$$(CH_3)_3C—C≡CH \xrightarrow[\text{2. CH}_3\text{CH}_2\text{CH}_2\text{CHO}]{\text{1. 9-BBN}} \quad (5)$$

$$(CH_3)_3C—C≡C—CH_3 \xrightarrow[\text{2. CH}_3\text{CHO}]{\text{1. 9-BBN}} \quad (6)$$

The following procedure is representative. An oven-dried 100-ml flask fitted with a reflux condenser and magnetic stirring bar was flushed with nitrogen and charged with 50 ml of 0.50 M 9-BBN[3] (25 mmol) in THF. To the solution was added 2.7 g (28 mmol) of 4,4-dimethyl-2-pentyne, and the solution was stirred overnight to ensure complete hydroboration. Acetaldehyde (2.2 g, 50 mmol[6]) was added, and the solution was heated under reflux for 16 h. After cooling to room temperature, the reaction mixture was oxidized by adding 15 ml of 3 N sodium hydroxide followed by the slow addition of 15 ml of 30% hydrogen peroxide (*Caution:* exothermic!). The solution was maintained at 50 °C to ensure complete oxidation. The aqueous layer was saturated with anhydrous potassium carbonate, separated, and extracted with hexane. The combined organic layer was dried over anhydrous magnesium sulfate and analyzed by GC, which indicated a 69% yield of 3,5,5-trimethyl-3-hexen-2-ol. Distillation provided 1.97 g (56%) of colorless liquid: bp 80–81 °C (12 mm); n^{20}D 1.4472; IR (neat) 3350 cm^{-1}; ^{1}H NMR (CCl$_4$, TMS) δ 1.1–1.2 (s + d, 12 H), 1.7 (d, J = 1.5 Hz, 3 H), 4.1 (q, J = 6 Hz, 1 H), 5.4 (q, J = 1.5 Hz, 1 H).

Since the hydroboration reaction is known to be tolerant of a variety of functional groups,[5] we were intrigued with the possibility of achieving a "Grignard-like" synthesis with a reactive substituent present on the organometallic reagent. Thus, 5-chloro-1-pentyne was hydroborated with 9-BBN and then reacted with propionaldehyde to give *trans*-8-chloro-4-octen-3-ol (eq 7). Past experience with the application of

$$Cl(CH_2)_3C≡CH \xrightarrow[\text{2. CH}_3\text{CH}_2\text{CHO}]{\text{1. 9-BBN}} \quad (7)$$
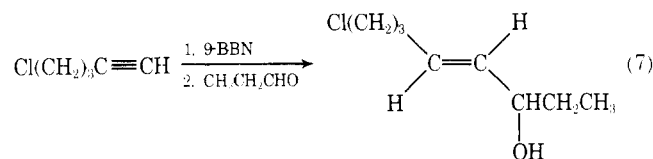
such organoborane intermediates indicate that this reaction should accommodate many functional groups, such as ester and nitrile, providing chemists with a versatile new approach to the synthesis of functionalized allylic alcohols.

It should be emphasized that this communication describes an unexpected development. All previous attempts to achieve a Grignard-like reaction of organoboranes had failed.[1] Evidently, the present development provides a remarkably simple, stereospecific, synthetic route to allylic alcohols. Furthermore, there is the definite implication that such alkenylboranes will undergo other reaction types previously believed to be possible only with far more reactive organometallic compounds. This represents a promising new area.

References and Notes

(1) Heating *B-n-butyl-9-BBN* with benzaldehyde resulted in reduction of the carbonyl group: J. D. Buhler, Ph.D. Thesis, Purdue University, West Lafayette, Ind., 1973. In contrast, *B-allyl-9-BBN* (G. W. Kramer and H. C. Brown, manuscript in preparation) and other allylboranes readily add to the carbonyl groups: B. M. Mikhailov, *Organomet. Chem. Rev. A*, 1 (1972).
(2) H. C. Brown, E. F. Knights, and C. G. Scouten, *J. Am. Chem. Soc.*, **96**, 7765 (1974); C. G. Scouten, Ph.D. Thesis, Purdue University, West Lafayette, Ind., 1974.
(3) Available from Aldrich-Boranes, a subsidiary of the Aldrich Chemical Co.
(4) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds", Wiley, New York, N.Y., 1975.
(5) The hydroboration of acetylenes involves a clean cis addition of the B–H bond: H. C. Brown, "Boranes in Organic Chemistry", Cornell University Press, Ithaca, N.Y., 1972; H. C. Brown, G. W. Kramer, A. B. Levy, and M. M. Midland, "Organic Syntheses via Boranes", Wiley-Interscience, New York, N.Y., 1975.

(6) Because of the high volatility of acetaldehyde (bp 21 °C), we employed a large excess. In most cases, the use of excess aldehyde is unnecessary.
(7) Graduate research assistant on grants provided by the National Science Foundation (GP-41169X) and by the G. D. Searle and Co. Chicago, Ill.

Peyton Jacob, III,[7] Herbert C. Brown*

Richard B. Wetherill Laboratory
Purdue University, West Lafayette, Indiana 47907

Tetraneopentylethylene

Summary: The highly hindered tetraneopentylethylene has been synthesized and was shown to exhibit a temperature dependent ^{1}H NMR spectrum demonstrating the nonequivalence of methylene protons, with the barrier of rotation across the sp^2–sp^3 bond being $\Delta G^{\ddagger}$ = 21.7 ± 5 kcal/mol at 145 °C.

Sir: In continuation of our studies on highly hindered olefins and their electrophilic reactions,[1,2] such as adamantylideneadamantane and homoadamantylidenehomoadamantane, the extremely hindered tetra-*tert*-butylethylene **1** would

1   **2**
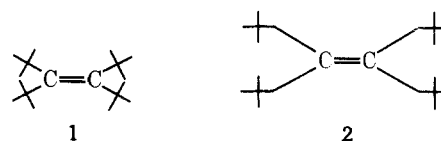
be of great interest, but it remains elusive despite efforts in different laboratories.[3] Recent methods developed by McMurry and Flemming[4] and their modifications[4d] for the reductive coupling of carbonyl compounds with low-valent titanium reagent has greatly facilitated attempts to prepare hindered olefins.[5-7] We wish now to report the synthesis of tetraneopentylethylene (**2**), one of the most crowded symmetrical tetraalkyl-substituted ethylenes.

Tetraneopentylethylene, mp 59 °C, a white crystalline solid was obtained in 38% yield by the reductive coupling of dineopentyl ketone[7b] using titanium(II) reagent[2,4] in tetrahydrofuran solution. In a 500-ml three-necked flask fitted with a reflux condenser under nitrogen is weighed TiCl$_3$ (31.3 g, 0.2 mol); 200 ml of anhydrous THF is added to it under stirring, and the flask is cooled to −40 °C (dry ice/acetone bath). Under stirring LiAlH$_4$ (3.8 g, 0.1 mol) is added in portions; rapid gas evolution is seen. After the addition, the mixture is warmed to room temperature and refluxed for 1 h, dineopentyl ketone (16.8 g, 0.1 mol) in 50 ml of THF is added dropwise, and the mixture is refluxed for 8 h more. Then the mixture is cooled, poured over 10% ice-cold NH$_4$Cl solution, and worked up with ether in the usual manner. The product is purified by chromatography on alumina (petroleum ether eluent): ^{13}C NMR (25.1 MHz, CDCl$_3$, from capillary TMS, 37 °C) δ 136.56 (vinylic carbon), 47.36 (CH$_2$, J_{CH} = 121.0 Hz), 35.23)quaternary carbon), 32.47 (CH$_3$, J_{CH} = 128.1 Hz); mass spectrum (70 eV) (relative abundance) m/e 308 (78.1, M$^+$), 252 (40.6), 251 (50.2), 196 (30.2), 195 (63.8), 167 (11.2), 154 (7.7), 140 (18.7), 139 (58.3), 125 (20.6), 111 (15.8), 99 (10.5), 85 (11.4), 83 (19.6), 71 (13.0), 57 (100), 41 (24.3), 29 (15.7). Elemental Anal.[8a] Calcd for C$_{22}$H$_{44}$: C, 85.71; H, 14.29. Found: C, 85.76; H, 14.39.

Of particular interest is the marked temperature dependence of the ^{1}H NMR spectrum[8b] of **2**. The methylene protons show an AB pattern, centered at δ 2.18 (J_{AB} = 13.0 Hz) up to 104 °C; coalescence occurs at 145 °C. The methyl groups resonate at δ 0.97 as a singlet without any change with temperature. The appearance of two different methylene protons is
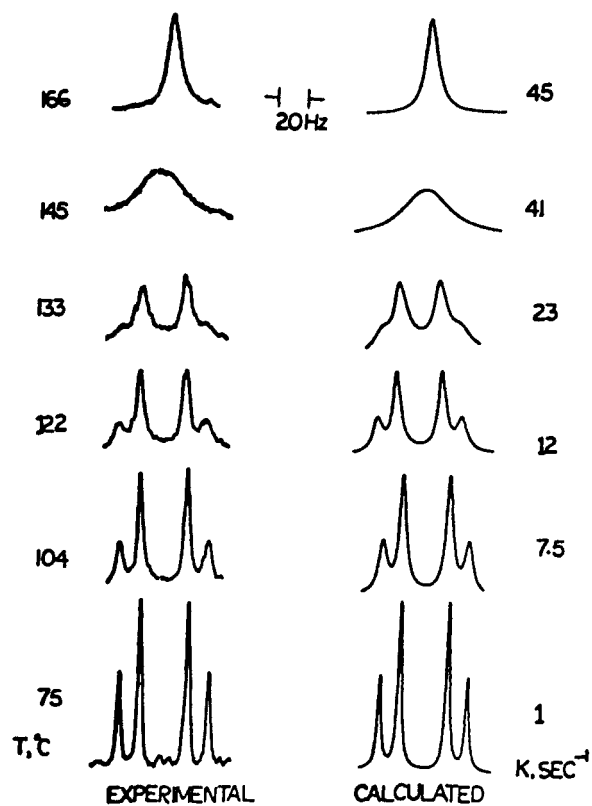
Figure 1. Experimental and calculated 60-MHz NMR absorptions of methylene protons of **2** at various temperatures, T, °C; K, rate constant.

Table I. Raman C=C Bond Stretching Frequencies of Alkyl-Substituted Olefins

Compd	$\nu_{C=C}$, cm^{-1}
	1656
	1638
	1636
	1629
	1615.5
	1607
	1583

as expected. This type of hindered rotation across sp^2–sp^3 carbon–carbon bonds has been observed in many neopentyl-substituted benzenes.[9] The coalescence temperature at which collapse of the nonequivalent proton absorptions occurs is rather high.[10] A complete NMR line-shape analysis (Figure 1) using the "QUABEX" computer program[11] shows the activation energy barrier at coalescence to be $\Delta G^{\ddagger} = 21.7 \pm 0.5$ kcal/mol. This is one of the highest energy barriers yet reported for this kind of hindered rotation in comparison with other neopentyl-substituted systems.[10] The olefinic carbons are more shielded (by 8.34 ppm) compared to the olefinic carbons of tetraisopropylethylene **3**.[5b] This effect is, however, in great part due to the neighboring-group effects, as a similar ipso carbon shift difference[11c] (9.1 ppm) is observed between cumene and neopentylbenzene. The methylene carbons did not show any change in coupling with the nonequivalent hydrogens at different temperatures.

The laser Raman spectrum of **2** (488.0 nm, crystalline sample) shows bands at 1607 cm^{-1} (C=C stretch), 1450 (sh), 1445, 1430 (sh), 1394, 1364, 1357, 1316, 1226, 1199, 1175, 1157, 934, 907, 900, 890, 862, 778, 641, 500, 467, 386, 257, 240, and 215. The C=C stretching frequency is rather low compared to that of other crowded olefins[3a,5b] (Table I).

The continuous decrease in C=C stretching frequency with the increase in steric crowding of the double bond is apparent, though such a correlation cannot be generalized.[11d] Such shift in stretching frequency is considered to arise from change in bond angles and hence change in hydridization.[12-14] It has also been argued[12b,13] that the primary contributor for the shift in frequencies is the coupling of the double-bond stretching with the adjacent single bonds, such that the compression and elongation of the single bond occurs during double-bond vibration which is also angle dependent.

Tetraneopentylethylene (**2**) does not react with bromine in CCl_4 solution and the system stays unchanged for days. The

^{13}C NMR spectrum of **2** in $Br_2/CDCl_3$ shows no shift changes indicating absence of any detectable π-complex formation. **2** also shows no evidence of protonation and is unchanged in FSO_3H/SO_2ClF solution. However, the much stronger FSO_3H/SbF_5 system cleaves the neopentyl groups giving *tert*-butyl cation and polymeric products. The lack of reactivity of **2** to electrophilic additions further demonstrates the steric constraints imposed by the four neopentyl groups.

Conformation **2a** is consistent with the nonequivalence of the methylene protons in the ^{1}H NMR spectrum and mini-

2a
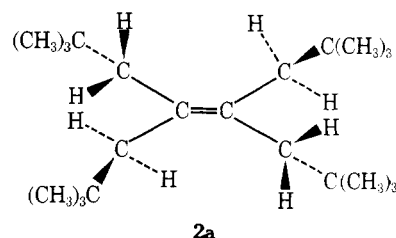
mizes steric interactions between the four neopentyl groups. It also explains the lack of reactivity of the double bond in **2**, since both sides of the molecule are shielded by two *tert*-butyl groups.

In the mass spectrum of **2** the base peak at m/e 57 corresponds to C_4H_9, i.e., *tert*-butyl group. The molecular ion peak at m/e 308 is also intense. The fragmentation peaks can be accounted for by the progressive loss of *tert*-butyl, isobutylene, ethylene, or methyl moities. The peak at m/e 154 should come from the cission of the C=C bond as observed in the case of tetraisopropylethylene.[5b]

Di-*tert*-butyl ketone, *tert*-butyl isopropyl ketone, and neopentyl *tert*-butyl ketone failed to undergo coupling reaction. We are continuing our studies on **2** and other related highly crowded olefins[3c] and their behavior under electrophilic conditions.

References and Notes

(1) G. A. Olah, P. Schilling, P. W. Westermann, and H. C. Lin, *J. Am. Chem. Soc.*, **96**, 3581 (1974).
(2) G. A. Olah, G. K. Surya Prakash, and G. Liang, *Synthesis*, 318, (1976).

(3) (a) G. J. Abruscato and T. T. Tidwell, *J. Am. Chem. Soc.*, **92**, 4125 (1970); (b) D. H. R. Barton, F. S. Guziec, Jr., and I. Shahak, *J. Chem. Soc., Perkin Trans 1*, 1793 (1974); (c) unpublished results in our laboratory.
(4) (a) J. E. McMurry, *Acc. Chem. Res.*, **7**, 281 (1974); (b) J. E. McMurry and M. P. Flemming, *J. Am. Chem. Soc.*, **96**, 4708 (1974); (c) J. E. McMurry and M. P. Flemming, *J. Org. Chem.*, **41**, 896 (1976); (d) E. J. Corey, R. L. Danheiser, and S. Chandrasekaran, *ibid.*, **41**, 260 (1976).
(5) (a) R. F. Langler and T. T. Tidwell, *Tetrahedron Lett.*, 777 (1975); (b) D. S. Bombse and T. H. Morton, *ibid.*, 781 (1975).
(6) H. Wynberg, K. Lammertsma, and L. A. Hulshoff, *Tetrahedron Lett.*, 3749 (1975).
(7) (a) See also W. H. Richardson and K. W. Gunderson, *J. Org. Chem.*, **41**, 2054 (1976); (b) J. Ciabattoni, E. C. Nathan, A. E. Feiring, and P. J. Kocienski, *Org. Synth.*, **54**, 97 (1975).
(8) (a) Analysis by Galbrath Laboratories, Inc., Knoxville, Tenn. (b) Spectrum was taken in hexachloroacetone, shifts from capillary TMS.
(9) (a) D. T. Dix, G. Frankel, H. A. Karnes, and M. S. Newman, *Tetrahedron Lett.*, 517 (1966); (b) A. J. M. Reuvers, A. Sinnema, T. J. Nieumstad, F. V. Rantwijk, and H. V. Bekkum, *Tetrahedron*, **27**, 3713 (1971).
(10) S. Sternhell in "Dynamic Nuclear Magnetic Resonance Spectroscopy", L. M. Jackmann and F. A. Cotton, Ed., Academic Press, New York, N.Y., 1975, p 170.
(11) (a) G. Binch in "Topics in Stereochemistry", Vol. 3, E. L. Eliel and N. L. Allinger, Ed., Wiley-Interscience, New York, N.Y., 1968, pp 180, 181. (b) Calculations were performed on a Univac 1108 computer equipped with a CALCOMP plotter. $\Delta G^{\ddagger}$ was calculated from the rate constants using the Eyring equation

$$\Delta G^{\ddagger} = 4.576 \, TC \, (10.319 + \log TC/K)$$

In the equation the transmission coefficient (TC) was assumed to be unity. E_a was found to be 13.07 ± 0.5 kcal/mol from a linear Arrehenious plot. $\Delta H^{\ddagger}$ and $\Delta s^{\ddagger}$ were found to be 11.68 ± 0.5 kcal/mol and −20 ± 2.0 eu, respectively. (c) ^{13}C NMR: cumene, δ_{ipso} 149.40; neopentylbenzene, δ_{ipso} 140.30. (d) O. Ermer and S. Lifson, *Tetrahedron*, **30**, 2425 (1974).
(12) (a) N. Sheppard and D. M. Simpson, *Quart. rev. Chem. Soc.*, **6**, 1 (1962); (b) D. G. Rea, *Anal. Chem.*, **32**, 1638 (1960); (c) F. h. A. Rummens, *Recl. Trav. Chim., Pays-Bas*, **84**, 5 (1965).
(13) L. J. Bellamy. "Advances in Infrared Group Frequencies", Methuen and Co., London, 1968, pp 22–26, 30–32, 132–135.
(14) S. Bank, W. D. Closson, and L. T. Hodgins, *Tetrahedron*, **24**, 381 (1968).

George A. Olah,* G. K. Surya Prakash

Department of Chemistry
Case Western Reserve University
Cleveland, Ohio 44106

Received October 18, 1976

Stereochemistry and Kinetics of Photochemical Fragmentation of 1-Phenyl-3-Phospholene Oxides

Summary: The rate and stereospecificities of the novel photochemical extrusion of phosphinidene oxide from the excited singlet states of 3-phospholene oxides are shown to be sensitive to the configuration of an asymmetric leaving group, indicating that the steric influence on the transition state is substantial.

Sir: During a study of the photochemical reactions of phosphorus heterocycles,[1] we have found, upon UV irradiation, that 1-phenyl-3-phospholene oxides efficiently cleave to dienes and phenylphosphinidene oxide. In contrast to the
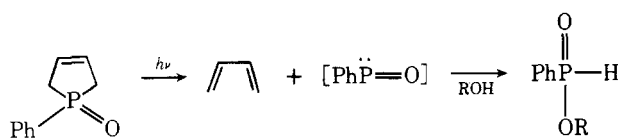
other closely related five-membered cheletropic cycloregressions,[2,3] this formally cheletropic reaction[4] has an asymmetric leaving group and would be expected to reveal how the direction of ring opening and the rate of the reaction depend on the stereochemical disposition of the leaving group.

It was found that the stereochemical disposition of the

leaving group exerted a substantial effect on the rate of the fragmentation. This can be explained by considering the steric influence in the transition state during bond reorganization. The all-trans isomers furnished a mixture of dienes, whereas the all-cis isomers gave predominantly the all-trans olefins. This is the first five-membered cheletropic cycloregression observed to proceed through the singlet excited state.

The stereoisomeric pairs of 3-phospholene oxides (**1** and **2**) were prepared according to Quin[5] and the isomers[6] were separated by silica gel chromatography followed by short-path distillation at 10^{-3} mm.

Direct irradiation of **1** and **2** with 254-nm light from a monochromator was performed in methanol containing methylcyclohexane as the internal standard. This resulted in quantitative formation of 1,3-dienes (**3** and **4**) and methyl phenylphosphinate. No photochemical cis–trans isomerization of **1** and **2** was observed even after prolonged irradiation. These phospholene oxides were thermally stable and gave no trace of dienes in refluxing diethyl phthalate (300 °C). Prolonged refluxing caused rearrangement to the 2-phospholene oxide isomer.

Irradiations were interrupted at low conversion (<2%) and yields of 1,3-diene were extrapolated to zero conversion[7] as an appropriate correction for possible sensitized diene isomerization by phospholene oxide (vide infra). The results are shown in eq 1 and 2.[8]
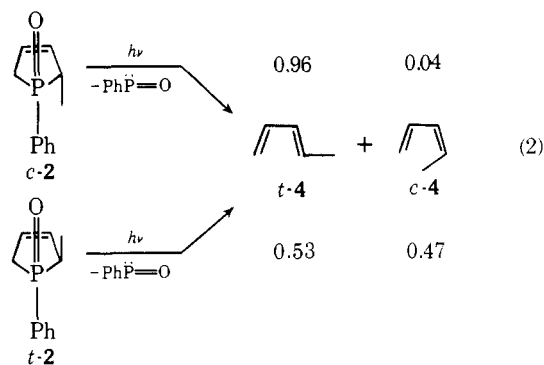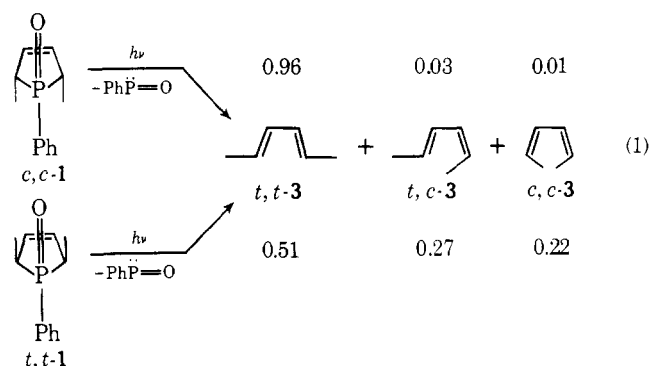
Quenching of the reactions 1 and 2 occurred with 1,3-dienes (e.g., 2,5-dimethyl-2,4-hexadiene) to yield linear Stern–Volmer plots. The 1,3-diene photoproduct compositions were the same as those obtained by extrapolation. Triplet sensitization[9] (benzophenone) of **1** and **2**, however, gave no detectable amount of **3** and **4**. Fluorescence quenching of **1** and **2** by 1,3-diene also occurred. The quenching gave good linear Stern–Volmer plots whose slopes are in agreement within experimental errors with those obtained in the quenching of the photochemical reactions (Table I). Unlike other closely related systems,[3] photofragmentation of the phospholene oxides proceeds via the lowest excited singlet state.