that solvolysis of acetates of α-ferrocenyl alcohols is rapid[10] and α-halomethylferrocenes are unstable.[11]

An alternate mechanistic possibility involving the decomposition of the diazonium salts to phenonium ions, which might abstract hydride from the halohydrocarbons to produce electrophilic carbonium ions, is excluded by the last experiment in Table I, wherein bromotrichloromethane solvent gives rise to ferrocenoic acid. Bromotrichloromethane is known to react readily with phenyl radicals to produce trichloromethyl radicals.[4]

We have found that ordinarily methylene chloride is a good solvent for arylation of ferrocene with diazonium salts other than o-alkylbenzenediazonium salts, which give significant amounts of the aldehyde to the exclusion of normal arylation products.[12] The anomalous reaction of o-alkylbenzenediazonium salts is not due to steric effects alone, for the aldehyde is not produced from reaction with the diazonium salts derived from o-nitroaniline, o-bromoaniline, 2-methyl-6-nitroaniline, or 2-methyl-4-nitroaniline, though it is produced in small amounts with the salts from o-iodoaniline, o-aminobiphenyl, 2,6-dimethyl-4-nitroaniline, and 2,4-dimethyl-6-nitroaniline. These substrates all give reasonable yields of normal arylation products. In general, the presence of a nitro group in an o-alkylbenzenediazonium salt discourages the aldehyde formation, but electronic effects alone are not responsible. No aldehyde was obtained from o-anisidine or o-phenetidine and only a trace amount of the aldehyde was obtained from p-toluidine. Most likely, a combination of both electronic and steric effects of substituents on the diazonium salts are responsible for the preferential reaction with the solvent.

The aldehyde[13] was identified by its melting point and its infrared, ultraviolet, and n.m.r. spectra; ferrocenoic acid[14] and acetylferrocene[15] were identified by mixture melting points and the identity of their infrared spectra to those of authentic samples.

Acknowledgment.—The authors wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial assistance.

(10) E. A. Hill and J. H. Richards, J. Am. Chem. Soc., **83**, 4216 (1961).

(11) R. A. Benkeser and W. P. Fitzgerald, Jr., J. Org. Chem., **26**, 4179 (1961).

(12) With 2,6-dimethylbenzenediazonium fluoroborate and o-toluenediazonium fluoroborate some arylation products were also obtained.

(13) M. Rosenblum, Chem. Ind. (London), 72 (1957).

(14) W. F. Little and R. Eisenthal, J. Am. Chem. Soc., **82**, 1577 (1960).

(15) V. Weinmayr, ibid., **77**, 3009 (1955).

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A New Synthesis of α,β-Dihydroxy-γ-ketoesters and of α,β-Dihydroxyketones via Cyclic Oxyphosphoranes[1]

Sir:

This communication generalizes further a new carbon–carbon condensation reaction recently described.[2] The reaction is induced by trialkyl phosphites, involves as intermediates compounds with pentavalent phosphorus, and produces polyoxygenated functions in acceptable yields. The previous examples[2] dealt with the formation of diketols from two molecules

of an α-diketone, and of tartaric esters from two molecules of an α-ketoester.

Biacetyl and trimethyl phosphite form a 1:1 adduct (I) very rapidly.[2a] Adduct I reacted further with methyl pyruvate and yielded the crystalline cyclic saturated oxyphosphorane IIa, isolated in 60% yield. The material balance is a noncrystalline mixture of the two possible diastereomers: IIa, with the acetyl trans to the carbomethoxy, and IIb, with the acetyl cis to the carbomethoxy.
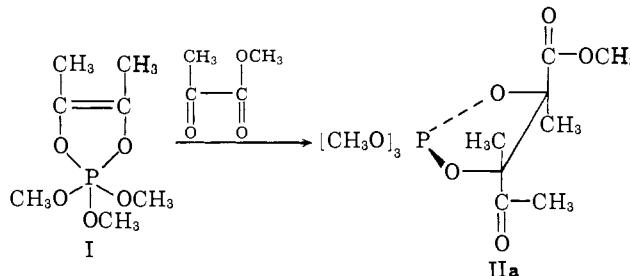

The trans-oxyphosphorane IIa reacted very rapidly with one mole equivalent of water in benzene solution at 20° and gave a crystalline cyclic phosphate ester IIIa. This compound (or the parent oxyphosphorane IIa) was converted into DL-threo-methyl-α,β-dimethyl-α,β-dihydroxylevulinate (IVa) in aqueous solution at pH 4–4.5 (6 hr. at 100°).
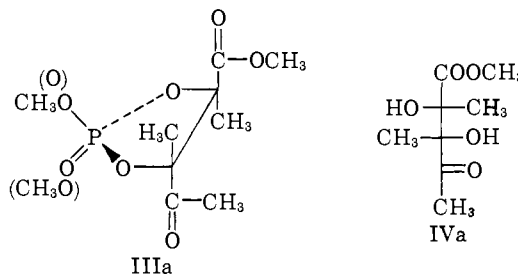
The biacetyl–trimethyl phosphite 1:1 adduct I reacted with anhydrous propionaldehyde and yielded mainly the liquid oxyphosphorane Va.
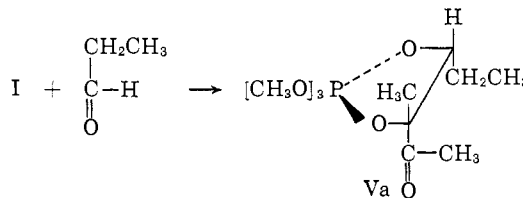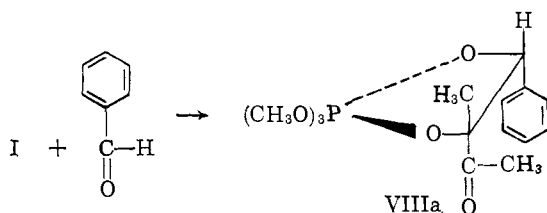

Hydrolysis of the oxyphosphorane Va with one mole equivalent of water in benzene solution (20°) gave a liquid cyclic phosphotriester, VIa. The phosphate VIa, or the oxyphosphorane Va, were converted into DL-threo-3-methylhexane-3,4-diol-2-one (VIIa) in aqueous solution at pH 4–4.5 (6 hr. at 100°).
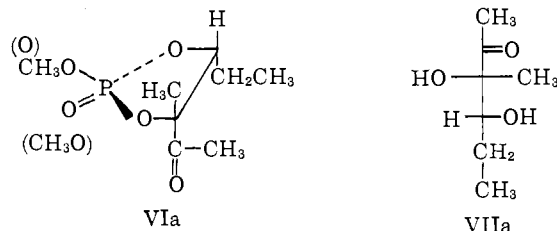
Benzaldehyde also reacted with the 1:1 adduct I and gave predominantly the oxyphosphorane VIIIa in which the acetyl is cis to the phenyl.

The P³¹ n.m.r. spectra of the oxyphosphoranes IIa, Va,[2a] and VIIIa had one peak at ca. +50 p.p.m. to high-

field of 85% H_3PO_4, like other related compounds.[2] We have described the partial hydrolysis of oxyphosphoranes to cyclic phosphate esters.[3]

The configurations shown for the predominant adducts and for the cyclic phosphates are highly probable but not definitive. They are based on comparisons between the H^1 n.m.r. spectra and the corresponding spectra in the series of *meso* and DL 2:1 biacetyl–phosphite[3] and 2:1 methyl pyruvate–phosphite adducts[4] and cyclic phosphates.[3]

The adduct I and the methyl pyruvate were mixed in a 3:1 mole ratio and kept 90 hr. at 20° with stirring (N_2). The excess of I was removed *in vacuo*, and the colorless residue (88% yield; $n^{25}D$ 1.4465; infrared similar to that of pure IIa) was dissolved in ether and allowed to crystallize at −10°. Crystalline IIa (m.p. 33–35°, ca. 60%) separated out. *Anal.* Calcd. for $C_{11}H_{21}O_8P$: C, 42.3; H, 6.8; P, 9.9. Found: C, 42.2; H, 7.0; P, 10.3. Bands at 5.76 (ester C=O), 5.84 (ketone C=O), and 9.2–9.3 μ (POCH$_3$) (in CCl_4). Singlet at 6.35 (COOCH$_3$), doublet at 6.52, J_{HP} = 13 c.p.s. (POCH$_3$), singlet at 7.83 (acetyl), and singlets

at 8.57 and 8.76 τ (CH$_3$C—) (in CCl$_4$ vs. TMS).

The cyclic phosphate IIIa had m.p. 81–83° (ether). *Anal.* Calcd. for $C_9H_{15}O_7P$: C, 40.6; H, 5.7; P, 11.6. Found: C, 40.7; H, 5.9; P, 11.7. Bands at 5.74 (ester C=O), 5.84 (ketone C=O), 7.70 (P=O), and 9.52 μ (POCH$_3$) (in CCl_4). The H^1 n.m.r. spectrum in $CDCl_3$ is complex; two sets of peaks are observable, the stronger set consists of a singlet at 6.20 (COOCH$_3$), doublet at 6.17, J_{HP} = 12.5 c.p.s. (POCH$_3$), singlet at 7.68 (acetyl), and two singlets at 8.28 and

8.38 τ (CH$_3$C—). The weaker set has a singlet at 6.25

τ (COOCH$_3$), under the high field component of the strong POCH$_3$ doublet; a doublet at 6.08, J_{HP} = 12.5 c.p.s. (POCH$_3$), a singlet at 7.64 (acetyl), and sin-

glets at 8.32 and 8.35 τ (CH$_3$C—). (A stereomutation

at phosphorus in the *meso*-cyclic phosphate derived from the 2:1 biacetyl–phosphite adduct, which doubles the number of peaks, has been mentioned.)[3]

α,β-Dihydroxylevulinate (IVa) had m.p. 72–73° (cyclohexane). *Anal.* Calcd. for $C_8H_{14}O_5$: C, 50.6; H, 7.4. Found: C, 50.5; H, 7.4. Bands at 2.92 (broad OH), 5.83–5.88 μ (broad ester and ketone C=O) (in $CHCl_3$). Singlet at 6.1 (OH), 6.20 (COOCH$_3$), 7.71 (acetyl), and 8.57 and 8.61 τ (CH$_3$C—).

The adduct I and propionaldehyde (dried over Drierite) (1:3 mole ratio) were stirred 88 hr. at 20°.

Mc./sec. showed 16 of the 20 lines expected for the P^{31} nucleus coupled with nine methoxyl protons (J_{PH} = 12.6 c.p.s.) and with one methine proton (J_{PH} = 6.3 c.p.s.); the center of this multiplet was at +51.27 ± 0.03 p.p.m vs. H_3PO_4. A much weaker multiplet, possibly due to a diastereomer, was centered at +48.9 ± 0.1 p.p.m. (measurements by Mr. S. R. Heller of this Department).

(3) F. Ramirez, N. B. Desai, and N. Ramanathan, *J. Am. Chem. Soc.*, **85**, 1874 (1963).

(4) New data on mixtures of DL plus *meso* 2:1 methyl pyruvate–trimethyl phosphite adducts show that the carbomethoxy group of the DL form is at lower field than that of the *meso* form (see ref. 2b).

The oxyphosphorane Va ($n^{25}D$ 1.4356; 60% yield) was collected at 88–89° (1.5 mm.) using a 12-in. spinning band column.[4a] In addition, some cyclic phosphate VIa ($n^{25}D$ 1.4381; 20%) was collected at 90–93° (0.5 mm.). The latter was identical with the product of the hydrolysis of Va with one mole of water in benzene. The dihydroxyketone VIIa had $n^{25}D$ 1.4489; b.p. 50–51° (0.3 mm.).

The adduct I and benzaldehyde (1:3 mole ratio) were stirred 112 hr. at 20°. The oxyphosphorane VIIIa ($n^{25}D$ 1.4935, 80% yield) was collected at 95–102° (1 mm.). Under certain conditions VIIIa loses trimethyl phosphate and forms a β-diketone enol. All structures given are consistent with the analytical data and the infrared and H^1 n.m.r. spectra.

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RECEIVED JUNE 14, 1963

Quadricyclo[2.2.1.0²,⁶.0³,⁵]heptan-7-ol (Quadricyclanol)

Sir:

We have prepared quadricyclo[2.2.1.0²,⁶.0³,⁵]heptan-7-ol (quadricyclanol, I). Carbonium ion II that might form directly from I or its derivatives could isomerize
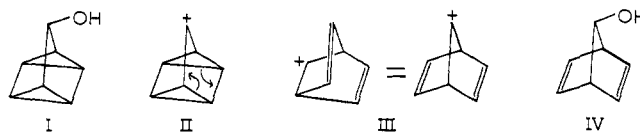
readily, as shown by the arrows, to the 7-norbornadienyl cation III thought to be remarkably stable.[1,2] Alternatively, II and III might represent resonance structures of a hybrid ion formed directly from both the quadricyclic and dienylic systems. The product of acetolysis of the β-naphthalenesulfonate ester of I contains approximately 20% of the acetate of I, 70% of the acetate of IV, and 10% of unidentified material (though the quadricyclic acetate was shown to be far less stable by its quantitative isomerization to the dienylic acetate on attempts at g.p.c.). In contrast, Winstein and Ordronneau reported[1] that hydrolysis of 7-norbornadienyl chloride or trifluoroacetate gave only IV and Story and Saunders[2] that acetolysis of the fluoroborate of III gave only the acetate of IV. Therefore, different intermediates (presumably II and III) must be formed initially in solvolysis reactions of these quadricyclic and dienylic derivatives. A solution of I in 96% sulfuric acid has λ_{max} 350 mμ (ε 5000), the same absorption reported for IV in sulfuric acid, suggesting formation of the same absorbing species from I and IV. The slow rate of formation of this absorption from solutions of I in less concentrated acid suggests that this species is not II or III.

The acetolysis rate of naphthalenesulfonate VII is 8.9 × 10⁻⁵ sec.⁻¹ at 25°. This rate is 10¹⁰ times that

(1) S. Winstein and C. Ordronneau, *J. Am. Chem. Soc.*, **82**, 2084 (1960).
(2) P. R. Story and M. Saunders, *ibid.*, **82**, 6199 (1960); **84**, 4876 (1962).