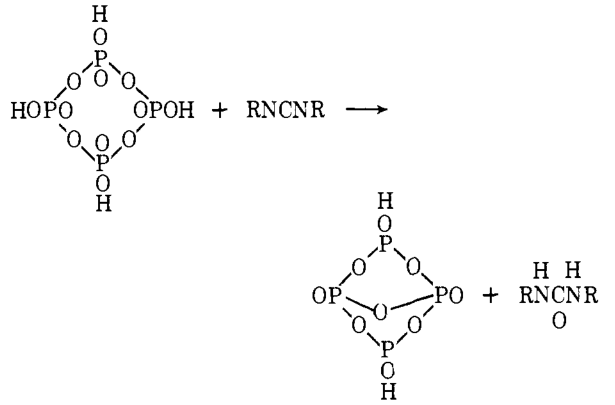


(1)

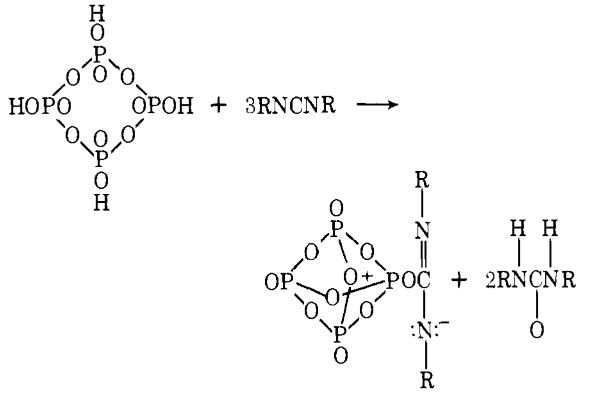
condensation so that the P_4O_{10} molecule would be a product. Thus, in the solution, the carbodiimide concentration should be increased while that of its urea hydrolysis product should be decreased concomitantly. Fortunately, dicyclohexylcarbodiimide ($R = C_6H_{11}$ in eq 1), which exhibits a melting point near room temperature, is a poor solvent for its urea while being a good solvent for small ultraphosphate molecules.

Although other procedures have proven suitable, we have obtained good results in carrying the condensation beyond the 1,5-μ-oxo-tetrametaphosphoric acid stage by using the following sequences of steps. To a solution of 0.4 m*M* tetrakistetra-*n*-butylammonium tetrametaphosphate in 5 ml of tetramethylurea, 3.04 m*M* of the hydrochloride of dicyclohexylurea is added to give a clear homogenous solution exhibiting only a single peak in its ^{31}P nmr pattern, the peak corresponding to the tetrametaphosphate anion. An equal volume of molten dicyclohexylcarbodiimide is then added and the resulting precipitated urea is removed by decantation after centrifugation (*Note:* All operations must be carried out with careful avoidance of contamination by moisture.[2]) The resulting solution shows only ^{31}P nmr resonances attributable to the 1,5-μ-oxo-tetrametaphosphate anion.[1,2] Additional molten carbodiimide is added in several steps, removing the precipitated urea after each addition. After each step a diminution is seen in the area of the second-order double-triplet nmr pattern of the 1,5-μ-oxo-tetrametaphosphate anion appearing approximately 35 ppm upfield of the resonance position of 85% H_3PO_4, while concomitantly a new set of resonances lying approximately 60 ppm above that of 85% H_3PO_4 is seen to appear and grow in area. Finally, when approximately 90 weight per cent of the clear homogenous solution consists of dicyclohexylcarbodiimide, the sole ^{31}P resonances consist of the new pattern appearing near +60 ppm.

This new pattern consists of a pair of barely resolvable multiplets composed of a doublet having a relative area of 3.0 at +59.5 ppm and a quartet having a relative area of 1.0 at +64.2 ppm, with a single coupling constant of 18.0 Hz applying to both multiplets. This classic pseudo-first-order pattern has been well simulated by a calculation corresponding to an a_3x system. Heteronuclear decoupling experiments show that there is no coupling between phosphorus and hydrogen atoms in this molecule; and signal-averaged homonuclear ^{31}P–^{31}P INDOR experiments demonstrate that the two multiplets are in fact coupled. By completely dissolving the urea precipitates removed during the preparation of this entity and obtaining time-averaged ^{31}P nmr patterns of the resulting solutions, it was shown that the amount of phosphorus lost during these precipitation steps was slight, being due to the usual occlusion of the solution by the precipitate.

Dilution of the system with dry, but not scrupulously dry, tetramethylurea causes the area of the ^{31}P nmr pattern at +60 ppm to decrease while that of the pattern at +40 ppm increases. Likewise similar behavior is found upon dilution with the urea dissolved in scrupulously dry (CaH_2) tetramethylurea. Controlled hydrolysis[2] of the solution exhibiting the ^{31}P nmr pattern at +60 ppm leads to the quantitative production of the tetrametaphosphate starting material.

The reasonable interpretation of these results is that the entity exhibiting the nmr pattern at +60 ppm consists of a P_4O_{10} birdcage molecule which is solvated at only one of its apices with a carbodiimide molecule. Since there is no coupling between phosphorus and hydrogen, the point of coordination to the carbodiimide must be at the electropositive carbon atom, as indicated in the product of eq 2 in which the formal charges are indicated for one resonance form.



(2)

Acknowledgment. This work was supported in part by Grants USPHS-11702 and NSP-GP-28698X, as well as by the General Research-Support Grant awarded to the University of Illinois, College of Medicine.

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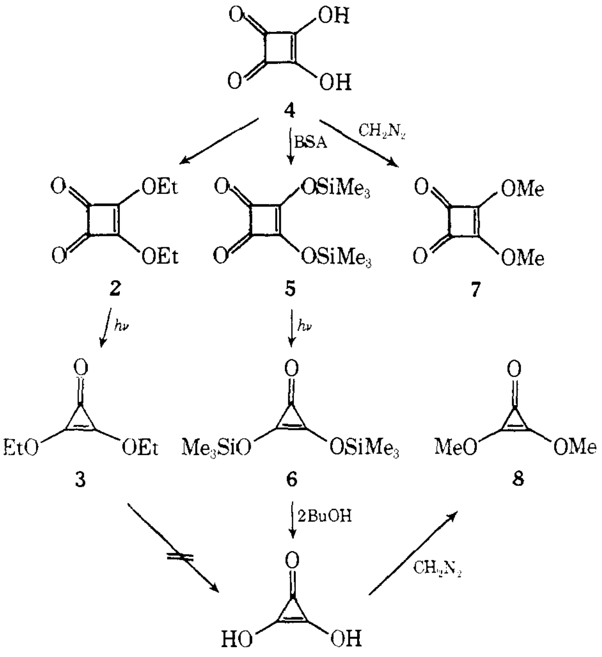
Received October 3, 1974

Synthesis of Dihydroxycyclopropenone (Deltic Acid)

Sir:

The cyclic oxycarbon anions, $C_nO_n^{m-}$, have been recognized as a series of aromatic compounds,[1] and the unknown deltate dianion ($n = 3$, $m = 2$) has been predicted to have an exceptionally high delocalization energy per π-electron.[2]

Scheme I



We report here the synthesis of deltic acid (dihydroxycyclopropenone, **1**) the conjugate acid of this anion.

Several unsuccessful attempts to synthesize the deltate dianion or deltic acid have been reported.[3-5] Recently, the photochemical extrusion of carbon monoxide from diethyl squarate (diethoxycyclobutendione, **2**) gave diethoxycyclopropenone (**3**), but **3** could not be hydrolyzed to **1**. Our route to **1** is similar but with the ethyl groups replaced by trimethylsilyl. The resulting bis(trimethylsiloxy)cyclopropenone (**6**) can be smoothly and quantitatively cleaved to deltic acid.

Squaric acid (**4**) was converted to bis(trimethylsilyl) squarate (**5**) by treatment with 2 equiv of bis(trimethylsilyl)acetamide in refluxing acetonitrile (Scheme I). Work-up by vacuum distillation gave **5** as a low-melting colorless solid: pmr δ 0.44; ir in CCl_4 ν 1820, 1745, 1610 cm^{-1}.[6] (*Cf.* diethyl squarate, 1810, 1735, 1605 cm^{-1}.)

Prolonged photolysis of **5** in hexane using a Vycor-filtered 450-W Hanovia lamp results in the disappearance of **5** and the formation of several products. After removal of solvent, Kugelrohr distillation at 60-70° (0.1 Torr) followed by crystallization from hexane at $-78°$ and redistillation gave nearly pure bis(trimethylsiloxy)cyclopropenone (**6**), a low-melting solid, in ~15% yield. The identity of **6** is established by its infrared spectrum which shows characteristic cyclopropenone bands at ν 1870 and 1655 cm^{-1} (*cf.* diethoxycyclopropenone, 1890 and 1680 cm^{-1} [5]).

When an ethereal solution of **6** at $-78°$ was treated with 2 equiv of 1-butanol, **1** was formed quantitatively as a white precipitate. *Anal.* Calcd for $C_3O_3H_2$: C, 41.87; H, 2.35. Found: C, 41.79; H, 2.43. The infrared spectrum of **1** in the 2000-4000-cm^{-1} region is quite similar to that of squaric acid,[7] showing a very strong broad band with a maximum near 2300 cm^{-1}. The structure of **1** was further established by its reaction with diazomethane to give dimethoxycyclopropenone (**8**) in 75% yield, identified by comparison of its ir spectrum (1890, 1680, 1305, 1030 cm^{-1}) with that of cyclopropenone **3** (1890, 1680, 1310, 1045 cm^{-1}).[5] High resolution mass spectroscopy showed the expected molecular ion at *m/e* 114.03168 (calcd for $C_5H_6O_3$, 114.03168). Squaric acid is converted analogously to dimethyl squarate by diazomethane.[8]

Deltic acid decomposes at *ca.* 180° but is unchanged by brief heating to 150°. The compound is stable to atmospheric moisture and oxygen but appears to decompose when dissolved in water-ethanol. The pH of the solution is initially *ca.* 1 but increases with time. Further studies of **1** and attempts to prepare the deltate dianion are currently in progress.

Acknowledgment. This work was supported by a grant from the National Science Foundation.

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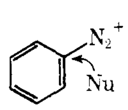
Received September 24, 1974

Onium Ions. XII.[1] Heterolytic Dediazoniation of Benzenediazonium Ions by Halide Ions in Pyridinium Polyhydrogen Fluoride Solution Giving Isomeric Halobenzenes Reflecting Ambident Reactivity of Benzenediazonium Ions and Intermediate Phenyl Cation as Well as Subsequent Aryne Formation

Sir:

The structure and reactivity of arenediazonium ions have been well reviewed.[2] In a recent article,[3] Zollinger reviewed the reactivity of arenediazonium ions and classified their reactions with nucleophiles (Nu) as (a) heterolytic dediazoniations at carbon-1 (*i.e.*, the ipso carbon) (I), (b) reactions with nucleophiles at the β-nitrogen (II), (c) substitution of nucleofugal leaving groups (such as nitro and halogens) in the ortho and para positions of the diazonium ions (III), and (d) aryne formation *via* the loss of N_2 and deprotonation (IV).



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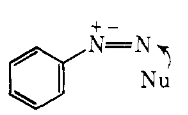
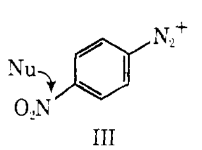
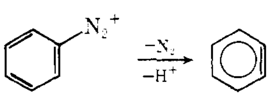


II



III



IV

Early examples of what now can be considered substitution of nucleofugal leaving groups can be found in the work of Hantsch (1896),[4a-c] Hirsch (1898),[4d] and Orton (1903)[5] but generally were given little attention. More recent examples of nucleofugal substitution were provided by the work of Meerwein[6] and Huisgen.[7] These reactions can be readily explained as nucleophilic aromatic substitutions (SNAr reactions), the diazonium group being an extremely strong withdrawing group, thus facilitating the displacement of suitable leaving groups.