(12) A. Wolberg and J. Manassen, *J. Am. Chem. Soc.*, **92**, 2982 (1970).
(13) λ_{max} in nm in THF (log ϵ): CrCl(TPP) 629 (3.7), 601 (3.9), 561 (4.0), 520 (3.6), 446 (5.2), 394 (4.5); Cr(TPP) 655 (3.65), 601 (3.75), 516 (3.95), 460 sh (4.2), 421 (5.3), 402 sh (4.5); Cr(TPP)(py) 675 (4.1), 610 sh (3.8), 530 (4.1), 455 sh (4.3), 420 (5.0); Cr(TPP)(NMeIm) 775 (3.4), 682 (4.0), 620 br (3.8), 532 (3.9), 453 (4.8), 423 (4.7), 404 sh (4.5).
(14) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **85**, 818 (1963).
(15) By way of antithesis porphyrin *π-cation* radicals typically undergo a marked blue shift of the Soret. See ref 16.
(16) J. H. Fuhrhop, *Struct. Bonding* (*Berlin*), **18**, 1 (1974).
(17) Zinc pellets were cleaned with dilute aqueous HCl followed by treatment with dilute aqueous $HgCl_2$, washed, dried, and stored under nitrogen.
(18) L. J. Boucher, *Coord. Chem. Rev.*, **7**, 289 (1972).
(19) The metal vs. ligand *oxidation* crossover point has actually been observed in $Ni(TPP)^+$: D. Dolphin, T. Niem, R. H. Felton, and I. Fujita, *J. Am. Chem. Soc.*, **97**, 5288 (1975).
(20) J. L. Hoard in "Porphyrins and Metalloporphyrins", K. M. Smith, Ed., Elsevier, Amsterdam, 1975, p 350.
(21) E. B. Fleischer and M. Krishnamurthy, *Ann. N.Y. Acad. Sci.*, **206**, 40 (1973).
(22) M. Tsutsui, R. A. Velapoli, K. Suzuki, F. Vohwinkel, M. Ichikawa, and T. Koyano, *J. Am. Chem. Soc.*, **91**, 6262 (1969).
(23) N. J. Gogan and Z. U. Siddiqui, *Can. J. Chem.*, **50**, 720 (1972); B. B. Wayland, L. W. Olson, and Z. U. Siddiqui, *J. Am. Chem. Soc.*, **98**, 94 (1976).
(24) A. L. Crumbliss and F. Basolo, *J. Am. Chem. Soc.*, **92**, 55 (1970).
(25) Noted Added in Proof. We now have evidence for six-coordination.

Stephen K. Cheung, Carol J. Grimes, Janice Wong
Christopher A. Reed*
Chemistry Department, University of Southern California
Los Angeles, California 90007

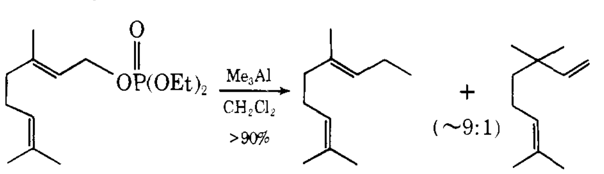
Received April 2, 1976

Novel Nonenzymic Heterolysis of an Allyl Phosphate Ester by Organoaluminum Reagents

Sir:

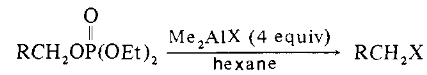
Although nonenzymic polyolefin terminal epoxide cyclizations are among the most fascinating biogenetic-like terpenoid syntheses and have received an immense amount of study,[1] another important counterpart of terpene biosynthesis, an allyl phosphate ester cyclization, has never been developed to a useful level due to the lack of a satisfactory reagent to promote the controlling heterolysis of these esters.[2] We now report the nonenzymic SN1-like heterolysis of the phosphate ester with concurrent regioselective generation of new C–S, C–N, C–O, and C–C bonds akin to that occurring in the biological process.[3]

Reaction of geranyl diethyl phosphate (**1**)[4] with trimethylaluminum (4.0 equiv) in methylene chloride under argon at −78° for 30 min, 0° for 1 h, and 20° for 2.5 h led to efficient (>90%) cross coupling in a stereospecific manner; none of the *Z*-isomer of **2** was present in the crude reaction mixture by GLC analysis.[5] A dramatic alteration in the course of the reaction occurred when the reaction of trimethylaluminum was conducted with neryl diethyl phosphate (**3**);[4] although limonene (**4**) and terpinolene (**5**) were formed with no trace of **2**, the predominant product (68%) was 4-*tert*-butyl-1-methylcyclohexene (**6a**), resulting either from a direct alkylation of nonclassical carbonium ion **7** or an alkylation of classical terpinyl ion **8** (or **9**).[2] The analogous alkylative cyclization using triethylaluminum or triisobutylaluminum in methylene chloride afforded **6b** or **6c** in 70 and 68% yields, respectively, starting from **3**. These striking observations demonstrate unequivocally that intermediary allylic carbonium ions (or equivalents) from **1** and **3** strictly preserve their steric integrities in the above transformations.[6]



1 **2**

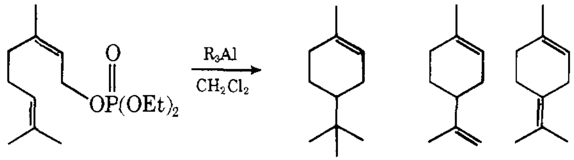
Table I.[a] Substitution of **1** and **3**



$$RCH_2O\overset{\overset{\displaystyle O}{\|}}{P}(OEt)_2 \xrightarrow[\text{hexane}]{Me_2AlX\ (4\ \text{equiv})} RCH_2X$$

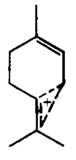
Aluminum reagent (method of preparation)[b]	Substrate	Reaction conditions Time (h) Temp (°C)	Product X	Product Isolated yield[c] (%)
Me_2AlS-*t*-Bu^7 (A)	1	0.5, 0	S-*t*-Bu	97
Me_2AlS-*t*-Bu^7 (A)	3	0.5, 0	S-*t*-Bu	92
Me_2AlSPh^7 (A)	3	0.5, 0	SPh	83
$Me_2AlNHPh^8$ (B)	1	0.5, 0; 12, 20	NHPh	74
$Me_2AlNHPh^8$ (B)	3	0.5, 0; 12, 20	NHPh	82
Me_2AlOPh^9 (B)	1	0.3, 0; 1.5, 20	OPh	85
Me_2AlOPh^9 (B)	3	1, 0; 1, 20	OPh	77

[a] Most of these reactions were run on a 1 mmol scale. The yields are not necessarily optimum. [b] Method of preparation: A, prepared in situ by treatment of the corresponding thiol with trimethylaluminum (1.0 equiv) in hexane at 0°; B, prepared by the reported procedure and isolated by recrystallization. [c] Isolated by chromatography on silica gel and adequately characterized by analytical and spectral data.

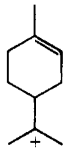


3 **4** **5**

6a, R = Me
6b, R = Et
6c, R = *i*-Bu



7



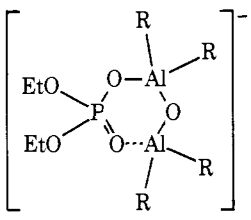
8

9

In view of the efficiency of the mild and stereospecific heterolysis of allyl phosphate ester by trialkylaluminum reagents, the behavior of certain organoaluminum reagents of type R_2AlX (X = SR, NHR, or OR)[7-9] was studied. Treatment of geranyl or neryl phosphate ester in hexane with aluminum reagents (4 equiv) results in formation of substitution products *with regio- and stereospecific manner.* The examples cited in Table I illustrate the synthesis of sulfides, amines, and ethers using the indicated reactants and reaction conditions.

In contrast to the substitution of **3** by aluminum reagents in hexane (Table I) that gave only a small amount or (in most cases) none of the cyclic products, *the cyclic dienes predominated using methylene chloride as solvent.* Thus, treatment of the ester **3** with dimethylaluminum phenoxide in methylene chloride at 0° for 1 h and 20° for 3 h furnished limonene (**4**) and terpinolene (**5**) in 58 and 11% yields, respectively, contaminated by only 8–10% of neryl phenyl ether. Similarly, dimethylaluminum anilide gave rise to **4** and **5** in 49 and 13% yields, respectively. The pronounced solvent effect on the course of the reaction must be related in part to the nature of the ion pair in the transition state. In nonpolar solvent a tight ion pair might be involved, while in a more polar solvent system the ion pair might be more widely separated and the cyclization takes place rather easily.

For preparing the cyclized products even more selectively, we next examined the behavior of certain aluminum reagents of type $R_2AlXAlR_2$ (X = S, PhN, and O)[10] which may form a "chelate" anionic complex with the phosphate residue, e.g., **10**.[11] Of these reagents, tetraisobutyldialuminoxane (**11**)



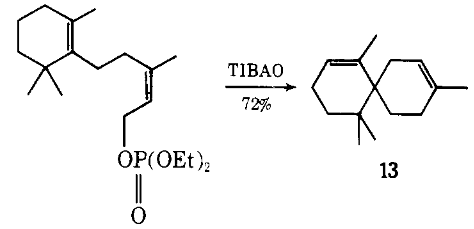
10

$(i\text{-Bu})_2Al—O—Al(i\text{-Bu})_2$

11

prepared by the action of 0.5 equiv of water on diisobutylaluminumhydride in dry THF (at −78° under argon)[12] followed by concentration in vacuo was clearly the most effective; the reagent is designated herein as TIBAO. The reaction of the ester **3** with 4.0 mol equiv of TIBAO in methylene chloride at 0° for 1 h and 20° for 3 h produced limonene (66%) and terpinolene (9%) exclusively: none of the other by-products were detected by GLC and TLC analyses. TIBAO-promoted cyclization did not suffer the significant solvent effects and the use of hexane or THF as solvent afforded **4** and **5** in yields of 54 (**4**:**5** = 9:1) and 80% (5:3), respectively. Surprisingly, the geranyl ester **1** also experienced the similar cyclization with equal efficiency (75% yield; 5:3) by exposure to excess TIBAO in THF, probably due to the intermediacy of "free" allylic carbonium ion in this reagent-solvent system.[13]

To illustrate the utility of the "aluminum promoted" cyclization process in an even more complex case, the cyclization of (*Z*)-monocyclofarnesyl diethyl phosphate (**12**)[14] was chosen to study. Previously (*Z*)-monocyclofarnesol was transformed into α-chamigrene (**13**) in low relative yield.[15,16] After examining several organoaluminum reagents in various solvent systems, we soon found that TIBAO was the reagent of choice for the substrate **12**.[17] Thus, the cyclization was carried out with excess TIBAO (10 equiv) in hexane at −78° for 10 h and 20° for 3 h to produce *dl*-α-chamigrene (**13**)[18] in 72% yield accompanied by only ~3% of the β-isomer.



12 **13**

The investigation is currently being extended to ascertain in more detail the scope of these reactions which may have theoretical and synthetic value. We are particularly intrigued with possibilities to control the cyclization process regio- and stereoselectively.

References and Notes

(1) For a review dealing with terpene terminal epoxide cyclization, see E. E. van Tamelen, *Acc. Chem. Res.*, 1, 111 (1968). For a related biogenetic-like cyclizations, see W. S. Johnson, *Ibid.*, 1, 1 (1968); K. E. Harding, *Bioorg. Chem.*, **2**, 248 (1973).

(2) Haley, Miller, and Wood have examined the behavior of geranyl and neryl phosphate, as model for the biosynthetic process. These compounds decompose slowly at 37° in inert solvents to give a complex mixture of acyclic and cyclic hydrocarbons: R. C. Haley, J. A. Miller, and H. C. S. Wood, *J. Chem. Soc. C*, 264 (1969). See also W. Rittersdorf and F. Cramer, *Tetrahedron*, **24**, 43 (1968), **23**, 3015, 3023 (1967); P. Valenzuela and O. Cori, *Tetrahedron Lett.*, 3089 (1967).

(3) General review: J. H. Richards and J. B. Hendrickson, "The Biosynthesis of Steroids, Terpenes, and Acetogenins", W. A. Benjamin, New York, N.Y., 1964. A reasonable biosynthetic route for presqualene pyrophosphate, which involves the formation of a C-S bond from an allyl pyrophosphate, was reported: T. Cohen, G. Herman, T. M. Chapman, and D. Kuhn, *J. Am. Chem. Soc.*, **96**, 5627 (1974).

(4) Prepared in 80-90% yields from diethyl chlorophosphate and geraniol: A solution of geraniol (or nerol) in ether at −78° was treated with *n*-butyllithium (1 equiv) using *o*-phenanthroline as the internal indicator, followed by diethyl chlorophosphate (2 equiv) in ether–triethylamine (treatment of the chloride with triethylamine at 0° in ether produced the white precipitate and the clear supernatant was used) at −20° for 20 h. Chromatography on silica gel column (hexane–ethyl acetate) furnished the pure ester, homogeneous by TLC analysis and spectroscopically consistent with the indicated structure.

(5) An *E,Z* mixture of the diene **2** was prepared independently from 6-methyl-5-hepten-2-one and propylidenetriphenylphosphorane in THF. Reaction of 1 or 3 with MeMgI in ether produced a low yield of **2** (*E-Z* mixture), see also ref 2.

(6) The formation of cyclic hydrocarbons from geranyl diphenyl phosphate under solvolysis conditions was reported by Miller (ref 2). It is suggested that participation by the P═O bond occurs and that geranyl phosphate rearranges to linalyl phosphate which cyclizes with ease, although they were unable to identify linalyl phosphate in the reaction mixture.

(7) N. Davidson and H. C. Brown, *J. Am. Chem. Soc.*, **64**, 316 (1942).

(8) J. I. Jones and W. S. McDonald, *Proc. Chem. Soc., London*, 366 (1962).

(9) E. A. Jeffery and T. Mole, *Aust. J. Chem.*, **21**, 2683 (1968).

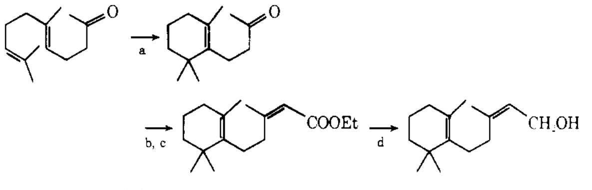
(10) Bis(diethylaluminum) sulfide: H. Imaeda, T. Hirabayashi, K. Itoh, and Y. Ishii, *Organomet. Chem. Synth.*, 1, 115 (1970/1971). Bis(dimethylaluminum) anilide: H. Tani and N. Oguni, *J. Polym. Sci. B*, **3**, 123 (1965). Tetraisobutyldialuminoxanes: T. R. Crompton, *Anal. Chem.*, **39**, 1464 (1967).

(11) The requirement for a divalent metal ion is found in most enzymic reactions of phosphate ester heterolysis, see T. C. Bruice and S. Benkovic, "Bioorganic Mechanisms", Vol 2, W. A. Benjamin, New York, N.Y., 1966, p 167. TIBAO might play a similar important role for the present reaction.

(12) G. B. Sakharovskaya, N. N. Korneev, A. F. Popov, Y. V. Kissin, S. M. Mezhikovskii, and E. Kristalnyi, *J. Gen. Chem. USSR (Engl. Transl.)*, **39**, 749 (1969).

(13) The ether solvent–TIBAO combination might increase the lifetime of geranyl carbonium ion so that it can be converted into neryl carbonium ion which cyclizes with ease. For similar solvent effects, see C. A. Bunton, J. P. Leresche, and D. Hachey, *Tetrahedron Lett.*, 2431 (1972).

(14) The phosphate **12** was prepared by esterification (ref 4) of (*Z*)-monocyclofarnesol, in turn made readily available by a synthesis developed in this laboratory:



where (a) HCOOH; (b) $Me_3SiCHLiCOOEt$; (c) *E,Z* separation by chromatography on silica gel; (d) AlH_3.

(15) S. Kanno, T. Kato, and Y. Kitahara, *Chem. Commun.*, 1257 (1967).

(16) The acid-catalyzed isomerization of (−)-thujopsene under nonaqueous conditions was known to proceed via α- and β-chamigrene to a complex mixture of isomeric tricyclic hydrocarbons: H. U. Daeniker, A. R. Hochstetler, K. Kaiser, and C. C. Kitchens, *J. Org. Chem.*, **37**, 1 (1972); W. G. Dauben and L. E. Friedrich, *ibid.*, **37**, 241 (1972); W. G. Dauben and E. I. Aoyagi, *ibid.*, **37**, 251 (1972).

(17) Other aluminum reagents or TIBAO in other solvent systems gave relatively low yields of desired products.

(18) Identical in all respects with the authentic sample. We thank Professor S. Torii and associates for a generous comparison sample and spectral data of α-chamigrene; J. D. White, S. Torii, and J. Nogami, *Tetrahedron Lett.*, 2879 (1974).

Yoshizo Kitagawa, Shinsuke Hashimoto, Satoshi Iemura
Hisashi Yamamoto,* Hitosi Nozaki
Department of Industrial Chemistry, Kyoto University
Yoshida, Kyoto 606, Japan

Received March 12, 1976

Zero-Coordinate Rb$^+$. A Rubidium Ion Whose Interionic Contacts Are All Unconventionally Long by More Than 1.5 Å

Sir:

Large monovalent cations were observed to be under-coordinated in the crystal structures of the dehydrated zeolites Cs_7Na_5-A[1,2] and K_{12}-A.[2,3] In the latter structure, a zero-coordinate K$^+$ ion is located deep within the zeolite's large cavity, 4.25 Å from the nearest framework ion, an oxygen.[4] This distance is 1.6 Å greater than the sum of the corresponding ionic radii.[5]

Herein is reported a substantiation of that result, the existence of an uncoordinated Rb$^+$ ion in Rb$^+$-exchanged zeolite A. This work is more precise than that involving K_{12}-A because