

Mixtures were made containing one part of 95% oxygen-18 enriched water vapor, one part of ozone, and eight parts of argon. The photolysis cell was filled with 10 torr of this mixture for each exposure. The effective exposure time was about 15 μ sec. directly following the photolysis flash. A number of spectra in the hydroxyl absorption bands between 3060 and 3300 Å. were taken using flash photolysis and this gas mixture.

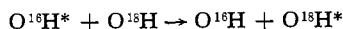
Figure 1 shows three small sections of the hydroxyl spectrum. The bottom spectrum is about 6 Å. of the (0,0) band around 3090 Å. Both O¹⁸H and O¹⁶H are strong and approximately equal in intensity in the (0,0) band. The isotope shift is about 0.1 Å. The section labeled C.L. is an artifact of the spectrograph.

The middle spectrum is in the (1,1) band around 3148 Å. The O¹⁶H spectrum is strong, but only at the calculated positions (dotted lines above spectrum) of the strongest O¹⁸H lines is there any indication of absorption, for example at the Q₂(3) and Q₂(2). It is estimated that the ratio O¹⁸H ($\nu'' = 1$)/O¹⁶H ($\nu'' = 1$) is around 10⁻². This is somewhat more than expected on the basis of the 0.2% natural abundance of O¹⁸.

The top spectrum is in the (2,2) band around 3197 Å. The O¹⁶H spectrum is fairly strong, but no O¹⁸H was detected at the calculated positions. The sensitivity for detecting O¹⁸H in the (2,2) band is not as high as it is in the (1,1) band.

No evidence for OH of either isotope was found at the location of the (3,3) band. This result has been obtained before,⁴ but the sensitivity in the present high resolution experiments is thought to be considerably greater. The $\nu'' = 3$ state of OH corresponds to 29.2 kcal., or slightly more than the exothermicity of reaction 4. Some highly excited oxygen molecules from the oxygen atom-ozone side reaction were detected in the Schumann-Runge absorption band system. Both the hydroxyl and oxygen molecular spectra had rotational distributions and line widths consistent with approximately room temperature.

The most important conclusion of this study is that the newly formed OH bond receives most of the available vibrational energy, while the old OH bond remains vibrationally cold. This result is not too unexpected since the OH bond length in water is almost identical with that in the free OH radical. While no absolute measurements of OH concentrations have been made, it appears that about one out of six radicals coming from reaction 4 is vibrationally excited. The vibrational energy exchange process



is slow under the conditions of these experiments.

Further studies of (4) and similar reactions are in progress.

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Facile Addition of a Grignard Reagent to an Unconjugated Ethylenic Linkage

Sir:

Despite their pronounced ability to add to diverse unsaturated organic compounds, Grignard reagents hitherto have not been found to add across unconjugated carbon-carbon multiple bonds. Only in the case of ethylenic linkages conjugated with carbonyl or related groups¹ or of the exocyclic ethylenic linkage in substituted fulvenes² have additions of Grignard reagents to olefinic linkages been well substantiated. Occasional reports of successful Grignard additions to ordinary ethylenic or acetylenic linkages have been discredited subsequently by the careful investigations of Gilman and co-workers.³ In the light of previous work, therefore, we were surprised recently to observe the smooth addition of a Grignard reagent to an unconjugated ethylenic linkage. To our knowledge, this constitutes the first authenticated case of such a Grignard addition. Moreover, since appealing extensions of this type of reaction to other systems appear possible, we wish to put forward our findings at this time.

In the preparation of allyldiphenylcarbinol (I) by the interaction of benzophenone with allylmagnesium bromide in ethyl ether,⁴ we obtained both I (70-75%) and a new carbinol II (10-20%, b.p. 160° (0.5 mm.)). Both carbinols were dehydrated in individual runs by heating their benzene solutions with traces of *p*-toluenesulfonic acid. As anticipated, allyldiphenylcarbinol (I) yielded 1,1-diphenyl-1,3-butadiene (III).⁵ The new carbinol II, however, gave a hydrocarbon (b.p. 130° (0.4 mm.)) which proved to be 1,1-diphenyl-1,6-heptadiene (IV). The structure of IV is supported by the following data: (a) elemental analysis (*Anal.* Calcd. for C₁₉H₂₀: C, 91.88; H, 8.12. Found: C, 91.83; H, 8.01); (b) oxidation with hot KMnO₄ to yield benzophenone; (c) infrared spectrum (bands (cm.⁻¹) at 1650 (C=C), 1610 and 1585 (C=C conjugated with phenyl), 910 and 990 (CH=CH₂), and 695 and 760 (C₆H₅)); (d) n.m.r. spectrum in CCl₄ (peaks [δ in p.p.m. (integrated areas)] at 7.22 (10.0, phenyl), triplet at 6.06 ($J = 8$ c.p.s.), and multiplets between 4.7 and 6.0 (total vinyl of 4.1), multiplets at 2.04 (4.0) and at 1.5 (2.1)); and (e) ultraviolet spectrum in cyclohexane (λ_{max} 250 m μ ($\log \epsilon$ 2.13); 1,1-diphenyl-1-butene has λ_{max} 251 m μ). Accordingly, the structure of the new carbinol II as 1,1-diphenyl-6-hepten-1-ol can be deduced from its spectral properties [e.g., infrared spectral bands (cm.⁻¹) at 3600 (OH), 1645 (C=C), 1600 (aromatic C=C), and 910 and 990 (CH=CH₂)] and from its smooth dehydration to form 1,1-diphenyl-1,6-heptadiene. The foregoing reactions are summarized in Chart I.

In considering the origin of the interesting carbinol II, the question arises whether the benzophenone need

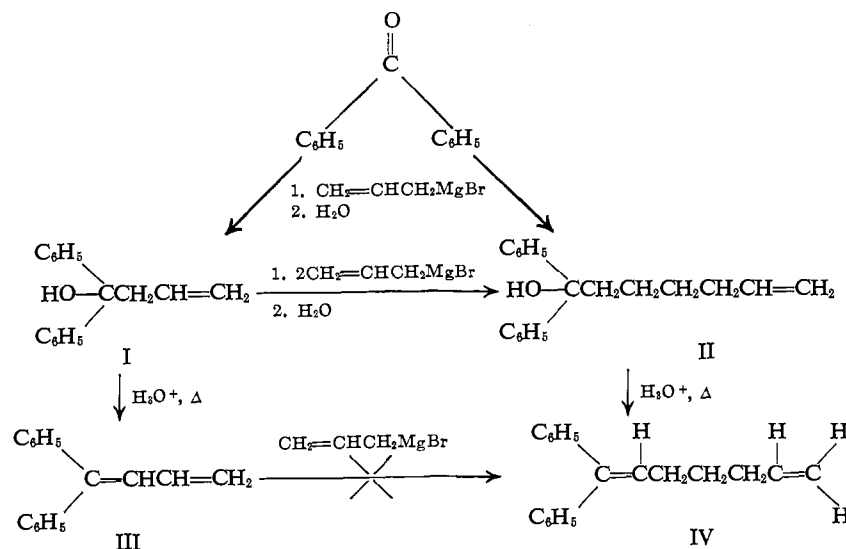
(1) R. C. Fuson, *Advan. Organometal. Chem.*, **1**, 221 (1964).

(2) Cf. R. C. Fuson and O. York, Jr., *J. Org. Chem.*, **18**, 570 (1953), for leading references.

(3) (a) Cf., *inter alia*, H. Gilman and J. H. McGlumphy, *Rec. trav. chim.*, **47**, 418 (1928). (b) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, pp. 87-90, presents a precis of previous literature.

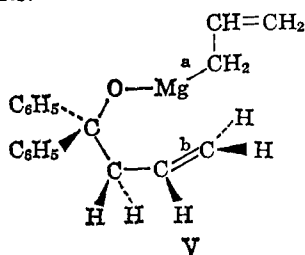
(4) M. S. Kharasch and O. Weinhouse, *J. Org. Chem.*, **1**, 209 (1936).

(5) All compounds involved in this study were characterized by satisfactory spectroscopic and analytical data. Cf. G. R. Husk, doctoral dissertation, University of Michigan, 1964.



participate directly in the formation of II. Clearly the presence of benzophenone is not essential, for the carbinol II could be obtained in good yield (>70%) merely by treating allyldiphenylcarbinol in ether with 2 equiv. of allylmagnesium bromide (25° for 36 hr.). (Incidentally, III was shown not to add allylmagnesium bromide.) There is no reasonable doubt, therefore, that allylmagnesium bromide can add to the unconjugated, unactivated ethylenic linkage of the magnesium carbinolate salt of I.

As a working hypothesis for further synthetic and mechanistic studies of this reaction, we suggest that this addition is facilitated by the intramolecular proximity of the reacting bonds. When allyldiphenylcarbinol is treated with the allyl Grignard reagent, it is reasonable to assume that the presence of diallylmagnesium in the latter⁶ would lead to the production of intermediate V. Inspection of a Stuart-Briegleb model of V reveals that the allyl-magnesium bond (a) can easily become contiguous to the vinyl bond (b) of the carbinolate. Further research will probe the generality of this reaction by use of other unsaturated carbinols and amines, as well as a variety of organometallic reagents.



Acknowledgment. The authors wish to express their appreciation to the donors of the Petroleum Research Fund for their support of this research by PRF Grant No. 723-A, both at the University of Michigan and The Catholic University of America.

(6) G. O. Johnson and H. Adkins, *J. Am. Chem. Soc.*, **54**, 1943 (1932).

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Mixed Metal Complexes as Enzyme Models. I. Intracomplex Nucleophilic Catalysis by an Oxime Anion

Sir:

Studies on esterolytic enzymes and peptidases have proceeded to the point that a general mechanism of their action may be described: acyl transfer occurs to a nucleophilic group of the enzyme within an enzyme-substrate complex, and the acyl group is then hydrolytically removed in a second step. The hope of utilizing such principles to achieve rapid and selective organic reactions has stimulated the construction of various enzyme model systems. We have considered that catalysis by attack of one ligand on another within a mixed metal complex could include the strong catalyst-substrate binding which is a key feature of enzymatic catalysis; furthermore, such enzymes as (zinc-containing) carboxypeptidase use metal bridging between protein and substrate for at least part of the ES binding energy. The problem of providing a strong free nucleophile in a metal complex has been solved by utilizing zinc pyridinecarboxaldoxime anion (I).¹ We wish to report that I is indeed a particularly effective nucleophilic catalyst in the hydrolysis of 8-acetoxyquinoline 5-sulfonate (II), a weakly complexing substrate,² by a two-step mechanism involving acyl transfer within a catalyst-substrate complex. Models show

Table I. Equilibria of PCA with Zn^{2+} ^a

	<i>K</i> , <i>M</i>
$\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$	$(9.1 \pm 0.9) \times 10^{-11}$
$\text{HA} + \text{Zn}^{2+} \rightleftharpoons \text{ZnAH}^{2+}$	150 ± 15
$\text{A}^- + \text{Zn}^{2+} \rightleftharpoons \text{ZnA}^+$	$(5.0 \pm 1.2) \times 10^5$
$\text{ZnAH}^{2+} \rightleftharpoons \text{ZnA}^+ + \text{H}^+$	$(3.0 \pm 0.7) \times 10^{-7}$
$\text{HA} + \text{Zn}^{2+} \rightleftharpoons \text{ZnA}^+ + \text{H}^+$	$(4.5 \pm 1.0) \times 10^{-5}$
$\text{ZnA}(\text{H}_2\text{O})^+ \rightleftharpoons \text{ZnA}(\text{OH}) + \text{H}^+$	$(1.8 \pm 0.4) \times 10^{-5}$

^a At 25.0°. HA = neutral PCA molecule.

(1) Cf. S. Balton and A. Beckett, *J. Pharm. Soc.*, **53**, 55 (1964).
(2) E. J. Corey and R. L. Dawson, *J. Am. Chem. Soc.*, **84**, 4899 (1962), report metal-catalyzed hydrolyses of 8-carbamoylquinolines. Compound II was prepared by acetylation and fully characterized. Spectrophotometric studies show that *K*_s for Zn^{2+} and II is $<5 \text{ M}^{-1}$.