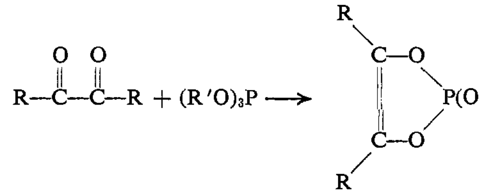
was allowed to react with I for 2 months, *ca.* 50% of diethyl diethylmalonate was formed.

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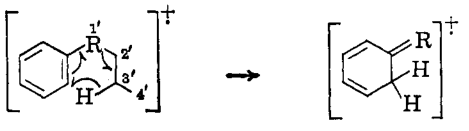
Mass Spectrometry in Structural and Stereochemical Problems. CIX.[1] The Nonspecificity of Hydrogen Rearrangements in Aryl Alkyl Ethers[2]

Sir:

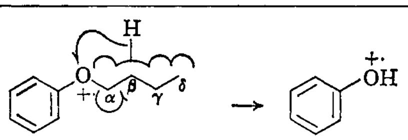
The McLafferty rearrangement[3] has been recognized as one of the most common forms of hydrogen transfer in mass spectrometric fragmentation processes. For alkylbenzenes[4] and for those related ethers and alcohols containing the oxygen atom at the 2',[1] 3',[5] or 4'[6] position, there is ample evidence 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.

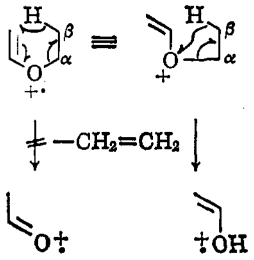
(7) F. W. McLafferty, *Anal. Chem.*, **31**, 2072 (1959); see also ref 3.

(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.

less likely than transfer to oxygen to furnish the charged enol species II.



I II

Furthermore, our studies demonstrate again that site-specific hydrogen rearrangements, regardless of their plausibility, should not be postulated unless at least one typical case of each structural type is documented by isotope-labeling experiments.

To investigate the relative charge-localizing abilities of differing aromatic systems and heteroatoms, a series of β-d_2-labeled aryl alkyl ethers and thioethers was prepared. The per cent contribution from the side-chain β' position in α- and β-naphthyl *n*-butyl ethers (26 and 28%, respectively) indicated no significant enhancement of transfer to the naphthyl as compared to the phenyl nucleus. On the other hand, *m*-dimethylaminophenyl *n*-butyl-β-d_2 ether exhibited a minimum of 45% deuterium transfer (calculations were complicated by a strong peak one mass unit less than the rearrangement peak), suggesting that the *m*-dimethylamino group partially stabilizes the radical site at the *ortho* and *para* positions, facilitating deuterium migration to the aromatic ring *via* the McLafferty rearrangement. This was supported by the calculated value of β-hydrogen transfer in *m*-trifluoromethylphenyl *n*-butyl ether (22%) where the charge-stabilizing effect of the *m*-trifluoromethyl substituent would be opposite to that of the dimethylamino group.

Finally, replacement of the oxygen atom by sulfur resulted in a diminution of hydrogen transfer (19% *vs.* 25% in Table I) from the β position as calculated from the mass spectrum of phenyl *n*-butyl-β-d_2 sulfide. Since labeling experiments in dialkyl ethers[9] and sulfides[11] have shown that there is no significant difference between the extent of β-hydrogen transfer to oxygen and sulfur, the decrease in migration from this position in the sulfur analog can be reasonably attributed to suppression of the contributing McLafferty rearrangement species (A) in the sulfide, due to the greater charge-stabilizing ability of sulfur.[12]

All mass spectra were recorded on an Atlas CH-4 mass spectrometer at 70 ev using a heated gas inlet system. The ethers were prepared by the Williamson synthesis[13] and purified for mass spectrometric analysis by vapor phase chromatography. Standard techniques[14] were employed for the preparation of the deuterated *n*-butyl bromides.

Acknowledgment. We are grateful to Dr. A. M. Duffield for recording the mass spectra and to Miss S. Sample for providing a sample of *n*-butyl-β-d_2 bromide.

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[11] S. Sample and C. Djerassi, *J. Am. Chem. Soc.*, in press.

[12] Reference 8, pp 87 and 124.

[13] A. I. Vogel, "Practical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p 665.

[14] A. M. Duffield, R. Beugelmans, H. Budzikiewicz, D. A. Lightner, D. H. Williams, and C. Djerassi, *J. Am. Chem. Soc.*, **87**, 805 (1965).

Reactions of Triethyl Phosphite with 4-Trihalomethylcyclohexa-2,5-dienones. Evidence for Displacement of a Tribromomethyl Anion by SN2′ Attack on Oxygen[1]

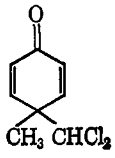
Sir:

Nucleophilic attack by trivalent phosphorus derivatives on carbonyl oxygens of α-halocarbonyl compounds has frequently been postulated.[2] It has never been possible, however, to distinguish between attack of the phosphorus compound at the carbonyl oxygen and its addition to the carbonyl carbon, followed by rearrangement to oxygen.[2]

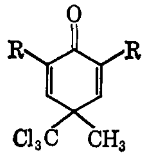
We wish to report evidence that triethyl phosphite directly attacks the carbonyl oxygen of 4-tribromomethyl-4-methylcyclohexa-2,5-dienone and simultaneously displaces a tribromomethyl anion in an SN2′ reaction.

It was recently reported that an attempt to force triethyl phosphite to attack a chlorine atom of 4-dichloromethyl-4-methylcyclohexa-2,5-dienone (**1**) gave only recovered starting materials,[3a] although 4-bromocyclohexa-2,5-dienones react essentially instantaneously with trialkyl phosphites.[3]

Attack at halogen atoms in compounds similar to **1** should be aided by further halogen substitution, to stabilize any carbanions formed in the reaction, and by substitution of bromine or iodine for chlorine on the methyl group.[4] Substitution of additional halogen atoms in **1**, however, did not suffice to activate the molecule toward reaction with triethyl phosphite. 4-Trichloromethyl-4-methylcyclohexa-2,5-dienone (**2a**)[5] was recovered unchanged after 124-hr refluxing in toluene in the presence of 1.5 equiv of triethyl phosphite, or after 24 hr at 150° in the absence of solvent. Similarly, 2,6-dibromo-4-trichloromethyl-4-methylcyclohexa-2,5-dienone (**2b**)[6] was recovered unchanged from reaction with triethyl phosphite at 150°.



1



2a, R = H
2b, R = Br

In contrast, reaction of triethyl phosphite with 4-tribromomethyl-4-methylcyclohexa-2,5-dienone (**3**)[7] in

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[1] Reactions of Cyclohexadienones. XV. Part XIV: B. Miller, *J. Am. Chem. Soc.*, **87**, 5515 (1965).

[2] (a) See F. W. Lichtenthaler, *Chem. Rev.*, **61**, 607 (1961), for leading references; (b) P. A. Chopard, V. M. Clark, R. F. Hudson, and A. J. Kirby, *Tetrahedron*, **21**, 1961 (1965).

[3] (a) B. Miller, *J. Org. Chem.*, **28**, 345 (1963); (b) B. Miller, *ibid.*, **30**, 1964 (1965).

[4] B. Miller in "Topics in Phosphorus Chemistry," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1965, pp 133–199.

[5] T. Zincke and R. Suhl, *Ber.*, **39**, 4148 (1906).

[6] K. v. Auwers and W. Jülicher, *ibid.*, **55**, 2167 (1922).

[7] J. R. Merchant and V. B. Desai, *J. Chem. Soc.*, 2258 (1964).