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.
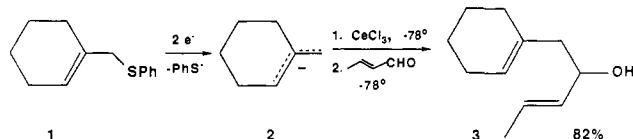
The propensity of terminal allyl anions to exist largely in the cis configuration[11] has rarely if ever been used in synthetic chemistry, probably because even in those cases in which such anions can be prepared readily electrophiles attack to a significant extent at the inner terminus, thus destroying 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.
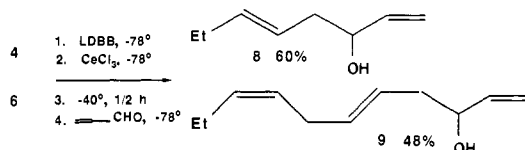
In conclusion, dramatic changes in regio- and stereochemistry result by addition of cerium(III) chloride to a solution of thermodynamically stable *cis*-allyllithiums to form unstable *cis*-π-allylceriums capable of isomerizing at elevated temperatures to *trans*-π-allylceriums.[16] Both react with carbonyl 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 CeCl₃ (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.

(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═N₂): New Phosphacumulene Ylides and First Stable Pseudounsaturated Diazo Derivatives

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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

(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.

(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.

Scheme I
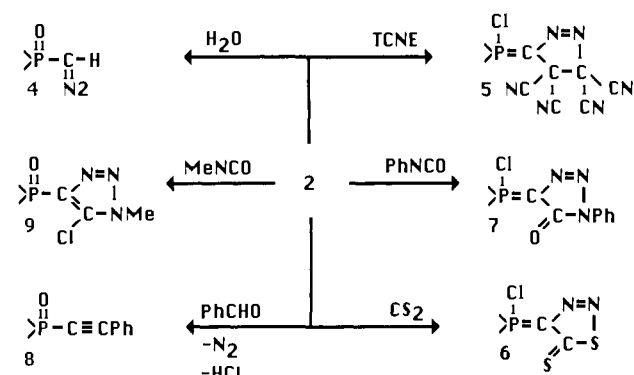
allows the synthesis of the *P*-bromo analogue **3**. Note that oxidative ylidation of methylphosphines is well documented.[7]

1a : R = H

1b : R = SiMe3

2 : X = Cl

3 : X = Br
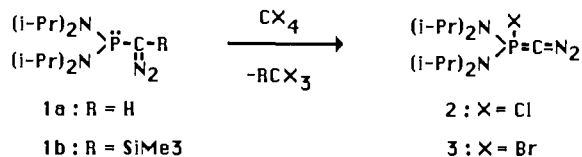
Compounds **2** and **3** are water-sensitive, red oily materials. They are stable in solution for several weeks but slowly decompose in the absence of solvent. The infrared (2035 cm^{-1} (**2** and **3**)), ^{13}C NMR (26.1 ppm, ^1J(PC) = 47 Hz (**2**)), and ^{31}P NMR spectra (+31 ppm (**2**), +15 ppm (**3**)) strongly support the proposed structure.[8]

As expected, diazomethylenephosphoranes appear to be extremely versatile reagents as illustrated in Scheme I. Hydrolysis on silica gel leads to (diazomethyl)phosphine oxide **4**,[8] probably by nucleophilic substitution of the halogen atom followed by a classical 1,3 hydrogen shift. Tetracyanoethylene, carbon disulfide, and phenyl isocyanate afford derivatives **5**, **6**, and **7**,[8] respectively, which are the [2 + 3] adducts on the diazo moiety. We believe that benzaldehyde and methyl isocyanate react via a [2 + 2] cycloaddition on the phosphorus ylide center leading to transient oxaphosphetanes **10a,b** (Scheme II). Then, as is usual in the case of *P*-halogenophosphorus ylides, **10a,b** do not undergo a P–C bond cleavage but rearrange either with HCl elmination,[7f,e] leading to **8**, or via a 1,3 halogen shift,[7d,f] leading to α-diazoimine **11**, which subsequently[9] affords **9**[8] (Scheme II). The nucleophilicity of the ylidic carbon is certainly the driving force for all these reactions, inducing the primary formation of zwitterionic intermediates **12a** (or **12b**).[5] Then, depending on the affinity of X (or X and Y)
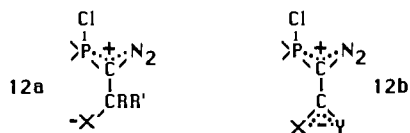
toward nitrogen and phosphorus, a 1,5 cyclization involving the diazo group, or alternatively a 1,4 ring closure involving the phosphorus ylide, occurs. This mechanistic hypothesis is strongly supported by the difference of reactivity observed between phenyl and methyl isocyanate.
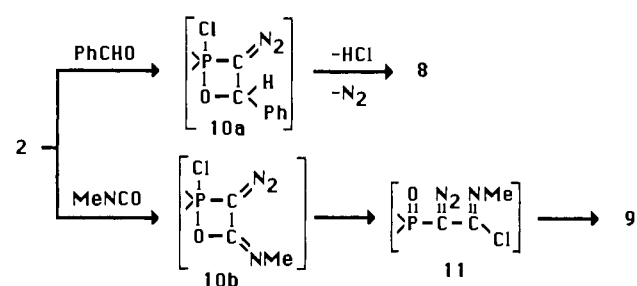
All the reactions described in Scheme I occur in quantitative yield, demonstrating the potential synthetic interest of this new type of phosphacumulene ylide. Moreover, derivative **2** displays an intriguing thermal behavior. Attempted distillation under vacuum leads to the corresponding chlorophosphine **13** along with

Scheme II

Scheme III

carbon. In the presence of sulfur, an 88% yield of carbon disulfide is obtained, suggesting the transient formation of a diazocarbene (:C=N$_2$) or a naked carbon atom (Scheme III). Trapping of these small highly unsaturated species is under active investigation.

A Model for the Sweet Taste of Stereoisomeric Retro-Inverso and Dipeptide Amides

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We have recently reported the synthesis of several *N*-(L-aspartyl)-1,1-diaminoalkanes, a class of sweeteners whose structure is based on a "retro-inverso" peptide modification.[1] Here we report the results from the conformational analysis, employing ^{1}H NMR spectroscopy and energy minimizations, of the L- and D-alanylamides[2] and the corresponding retro-inverso analogues incorporating a tetramethylcyclopentanyl group, *N*-(L-aspartyl)-*N'*-[(2,2,5,5-tetramethylcyclopentanyl)carbonyl]-(*R* or *S*)-1,1-diaminoethane (A) and L-aspartyl-(L or D)-alanyl-2,2,5,5-tetramethylcyclopentanylamide (B).
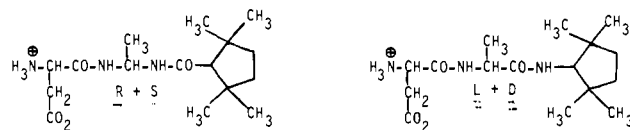
These four stereoisomeric compounds present a unique opportunity to study structure–taste relationships. Small changes in the overall topology affect the taste of these analogues (the L,L amide is bitter

(7) For examples, see: (a) Appel, R.; Waid, K. *Angew. Chem.* **1979**, *18*, 169. (b) Appel, R.; Peters, J.; Schmitz, R. *Z. Anorg. Allg. Chem.* **1981**, *475*, 18. (c) Kolodiaznhyi, O. I. *Zh. Obshch. Khim.* **1977**, *47*, 956. (d) Kolodiaznhyi, O. I.; Kukhar, V. P. *Phosphorus Sulfur* **1983**, *18*, 191. (e) Kolodiaznhyi, O. I. *Tetrahedron Lett.* **1980**, *21*, 3983. (f) Kolodiaznhyi, O. I. *Tetrahedron Lett.* **1985**, *26*, 439.
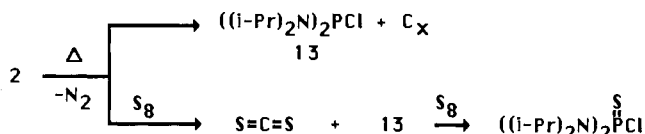
(8) Mass spectral, IR, and NMR data for each new compound are given in the supplementary material.

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(1) Fuller, W. D.; Goodman, M.; Verlander, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 5821–5822.

(2) Brennan, T. M.; Hendrick, M. E. U. S. Patent 4 411 925, October 25, 1983.