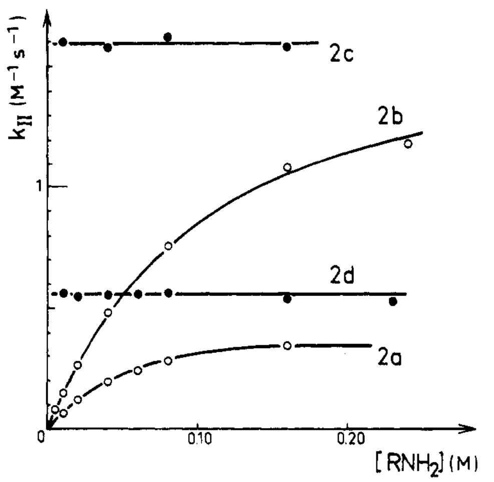


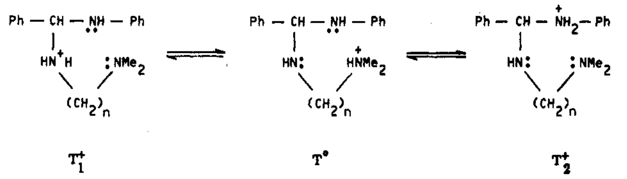
Figure 1. Amine concentration effect on the second-order rate constant (first order with respect to the substrate and to ammonium ion) for N-benzylideneaniline transimination by monofunctional amines (○) and (dimethylamino)alkylamines (●) (25 °C) [μ = 0.08 M (NMe_4Br); because of a slight downward curvature of the plots of k_ψ vs. [RNH_3^+] ($RNH_3^+NO_2^-$), k_{II} values were extrapolated to zero ammonium ion concentration].

Table I. Asymptotic Rate Constants at High Amine Concentration or Amine Concentration-Independent Rate Constants for Transimination of N-Benzylideneaniline by Monofunctional and Bifunctional Amines (25 °C)

compound	pK_a [a]	$(k_{II})_{max}$ [b] (M^{-1} s^{-1})	k_{II} [b] (M^{-1} s^{-1})
propylamine (**2a**)	12.20	0.488 ± 0.020	
2-methoxyethylamine (**2b**)	11.52	1.75 ± 0.15	
2-(dimethylamino)ethylamine (**2c**)	11.60		1.59 ± 0.03
3-(dimethylamino)propylamine (**2d**)	12.04		0.55 ± 0.03

[a] In methanol; see ref 6. [b] The listed uncertainties are estimated error limits (about twice the standard deviations).

Scheme II



value observed for **2b** at high concentration of base. This clearly shows that the dialkylamino group makes the proton transfer fast by intramolecular base catalysis (Scheme II); the rate of transimination of **1** by **2c** and **2d** is wholly controlled by the expulsion of aniline and is similar to that observed for monofunctional amines when base concentration is so high that intermolecular proton transfer no longer controls the rate of the overall reaction. Moreover, when k_{II} values from Table I for **2c** and **2d** are plotted vs. pK_a, together with $(k_{II})_{max}$ for **2a** and **2b**, a rough straight line with a slope close to unity is observed. This is in agreement with what expected from a rate-limiting expulsion step with an early transition state.

It is noteworthy that the identity of the overall rate constants for amines of same basicity when proton transfer is fast—whether proton transfer occurs intramolecularly or intermolecularly—means that proton transfer and C–N bond cleavage are not energetically coupled processes, despite the good leaving group ability of aniline. C–N bond cleavage requires full protonation of nitrogen, in contrast to the C–O bond cleavage which, in the case of many tetrahedral intermediates,[7] is coupled with proton transfer.

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(6) The pK_a values of the RNH_3^+ ions were measured by UV spectroscopy with 4-nitrophenol as indicator [pK_a = 11.2 (Clare, B. W.; Cook, D.; Ko, E. C. F.; Mac, Y. C.; Parker, A. J. *J. Am. Chem. Soc.* **1966**, *88*, 1911–1916)].

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Novel Products from the Reaction of Tris(p-methoxyphenyl)phosphine with Neopentyl Iodide

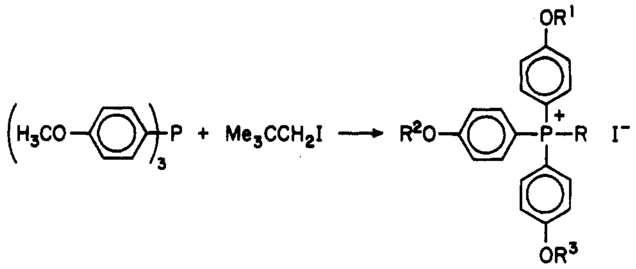
Summary: The title reaction gave a mixture of eight phosphonium salts. Intermediacy of phosphonium inner salts, $\geqslant P^+C_6H_4O^-$-p, is suggested for their formation.

Sir: Recently, we have observed that in a reaction between tris(p-methoxyphenyl)phosphine and neopentyl iodide eight phosphonium salts were formed (**1**–**8**, see Table I). The reaction was carried out by using 3.52 g (0.01 mol) of the phosphine with 3.96 g (0.02 mol) of Me_3CCH_2I under N_2 at 150 °C for 18 h. Addition of 100 mL of ethyl acetate and 100 mL of anhydrous ether precipitated a mixture (4.3 g) of phosphonium salts. Their structures were assigned, without separation, from the ^{31}P and ^1H NMR spectra of the mixture. The ^{31}P spectrum showed four absorptions in the chemical shift region of neopentylphosphonium salts and four corresponding to the methylphosphonium salts. The ^1H NMR spectrum corroborated the structures of **1**, **2**, **5**, and **6** whose absorptions were clearly observed due to their higher concentrations in the mixture. The presence of methyltris(p-methoxyphenyl)phosphonium iodide in the mixture was established by comparison of its NMR data to that of a pure sample. Table I lists the spectral data and the approximate molar ratios of phosphonium salts estimated from the ^{31}P NMR spectrum.

The FAB mass spectrum of the mixture, run in glycerol–thioglycerol–methylene chloride as matrix, showed main peaks corresponding to the masses of the parent phosphonium ions: 367 (**5**), 423 (**1**, **6**), 479 (**2**, **7**), 535 (**3**, **8**), and 591 (**4**). Next in intensity were peaks at masses 353, 409, 465, and 521 due to the phosphonium species in which the methyl of a OCH_3 group has been substituted by H from matrix. There were three more peaks of much lower intensity at masses 337, 393, and 449. They are apparently due to the phosphonium ions in which a p-methoxy group has been replaced by H.

Apparently, quaternization of phosphorus in **1** activates the p-methoxy groups on the phenyl rings making them prone to nucleophilic attack by the unreacted phosphine to give methyltris(p-methoxyphenyl)phosphonium salt (**5**)

Table I. ^{31}P and ^1H NMR Data of Phosphonium Salts Formed in the Reaction



compd	R	R¹	R²	R³	molar ratio	$\delta_{^{31}P}$	proton data of R groups
1	CH_2CMe_3	Me	Me	Me	8.1	17.67	δ_{CH_2} 3.50 ($^2J_{PH}$ = 12.8 Hz); $\delta_{C(CH_3)_3}$ 1.008
2		Me	Me	CH_2Me_3[a]	6.3	17.40	δ_{CH_2} 3.34 ($^2J_{PH}$ = 12.8 Hz); $\delta_{C(CH_3)_3}$ 1.986
3		Me	CH_2CMe_3	CH_2CMe_3	2.0	17.60	*b*
4		CH_2CMe_3	CH_2CMe_3	CH_2CMe_3	1.0	17.33	*b*
5	Me	Me	Me	Me	15.6	19.43	δ_{CH_3} 2.91 ($^2J_{PH}$ = 13.1 Hz)
6		Me	Me	CH_2CMe_3[c]	12.4	19.08	δ_{CH_3} 2.80 ($^2J_{PH}$ = 13.1 Hz)
7		Me	CH_2CMe_3	CH_2CMe_3	3.1	19.38	*b*
8		CH_2CMe_3	CH_2CMe_3	CH_2CMe_3	1.6	19.02	*b*

[a] $\delta_{C(CH_3)_3}$ 1.038. [b] Absorption peaks not clearly observed due to overlap with those of the more abundant components of the mixture. [c] $\delta_{C(CH_3)_3}$ 1.045.

which, in turn, undergoes similar reactions. From the relative molar ratios of the products, it is clear that these reactions start to dominant the inherently slower S_N2 reaction of neopentyl iodide with the phosphine.

The phosphine attack on the *p*-methoxy groups of phosphonium salts probably results in the formation of a resonance-stabilized inner salt (eq 1). Horner et al.[1] have observed the formation of such species from (*p*-hydroxyphenyl)phosphonium salts in the presence of aqueous sodium hydroxide. The inner salt then reacts with neopentyl iodide to give the (*p*-neopentoxyphenyl)phosphonium derivatives.


(1)

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