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α-ALKOXYALKYLIDENETRIPHENYLPHOSPHAZINES AS YLIDE REAGENTS AND AS A SOURCE OF α-ALKOXYCARBENES

Glory B. Merrill[1] and Harold Shechter

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

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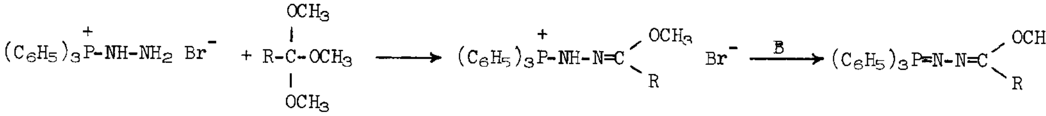
Acyl and sulfonyl hydrazides react with ortho esters to form hydrazimidocarboxylate ester derivatives (RCONHN=CROR and RSO_2NHN=CROR, respectively).[2] It has now been found that α-methoxyalkylidenetriphenylphosphazinium bromides (3) are obtained efficiently by reaction of trimethyl ortho esters (2) with hydrazinotriphenylphosphonium bromide (1, Eq 1) as prepared



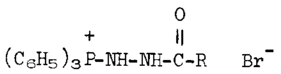
$$(C_6H_5)_3\overset{+}{P}\text{-NH-NH}_2\ Br^- + R\text{-}\underset{OCH_3}{\overset{OCH_3}{C}}\text{-OCH}_3 \longrightarrow (C_6H_5)_3\overset{+}{P}\text{-NH-N=C}\genfrac{}{}{0pt}{}{OCH_3}{R}\ Br^- \xrightarrow{B} (C_6H_5)_3P\text{=N-N=C}\genfrac{}{}{0pt}{}{OCH_3}{R} \qquad (1)$$

1 2a, $R = C_6H_5$ 3a 4a

2b, $R = CH_3$ 3b 4b

2c, R = H 3c 4c

conveniently from triphenylphosphine dibromide and hydrazine[3] Phosphazinium bromides 3a-c are solids of proper analysis and spectral properties and can be handled without difficulty in anhydrous, oxygen-free environments As indicated by two nmr signals for their respective methoxyl protons (Table 1), 3a-c exist in *syn* and *anti* forms.[4] Upon exposure to water, 3a-c convert rapidly to N-acylamidotriphenylphosphiniminium bromides (5). Of particular present interest is that 3a-c are dehydrobrominated efficiently by tetramethylguanidine, triethylamine, basic alumina or aqueous sodium hydroxide-chloroform to *syn*- and *anti*-α-methoxyalkylidenetriphenylphosphazines (4a-c, Eq 1, Table 1)



$$(C_6H_5)_3\overset{+}{P}\text{-NH-NH-}\overset{O}{\overset{\|}{C}}\text{-R}\quad Br^-$$

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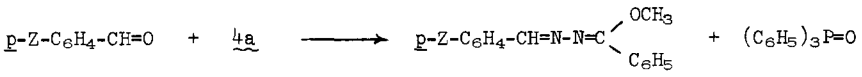
Table 1

Phosphazinium Bromides (3a-c) and Phosphazines (4a-c)

Compound	Yield, %	Chemical Shifts (δ) for Methoxyl Protons[a] Syn[b]	 Anti
3a	88	3.95	3.64
3b	89	3.90	3.41
3c	84	3.53	3.32
4a	82-90	4.25	3.54
4b	93	3.86	3.50
4c	70	3.78	3.54

[a] Determined in chloroform-d_1 containing tetramethylsilane. [b] Syn protons resonate downfield from the corresponding anti protons in similar compounds, L. M. Jackman and S. Sternhell, ''Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,'' Pergamon Press, N.Y., 1969, p 226

α-Alkoxyalkylidenetriphenylphosphazines are active ylide reagents in that they are converted efficiently by various aldehydes to mixed azines of carboxylic esters and aldehydes (Eq 2). Thus 4a reacts with p-nitrobenzaldehyde (6a) and with p-methoxybenzaldehyde (6b) to yield methyl benzoate p-nitrobenzalazine (7a, 96%, yellow, mp 104-105°) and methyl benzoate p-methoxybenzalazine (7b, 74%, yellow oil) of proper analyses and spectra.[5] The structure of 7a is confirmed upon its acidic hydrolysis to N-benzoyl p-nitrobenzaldehyde hydrazone ($p\text{-}O_2NC_6H_4CH{=}NNHCOC_6H_5$). Attempted syntheses of 7a and 7b by reactions of trimethyl orthobenzoate with hydrazones of p-nitrobenzaldehyde and p-methoxybenzaldehyde give however p-nitrobenzalazine and p-methoxybenzalazine, respectively, in high yields rather than the desired products.

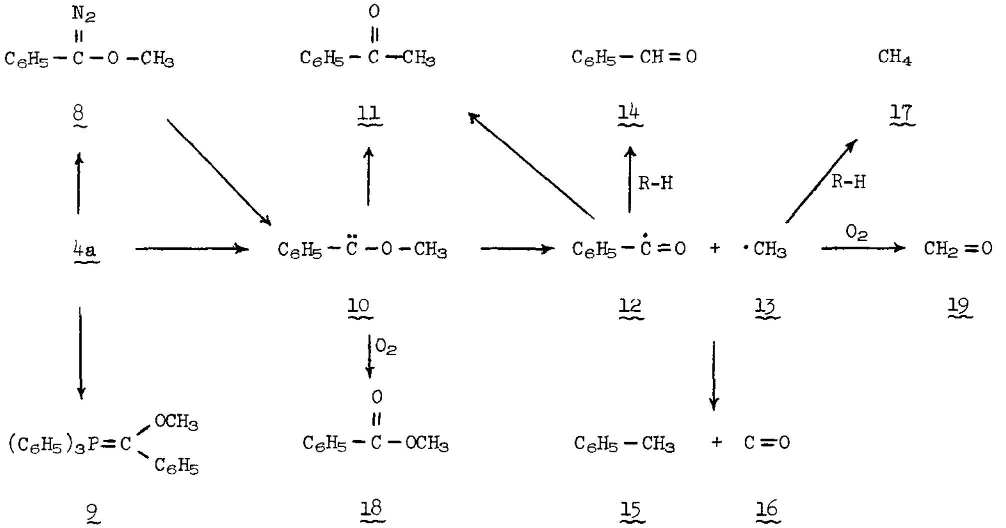


$$p\text{-Z-}C_6H_4\text{-CH=O} \quad + \quad \mathbf{4a} \quad \longrightarrow \quad p\text{-Z-}C_6H_4\text{-CH=N-N=C}\begin{array}{l}\diagup OCH_3 \\ \diagdown C_6H_5\end{array} \quad + \quad (C_6H_5)_3P{=}O \qquad (2)$$

6a, Z = NO_2
6b, Z = OCH_3

7a, Z = NO_2
7b, Z = OCH_3

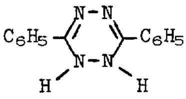
Phosphazines **4a-c** are quite stable thermally Decomposition of **4a** does not occur advantageously to α-methoxyphenyldiazomethane (**8**) or α-methoxybenzylidenetriphenylphosphorane (**9**) At > 200° **4a** is converted to triphenylphosphine (95%), phosphorous-containing residues, and nitrogen along with the volatile products (~ 49%) acetophenone (**11**, 6-11%), benzaldehyde (**14**, 56%) and methane (**17**, 19%), and toluene (**15**, 5-6%) and carbon monoxide (**16**, 9%) In a limited amount of oxygen, **4a** pyrolyzes to methyl benzoate (**18**, 10%) and formaldehyde (**19**, 5%) along with the above gaseous products[6] Thermolysis of **4a** thus appears to generate α-methoxybenzylidene (**10**) which undergoes isomerization, fragmentation, and oxidation as indicated in Eq 3. The behavior of **10** is generally analogous to that of alkyl aryl azo compounds (Ar-N=N-R)[7a] and similar to that of 1-alkoxy-1-alkylidenes (R-O-C̈-R) believed generated by aprotic decomposition of salts of α-alkoxycarbonyl sulfonylhydrazones[2b-c,7b] and by photolysis of strained ring ketones[7c] Decomposition (thermal and photochemical) of α-alkoxyalkylidenetriphenylphosphazines gives promise for advantageous study of a variety of α-alkoxycarbenes.



(3)

Phosphazines **4a-c** are moisture sensitive. Hydrolysis of **4a** yields 1,2-dihydro-3,6-diphenyl-1,2,4,5-tetrazine (**20**),[8a,b] possibly *via* **3a** and then methyl benzoate hydrazone (**21**).

The structure of 20 is established from its properties (mp 190-191.5°, spectra) and origins and upon its dehydrogenation to 3,6-diphenyl-1,2,4,5-tetrazine (22)[8c] by 2,3-dichloro-5,6-dicyanoquinone.



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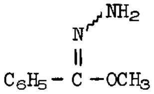
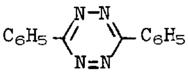


$C_6H_5-\overset{\overset{N-NH_2}{\|}}{C}-OCH_3$

21



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α-Thioalkoxyalkylidenetriphenylphosphazines and α-dialkylaminoalkylidenetriphenylphosphazines are to be studied in this laboratory.

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4 Syn and anti isomers have been observed for 1-acyl-2-ethoxymethylenehydrazines[2a] and for ester p-tosylhydrazones [2b,c]

5. Sodium methyl benzoate p-tosylhydrazonate pyrolyzes to α-methoxybenzalazine [2b]

6. Methanol and benzaldehyde dimethyl acetal are also formed in small yields.

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