

trans butatriene moiety, although this point remains to be established. Finally, the exclusive formation of the trans isomer **3** is in agreement with the formation of **4** as an intermediate and its base-assisted anti elimination reaction.¹⁴ We are currently trying to achieve (a) a stereospecific transformation of **3** into their cis isomers and (b) a synthesis of unsymmetrically 1,4-disubstituted analogs for observation of the pmr coupling constants for the two vinylic protons.¹⁵

Acknowledgment. Financial support by Syracuse University is gratefully acknowledged.

(14) For related transformations, see (a) G. Köbrich and M. R. Merkle, *Angew. Chem., Int. Ed. Engl.*, **6**, 74 (1967); (b) G. Zweifel, H. Arzoumanian, and C. C. Whitney *J. Amer. Chem. Soc.*, **89**, 3652 (1967); (c) G. Zweifel and H. Arzoumanian, *ibid.*, **89**, 5086 (1967); (d) E. Negishi, J. J. Katz, and H. C. Brown, *Synthesis*, 555 (1972).

(15) A value of 7.8 Hz has been predicted: M. Karplus, *J. Amer. Chem. Soc.*, **82**, 4431 (1960).

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Alkyl Carbon-Oxygen Bond Cleavage in the Hydrolysis of Imidate Esters to Amides in Acid Solution

Sir:

The hydrolysis of imidate esters has seen considerable investigation, particularly since this reaction offers an alternative approach to the study of the type of tetrahedral addition intermediate implicated in many acyl transfer reactions. In general the hydrolysis produces ester and amine at low pH with a change over to amide and alcohol at high pH,^{1,2} although exceptions to this behavior have been observed.^{2,3}

Recently a study of the sulfuric acid catalyzed hydrolysis of a series of methyl benzimidates was reported.⁴ In 5% H₂SO₄ only the expected ester product was obtained, but in 65% H₂SO₄ considerable amide was formed, the relative amount increasing with the degree *N*-methyl substitution. This result was interpreted in terms of acidity dependence of the breakdown of the tetrahedral intermediate. The suggestion then followed that the analogous benzamides could not be hydrolyzing *via* similar tetrahedral intermediates, since these reactions show no detectable ¹⁸O exchange during hydrolysis at these or any other acidities. That is, if the tetrahedral intermediate obtained in an acid-catalyzed imidate hydrolysis can expel alcohol to give amide, the analogous tetrahedral intermediate for an acid-catalyzed amide hydrolysis could expel water, a process which (assuming rapid proton transfers) would result in ¹⁸O exchange.

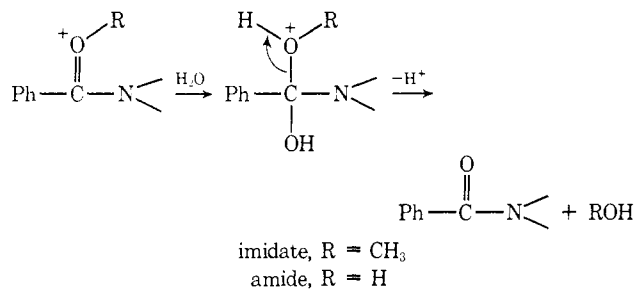
An alternative explanation is that the pathway by which the imidates hydrolyze to give amide does not involve a tetrahedral intermediate. Study was therefore initiated into the nature of this reaction. The following results present evidence concerning the posi-

(1) G. L. Schmir and B. A. Cunningham, *J. Amer. Chem. Soc.*, **87**, 5692 (1965); G. M. Blackburn and W. P. Jencks, *ibid.*, **90**, 2638 (1968); R. K. Chaturvedi and G. L. Schmir, *ibid.*, **90**, 4413 (1968); T. C. Pletcher, S. Koehler, and E. H. Cordes, *ibid.*, **90**, 7072 (1968).

(2) T. Okuyama, T. C. Pletcher, D. J. Sahn, and G. L. Schmir, *J. Amer. Chem. Soc.*, **95**, 1253 (1973).

(3) P. Deslongchamps, C. Lebreux, and R. Taillefer, *Can. J. Chem.*, **51**, 1666 (1973).

(4) C. R. Smith and K. Yates, *J. Amer. Chem. Soc.*, **94**, 8811 (1972).



tion of bond cleavage. Amide products would arise from cleavage of either the acyl carbon-oxygen bond or the alkyl carbon-oxygen bond;⁵ a tetrahedral intermediate requires the former (see above equation).

N,O-Dimethylbenzimidate-¹⁸O (Ia), *N,O*-dimethylbenzimidatonium-¹⁸O fluoroborate (Ib), and *N,N,O*-trimethylbenzimidatonium-¹⁸O fluoroborate (II) were prepared by methylation⁴ of labeled benzamides,⁴ and the ¹⁸O content of the amide product isolated from hydrolysis in 65% H₂SO₄ was determined. For comparison purposes a similar study was carried out on the hydrolysis of compound I in dilute base, where amide is also formed. The results are reported in Table I.

Table I. ¹⁸O Content of Amides Obtained from Hydrolysis of Labeled Imidates

Substrate ^a	Solvent	Time (hr)	Temp (°C)	% ¹⁸ O in amide ^c	Mode of cleavage
Ia	65% H ₂ SO ₄	55	85	1.52	O-CH ₃
Ib	65% H ₂ SO ₄	50	85	1.61	O-CH ₃
II	65% H ₂ SO ₄	110	85	1.59	O-CH ₃
Ia	0.01 <i>N</i> NaOH	6	25	0.19 ^d	O-acyl
Ib	0.01 <i>N</i> NaOH ^b	6	25	0.25 ^d	O-acyl

^a 1.60% ¹⁸O. ^b Corrected for deprotonation of Ib. ^c Amides were purified by recrystallization or distillation and analyzed on an AEI Model Ms 902 mass spectrometer, error ±0.05. ^d Labeled amide showed no loss of ¹⁸O under identical conditions.

In the basic hydrolysis the results are consistent with a tetrahedral intermediate; unlabeled amide is obtained, implying acyl carbon-oxygen cleavage. This is reassuring since to date all studies of imidate hydrolysis in the pH range have dealt with the results in terms of tetrahedral intermediates in various forms.¹⁻³

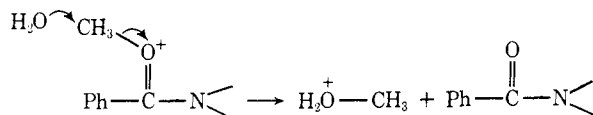
However, in 65% H₂SO₄, the amides retain the label of the imidates, demonstrating alkyl carbon-oxygen cleavage. Thus a tetrahedral intermediate must be ruled out as the precursor. Consequently arguments relating to a comparison of imidate and amide hydrolysis in concentrated acids cannot hold, since an analogous hydrolysis reaction cannot occur for amides. In particular the problem of explaining the lack of ¹⁸O exchange during amide hydrolysis in the light of the imidate results is resolved. It is the imidate hydrolysis (to amide) that does not involve a tetrahedral intermediate. The question of the mechanism of amide hydrolysis is still open.⁶

The reaction responsible for the amide products is an interesting one. From the negative entropies of

(5) The terms acyl and alkyl carbon are used in analogy with normal carboxylate esters.

(6) See, for example, ref 4 and the following: C. A. Bunton, S. J. Farber, A. J. G. Milbank, C. J. O'Connor, and T. A. Turney, *J. Chem. Soc., Perkin Trans. 2*, 1869 (1972); C. R. Smith and K. Yates, *J. Amer. Chem. Soc.*, **93**, 6578 (1971); *Can. J. Chem.*, **50**, 771 (1972); M. Liler, *J. Chem. Soc. B*, 334 (1971).

activation⁴ and positive "r" hydration parameters⁷ previously observed, it appears to be a bimolecular (A-2) process. In addition a unimolecular reaction involving methyl-oxygen cleavage would give the unlikely methyl carbonium ion. What is apparently occurring is an SN2 type of displacement on the methyl carbon of the protonated imidate, with a neutral amide as the leaving group. An analogous reaction has been



suggested as a possibility for the acid-catalyzed hydrolysis of carboxylate esters (the A_{A1}-2 reaction)⁸ but has not yet been observed.

A further interesting facet of this reaction is its take-over in the more concentrated acids from the normal acid-catalyzed imidate hydrolysis (*i.e.*, tetrahedral intermediate and ester product). Changes in reaction mechanism with increasing acidity have been observed in the hydrolysis of carboxylate esters⁹ and amides¹⁰ but have all involved a change from a bimolecular to a unimolecular reaction. In this case the change involves the position of nucleophilic attack, the acyl carbon being the more reactive site in dilute acid and the methyl carbon in concentrated acid. The explanation for this behavior is not immediately apparent, but could lie in the hydration requirements for the two reactions. Work is currently in progress on this unusual behavior and will be reported at a later date.

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- (7) C. R. Smith, Ph.D. Thesis, University of Toronto, 1971.
 (8) J. N. E. Day and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 686 (1941).
 (9) K. Yates, *Accounts Chem. Res.*, **4**, 136 (1971).
 (10) J. A. Duffy and J. A. Leisten, *J. Chem. Soc.*, 583 (1960); J. W. Barnett and C. J. O'Connor, *J. Chem. Soc., Perkin Trans. 2*, 2378 (1972).

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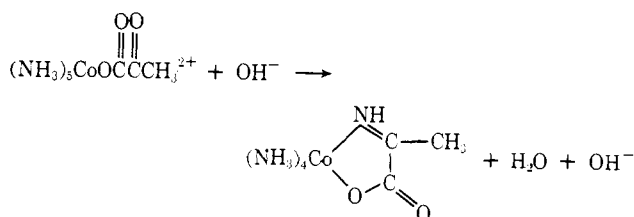
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Intramolecular Chelation *via* Imines. A Novel Condensation of Acetylacetone with Pyruvildinatotetraamminecobalt(III) Ion

Sir:

The synthesis of the chelated imine species by a base-



catalyzed reaction of pyruvopentaamminecobalt(III) ion has been described previously.¹ The imine species

- (1) J. MacB. Harrowfield and A. M. Sargeson, *J. Amer. Chem. Soc.*, **96**, 2634 (1974).

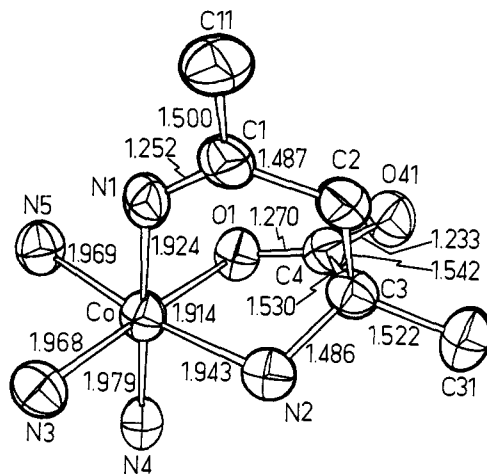


Figure 1. The overall stereochemistry of the cation. Typical bond length esd's are: Co-O, 0.004; Co-N, 0.005; C-O, 0.007; C-N, 0.007; C-C, 0.008 Å.

was readily deprotonated at the imine N center ($pK \sim 10.5$) and proton exchange was also observed at the methyl group. These properties indicated that it might condense with acetylacetone in a basic medium to give a chelated 3,5-dimethylpyridine-2-carboxylate ligand. Condensation of the carbonyl center at the imine site with elimination of H₂O followed by attack of the deprotonated methyl (-CH₂-) at the other carbonyl site, again with elimination of H₂O, would yield the pyridine species.

The pyruvildinimine chloride (1.5 g in 25 ml of H₂O) was treated therefore with acetylacetone in basic aqueous solution (4 g of acacH in 25 ml of 1 M NaOH) at 25°. Condensation occurred over 24 hr and the product was isolated as the perchlorate (1.5 g) or dithionate. However, analysis indicated that only three new carbon atoms were incorporated into the product (*Anal. Calcd for (CoC₆H₂₀N₅O₂(S₂O₆): Co, 14.26; C, 17.44; H, 4.88; N, 16.94; S, 15.52. Found: Co, 14.6; C, 17.49; H, 4.95; N, 16.83; S, 15.51). Pmr spectroscopy indicated the presence of one methyl group $\delta -2.30$ (ppm relative to TMS) on the C atom of an -N=C< group and another methyl ($\delta -1.40$) attached to a saturated carbon atom. A two-proton singlet at $\delta -2.98$ was tentatively assigned to a methylene group flanked by the imino C atom and the saturated carbon atom. Signals at $\delta -2.65$, -3.48 , and -3.78 accounted for three coordinated ammonia molecules. Hence, one ammonia of the starting complex had disappeared being replaced by an imino NH ($\delta -10.26$). The analysis and pmr results implied that acetylacetone had condensed with a coordinated ammonia through a >C=O center. Cleavage of acetylacetone and condensation at the imine center of the starting complex was also indicated.*

A three-dimensional X-ray diffraction study of the dithionate salt has established that the complex cation has the structure shown in Figure 1. The crystals were monoclinic, space group *P*2₁/*c*, with $a = 7.576$ (4), $b = 18.209$ (7), $c = 14.068$ (6) Å, $\beta = 125.25$ (2)°, and $Z = 4$. Reflection data were collected on a Picker FACS-I four-circle diffractometer using graphite-crystal monochromated Cu K α radiation [1479 unique reflections with $I/\sigma(I) \geq 3.0$]. Data have been corrected for absorption effects. Block-diagonal least-squares refine-