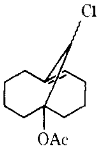
References and Notes

(1) We thank the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and the U.S. ERDA for support of this work.
(2) Taken, in part, from the Ph.D. Dissertation of Shih-Lai Lu.
(3) Fellow of the Alfred P. Sloan Foundation, 1976–1978.
(4) (a) P. M. Warner, R. C. LaRose, C.-M. Lee, and J. C. Clardy, *J. Am. Chem. Soc.*, **94**, 7607 (1972); (b) C. B. Reese and M. R. D. Stebles, *J. Chem. Soc., Chem. Commun.*, 1231 (1972); (c) P. Warner, J. Fayos, and J. Clardy, *Tetrahedron Lett.*, 4473 (1973); (d) W. E. Parham, D. C. Egberg, and W. C. Montgomery, *J. Org. Chem.*, **38**, 1207 (1973); (e) P. Warner and S. Lu, *J. Am. Chem. Soc.*, **97**, 2356 (1975); (f) P. Warner, S. Lu, E. Myers, P. DeHaven, and R. A. Jacobson, *Tetrahedron Lett.*, 4449 (1975); (g) P. Warner, R. LaRose, R. F. Palmer, C. Lee, D. O. Ross, and J. C. Clardy, *J. Am. Chem. Soc.*, **97**, 5507 (1975); (h) P. Warner and S. Lu, *ibid.*, **98**, 6752 (1976).
(5) (a) G. Köbrich, *Angew. Chem., Int. Ed. Engl.*, **12**, 464 (1973); (b) G. L. Buchanan, *Chem. Soc. Rev.*, **3**, 41 (1974); (c) D. B. Ledlie, J. Knetzer, and A. Gitterman, *J. Org. Chem.*, **39**, 708 (1974); (d) R. Keese, *Angew. Chem., Int. Ed. Engl.*, **14**, 528 (1975); (e) D. B. Ledlie and L. Bowers, *J. Org. Chem.*, **40**, 792 (1975); (f) D. B. Ledlie, T. Swan, J. Pile, and L. Bowers, *ibid.*, **41**, 419 (1976).
(6) L. A Paquette, I. Itoh, and W. B. Farnham, *J. Am. Chem. Soc.*, **97**, 7280 (1975). These authors found the protons cis to a hydroxyl group in a five-membered ring to show LIS's of −13.9, −11.9, and −12.4, while the trans protons had LIS's of −6.3, −7.8, and −7.1 ppm.
(7) In the corresponding hydrolysis of 11,11-dibromo[4.4.1]propellane,[4e] three acids are formed.
(8) P. Warner, R. F. Palmer, and S.-L. Lu, *J. Am. Chem. Soc.*, **99**, 3773 (1977).
(9) Precedent for the solvolytic rearrangement of a bicyclo[4.3.1]decane to bicyclo[5.3.0]decane ring system exists: J. A. Marshall, *Synthesis*, 517 (1972).
(10) We thank Professor Reese for this information prior to publication.
(11) R. F. Bryan and J. D. Dunhitz, *Helv. Chim. Acta*, **43**, 3 (1960).
(12) S. Dahl and P. Groth, *Acta Chem. Scand.*, **25**, 1114 (1971).
(13) P. Iwasaki, M. Sato, and A. Aihara, *Acta Crystallogr., Sect. B*, **32** (1), 102 (1976).
(14) F. J. Andrian, *J. Chem. Phys.*, **29**, 1381 (1958).
(15) P. Romain, *Bull. Soc. Fr. Mineral. Cristallogr.*, **81**, 35 (1958).
(16) We doubt that I could have been present in the mixture of enol acetates and then be reconverted to **21** upon hydrolysis, since **24** readily gave **24-OH** without any trace of **3** upon hydrolysis (see Experimental Section).



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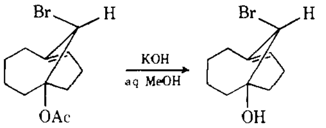

24 **24-OH**

(17) In contrast, both 5-cyclononynone[18a] and 5-cyclodecynone[18b] undergo transannular acid-catalyzed cyclization to afford bicyclo[4.3.0]non-1(6)-en-2-one and bicyclo[4.4.0]dec-1(6)-en-2-one, respectively.
(18) (a) G. L. Lange and T. Hall, *J. Org. Chem.*, **39**, 3817 (1974); (b) C. E. Harding and M. Hanack, *Tetrahedron Lett.*, 1253 (1971).
(19) P. G. Gassman, R. N. Steppel, and E. A. Armour, *Tetrahedron Lett.*, 3287 (1973); (b) P. G. Gassman, G. M. Lein, Jr., and R. Yamaguchi, *ibid.*, 3113 (1976).
(20) K. B. Wiberg and R. A. Fenoglio, *J. Am. Chem. soc.*, **90**, 3395 (1968).
(21) P. Warner, unpublished results.
(22) R. L. Kronenthal and E. I. Becker, *J. Am. Chem. Soc.*, **79**, 1095 (1957).
(23) P. Warner and S. Lu, *J. Org. Chem.*, **41**, 1459 (1976).
(24) S. Winstein, E. C. Friedrich, R. Baker and Y. Lin, *Tetrahedron, Suppl.*, **No. 8**, pt 2, 621 (1966).
(25) R. O. Hutchins, C. Milewski, and B. Maryanoff, *J. Am. Chem. Soc.*, **95**, 3662 (1973).
(26) G. W. Kabalka and J. D. Baker, Jr., *J. Org. Chem.*, **40**, 1834 (1975).
(27) K. Ohkata, *J. Org. Chem.*, **41**, 2162 (1976).
(28) J. Tadanier, *J. Org. Chem.*, **31**, 3204 (1966).
(29) E. Vogel, W. Wiedemann, H. Roth, J. Eimer and H. Günther, *Justus Liebigs Ann. Chem.*, **759**, 1 (1972).
(30) W. Hückel, R. Danneel, A. Schwarz, and A. Gercke, *Justus Liebigs Ann. Chem.*, **474**, 121 (1929).
(31) L. F. Fieser, "Organic Experiments", D. C. Heath, Boston, Mass., 1964, p 96.
(32) W. Hückel and H. Schlee, *Chem. Ber.*, **88**, 346 (1955).
(33) W. J. Rohrbaugh and R. A. Jacobson, *Inorg. Chem.*, **13**, 2535 (1974).
(34) R. A. Jacobson, *J. Appl. Crystallogr.*, **9**, 115 (1976).
(35) D. E. Williams, *U.S.A.E.C.*, **IS-1052** (1964).
(36) S. L. Lawton and R. A. Jacobson, *Inorg. Chem.*, 7, 2124 (1968).
(37) E. R. Howells, D. C. Phillips, and D. Rogers, *Acta Crystallogr.*, **3**, 210 (1950).
(38) C. A. Hubbard, C. O. Quicksall, and R. A. Jocobson, *U.S.A.E.C.*, **IS-2625** (1971).
(39) W. R. Busing, K. O. Martin, and H. A. Levy, *U.S.A.E.C.*, **ORNL-TM-305** (1965).
(40) D. W. Cruickshank and D. E. Pilling in "Computing Methods and the Phase Problem in X-Ray Crystal Analysis", R. Pepinsky, J. M. Roberts, and J. C. Speakman, Ed., Pergamon Press, New York, N.Y., 1961.
(41) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1960).
(42) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(43) D. H. Templeton in "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962, pp 215–216, Table 3.3.2c.
(44) C. A. Johnson, *U.S.A.E.C.*, **ORNL-3794** (1971).
(45) F. Takusagawa, personal communication, 1976.
(46) Supplementary material.

On the Mechanism of Reductive Cleavage of Aryl Phosphates[1a]

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Abstract: Evidence is presented which strongly indicates that cleavage of aryl phosphates with electron donors may occur either by a one-electron or two-electron pathway. Thus, high concentrations and greater reducing power of the electron donor favor production of arene (C–O cleavage product) while low concentrations and/or lower reducing power of the electron donor favor production of phenol (P–O cleavage product) from aryl phosphates. A rationale based on the intermediacy of a trigonal bipyramidal phosphate ester anion radical which either undergoes P–O (α) scission or is reduced further and undergoes C–O (β) scission, is presented. Comparison is also made with the electron transfer chemistry of sulfonate esters.

In our studies of the reaction of sulfonyl derivatives with electron donors we have discovered several rather different types of cleavage mechanisms. With arenesulfonamides (**1**) the initial electron transfer step is rate controlling and results in exclusive S–N cleavage.[2] This is followed by rapid further reduction resulting in overall formation of arenesulfinate and amide anions. With alkyl alkanesulfonates (**2**) initial electron transfer apparently results in a metastable substrate anion radical which, if nothing further transpires, undergoes C–O cleavage yielding alkyl radical and alkanesulfonate anion.[3] If,

Table I. Cleavage of Aryl Diethyl Phosphates with Electron Donors

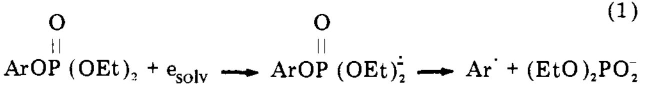
Aryl group	Electron donor	Mode of addition[a]	% arene[b]	% phenol[b]
Phenyl (**4a**)	$Na^+Naph^{-\cdot}$/THF	Inverse	88	10
	$Na^+Naph^{-\cdot}$/THF	Normal	34 (68)	66 (29)
	Na/liq NH_3	Normal	*c*	(29)
p-Tolyl (**4b**)	$Na^+Naph^{-\cdot}$/THF	Inverse	76	<1
	$Na^+Naph^{-\cdot}$/THF	Normal	23 (51)	59 (30)
	$Na^+Anth^{-\cdot}$/THF	Normal	<1	74
	Na/liq NH_3	Inverse	55	<1
	Na/liq NH_3	Normal	(55)	(27)
	$Na^+Naph^{-\cdot}$THF-TG[d]	Normal	(53)	(42)
	$Na^+Naph^{-\cdot}$/THF-TG[d]	Inverse	70	12
p-Anisyl (**4c**)	$Na^+Naph^{-\cdot}$/THF	Inverse	54	8
	$Na^+Naph^{-\cdot}$/THF	Normal	16 (40)	69 (33)
	$Na^+Anth^{-\cdot}$/THF	Normal	<1	86
	Na/liq NH_3	Inverse	62	<1
	Na/liq NH_3	Normal	(76)	(17)
p-Biphenylyl (**4d**)	$Na^+Naph^{-\cdot}$/THF	Inverse	61	<1
	$Na^+Naph^{-\cdot}$/THF	Normal	(43)	(21)
p-chlorophenyl (**4e**)	$Na^+Anth^{-\cdot}$/THF	Normal	<1	60

[a] In inverse addition ester was added rapidly to 0.5 M electron donor solution; normal addition involved slow addition of electron donor solution to 0.1 M ester solution. [b] Yields quoted are averages of at least two separate experiments. Reproducibility of arene yields is about ±3%, of phenol yields, about ±5%. Data in parentheses refer to experiments where 0.5 M electron donor solutions were used for normal addition rather than 0.2 M. [c] Benzene detected but not measured. [d] Solvent system was 50:50 (v/v) THF–tetraglyme (TG).

however, electron donor concentration and/or reducing power is high, further reduction may take place and a different mode of cleavage, S–O, occurs, yielding alkoxide and alkanesulfinate ions.[3] Recently, we have noted that the mode of reductive cleavage of aryl alkanesulfonates (**3**) is also quite sensitive to reducing power of the electron donor, though not particularly sensitive to its concentration. Thus, use of sodium in liquid ammonia results in production of high yields of arene (C–O cleavage),[4,5] use of sodium naphthalene in THF ($-E_{1/2} = 2.50$ V)[6] gave some arene but mostly phenoxide (S–O cleavage) product, while sodium anthracene ($-E_{1/2} = 1.96$ V)[6] resulted in exclusive S–O cleavage, yielding only alkanesulfinate and phenoxide anions.[5]

In 1955 Kenner and Williams reported that aryl diethyl phosphates (**4**) gave fairly good yields of arenes on treatment with sodium in liquid ammonia and recommended this reaction as a useful procedure for deoxygenation of phenols.[4] They also noted formation of small amounts of phenol in the reactions and a "bicarbonate soluble oil, possibly aryl ethyl hydrogen phosphate".[4] Recently, Rossi and Bunnett have elaborated on this work and have shown that yields of arene can be as high as 90%.[7] Their ability to trap the aryl group with amide ion (to form aniline)[8] (via a proposed $S_{RN}1$ mechanism)[9] led them to postulate the intermediacy of an aryl radical.[10] Their interpretation of the mechanism is given in eq 1. This fits with their

$$\underset{\mathbf{1}}{ArSO_2NR_2} \qquad \underset{\mathbf{2}}{RSO_2OR'} \qquad \underset{\mathbf{3}}{ArOSO_2R}$$



$$\underset{\mathbf{4}}{Ar\overset{\overset{\displaystyle O}{\|}}{O P}(OEt)_2} + e_{solv} \longrightarrow Ar\overset{\overset{\displaystyle O}{\|}}{O P}(OEt)_2^{\dot{-}} \longrightarrow Ar^{\cdot} + (EtO)_2PO_2^- \qquad (1)$$

"sense of cleavage" scheme based on the relative electronegativities of the atoms attached to the bond being broken.[10]

Our experience with reductive cleavages of sulfonate esters, the earlier report of phenol being a minor product from the aryl phosphate reduction,[4] and the quite curious behavior of **4** on attempted photostimulated $S_{RN}1$ reaction with acetone enolate ion (phenol, not phenylacetone, is the major product after relatively long periods of irradiation)[11] prompted us to reinvestigate this reaction using electron donors of different reducing power, i.e., arene anion radicals.

Results and Discussion

The reactions of several aryl diethyl phosphate esters (**4a–e**) with sodium naphthalene and sodium anthracene in tetrahydrofuran (THF) and with sodium in liquid ammonia were examined using several different combinations of electron donor concentration and mode of mixing the reactants. The results are shown in Table I.

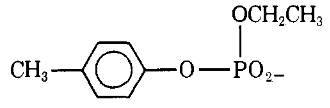
In all cases examined the poorest electron donor, sodium anthracene, gave only one cleavage product, the corresponding phenoxide ion. The reaction was rather slow in all cases and there appeared to be little effect of mode of mixing the reactant solutions on the nature or yield of products. The phosphorus-containing salts from these reactions were not examined.

Use of sodium naphthalene, however, gave mixtures of arene and phenoxide ion whose composition was highly dependent on both anion radical concentration and mode of mixing. For example, adding phenyl diethyl phosphate (**4a**) slowly to an excess of 0.5 M sodium naphthalene in THF ("inverse addition") results in a high yield of benzene (88%) and very little phenol (10%), while dropwise addition of 0.2 M anion radical solution to an 0.15 M solution of **4a** ("normal addition") until the green color of the reagent persists results in formation of only 34% benzene and 66% phenol. "Normal addition" of 0.5 M sodium naphthalene to **4a** shifts the product composition back toward mostly benzene. Similar results were seen with most of the other aryl phosphates. The *p*-chlorophenyl ester (**4e**) underwent considerable dechlorination with sodium naphthalene, however, making interpretation of its behavior rather difficult.

The reactions of some of the esters (**4a–c**) with sodium in liquid ammonia were examined in similar fashion. Here, "inverse addition" (most similar to the manner in which sodium–liquid ammonia reductions are normally performed) gave good yields of arene and no detectable phenol, while "normal addition" gave equally good yields of arene but now accompanied by significant quantities (17–29%) of phenol.

Analysis of the water-soluble salts from reaction of **4b** with sodium naphthalene ("normal addition") by means of high-pressure liquid chromatography (HPLC) revealed the presence of not only the expected diethyl phosphate and phosphite anions but also of an additional material of longer retention time.

Isolation of this material and examination by NMR showed that it contained a *p*-tolyl group and an ethoxy group in 1:1 ratio (see Experimental Section). It was tentatively identified as *p*-tolyl ethyl sodium phosphate (**5**).



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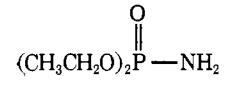


$(CH_3CH_2O)_2P(=O)-NH_2$

6

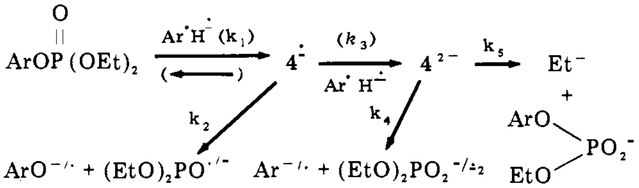
Production of phenol from these phosphate esters could easily result from nucleophilic attack rather than by an electron-transfer mechanism. To check against this and other possible routes to phenol or arene, several control reactions were performed. A solution of 0.5 M sodium naphthalene in THF was quenched by addition of a small amount of water and then ester **4b** added to the mixture and stirred for 10 min at 25 °C. Analysis showed formation of neither *p*-cresol nor toluene. The *p*-anisyl ester (**4c**) was cleaved with 0.5 M sodium naphthalene (normal addition) and then ester **4b** was added and the resulting mixture stirred for 10 min. Again, analysis showed neither *p*-cresol nor toluene to be present. Treatment of the sodium salt of *p*-cresol with 0.5 M sodium naphthalene in THF produced no detectable toluene. With respect to the reactions carried out in liquid ammonia (actually a mixture of liquid ammonia in THF; see Table I), the solvent itself is quite nucleophilic. However, it was shown that treatment of a solution of **4b** in THF with liquid ammonia under conditions of the "normal addition" cleavage reaction produced no detectable amount of *p*-cresol. Treatment of **4b** with 1 equiv of sodium amide in liquid ammonia-THF for 18 min at −50 °C did yield 4% *p*-cresol but this is far from the 27% yield of cresol obtained from "normal addition" of Na-liquid ammonia to a THF solution of **4b**. Formation of phenoxide ion via displacement by ammonia or amide ion would also require production of *O,O*-diethylphosphoramide (**6**). Examination of products from a "normal" addition sodium-liquid ammonia cleavage of **4b** showed the presence of about 1% of **6**. It was also shown that **6** was stable under the conditions required for cleavage of **4b**. In addition it was shown that the sodium salt of *p*-cresol was stable to sodium-liquid ammonia under our usual reaction conditions and that no detectable amount of *p*-toluidine was formed from **4b** during our sodium-liquid ammonia cleavages.

The states of ion pairing are known to play an important role in many electron transfer reactions.[12,13] Sodium naphthalene in THF is known to exist almost entirely as tight ion pairs while in mixtures of THF and tetraglyme it exists as a "glymated" ("loose") ion pair.[12] Bank and Juckett have shown that in the reductive cleavage of *n*-hexyl chloride with sodium naphthalene there is a rate increase of nearly an order of magnitude on going from THF to THF-tetraglyme as solvent.[14] This was interpreted as indicating more rapid electron transfer by the freer ions. Accordingly, the reaction of **4b** with sodium naphthalene in 50% THF-tetraglyme was examined to see if this change would affect the yields of arene and phenol. From Table I it is seen that the result using this reagent in either "normal" or "inverse" addition are almost the same as obtained with pure THF solutions; "normal" addition greatly increases the yield of phenol and "inverse" addition favors toluene formation. About the only conclusion that can be drawn is that either the steps of this reaction are not very sensitive to the ion pairing state of the electron donor, or that there are nearly compensating effects occurring. It was also found that buffering the phosphate ester solution with a tenfold excess of sodium perchlorate (ca. 1.5 M) had only minor effects on the observed yields of arene and phenol.

The fate of the ethyl fragment lost in formation of **5** was of interest. Ethanol, diethyl ether, and ethylene were shown to be absent from reaction mixtures from sodium naphthalene and **4a–c**. A small amount of very volatile material with GC retention time similar to that of ethane was observed in all these reaction mixtures and while quantitative measurements were not successful we feel that most of the ethyl group must be converted to ethane. If so, this is rather similar to the C-O cleavage reactions undergone by alkyl *N,N,N′,N′*-tetramethylphosphorodiamidates and certain other alkyl phosphate esters on reduction with lithium in ethylamine.[15] About the two most likely precursors of ethane would be ethyl anion and ethyl radical. Sodium naphthalene is known to be a quite efficient trap for alkyl radicals, converting about 50% of them to 1-alkyldihydronaphthalene species.[16] Careful examination of the product mixture from reaction of **4b**, with sodium naphthalene under conditions ("inverse" addition) where the material balance would indicate ca. 20% loss of ethyl group revealed the presence of much less than 1% of 1-ethyldihydronaphthalene, much less than the expected 8–10% of substitution product. (This small trace of ethyldihydronaphthalene could frequently be found after water quenching of our original sodium naphthalene-THF solutions and probably results from the very slow reaction between THF and anionic naphthalene species.)[17] Inspection of several other product mixtures from reaction of sodium naphthalene with phosphates **4** also showed only traces of ethyldihydronaphthalene. The other possible precursor of ethane, ethyl anion, should be capable of being trapped by anhydrous magnesium bromide.[18] Ester **4b** was treated with sodium naphthalene in the presence of an excess of anhydrous $MgBr_2$, followed by addition of acetaldehyde. No 2-butanol was observed in the product mixture. Unfortunately, a control experiment showed that ethylmagnesium bromide reacts rapidly with aryl diethyl phosphates, producing phenol and presumably a phosphonate ester. Thus, formation of ethane via an ethyl anion cannot be ruled out.

The most economical rationale for the striking effects of concentration and reducing power of the electron donor on the mode of cleavage of aryl phosphates is similar to the stepwise mechanisms proposed for aryl[5] and alkyl alkanesulfonates.[3] It is set forth in Scheme I. A finite lifetime for species $4^{-}\cdot$ is required but not for 4^{2-}. The reactions with sodium naphthalene and sodium in liquid ammonia are very fast so it is not possible to estimate effective concentrations of electron donor at given stages of reaction, but for "inverse" addition it must be at least close to 0.4 M during a large part of the reaction and much lower for "normal" addition. Assuming that the electron transfer steps are not reversible and using the relationship k_3 [electron donor]/k_2 = [arene + ethane]/[phenol], one can estimate that the ratio k_3/k_2 is ca. 0 for sodium anthracene, in the range 10–10^2 for sodium naphthalene, and ca. 10^3 for sodium in liquid ammonia, in keeping with the increasing reducing power of this series of reagents. Also, if one examines the yield of arene from esters **4a–c** under similar conditions, the order is always **a** > **b** > **c** in keeping with the expected inductive effects of the substituents in **b** and **c** upon the ease of introducing negative charge into the esters. (The *p*-biphenylyl ester, **4d**, does not seem to fit a pattern based on simple Hammett substituent constants, but is not too far out of line.) If one considers combined yields of arene plus estimated ethane (determined assuming that all unaccounted-for material has

Scheme I



gone into production of ethane) there is little difference between the different esters. Whether this is meaningful or not, however, is clouded by the obviously larger error in estimating ethane yield and by the fact that other unknown minor side reactions may be taking place. The relative yields of phenol from esters **4a–d** also seem not to follow any easily decipherable pattern.

We have no evidence with respect to the "sense of cleavage"[10] of $\mathbf{4}^{-}\cdot$ and $\mathbf{4}^{2-}$ with respect to the aryl fragment. Either possible radical fragment from cleavage of $\mathbf{4}^{-}\cdot$ would be expected to be rapidly reduced to an anion by either sodium naphthalene or possibly unreacted $\mathbf{4}^{-}\cdot$. Bunnett and co-workers have been able to trap phenyl radicals from reaction of **4a** in alkali metal-liquid ammonia solution,[10,19] implying, if our mechanism is correct, that the unusual dianion radical **7** is the coproduct. This highly charged ion might appear rather unlikely, but the fact that *p*-toluenesulfonate ion is slowly reduced to toluene by sodium naphthalene in THF[20] strongly implies that species **8** is at least attainable and therefore **7** not implausible. Whether the precursor of arene in THF is a radical, however, is not easily predictable. The sense of cleavage of anion radicals is often solvent sensitive[21] and as yet good radical traps for aryl radicals in THF have not been developed. Sodium naphthalene, unlike its behavior with alkyl radicals,[16] apparently reduces aryl radicals entirely to anions.[22]

$(EtO)_2PO_2^{2\dot{-}}$

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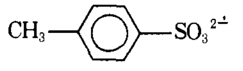

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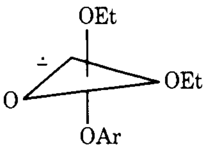
The sense of cleavage of $\mathbf{4}^{2-}$ with respect to production of ethyl fragment is most likely as indicated in Scheme I. Ethyl radical would almost certainly be intercepted by naphthalene anion radical to a significant extent since the reaction has been shown to proceed at close to the diffusion-controlled rate.[16] Dissociation to ethyl radical and **7**, followed by rapid electron transfer between them, is of course plausible but presents awkward detection problems.

One should note that the most stable fragments obtainable from $\mathbf{4}^{2-}$ would be phenoxide and phosphite anions, yet this pathway is not followed. As in the case of aryl alkanesulfonates (**3**)[5] we would like to propose the following explanation for the unusual behavior of $\mathbf{4}^{2-}$: (1) Initial electron transfer is directly to the phosphorus atom. (2) This anion radical adopts a trigonal bipyramidal configuration with the extra electron occupying one of the basal positions, as in **9**. Considerable evidence for this configuration exists for many neutral and charged phosphoranyl radicals.[23] Following the usual polarity rules[24] one would expect the aryloxy group to occupy an apical position as shown. (3) In accordance with the rules developed for phosphate ester hydrolysis,[24a] and which appear to hold for α-scission of neutral phosphoranyl radicals,[25] one would expect the aryloxy group to be lost easily at this stage. One might also expect loss of the apical ethoxy group in **9** to compete with this reaction but it may be that the greater stability of either the aryloxy radical or anion precludes this. (4) Introduction of a second electron onto phosphorus should be difficult and if one of the attached groups is of suitable electron affinity, e.g., the aryloxy group, it may be placed there. Such a group, now being electron rich, might migrate to a basal position as in **10**. (5) If such a reduced group is in the basal position and if the rules for phosphate ester displacement[24a] apply, then it cannot be expelled entire but must fragment internally if it is to react at all. On the other hand, if the reduced aryloxy group remains apical, as in **11**, it may be that the expected weakening of the C–O bond brought about by the negative charge in the ring is sufficient to make β-scission the preferred course of reaction. It has been argued that for neutral phosphoranyl radicals both bond energy and stereoelectronic factors favor β-scission at an apical position,[25a] and some recent evidence supports this.[26]



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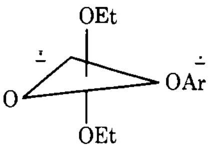

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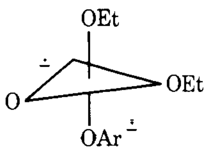

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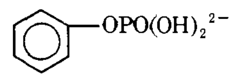
Table II. CNDO/2 Results for Different Geometries and Electronic States of **12**

Species	Energy au	Ring charge	O-Atom charge
Basal phenoxy, singlet	−127.864	−0.0829	−0.496
Basal phenoxy, triplet	−127.810	−0.7165	−0.443
Apical phenoxy, singlet	−124.714	−0.2704	−0.268
Apical phenoxy, triplet	−124.604	−0.9271	−0.268

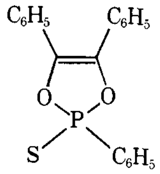
To gain some insight into whether **10** or **11** would be the preferred configuration of the dianion, some CNDO/2 calculations were performed for the hypothetical dianion **12**.[27]



12

All distances and angles were standard values or were optimized previously.[27] A total of four structures were examined: singlet and triplet states with the aryloxy group basal, and singlet and triplet states with the aryloxy group apical. The results for total energy, net ring charge, and basal oxygen atom charge are shown in Table II. The calculations clearly show that a basal phenoxy group is strongly favored over an apical one but do not distinguish between a singlet species with relatively little charge in the aryl ring and a triplet species with charge distribution close to that of our postulated dianion **10**. While the results favor slightly the singlet species it should be noted that the calculations were not optimized for bond angles and distances, and solvent effects might easily reverse the stabilities of the two species, particularly considering that the two states have very different charge distributions. The calculations at least suggest that **11** would not be a long-lived intermediate.

The C–O cleavage reactions between vinyl phosphates and lithium in liquid ammonia[28] probably proceed by a mechanism very similar to that of aryl phosphates. It was noted that an "excess" of lithium was required in order to obtain good yields of alkenes.[28] Nakayama et al. reported that the magnesium reduction of cyclic thionephosphinate ester **13** resulted in a



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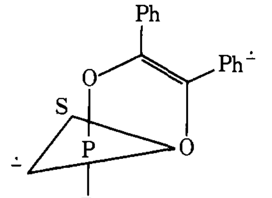
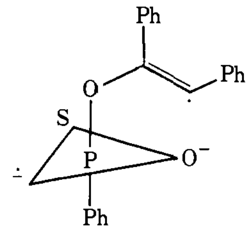


$\mathbf{13}^{2-}$



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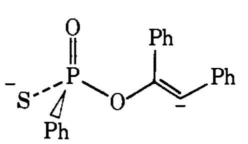


15

Table III. Properties of Aryl Diethyl Phosphates

Aryl group	Yield, %	Bp, °C (Torr)	$n^{20}{}_D$	Lit. values	
				Bp, °C (Torr)	n_D
Phenyl (**4a**)	76	120 (0.2)[a]	1.4815	90(0.1)[b]	1.4785[b]
p-Tolyl (**4b**)	77	115 (0.1)	1.4825		1.473[c]
p-Anisyl (**4c**)	67	125 (0.02)	1.4890	119(0.25)[b]	1.4869[b]
p-Biphenylyl (**4d**)	82	110 (0.25)[a]			1.548[c]
p-Chlorophenyl (**4e**)	88	181 (0.2)[a]	1.4895	114(0.01)[b]	1.4897[b]

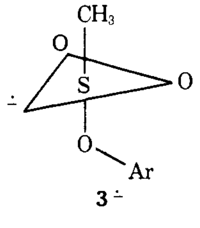
[a] Kugelrohr distillation. [b] C. van Hooidonk and L. Ginjaar, *Recl. Trav. Chim. Pays-Bas*, **86**, 449 (1967); refractive indices at 25 °C. [c] Reference 4; refractive indices at 17 °C.

considerable yield of diphenylacetylene.[29] On the basis of stoichiometry, etc., they argued that the reaction proceeded through a dianion. If the first step in cleavage of **13**$^{2-}$ follows our postulated mechanism, it would generate species **14** which might easily undergo an electron shift, giving **15** which could easily fragment to diphenylacetylene and a stable thiophosphinate dianion.

If our proposed mechanism for reductive cleavage of **4** is correct it would explain the rather poor results in Rossi and Bunnett's attempted "photostimulated $S_{RN}1$ reaction" between **4a** and acetone enolate ion.[11] Unlike aryl halides which gave quite good yields (60–80%) of substitution product after only brief periods of irradiation, **4a** gave only a small yield (13%) of phenylacetone after a quite long irradiation time.[11] A quite sizable amount of phenol (~71%) was also noted as a product, however.[11] The formation of phenol would actually be the expected result of this reaction since photochemical electron transfer could easily yield **4a**$^{-}\cdot$, but double photochemical reduction to obtain **4a**$^{2-}$ would be extremely unlikely. The small amount of substitution product (and benzene) noted may arise via production of phenyl radicals through some other process.

About the only other well-known reductive C–O cleavage reaction of phosphate esters is the interesting hydrogenolysis cleavage of aryl and vinyl diethyl phosphates discussed recently by Jung and Engel.[30] While this is formally a two-electron reduction, also, we hesitate to include it as a candidate for our proposed mechanism.

Of the sulfonyl derivatives we have studied previously, aryl alkanesulfonates (**3**) most closely resemble **4** in their behavior in electron transfer reactions.[5] The differences, however, are rather interesting. The sulfonate ester undergoes rapid one-electron (S–O) cleavage even with sodium anthracene, but C–O cleavage (presumably two-electron reduction) can be achieved in high yield only with alkali metal–liquid ammonia reagents. The aryl phosphates, on the other hand, react rather sluggishly with sodium anthracene (in some cases unreacted phosphate ester could be detected after 30 min reaction with an excess of sodium anthracene) but easily undergo even two-electron reduction with sodium naphthalene. The implication is that **3**$^{-}\cdot$ is more easily generated than **4**$^{-}\cdot$, but either has a much shorter lifetime or a greater resistance to further reduction.



3$^{-}\cdot$

Experimental Section[31]

Materials and Equipment. Tetrahydrofuran (THF) was reagent grade and was dried by distillation from lithium aluminum hydride and stored under nitrogen. Gas chromatographic analyses were performed on a Hewlett-Packard Model 5750 instrument equipped with flame ionization detectors, using a 10 ft × 0.125 in., 10% silicone rubber (UC-W98) on Chromosorb W column. The NMR spectra were recorded using either a Varian A-60A instrument or an HA-100D instrument modified by a Digilab FTS-3 Fourier transform system.[32] High-pressure liquid chromatography (HPLC) was performed on a Waters Associates liquid chromatograph equipped with a Model 6000A solvent delivery system, Model U6K injector system, and a differential refractometer detector. The column used was AX/Corasil (anion exchange) with a total length of 4 ft.

Aryl diethyl phosphates (4) were prepared by the method of Rossi and Bunnett[7] in 67–88% yield and had the properties described in Table III.

Arene anion radical solutions were prepared and handled as described previously.[2] Their molarity was determined by quenching with water and measuring the amount of dihydroarene produced, by GC.[33]

Reaction of Phosphate Esters with Arene Anion Radicals. "Normal addition" reactions were carried out as follows. In a 2-dram vial equipped with a stirrer and sealed with a rubber septum were placed 0.2 mmol of phosphate ester, about 0.1 mmol of an appropriate alkane (GC standard), and 1.5 mL of dry THF or other solvent mixture. The system was flushed with argon or nitrogen and stirred in a 25 °C water bath. Freshly prepared anion radical solution was then added dropwise via syringe. Reactions with sodium naphthalene were complete when the solution remained green. Those using sodium anthracene were allowed to stir for 1 h after an excess of anion radical had been added. The reaction mixture was then quenched with 0.35 mL of BSTFA (bis(*N*,*O*-trimethylsilyl)trifluoroacetamide) (converting phenoxide ion to aryl trimethylsilyl ether), stirred for 1 min, and analyzed by GC. "Inverse addition" was done as follows. In a 2-dram vial sealed with a rubber septum were placed 0.2 mmol of phosphate ester, 0.1 mmol of hydrocarbon standard, and 1.5 mL of dry THF. This was degassed and placed under nitrogen. In a 4-dram vial equipped with a stirrer and sealed with a rubber septum was placed 6 mL of freshly prepared 0.5 M anion radical solution. This was placed in a water bath (25 °C) and stirred vigorously while the phosphate ester solution was slowly added dropwise via syringe. The sodium naphthalene reactions were quenched with 0.75 mL of BSTFA about 1 min after addition was complete, stirred for an additional 1 min, and analyzed by GC. Those using sodium anthracene were stirred for an additional 1 h before the BSTFA was added.

Reaction of Phosphate Esters with Sodium in Liquid Ammonia. "Normal addition" was carried out as follows. To a 50-mL round-bottom flask equipped with a stirrer were added 0.6 mmol of phosphate ester, 0.3 mmol of decane or dodecane, and 4.5 mL of THF. This solution was cooled with a dry ice–acetone bath and rapidly stirred while a 0.5 M solution of sodium in liquid ammonia was added dropwise from a dry ice–acetone jacketed addition funnel. Addition was continued till the blue color of sodium in liquid ammonia persisted in the reaction mixture. The ammonia was then allowed to evaporate under a slow stream of nitrogen, 10 mL of dry THF added to the residual material, and 1.0 mL of the resulting solution withdrawn and treated with 0.35 mL of BSTFA. This solution was stirred for 1 min and analyzed by GC. "Inverse addition" was carried out as follows. To 15 mL of 0.5 M sodium in liquid ammonia, cooled by a dry ice–acetone bath, was added dropwise a solution of 0.6 mmol of phosphate ester and 0.3 mmol of decane or dodecane in 4.5 mL of dry THF. After addition was complete the reaction mixture was worked up and analyzed in a fashion similar to that used for "normal addition".

Identification of Water-Soluble Salts from Reaction of *p*-Tolyl

Diethyl Phosphate with Sodium Naphthalene. Phosphate ester **4b** (5 mmol) was dissolved in 35 mL of dry THF under a nitrogen atmosphere and titrated dropwise with 0.5 M sodium naphthalene delivered via syringe through a septum-fitted side arm. After addition was complete 50 mL of water and 50 mL of ether were added, and the aqueous layer was separated and washed with two 50-mL portions of ether. It was then acidified to pH 5 using hydrochloric acid, and then concentrated under vacuum at room temperature. It was then analyzed by HPLC using an acetate buffer solvent (6 g (0.1 mol) of acetic acid and 8.2 g (0.1 mol) of sodium acetate dissolved in 1.0 L of water) and a flow rate of 0.3 mL/min. Under these conditions known samples of diethyl phosphate and phosphite gave peaks separated by 1 min. The reaction mixture showed two peaks coinciding with diethyl phosphate and phosphite, the phosphate:phosphite ratio (determined from peak height comparisons) being about 5:3. In addition the reaction mixture exhibited a peak of much longer retention time (8 min at a flow rate of 1 mL/min). This peak was collected and the resulting solution (ca. 150 mL) concentrated under vacuum at 25 °C. The resulting syrup was acidified to pH 1 with dilute hydrochloric acid and reconcentrated under vacuum at 25 °C. The crude material was then extracted with 75 mL of hot 95% ethanol and the extract thoroughly concentrated under vacuum leaving a small amount of viscous material. Its NMR spectrum (D_2O) was as follows: δ 1.0 (t, 3 H, CH_3), 1.9 (s, 3 H, CH_3) 3.7 (m, 2 H, CH_2), 6.6-7.2 (m, 4 H, aromatic). It was tentatively identifed as *p*-tolyl ethyl hydrogen phosphate.

Reaction of *p*-Tolyl Diethyl Phosphate (4b) with Sodium Amide in Liquid Ammonia. To a solution of 0.8 mmol of sodium amide in 20 mL of liquid ammonia surrounded by a dry ice-acetone bath was added rapidly with stirring a solution of 0.8 mmol of **4b** and 0.4 mmol of alkane standard in 6 mL of dry THF. The resulting mixture was allowed to stir for 30 min, and then quenched with 1.0 mmol of ammonium chloride. The ammonia was allowed to evaporate and 10 mL of dry THF added. A 1-mL sample of the resulting solution was withdrawn and treated with 0.35 mL of BSTFA. Analysis by GC indicated a 4% yield of *p*-cresol.

Yield of ethyl phosphoramidate (6) on cleavage of 4b with sodium in liquid ammonia was determined in a reaction carried out as described above for "normal addition", except that the reaction mixture was quenched with ammonium chloride and analyzed (GC) without silylation. Comparison with GC measurements on solutions with known concentrations of **6** (prepared after the method of Goehring and Niedenzu)[34] revealed the presence of ca. 1% of the phosphoramide.

Reaction of *p*-Tolyl Diethyl Phosphate (4b) with Sodium–Liquid Ammonia in the Presence of Ethyl Phosphoramidate (6). A solution of 0.8 mmol of **4b**, 0.1 mmol of **6**, and internal standard in 6 mL of dry THF was cooled in a dry ice-acetone bath and treated with a solution of 0.5 M sodium in liquid ammonia in the manner described for "normal addition". After evaporation of the ammonia 0.15 g of ammonium chloride and 10 mL of THF was added. Analysis by GC indicated the presence of 0.102 ± 0.005 mmol of **6**.

Low-Boiling Materials from Reaction of 4b with Sodium Naphthalene. A "normal addition" (0.5 M sodium naphthalene) was run as previously described. Analysis by GC of the unquenched reaction mixture (at 25 °C) revealed a peak with retention time identical with that of ethane on both UC-W98 and Carbowax 20M columns. Attempts to obtain a quantitative measure of the amount of ethane were unsuccessful. A separate reaction was carried out in similar fashion except that a stream of nitrogen was passed through the reaction mixture (during and after reaction) and then through a solution of bromine in carbon tetrachloride. Analysis of the carbon tetrachloride solution by GC revealed no detectable amount (less than 0.5%) of 1,2-dibromoethane. Analysis of these and other prosphate ester–sodium naphthalene reaction mixtures for 1-ethyldihydronaphthalene never indicated the presence of more than ca. 0.5% of the ethylated material.

Cleavage of *p*-Tolyl Diethyl Phosphate (4b) in the Presence of Magnesium Bromide. To 1.5 mL of 0.4 M magnesium bromide in dry THF in a 2-dram vial equipped with stirrer and sealed with a septum were added 0.2 mmol of **4b** and 0.1 mmol of dodecane. The solution was then flushed with nitrogen and stirred in a 25 °C water bath. It was then titrated with 0.5 M sodium naphthalene until the green color persisted. Acetaldehyde (0.2 mL) was then added, and the solution was stirred for 2 min and then quenched with water. Analysis by GC (5 ft × 0.125 in. Carbowax 20M (17.5%) on Anakrom SD column) revealed no detectable amount of 2-butanol. In a separate experiment it was shown, however, that ethylmagnesium bromide reacted very rapidly with **4b** in dry THF, to produce *p*-cresol.

References and Notes

(1) (a) Presented in part at the 168th National Meeting of the American Chemical Society, Atlantic City, N.J., Sept 1974, Abstract No. ORGN-020. (b) State University of New York at Albany. (c) Eindhoven University of Technology.
(2) W. D. Closson, S. Ji, and S. Schulenberg, *J. Am. Chem. Soc.*, **92,** 650 (1970). Electrochemical reduction, however, may follow a somewhat different mechanism; see P. T. Cottrell and C. K. Mann, *ibid.*, **93,** 3579 (1971).
(3) (a) J. R. Ganson, S. Schulenberg, and W. D. Closson, *Tetrahedron Lett.*, 4397 (1970); (b) J. C. Carnahan, Jr., and W. D. Closson, *ibid.*, 3447 (1972).
(4) G. W. Kenner and N. R. Williams, *J. Chem. Soc.*, 522 (1955).
(5) J. C. Carnahan, Jr., W. D. Closson, J. R. Ganson, D. A. Juckett, and K. S. Quaal, *J. Am. Chem. Soc.*, **98,** 2526 (1976).
(6) Half-wave reduction potential of arene in 75% aqueous dioxane. A. Streitwieser, "Molecular Orbital Theory for Organic Chemists", Wiley, New York, N.Y., 1968, p 178.
(7) R. A. Rossi and J. F. Bunnett, *J. Org. Chem.*, **38,** 2314 (1973).
(8) R. A. Rossi and J. F. Bunnett, *J. Org. Chem.*, **37,** 3570 (1972).
(9) J. K. Kim and J. F. Bunnett, *J. Am. Chem. Soc.*, **92,** 7463 (1970).
(10) R. A. Rossi and J. F. Bunnett, *J. Am. Chem. Soc.*, **96,** 112 (1974).
(11) R. A. Rossi and J. F. Bunnett, *J. Org. Chem.*, **38,** 1407 (1973).
(12) M. Szwarc and J. Jagur-Grodzinski, "Ions and Ion Pairs in Organic Reactions", Vol. 2, Wiley-Interscience, New York, N.Y., 1974, Chapter 1.
(13) K. S. Chen, S. W. Mao, N. Kahamura, and N. Hirota, *J. Am. Chem. Soc.*, **93,** 6004 (1971); N. Hirota, *ibid.*, **90,** 3603 (1968); A. Crowley, N. Hirota, and R. Kreilich, *J. Chem. Phys.*, **46,** 3815 (1967).
(14) S. Bank and D. A. Juckett, *J. Am. Chem. Soc.*, **97,** 567 (1975).
(15) R. E. Ireland, D. C. Muchmore, and U. Hengartner, *J. Am. Chem. Soc.*, **94,** 5098 (1972).
(16) J. F. Garst, *Acc. Chem. Res.*, **4,** 400 (1971).
(17) J. C. Carnahan, Jr., and W. D. Closson, *J. Org. Chem.*, **37,** 4469 (1972).
(18) S. Bank and J. F. Bank, *Tetrahedron Lett.*, 4533 (1969).
(19) J. F. Bunnett and B. F. Gloor, *J. Org. Chem.*, **38,** 4156 (1973).
(20) W. D. Closson, P. Wriede, and S. Bank, *J. Am. Chem. Soc.*, **88,** 1581 (1966).
(21) S. P. Mishra and M. C. R. Symons, *J. Chem. Soc., Chem. Commun.*, 606 (1974).
(22) G. D. Sargent, *Tetrahedron Lett.*, 3279 (1971).
(23) J. Higuchi, *J. Chem. Phys.*, **50,** 1001 (1969); A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 993, 2224 (1972); P. J. Krusic, W. Mahler, and J. K. Kochi, *J. Am. Chem. Soc.*, **94,** 6033 (1972); G. Boekestein, J. M. Jansen, and H. M. Buck, *J. Chem. Soc. Chem. Commun.*, 118 (1974); A. G. Davies, M. J. Parrot, and B. P. Roberts, *ibid.*, 973 (1974).
(24) (a) F. H. Westheimer, *Acc. Chem. Res.*, **1,** 70 (1968); (b) F. Ramirez, *ibid.*, **1,** 168 (1968); E. L. Muetterties, *ibid.*, **3,** 266 (1970); C. K. Mislow, *ibid.*, **3,** 321 (1970).
(25) (a) A. G. Davies, R. W. Dennis, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1101 (1974); (b) J. W. Cooper and B. P. Roberts, *ibid.*, 808 (1976).
(26) W. G. Bentrude and T. B. Min, *J. Am. Chem. Soc.*, **98,** 2918 (1976).
(27) For the general procedure for these calculations see J. M. F. van Dijk, J. F. M. Pennings, and H. M. Buck, *J. Am. Chem. Soc.*, **97,** 4836 (1975).
(28) M. Fetizon, M. Jurion, and N. T. Anh, *Chem. Commun.*, 112 (1969); R. E. Ireland and G. Pfister, *Tetrahedron Lett.*, 2145 (1969).
(29) S. Nakayama, M. Yashifugi, R. O. Kazaki, and N. Inamoto, *J. Chem. Soc., Perkin Trans. 1*, 2069 (1973).
(30) A. Jung and R. Engel, *J. Org. Chem.*, **40,** 244, 3652 (1975).

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(33) S. Bank and W. D. Closson, *Tetrahedron Lett.*, 1349 (1965).
(34) M. Goehring and K. Niedenzu, *Chem. Ber.*, **89,** 1768 (1956).