theory,[4] and that the mean ionic activities can be adequately approximated by extended Debye–Hückel theory with an interionic size parameter of 5.5 Å.,[5] we have determined the equilibrium constant for the oxidation–reduction reaction by fitting to the magnetic susceptibility data of Hutchison and Pastor.[6] For solutions of sodium in liquid ammonia less concentrated than *ca.* 0.1 *M*, we find that (assuming the solvent to be at unit activity)

$$\log K_1 \ (\text{l.}^2/\text{g. mole}^2) = \frac{2.09 \times 10^3}{T} - 3.42$$

where *T* is the absolute temperature. The equilibrium constants at each temperature, determined for each measured susceptibility, showed no trends with changing metal concentration and gave a mean value with an average deviation of *ca.* 15%. An analogous treatment of potassium solutions also has been made.

With no further adjustments of parameters implicit in K_2 and the relevant activity coefficients, calculations were made at a variety of compositions to test the validity of the proposed equilibria as follows.

(1) The vapor pressure depression data of Kraus[7] were compared with calculated values. The maximum deviation obtained for solutions <0.1 *M* was *ca.* 5%, with a trend toward better agreement for the smaller concentrations.

(2) The dilute solution conductance data have been found by others[8] to yield a value of K_2 substantially in accord with the value obtained from Fuoss' theory and indicating support for ion pairing. From the calculated temperature coefficient of composition, an estimate of *ca.* 3 × 10⁻² deg.⁻¹ was obtained for the temperature coefficient of conductance at −33°. The experimental value obtained by Gibson and Phipps[9] is 2 × 10⁻² deg.⁻¹.

(3) The Knight shift data[10] for N¹⁴ give values which are essentially proportional to the sum of the computed fractions of S⁻ and Na⁺·S⁻. The Knight shift data[10] for Na²³ give values which are essentially proportional to the computed fractions of Na⁺·S⁻.

(4) The dominant species (apart from Na⁺) at −65° for total metal concentrations >5 × 10⁻³ *M* were calculated to be Na⁻ and Na⁺·Na⁻, and these exhibited very nearly a linear variation in concentration with the concentration of total metal. As a result, the following of Beer's law for absorption, observed by Gold and Jolly,[11] is to be expected on the basis that the absorbing species may have broad, overlapping absorption spectra, not necessarily identical. The deviations from Beer's law observed at very long wave lengths correlates, apart from temperature dependence, with calculated fractions of Na⁺·Na⁻, the observed extinction coeffi-

cients being essentially proportional to the latter. A similar result is obtained at −45°.

The species S⁻·Na⁺·S⁻ (in our notation) has been suggested[12] as being present in sodium–ammonia solutions. Though formally similar to the Na⁻ proposed here, it is quite different. With the aid of the theory of Kraus and Fuoss,[3] and the noted values of K_1 and K_2, we have been able to estimate that [Na⁻]/[S⁻·Na⁺·S⁻] > 2500 in sodium–ammonia solutions for temperatures < −23°. The difference in the molal enthalpies of the two species is estimated to be *ca.* 9 kcal. Unless the electronic structure of the ion triple is altered appreciably, it cannot be identified with solvated metal anion introduced here.

A more detailed analysis of the experimental data leading to the above conclusions is currently being prepared for publication.

(12) See, for example, K. S. Pitzer, "Metal-Ammonia Solutions," W. A. Benjamin, Inc., New York, N. Y., 1964, p. 198.
(13) NDEA Graduate Fellow, 1961–1964; NSF Cooperative Fellow, 1964.

Sidney Golden, Charles Guttman,[13] Thomas R. Tuttle, Jr.
Department of Chemistry, Brandeis University
Waltham, Massachusetts

Condensation Reactions of Cyclooctatetraene Dianion with Aldehydes and Ketones

Sir:

Cyclooctatetraene dianion (I) is of recent interest with respect to structural theory and its chemical disciplines.[1] It has been reported that dilithium cyclooctatetraenide (I) condenses with aldehydes and ketones such as benzaldehyde, acetone, and benzophenone, etc., to yield 7,8-bis(α-hydroxyalkyl)-1,3,5-cyclooctatrienes (II) which may be dehydrated to tetrahydrofurans (III) by *p*-toluenesulfonic acid.[2] It has been presently found that I reacts with 2 equiv. of these aldehydes and ketones by (1) 1,2-bis addition to give II as probable intermediates which reorganize to 7,8-bis(α-hydroxyalkyl)-bicyclo[4.2.0]octa-2,4-dienes (IV, VI, and VIII) and
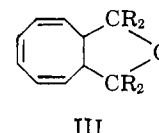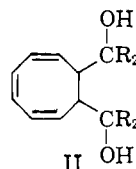
1,1,10,10-tetrasubstituted 2,4,6,8-decatetraene-1,10-diols (XII); and (2) 1,4-bis addition to yield 5,8-bis(α-hydroxyalkyl)-1,3,6-cyclooctatrienes (V, X, and XIV). The results thus described illustrate the much greater complexity in condensation reactions of I with carbonyl compounds than previously established[2] and the potential of I as a dicarbanionic reagent of the Grignard type. It has also been found that there are unusual rearrangements and real synthetic utility in acid-catalyzed de-

(4) R. M. Fuoss, *J. Am. Chem. Soc.*, 80, 5059 (1958).
(5) This value has been used by others: *e.g.*, J. L. Dye, G. E. Smith, and R. F. Sankuer, *ibid.*, 82, 4797 (1960). It was not adjusted in the analysis described here.
(6) C. A. Hutchison, Jr., and R. C. Pastor, *J. Chem. Phys.*, 21, 7959 (1953).
(7) C. A. Kraus, *J. Am. Chem. Soc.*, 30, 1192 (1908). The solvent activity was estimated by extended Debye–Hückel theory.
(8) See, for example, C. A. Kraus, *ibid.*, 43, 749 (1921); E. C. Evers and P. W. Frank, Jr., *J. Chem. Phys.*, 30, 61 (1959).
(9) G. E. Gibson and T. E. Phipps, *J. Am. Chem. Soc.*, 48, 312 (1926).
(10) J. V. Acrivos and K. S. Pitzer, *J. Phys. Chem.*, 66, 1993 (1962); H. M. McConnell and C. H. Holm, *J. Chem. Phys.*, 26, 1917 (1957).
(11) M. Gold and W. L. Jolly, *Inorg. Chem.*, 1, 818 (1962).

(1) T. J. Katz, *J. Am. Chem. Soc.*, 82, 3785 (1960); T. S. Cantrell and H. Shechter, *ibid.*, 85, 3300 (1963), and the references therein.
(2) V. D. Azatyan and R. S. Gyuli-Kevkhyan, *Izv. Akad. Nauk Arm. SSR Khim. Nauk*, 14, 451 (1961), and previous references.

hydration of the intermediate diols as derived from 1,2 (VI and VIII) and 1,4 (XI and XV) addition.

Addition of I in ether to benzaldehyde at 0° and acidification (eq. 1) gives 7,8-bis(α-hydroxybenzyl)-bicyclo[4.2.0]octa-2,4-diene (IV, 15%) and 5,8-bis(α-hydroxybenzyl)-1,3,6-cyclooctatriene (V, 80%). Bicyclic diol IV, m.p. 175°, is apparently derived by valence tautomerism of an intermediate cyclooctatriene II.[3]
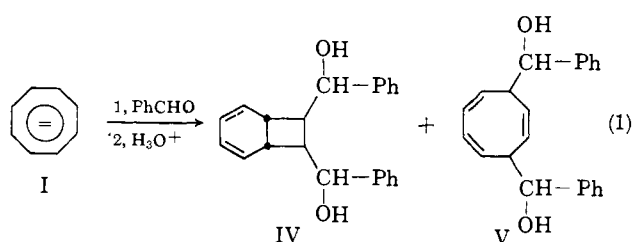
The structure of IV was deduced from its analysis, spectra,[4a] and its great Diels–Alder reactivity with N-phenylmaleimide and maleic anhydride. Diol V,[4b] from 1,4 addition, is a viscous liquid and is probably of *trans* stereochemistry.[4c]

Reaction of I with phthalaldehyde occurs by 1,2-bis addition and reorganization to yield diol VI, m.p. 190–191°. Its structure (VI) was based on its ultraviolet absorption[3] (λ_{max} 273 mμ, (ϵ 3200)), its rapid Diels–Alder addition to N-phenylmaleimide, and its dehydration and rearrangement (eq. 2) by acid to 2-phenyl-naphthalene (VII, 85%).
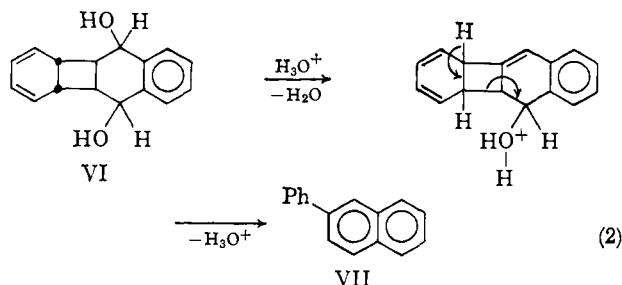

Excess acetone and I give (eq. 3) a mixture of 7,8-bis(2-hydroxy-2-propyl)bicyclo[4.2.0]octadiene (VIII, 62%) and 5,8-bis(2-hydroxy-2-propyl)-1,3,6-cycloocta-triene (X, 38%) which could not be separated adequately. Dehydration of the mixture with p-toluene-sulfonic acid yields o-bis(2,2-dimethylvinyl)benzene (IX, 36%) and 3,3-dimethyl-9-isopropylidene-2-oxa-tricyclo[4.3.1.0⁴,¹⁰]dec-7-ene (XI, 28%). The structure of IX, b.p. 55–56° (0.3 mm.), was established from its analysis, its infrared (λ_{max} 13.34 μ), ultraviolet[5a] (λ_{max} 229 mμ (ϵ 22,000)), and n.m.r.[5b] spectra, and its ozonolysis to 2 equiv. (61%) of acetone. The tricyclic ether (XI), b.p. 77–79° (0.5 mm.), was characterized from its analysis, infrared and ultraviolet[6a] absorption (λ_{max} 244 mμ (ϵ 15,500)), and most importantly its n.m.r.

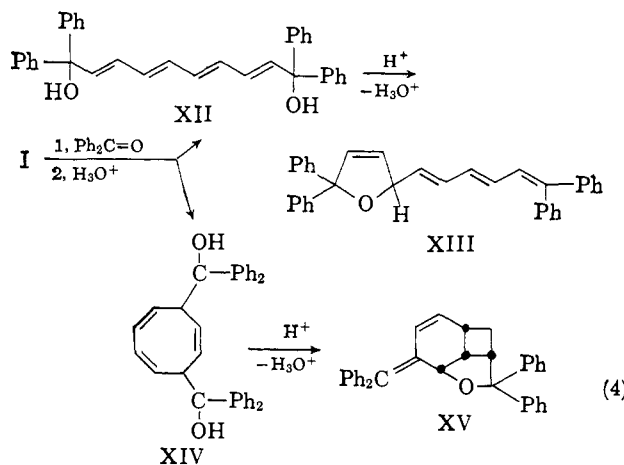(3) A. C. Cope, A. C. Haven, F. L. Ramp, and E. R. Trumbull, *J. Am. Chem. Soc.*, **74**, 4867 (1952).

(4) (a) Its ultraviolet spectrum (λ_{max} 274 mμ (ϵ 3100); λ_{min} 237 mμ (ϵ 780)) is similar to that of bicyclo[4.2.0]octadienes.[3] (b) Infrared spectrum: λ_{max} 2.91, 2.98, 13.14, and 14.4 μ; ultraviolet spectrum: λ_{max} 248 mμ (ϵ 2000). (c) *cis*-5,8-Disubstituted 1,3,6-cyclooctatrienes, in which one substituent must occupy a quasi-axial position, will be extremely crowded.

(5) (a) Compare with the spectrum of o-divinylbenzene (λ_{max} 229 mμ (ϵ 23,000)): F. W. Hoover, O. H. Webster, and C. T. Handy, *J. Org. Chem.*, **26**, 2234 (1961). (b) Signals at τ 2.94 (4H, singlet, phenyl hydrogens), 3.87 (2H, septet, J = 1.3 c.p.s., vinyl hydrogens), and 8.13 and 8.33 (6H each, doublets, J = 1.3 c.p.s., allylic methyls).
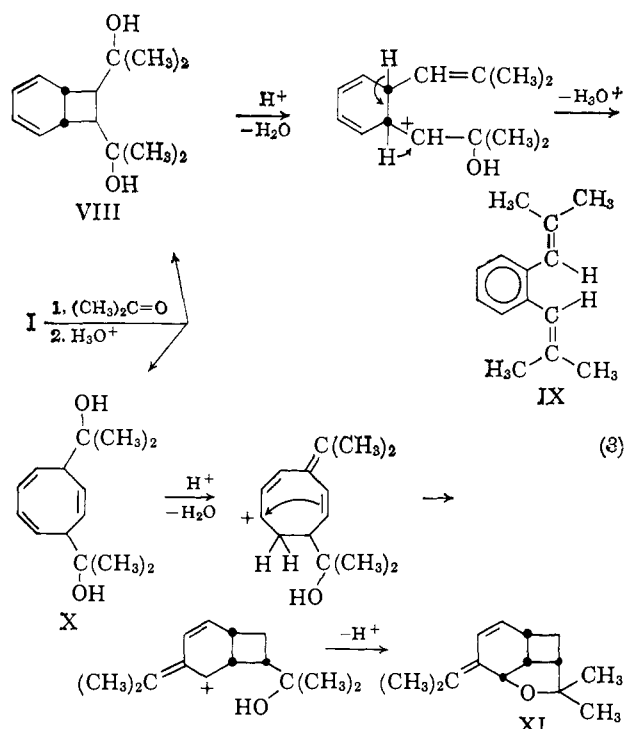
spectrum.[6b] Alternate structures containing a five-membered ring are eliminated by the size of the coupling constant[6c] between the hydrogens on C-7 and C-8.

Benzophenone condenses with I (eq. 4) to yield all-*trans*-1,1,10,10-tetraphenyl-2,4,6,8-decatetraene-1,10-diol (XII, 28%) and 5,8-bis(α-hydroxybenzhydryl)-1,3,6-cyclooctatriene (XIV, 64%). Diol XII is apparently formed by ring opening of the intermediate 1,3,5-cyclooctatriene (II). Such rearrangements have hitherto been observed only with 1,3,5-cyclooctatrienes bearing unsaturated substituents in the 7- and 8- positions.[7] In the present case ring opening is due primarily to relief from the steric strain of the bulky α-

hydroxybenzhydryl groups.

The gross structure of XII, m.p. 220°, was established upon its hydrogenation to 1,1,10,10-tetraphenyldecane-

(6) (a) Compare with 3-isopropylidene-6-methylcyclohexene (λ_{max} 243 mμ (ϵ 16,000)): H. Pines and H. Eschinazi, *J. Am. Chem. Soc.*, **7 7**, 6314 (1955). (b) Signals at τ 3.58 (1H, doublets, J = 10.3 and 0.8 c.p.s., C-8), 4.42 (1H, two doublets, J = 10.3 and 4.0 c.p.s., C-7), 5.27 (1H, doublet, J = 6.4 c.p.s., C-1), 6.2–7.3 (5H, multiplets, C-4, C-5, C-6, and C-10), 8.13 and 8.18 (3H each, singlets, allylic methyls), and 8.90 (6H, broadened singlet, methyls on C-3). (c) O. L. Chapman, *ibid.*, **85**, 2014 (1963).

(7) A. C. Cope and D. J. Marshall, *ibid.*, **75**, 3208 (1953).

1,10-diol.[8] Its stereochemistry is assigned all-*trans* because its ultraviolet spectrum[9a] is similar to that of *trans*-polyenes[9b] but different from those containing one or more *cis* double bonds.[9b] Tetraenediol XII reacts with 1 equiv. of excess N-phenylmaleimide to give a mono 4,7-adduct, m.p. 303°, which can be dehydrated to the fully conjugated pentaene, m.p. >300° (λ_{max} 264 and 361 mμ (ϵ 21,000 and 36,000)). Reaction of XII with *p*-toluenesulfonic acid yields 2,2-diphenyl-5-(6,6-diphenylhexatrienyl)-2,5-dihydrofuran (XIII, 71%), m.p. 132–133° (eq. 4); its structure is consistent with its analysis, spectra,[10a] and n.m.r. absorption.[10b] Tetraphenyldiol XIV is converted by *p*-toluenesulfonic acid (eq. 4) to the tricyclic ether XV (45%, m.p. 231°, λ_{max} 287 mμ (ϵ 19,500)); the transformation of XIV and proof of structure of XV are analogous to that of X and XI.[10b]

(8) M. Godchot, *Compt. rend.*, **171**, 198 (1920).

(9) (a) Maxima at 320 mμ (ϵ 66,000), 306 (70,000), and 294 (52,000); (b) L. Zechmeister and J. H. Pinckard, *J. Am. Chem. Soc.*, **76**, 4144 (1954).

(10) (a) λ_{max} at 239 and 326 mμ (ϵ 16,500 and 42,000); (b) the n.m.r. absorption will be discussed in detail in future publications.
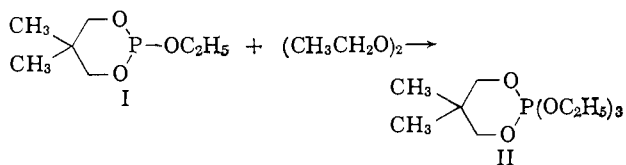
Thomas S. Cantrell, Harold Shechter

Department of Chemistry
The Ohio State University, Columbus 10, Ohio

Pentaalkoxyphosphoranes[1]

Sir:

Recently it was reported that a material believed to be pentaethoxyphosphorane could be prepared by reaction of triethyl phosphite and diethyl peroxide.[2] It is the purpose of this report to describe the preparation of two new pentaalkoxyphosphoranes. They are the cyclic oxyphosphorane II and pentamethoxyphosphorane. The phosphite (I) was allowed to react with diethyl peroxide at room temperature for 20 days. At this

$$\underset{\text{I}}{\overset{CH_3}{\underset{CH_3}{>}}\!\!<\!\!\overset{O}{\underset{O}{>}}\!P\!-\!OC_2H_5} + (CH_3CH_2O)_2 \longrightarrow$$

$$\underset{\text{II}}{\overset{CH_3}{\underset{CH_3}{>}}\!\!<\!\!\overset{O}{\underset{O}{>}}\!P(OC_2H_5)_3}$$

time the n.m.r. spectrum indicated that there was present unreacted phosphite, the phosphate (III) derived from I, a new material, and possibly minor amounts of other substances. Distillation at 65° (block) (0.25 mm.) gave a 60% fraction, whose n.m.r. spectrum indicated it was composed of *ca.* 15% I, very little III, and a new substance. This substance has been assigned the structure II on the basis of the following data. The phosphorus-31 n.m.r. spectrum taken on a sample 38 days after distillation showed absorption at −124.1, +1.9, +8.9, and +71.6 p.p.m. relative to 85% phosphoric acid. The absorptions can be assigned to I, triethyl phosphate, III, and II, respectively.[3] Large positive shifts are characteristic of phosphorus com-

(1) This research has been supported by the National Science Foundation under Grant GP-202.

(2) D. B. Denney and H. M. Relles, *J. Am. Chem. Soc.*, **86**, 3897 (1964).

(3) The proton n.m.r. spectrum of the 38 day old sample showed considerable changes from that obtained on the freshly distilled material. These changes clearly indicate that III was formed over the 38 days.

pounds with five electronegative groups attached to phosphorus.[4] The proton n.m.r. spectrum of the freshly distilled sample showed a singlet at τ 9.04 and a triplet at 8.98 ($J = 7$ c.p.s.) further split into doublets ($J = 2$ c.p.s.). There was also a complex multiplet centered at τ 6.2. The 9.04 absorption can be assigned to the *gem*-dimethyl group,[5] the 8.98 to the methyls of the ethyl groups, and the remainder to methylene groups. Some phosphite (I) was also detected by the presence of an absorption at τ 9.3.

The infrared spectrum of II is similar in many respects to those of I and III; however, each can be distinguished from the other by characteristic absorptions. In particular II has broad absorptions at 12.35 and 13.2 μ, I at 12.5 (sharp) and 13.5 μ (broad), and III has strong sharp bands at 11.65 and 12.0 μ. There is also a strong absorption at 7.6 μ in III which is weak in II and absent in I.

Attempted g.l.p.c. analysis, 10-ft. silicone grease column, 175°, injection port 195°, gave at least seven products. Two of the major components were shown to be triethyl phosphate and III by adding each and rechromatographing.

All of the above physical data support the assignment of structure II. The reactions of II lend support to this structural assignment. Benzoic acid reacted exothermically with II[6] at room temperature to give ethanol, ethyl benzoate (78%), triethyl phosphate (24%), III (42%), and uncharacterized materials. Reaction of II with phenol was mildly exothermic and led to the formation of ethanol, phenetole (78%), III (33%), and triethyl phosphate (19%). Treatment of II with an equimolar amount of butanol gave very little reaction; after 7 days a trace of butyl ethyl ether had been formed. Hydrolysis of II was rapid and resulted in the formation of phosphates and ethanol.

Trimethyl phosphite was allowed to react with dimethyl peroxide in methylene chloride for 2 months in a refrigerator. Evaporation of the methylene chloride afforded a residue whose n.m.r. spectrum in carbon tetrachloride showed two doublets at τ 6.26 ($J = 11$ c.p.s.) and 6.56 ($J = 12$ c.p.s.). A weak doublet with $J = 10$ c.p.s. appeared on the sides of the peaks of the τ 6.56 doublet. The doublet at τ 6.26 was increased in intensity when trimethyl phosphate was added. The small doublet may have been due to trimethyl phosphite; it has the same chemical shift and coupling constant. Distillation at 40° (block) (10 mm.) concentrated the unknown material in the distillate.[7] Treatment of a carbon tetrachloride solution of this material with water yielded trimethyl phosphate and methanol. Treatment with benzoic acid yielded methyl benzoate (70%) based on the mole ratio determined by n.m.r.,[7] trimethyl phosphate (100%), and a low-boiling material, possibly methanol. On the basis of these data it is concluded that the reactive material is pentamethoxyphosphorane.[8]

(4) F. Ramirez and N. B. Desai, *J. Am. Chem. Soc.*, **85**, 3252 (1963).

(5) It is very interesting to note that the *gem*-dimethyls are not equivalent (τ 9.3 and 8.82) in the phosphite (I) and (τ 9.13 and 8.8) in the phosphate (III), whereas they are apparently equivalent in II.

(6) The material was freshly distilled and by n.m.r. showed *ca.* 15% I and very little III.

(7) If it is assumed that this material is pentamethoxyphosphorane the mole ratio changed from 0.67:1 to 1.62:1.

(8) Unfortunately it was not possible to obtain a phosphorus-31 n.m.r. spectrum of this material.