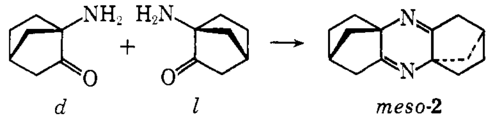
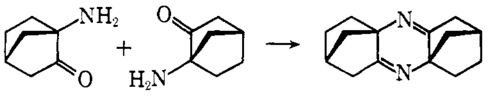
pure samples of **1** (mp 160–170°) whose spectral properties were almost identical with those of the mixture. *Anal.* Found: C, 78.53; H, 8.46; N, 13.01.

Fortunately, the problem of isomer separation could be largely avoided by generating compound **1** from optically active amino ketone. Examination of eq 3 shows the unwanted *meso*-**2** can only arise from the combination of one *d* and one *l* form of the amino ketone. On the other hand, **1** results when a *d* reacts with another *d*, or an *l* with an *l* (eq 4). Consequently, if one enatiomer is present in excess, optically active **1** is formed.



meso-**2** (3)



optically active **1** (4)

The amino ketone was resolved as its *d*-10-camphorsulfonic acid salt.[3] The two diastereomeric salts were fractionally recrystallized from acetone to constant rotation. The salt with the lower rotation, mp 208–209°, $[\alpha]_{578}$ +23.9° (MeOH), $[\alpha]_{365}$ +173°, was treated with dilute aqueous base and the product sublimed to yield optically active dihydropyrazine **1**, $[\alpha]_{578}$ −106.8° (CH_3OH), $[\alpha]_{365}$ −353°, apparently still containing some meso compound (mp 160–167°, sealed tube).

Dilute solutions of optically active **1** (50–90 mg (100 ml)) in methanol were prepared. These were irradiated through quartz under a positive pressure of nitrogen at 25°, 1.5 in. from a Hanovia 200-W mercury lamp. After 30 hr, racemization was greater than 90% complete ($[\alpha]_{365}$ −25°). No racemization occurred when Pyrex or Vycor filters were used.

Loss of optical activity by photoreactions other than racemization has been ruled out by continuously monitoring the shape and intensity of the characteristic ultraviolet spectrum of **1** (λ_{max} 208, ϵ 2.2×10^3; 250, ϵ 2.5×10^2) and observing that no changes take place. In addition, partially racemized dihydropyrazine with an optical rotation identical with that of the solution and other properties identical with the starting material could be recovered in 50% yield[4] by sublimation after 60–70% racemization. Rearrangement of **1** catalyzed by other photoproducts generated during the reaction might also account for our observations. However, we reject this hypothesis since photolysis was cleanly first order in starting material over four half-lives.

So far **1** does not appear to racemize thermally or in the presence of toluenesulfonic acid. It easily survived routine sublimation at 110–130°, and solutions in heptane were indefinitely stable at 25° and did not lose any optical activity after 4 days in a nitrogen-filled sealed tube at 110°. Longer periods of heating resulted in slow decomposition to a brown tar. The presence of magnesium oxide as an acid scavenger retarded but did not halt this process. The optical rotation of solutions in ethylene dichloride *ca.* 5 m*M* in **1** and 5–10 m*M* in toluenesulfonic acid gave a small initial loss of optical activity at 50°, then remained unchanged. The initial loss of optical activity was greater when less care was taken to exclude water from the system and was probably due to acid-catalyzed hydrolysis of **1**.

The thermal stability and photolability of **1** are in accord with the orbital symmetry considerations of Woodward and Hoffmann.[5] If the synchronous rearrangement of **1** proceeds with retention of configuration at both migrating centers, then, using Woodward–Hoffmann notation,[5] it must be a $[\sigma^2s + \pi^2s + \sigma^2a + \pi^2a]$ or entirely suprafacial or entirely antarafacial process, hence photochemically allowed and thermally forbidden, as observed. The thermally allowed process would require inversion at one center and retention at the other, very likely an energetically unfavorable process.

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[3] The camphor-10-sulfonic acid salt could be prepared by evaporation of an aqueous solution of 1 equiv of the amine hydrochloride and 1 equiv of camphor-10-sulfonic acid, and crystallization of the residue from acetone.

[4] The low recovery yield can be ascribed to the small quantity of material (<10 mg), the partial decomposition occurring during photolysis, and the partial decomposition which always accompanied sublimation of dihydropyrazine **1**.

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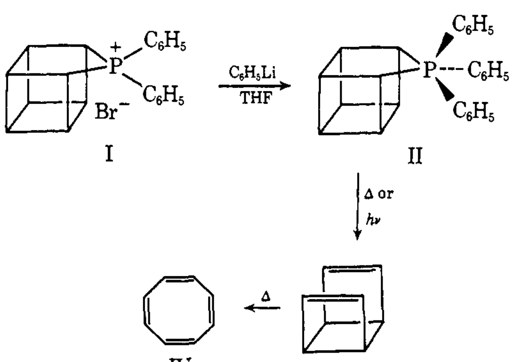
Stable Cycloalkyl Pentavalent Phosphoranes

Sir:

Tetraarylphosphonium salts react with phenyllithium to give pentaarylphosphoranes,[1] but phosphonium salts that have hydrogen atoms attached to one of the carbons bonded to phosphorus give ylides instead.[1b,2] We are reporting below that the phosphonium salt I, although it has hydrogen atoms attached to carbons bonded to phosphorus, reacts with phenyllithium to give not the ylide, but the corresponding pentavalent phosphorane, II. We are also reporting that when



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this unusual phosphorane (homocubyltriphenylphosphorane) is warmed to 75° or irradiated with ultraviolet light it fragments to give III. This is one of only few known fragmentations of a five-membered ring to two two-atom components and one one-atom component[3] and the only known cheleotropic reaction[4] of phosphorus.

Homocubyltriphenylphosphorane (II) is a white crystalline solid, mp 118–119°, is unaffected by water, and can be stored at room temperature in the atmosphere.[5] However when heated to 120°, just above its melting point, it decomposes in 85% yield to triphenylphosphine and a mixture of *syn*-tricyclo-[4.2.0.$0^{2,5}$]octa-3,7-diene (III, four parts)[7] and cyclooctatetraene (IV, one part).[8] In benzene solution the half-life[9] of II is about 7 hr at 75° and 50 hr at 60°. Photolyzed through Pyrex in C_6D_6 or CH_2Cl_2 it gives III (*ca.* 48% conversion after 6 hr in C_6D_6) and no IV. The hydrocarbon was isolated (15% yield) by glpc of the CH_2Cl_2 photolysate.

There are two possible reasons why the reaction of the phosphonium salt I with phenyllithium gives the pentavalent phosphorane rather than the ylide and why this pentavalent phosphorane is stable. Either (1) there is especial difficulty in the phenyllithium removing a proton from the carbon adjacent to phosphorus—although phenyllithium is known to be an effective reagent for forming many ylides,[2b] and the geometrical constraints of bridged ring systems have previously not inhibited ylide formation[10]—or (2) the formation of a pentavalent phosphorane is here especially favored. The latter is probably the true reason. In phosphonium salts the four groups attached to phosphorus should be tetrahedrally arranged,[11] and compound I must therefore be strained because the internal angle at phosphorus is close to, and probably less than, 90°.[12] This strain is unrelieved if the ylide is formed because the four groups should still be tetrahedrally arranged.[13] However if the pentavalent phosphorane forms, the strain is relieved because the trigonal-bipyramidal configuration normal for pentavalent phosphorus compounds[14] allows the ring to span without strain coordination positions separated by 90°.

It is probably for the same reason that the phosphonium salt I can be easily prepared by treating at −78° the corresponding phosphine oxide[15] in tetrahydrofuran with phenyllithium in benzene–ether (70:30),[16] followed by 20% aqueous HBr. (The salt melts at 310–311°, and the yield is 70%.)[17] Phosphonium salts are not usually prepared in this way[18] because phosphine oxides with α hydrogens usually give ylides instead,[19] and even when there are no α hydrogens the phosphonium salts form in only poor yield.[20]

The reason for the ease and efficiency with which the procedure gives the salt I is almost surely the reason II is so readily prepared: angle-strained tetravalent organophosphorus compounds react especially easily with nucleophiles to give their pentavalent derivatives. This is, of course, the reason given by Westheimer[6,21] why small-ring phosphate esters (and related substances) hydrolyze rapidly. The theory manifests itself in our experiments in the pentavalent derivative being isolable. We anticipate this to be a general phenomenon.[22]

Acknowledgments. We are grateful to the National Institutes of Health (MH-08912) for its support and Badische Anilin und Sodafabrik, A.G. for gifts of cyclooctatetraene.

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[5] The analyses for carbon, hydrogen, and phosphorus, the mass spectrum, and the proton nmr spectrum are all satisfactory. The proton nmr spectrum (100 MHz) in $CDCl_3$ at ambient temperature shows the resonances of the 15 aromatic protons and multiplets at τ 6.43, 6.71, and 7.04 of intensity 2, 2, and 4. The resonance at τ 6.43 is split into a doublet, $|J| = 13.0$ Hz, by coupling with ^{31}P, and this splitting is removed by irradiation at the phosphorus resonance frequency. The simplicity of the spectrum indicates that the molecule is pseudorotating rapidly.[6]

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[8] Compound III is transformed by heating into cyclooctatetraene.[7] The half-life in benzene at 75° is about 7.5 hr.

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[22] This probably accounts for the stability of the alkylbisbiphenylenephosphoranes.[23] Simple alkylphosphoranes are rapidly converted to a hydrocarbon and an ylide.[2a,24]

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Alkylation of the Dianion of β-Keto Esters

Sir:

Recently we required a method to substitute a β-keto ester at the γ carbon (eq 1). One method to

$$CH_3COCH_2CO_2R' \longrightarrow \underset{\textbf{1}}{RCH_2COCH_2CO_2R'} \qquad (1)$$

$$\underset{\textbf{2}}{\bar{C}H_2CO\bar{C}HCO_2R'} \qquad \underset{\textbf{3}}{CH_3CO\bar{C}HCO_2Me}$$