

relaxed $d-\pi^*$ level and a corresponding excited level would likely require activation and, as a result, could be inefficient in a low-temperature glass.

Like the 115- μ s component, the ≤ 1 -ns component exhibits a broad structureless spectrum.²⁰ In view of the relative energy and lifetime of the ≤ 1 -ns component compared with the 115- μ s component, it is tempting to consider that the former might be prompt fluorescence from the corresponding singlet $d-\pi^*$ state.¹⁷ However, because the ≤ 1 -ns component is so weak and because its excitation spectrum has so far not been measured, an assignment would be premature.¹⁹ Even if the component could confidently be associated with photoexcited $[\text{Cu}(\text{PPh}_3)_2(\text{phen})]^+$, the singlet $d-\pi^*$ assignment would not be unambiguous. Other possibilities would be a triplet $d-\pi^*$ state involving another geometry and a triplet $d-\pi^*$ species in another state of solvation.³

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- Actually, the comparisons indicated that the lifetime of the ≤ 1 -ns component was ~ 500 ps, but, in view of the difficulties in accurately resolving such short lifetimes from an instrumental signal of this width, we are reporting the more conservative figure of ≤ 1 ns.
- We cannot specify the relative quantum yields of the ≤ 1 -ns and 115- μ s components with the data at hand, but it is apparent from the relative areas under the emission profiles in Figure 2 that the yield of the ≤ 1 -ns component is considerably less than that of the 115- μ s component.
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- Assuming this assignment, from the spectra in Figure 3 we would estimate that energy gap between the singlet and triplet $d\pi^*$ levels is ~ 1000 cm^{-1} —a figure which appears reasonable when compared with recent spectroscopic studies of $\text{Fe}(\text{bipyridyl})_3^{2+}$.¹⁸
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- It can, however, be noted that the emission spectrum of the ≤ 1 -ns component is quite distinct from those that would be observed for the obvious ligand redistribution products of the complex, i.e. PPh_3 , $\text{Cu}(\text{I})$ complexes of PPh_3 , and $[\text{Cu}(\text{phen})_2]^+$.¹¹ However, other as yet unisolated complexes, e.g., $[\text{Cu}(\text{PPh}_3)(\text{phen})(\text{S})]^+$ where S is solvent, are conceivable derivatives and their presence in solution cannot be excluded at this point.
- Comparably short-lived emission has also been observed from bipyridyl analogues of $[\text{Cu}(\text{PPh}_3)_2(\text{phen})]^+$.¹¹
- In fact the spectrum obtained in this way also reflects a small contribution from the 115- μ s component since the latter exhibits weak intensity at the time of the maximum in the laser output (Figure 2).

Michael T. Buckner, Thomas G. Matthews
Fred E. Lytle, David R. McMillin*

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

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Lanthanoids in Organic Synthesis. 5.¹ Selective Reductions of Ketones in the Presence of Aldehydes

Sir:

The central role of the carbonyl group in organic chemistry has generated substantial interest in developing methods that allow its selective reduction in the presence of other functional groups.² With several new reagents^{3–10} a selectivity is observed that permits the reduction of aldehydes in the presence of ketones. In contrast, there is no efficient method for selectively effecting this type of reduction in the opposite sense, i.e., the reduction of a ketone in the presence of an aldehyde. Usually, this transformation necessitates a three-step process: protection of the aldehyde (e.g., ketalization), reduction of the ketone, and finally liberation of the aldehyde. Not only is a three-step process synthetically undesirable, but, in addition, the ketalization catalyst¹¹ is often not sufficiently selective, thus leading to low yields and/or separation problems.

We described in the previous paper of this series an approach for the simplification of this problem, based on the preferential *in situ* ketalization of aldehydes relative to ketones using a lanthanoid ion as the catalyst.¹ However, this method cannot be used with easily ketalized ketones.

We now report another solution to the problem which is an even easier and more attractive "one flask" method than the previous, achieving the desired selective reduction *without* the need for any stable, isolable protective group. Moreover, the scope of this method shows that it can be used in cases when the first method fails.

When an equimolar mixture of an aldehyde and a ketone in aqueous ethanol (EtOH–H₂O, 1:1.5) in the presence of cerium trichloride ($\text{CeCl}_3 \cdot 6\text{H}_2\text{O}$, 1 molar equiv), is cooled to -15 °C and treated with 1.5 molar equiv of NaBH_4 ,¹² a selective reaction occurs. The aldehyde is recovered almost quantitatively and the secondary alcohol is generated in high yield. The results given in Table I are illustrative of the selectivity that can be obtained by this process. With most nonconjugated aliphatic and alicyclic carbonyl compounds this selectivity is excellent. On the other hand, benzaldehyde and citral undergo substantial reduction under these conditions, results which suggest that sufficient selectivity cannot be expected with conjugated aldehydes. This observation, however, may be of synthetic value for it permits a discrimination in the reduction of aldehydes of various types. For instance, an equimolar benzaldehyde–hexahydrobenzaldehyde, when treated as above, affords benzyl alcohol in 85% yield and 98% recovery of hexahydrobenzaldehyde.

It is known that in general conjugated aldehydes are not hydrated and that nonconjugated aldehydes yield hydrates to a larger extent than ketones.¹¹ Thus, the efficient protection of the nonconjugated aldehyde function is most certainly achieved by the formation of a geminate diol. Hemiketal or ketal formation¹ can be excluded as the observed selectivity is almost the same ($\pm 5\%$) when the solvent is changed from ethanol–water to methanol– or 2-propanol–water. A second point is that the stability of the geminate diol is increased by Ce^{3+} . This effect was demonstrated for a mixture of cyclohexanone and hexanal. In a $\text{CD}_3\text{OD}-\text{D}_2\text{O}$ solution, the NMR spectrum of this mixture exhibits no signal in the usual CHO resonance domain, suggesting that the aldehyde is totally converted into its hydrate. Reduction (NaBH_4 , 1.5 equiv, -15 °C) yields cyclohexanol (100%), hexanol (49%), and hexanal (51%). The same reaction when performed in the presence of 1 equiv of CeCl_3 gives cyclohexanol (100%), hexanol (2%), and 98% recovered hexanal. The stabilization of the geminate diol under the reaction conditions was also tested with various ions (H^+ , Cu^{2+} , Zn^{2+} , Ba^{2+} , Ti^{3+} , Cr^{3+} , Fe^{3+}), but they proved to be less effective¹³ than Ce^{3+} . Thus, the effect of Ce^{3+} is large enough to ensure an adequate protection during the reduction

Table I. Reduction of Ketones in the Presence of Aldehydes^a

initial compound or mixture	% reduction ^b
hexanal	2 (7) ^c
cyclohexanone	100 (93) ^c
hexanal	13
2-octanone	96
hexahydrobenzaldehyde	15
cyclohexanone	100
hexahydrobenzaldehyde	22
phenyl-2-propanone	93
norbornenecarboxaldehyde	19
2-octanone	90
1,2,5,6-tetrahydrobenzaldehyde	14 ^c
acetophenone	98 ^c
1,2,5,6-tetrahydrobenzaldehyde	14
5-nonanone	48
1	2, 95^d (78^e)
3	4, 85^d (75^e)
benzaldehyde	60
acetophenone	100
citral	70
2-cyclohexenone	100

^a The standard procedure is as follows. The two carbonyl compounds (1 mmol each)—or the dicarbonyl compound (2 mmol)—and 355 mg of $\text{CeCl}_3 \cdot 6\text{H}_2\text{O}$ are dissolved in 6 mL of ethanol and 10 mL of water. The mixture is cooled to -15°C , and then 60 mg of NaBH_4 is added in one portion. Stirring is continued for 10 min. Excess NaBH_4 is destroyed with 2 mL of acetone, and the mixture is then diluted with aqueous NaCl and extracted with ether. Usual workup of the ethereal layer affords a crude mixture which is analyzed and/or purified. ^b Identification of reduction products was made by comparison with authentic samples. Yields were calculated by VPC (Carlo Erba Fractovap, Carbowax column 2.5×2 mm, N_2 carrier). ^c $\text{ErCl}_3 \cdot 5\text{H}_2\text{O}$ was used instead of $\text{CeCl}_3 \cdot 6\text{H}_2\text{O}$. ^d Yields of crude material were obtained by NMR analysis. ^e Isolated yields after column (SiO_2) chromatography.

step, but at the same time allows the ready recovery of the aldehyde during the workup of the reaction mixture. This procedure represents the first *direct* solution to the problem of reverse selectivity and should find wide use in organic synthesis due to the ease of operation and exceptional rapidity.

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- (13) The larger stabilization effect is observed with Ce^{3+} , Er^{3+} which gives satisfactory results is followed by Cr^{3+} . The other ions tested gave poor selectivities.

Jean-Louis Luche,* André Luis Gemal

Laboratoire de Chimie Organique C.E.R.M.O.
Université Scientifique et Médicale
38041 Grenoble, France
Received May 22, 1979

An ab Initio Approach to Organic Reaction Rates. Kinetic Isotope Effects in the Reaction $\text{H} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5$

Sir:

It is of general interest to predict rate constants of organic reactions entirely from a nonempirical standpoint. Recent advances in the ab initio energy gradient method^{1,2} are expected to provide a reliable assistance to such predictions. We here report the results of a transition state theoretical (TST)³ study, reinforced by the relevant ab initio molecular orbital computation, of the addition reaction $\text{H} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5$. The TST procedure, which would otherwise entail a considerable extent of empiricism on the transition state characteristics, has proved to be valuable indeed as a quantitative tool for kinetic considerations.

In the first place, geometries of ethylene and the transition state were optimized⁴ by analytic evaluation of the potential energy gradients. The unrestricted Hartree-Fock (UHF) method with the 4-31 split-valence basis set⁵ was used. The calculated barrier height for the reaction was 2.2₀ kcal/mol. The force constant matrices for both ethylene and the transition state were then constructed by numerical differentiation of the energy gradients.⁶ The resultant normal mode

Table I. Comparison of the Experimental and the Present Theoretical Rate Constants k for the $\text{H} + \text{C}_2\text{H}_4$ Reaction

temp (T), K	k (10^{-13} cm ³ molecule ⁻¹ s ⁻¹)	
	expt ^a	theory, this work
320	14.5 ± 1.1	16.9
298	11.3 ± 0.5 ^b	12.7
283	9.4 ± 0.6	10.3
258	6.3 ± 0.4	6.8
234	4.1 ± 0.2	4.3
216	3.0 ± 0.3	2.9
198	2.0 ± 0.1	1.8

^aReference 12. ^b Room-temperature values reported by other workers: 9.1 ± 0.9,⁷ 12.2 ± 1.0,⁸ 11.0 ± 1.3,⁹ 12.5 ± 0.3,¹⁰ and 11.0 ± 1.0.¹¹