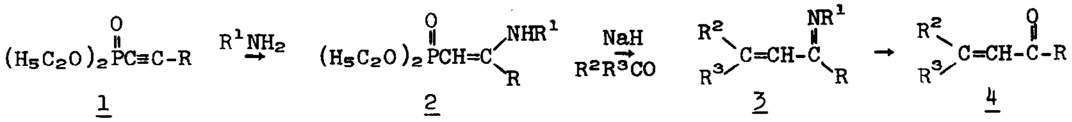
Tetrahedron Letters No.18, pp. 1419-1420, 1971. Pergamon Press. Printed in Great Britain.

ENAMINE PHOSPHONATES: THEIR USE IN THE SYNTHESIS OF α,β-ETHYLENIC KETIMINES AND THE CORRESPONDING KETONES

Mohinder S. Chattha and Adam M. Aguiar[1]
Department of Chemistry, Tulane University
New Orleans, Louisiana 70118

(Received in USA 8 March 1971; received in UK for publication 30 March 1971)

As a continuation of our interest in the chemistry of phosphorus(V) enamines,[2] we wish to report the usefulness of enamine phosphonates 2 in the preparation of α,β-ethylenic ketones 4. Reported information on the preparation of compounds like 2 is rather limited.[3,4,5] We have found that 2 can be prepared in essentially quantitative yields by the addition of a primary amine to diethyl alkynyl-1-phosphonates (1). Treatment of 2 with NaH followed by addition of a carbonyl compound produces ketimines 3 in good to excellent yields; and hydrolysis of 3 yields 4 as outlined below.



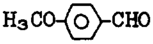
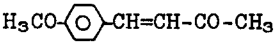
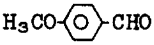
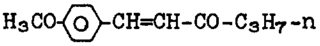
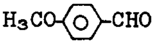
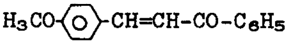
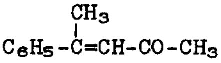
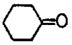
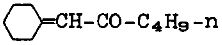
$$\underset{\mathbf{1}}{(H_5C_2O)_2\overset{O}{\overset{\|}{P}}C\equiv C\text{-}R} \xrightarrow{R^1NH_2} \underset{\mathbf{2}}{(H_5C_2O)_2\overset{O}{\overset{\|}{P}}CH{=}C(NHR^1)R} \xrightarrow[R^2R^3CO]{NaH} \underset{\mathbf{3}}{R^2R^3C{=}CH\text{-}\overset{NR^1}{\overset{\|}{C}}\text{-}R} \rightarrow \underset{\mathbf{4}}{R^2R^3C{=}CH\text{-}\overset{O}{\overset{\|}{C}}\text{-}R}$$

R = alkyl, phenyl; R^1 = alkyl; R^2 = alkyl, phenyl; R^3 = alkyl, H

Compound 1 was dissolved in ten-twelve molar excess of amine and refluxed for 2-3 days until the ir spectrum of the reaction mixture showed a complete disappearance of absorption in the region of 4.55 μ ($C\equiv C$) and appearance of a strong absorption at 6.25 μ ($C{=}C$). Excess amine was evaporated *in vacuo*. The resulting adduct was dissolved in THF, treated at 0° C with an equivalent amount of NaH and then with the carbonyl compound. The mixture was stirred at 0° C for 1 hr and then at room temperature for 5-6 hr. The resulting 3 was purified in one case ($R = R^1 =$ *n*-C_4H_9, $R^2 = C_6H_5$, $R^3 = H$); in all other cases, 3 was hydrolyzed directly to 4 by stirring an ethereal solution with 2% aqueous oxalic acid. Ketones 4 produced in this manner are listed in Table I.

TABLE I

PREPARATION OF $R^2R^3C{=}CH\text{-}\overset{O}{\overset{\|}{C}}\text{-}R$ (4) FROM R^2R^3CO AND ENAMINES 2

Enamine 2		Aldehyde or Ketone	α,β-ethylenic Ketone	Yield[a] (%)	Mp or Bp °C (mm)
R	R^1				
n-C_3H_7	C_6H_{11}	C_6H_5CHO	$C_6H_5\text{-CH=CH-CO-}C_3H_7\text{-n}$	55	90-1 (0.10)
n-C_4H_9	n-C_4H_9	C_6H_5CHO	$C_6H_5\text{-CH=CH-CO-}C_4H_9\text{-n}$	65	95-8 (0.05)
CH_3	n-C_4H_9			66	110-12 (0.06)
n-C_3H_7	C_6H_{11}			60	131-2 (0.07)
C_6H_5	C_6H_{11}			53	75-6
CH_3	C_6H_{11}	$C_6H_5\text{-CO-}CH_3$	 $C_6H_5\text{-}\overset{CH_3}{\overset{\mid}{C}}\text{=CH-CO-}CH_3$	46	60-1 (0.05)
n-C_4H_9	n-C_4H_9			67	66-70 (0.06)[b]

a. This is the yield of the distilled or recrystallized material based upon 1.

b. The product is found to be a mixture of α,β- and β,γ-ethylenic ketones.

Compounds 1 were prepared by treating diethylphosphorochloridate with alkynylmagnesium bromides in ether at 0° C.

Acknowledgment. We wish to acknowledge National Institutes of Health support of this work under Grant GM-16828 and the National Science Foundation under Grant GP-10739. We also thank Dr. Joseph A. Kuczkowski for his useful suggestions during the course of this work.

REFERENCES

1. To whom correspondence should be addressed.
2. C. J. Morrow, Ph.D. Dissertation, Tulane University, New Orleans, La., 1970.
3. B. C. Saunders and P. Simpson, J. Chem. Soc., 3464 (1963).
4. A. N. Pudovik, N. G. Khusainova and A. B. Agreeva, Zh. Obshch. Khim., 34, 3938 (1964).
5. W. Nagata and Y. Hayase, Tetrahedron Lett., 4359 (1968).