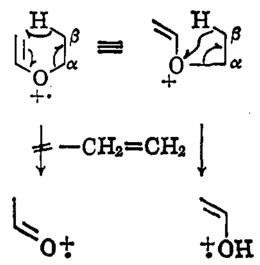
less likely than transfer to oxygen to furnish the charged enol species II.



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.

J. K. MacLeod, Carl Djerassi
Department of Chemistry, Stanford University
Stanford, California
Received February 21, 1966

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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]

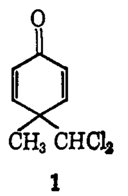
Sir:

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]

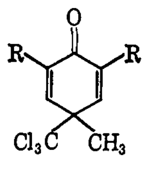
We wish to report evidence that triethyl phosphite directly attacks the carbonyl oxygen of 4-tribromomethyl-4-methylcyclohexa-2,5-dienone and simultaneously displaces a tribromomethyl anion in an SN2′ reaction.

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).

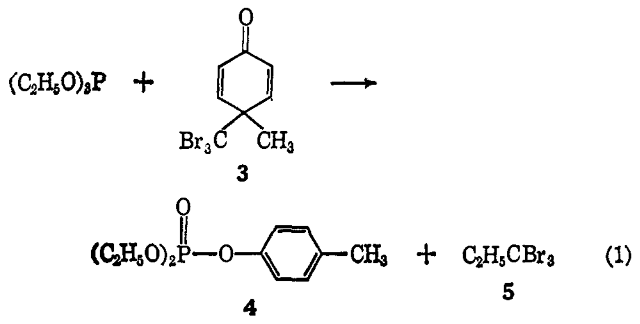
[4] B. Miller in "Topics in Phosphorus Chemistry," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1965, pp 133–199.

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

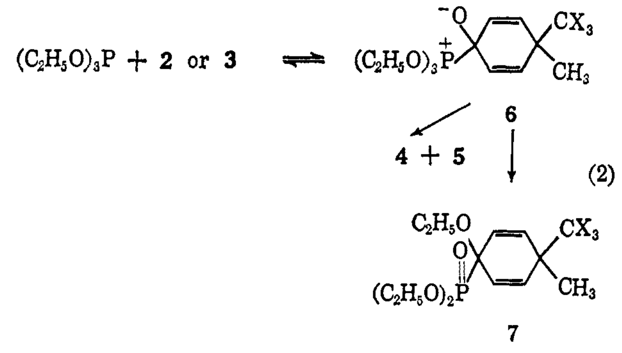
[6] K. v. Auwers and W. Jühlicher, *ibid.*, 55, 2167 (1922).

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

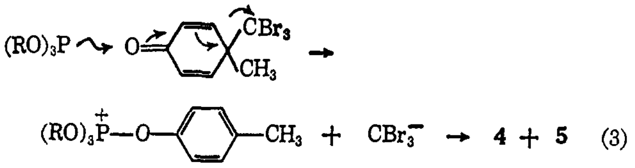
refluxing toluene for 42 hr gave (in addition to 20% of recovered **3**) a 60% yield of diethyl *p*-tolyl phosphate (**4**)[8] and a 43% yield of 1,1,1-tribromopropane (**5**).[9]



Formation of **4** and **5** would be quite difficult to explain by any reasonable mechanisms involving free-radical paths or nucleophilic attack at halogen. Attempts to rationalize the relative reactivities of **2a** and **3** by postulating initial addition of triethyl phosphite to the carbonyl carbon and a subsequent rearrangement to oxygen would also run into difficulties. If the addition step were rate determining and the subsequent rearrangement step were fast, **2a** should be more reactive than **3**, since addition to the carbonyl should be aided by the inductive effect of the trichloromethyl group. If addition to the carbonyl group were fast and reversible and the rearrangement step were rate determining (eq 2), the intermediate zwitterion **6** would be expected to undergo transfer of an alkyl group to oxygen to give **7** in an Arbuzov rearrangement[10,11] since dealkylation of tetraalkoxyphosphonium salts occurs very rapidly at temperatures far below that of refluxing toluene.[2a,4] The absence of **7** or any related product, particularly from the prolonged reaction with **2**, suggests that no addition to the carbonyl group of **2** or **3** occurs.



The most probable mechanism for reaction 1 is a nucleophilic attack of the phosphite upon the carbonyl oxygen with simultaneous elimination of the tribromomethyl anion (eq 3).[12] The relative ease of formation of the tribromomethyl anion compared to the trichloromethyl anion is consistent with previous demonstrations that the tribromomethyl anion is far more rapidly formed in reactions of haloforms with alkali[13] and in decarboxylation of trihaloacetic acid salts.[14] It is possible that displacement of a tribromomethyl anion from **3** is further favored by steric repulsions between the tribromomethyl group and the adjacent quaternary carbon.



Nucleophilic displacement of a tribromomethyl anion from a saturated carbon and alkylation of that anion appear to be novel reactions.

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(8) G. W. Kenner and N. R. Williams, *J. Chem. Soc.*, 522 (1955).

(9) J. C. Conly, *J. Am. Chem. Soc.*, **75**, 1148 (1953).

(10) V. S. Abramov and N. A. Il'ina, *Dokl. Akad. Nauk SSSR*, **125**, 1027 (1959); *Chem. Abstr.*, **53**, 21747 (1959).

(11) B. A. Arbusow, *Pure Appl. Chem.*, **9**, 307 (1964).

(12) A referee has suggested that a pentacovalent intermediate may be formed by addition of phosphorus to both carbon and oxygen. The effects of the leaving group, however, make it clear that formation of such an intermediate cannot be rate determining. The alternative possibility that formation of a complex is rapid and reversible, and that occasionally the carbon–phosphorus bond in the complex breaks, seems, even conceptually, almost indistinguishable from complete dissociation followed by attack at the carbonyl oxygen.

(13) J. Hine, N. W. Burske, M. Hine, and P. B. Langford, *J. Am. Chem. Soc.*, **79**, 1406 (1957).

(14) R. A. Fairclough, *J. Chem. Soc.*, 1187 (1938).

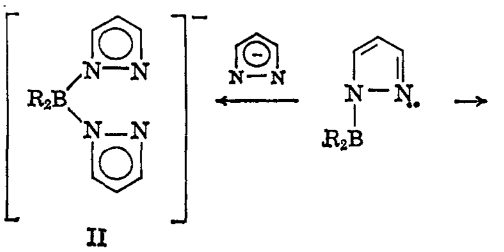
Bernard Miller
Chemical Research and Development, Agricultural Division
American Cyanamid Company, Princeton, New Jersey
Received December 4, 1965

Boron–Pyrazole Chemistry

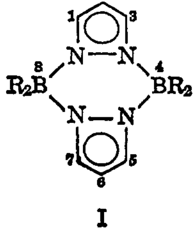
Sir:

Boron–pyrazole chemistry, which deals with compounds containing boron bonded to nitrogen of a pyrazole nucleus,[1] is a new and fertile field of remarkable scope. It has yielded novel classes of boron heterocycles, chelating ligands, and transition metal compounds.

Such versatility stems from the singular combination of electronic and geometric features of the 1-borylpyrazole fragment that leads to its facile stabilization either through dimerization or through coordination with a pyrazolide ion.[2] In this manner structures I and II, respectively, are produced; they are representa-



II



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(1) The only reported boron–pyrazole compound is 4,5(3)-diphenylpyrazole-3(5)-boronic acid: D. S. Matteson, *J. Org. Chem.*, **27**, 4293 (1962).

(2) Coordination with a neutral pyrazole molecule gives rise to the free acid derived from II.