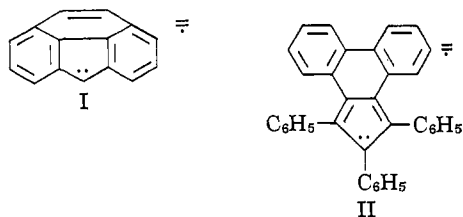


cyclopentadienide dianion radical or the corresponding ring closed compound II.¹³



All g -values were found to be higher than most previously described radicals. Anion radicals have slightly larger g -values than cation radicals of the same structure.¹⁴ The g -values for dianion radicals are consistent with the trend that the g -value of the radical increases with increase in negative charge on the radical.¹⁵

Samples were prepared in a high vacuum system and studied at room temperature in quartz tubes sealed under vacuum. Potassium mirrors were made by depositing distilled metal on the walls of a side arm under vacuum. A Varian 4502 e.p.r. spectrometer with a 12-in. magnet was used. g -Values were determined by means of a dual cavity using solid DPPH (diphenylpicrylhydrazyl) dispersed in NaCl as a g -value marker ($g = 2.0036$). By this means reported g -values could be reproduced to ± 0.0003 or better. Line widths were measured from first resolved maxima to last resolved minima.^{15a}

Acknowledgments. We are grateful to Dr. R. C. Lamb and to the Air Force Office of Scientific Research (AF-AFOSR-62-53) for their support of J. G. P. in this work.

(13) The formation of II in the reduction of pentaphenylcyclopentadienide would be analogous to the observed reduction of benzil dianion to phenanthrenequinone trianion radical (ref. 5b).

(14) M. S. Blois, Jr., H. W. Brown, and J. E. Mailing, "Free Radicals in Biological Systems," M. S. Blois, Ed., Academic Press Inc., New York, N. Y., 1961, p. 117.

(15) See A. J. Stone, *Mol. Phys.*, **6**, 507 (1963); **7**, 311 (1963).

(15a) NOTE ADDED IN PROOF. Recently cycloheptatrienide and tetraphenylallyl dianion radicals have been reported: N. L. Bauld and M. S. Brown, *J. Am. Chem. Soc.*, **87**, 4390 (1965); P. Dowd, *ibid.*, **87**, 4968 (1965).

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Condensation of Nitroethanol and Ribose 5-Phosphate. A Novel Route to Sedoheptulose 7-Phosphate¹

Sir:

The base-catalyzed condensation of nitroethanol with aldoses in methanol has been applied with some success as a key step in the synthesis of several ketoses.² We wish to report the first chemical synthesis of D-sedoheptulose 7-phosphate (S-7-P) using an analogous method in aqueous solution. This compound, which is unavailable commercially, is a very important metabolite³

(1) Supported in part by the Medical and Biological Research Fund of Washington State University and by Research Grant RG-5904 from the National Institutes of Health.

(2) J. C. Sowden, *Advan. Carbohydrate Chem.*, **6**, 316 (1951); J. C. Sowden and D. R. Strobach, *J. Am. Chem. Soc.*, **80**, 2532 (1958).

(3) J. S. Fruton and S. Simmonds, "General Biochemistry," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 530, 551, and 552.

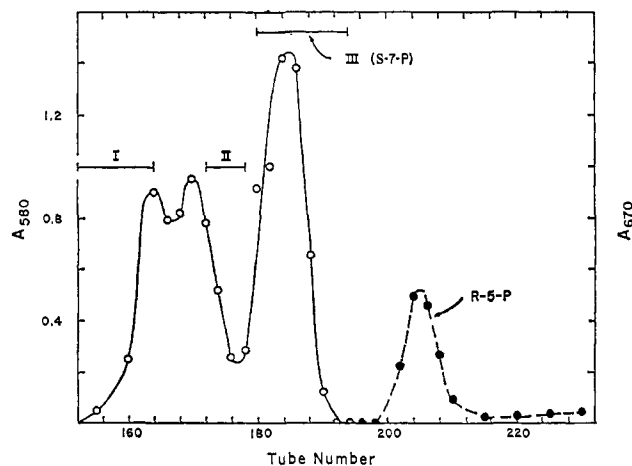


Figure 1. Column chromatography of the HBr-treated reaction mixture at an average rate of 0.7 ml./min. Fractions (22 ml./tube) were collected and 0.05 ml. was analyzed with orcinol⁸ to give: O—O, absorbancy at 580 $m\mu$ (A_{580}) due to heptulose phosphate, and ●—●, absorbancy at 670 $m\mu$ (A_{670}) due to ribose 5-phosphate. Absorbancies at 670 and 580 $m\mu$ due to heptulose phosphate and ribose 5-phosphate, respectively, are not shown.

and has been prepared by lengthy enzymatic methods^{4,5} and isolated in a partially purified state. Consequently its synthesis by more direct techniques and isolation in essentially pure form as described here are of considerable interest. Of additional interest is the likelihood that the present procedure opens an entirely new synthetic avenue to rare or unknown ketose phosphates.

An aqueous solution (97 ml.) of 6 mmoles of sodium D-ribose 5-phosphate (R-5-P) was prepared from the barium salt trihydrate (Nutritional Biochemicals Corp.). Then 1 *N* NaOH (30 mequiv.) and water were added at 2° to bring the volume to 180 ml., followed by the dropwise addition of 8.6 ml. (120 mmoles) of cold β -nitroethanol (Columbia Organic Chemicals Co.). After stirring for 24 hr. at 2° (kinetic experiments⁶ have established that the time may be shortened to 1 hr. or less), the amorphous sodium C-nitroalcohols were precipitated with ten volumes of cold acetone. The suspension was centrifuged at 2° and the supernatant solution was discarded. Cold 4 *N* HBr (250 ml.) was slowly added to the pellet which dissolved with concomitant evolution of N_2O . Then the pH was adjusted to 7.7 with LiOH, and 2.3 g. (6.9 mmoles) of $BaBr_2 \cdot 2H_2O$ was added. A small amount of precipitate was removed by filtration and the barium heptulose phosphate salts were precipitated from the filtrate by addition of five volumes of either cold acetone or cold ethanol. The barium salts were converted to a solution (80 ml.) of sodium salts with Na_2SO_4 . An aliquot assayed with transaldolase⁶ revealed that the yield of S-7-P was 30%. The solution of sodium salts was then chromatographed on a 2 \times 61 cm. Dowex 1-X8 column in the formate form by the general method of Horecker, *et al.*,^{7,8} except that

(4) B. L. Horecker, *Methods Enzymol.*, **3**, 195 (1957).

(5) J. R. Sokatch and B. A. McFadden, *Biochem. Prepn.*, **12**, in press.

(6) E. Racker in "Methods of Enzymatic Analysis," H. U. Bergmeyer, Ed., Academic Press Inc., New York, N. Y., 1963, p. 107. We are indebted to Dr. B. L. Horecker for a generous gift of highly purified transaldolase.

(7) B. L. Horecker, P. Z. Smyrniotis, H. Hiatt, and P. Marks, *J. Biol. Chem.*, **212**, 827 (1955).

(8) B. L. Horecker, *Methods Enzymol.*, **3**, 105 (1957).

fivefold lower concentrations of formate and formic acid were employed and 1 l. of water was used in the mixing chamber. It has proven essential to conduct a slow elution for optimal separation of products. Figure 1 shows the elution pattern. All efforts to date to separate the heptulose phosphates by other techniques have failed. Dephosphorylation with Polidase S⁹ of portions of each fraction and subsequent paper chromatography with D-*allo*-heptulose and D-sedoheptulose¹⁰ as standards established that fractions I and II, which were from overlapping peaks (Figure 1), both contained D-*allo*-heptulose 7-phosphate. The results also established that fraction III contained D-sedoheptulose 7-phosphate.

Fractions I, II, and III (Figure 1) were reduced to *ca.* 30% of the original volume and the barium salts were precipitated with cold alcohol and assayed enzymatically.⁶ Table I shows the yield of each product and results of the assays, and compares results of elemental analyses (Galbraith Laboratories, Inc., Knoxville, Tenn.) with theory.

Table I. Analyses of Heptulose Phosphate Products

Fraction	Yield of mono-hydrate, ^a mg. (%)	S-7-P-H ₂ O by trans-aldolase assay, %	% C ^b	% H	% P
I	90 (3)	0	19.14	3.27	6.97
II	112 (4)	9	18.95	3.40	6.94
III	428 (16)	101	18.86	3.47	6.85

^a Percentage yields assume that starting material was pure.

^b Theory for heptulose phosphate monohydrate for C, H, and P, respectively, is: 18.95, 3.41, 6.98.

In conclusion, the described condensation results in intermediate nitroalcohol salts which can be decomposed smoothly through the novel use of cold HBr. The principal product, D-sedoheptulose 7-phosphate, can be isolated in reasonable yield. We are currently investigating the scope of this reaction.

(9) I. Smith in "Chromatographic and Electrophoretic Techniques," Vol. I, I. Smith, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 527.

(10) We are indebted to Dr. N. K. Richtmeyer for samples of these sugars.

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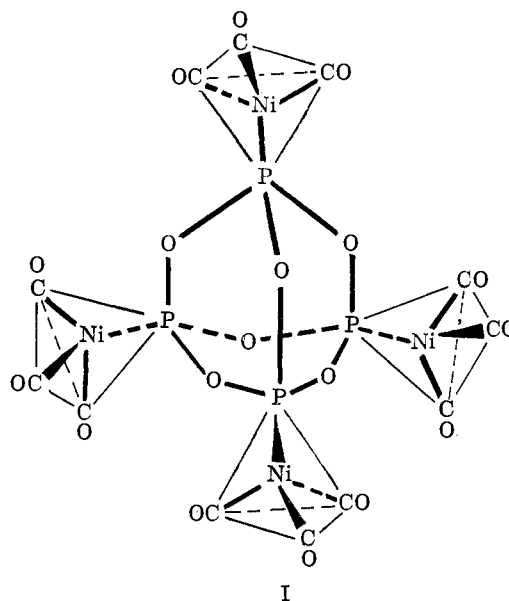
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P,P',P'',P'''-Tetrakistricarbonylnickel(tetraphosphorus hexaoxide)

Sir:

Phosphorus trioxide (P₄O₆) reacts with metal carbonyl complexes to give a new class of coordination compounds, including polymers, where P₄O₆ behaves as a polydentate ligand. When allowed to react with an excess of nickel carbonyl, the symmetric bird-cage structure of P₄O₆, which has four unshared pairs of electrons (one on each phosphorus), will coordinate with as many as four nickel tricarbonyl groups per

P₄O₆ molecule to give the tetrahedrally symmetric P,P',P'',P'''-tetrakistricarbonylnickel(tetraphosphorus hexaoxide) (I).



This is believed to be the first reported coordination complex built around a tetradentate phosphorus(III) molecule and is also the first complex having metal-phosphorus bonds where metal atoms are bridged by P-O-P linkages. Compound I is best obtained by treating 1 mole of P₄O₆ with 5 moles of Ni(CO)₄, mixed as neat liquids. Within about 10 min. at 24°, with evolution of 4 equiv. of carbon monoxide, I is formed as a white crystalline powder containing some unreacted Ni(CO)₄. It is essential to remove quickly this excess of Ni(CO)₄ in order to obtain a stable, storable product. The excess Ni(CO)₄ was removed by repeated crushing of the crystalline powder with Dry Ice cooled, dry pentane, followed by filtration. The pure compound shows unexpectedly good resistance to thermal decomposition and to reaction with moist air.

The structure of I is proven by the following: (a) a single sharp P³¹ n.m.r. peak at -32.9 p.p.m. for solutions (this is 10 p.p.m. downfield from P₄O₆ as expected¹ from the decrease of electron density on the phosphorus atoms in the complex); (b) the proper elemental analysis (Calcd.: P, 15.66; C, 18.22. Found: P, 15.47; C, 18.05); (c) a partial structure determination based on the X-ray powder diffraction pattern (1 mole per unit cell in the simple cubic system with a₀ = 8.81 Å.); and (d) the infrared stretching frequencies for the carbonyl which are close to those of the Ni(CO)₄ itself.

Additional structural evidence is obtained by following kinetically by P³¹ n.m.r. the formation of I. In this case, all of the intermediate species having from one to three tricarbonylnickel groups per P₄O₆ molecule are observed to form and maximize successively. These intermediate compounds exhibit the correct splitting patterns and reasonable n.m.r. chemical shifts and splitting constants for Ni-P bonding at the various :P< sites of P₄O₆. Thus, the over-all P³¹ n.m.r. spectrum at the beginning of the reaction exhibits the

(1) J. H. Letcher and J. R. Van Wazer, *J. Chem. Phys.*, submitted for publication.