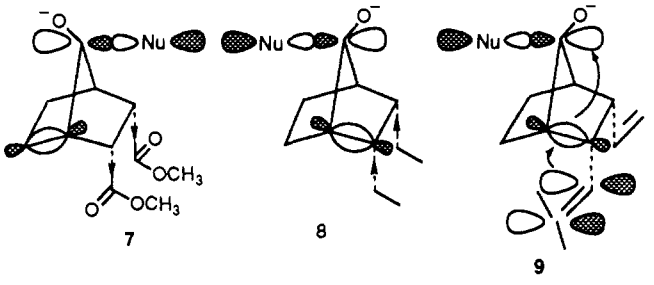
E alcohols in the ^1H NMR spectrum.[8] This trend was further confirmed through Eu(fod)$_3$ induced shift reagent studies.

The results summarized in Table I demonstrate a very significant variation in face selectivity as a function of 2,3-endo,endo substitution, the most dramatic being the reversal in *E*:*Z* ratio in going from **2a** (84:16) to **2e** (20:80). The predominant approach of nucleophiles to the syn face in **2a** and to the anti face in **2e** is fully consonant with the prediction based on the Cieplak's hyperconjugative model[3] according to which delocalization of σ electrons in the electron-rich antiperiplanar bond into the incipient σ^* orbital lowers the transition-state energy as indicated in **7** and **8**, respectively. The anti-face preference in the case of **2b** and **2c**, having groups traditionally considered as electron withdrawing ($-I$),[10] is somewhat unexpected at first sight but may be attributed to through-space donation in a perpendicular conformation as shown in **9** for **2c**.[11]



In summary, we have shown for the first time that π-facial selectivities in nucleophilic additions to 7-norbornanones can be electronically fine-tuned, and further theoretical and experimental work is currently underway.

Supplementary Material Available: Tables of ^1H and ^{13}C NMR and LRMS/HRMS data on all key compounds mentioned in this paper along with copies of spectra (16 pages). Ordering information is given on any current masthead page.

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(11) We thank Professor W. J. le Noble for this suggestion.

Synthesis of New Tricyclic Chiral P-H Bond Phosphoranes, "Triquinphosphoranes", from Chiral Diaminodiols. Asymmetric Addition on an Activated Carbonyl Compound

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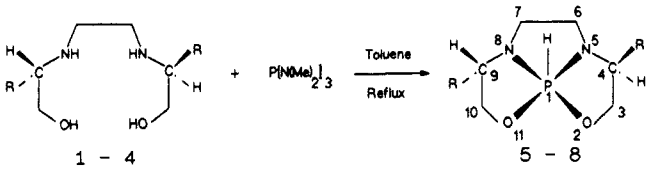
Received October 31, 1989

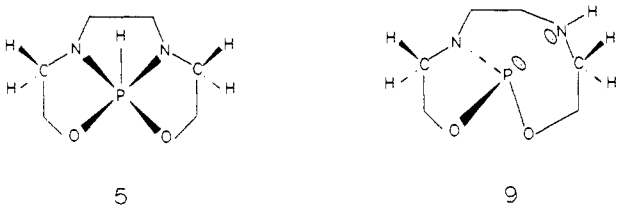
It is well-known that the P-H bond in hydridophosphoranes reacts with carbonyl compounds, leading to P–C bond formation.[1,2] However, to our knowledge, asymmetric addition of chiral hydridophosphoranes[3,4] to carbonyl compounds is without precedent. We report herein the synthesis (Scheme I) of a new class of tricyclic, chiral hydridophosphoranes, the "triquinphosphoranes",[5] from chiral diaminodiols, as well as their asymmetric addition to an activated carbonyl compound, ketopantolactone.[6]

Scheme I[a]

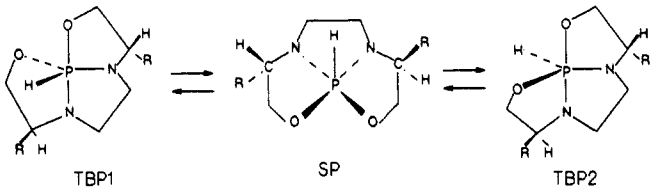


[a] **1** and **5**, R = H; **2** and **6**, R = CH_3; **3** and **7**, R = $CH(CH_3)_2$; **4** and **8**, R = CH_2Ph.

Scheme II



Scheme III



Compounds **5–8** were easily prepared in 80–90% chemical yields by the usual stoichiometric exchange reaction between diaminodiol[7] (0.3 M) (**1–4**) and hexamethylphosphorous triamide (1 equiv), in refluxing toluene under a nitrogen atmosphere, for 1 h.[8] Chiral C_2 symmetry axis diaminodiols **2–4** are particulary promising for the synthesis of chiral phosphoranes. They were synthesized in two steps from the methyl ester hydrochloride of the corresponding natural amino acid[9] (for **2**, (*S*)-(+)-alanine, **3**, (*S*)-(+)-valine; **4**, (*S*)-(−)-phenylalanine).

The $^{31}P\{^1H\}$ NMR spectra of these hydridophosphoranes exhibit only one single high-field signal ($\delta \approx -36.5$),[8] characteristic of 5-coordinated phosphorus compounds,[10] and a large coupling constant ($^1J_{PH} \approx 715$ Hz)[8] revealing a pronounced s character for the P-H bond. No signal was detected for the bicyclic alk-

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(4) Jeanneaux, F.; Riess, J. G.; Wachter, J. *Inorg. Chem.* **1984**, *23*, 3036.
(5) (4*S*,9*S*)-4,9-Dialkyl-2,11-dioxa-5,8-diaza-1λ^5-phosphatricyclo-[6.3.0.0^{1,5}]undecane: "triquinphosphorane" by analogy with the name "triquinacene" coined by Woodward et al. (*J. Am. Chem. Soc.* **1964**, *86*, 3162).
(6) Dihydro-4,4-dimethyl-2,3-furandione: ketopantolactone.
(7) *N*,*N*'-Bis(1-alkyl-2-hydroxyethyl)ethylenediamine: diaminodiol.
(8) After the removal of toluene under reduced pressure, the compounds were isolated by either distillation or recrystallization. **5** is obtained in 80% chemical yield: bp 75 °C/0.05 mmHg; $^{31}P\{^1H\}$ NMR δ −37.3 ($^1J_{PH}$ = 721 Hz). **6** (82%): bp 80 °C/0.05 mmHg; $[\alpha]^{22}_D$ +94.0° (*c* 1.18, $PhCH_3$); $^{31}P\{^1H\}$ NMR (toluene-d_8) δ −37.1 ($^1J_{PH}$ = 711 Hz). **7** (85%): bp 110 °C/0.05 mmHg; $[\alpha]^{22}_D$ +28.6° (*c* 1.10, $PhCH_3$); $^{31}P\{^1H\}$ NMR δ −35.2 ($^1J_{PH}$ = 712 Hz). **8** (80%): mp 71 °C (recrystallized from cyclohexene); $[\alpha]^{22}_D$ +49.5° (*c* 0.98, $PhCH_3$); $^{31}P\{^1H\}$ NMR δ −36.3 ($^1J_{PH}$ = 723 Hz).
(9) (a) For compound **4**, see: Vriesema, B. K.; Lemaire, M.; Buter, J.; Kellogg, R. M. *J. Org. Chem.* **1986**, *51*, 5169. (b) For an analogous compound with (*S*)-(−)-proline, see: Colombo, L.; Gennari, C.; Poli, G.; Scolastico, C. *Tetrahedron* **1982**, *38*, 2725. Marchelli, R.; Dradi, E.; Dossena, A.; Casnati, G. *Tetrahedron* **1982**, *38*, 2061. Lodi, T.; Marchelli, R.; Dossena, A.; Dradi, E.; Casnati, G. *Tetrahedron* **1982**, *38*, 2055.
(10) Tebby, J. C. *Methods in Stereochemical Analysis: Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, D. L., Eds.; VCH Publishers: Deerfield Beach, FL, 1987; Vol. 8, p 40.

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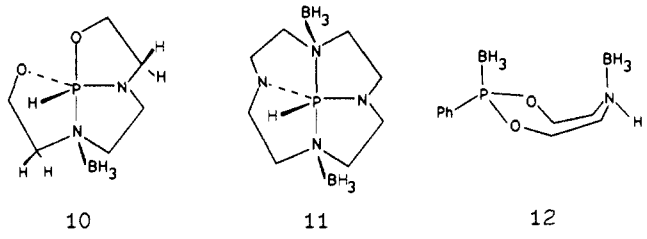
Scheme IV



10 11 12

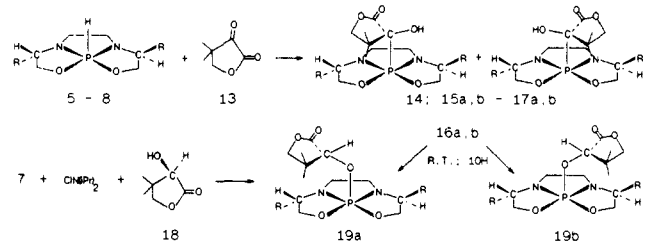
oxyoxazaphospholane **9**[11] (Scheme II), even at higher temperature[11a] (80 °C), or in a polar solvent such as DMSO-d_6 at room temperature.

The ^{13}C NMR spectrum of **5** shows magnetic equivalence of carbon atoms C_3 and C_{10} (δ 59.1), C_4 and C_9 (δ 44.9), and C_6 and C_7 (δ 43.4), and they remain unchanged between −90 and 25 °C. With chiral phosphoranes **6–8**, the same carbon atoms become anisochronous; for **6**: C_3, C_{10} (δ 67.0, 65.7); C_4, C_9 (δ 51.7, 48.7); C_6, C_7 (δ 42.7, 38.6); and the methyl groups (δ 19.2, 17.8). The NMR spectroscopic data for **5** are consistent with either a time-averaged spectrum characteristic of a low-energy Berry pseudorotation process[12] of the trigonal-bipyramidal structure (TBP) (with racemization of the phosphorus atom and exchange of corresponding methylene carbons of the tricyclic structure) or the achiral square-pyramidal structure (SP) (Scheme III). In the TBP structure the five-membered rings are in apical equatorial positions with one nitrogen atom in the uncustomary apical position;[13] in the SP structure the five-membered rings occupy basal positions. The same is true for **6–8**, but in these cases there are two possible diastereomeric TBP structures (TBP1, TBP2) (with epimerization at the phosphorus atom and interchange of anisochronous carbon atoms) or one chiral SP structure. The difference in conformational energies,[14] 2.0 ± 1.5 kcal/mol of relative stability for the TBP form over the SP structure, reflects a small energy barrier between these structures and accounts for a fast pseudorotation process (Scheme III).

Hydridophosphorane **5** (0.3 M) in benzene solution reacts with BH_3·SMe_2 complex in THF (1.1 equiv) at room temperature, in 20 min under a nitrogen atmosphere, to afford the stable monoborane adduct **10** in 90% chemical yield (recrystallized from diethyl ether): mp 110 °C; $^{31}P\{^1H\}$ NMR (in toluene-d_8) δ −24.5 ($^1J_{PH}$ = 820 Hz); $^{11}B\{^1H\}$ NMR δ −15.6 ($^1J_{BH}$ = 93 Hz). This reactivity can be compared with that of cyclenphosphorane, in which the two apical nitrogen atoms react with B_2H_6, giving the bis(borane) adduct **11**,[15] rather than that of a bicyclophosphorane, in which the equatorial nitrogen atom reacts with B_2H_6, leading to an open-form diborane like **12**[16] (Scheme IV).

Hydridophosphoranes **5–8** react readily with ketopantolactone (Scheme V). Indeed, $^{31}P\{^1H\}$ NMR spectroscopy shows that at room temperature **6–8** in toluene-d_8 solution (0.4 M) react quantitatively with **13** (1 equiv) to afford in less than 1 min chiral diastereomer phosphorane alcohols[17] **15a,b** (ratio, 93:7), **16a,b** (95:5), and **17a,b** (92:8). Nominal structures of these phosphorane alcohols are unambiguously established by spectroscopic data.[18,19] The observed diastereoselectivity (90% for **16a,b**) results from the asymmetric induction during the C–P bond formation. The inertness of the monoborane adduct **10** (one nitrogen atom lone pair is coordinated with BH_3) toward **13** indicates that in triquinphosphoranes **5–8** the nucleophilicity of the apical nitrogen atom (in a favorable TBP structure) is the key fact, as it is presumed to be, for their reactivity. Nevertheless, the mechanism of phosphorane alcohol formation remains unknown and requires complementary experimental work.[20]

Scheme V[a]



5 - 8 13 14; 15a,b - 17a,b 16a,b R.T.; 10H 7 18 19a 19b

[a] **14**, R = H; **15a,b** R = CH_3; **16a,b**, R = $CH(CH_3)_2$; **17a,b**, R = CH_2Ph.

Phosphorane alcohols, pure or in solution, are transformed quantitatively into alkoxyphosphoranes when they are kept at room temperature for 10 h (e.g., compounds **16a,b** lead to **19a** and **19b**[21]) (Scheme V). Such a rearrangement is analogous to that of Brook[22] and found in silylcarbinol compounds. These alkoxyphosphoranes can be independently synthesized by the action of pantolactone[23] (**18**) on **7** in CH_2Cl_2 solution in the presence of chlorodiisopropylamine (2 equiv). Thus, when (*R*)-pantolactone was used, only **19a**, corresponding to the major diastereomer obtained from the rearrangement, was formed.

The chemistry of "triquinphosphoranes" **5–8** and their possible applications in coordination chemistry and asymmetric catalysis are currently under investigation, and results will be reported.

Acknowledgment. We thank Prof. W. G. Bentrude of the University of Utah, who has played a great part in the correction of this manuscript.

Supplementary Material Available: ^{13}C NMR data, IR data, and elemental analyses for compounds **5–8**, **10**, **16a,b**, and **19a** and experimental procedures for **16a,b** and **19a** (2 pages). Ordering information is given on any current masthead page.

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(16) Contreras, R. *Tetrahedron Lett.* **1981**, 3953.

(17) Each diastereomeric compound possesses an asymmetric extracyclic carbon and an asymmetric phosphorus atom and should therefore exist as a pair of diastereomers. The detection of only two signals is due to the pseudorotation process described for the phosphoranes (Scheme III).

(18) Compounds **16a,b** (in toluene-d_8) exhibit two $^{31}P\{^1H\}$ NMR signals at δ −12.5 (95%) and δ −13.5 (5%), the ^{13}C NMR spectrum shows only the doublet of the major product (for PCOH) at δ 82.8 ($^1J_{PC}$ = 145 Hz),[19] and the ^1H NMR spectrum exhibits the two doublets (for PCO*H*) at δ 8.80 ($^3J_{PH}$ = 25.0 Hz) (5%) and at δ 8.25 ($^3J_{PH}$ = 24.5 Hz) (95%). However, from the spectral data the assignment of the diastereomers cannot be established. **14**: $^{31}P\{^1H\}$ NMR δ −17.4. **15a,b**: δ −15.1 (93%), δ −16.0 (7%). **17a,b**: δ −13.3 (92%), δ −14.4 (8%).

(19) Cavell, R. G. *Methods in Stereochemical Analysis: Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, D. L., Eds.; VCH Publishers: Deerfield Beach, FL, 1987; p 239. Schmidbauer, A.; Buchner, W.; Kohu, F. H. *J. Am. Chem. Soc.* **1974**, *96*, 6208.

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(21) **19a** (75%) (recrystallized from hexane): mp 72 °C; $^{31}P\{^1H\}$ NMR δ −18.5 (75%); ^{13}C NMR (for POCH) δ 77.7 ($^2J_{PC}$ = 10.2 Hz); ^1H NMR (for POC*H*) δ 4.84 ($^3J_{PH}$ = 13.4 Hz). **19b**: $^{31}P\{^1H\}$ NMR δ −18.0 (25%); ^{13}C NMR (for POCH) δ 78.2 ($^2J_{PC}$ = 4.7 Hz); ^1H NMR (for POC*H*) δ 4.77 ($^3J_{PH}$ = 13.8 Hz).

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