Carbon–Phosphorus Heterocycles. A Study of the Mechanism of Cyclization of Alkenyl-Substituted Phosphonium Salts by 115% Polyphosphoric Acid via Stereochemical and Phosphorus-31 Nuclear Magnetic Resonance Analyses

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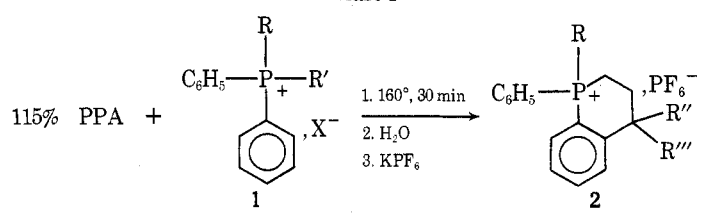
Evidence is presented that intramolecular cyclization of alkenyl-substituted phosphonium salts $(C_6H_5)_2(R)[R'CH{=}CH(CH_2)_n]P^+$, X^- or $(C_6H_5)_2(C_6H_5CH_2)(CH_2{=}CHCH_2)P^+$, PF_6^-, via reaction with polyphosphoric acid (PPA) at 150°, proceeds through a mechanism reminiscent of a cation-alkylation process to give phosphinolinium systems and an isophosphinolinium salt, respectively. Stereochemical analysis of the products and ^{31}P NMR monitoring of the cyclization support a mechanism of marked resemblance to a cation alkylation of an arene, i.e., an electrophilic substitution process. An intermediate with strong ^{31}P NMR signal was observed in the reaction of 2-butenyltriphenylphosphonium bromide (**1j**) with PPA to give **2d** but such a signal was absent when allylbenzyldiphenylphosphonium bromide (**7**) was converted to 1,2,3,4-tetrahydro-4-methyl-2,2-diphenylisophosphinolinium hexafluorophosphate (**8**). The latter observation was rationalized on the basis of a rapidly formed intermediate of a classic type in electrophilic aromatic substitution. Fast loss of a proton to re-form the aromatic ring to yield 8 ensues and no intermediate detectable by ^{31}P NMR accumulates.

The recent discovery that alkenyl-substituted arylphosphonium salts undergo cyclization in the presence of commercial 115% polyphosphoric acid (PPA) to yield tetrahydrophosphinolines and tetrahydroisophosphinolines has not heretofore been investigated from a mechanistic standpoint.[1] We wish to report that a careful study of selected salts (Table I contains data on the open salts) indicates that the ring closure shown in Chart I follows a course predictable, in part, from current carbonium ion theory.

When the 4-pentenyl compound **1g** was subjected to the same conditions, the six-membered ring analogue **2g** formed as evidenced by ^1H NMR, ^{31}P NMR, ir, mass spectral, and elemental analysis.[2] This shows that the six-membered ring is formed in preference to the seven-membered ring which would have resulted from initial protonation at the terminal carbon atom to generate a secondary cation. The observation suggests that either hydride transfer and cyclization to **2g** together are faster than cyclization to the

Chart I



Compd[a]	R	R′	X⁻	Compd	R	R″	R‴
1a	C_6H_5	$CH_2CH{=}C(CH_3)_2$	Cl	2a	C_6H_5	CH_3	CH_3
1b	CH_3	$CH_2CH{=}C(CH_3)_2$	Cl	2b	CH_3	CH_3	CH_3
1c	C_2H_5	$CH_2CH{=}C(CH_3)_2$	Cl	2c	C_2H_5	CH_3	CH_3
1d	C_6H_5	$CH_2CH_2CH{=}CH_2$	Br	2d	C_6H_5	H	CH_3
1e	CH_3	$CH_2CH_2CH{=}CH_2$	PF_6	2e	CH_3	H	CH_3
1f	C_2H_5	$CH_2CH_2CH{=}CH_2$	PF_6	2f	C_2H_5	H	CH_3
1g	C_6H_5	$CH_2(CH_2)_2CH{=}CH_2$	Br	2g	C_6H_5	H	C_2H_5
1h	CH_3	$CH_2(CH_2)_2CH{=}CH_2$	PF_6	2h	CH_3	H	C_2H_5
1i	C_2H_5	$CH_2(CH_2)_2CH{=}CH_2$	PF_6	2i	C_2H_5	H	C_2H_5
1j	C_6H_5	$CH_2CH{=}CHCH_3$	Br	2d	C_6H_5	H	CH_3

When R′ = $(CH_3)_2C{=}CHCH_2^-$, the cyclization proceeded smoothly for R = CH_3, C_2H_5, or C_6H_5 in high yields (86, 89, and 88%) as shown in Chart I (Table II contains data on the phosphinolinium salts). The loss of HBr was instantaneous with the mixing of reagents at 160°. Thus, any intermediate involved is *not* likely dependent to an influential degree upon R as a *stabilizing group* under the conditions illustrated. The open-chain 3-butenyl analogue **1d** closed to give **2d** which was the identical product obtained previously[1] from the 2-butenyl precursor **1j**. Consequently, the same transitory secondary cation 4 is likely to be involved in both cases. Similarly, **2e** and **2f** were prepared and have ^1H NMR spectra very nearly superimposable on that of **2d**, except for the signals arising from R.

seven-membered ring or all three species equilibrate. The latter is a separate problem under study. The stability of the phosphorinane ring both singly and as a part of a fused system is well known.[3] As noted previously, it was observed

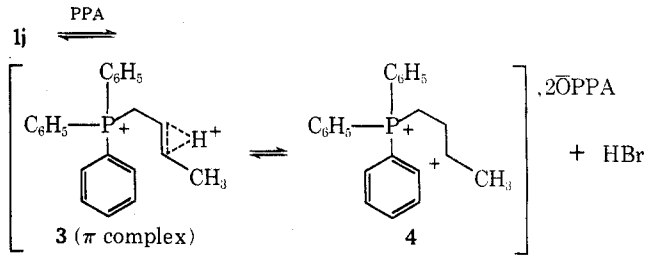
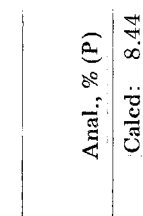


Table I



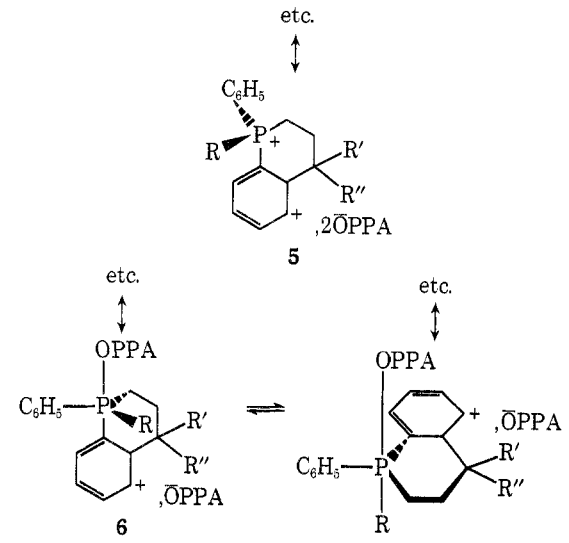
Compd	R	R′	X⁻	Mp, °C	Quaternizing solvent (reaction time, hr)	Equivalent halide	Yield, %	Molecular formula	Anal., % (P)
1a	C_6H_5	$CH_2CH{=}(CH_3)_2$	Cl	253–254.5	Toluene (24)	0.88	57	$C_{23}H_{24}ClP$	Calcd: 8.44 Found: 8.24
1b	CH_3	$CH_2CH{=}C(CH_3)_2$	Cl	189.5–191.5	Benzene (24)	0.88	69	$C_{18}H_{22}ClP$	Calcd: 10.16 Found: 9.96
1c	C_2H_5	$CH_2CH{=}C(CH_3)_2$	Cl	163–165	Toluene (48)	1.43	73	$C_{19}H_{24}ClP$	Calcd: 9.71 Found: 9.51
1d	C_6H_5	$CH_2CH_2CH{=}CH_2$	Br	224–226[a]	Xylene (50)	0.73	71	$C_{22}H_{22}BrP$	
1e	CH_3	$CH_2CH_2CH{=}CH_2$	PF_6	117.5–119	Benzene (60)	1.50	69	$C_{17}H_{20}F_6P_2$	Calcd: 15.47 Found: 15.07
1f	C_2H_5	$CH_2CH_2CH{=}CH_2$	PF_6	129–131	Benzene (48)	1.50	52	$C_{18}H_{22}F_6P_2$	Calcd: 14.95 Found: 15.00
1g	C_6H_5	$CH_2(CH_2)_2CH{=}CH_2$	Br	189–191[b]	Xylene (50)	0.73	76	$C_{23}H_{24}BrP$	Calcd: 7.53 Found: 7.64
1h	CH_3	$CH_2(CH_2)_2CH{=}CH_2$	PF_6	89.5–91.5	Benzene (60)	1.50	77	$C_{18}H_{22}F_6P_2$	Calcd: 14.95 Found: 14.69
1i	C_2H_5	$CH_2(CH_2)_2CH{=}CH_2$	PF_6	108–110	Benzene (48)	1.43	50	$C_{19}H_{24}F_6P_2$	Calcd: 14.46 Found: 14.44
1j	C_6H_5	$CH_2CH{=}CHCH_3$	Br	241–242[c]	Xylene (24)	1.36	90	$C_{22}H_{22}BrP$	

[a] Lit. mp 288° [E. Schweizer, J. Thompson, and T. Ulrich, *J. Org. Chem.*, 33, 3082 (1968)]. [b] Lit. mp 134–140° [C. Hauser, T. Brooks M. Miles, M. Raymond, and G. B. Butler, *J. Org. Chem.*, 28, 372 (1963)]. [c] Reported previously in ref 1.

that the phosphorinane system **2d** formed in preference to a phosphindoline system when 2-butenyltriphenylphosphonium bromide (**1j**) was the starting material. Again, this hints at ring stability and intermediate cation stability as governing factors in controlling the ring closure.

Attempts to cyclize **1h** and **1i** appeared successful but mixtures of isomers were obtained in both cases as suggested by a melting range for products and ^1H NMR analysis. All efforts to separate these isomers have not been fruitful in view of the nearly identical solubility properties of the components in the mixtures.

Assuming **5** or **6** as tentative candidates for cyclic intermediates in the reaction, a ^{31}P NMR study of the cyclization was conducted on **1j** in an NMR tube at 150°. At this temperature, the rate of reaction permitted reasonable monitoring ease, and the viscosity of the medium was such that fine structure of the ^{31}P NMR signals was clearly visible.



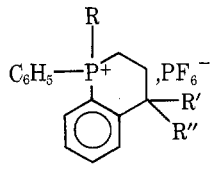
Within 5 min (t_0 + 5) after mixing **1j** with 115% PPA at 150° and inserting the tube into the probe (heated 150°), broad signals appeared at −8.7, −19.4, and −22.5 ppm (1.2:1.2:1) relative to external 85% H_3PO_4. Signals at −0.03, +15.3, and +31.6 ppm (1:10.2:9.6) were discernible for PPA in all samples examined and were continuously monitored in all experiments.

At t_0 + 45, only two signals at −8.7 and −22.5 ppm (5.2:1) were detected. Addition of one-half of an equivalent weight of **2d** (or **2d** as the Br^- salt) caused the ratio of the two peaks to change to 13.7:1. Thus, the signal at −8.7 ppm was for product. Moreover, after hydrolysis of the reaction mixture in the NMR tube, solid **2d** was isolated in high yield. A separate ^{31}P NMR analysis of the water solution also gave a strong signal at −8.7 ppm.[4] The signal at −22.5 ppm disappeared, however.

Freshly prepared 115% PPA (84% by weight of P_2O_5 in 85% H_3PO_4) or commercial 105% PPA gave identical results but the rate of reaction was much slower. In fact, in 105% PPA only one signal at −19.3 ppm was observed at t_0 + 5. Only at t_0 + 20 did three peaks appear in the spectrum of the reaction with 105% PPA as seen previously when 115% PPA was used. In the latter, the signal at −19.4 ppm[5] vanished after t_0 + 45 at 150°. Thus, the signal at −19.4 ppm must be for **1j**.

Related experiments with **1d** and commercial 115% PPA at 150° showed three peaks at −9.5, −20.0, and −23.1 ppm. The addition of **1d** and **2d** showed reinforcement of the signals at −20.0 and −9.5 ppm, respectively. Persistence of the signal at −23.1 ppm for the intermediate was very rem-

Table II

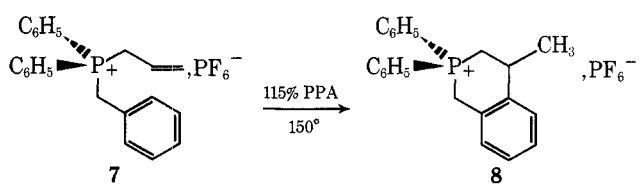


Compd	R	R′	R″	Mp, °C	Yield, %	Molecular formula	Anal., % P
2a	C_6H_5	CH_3	CH_3	209–211	89	$C_{23}H_{24}F_6P_2$	Calcd: 13.00 Found: 12.94
2b	CH_3	CH_3	CH_3	211–213.5	86	$C_{18}H_{22}F_6P_2$	Calcd: 14.95 Found: 15.04
2c	C_2H_5	CH_3	CH_3	144–146	89	$C_{19}H_{24}F_6P_2$	Calcd: 14.46 Found: 14.49
2d	C_6H_5	H	CH_3	203.5–205[a]	95	$C_{22}H_{22}F_6P_2$	
2e	CH_3	H	CH_3	177.5–179	73	$C_{17}H_{20}F_6P_2$	Calcd: 15.47 Found: 15.09
2f	C_2H_5	H	CH_3	145.5–147	45	$C_{18}H_{22}F_6P_2$	Calcd: 14.95 Found: 14.90
2g	C_6H_5	H	C_2H_5	159–161	60	$C_{23}H_{24}F_6P_2$	Calcd: 13.00 Found: 13.30

[a] Reported previously; see ref 1.

iniscent of the signal at −22.5 ppm found in the reaction with **1j**. Since **2d** was formed in the reaction of **1d**, the intermediates must be identical.

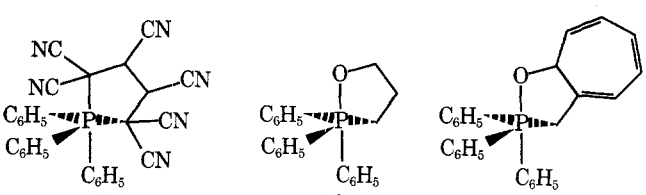
When the phosphorus atom was moved one position in the ring system as in allyldiphenylbenzylphosphonium hexafluorophosphate (**7**), a somewhat similar pattern was observed in the conversion to **8** with but one exception. Sig-



7 **8**

nals for ^{31}P at −16.1 and −21.9 ppm (3:6:1) were strong at t_0 + 15 but *only* the signal at −21.9 ppm was noted at t_0 + 5. The ratios of **8**:**7** changed to 4.6:1 (t_0 + 125), 4.9:1 (t_0 + 134), and 10.2:1 (t_0 + 180). Addition of an authentic sample of **8** at t_0 + 30 in a separate experiment resulted in a large increase in the signal at −16.1 ppm, thus confirming it to be assigned to **8**. Hydrolysis of the reaction mixture in the NMR tube revealed that **8** had formed in high yield (>90%) and was identical with the reported compound.[1] Similarly, addition of authentic **7** caused the signal at −21.9 ppm to increase, substantiating its assignment. In no experiment studied up to t_0 + 180 did another signal appear in **7** → **8**.

A search of the literature did not reveal a similar system with sulfur or arsenic involved. Likewise, no data could be uncovered for molecular structures (or intermediates) in which a pentavalent phosphorus as part of a *six-membered ring* system was bound to four carbons and one oxygen atom in a trigonal bipyramid or tetragonal pyramid. However, the phosphorus is bound to five carbon atoms in **9**[6] and to four carbons and one oxygen atom in **10**[7] and **11**[8]

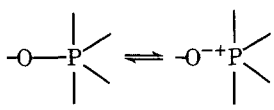


9 (−22.0 ppm, dioxane) **10** (+49.5 ppm, H_2CCl_2) **11** (+66.9 ppm, $DCCl_3$)

$R(R')(R'')(R''')P^+,X^-$

12

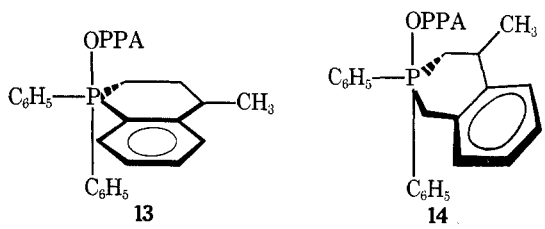
but the ring system is five membered. Moreover, a dipolar ion (**A**) may exist in solution as suggested by a long P–O



A

distance of 2.14 Å in **11**.[8] The dependence of ^{31}P shifts upon the nature of substituents is well known,[9,10] and there are several other pentavalent P-containing systems reported to have *negative shifts*.[11] Most simple phosphonium salts like **12** have negative ^{31}P values commonly ranging from −10 to −40 ppm.[9]

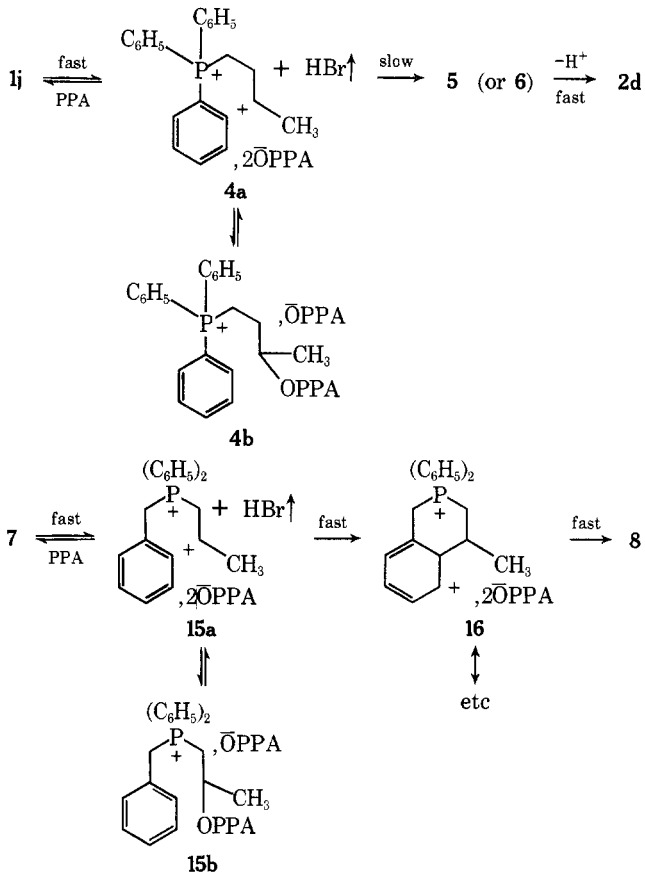
Intuitively, one would estimate the inherent stability of **5** or **6** to be low under the reaction conditions since the stabilization energy gained via aromatization would be significant. The same should be true for a similar intermediate formed in the conversion **7** → **8**. In **1j** → **2d**, the ^{31}P NMR signal at −22.5 ppm is not much different from the signal for **1j** at −19.4 ppm. Initially, it is tempting to consider candidates like **13** (or rotamer thereof) since **2d** accumu-



13 **14**

lates as the intermediate at −22.5 ppm decreases (as evidenced by the change in ^{31}P NMR signals after t_0 + 45). However, in **7** → **8** a third ^{31}P NMR signal did *not* appear, and the other peaks were confirmed as for **7** and **8**. Thus, there is no intuitively obvious reason why **13** or **14** should not be stable candidates as intermediates in **7** → **8** as well. Consequently, an intermediate does not form or is very reactive and does *not* accumulate.

Several other observations in the cyclization are relevant. The intermediate (at −22.5 ppm) in **1j** → **2d** is relatively stable since the signal persisted to t_0 + 90 min and the ^{31}P NMR signal is close in field position to that of **1j** (−19.4 ppm). Thus, an intermediate with an environment around phosphorus similar to that of **1j** would seem defensible.



One reasonable compromise could involve equilibria such as with **4a** (or **4b**) and **15a** (or **15b**). In **1j** → **2d**, a conversion of **4a** (or **4b**) to **5** (or **6**) would be expectedly slow since the process should have a high energy barrier. Thus **4a** or **4b** could accumulate in the high acid media and could account for the ^{31}P signal at −22.5 ppm indicating a similar environment for P as in **1j** (−19.4 ppm). Rapid loss of a proton from **5** (or **6**) should follow since it is known that >P⁺< has an electron-withdrawing effect on electrophilic substitution processes[12] and regeneration of the aromatic nucleus would be energetically favorable. This is also in accord with the observation that the intermediates accumulate at the expense of **1j** and decreases with time as **2d** amasses.

In contrast, conversion of **7** to **15a** (or **15b**) would be fast followed by a rapid intramolecular cyclization to **1b**. An insulating methylene group prevents direct electronic interaction between >P⁺< and the ring under attack. Thus, a rather classic intermediate **16** in a classic electrophilic substitution rapidly loses a proton to yield **8**. Consequently, **15a** (or **15b**) and **16** do not persist significantly at 150° to produce a ^{31}P NMR signal.

PPA is known to attack conjugate double bonds in unsaturated phosphine oxides.[13] In fact, a postulate was made that Ō–PPA adds to the sp^2 carbon.[13] To be sure, attack on salts **1j** or **7** should be more difficult but at 150° the problem is circumvented. The evidence available does not support the pentavalent intermediates **13** or **14**, and we interpret the data with the more classical type intermediate, i.e., **5**.

Experimental Section

General Data. Melting points were obtained on a Thomas-Hoover melting point apparatus and are uncorrected. ^{31}P NMR data were obtained on a XL-100(15) Varian spectrometer operating at 40.5 MHz and with 85% H_3PO_4 as an external standard with the total scan area examined being −123 to +184 ppm without ^1H decoupling. Of course, the ratios of ^{31}P signals is only roughly qualitative because of probable differential NOE effects.[9] Ir, mass spectral, and ^1H NMR data were collected on a Beckman IR-5A unit (as KBr pellets), a CEC Model 21 HR unit, and an XL-100(15) spectrometer, respectively, and are available upon request. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

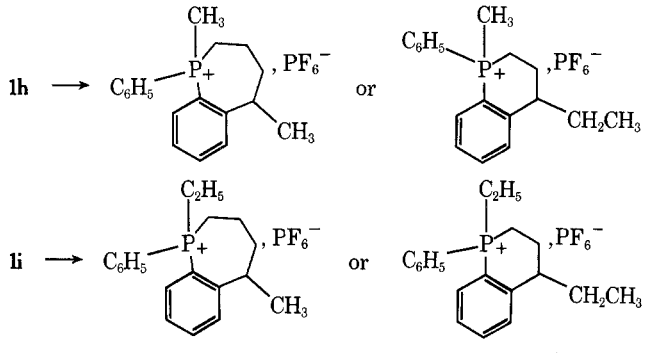
Starting Materials. The phosphine $(C_6H_5)_2PR$ (R = CH_3, C_2H_5, or C_6H_5) required to prepare the open-chain salts in Table I were synthesized as described previously.[1] Allylbenzyldiphenylphosphonium hexafluorophosphate (**7**) was prepared by a metathetic exchange from the corresponding bromide[1] in water when treated with a saturated aqueous solution; mp of **7** was 118–119.5°.

Anal. Calcd for $C_{22}H_{22}F_6P_2$: C, 57.12; H, 4.76; P, 13.41. Found: C, 57.18; H, 4.52; P, 13.18.

Commercial 115% and 105% PPA was obtained from FMC Corp., Inorganic Division, via Mr. J. P. Cassidy.

Quaternization and Cyclization Techniques. Both of these techniques have been outlined in detail previously.[1] All salts of families **1** and **2** as well as **7** and **8** were prepared in a similar fashion. The work-up was modified slightly from that reported.[1] The tube was removed from the probe and allowed to cool to about 80–90°. The various contents were added to 25 ml of distilled H_2O, and the resulting mixture was allowed to stand overnight. A solution resulted and was analyzed at 80° via ^{31}P NMR analysis to confirm the signal for product **2d**. In the case of **8**, the PF_6^- salt precipitated at once when the contents of the tube were discharged into the H_2O. In the work-up for **2d**, the solution of 80° was allowed to cool to room temperature, and a saturated solution of KPF_6 was added. The corresponding salt precipitated and was purified and identified as described.[1]

In the reactions of **1h** and **1i** with 115% PPA, solids were isolated by the standard procedure. However, the melting ranges were



long for the products from both open-chain compounds. ^1H NMR analysis revealed a very complex spectrum in each case. Absent were simple doublets for methyl protons at high field if a seven-membered ring had formed. Neither did the spectrum show a triplet at high field for the terminal methyl group if a six-membered ring had formed. Of course, two sets of geometrical isomers are possible in each example and may be present. All attempts to separate the isomeric mixture have been unsuccessful to date.

Acknowledgment. We gratefully acknowledge support of this work by the USPHS National Cancer Institute, Grant CA 11967.

Registry No.—**1a**, 52750-95-5; **1b**, 56771-23-4; **1c**, 56771-24-5; **1d**, 16958-42-2; **1e**, 56771-26-7; **1f**, 56771-28-9; **1g**, 56771-29-0; **1h**, 56771-31-4; **1i**, 56771-33-6; **1j**, 28975-45-3; **2a**, 56771-35-8; **2b**, 56771-37-0; **2c**, 56771-39-2; **2d**, 54230-12-5; **2e**, 54293-29-7; **2f**, 54230-14-7; **2g**, 56771-41-6; **7**, 56771-43-8.

References and Notes

(1) G. A. Dilbeck, D. L. Morris, and K. D. Berlin, *J. Org. Chem.*, **40**, 1150 (1975). The 115% PPA was obtained from FMC Corp. of New York through the kindness of Mr. J. P. Cassidy.
(2) All new compounds gave satisfactory elemental (±0.3% P or C, H, and P) analysis as well as the expected ^1H NMR, ^{31}P NMR, ir, and mass spectral data.
(3) G. M. Kosolapoff and L. Maier, Ed., "Organic Phosphorus Chemistry", Wiley-Interscience, New York, N.Y., 1972, Vol. 1–6; D. M. Hellwege and K. D. Berlin, *Top. Phosphorus Chem.*, **6**, 1 (1969); G. A. Dilbeck, Ph.D. Dissertation, Oklahoma State University, 1974.
(4) This sample had a peak at −10.74 ppm in CH_3CN (see ref 1).
(5) In $DCCl_3$ (plus 3 drops of trifluoroacetic acid), the signal for **1j** occurred at −21.14 ppm (ref 1).
(6) G. S. Reddy and C. T. Weiss, *J. Org. Chem.*, **28**, 1822 (1963).

(7) E. E. Schweizer, W. S. Creasy, J. G. Liecher, M. E. Jenkins, and P. L. Dalrymple, *J. Org. Chem.*, **35**, 601 (1970).
(8) I. Kawamoto, T. Hata, Y. Kishida, and C. Tamura, *Tetrahedron Lett.*, 1611 (1972).
(9) M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, *Top. Phosphorus Chem.*, **5**, 1 (1967).
(10) The stability of pentasubstituted phosphorus interemediates is well known and has been reviewed; see R. Luckenbach, "Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements", Georg Thieme Verlag, Stuttgart, 1973.
(11) N. J. De'Ath and D. B. Denney, *Chem. Commun.*, 395 (1972); C. D. Hall, J. D. Bramblett, and F. F. S. Liu, *J. Am. Chem. Soc.*, **94**, 9264 (1972).
(12) A. Gastaminza, T.-R. Modro, J. H. Ridd, and J. H. P. Utley, *J. Chem. Soc. B*, 534 (1968), and references cited therein.
(13) J. M. Conia and M. L. Leriverend, *Bull. Soc. Chim. Fr.*, 2992 (1970); M. Simalty and L. Van Chau, *Tetrahedron Lett.*, 4371 (1970).

Oxymercuration–Demercuration and Hydroboration–Oxidation of *endo*-Tricyclo[5.2.2.0^{2,6}]undeca-3,8-diene. Stereospecific Oxymercuration Leading to the 4-*exo*-Hydroxy Derivative

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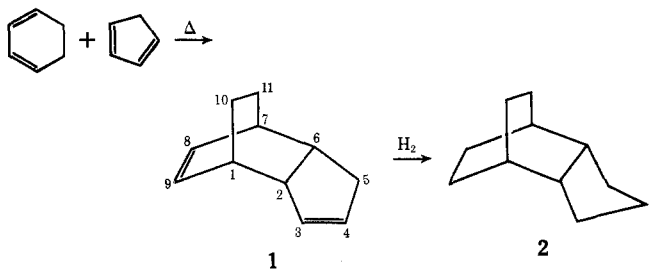
Oxymercuration–sodium borohydride reduction of *endo*-tricyclo[5.2.2.0^{2,6}]undeca-3,8-diene (1) was found to proceed highly regioselectively and stereospecifically, giving 4-*exo*-hydroxy-*endo*-tricyclo[5.2.2.0^{2,6}]undec-8-ene (3). Saturation of the 8,9 ethylenic bond in 1 resulted in a great reduction in the reactivity as well as the stereoselectivity. In contrast to this, hydroboration of 1 proceeded stereospecifically but not regiospecifically, to give three *exo*-hydroxytricycloundecene isomers. The result suggests a trans addition mechanism for the oxymercuration of 1 with the attack of mercuric ion from the endo side of the diene, the transition state being stabilized with the coordination of the 8,9 ethylenic bond to the mercuric ion.

In a series of the studies on biological activities of substituted polycycloalkanes,[1] we have been interested in the plant-hormonal properties of hydroxypolycycloalkanes. After some hydroxynorbornanes and -adamantanes as well as 3-[2] and other hydroxy derivatives of 4-homoisotwistane (tricyclo[5.3.1.0^{3,8}]undecane) had been tested,[3] examination of the activity of tricyclo[5.2.2.0^{2,6}]undecane (2) with hydroxy substituents was planned. The hydrocarbon 2 was prepared for the first time by us[4–6] through hydrogenation of the Diels–Alder adduct (1)[7] of cyclohexa-1,3-diene and cyclopentadiene. Although adamantane rearrangement of 2 under the catalysis of Lewis[4,5] and Bronsted[5,6,8] acids was studied, no functionalization reaction has been attempted to date. In this paper, oxymercuration–demercuration and hydroboration–oxidation of *endo*-tricyclo[5.2.2.0^{2,6}]undeca-3,8-diene (1) giving a variety of hydroxy compounds related to 2 are described.

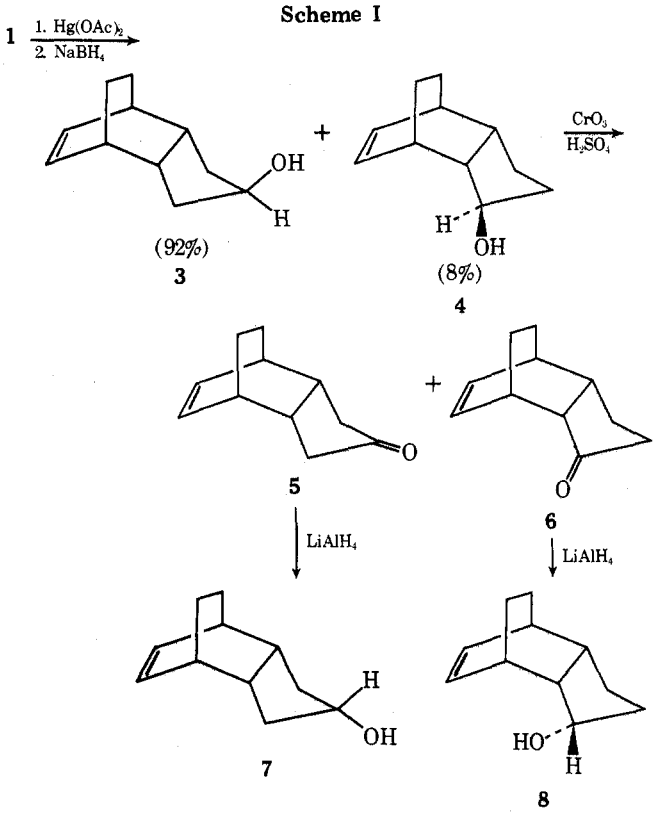


Results

Oxymercuration–sodium borohydride reduction[9,10] of *endo*-tricyclo[5.2.2.0^{2,6}]undeca-3,8-diene (1) in aqueous tetrahydrofuran at ambient temperature for 1 hr gave in 96% yield a mixture of 92% 4-*exo*-hydroxy (3) and 8% 3-*exo*-hydroxy (4) derivatives of *endo*-tricyclo[5.2.2.0^{2,6}]undec-8-ene (13) (Scheme I). The ratio of the two isomeric alcohols in the product was determined on a Golay GC–MS, since conventional VPC could not separate them. However, a pure sample of 3 could be isolated by repeated recrystallizations.

The structure of the alcohol 3 was established as follows.

Scheme I



The ^{13}C NMR spectrum indicated that the molecule had a C_s symmetry, showing a correct chemical shift,[11] fine structure, and relative intensity of the signal for the hydroxy-substituted 4-carbon atom. The structure assignment was supported by the ^{1}H NMR spectrum, which had a olefinic proton signal corresponding to that of bicyclo[2.2.2]oct-2-ene,[12] and in which no resonance similar to that of the olefinic protons of 3,4-dimethylcyclopentene[13] was observed.

Jones oxidation[14] of the above oxymercuration–demercuration product from 1 gave a mixture of *endo*-tricy-