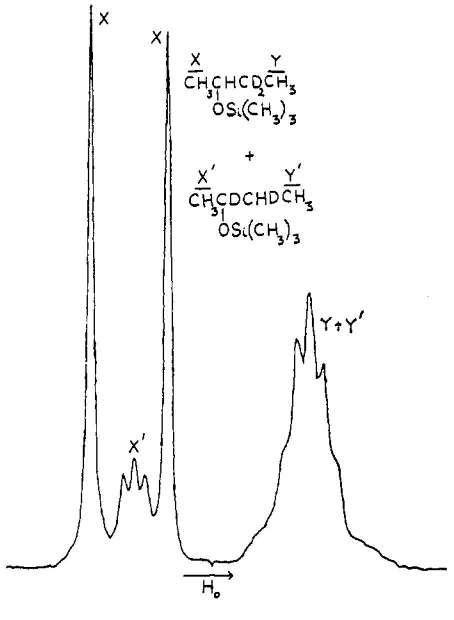
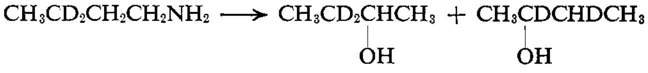


Figure 1.

The integrated area ratio of the signals from the 1-methyl and 4-methyl is 1.06:1.00. Since the corresponding ratio of the ether of unlabeled 2-butanol is 1.07:1.00 under our instrumental conditions, VI cannot be present in significant amount. From the ratio 83:17 of A:B, the following may be written.

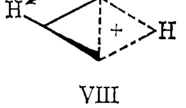


$$CH_3CD_2CH_2CH_2NH_2 \longrightarrow CH_3CD_2\underset{OH}{\underset{|}{C}}HCH_3 + CH_3\underset{OH}{\underset{|}{C}}DCHDCH_3$$

$100\%\ d_2$ 83% 17%

In turn, this product distribution accounts satisfactorily for the isotopic distribution of the $(P - C_2H_5)$ ions in the mass spectrum of the derived trimethylsilyl ether.

The only experimental evidence therefore for the intermediacy of I and II is the formation of methylcyclopropane. As only 2% of the hydrocarbon fraction is methylcyclopropane,[2a] and the hydrocarbon fraction comprises less than 30% of total product, I and II can be responsible for less than 0.6% of product. This should be contrasted with the 6% product—cyclopropane and isotopically rearranged 1-propanol—arising from the corresponding species in the deamination of 1-propylamine. Repulsive interactions in VIII, analogous to those suggested for the isobutyl and neopentyl systems,[1] can account for these differences.



VIII

Finally, we wish to point out that the rearrangement 2-butyl cation ⇌ 2-butyl cation is only slightly slower than its capture by water. Assuming capture by water to be diffusion controlled leads to the conclusion that the activation energy of this rearrangement is *ca.* 2 kcal/mole. Under the experimental conditions isotopically labeled 2-butanol did not undergo isotope position rearrangement.

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(5) Fellow of the Alfred P. Sloan Foundation.

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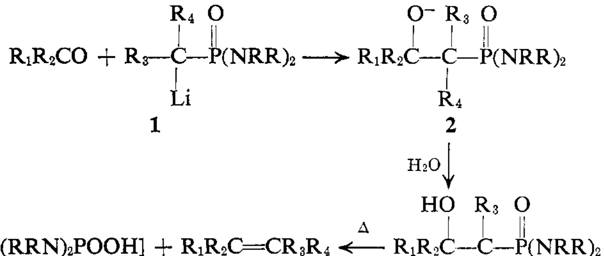
The Synthesis of Olefins from Carbonyl Compounds and Phosphonic Acid Bisamides

Sir:

We report herein a new and useful two-step synthesis of olefins from carbonyl compounds and α-lithiophosphonic acid bisamides (**1**) according to the sequence



$$R_1R_2CO + R_3-\underset{Li}{\underset{|}{\overset{R_4}{\overset{|}{C}}}}-\overset{O}{\overset{\|}{P}}(NRR)_2 \longrightarrow R_1R_2\overset{O^-}{\overset{|}{C}}-\underset{R_4}{\underset{|}{\overset{R_3}{\overset{|}{C}}}}-\overset{O}{\overset{\|}{P}}(NRR)_2$$

1 **2**

$$\big\downarrow H_2O$$

$$[(RRN)_2POOH] + R_1R_2C{=}CR_3R_4 \xleftarrow{\Delta} R_1R_2\overset{HO}{\overset{|}{C}}-\underset{R_4}{\underset{|}{\overset{R_3}{\overset{|}{C}}}}-\overset{O}{\overset{\|}{P}}(NRR)_2$$

4 **3**

The possibility that the key transformation of **3** to **4** might occur was indicated in part by the discovery that β-hydroxy sulfinamides undergo thermal decomposition to olefins, amines, and sulfur dioxide.[1]

The carbanionic reagents of type **1** are readily generated. Thus, treatment of methylphosphonic acid bis(dimethylamide)[2,3] in tetrahydrofuran at −78° under nitrogen with 1 equiv of *n*-butyllithium produces the α-lithio derivative **1** ($R_3 = R_4 = H$; $R = CH_3$) in high yield,[4] as shown by reaction with the carbonyl function of aldehydes and ketones to form β-hydroxyphosphonic acid bisamides of type **3**, $R = CH_3$, almost quantitatively. The lithio derivative **1** ($R_3 = R_4 = H$; $R = CH_3$) is quite stable even at 0° in tetrahydrofuran solution under nitrogen. The adducts of general type **3**, $R_3 = R_4 = H$, derived from ketones and aldehydes undergo elimination to form olefins **4**, $R_3 = R_4 = H$, upon heating at reflux in dry benzene or toluene solution in the presence of silica gel catalyst for 10–12 hr.[5] The intermediate *alkoxy* adducts **2**, in contrast to the *β-hydroxy* phosphonic acid amides **3** and in contrast

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(1) E. J. Corey and T. Durst, *J. Am. Chem. Soc.*, **88**, 5656 (1966).

(2) The phosphonyl amides used in this work were obtained from the corresponding phosphonyl dichlorides by a minor modification of the method of G. M. Kosolapoff and L. B. Payne, *J. Org. Chem.*, **21**, 413 (1956). The dichlorides were prepared by the procedures of A. M. Kinnear and E. A. Perren, *J. Chem. Soc.*, 3437 (1952).

(3) New compounds prepared in this work have been characterized satisfactorily by elemental analysis and infrared and nmr spectroscopy.

(4) Metalation was complete after 15 min at −78°. The homologs **1** (R_3 = alkyl, $R_4 = H$, $R = CH_3$) require 2 hr at −50°, and **1** ($R_3 = R_4 = R = CH_3$) requires 5 hr at −40°.

(5) A solution of **3** in about 10 times the weight of benzene with 2–3 times the weight of silica gel ("Woelm") has generally been employed. The elimination also occurs if silica gel is not used as catalyst, but the rate is reduced roughly by a factor of 2. Olefin formation proceeds more rapidly with the adducts derived from ketones than with those derived from aldehydes.

Table I. Conversion $R_1R_2C{=}O \rightarrow R_1R_2C{=}CH_2$ *via* Methylphosphonic Acid Bis(dimethylamide) Adducts

Carbonyl compd	Yield of adduct, %	Yield of olefin, %[a]
Benzophenone	95	93
4-*t*-Butylcyclohexanone	98	65[b]
2-Cyclohexenone	96	78[c, d]
Benzaldehyde	95	53[c]
Δ^3-Cyclohexenecarboxaldehyde	95	67[c]
Dodecanal	89	70[c]

[a] Yields given refer to reaction in benzene at reflux for 12 hr. [b] Yield of isolated product. [c] Yield as determined by vpc or nmr analysis. [d] Elimination carried out without silica gel and in the presence of triethylamine to prevent isomerization of the olefinic product.

Table II. Conversion $R_1R_2CO \rightarrow R_1R_2C{=}CHCH_3$ *via* Ethylphosphonic Acid Bis(dimethylamide) Adducts

Carbonyl compd	Yield of adduct, %	Yield of olefin, %
Benzophenone	97	90
4-*t*-Butylcyclohexanone	92	80
Benzaldehyde	98	90[a,b]
Δ^3-Cyclohexenecarboxaldehyde	96	79[a]

[a] For stereochemistry see E. J. Corey and G. T. Kwiatkowski, *J. Am. Chem. Soc.*, **88**, 5653 (1966). [b] Yield for reaction in toluene at reflux for 12 hr; all other yields for reaction in benzene at reflux for 12 hr.

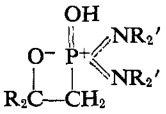
to β-alkoxy phosphonium (Wittig) betaines, do not undergo olefin-forming elimination under normal conditions. Results for a variety of carbonyl components are summarized in Tables I and II.

The phosphonic amide route to olefins is general in the sense that it can be applied to the formation of mono-, di-, tri-, and tetrasubstituted ethylenic systems. Table II shows the yields of adducts and olefins obtained from aldehydes and ketones using as reagent the α-lithio derivative of ethylphosphonic acid bis(dimethylamide), prepared by metalation with butyllithium as described above. The α-lithio derivative of isopropylphosphonic acid dimethylamide, similarly available, also is useful; for example, with benzophenone the β-hydroxy phosphonic acid amide **3** ($R_1 = R_2 = C_6H_5$; $R_3 = R_4 = CH_3$; $R = CH_3$) is obtained in 94% yield, and 1,1-diphenyl-2-methylpropene is formed in 92% yield.[6]

A wide variety of phosphonic acid chlorides and amides are readily available by known procedures.[2] In addition, it has been found that lithio derivatives of type **1** can be alkylated with alkyl iodides and bromides which are not excessively prone to elimination. Thus, reaction of the lithio derivative **1** ($R_3 = R_4 = H$; $R = CH_3$) with 1 equiv of methyl iodide, followed by sequential addition of 1 equiv of *n*-butyllithium and 1 equiv of benzophenone, produces the β-hydroxy phosphonic amide **3** ($R_1 = R_2 = C_6H_5$; $R_3 = CH_3$, $R_4 = H$, $R = CH_3$) in 96% yield; the analogous sequence using *n*-butyl bromide in the alkylation affords the adduct **3** ($R_1 = R_2 = C_6H_5$; $R_3 = n\text{-}C_4H_9$; $R_4 = H$; $R = CH_3$) in 96% yield.

These findings open up a host of interesting synthetic possibilities and a number of questions. The phosphonamide and the sulfinamide[1] routes to olefins are now available as alternatives to the Wittig reaction with phosphonium ylides,[7] as well as the somewhat less general, but often very useful, Horner–Emmons reaction with certain stabilized carbanions derived from phosphonate esters and phosphine oxides,[8,9] and the newer variation which employs carbanions derived from thiophosphonate esters.[10] Several general advantages of the phosphonamide route to olefins compared to the Wittig reaction are apparent; these include (1) the absence of reaction products, such as triphenylphosphine oxide in the case of the Wittig reaction, which can complicate the isolation of olefin; (2) the ready availability and potential low cost (especially on a molar basis) of the phosphonamide reagents; (3) the possibility of purification at the stage of the intermediate β-hydroxy phosphonic amide;[11] (4) the relatively greater opportunity to control the stereochemistry of the intermediate β-hydroxy phosphonic amide and, hence, of the olefin;[12] and (5) the availability of phosphonamide reagents by routes involving alkylation on carbon (usually impractical with phosphonium ylides).

This investigation is being continued along a broad front to determine the full range of utility in synthesis of the new reagents reported here and to clarify the underlying reaction mechanisms. In regard to the mechanism of olefin formation from β-hydroxy phosphonic amides, it seems attractive to consider oxygen attack on phosphorus from a dipolar intermediate **5** followed by *cis* cycloelimination, although this is speculative at present.[13]



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[6] In general, the rate of elimination from the adducts of type **3** to form olefin increases with the number of carbon substituents at the ethylenic function; yields also appear to improve with substitution.

[7] For a review see A. Maercher, *Org. Reactions*, **14**, 270 (1965).

[8] L. Horner, H. Hoffman, W. Klink, H. Ertel, and V. G. Toscano, *Ber.*, **95**, 581 (1962).

[9] W. S. Wadsworth and W. D. Emmons, *J. Am. Chem. Soc.*, **83**, 1733 (1961).

[10] E. J. Corey and G. T. Kwiatkowski, *ibid.*, **88**, 5654 (1966).

[11] These substances have been found uniformly to be nicely crystalline substances which are readily and efficiently purified by a single recrystallization.

[12] See Table II, footnote *a*.

[13] We thank the National Institutes of Health for generous financial aid in the form of a research grant and postdoctoral fellowship.

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The Synthesis of *cis* and *trans* Olefins *via* β-Keto and β-Hydroxy Phosphonamides

Sir:

The Wittig synthesis of olefins combines the extension of carbon skeleton with the feature of position-specific introduction of an ethylenic unit and in consequence has proved to be tremendously useful.[1] One serious limitation, however, arises from the frequent difficulty of synthesizing a particular geometrical form of an

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[1] For a recent review see A. W. Johnson, "Ylid Chemistry," Academic Press Inc., New York, N. Y., 1966.