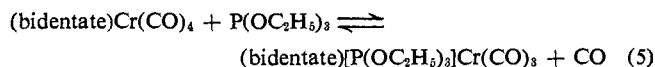


Figure 1. Plots of K_{obsd} vs. $[L]$ at various temperatures for the reaction of $(\text{tmen})\text{Cr}(\text{CO})_4$ with triethyl phosphite in methylcyclohexane.

$\Delta S_2^\ddagger - \Delta S_3^\ddagger = -33.4 \pm 17.2$ eu. The positive entropy of activation for the dissociation of one end of the chelating tmen is consistent with the indicated mechanism. The results strongly suggest that mechanism II may be important for other reactions involving octahedral metal carbonyl derivatives containing chelating groups and which exhibit rate dependence on ligand concentration. This should be especially true for the smaller metal atoms of the first transition series for which an associative mechanism is less plausible.

These results may also be contrasted with those reported by Angelici and Graham for the reaction of $(\text{dmp})\text{Cr}(\text{CO})_4$ ($\text{dmp} = 1,2\text{-diamino-2-methylpropane}$) with phosphites, for which a ligand-independent rate law was found, and for which replacement of CO to give $(\text{dmp})(\text{L})\text{Cr}(\text{CO})_3$ rather than replacement of the chelating group was observed.⁹ Reaction of $(\text{tmen})\text{Cr}(\text{CO})_4$ with triethyl phosphite in refluxing *n*-heptane results in the formation of *trans*- $[\text{P}(\text{OC}_2\text{H}_5)_3]_2\text{Cr}(\text{CO})_4$, as shown by infrared spectrum and chemical analysis; no carbonyl replacement was noted.

The difference in behavior of $(\text{dmp})\text{Cr}(\text{CO})_4$ and $(\text{tmen})\text{Cr}(\text{CO})_4$ in their reactions with phosphites may arise as a consequence of the more stringent steric requirements of tmen. For reactions of $(\text{tmen})\text{Mo}(\text{CO})_4$ with Lewis bases, bulky triphenylphosphine and triphenyl phosphite replace tmen without CO loss, while trimethyl phosphite replaces CO to give *cis*- $(\text{tmen})\text{P}(\text{OCH}_3)_3\text{Mo}(\text{CO})_3$.¹⁰ These observations suggest that the equilibrium



may be shifted further to the left for tmen than for

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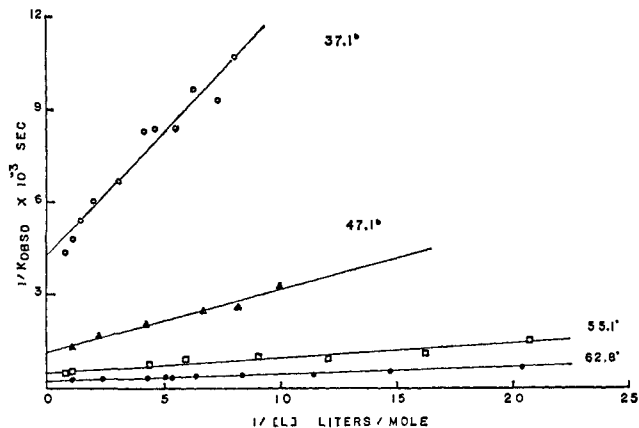


Figure 2. Plots of $1/k_{\text{obsd}}$ vs. $1/[L]$ at various temperatures for the reaction of $(\text{tmen})\text{Cr}(\text{CO})_4$ with triethyl phosphite in methylcyclohexane.

dmp. On the other hand, the correlation between a ligand's "hardness"¹¹ and its ability to labilize carbonyls⁹ has been attributed to inhibition of carbonyl-to-metal σ -bond formation by strongly basic substituents.¹⁰ The steric demands of tmen may diminish its basicity toward the chromium carbonyl moiety, thus strengthening carbonyl-to-metal σ bonds in $(\text{tmen})\text{Cr}(\text{CO})_4$ relative to those in $(\text{dmp})\text{Cr}(\text{CO})_4$.

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A Revised Structure for Ceanothine-B

Sir:

Peptide alkaloids have been found in a number of plants of the family Rhamnaceae.¹⁻¹¹ Among these

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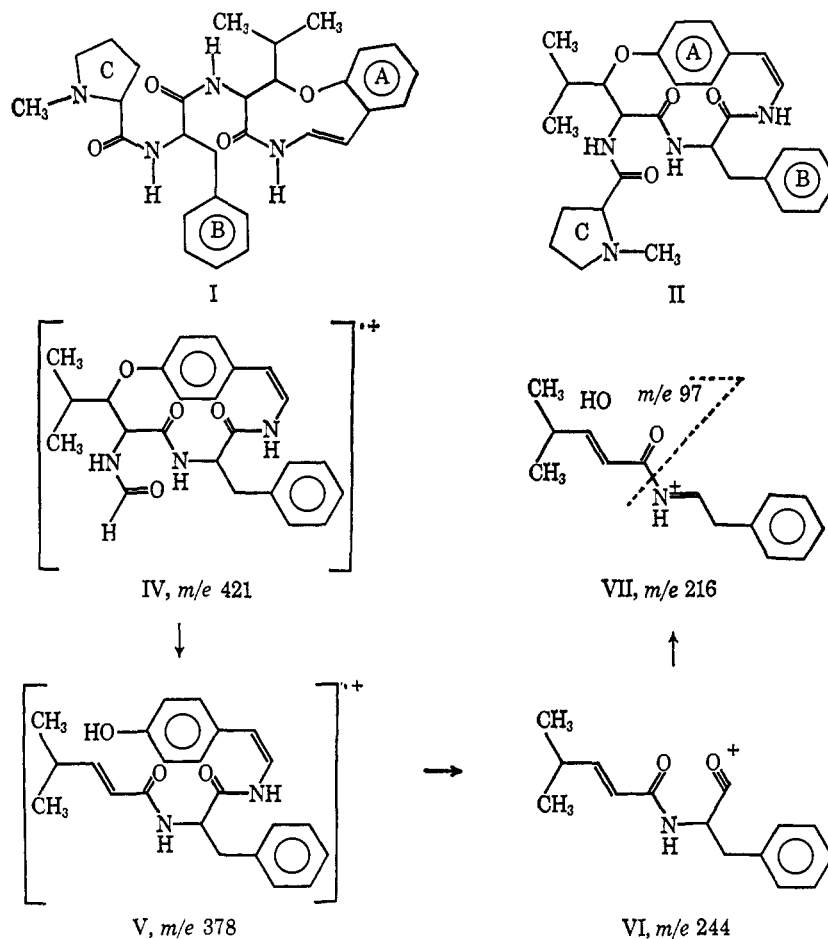
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is ceanothine-B, a component of *Ceanothus americanus*, which was first isolated by Bertho and Liang¹² in 1933, and later in pure form by Saltzman¹⁰ and by Warnhoff, *et al.*;⁴ these last workers proposed I as the structure. We believe, on the basis of the evidence cited below, that II better represents ceanothine-B.

Complete hydrolysis (6 *N* hydrochloric acid) of dihydroceanothine-B (III) yielded *p*-aminoethylphenol (tyramine) rather than *o*-aminoethylphenol which would be expected from dihydro-I, in addition to *N*-methylproline, β -phenylalanine, and α -ketoisocaproic acid. These compounds were all identified by comparison with authentic samples by paper chromatography, tlc, gas chromatography (trimethylsilyl derivatives), and mass spectroscopy.

The previous assignment⁵ of *ortho* substitution in ring A was assigned on the basis of absorption at 757 cm^{-1} in the infrared spectrum of II. We suggest that this band and one of nearly equal intensity at 707 cm^{-1} arise from the C-H out-of-plane bending vibrations of the monosubstituted ring B, and the *para*-substituted A ring gives rise to a somewhat weaker band at 839 cm^{-1} .¹³

The 60-MHz nmr spectrum of the alkaloid does not allow one to corroborate the substitution pattern of ring A since the aromatic protons of this ring and those of ring B overlap.

The mass spectra of II, III, and dideuterio-II are similar to those obtained by Tschesche for scutianine,⁶ frangulanine,⁸ integerressine,⁷ integerrenine,⁷ and inte-

gerrine⁹ which all have been shown to have the 14-membered ring of II. A 14-membered ring has also been very recently proposed for americine,¹¹ another alkaloid from *Ceanothus americanus*. Of particular interest in the mass spectrum of the alkaloid (parent: m/e 504) are the ions at m/e 421, 378, 244, and 216 (IV-VII). This sequence of ions can only be accounted for by a 14-membered-ring compound such as II and not by I. If the alkaloid possessed a nine-membered ring such as I, its mass spectrum would contain an ion at m/e 274 (*cf.* IV) resulting from cleavage of the dipeptide residue; no ion is found at m/e 274.

The partial hydrolysis of III yielded a product whose mass spectrum shows a large parent peak at m/e 395 (derived from III by loss of the *N*-methylprolyl group) and a base peak at m/e 120 (in contrast to the base peak of II or III at m/e 84). This spectrum is identical with that of the partial hydrolysis product of scutianine.⁶

The revised structure of ceanothine-B shows the similarity of the alkaloids of *Ceanothus americanus* to those from other members of the Rhamnaceae family whose structures have been reported. We have found that ceanothamine-B⁴ is identical with frangulanine⁸ (isolated from *Rhamnus frangula*) and that ceanothamine-A⁴ is identical with adouetine-X^{2,8} (isolated from *Waltheria americana*). A further report is in preparation.

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