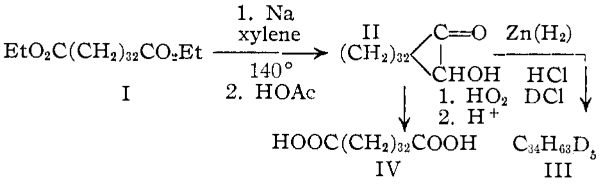
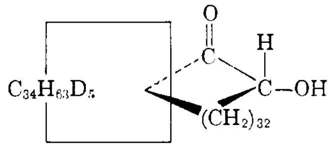
with sodium yielded the cyclic acyloin (II). *Anal.* Calcd. for $C_{34}H_{66}O_2$: C, 80.56; H, 13.12; O, 6.31. Found: C, 80.66; H, 13.00, O, 6.44. Clemmensen reduction of II with deuterated hydrochloric acid produced the cyclic hydrocarbon (III), in 50% yield from I, m.p. 67–68,°[6] with *ca.* 5 atoms of deuterium per molecule. The transformation of I to II was then carried out with a 1:1 mixture of III and xylene as solvent.



Unchanged III was separated *cleanly* from the other products by chromatography using pentane as eluent. The fraction containing II, which was removed with ether–methanol, had infrared bands at 2105, 2160 and 2200 cm.$^{-1}$ (C–D stretch) which were also observed in the spectrum of III. Rechromatography of this material demonstrated that the deuterium was associated with the acyloin and was not due to contamination by unaltered III. This acyloin fraction was oxidized with alkaline hydrogen peroxide giving the diacid (IV). The presence of III among the products was demonstrated by its chromatographic behavior, infrared spectrum, m.p. and mixed m.p. The yield of II, formed in the presence of III, varied between 5 and 20%. The yield of III in a given oxidation was roughly proportional to that of II and constituted about 1% of the acyloin.[7]

It is proposed that the acyloin fraction contains V, a species comprised of two interlocking but otherwise non-bonded rings. Oxidation of V cleaves the acyloin containing ring and this is followed by unthreading to give III. It is unlikely that some other deuterated system would give rise to III under oxidative conditions. Chromatography of the material obtained by heating III, xylene and sodium with II, previously formed in the absence of III, gave *no* deuterium in the acyloin fraction. Oxidation of that fraction produced no hydrocarbon.

V



We note that V is the first demonstrated example of a compound in which the topology of the system must be considered in describing its structure. For example, V is a topological "isomer" of the non-interlocked system II plus III.[8] Other possibilities for topological isomers exist,[9] *e.g.*, models indicate that a cycloalkane of more than 50 carbon atoms can take the form of a simple or a knotted ring. In addition, this latter species can exist in two optical isomers.

Further work with larger quantities of material to permit isolation of V is in progress.

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(6) L. Ruzicka, M. Hürbin and M. Furter, *Helv. Chim. Acta*, **17**, 78 (1934) found m.p. 66°–67° for non-deuterated III.

(7) Calculations by H. Frisch have given a probability of 10^{-2} for this statistical threading. This small value renders the hypothesis of extended chains of references 2 and 3 somewhat less likely. It also reduces the probability that more than 1% of III, from the oxidation reaction, arose from higher interlocked systems.

(8) Thus two separate molecules are to be viewed as isomeric with V, which resembles a single molecule in many respects. It should be noted that topological isomers necessarily have identical chemical bonding and arrangements of atoms about rigid centers.

(9) H. Frisch and E. Wasserman, Division of Polymer Chemistry, 138th Meeting A.C.S., New York, Sept., 1960.

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RECEIVED JULY 5, 1960

THE MECHANISM OF BASE HYDROLYSIS AND BASE CATALYZED REACTIONS OF SOME COBALT(III) AMMINE COMPLEXES

Sir:

Two mechanisms have been proposed for the reaction of hydroxide ion with complexes of cobalt (III) containing a replaceable ligand. One is the direct displacement, or SN2 mechanism[1] and the other the conjugate base dissociation, or SN1 CB mechanism.[2] In water solvent the two mechanisms give rise to the same product, since the intermediate in the conjugate base mechanism would react with the solvent to yield a hydroxo product. However in a non-hydroxylic solvent different products are predicted for the two mechanisms in the event that an excess of some nucleophilic reagent other than hydroxide ion or water is present.

We wish to report some results which are easily explained by the SN1 CB mechanism and cannot be explained by the SN2 mechanism. The solvent used is dry dimethylsulfoxide. As examples of a large number of similar experiments with various cobalt(III) complexes and nucleophilic reagents, these reactions illustrate the chief points. Spectral data were used to follow the reactions and identify the reaction products.

$$\underset{0.001\ M}{trans\text{-}\mathrm{Co(en)_2NO_2Cl^+}} + \underset{0.01\text{–}0.10\ M}{\mathrm{NO_2^-}} \longrightarrow \mathrm{Co(en)_2(NO_2)_2^+} + \mathrm{Cl^-} \quad (1)$$

$$\underset{0.001\ M}{trans\text{-}\mathrm{Co(en)_2NO_2Cl^+}} + \underset{0.001\ M\text{ or less}}{\mathrm{OH^-}} \longrightarrow \mathrm{Co(en)_2NO_2OH^+} + \mathrm{Cl^-} \quad (2)$$

$$\underset{0.001\ M}{trans\text{-}\mathrm{Co(en)_2NO_2Cl^+}} + \underset{0.10\ M}{\mathrm{NO_2^-}} + \underset{0.001\ M}{\mathrm{OH^-}} \longrightarrow \mathrm{Co(en)_2(NO_2)_2^+} + \mathrm{Cl^-} + \mathrm{OH^-} \quad (3)$$

$$\underset{0.001\ M}{\mathrm{Co(en)_2(NO_2)(OH)^+}} + \underset{0.10\ M}{\mathrm{NO_2^-}} \longrightarrow \text{indefinite product, some } \mathrm{Co(en)_2(NO_2)_2^+} \quad (4)$$

Reaction (1) shows first order kinetics and has a half-life of 5–6 hr., nearly independent of the nitrite ion concentration. Reaction (2) is very fast, being complete in less than 2 min. when the first reading was made. Reaction (3) is also complete in less than 2 min. yet the product is cleanly the dinitro complex. Reaction (4) is very much slower than (2) or (3) and gives a spectrum lacking sharp bands which steadily changes over several days.

The following points are also significant: Only catalytic quantities (10%) of hydroxide ion are required to cause a rapid reaction of the cobalt(III)

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(1) D. D. Brown, C. K. Ingold and R. S. Nyholm, *J. Chem. Soc.*, 2678 (1953); C. K. Ingold, Fifth Weizmann Memorial Lecture Series, the Weizmann Science Press of Israel, 1959.

(2) F. J. Garrick, *Nature*, **139**, 507 (1937); F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons Inc., New York, N. Y. 1958, pp. 124–132.

complex with a number of nucleophilic reagents. Other bases such as piperidine also act as catalysts. The rates then increase with increasing concentration of piperidine, though not in a simple fashion. The rates vary inversely with the concentration of added piperidinium ion when piperidine is used as a base, again not in a simple fashion. In all these cases first order kinetics are observed.

For a given concentration of catalyst, the rate of reaction is independent of the concentration of the nucleophilic reagent, for example, the nitrite ion. For a given concentration of catalyst the rate is the same for the three nucleophilic reagents, nitrite ion, thiocyanate ion and azide ion.

Allowing for the fact that acid-base reactions in non-aqueous solvents often do not yield simple equilibria, it is clear that the above observations are accounted for by the S_N1 CB mechanism

$$\mathrm{Co(en)_2NO_2Cl^+ + B \rightleftarrows Co(en)(en\text{-}H)NO_2Cl + BH^+} \tag{5}$$

$$\mathrm{Co(en)(en\text{-}H)NO_2Cl \longrightarrow Co(en)(en\text{-}H)NO_2^+ + Cl^-} \tag{6}$$

$$\mathrm{Co(en)(en\text{-}H)NO_2^+ + NO_2^- \longrightarrow Co(en)(en\text{-}H)(NO_2)_2} \tag{7}$$

$$\mathrm{Co(en)(en\text{-}H)(NO_2)_2 + BH^+ \longrightarrow Co(en)_2(NO_2)_2^+ + B} \tag{8}$$

In water the direct reaction with nucleophilic reagents generally does not occur for complexes of cobalt(III), chromium(III), rhodium(III), iridium(III) and platinum(IV). Therefore base catalysis of substitution reactions in non-aqueous media has important synthetic applications, since often the direct reactions are extremely slow in these media.

This work was supported by the U. S. Atomic Energy Commission under Contract AT(11-1)-89-project No. 2.

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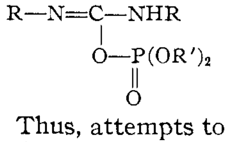
RECEIVED JUNE 21, 1960

1-ALKOXYVINYL ESTERS OF PHOSPHORIC ACIDS AS PHOSPHORYLATING AGENTS

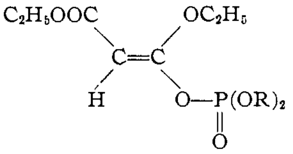
Sir:

Among the most successful methods for carrying out phosphorylation reactions is the use of carbodiimides as developed by Khorana and Todd.[1] It has, however, proved impossible to isolate the postulated intermediates (I) despite their obvious usefulness in synthesis.

I 

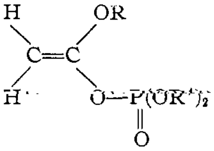
$$\mathrm{R{-}N{=}C(NHR){-}O{-}P(=O)(OR')_2}$$

Thus, attempts to make unsymmetrical pyrophosphates using carbodiimides have invariably led to the formation of mixed products.[2] Cramer, making use of the *Perkow* reaction, obtained II[3] from the reaction of trialkyl phosphites with bromomalonic ester. This type of intermediate was shown to be a very reactive phosphorylating agent for carboxylic, sulfonic and phosphoric acids and, more recently, also adenylic acid.[4] However, this preparation of substituted ketene acylals (II) is limited by the restricted accessibility of triesters of phosphorous acid.



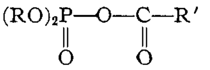
II

We now describe a general method for the preparation of 1-alkoxyvinyl phosphates (III) from esters of phosphoric acid in a manner similar to that described recently for the preparation of 1-alkoxyvinyl esters of carboxylic acids.[5,6,7] The formation of the alkoxyvinyl esters and their subsequent reactions can be followed by observing their infrared spectra (characteristic peaks at 5.96, 5.74μ). In this way, formation of compounds of the type III ($R' = C_6H_5, C_6H_5CH_2, p\text{-}NO_2C_6H_4$) has been demonstrated. These compounds can be obtained as oils which tend to polymerize on heating, but which, as described below, may be obtained in a pure state by cautious distillation in high vacuum. Thus, III ($R = C_2H_5$, $R' = C_6H_5$) has been isolated from the reaction of ethoxyacetylene with diphenylphosphoric acid in methylene chloride[8] solution at 0° in the presence of a mercuric acetate catalyst. After removal of solvent, III ($R = C_2H_5$, $R' = C_6H_5$) was obtained as a pale yellow liquid by molecular distillation (2×10^{-4} mm., 100° (Calcd. for $C_{16}H_{17}O_5P$: C, 60.0; H, 5.31; P, 9.68. Found: C, 59.9; H, 5.47; P, 9.67)).



III

The active intermediates (III) will react *in situ* without purification, and in this way rapid phosphorylation of alcoholic, phenolic and nucleosidic hydroxyls, phosphoric acids, amines and carboxylic acids has been observed, the only other product being ethyl acetate. (Diphenyl N-cyclohexylphosphoroamidate, obtainable analytically pure, may be used as a method of estimating III ($R = C_6H_5$).) The mixed anhydride (IV) ($R = C_6H_5CH_2$, $R' = C_6H_5$), prepared in this manner reacted with cyclohexylamine to give the anticipated N-cyclohexylbenzamide and cyclohexylammonium dibenzyl phosphate.[9]



$$\mathrm{(RO)_2P(=O){-}O{-}C(=O){-}R'}$$

IV

Further reactions of these alkoxyvinyl phosphates, and the reactions of monoesters of phosphoric

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[1] H. G. Khorana and A. R. Todd, *J. Chem. Soc.*, 2257 (1953).

[2] See review by A. R. Todd, *Gazz. chim. ital.*, **89**, 126 (1959).

[3] F. Cramer, *Angew. Chem.*, **69**, 727 (1957).

[4] F. Cramer, *ibid.* **72**, 236 (1960).

[5] H. H. Wasserman and P. S. Wharton, *Tetrahedron*, **3**, 321 (1958).

[6] H. H. Wasserman and P. S. Wharton, THIS JOURNAL, **82**, 661 (1960).

[7] J. P. Arens and T. Doornbos (*Rec. trav. chim.*, **74**, 79 (1955)), prepared tetraethyl pyrophosphate by the reaction of diethyl phosphate with ethoxyacetylene without isolation of any intermediate.

[8] For III ($R' = p\text{-}NO_2C_6H_4$), di-p-nitrophenylphosphoric acid is dissolved in a dimethylformamide–methylene chloride mixture.

[9] Compare peptide synthesis by F. Cramer and K. G. Gärtner, *Ber.*, **91**, 1562 (1958).