tion to produce products of Birch reduction to the exclusion of those due to reductive amination.

A typical reductive amination, that of naphthalene with sodium and hexamethylenimine, may be carried out as follows. To 6.4 g (0.05 mole) of naphthalene and 4.6 g (0.2 g-atom) of dispersed sodium contained in a 500-ml, three-necked flask equipped with a stirrer, air condenser, and nitrogen inlet tube was added 100 ml of hexamethylenimine. A red color developed within 20 min. The mixture was stirred at 25° for 12 hr, and the unreacted sodium, which had agglomerated, was removed. The remaining solution was cooled and treated cautiously with water until the reaction mixture became colorless, then acidified with 10% aqueous hydrochloric acid. After the hydrocarbons had been removed by extraction with ether, the aqueous layer was basified with dilute sodium hydroxide, and surplus hexamethylenimine was removed by steam distillation. The steam distillation residue was extracted with ether. Drying over anhydrous sodium sulfate and distillation yielded 6.2 g (55% yield) of I.

Acceptable C, H, and N analyses[4] were obtained for each amine in Tables I and II. The structures of these amines were unequivocally established through nmr and mass spectroscopic[5] studies except as noted in Tables I and II.

Since the reductive amination is generally selective as to position of attachment of nitrogen to the tetralin nucleus[6] and proceeds in reasonable yield, it offers an attractive synthetic route to novel secondary and tertiary amines.

Acknowledgment. We are grateful to the American Petroleum Institute for generous support of this research, and to the Research Foundation, Oklahoma State University, for their assistance. We wish to thank Dr. O. C. Dermer for valuable discussions and for having read the manuscript.

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[4] Galbraith Laboratories, Inc., Knoxville, Tenn.

[5] We are indebted to Mr. M. C. Hamming, Continental Oil Co., Ponca City, Okla., for these data.

[6] The majority of the amines were found to have nitrogen attached at the 2 position of the 1,2,3,4-tetrahydronaphthyl nucleus. Nitrogen attachment at both the 1 and 2 positions was observed in some cases.

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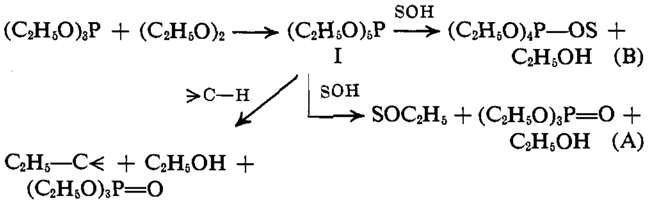
Reactions of Pentaethoxyphosphorane[1]

Sir:

Recently it was reported that pentaalkoxyphosphoranes can be prepared by the reaction of a trisubstituted phosphite and a dialkyl peroxide such as diethyl or dimethyl peroxide.[2] The only other synthetic method leads to pentaalkoxyphosphoranes containing five-membered rings,[3] and thus this new method is potentially of much greater generality. Recent work has suggested that this is the case.[4] Moreover, it has become increasingly clear that the pentaalkoxyphosphoranes are extremely reactive substances and that some of these reactions may have considerable synthetic value. It is the purpose of this report to elaborate on some of these reactions. These studies have been conducted with pentaethoxyphosphorane (I). This compound has been chosen because of its ready availability and the ease of characterization of the products of its reactions.



$$(C_2H_5O)_3P + (C_2H_5O)_2 \longrightarrow \underset{\text{I}}{(C_2H_5O)_5P} \xrightarrow{SOH} (C_2H_5O)_4P{-}OS + C_2H_5OH \quad (B)$$

$$(C_2H_5O)_5P \xrightarrow{SOH} SOC_2H_5 + (C_2H_5O)_3P{=}O + C_2H_5OH \quad (A)$$

$$(C_2H_5O)_5P \xrightarrow{>C-H} C_2H_5{-}C< + C_2H_5OH + (C_2H_5O)_3P{=}O$$

Pentaethoxyphosphorane is most conveniently prepared by allowing triethyl phosphite to react with diethyl peroxide at room temperature. After 15 days the content of I in the reaction mixture reaches *ca.* 60%. Subsequent standing at room temperature leads to a steady diminution in the content of I.[5] Storage at low temperatures inhibits the decomposition. The crude reaction mixture can be enriched in I by distillation at reduced pressure. The major contaminants are triethyl phosphate, triethyl phosphite, and ethanol. These substances do not interfere with the reactions being reported and thus they have been conducted using the crude reaction mixture of I.

Several modes of reaction are available to I depending upon the coreactant. These include reactions in which alkylation (A) occurs and also those in which exchange (B) between the reactant and ethoxy groups takes place.

The alkylation reactions are most facile with acidic materials. For example, carboxylic acids are rapidly and quantitatively converted to the corresponding ethyl ester. Triethyl phosphate and ethanol are also formed. Of greater interest are the reactions with phenols. Hydroquinone reacted exothermically with I to give *p*-ethoxyphenetole, triethyl phosphate, and ethanol. No other major products were detected by glpc. Similarly *p*-nitrophenol reacted vigorously with I to give *p*-nitrophenetole in quantitative yield.[6] *p*-Methoxyphenol yielded *p*-methoxyphenetole. Reaction of I with 2,6-di-*t*-butyl-*p*-cresol was slow, and after 15 days only a small amount of the corresponding ether was formed.

Of particular interest are the reactions of I with enolic substances. Acetylacetone reacted vigorously at room temperature or 0° to give mainly the enol ether of acetylacetone. A small amount of 3-ethyl-2,4-pentanedione was also formed. Reaction with diethyl malonate was not exothermic at room temperature. After 14 days analysis by glpc showed that the major products were diethyl ethylmalonate (88%), triethyl phosphate, and ethanol. Little or none of the dialkylated product was formed. When diethyl ethylmalonate

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[1] This research has been supported by the National Science Foundation under NSF GP202 and GP4997.

[2] (a) D. B. Denney and H. M. Relles, *J. Am. Chem. Soc.*, **86**, 3897 (1964); (b) D. B. Denney and S. T. D. Gough, *ibid.*, **87**, 138 (1965).

[3] F. Ramirez, *Pure Appl. Chem.*, **9**, 337 (1964).

[4] Unpublished results from these laboratories.

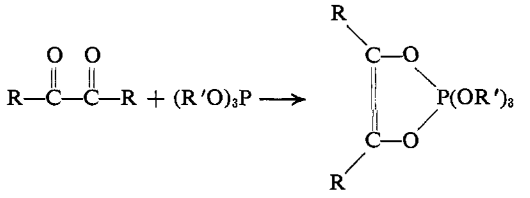
[5] The percentage of I in a reaction mixture can be determined by adding excess benzoic acid and measuring the amount of ethyl benzoate formed by glpc or by titrating unreacted benzoic acid.

[6] Yields were determined by glpc on the reaction mixtures.

was allowed to react with I for 2 months, *ca.* 50% of diethyl diethylmalonate was formed.

Reaction of pentaalkoxyphosphoranes with water leads to rapid hydrolysis with the production of phosphates and alcohols;[7] I is hydrolyzed to triethyl phosphate and ethanol. Reaction of I (1 mole) with *n*-propyl alcohol (5 moles) followed by the addition of benzoic acid gave ethyl benzoate and *n*-propyl benzoate in similar amounts. In another experiment a mixture of I and *n*-propyl alcohol was subjected to glpc analysis. Four phosphates were detected; these were the same as those prepared by allowing triethyl phosphite to react with *n*-propyl alcohol followed by oxidation with *t*-butyl hydroperoxide. It appears therefore that an exchange process has occurred between I and *n*-propyl alcohol (triethyl phosphate did not exchange with *n*-propyl alcohol under these conditions). This exchange may be relatively general; however, this has yet to be determined.

The alkylation reactions of I are unique and particularly facile. The most intriguing feature of these reactions is that no catalyst, *i.e.*, acid or base, is required nor are acids or bases generated during the reaction. Adventitious catalysis by impurities cannot be ruled out at this time. Thus although noncyclic pentaalkoxyphosphoranes cannot be considered to be readily available, their unique ability to alkylate in the absence of acids and bases may make their use profitable in some cases. It should also be noted that the cyclic oxyphosphoranes, II, are readily available, and a study of their ability to alkylate should be undertaken.[8]



II

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[7] References 2 and 3 and references cited in ref 3.

[8] V. A. Kukhtin and K. M. Orekhova, *Zh. Obshch. Khim.*, 30, 1208 (1960), report that II, R = C_2H_5, R′ = CH_3, reacts with acetic acid to give ethyl acetate in 60% yield.

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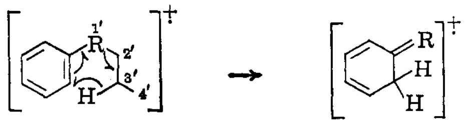
Mass Spectrometry in Structural and Stereochemical Problems. CIX.[1] The Nonspecificity of Hydrogen Rearrangements in Aryl Alkyl Ethers[2]

Sir:

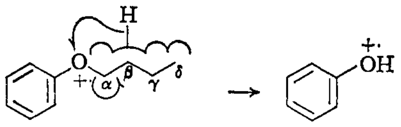
The McLafferty rearrangement[3] has been recognized as one of the most common forms of hydrogen transfer in mass spectrometric fragmentation processes. For alkylbenzenes[4] and for those related ethers and alcohols containing the oxygen atom at the 2′,[1] 3′,[5] or 4′[6] position, there is ample evidence from isotope-labeling experiments to show that this site-specific six-membered hydrogen rearrangement to the benzene ring takes place exclusively from the 3′ position to yield a charged species of mass 92. By analogy it has been assumed that in phenyl alkyl ethers (oxygen at the 1′ position) a similar specific 3′-hydrogen migration occurs to give an *m/e* 94 peak.[7,8] However, as a consequence of our investigation into the isotope effect[1] in McLafferty rearrangements, we prepared the complete series of side-chain labeled phenyl *n*-butyl ethers (Table I) and found that hydrogen transfer was nonspecific in this type of compound. The results are similar to those encountered in dialkyl ethers[9] and suggest that the rearrangement of hydrogen proceeds predominantly to a positively charged oxygen atom *via* three-, four-, five-, and six-membered cyclic transition states (B → *m/e* 94) together with a maximal contribution of 25% from a standard McLafferty rearrangement (A → *m/e* 94).



A, R = CH_2 or O

m/e 92, R = CH_2
m/e 94, R = O

Table I. Origin of Hydrogen Transfer in *m/e* 94 Ion Production in Phenyl *n*-Butyl Ether



B

m/e 94

Deuterated derivative	α-d_2	β-d_2	γ-d_2	δ-d_3
% transfer	15	25	29	16

The driving force behind such behavior is probably the opportunity for resonance stabilization of the phenol ion radical, which in the mass spectrum of the unlabeled phenyl *n*-butyl ether represents 63% of the total ionization $(\Sigma^{M}{}_{40})$ of this compound. The contribution to *m/e* 94 from all four positions, 85% as determined by deuterium labeling (Table I), is a reasonable measure of the D-H isotope effect[1] inherent in these transfer processes.

Such a result creates some doubt as to the specificity of β-hydrogen transfer in vinyl ethers[7] since Meyerson[10] has already shown by ionization potential measurements that a McLafferty rearrangement to the double bond in ethyl vinyl ether to give an acetaldehyde ion (1) is much

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[1] For paper CVIII, see J. K. MacLeod and C. Djerassi, *Tetrahedron Letters*, in press.

[2] Financial assistance by the National Institutes of Health (Grants No. AM-04257 and CA-07195) is gratefully acknowledged. The purchase of the Atlas CH-4 mass spectrometer was made possible by NASA grant NsG 81-60.

[3] F. W. McLafferty, *Anal. Chem.*, **31**, 82 (1959); see also G. Spiteller and M. Spiteller-Friedmann, *Monatsh.*, **95**, 257 (1964).

[4] J. D. McCollum and S. Meyerson, *J. Am. Chem. Soc.*, 81, 4116 (1959).

[5] J. A. Gilpin, *J. Chem. Phys.*, **28**, 521 (1958).

[6] J. D. McCollum and S. Meyerson, unpublished results quoted in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, p 510.

[7] F. W. McLafferty, *Anal. Chem.*, **31**, 2072 (1959); see also ref 3.

[8] K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 123.

[9] C. Djerassi and C. Fenselau, *J. Am. Chem. Soc.*, **87**, 5747 (1965).

[10] S. Meyerson and J. D. McCollum, "Advances in Analytical Chemistry and Instrumentation," Vol. 2, C. N. Reilly, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 211–213.