. ^{13}P NMR Spectra[a] of Some TBP Preparations

Preparation No.	Chemical Shifts[b]		Ratio of Intensities[c]	Solvent[d]
DK 13	54.05	23.12	0.7:1	$CDCl_3$
DK 15	53.53	22.10	4.5:1	$(CD_3)_2CO$
DK 18	54.33	22.31	4.9:1	CD_2Cl_2
FC 4	53.96	23.07	0.4:1	$CDCl_3$
FC 6	54.03	23.09	4.0:1	$CDCl_3$
FC 8	54.03	23.19	7.7:1	$CDCl_3$
FC 9A	53.54	22.10	2.2:1	$(CD_3)_2CO$
FC 11	54.03	23.14	9.1:1	$CDCl_3$

[a] Proton decoupled. [b] In ppm downfield from external 85% H_3PO_4, at ambient temperatures. [c] Relative integrated intensity of downfield to upfield signal. [d] Conc. ca 150 mg/ml.

Several preparations were also examined by ^{13}C NMR spectroscopy (Table 2). Although the chemical shifts and coupling constants of the two doublets agree with previously reported values,[1] we found that the intensity ratios differ markedly from the reported value[1] of ca 2:1 and vary widely from preparation to preparation. Of particular interest are observations on FC 10 and FC 9B, whose ^{31}P NMR spectra were remarkable by the absence of the signal at ca 22 ppm. The ^{13}C NMR spectra of these "pure" compounds nevertheless differed in the carbonyl region (Table 2): FC 10 exhibited a ca 3:1 ratio of signals, whereas FC 9B, whose NMR sample was sealed under vacuum, showed no trace of the upfield signal. The two signals manifestly arise from TBP (ca 206 ppm) and a contaminant (ca 199 ppm) which is present in varying amounts depending on the particular sample preparation. Contrary to the previous claim,[1] there is no evidence of coalescence, even at 70°C (Table 2, FC 9B).[5]

Table 2. Carbonyl ^{13}C NMR Signals of Some TBP Preparations

Preparation No.	Temp. (°C)	Downfield Doublet[a] δ ^{13}C ($^{1}J_{PC}$)	Upfield Doublet[a] δ ^{13}C ($^{1}J_{PC}$)	Ratio of Intensities[b]	Solvent[c]
DK 18	-49	206.48(32.8)	199.54(58.2)	4.4:1	CD_2Cl_2
	-75	206.52(32.3)	199.38(57.4)	4.1:1	CD_2Cl_2
FC 9A	29	205.40(33.1)	199.13(55.8)	5.0:1	$CDCl_3$(*)
	-54	206.53(32.3)	199.24(57.3)	4.3:1	$CDCl_3$
FC 10	30	205.59(33.6)	199.31(55.0)	2.9:1	$CDCl_3$(*)
	-47	206.50(32.2)	199.27(56.9)	2.7:1	$CDCl_3$
FC 9B	70	205.38(33.9)	d	e	$CDCl_3$(*)
	29	205.61(33.2)	d	e	$CDCl_3$(*)
	-30	206.15(32.3)	d	e	$CDCl_3$(*)

[a] Chemical shifts in ppm downfield from internal TMS, coupling constants in Hz. [b] Relative integrated intensity of downfield to upfield signal. [c] Conc. 200-250 mg/2 ml. The asterisk signifies the presence of relaxation agent ($Cr(acac)_3$) added to enhance signal intensity at room temperature. [d] No signal could be detected even under high amplification. [e] Greater than 10:1.

The conclusion is inescapable that the previously reported[1] coalescence is the result of an experimental artifact and that there is no evidence for hindered rotation about the P-C bonds in TBP.

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References and Notes

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3. R. Tyka and E. Plazek, Roczniki Chem., 35, 183 (1961).
4. V. P. Pospelov et al., USSR 497,224 (Chem. Abstr., 84, 107915p (1976)).
5. Samples sealed under vacuum show negligible change in the downfield signal on standing. However, the upfield signal rapidly decreases in intensity, owing to decomposition of the contaminant.

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