

of this reaction, produced bicyclo[4.2.0]octane by oxidative decomposition (bp 129–131 °C (760 mmHg)) which appeared to be the trans isomer, while the *cis*-2-nickelacyclopentane complex afforded the *cis* isomer (bp 136–139 °C (760 mmHg)); cf. bp 136–138 °C (760 mmHg) of A. T. Blomquist and J. Kwiatek, *J. Am. Chem. Soc.*, **73**, 2098 (1951). Details are given in ref 6b.

- (14) The product was compared with an authentic sample of *cis*- and *trans*-1,2-dicyanocyclobutane obtained from Aldrich Chemical Co.: NMR  $\delta$  3.45 (m, 2 H), 2.40 ppm (broadened d of d, 4 H). The GLC trace was similar to that of the commercial isomer mixture.
- (15) A. Miyashita and R. H. Grubbs, unpublished results.
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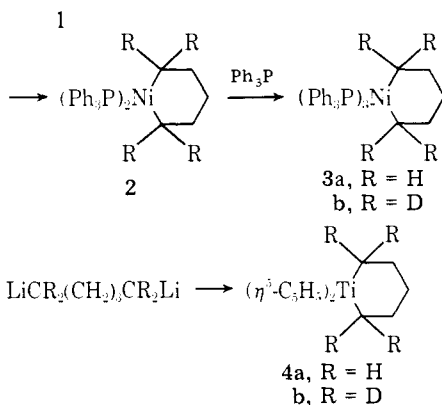
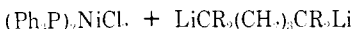
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### Carbon–Carbon Bond Cleavage Reactions in the Decomposition of Metallacycles

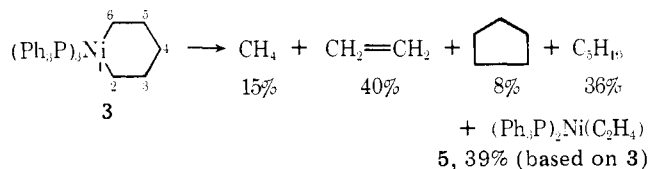
Sir:

We recently reported that trisphosphine and five-coordinate nickelacyclopentanes and titanacyclopentanes decomposed by  $\beta$ -C–C bond cleavage to produce ethylene. To determine if C–C bond cleavage would occur in systems which could not produce stable metal–olefin complexes, metallacyclohexanes were prepared. Bis(triphenylphosphine)dichloronickel(II) and titanocene dichloride were treated with 1,5-dilithiopentane (**1**) at low temperature to yield **2** and **4** which were purified and analyzed by procedures similar to those used in the preparation of the related metallacyclopentanes.<sup>1a,2,3</sup>



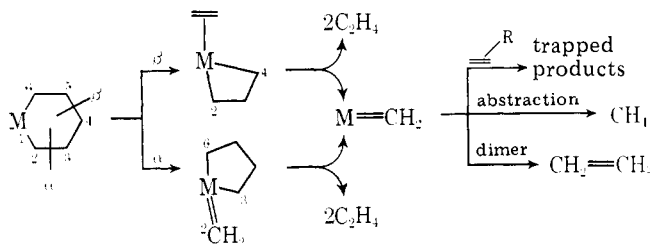
The yields of the decomposition products of **2**, **3**, and **4** and **4** are given in Table I. Those conditions which resulted in C–C

bond cleavage in the metallacyclopentanes also gave high yields of C–C bond cleavage products in the metallacyclohexanes. For example, the five-coordinate nickel complex **3** produced ethylene and  $\text{Ni}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$  (**5**) as the major products.<sup>4</sup> The chemistry of this complex will be examined first.

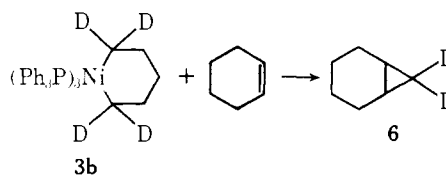


Either  $\alpha$ - or  $\beta$ -C–C cleavage would result in the ultimate production of a carbenoid complex which could yield the observed products (Scheme I).

Scheme I



Based on past results  $\beta$  cleavage would be expected to be the major pathway of decomposition of metal alkyls; however the  $\alpha$  cleavage route could be demonstrated to be the major route by deuterium labeling. Tris(triphenylphosphine)pentamethylenenickel(II)-2,2,6,6-*d*<sub>4</sub> (**3b**) was prepared and allowed to decompose in the presence of cyclohexene. Up to 10% (per Ni)



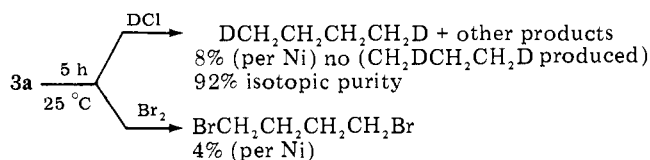
yields of norcarane (**6**) of high isotopic purity were isolated.<sup>5</sup> The isotopic purity decreased from 90 to 70% as the reaction progressed.<sup>6</sup> This suggested that the loss of isotopic purity was due to some competing reaction which moved the label from the 2,6 positions.<sup>7</sup> The fact that the isotopic purity was above 50% demonstrated that  $\alpha$ -C–C bond cleavage occurred first.  $\beta$  cleavage would have given a maximum of 50% purity since a labeled carbon and an unlabeled carbon become equivalent in the intermediate resulting from  $\beta$  cleavage.<sup>8</sup> Other evidence for initial  $\alpha$ -C–C bond cleavage was the lack of C<sub>3</sub> products

Table I. Decomposition Reactions of Metallacyclohexane Complexes<sup>a</sup>

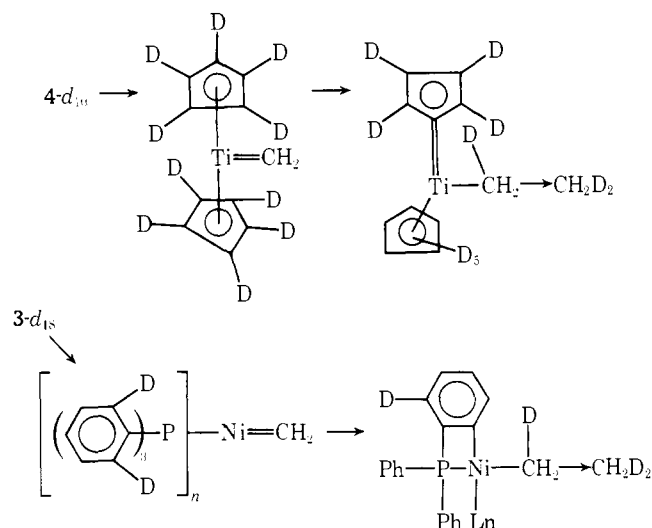
comps	reaction condition, °C, h	percent of decomposition products <sup>b</sup>					
		CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>4</sub> H <sub>8</sub>	c-C <sub>5</sub> H <sub>10</sub>	C <sub>5</sub> H <sub>10</sub>
Ni(CH <sub>2</sub> ) <sub>5</sub> (PPh <sub>3</sub> ) <sub>3</sub> ( <b>3a</b> )	23, 24	15	40	0	1	8	36
<b>3a</b> + PPh <sub>3</sub> <sup>c</sup>		4	64	0	1	4	27
Ni(CH <sub>2</sub> ) <sub>5</sub> (PPh <sub>3</sub> ) <sub>2</sub> ( <b>2a</b> )		3	8	0	5	68	16
<b>2a</b> + PPh <sub>3</sub> <sup>c</sup>		7	56	0	1	6	30
<b>2a</b> + <i>h</i> $\nu$ <sup>d</sup>	0, 2	30	43 <sup>e</sup>	5	5	15	0
Ti(CH <sub>2</sub> ) <sub>5</sub> Cp <sub>2</sub> ( <b>4a</b> )	23, 6	1	1	0	1	34 <sup>f</sup>	63
<b>4a</b> + PR <sub>3</sub> <sup>g</sup>		44	15	4	20	12 <sup>f</sup>	5
<b>4a</b> + <i>h</i> $\nu$ <sup>h</sup>	–40, 3	60	7	0	1	24 <sup>f</sup>	8

<sup>a</sup> Decomposition reactions were performed in toluene solution for **2a**, **3a**, and decalin solution for **4a**. <sup>b</sup> Product gases were analyzed by GLC in the vapor phase as well as the solution phase. These were average values of several experiments. <sup>c</sup> Up to ten times excess triphenylphosphine was used. <sup>d</sup> Photolysis was performed in a quartz tube. During photolysis 54% of **2a** decomposed, while only trace amounts of **2a** decomposed in the dark. Trisphosphine complex, **3a**, gave almost the same decomposition pattern as **2a**. <sup>e</sup> This value contains 46% ethane. <sup>f</sup> No cyclopentane was observed but *n*-pentane was observed. <sup>g</sup> Tertiary phosphines such as PEt<sub>3</sub>, P(*n*-Bu)<sub>3</sub>, PPh<sub>3</sub>, or PCy<sub>3</sub> were used and each phosphine showed almost the same effect on the decomposition reaction of **4a**. <sup>h</sup> By photolysis 20% of **4a** decomposed but **4a** was stable at –40 °C in the dark.

as would have been expected from the metallacyclobutane produced from initial  $\beta$  cleavage.<sup>9</sup> Evidence for a  $C_4$  fragment came from quenching studies. Treatment of partially decomposed solutions of **3a** with DCl or bromine produced terminally labeled butanes.<sup>11</sup>



The proposed carbenoid intermediate provides a route to the methane produced from these two complexes. When either **3b** or **4b** was allowed to decompose the majority (>80%) of the methane was  $\text{CH}_2\text{D}_2$ . Thus, the majority of the methane resulted from the  $\alpha$  carbons of the metallacycles. The ligands were the source of the other 2 hydrogens. When either **4-d**<sub>10</sub><sup>13</sup> or **3-d**<sub>18</sub><sup>14</sup> was decomposed,  $\text{CH}_2\text{D}_2$  was again the major product. The greater yield of methane from the titanocene (**4**)

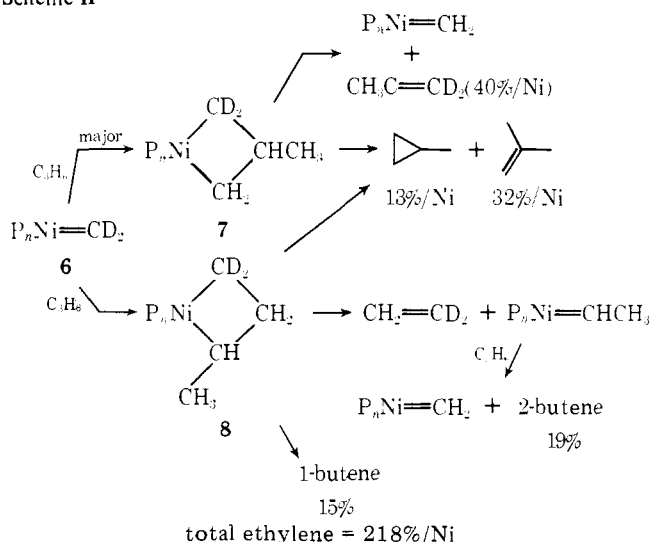


species suggested that the intramolecular C-H addition into the cyclopentadienyl ligand was more facile (compared with other reactions) than ortho metalation of the phosphine ligand.

This rapid intramolecular reaction also accounted for the low yield ( $\approx 1\%$ ) of norcarane produced when **4** was allowed to decompose in cyclohexene.

A very surprising reaction was observed when the nickel

Scheme II



complex **3** was decomposed in the presence of other olefins. 1,7-Octadiene was catalytically converted to cyclohexene (up to 560%/Ni) and ethylene. Also, propylene was converted to 2-butene and ethylene. These were the products of an *olefin metathesis reaction*.<sup>15</sup> As further confirmation, **3-d**<sub>4</sub> (**3b**) was used in the reaction with propylene. The propylene recovered at the end of the reaction contained propylene-1,1-d<sub>2</sub><sup>16</sup> (40%/Ni), a characteristic product of metathesis of primary olefins.<sup>17</sup> The by-products indicated in Scheme II show why the metathesis activity decayed rapidly.<sup>18</sup>

The competitive C-C bond cleavage (metathesis), reductive elimination, and  $\beta$ -hydride transfer reactions of the proposed metallacyclobutanes (**7**, **8**) were similar to the reactions of nickelacyclopentanes and nickelacyclohexanes<sup>19</sup> and the intermediates resulting from the reaction of other carbene and alkylidene complexes with olefins.<sup>20,21</sup>

Carbon-carbon bond cleavage can be a facile process in simple organometallic complexes and does not require the intervention of multimetal centers such as metal clusters or metal surfaces.

**Acknowledgment.** The financial support of the National Science Foundation is gratefully acknowledged.

## References and Notes

- (1) (a) R. H. Grubbs and A. Miyashita, *J. Am. Chem. Soc.*, **100**, 1300 (1978); (b) R. H. Grubbs and A. Miyashita, *J. Chem. Soc., Chem. Commun.*, 864 (1977).
- (2) (a) R. H. Grubbs, A. Miyashita, M. Liu, and P. Burk, *J. Am. Chem. Soc.*, **99**, 3863 (1977). (b) *ibid.*, **100**, 2418 (1978). (c) Bis(triphenylphosphine)nickelacyclohexane was prepared as bright yellow crystals in 49% yield from 1,5-dithiopentane and bis(triphenylphosphine)dichloronickel(II) by the same procedure used for the preparation of the nickelacyclopentane analogue.<sup>2a</sup> Anal. Calcd (2a): Ni, 9.00; P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, 83.4; C<sub>5</sub>/Ni, 1.00. Found: Ni, 9.13; P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, 84.0; C<sub>5</sub>/Ni, 0.97. The triphosphine **3a** was prepared from **2a** by allowing a toluene solution containing 3 g (4.6 mmol) of **2a** and 6.3 g (23 mmol) of triphenylphosphine to react at  $-10^\circ\text{C}$  for 4 h. Red-brown crystals of **3a** precipitated on cooling. The compound was obtained in 41% yield after recrystallization at  $-50^\circ\text{C}$  from toluene which had been saturated with triphenylphosphine at  $-60^\circ\text{C}$ . Anal. Calcd (3a): P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>/Ni, 3.00; C<sub>5</sub>/Ni, 1.00. Found: P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>/Ni, 2.87; C<sub>5</sub>/Ni, 0.98.
- (3) (a) J. X. McDermott, J. F. White, and G. M. Whitesides, *J. Am. Chem. Soc.*, **98**, 6521 (1976). (b) J. X. McDermott, M. E. Wilson, and G. M. Whitesides, *ibid.*, **98**, 6529 (1976). (c) To a suspension of titanocene dichloride (1.1 g, 4.4 mmol) in ether maintained at  $-70^\circ\text{C}$  was added 6.4 mmol of 1,5-dithiopentane in ether. After 4 h at  $-45^\circ\text{C}$  the titanocene dichloride had dissolved and 100  $\mu\text{L}$  of methanol was added. After filtration at  $-45^\circ\text{C}$  the solvent was removed in vacuo with the temperature below  $-45^\circ\text{C}$ . A hexane extract of the resulting orange brown solid was chromatographed over Florisil at  $-45^\circ\text{C}$ . The orange-red band was collected, concentrated, and cooled to  $-78^\circ\text{C}$ . Air-sensitive orange-red crystals, 0.3 g (27% yield) of **4a** were obtained. Anal. Calcd: Ti, 19.3; C<sub>5</sub>/Ti, 1.00. Found: Ti, 20.1; C<sub>5</sub>/Ti, 0.96.
- (4) The products were analyzed by GLC on a 20-ft Duopak, 10-ft 10% paraffin wax (Chromosorb W), and 12-ft Parapak Q columns. The ethylene complex **5** was isolated by precipitation with hexane and recrystallization at  $-78^\circ\text{C}$  from hexane-toluene (39% based on **3**).
- (5) Similar yields of methylene trapping products were obtained with norbornene. The isotopic purity was determined by mass spectrometry and <sup>1</sup>H NMR on GLC-purified samples.
- (6) The first sample of norcarane was collected after 10% of **3a** had decomposed and was 90% isotopically pure. The 70% isotopically pure sample was collected when the decomposition was complete.
- (7) More careful experiments suggested that the original pairs of deuteriums at the 2,6 positions had moved to other positions of the rings. Triphosphine complex **3a** was dissolved in toluene and stirred at  $0^\circ\text{C}$  for a few days. *n*-Pentane, which was produced by quenching with acid, was isolated by GLC and the labeled positions were determined by the mass spectral cracking pattern and by NMR spectroscopy. The two sets of deuterium originally bonded to the 2,6 carbons scrambled to the 3, 4, and 5 positions. More detailed mechanistic and kinetic studies are now in progress. This process provides a sufficient model for olefin metathesis.
- (8) This requires symmetry in the intermediate or an intramolecular rearrangement which equilibrates the two ends of the C<sub>3</sub> fragment more rapidly than attack by external olefin. Similar metallacyclopentanes undergo rapid pseudorotation processes<sup>18</sup> of the type required for this equilibration.
- (9) See discussion of trapping studies. Attempts to prepare nickelacyclobutanes by the addition of 1,3-dibromopropane to nickel(0) complexes resulted in the production of cyclopropane and propene as the major products.<sup>10</sup>
- (10) R. K. Stuart and R. H. Grubbs, unpublished results.
- (11) It was possible, but highly unlikely at the pressures used, that metallacyclopentanes are produced from **5** and the ethylene produced in the reaction.<sup>1,12</sup> Treatment of **3a** with bromine or HCl produced only C<sub>5</sub> products.
- (12) A. Miyashita and R. H. Grubbs, *J. Organomet. Chem.*, in press, and unpublished work.

- (13) Pentadeuteriocyclopentadiene (97.3% isotopic purity) was prepared by base catalyzed H-D exchange of cyclopentadiene with D<sub>2</sub>O.
- (14) Dry deuterium gas was slowly bubbled through a purple toluene solution containing RuHCl(PPh<sub>3</sub>)<sub>3</sub>·CH<sub>3</sub>Ph (1 g) and PPh<sub>3</sub> (7 g) at 90 °C for 2 days. After removal of the solvent under vacuum, tris(2,6-dideuteriophenyl)phosphine was obtained by sublimation from the white, purple residue (90–100 °C, 0.01 mmHg), 6.1 g (87% yield, 97.8% isotopic purity); G. W. Parshall, W. H. Knoth, and R. A. Schunn, *J. Am. Chem. Soc.*, **91**, 4990 (1969).
- (15) T. J. Katz, *Adv. Organomet. Chem.*, **16**, Chapter 9 (1977).
- (16) Isolated by GLC. The isotopic purity was determined by mass spectrometry and the position of the label was determined by NMR spectroscopy.
- (17) W. J. Kelly and N. Calderon, *J. Macromol. Sci., Chem.*, **9**, 911 (1975).
- (18) The titanocene analogue **4** did not catalyze the formation of metathesis products. Whether this was due to rapid destruction of the methylene by H abstraction or to electronic effects will require further investigation.
- (19) As further evidence, the intermediate produced from the reaction of 1,3-dibromobutane with Ni(COD)<sub>2</sub> yields ethylene (21%), methylcyclopropane (20%), and butenes (59%).<sup>10,22</sup>
- (20) S. J. McClain, C. O. Wood, and R. R. Schrock, *J. Am. Chem. Soc.*, **99**, 3519 (1977).
- (21) C. P. Casey and H. E. Tuinstra, *J. Am. Chem. Soc.*, **100**, 2290 (1978).
- (22) P. Diversi, G. Ingrassio, and A. Lucherini, *J. Chem. Soc., Chem. Commun.*, **52** (1977).
- (23) Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, Calif. 91125.

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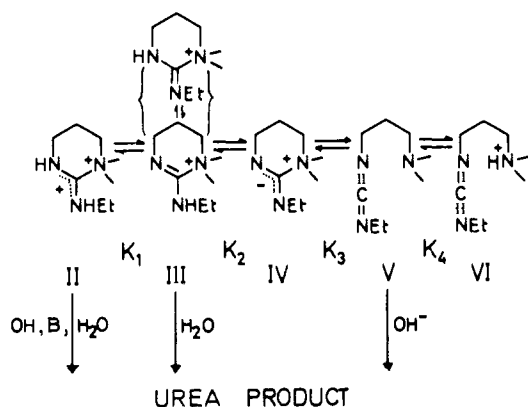
### Reaction of the Water-Soluble Reagent *N*-Ethyl-*N'*-(3-dimethylaminopropyl)carbodiimide with Nucleophiles: Participation of the Tautomeric Cyclic Ammonioamidinium as a Kinetically Important Intermediate

Sir:

Sheehan, Cruickshank, and Boshart<sup>1</sup> reported that *N*-ethyl-*N'*-(3-dimethylaminopropyl)carbodiimide (I), a water-soluble peptide coupling reagent, could undergo ring-chain tautomerism. This hypothesis was confirmed experimentally by Tenforde, Fawwaz, Freeman, and Castagnoli<sup>2a</sup> who used spectroscopic evidence to show that only some 7% of the total reagent exists as carbodiimide in neutral aqueous solution.

This communication reports data on the reactions of acetic acid and water with I consistent with the mechanisms of

Scheme I



Scheme II

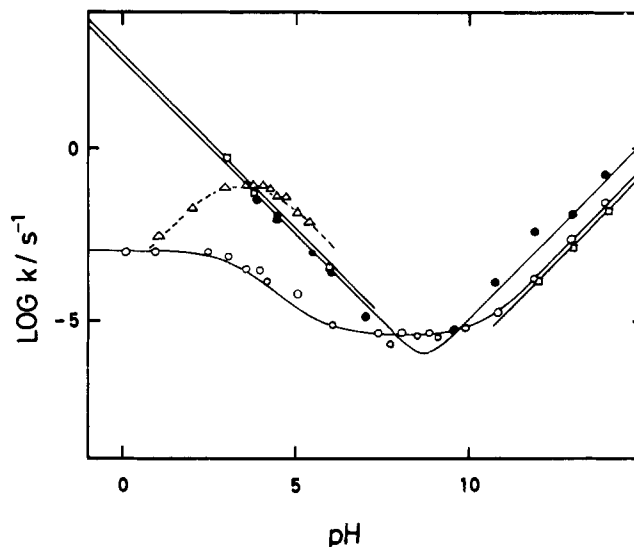
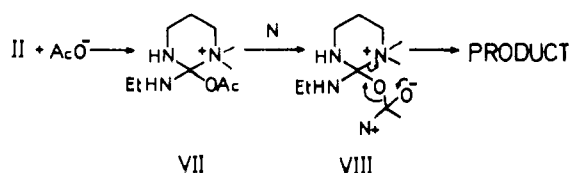


Figure 1. Dependence of rate constant on pH for hydrolysis of I (○); *N*-ethyl-*N'*-(3-trimethylammoniopropyl)carbodiimide (●); *N,N'*-di-*n*-propylcarbodiimide (□). The pH dependence for the reaction of I in 1 M acetate buffer (Δ). Lines for the hydrolyses of carbodiimides are theoretical and are from the following equations:  $k = 4 \times 10^{-6} + 10^{-3}/(1 + 10^{-3.2}/a_{\text{H}}) + 2.5 \times 10^{-2} [\text{OH}^-]$  (○);  $k = 320a_{\text{H}} + 0.14 [\text{OH}^-]$  (●);  $k = 400a_{\text{H}} + 1.4 \times 10^{-2} [\text{OH}^-]$  (□). Conditions are 25 °C, aqueous solution, ionic strength made up to 1 M with KCl.

Schemes I and II where the only participation of free carbodiimide is in the alkaline region of pH.

We report here the pH profiles for hydrolysis of *N*-ethyl-*N'*-(3-trimethylammoniopropyl)carbodiimide perchlorate, *N,N'*-di-*n*-propylcarbodiimide, and the coupling reagent I at zero buffer concentration; good pseudo-first-order kinetics were observed which obey equations given in the legend to Figure 1.

Water hydrolysis of the trimethylammonio carbodiimide model for VI has an upper limit for the rate constant ( $10^{-6} \text{ s}^{-1}$ ) close to that estimated from the Brønsted plot for nucleophilic attack.<sup>2b</sup> The proportion of free carbodiimide in the region of pH 7–10 present as the form VI is  $\sim 0.1$  using data from Tenforde and co-workers.<sup>2a</sup> Thus  $[\text{VI}]/[\text{III}]^{2c} = K_2K_3/K_4 \approx 0.1$  and, assuming  $K_4$  represents a normal  $\text{p}K_{\text{a}}$  for a dimethyl tertiary amine (9.99 for dimethylpropylamine),<sup>3</sup> then  $K_2K_3 \approx 10^{-11}$ . The rate constant for the mechanism through water attack on the carbodiimide VI therefore has the upper limit  $0.1 \times 10^{-6} = 10^{-7} \text{ s}^{-1}$ ; the observed value of  $4 \times 10^{-6} \text{ s}^{-1}$  indicates that the carbodiimide mechanism for this region of pH can only take at most  $1/40$  of the total reaction flux. At this stage we are not able to say whether the plateau is due to water attack on III or hydroxide attack on II.

Titration of reagent I with acid and base reveals two acidic groups of  $\text{p}K_{\text{a}} = 3.1$  and 11.1, respectively. We may calculate a  $\text{p}K_{\text{a}}$  for an ammonioamidinium dication such as II, using the data of Charton,<sup>4</sup> to be 3.83; we take the  $\sigma_1$  of the ammonio substituent to be 0.73.<sup>5a</sup> Perusal of Charton's correlation indicates that a conservative estimate of error would be  $\pm 2 \text{ p}K_{\text{a}}$  units. The apparent titration  $\text{p}K_{\text{a}}$  in the acid region may be derived from Scheme I (eq 1); substituting for  $K_2K_3$  and  $K_4$  leads to an apparent  $\text{p}K_{\text{a}}$  corresponding to  $K_1$  which therefore has a value (3.1) consistent with that for ammonioamidinium ionization within the limits of the prediction.

[II] =

$$\frac{[\text{total I}]K_4a_{\text{H}}}{K_1K_2K_3(1 + K_4/a_{\text{H}} + K_4/a_{\text{H}}K_3 + K_4/K_2K_3 + a_{\text{H}}K_4/K_1K_2K_3)}$$

(1)

The value of 11.1 is high for the  $\text{p}K_{\text{a}}$  of a dimethyl tertiary amine.<sup>3</sup> The apparent  $\text{p}K_{\text{a}}$  may be derived assuming equilib-