taken as the binuclear radical–cation VIII, formed *via* precursor complex VII (which cannot be chelated), the latter is present only at small steady-state concentrations, whereas conversion to VIII is very nearly complete. Intermediate VIII appears then, in the presence of excess Cr^{2+}, to be attacked by a second Cr^{2+} (very probably at one of the ring nitrogens).[5]

Complex VI is thus similar to I in that both heterocyclic systems readily accept an electron from Cr^{2+} to form a moderately stable radical–cation which can undergo internal electron transfer with reduction of Co(III). The cinnoline reduction is, however, complicated by the availability of an additional site at which further rapid external reductive attack may occur. Work is continuing in an effort to define the structural features within the ligand which favor one or the other type of behavior.[7,9]

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(5) Further elaboration of Scheme II is necessary to accommodate the earlier finding[1b] that when oxidant VI is in excess, just 1 equiv of Co^{2+} is eventually produced for each equivalent of Cr^{2+} taken. The alternatives appear to be a second, intramolecular path for reduction of Co(III) in VIII, which becomes important when only a deficiency of Cr^{2+} is taken, or, less likely, a slow reduction of Co(III) in VI by radical cation IX, in a manner similar to that proposed for radical–cations in the pyridine series.[6]

(6) C. Norris and F. R. Nordmeyer, *J. Amer. Chem. Soc.*, **93**, 4044 (1971); J. R. Barber, Jr., and E. S. Gould, *ibid.*, **93**, 4045 (1971).

(7) Although the rates of formation of the strongly absorbing intermediates derived from oxidants I and VI are independent of acidity in the (H^+) range 0.12–1.20 *M*, the rates of disappearance of these species are acid-dependent but in opposite directions. The fading of the intermediate from I is 0.7 times as rapid in 0.12 *M* $HClO_4$ (μ = 1.22) as in 1.2 *M* $HClO_4$, whereas the intermediate from VI disappears about twice as rapidly at the lower acidity. These trends correspond to those observed in the Cu^+ reductions of these complexes[8] and are in accord with the suggestion that protonation of the 4-nitrogen in the pyrazine complex facilitates electron transfer to Co(III) within a dinuclear intermediate, whereas with the cinnoline complex, H^+ and the reducing metal center compete for a basic "lead-in" site.

(8) E. R. Dockal, E. T. Everhart, and E. S. Gould, *J. Amer. Chem. Soc.*, **93**, 5661 (1971).

(9) A similar, but much more short-lived, Co(III)-bound radical–cation intermediate has recently been characterized in the e_{aq}^- reduction of *p*-nitrobenzoatopentaamminecobalt(III) by M. Z. Hoffman and M. Simic, *ibid.*, **94**, 1757 (1972). These authors report a specific rate of 2600 sec^{-1} for internal electron transfer, at pH 5.5–7.7, but there is evidence[10] that this radical–cation may be greatly stabilized by conversion to its conjugate acid in 1.2 *M* $HClO_4$.

(10) E. S. Gould, *ibid.*, **88**, 2983 (1966).

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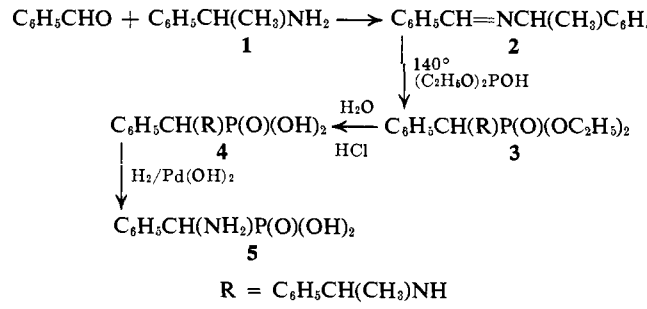
Synthesis of an Optically Active α-Aminophosphonic Acid

Sir:

Although various syntheses for α-aminophosphonic acids have been known for several years,[1-3] an optically active acid has not been reported to date. We wish to report the synthesis of the first optically active α-aminophosphonic acid. We have succeeded in preparing both enantiomers of α-aminobenzylphosphonic acid and we wish in further work to develop this synthesis into a general procedure for preparing the optically active phosphonic acid analogs of various amino acids.

The α-aminobenzylphosphonic acid enantiomers **5** were prepared by condensing benzaldehyde with either (*R*)-(+)- or (*S*)-(−)-α-methylbenzylamine (**1**) to form the respective Schiff's base **2**. The diethyl ester **3** was prepared by heating a mixture of **2** with diethyl hydrogen phosphonate at 140° for 1 hr.[4] The ester was hydrolyzed in concentrated HCl and evaporated to dryness. Treatment of the hydrochloride salt dissolved in a minimum amount of water with propylene oxide[5] gave **4**. The final product **5** was obtained by hydrogenolysis of the α-methylbenzyl group on a low-pressure Paar hydrogenator using 10% $Pd(OH)_2/C$[6] in glacial acetic acid at room temperature. Removal of the acetic acid gave a solid mass which was recrystallized from water–ethanol. Physical properties of both enantiomers were identical with the known racemic acid.[4c] Synthesis of **5** with (*S*)-(−)-α-methylbenzylamine gave the dextrorotatory enantiomer, $[\alpha]^{25}D$ +18.1° (*c* 2.0, 1 *N* NaOH), and the (*R*)-(+)-amine gave the levorotatory enantiomer, $[\alpha]^{25}D$ −18.1° (*c* 2.0, 1 *N* NaOH). Preliminary testing of each isomer with D-amino acid oxidase has failed to give an indication of absolute configuration.



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Biogenetically Patterned Approaches to Eudesmane Sesquiterpenes. A Total Synthesis of (±)-Junenol

Sir:

Nonenzymic cationic cyclizations of farnesol derivatives have been extensively investigated as a means for accomplishing biogenetic-type syntheses of sesquiterpenes.[1] While several representatives of sesquiterpene

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