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ON THE MECHANISM OF THE REACTION OF TRIPHENYLPHOSPHINE-CARBON TETRACHLORIDE WITH ALCOHOLS, ACIDS AND ENOLIZABLE KETONES

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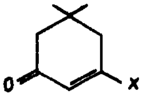
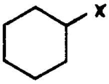
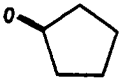
Triphenylphosphine with carbon tetrachloride or tetrabromide has found widespread use as a reagent for conversion of alcohols, acids and amide derivatives into the corresponding halides, nitriles and carbo imide derivatives.[1,2] The mechanism of these reactions has been interpreted[2,3], e.g., in terms of eq 1 involving the initial formation of interchangeable ion pairs that react directly with ROH, giving $CHCl_3$ and oxophosphonium salt which subsequently

$$\begin{tikzcd}
Ph_3P + CCl_4 \arrow[r] & {[Ph_3P^+Cl \quad {}^-CCl_3} \arrow[r, leftrightarrow] & {Ph_3P^+CCl_3 \quad {}^-Cl]} \arrow[d, "ROH"] \\
Ph_3PO + RCl & & {[Ph_3POR]^+Cl^- + CHCl_3} \arrow[ll]
\end{tikzcd} \qquad (1)$$

decomposes into Ph_3PO and RCl. Contrary to this scheme, formation of $[Ph_3PCH_2Cl]^+Cl^-$ (1) was observed in the course of preparation of β-halovinyl ketones from 1,3-dioxo compounds[4] in quantities corresponding to approx. 1/3 of the Ph_3P introduced. This product was identified by elemental analysis, ^1H and ^{13}C nmr data[5] and comparison with an authentic sample[6]. Formation of 1 was recently reported also by Appel *et al*[7]. in the reaction of the "Dreikomponentensystem" (Ph_3P - CCl_4 - amine) with amide derivatives.

In view of these facts we felt that interpretation based on eq 1 is erroneous even for conversions apparently studied in much detail. Reexamination

Starting Material: X=OH Product: X=Cl	Yield^a, %	**2**^{b} %^{d}	**1**^{c} %^{d}
	62 (1)		31 (94)
	82 (1.5)		32 (97)
	57 (1)		29 (87)
	89 (1.5)		31 (94)
$CH_3CH(Ph)CH_2CH_2X$	74 (1)		25 (75)
PhCOX	71 (1)		33 (100)
	86 (1.5)		33 (100)
$CH_3COCH{=}C(X)CH_3$	62 (1)	30 (76)	5
	75 (1.5)	31 (77)	5
 ^{e}	(1)	26 (72)	6-8

[a] Distilled poructs. Numbers in parentheses refer to moles Ph_3P per 1 mole substrate. [b] Mp 216-8° (dec). Anal. Calcd for $C_{19}H_{16}Cl_3P$: Cl, 27.86. Found: Cl, 27.64. [c] Mp 256-60° (dec), lit. 260-1° (dec), 216° (dec)[7]. Anal. Calcd for $C_{19}H_{17}Cl_2P$: Cl, 20.42. Found: Cl, 20.81. [d] Yields after recrystallization. Percentage relative to theoretical in parentheses. [e] Products[9] not identified.

of the typical experiments (see Table) revealed that in each case the conversion was accompanied by formation of either **1** or $[Ph_3CHCl_2]^+Cl^-$ (**2**). These salts were invariably separated as white crystalline precipitates[8]. Formation of **1** and **2** is compatible with the sequence of consecutive steps (eq 2-4) competing with process 1.

$$2Ph_3P + CCl_4 \longrightarrow Ph_3PCl_2 + Ph_3P{=}CCl_2 \xrightarrow{ROH} RCl + Ph_3PO + \mathbf{2} \qquad (2)$$

$$\mathbf{2} + Ph_3P \longrightarrow Ph_3PCl_2 + Ph_3P{=}CHCl \xrightarrow{ROH} RCl + Ph_3PO + \mathbf{1} \qquad (3)$$

$$\mathbf{1} + Ph_3P \longrightarrow Ph_3PCl_2 + Ph_3P{=}CH_2 \xrightarrow{ROH} RCl + Ph_3PO + (Ph_3PCH_3)^+Cl^- \qquad (4)$$

This mechanism is analogous to that proposed by Appel *et al*[7]. for the reaction of amides with this reagent. However, their statement concerning the equal contribution of the competitive routes is not borne out by our results: less than 5% of the theoretical $CHCl_3$ required by eq 1 was detected by means of gas chromatography and ^1H nmr analysis in the reaction mixture run with dimedone, whereas, accordingly, more than 95% of **1** was isolated preparatively. The negligible role of process 1 in the conversion of other compounds was attested by similarly high yields of phosphonium salt **1** or **2**.

Further evidence in support of this interpretation are provided by the following observations:

i. An increase of the phosphine to substrate molar ratio from 1 to the value required by the stoichiometry of processes 2 and 3 resulted in a 15 to 30% increase in the yield of the halides.

ii. Because of the low solubility of **1** in CCl_4 and the substantial consumption of phosphine in preceding steps, contribution of process 4 to the overall reaction is expected to be generally low. Its occurence[11], however, was demonstrated in separate experiments by boiling **1** with equimolar Ph_3P and cyclohexanol in $CHCl_3$. The reaction was complete in 4 hours and gave $[Ph_3PCH_3]^+Cl^-$ (**3**) (92), Ph_3PO (90), and cyclohexyl chloride (82%). Similarly, **2**, Ph_3P and cyclohexanol (molar ratio 1 : 2 : 2) yields **3** (82), Ph_3PO (91), and cyclohexyl chloride (76%). In a blank experiment with Ph_3P and cyclohexanol in $CHCl_3$ the unchanged starting materials were recovered after 8 hours.

Formation of **2** in reactions with less reactive molecules (cyclopentanone, acetylacetone) may be rationalized by assuming that the formation rate of $[Ph_3PCl_2 + Ph_3P{=}CCl_2]$ exceeds its consumption rate in consecutive steps. Under these conditions, due to the lack of available phosphine, process 3 can in principle not take place and, according to eq 2, the conversion gives **2**, rather than **1**.

References

(1) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis" Vol. 3, Wiley Intersience, New York, N. Y., 1972, p 320.

(2) J. I. G. Cadogan and R. K. Mackie, *Chem. Soc. Reviews*, **3**, 87 (1974) and references cited therein.

(3) R. Aneja, A. P. Davies, and J. A. Knaggs, *Tetrahedron Letters*, 67 (1974).

(4) L. Gruber, I. Tömösközi, and L. Radics, to be published.

(5) ^{1}H nmr ($CDCl_3$, 100.1 MHz): δ^{h}_{TMS} (**1**) 6.54 (d, 5.6 Hz, 2H), 7.6 - 8.1 (m, 15H); (**2**) 7.6 - 8.25 (m, 15H), 10.85 (d, 3.2 Hz, 1H). ^{13}C nmr ($CDCl_3$, 25.16 MHz); δ^{C}_{TMS} (**1**) Spectral parameters are identical with published values[12]; (**2**) 61.8 (d, 56.7 Hz, off.res.: 2d, P^+CHCl_2), 115.4 (d, 87.6 Hz, C-P^+), 135.0 (d, 10 Hz, C^o), 130.5 (d, 12.6 Hz, C^m), 136.0 (d, 2.5 Hz, C^p).

(6) G. Wittig and M. Schlosser, *Chem. Ber.*, **94**, 1373 (1961).

(7) R. Appel, K. Warning, and K. D. Ziehn, *Chem. Ber.*, **106**, 3450 (1973) and earlier papers cited therein. Their reported mp, 216°, however, seems to fit better **2** than **1**. The lack of sufficient characterization unfortunately permits no unequivocal identification (see also footnotes to Table).

(8) This precipitate has been referred[9,10] to as Ph_3PO and/or $Ph_3P.HCl$ without characterization.

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(12) G. A. Gray, *J. Amer. Chem. Soc.*, **95**, 7736 (1973).