yet understand the nature of the postulated excited state. It is interesting to note that the transition rate between the ground-state manifold and the excited-state configuration is slow on the time scale of Mössbauer spectroscopy ($\sim 10^{-7}$ s). Such a phenomenon has not yet been reported for iron–sulfur clusters. Interestingly, Borshch et al.[40] have published a theoretical study of electron delocalization in trinuclear mixed valence clusters taking into account vibronic interactions. These authors point out that localized and delocalized states can co-exist in certain temperature ranges and that such states may be observable by Mössbauer spectroscopy.

We have little information on the magnetic properties of the postulated excited state. The Hamiltonian of eq 7 is flexible enough to describe the fully delocalized configuration. This could be accomplished by adding delocalization between sites A and C and sites B and C. On the other hand, it is quite likely that a more comprehensible description requires some consideration of vibronic coupling.

The coupling Hamiltonian of eq 7 can be adapted to describe tetranuclear clusters. We are currently analyzing data of Fe_4S_4 and $CoFe_3S_4$ clusters, and the initial results are promising.

Acknowledgment. We thank Dr. J. LeGall for providing us generously with ^{57}Fe enriched *D. gigas* cells. We are grateful to Dr. O. Kahn, who suggested that the concept of double exchange may be applicable to Fd II. This work was supported by the National Science Foundation, the National Institutes of Health, the Instituto de Investigacão Cientifica Tecnologica, the Junta National de Investigacão Cientifica Tecnologica, and by a NATO Collaborative Research (RG86/0099) grant.

Registry No. Fe, 7439-89-6; S, 7704-34-9.

---

(40) Borshch, S. A.; Kotov, I. N.; Bersuker, I. B. *Chem. Phys. Lett.* **1982**, *89*, 381–384.

Communications to the Editor

Allylcerium(III) Compounds, Powerful New Synthetic Reagents. A New Stereocontrolled Approach to Olefins and Methylene-Interrupted Polyenes

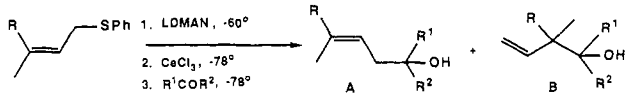
Bao-Shan Guo, Wendel Doubleday, and Theodore Cohen*

Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

Received February 25, 1987

We have recently reported that reductive metalation of allyl phenyl sulfides is a versatile and general preparative method for hydrocarbon allyl anions and that the latter, in the presence of titanium tetraisopropoxide, add in a 1,2-fashion to enals only *at the most substituted terminus of the allyl system*.[1,2] We now reveal simple procedures for securing 1,2-addition to aldehydes and enals mainly *at the least substituted terminus of such allyl anions*, a unique outcome[3] which results in *either cis or trans homoallylic alcohols with high stereocontrol.*

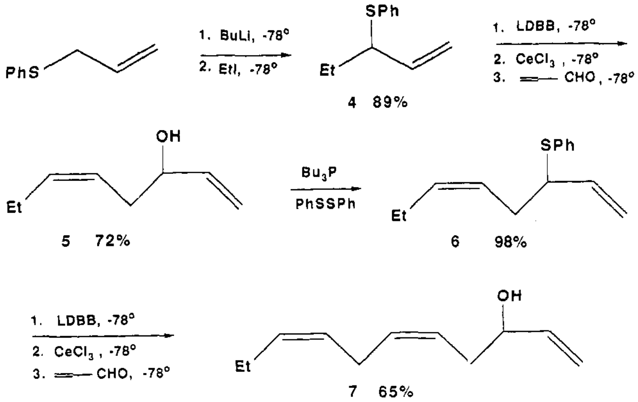
Table I.



R	R^1	R^2	% yield A^a	% yield B^a
CH_3	Ph	H	53	12
CH_3	*trans*-$CH_3CH{=}CH$	H	73	14
CH_3	$(CH_3)_2C{=}CH$	CH_3	58	34
CH_3	$(CH_2)_5$		45	16
CH_3	$CH{=}CH(CH_2)_3$		47	40
CH_3	*trans*-$PhCH{=}CH$	H	56	24
H	Ph	H	47	13
H	$CH_2{=}CH$	H	53	13
H	*trans*-$CH_3CH{=}CH$	H	59	25
H	*trans*-$PhCH{=}CH$	H	42	25
H	$(CH_2)_5$		48	35

^{a} Isolated, nonoptimized yields.

Scheme I



σ-Bonding between allyl and metal ions apparently occurs at the least hindered allyl terminus, and the metal behaves as a Lewis acid toward the carbonyl oxygen atom, thus positioning the carbonyl carbon atom for attack at the most substituted terminus.[1,2] In order to induce attack at the least sterically hindered terminus, we sought a metal which is unlikely to form a σ-bond to the allyl anion and yet which strongly complexes oxygen so as to encourage 1,2- rather than 1,4-addition to enals and enones.[4] Since certain allyllanthanides apparently involve trihapto bonding,[5] we examined cerium(III),[6] which had been found by Imamoto[7] to be highly oxophilic toward the carbonyl group and to cause 1,2-addition of an anion to an enal. Treatment of the lithium salt

---

(1) Cohen, T.; Guo, B.-S. *Tetrahedron* **1986**, *42*, 2803.

(2) Other recent work with allyltitaniums: Reetz, M. T.; Steinbach, R.; Westermann, J.; Peter, R.; Wenderoth, B. *Chem. Ber.* **1985**, *118*, 1441.

(3) Okude, Y.; Hirano, S.; Hiyama, T.; Nozaki, H. *J. Am. Chem. Soc.* **1977**, *99*, 3179 and note 4 therein.

(4) Lefour, J.-M.; Loupy, A. *Tetrahedron* **1978**, *34*, 2597. Wartski, L.; El Bouz, M. *Tetrahedron* **1982**, *38*, 3285 and references therein.

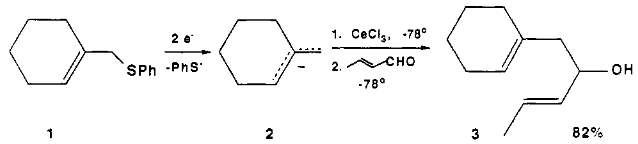
(5) Tsutsui, M.; Ely, N. *J. Am. Chem. Soc.* **1975**, *97*, 3551. See also: Hodgson, K.; Mares, F.; Starks, D.; Streitwieser, A., Jr. *Ibid.* **1973**, *95*, 8650.

(6) Reviews of organolanthanides: Marks, T. J.; Ernst, R. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Chapter 21. Schumann, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 474. Natale, N. R. *Org. Prep. Proced. Int.* **1983**, *15*, 389. Kagan, H. B.; Namy, J. L. *Tetrahedron* **1986**, *42*, 6573.

(7) Imamoto, T.; Sugiura, T.; Takiyama, N. *Tetrahedron Lett.* **1984**, *25*, 4233. Imamoto, T.; Kusumoto, T.; Tawarayama, T.; Sugiura, Y.; Mita, T.; Hatanaka, Y.; Yokoyama, M. *J. Org. Chem.* **1984**, *49*, 3904. After our discovery of the generality of the 1,2-addition of allylceriums to enals and enones, papers by Imamoto appeared indicating the generality of 1,2-additions of organocerium(III) compounds to enones: Imamoto, T.; Sugiura, Y. *J. Organomet. Chem.* **1985**, *285*, C21. Imamoto, T.; Takiyama, N.; Nakamura, K. *Tetrahedron Lett.* **1985**, *26*, 4763.

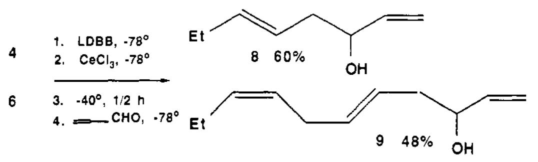
0002-7863/87/1509-4710$01.50/0

of **2**, prepared by reaction of **1** and lithium 1-(dimethylamino)naphthalenide (LDMAN),[1,8] with cerium(III) chloride at −78 °C, followed by the addition of crotonaldehyde, gave mainly **3**, the 1,2-addition product at the least substituted terminus;[9] the ratio of **3** to the product of 1,2-addition at the other allylic terminus, the only product formed from the corresponding allyltitanium,[1] was 18.[10] Although subsequent examples proved less selective (Table I), the yields and separability of the products are usually satisfactory, so the procedure should be of quite general utility.



The propensity of terminal allyl anions to exist largely in the cis configuration[11] has rarely if ever been used in synthetic chemistry, probably because even in those cases in which such anions can be prepared readily electrophiles attack to a significant extent at the inner terminus, thus destroying the integrity of the *cis*-alkene.[1,10,11b] However, the reversal of regiochemistry by cerium allows one to take advantage of this stereochemical preference. As indicated in the table, *trans*-crotyl phenyl sulfide is converted into an organocerium compound that yields, upon aldehyde capture, products possessing cis double bonds. Scheme I[12] shows a simple method of iteratively creating *cis*-alkene linkages to produce the biologically important class of compounds methylene-interrupted polyenes;[13] the acetate ester of **7** occurs in a brown alga and is a proposed biochemical precursor of some sex-specific substances.[14] *trans*-Olefins were detected as only minor contaminants.

We hoped that stereochemical control could be attained if allylceriums existed as π-complexes and if, like other π-allyls, the cis complexes isomerized to the trans upon warming.[15] We were gratified to find that the trans homoallylic enols **8** and **9** were by far the major products when the allylceriums derived from **4** and **6** were warmed to −40 °C and the clear solutions then cooled to −78 °C and treated with acrolein.[12] Newly created cis linkages could not be detected by NMR.



In conclusion, dramatic changes in regio- and stereochemistry result by addition of cerium(III) chloride to a solution of thermodynamically stable *cis*-allyllithiums to form unstable *cis*-π-allylceriums capable of isomerizing at elevated temperatures to *trans*-π-allylceriums.[16] Both react with carbonyl compounds mainly at the least sterically hindered terminus.

A typical procedure involves cannulating the allyllithium[1] (2 mmol in 5 mL of THF) into a suspension of CeCl$_3$ (3-4 mmol in 8 mL of THF)[17] at −78 °C. After the mixture has been stirred for 1 h (and optionally warmed to −40 °C and maintained at that temperature for 1/2 h), the carbonyl compound (4 mmol in 2 mL of THF, except in the case of acrolein in which addition is terminated upon decolorization) is added dropwise at −78 °C. After 10 min, 5% HCl (10 mL) is added and the solution is stirred at 25 °C for 1 h before being diluted with ether. The ether layer is washed with 10% HCl and 10% NaOH before isolation.

Acknowledgment. We thank the National Institutes of Health for support of this work (GM 22760), Dr. Alvin Marcus for recording the mass spectra, and Dr. John Cooper for a helpful discussion.

---

(8) Cohen, T.; Sherbine, J. P.; Hutchins, R. R.; Lin, M.-T. *Organomet. Synth.* **1986**, *42*, 2803.

(9) This result was reported in preliminary form by T.C. at the Euchem Stereochemistry Conference at Bürgenstock in May 1985.

(10) When lithium is the counterion of **2**, the major product arises from 1,2-attack *at the ring terminus*.[1] Related results: Miginiac, P. *Bull. Soc. Chim. Fr.* **1970**, 1077. Rautenstrauch, V. *Helv. Chim. Acta* **1974**, *57*, 496.

(11) (a) Schlosser, M.; Stahle, M.; Hartmann, J. *Helv. Chim. Acta* **1977**, *60*, 1730. (b) Bates, R. B.; Beavers, W. A. *J. Am. Chem. Soc.* **1974**, *96*, 5001. (c) Houk, K. N.; Strozier, R. W.; Rondan, N. G. *J. Am. Chem. Soc.* **1980**, *102*, 1426.

(12) The reductive lithiations in Scheme I and subsequent equations were performed with lithium *p,p'*-di-*tert*-butylbiphenylide (LDBB; Freeman, P.; Hutchinson, L. *J. Org. Chem.* **1980**, *45*, 1924), which gave better yields than LDMAN. The ratio of terminal to internal attack on the allyl anion was 10 or greater.

(13) (a) Moore, R. *Acc. Chem. Res.* **1977**, *10*, 40. Jaenicke, L.; Boland, W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 643. (b) Baker, R.; Herbert, R. H. *Nat. Prod. Rep.* **1984**, *1*, 299. Rokach, J.; Adams, J. *Acc. Chem. Res.* **1985**, *18*, 87.

(14) Yamada, K.; Ojika, M.; Hiroaki, T. *Chem. Lett.* **1980**, 1633.

(15) Tolman, C. A. In *Transition Metal Hydrides*; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971; Chapter 6.

(16) Heating the derived *allyllithium* from **4** to 0 °C and cooling it to −78 °C before quenching it with anisaldehyde give the same result observed in the absence of the heating, namely, predominant reaction at the internal terminus.

(17) The heptahydrate (Aldrich) is dried by stirring at 0.4 Torr in a flask which is warmed to 180 °C and maintained at that temperature for 2 h. A suspension in THF is stirred at ambient temperature for at least 3 h before use.

Synthesis and Reactivity of Diazomethylenephosphoranes (>P=C=N$_2$): New Phosphacumulene Ylides and First Stable Pseudounsaturated Diazo Derivatives

Jean-Marc Sotiropoulos, Antoine Baceiredo, and Guy Bertrand*

Laboratoire des Organométalliques
Université Paul Sabatier, 31062 Toulouse Cédex, France

Received March 3, 1987

Diazo derivatives[1] and Wittig reagents[2] are among the most useful building blocks not only in organic but also in inorganic chemistry. Diazoalkenes have attracted considerable interest in the last few years as potential generators of unsaturated carbenes[3] but have never been spectroscopically characterized.[4] Here we wish to report the synthesis and reactivity of a new type of phosphacumulene[2,5] possessing both phosphorus-ylide and diazo moieties. Since a Wittig reagent displays, to some extent, a double-bonded character, this is also an approach to unsaturated diazo derivatives.

Addition of a stoichiometric amount of carbon tetrachloride to a benzene solution of (bis(diisopropylamino)phosphino)diazomethane (**1a**) (or **1b**)[6] at room temperature leads, after loss of chloroform (or trimethylsilylchloroform), to the desired cumulene **2** in quantitative yield. Similarly, the use of carbon tetrabromide

---

(1) For reviews, see: (a) Patai, S. *The Chemistry of Diazonium and Diazo Groups*; Wiley: New York, 1978. (b) Regitz, M. *Diazoalkanes*; Georg Thieme Verlag: Stuttgart, 1977. (c) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159. (d) Hahn, J. E. *Prog. Inorg. Chem.* **1984**, *31*, 205. (e) Herrmann, W. A. *Pure Appl. Chem.* **1982**, *54*, 65. (f) Herrmann, W. A. *J. Organomet. Chem.* **1983**, *250*, 319.

(2) For reviews, see: (a) Bestmann, H. J.; Zimmermann, R. *Methoden der Org. Chem.*, Regitz, M., Ed.; Thieme: Stuttgart; 1982; Vol. EII, p 616. (b) Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 907.

(3) For reviews on alkylidenecarbenes, see: (a) Stang, P. J. *Acc. Chem. Res.* **1982**, *15*, 348. (b) Moss, R. A.; Jones, M., Jr. *Reactive Intermediates*; Jones, M., Jr., Moss, R. A. Eds; Wiley-Interscience: New York, 1981; Vol. II, Chapter 3, p 69. (c) Stang, P. J. *Chem. Rev.* **1978**, *78*, 383. (d) Stang, P. J. *Acc. Chem. Res.* **1978**, *11*, 107. (e) Schaeffer, H. F., III. *Acc. Chem. Res.* **1979**, *12*, 288.

(4) (a) Ando, W.; Furuhata, T.; Takata, T. *Tetrahedron Lett.* **1985**, *26*, 4499. (b) Herrmann, W. A.; Weber, C. *J. Organomet. Chem.* **1985**, *282*, C31. (c) Apeloig, Y.; Karni, M.; Stang, P. J.; Fox, F. P. *J. Am. Chem. Soc.* **1983**, *105*, 4781. (d) Fox, D. P.; Bjork, J. A.; Stang, P. J. *J. Org. Chem.* **1983**, *48*, 3994. (e) Lahti, P. M.; Berson, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 7011. (f) Gilbert, J. C.; Weerasooriya, U. *J. Org. Chem.* **1982**, *47*, 1837.

(5) For a review on phosphacumulene ylides, see: Bestmann, H. J. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 349.

(6) (a) Baceiredo, A.; Igau, A.; Bertrand, G.; Menu, M. J.; Dartiguenave, Y.; Bonnet, J. J. *J. Am. Chem. Soc.* **1986**, *108* 7868. (b) Baceiredo, A.; Bertrand, G.; Sicard, G. *J. Am. Chem. Soc.* **1985**, *107*, 4781.