thought to be more reliable than that determined from the methyl peak. Therefore we have weighted the parenthesized values of K_f' in Table II relatively lightly and taken as an average value and probable uncertainty $0.5 \pm 0.1\ M^{-1}$.

Determination of the Acidity Constant of the Formocholine Cation. Titrations were carried out at 25 ± 0.1° using a Radiometer Model 26 pH meter, G202B (pH 0–14) glass electrode, calomel reference electrode, and 2.5-ml Auto-Burette. It was assumed that in the titration solutions $-\log [H^+] = X + pH$, where X is a constant and pH is the reading on the meter. The meter was adjusted to read within 0.01 of the correct pH values for standard buffers with pH's of 7.413, 4.01, and 2.044 (0.01 M hydrochloric acid). It was then found to read 2.00 ± 0.01 for 0.01 M solutions of hydrochloric acid in 1.00 M trimethylammonium chloride and in 0.64 M formaldehyde plus 1.00 M trimethylammonium chloride. Therefore in this case, X is zero and the observed pH is equal to $-\log [H^+]$.

The addition of 0.631 M formaldehyde, as shown in Figure 1, increased the amount of sodium hydroxide required to reach a given pH in the titration of 25 ml of 0.96 M trimethylammonium chloride by as much as 2.0 mequiv. Blank experiments showed that the addition of 1.0 M formaldehyde never increased the amount of sodium hydroxide required to reach a given pH in the titration of 25 ml of water by more than 0.01 mequiv up to pH 9.5. When solutions of trimethylammonium chloride that had been titrated to pH 8.98 and 9.36 were made 0.6 M in ethylene glycol, their pH's decreased by 0.03 and 0.02, respectively.

Electron Spin Resonance Studies of the Reactions of Tris(1-naphthalene)phosphine and Its Oxide, Sulfide, and Selenide with Alkali Metals in Tetrahydrofuran and 1,2-Dimethoxyethane

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Abstract: Tris(1-naphthalene)phosphine (I) was allowed to react separately with lithium, sodium, potassium, and sodium–potassium alloy in tetrahydrofuran (THF) and in 1,2-dimethoxyethane (DME). In both solvents the reaction of I with sodium gave the naphthalene radical anion (II) while with potassium, $[(C_{10}H_7)_2PK]\cdot^-$(III) was formed. Reduction with sodium–potassium alloy gave a mixture of II and III. The reaction of I with lithium gave the 1,1′-binaphthyl radical anion, but when the lithium was allowed to react initially with glass and then with I, the perylene radical anion IV was formed. The oxide, sulfide, and selenide derivatives of I all behaved similarly to I in their reactions with the alkali metals in THF and DME. The electron spin resonance (esr) spectra of the 1,1′-binaphthyl radical anion was also studied. The mechanisms of the above reactions are discussed.

The reactions of arylphosphines with alkali metals in THF and DME have yielded interesting results. For example, Wittenberg and Gilman[1] reported the cleavage of triphenylphosphine by lithium to yield diphenylphosphinolithium and phenyllithium. Hanna[2]

$$(C_6H_5)_3P + 2Li \overset{THF}{\rightleftharpoons} (C_6H_5)_2PLi + C_6H_5Li$$

reported that this reaction with alkali metals produces the mononegative ion $[(C_6H_5)_3P]\cdot^-$ identified from its esr spectrum. The cleavage of phenyl groups from $(C_6H_5)_3P$ by alkali metals in THF is a well-known reaction,[1,3,4] and it has been reinvestigated in detail by Britt and Kaiser.[5] They studied the reaction as a function of the concentration of $(C_6H_5)_3P$ for the three alkali metals, K, Na, and Li, and the course of the reaction was followed by chemical methods and esr spectroscopy. They reported that the spectrum of the radical formed, as determined by the hyperfine splittings and the intensities of the lines, belongs to $[(C_6H_5)_2PK]\cdot^-$. Another esr study was reported by Kabachnik, *et al.*,[6] who observed the spectrum of the triphenylphosphine anion radical. This work was not in agreement with previous data on this compound.

In a comparison of the reactions of triphenylphosphine with those of triphenylphosphine oxide, Hein, Plust, and Pohleman[7] reported that triphenylphosphine oxide forms adducts with alkali metals which they formulated as Ar_3POM, Ar_2POM_3, and ArM, respectively. On the other hand, Hoffmann and Tesch[8] reported that solutions of triphenylphosphine oxide react with lithium or sodium to form the biphenyl radical anion in DME solution. A different paramagnetic species was obtained when potassium was used as the reducing agent. The spectrum consisted of eleven lines split by 1.75 G, which slowly disappeared when excess potassium was added due to formation of biphenyl radical anions.

Cowley and Hnoosh[9] reported that the free-radical species derived from $(C_6H_5)_3PO$ depends upon the alkali metal and the solvent. Like Hoffmann and Tesch,[8] they were able to detect only the biphenyl anion radical (*via* phenyl-P cleavage) in the reduction of $(C_6H_5)_3P(O)$ in DME by sodium. They obtained the same result by means of sodium reduction in THF.

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(2) M. W. Hanna, *J. Chem. Phys.*, 37, 685 (1962).

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(7) F. Hein, H. Plust, and H. Pohleman, *Z. Anorg. Allgem. Chem.*, 272, 25 (1959).

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However, the reduction of $(C_6H_5)_3P(O)$ with potassium in THF at −10° resulted in the formation of a blue solution having a 28-line esr spectrum which, on analysis, gave evidence which suggests that the species is $[(C_6H_5)_3PO]\cdot^-$. In contrast, potassium reduction in DME resulted in the formation of a red-brown solution with a 10-line spectrum which has an appearance very similar to that reported for $[(C_6H_5)_2PK]\cdot^-$ by Britt and Kaiser[5] which suggests that the radical is $[(C_6H_5)_2P(O)K]\cdot^-$. The latter spectrum has a hyperfine splitting of 7.7 G for the phosphorus nucleus which is less than that obtained from $[(C_6H_5)_2PM]\cdot^-$. This is attributed to the presence of an oxygen atom which decreases the electron density and consequently the hyperfine splitting constant. Complete analysis of the 10-line spectrum showed that the data correspond to the $[(C_6H_5)_2P(O)K]\cdot^-$ anion radical.

This paper describes an investigation of similar reactions with tris(1-naphthalene)phosphine as well as its oxide, sulfide, and selenide. These systems, because of their close similarity to Ph_3P and Ph_3PO, allow for the utilization of previously reported information along with that obtained from other investigations.[10] On the other hand, these mentioned systems differ from Ph_3P and Ph_3PO in that carbon–phosphorus bond cleavage of these molecules leads to different products, *viz.*, the naphthalene radical anion and the phosphorus-containing fragment. The reaction of tris(1-naphthalene)phosphine with lithium has been found to produce the 1,1′-binaphthyl radical anion, and under certain conditions this product is converted to perylene. The formation of 1,1′-binaphthyl has been reported[11] from tris(1-naphthalene)arsine by the action of Raney nickel. The conversion of the binaphthyl to perylene on silica–alumina[12] and under some other conditions also has been reported[13] along with the perylene esr spectrum.[14]

Experimental Section

THF and DME were purified by distillation following a period of drying over CaH_2 and potassium metal. They were further distilled into solvent storage flasks on a vacuum line where they were finally dried by magnetic stirring over sodium–potassium alloy. The solvent storage flasks were degassed frequently and the solvents were assumed to be sufficiently dry when they acquired a light blue color at room temperature which is due to solvation of electrons.

The alkali metals, lithium, sodium, and potassium (99.9% pure) were cleaned prior to the reaction, first by treatment with benzene and then ether. They were sublimed by heat under vacuum in reaction apparatus to produce a shiny metallic mirror in the reaction bulb. The sublimation of lithium was found to be exceedingly difficult because of its reactivity with glass materials. The lithium was cleaned with benzene followed by ethyl alcohol and then petroleum ether, after which it was placed in the reaction apparatus and heated until a clean, shiny metallic surface was exposed to the vacuum system.

Tris(1-naphthalene)phosphine and its sulfide were prepared as described in the literature.[15] They were purified thoroughly and analyzed prior to their use. Tris(1-naphthalene)phosphine oxide was prepared as follows.

Tris(1-naphthalene)phosphine was dissolved in xylene and placed in a 500-ml flask equipped with a reflux condenser. Hydrogen peroxide solution (30%) mixed with acetone was then added to the solution and heated for 2 hr. White crystals were precipitated from the reaction mixture. These were recrystallized twice from *n*-butyl alcohol. They melted at 348–349°.

Anal. Calcd: C, 84.11; H, 4.94; P, 7.23. Found: C, 84.20; H, 5.03; P, 7.01.

All free-radical anions described in this work were generated by reduction with alkali metals (Na, K, Li, or Na–K alloy) in THF or DME.

A vacuum line of conventional design was used for solvent transfer, drying, etc. The actual radical generation was carried out in an apparatus specially designed for this purpose which contains a stopcock joined to a large reaction bulb which is connected to a small alkali metal heating bulb on one side and to the esr sample tubes from the other side.

The general procedure was as follows: small pieces of clean, dry alkali metals were placed in the small alkali metal heating bulb of the reaction apparatus. A small measured quantity (to give the desired concentration in the range of 10^{-2}–10^{-4} *M*) of the compound to be reduced was then placed in the bottom of the stopcock of the apparatus in order to avoid thermal decomposition. The apparatus was then connected to the vacuum system in a horizontal position and evacuated. Next, a mirror of the alkali metal was introduced onto the surface of the large reaction bulb by evaporation of the alkali metal from the small bulb by external heating with a hand torch. The stopcock of the reaction apparatus was closed and attached to the line in a vertical position so that the sample of the compound dropped into the large bulb. Following evacuation and flaming of the vacuum line to ensure dryness, a suitable amount of solvent was distilled from the solvent reservoir into the large bulb. Samples were taken after various times and at various temperatures depending upon the observed color changes which, in turn, depended on the concentration of the free radical in the solution. The esr tubes attached to the reaction apparatus were flame sealed at −196°.

All esr[16] spectra were measured using the X band of a Varian V-4502-15 esr spectrometer. The spectrometer was equipped with a Varian V-4500 esr control unit, and a Varian G-14A-2 graphic strip chart recorder. The unit was operated in conjunction with a Varian V-3603 12-in. low-impedence electromagnet equipped with Varian V-3600 "tapered" pole caps. The temperature within the cavity was controlled by a Varian V-4557 variable-temperature controller.

Vapor phase chromatography was performed on an F & M Model 5750 research chromatograph, equipped with flame ionization detector. The analytical column was 8 × 1/8 in. of silica rubber Wc98.

Results and Discussion

Reactions of Tris(1-naphthalene)phosphine and the Resultant Esr Spectra. The reaction of this compound with different alkali metals gave results which are dependent on the alkali metal used, the solvent, and the temperature.

A. Reactions with Na in THF and DME. A light green solution formed from the reaction with sodium in THF at −65° which gave a weak esr signal. When the reaction mixture was permitted to stand in contact with the sodium metal until the temperature was raised to about 10°, the color became more intense. A sample of this solution gave a well-resolved and defined spectrum, recorded at temperatures between −60 and −20°. Broadening of the lines was observed when the recording temperature rose above −20°. When the reaction mixture was allowed to remain in contact with sodium metal at room temperature for 2 hr, its color turned to dark brown and gave a very broad, one-line spectrum. This solution is believed to contain a large concentration of the free radical.

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(10) A. D. Britt and E. T. Kaiser, *J. Org. Chem.*, 31, 112 (1966).

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(16) All esr spectra reported in this paper are first-derivative spectra.

The well-resolved and defined spectrum of the intense green solution consists of 25 lines. It has two hyperfine splitting constants (hsc) for 2-quintet patterns of lines, each pattern with line intensities of 1:4:6:4:1. The two hsc are 4.9 and 1.83 G. The analysis of this spectrum simply shows that there are two sets, each consisting of four equivalent protons. When this spectrum is compared with that of the naphthalene radical anion,[17] it is found to be identical in every respect.

Since there is no way for this molecule to produce any other radical which gives rise to a spectrum of the type observed, it appears to be well established that a naphthyl group has been cleaved from the tris(1-naphthalene)phosphine molecule, and abstracted a hydrogen to become a naphthalene molecule.

It was necessary to show that the tris(1-naphthalene)phosphine was very pure and that naphthalene was not present as an impurity. Two samples of the phosphine, whose concentration was equal to that used in the reaction for generating the free radical, were used. Each was mixed with different amounts of pure naphthalene so that the concentration of the naphthalene in the two mixtures when dissolved in THF would be 10^{-4} and 10^{-5} *M*. These two solutions were then analyzed by vapor phase chromatography along with a reference solution of tris(1-naphthalene)phosphine in THF without any added naphthalene. The solutions containing the added naphthalene each showed a peak which followed the THF peak. Such a peak was totally absent in the solution containing only tris(1-naphthalene)phosphine.

In order to further demonstrate that the sample was not contaminated with naphthalene, it should be pointed out that this compound (from the same source as in the reactions with sodium) gave different results in its reactions with potassium, lithium, or sodium–potassium alloy.

In order to account for the formation of naphthalene in this reaction, the following mechanism should be considered: (1) there occurs cleavage of the carbon–phosphorus bond by sodium; this leads to the formation of the fragments, $(C_{10}H_7)_2P^-Na^+$ and $C_{10}H_7Na$; (2) these two fragments can then undergo reduction by sodium; (3) a hydrogen atom is abstracted from the solvent molecules (THF or DME) by the $C_{10}H_7Na$ which leads to the formation of the naphthalene; (4) the naphthalene is reduced by another sodium atom to form the naphthalene radical anion.

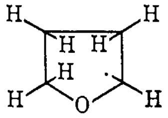
It has been reported that cleavage of the carbon–phosphorus bond occurs when either triphenylphosphine[5] (TPP) or triphenylphosphine oxide (TPPO)[9] reacts with alkali metals. In the case of TPP this cleavage leads to the formation of the $[(C_6H_5)_2PM]\cdot^-$ radical anion as determined by its esr spectrum. TPPO gave different results when it reacted with sodium or potassium in different solvents.[9] Thus, the biphenyl radical anion was formed in its reaction with Na in THF while the $[(C_6H_5)_2P(O)K]\cdot^-$ radical anion was formed in its reaction with K in DME. The cleavage of the C–P bond is well established.

The second stage, which follows the formation of $(C_{10}H_7)^-Na^+$ involves reduction by the addition of one electron to the naphthyl group. This results in formation of a free radical which can abstract a hydrogen atom from a solvent molecule. The hydrogen abstracted from the solvent replaces the sodium on the naphthyl group to form naphthalene as described in the third stage. At this point, it becomes necessary to investigate the nature of the solvent molecule following hydrogen abstraction.

In the case of unsaturated hydrocarbons, following their reduction by alkali metals in liquid ammonia in the presence of proton donors, as in the case of alcohols, hydrogen is abstracted from the donor to form the hydrogenated hydrocarbon.[18a,b]

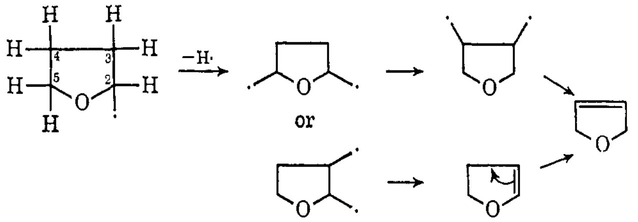
$$\mathrm{ArH} \xrightarrow{+e^-} \mathrm{ArH}\cdot^- \xrightarrow[\mathrm{ROH}]{} \mathrm{ArH_2}\cdot^-$$

Dixon and Norman[19] reported on the ability of the hydroxyl radical, OH·,· to abstract protons from alcohols, amines, and ethers, particularly THF.[20] When tetrahydrofuran was used as the proton donor, the radical formed following the hydrogen abstraction was identified from its esr spectrum and was reported to be



This molecule was found to possess a very short half-life. This means that this radical undergoes some other rearrangement to form a more stable product.

The abstraction of a second hydrogen atom from another carbon atom in either position 5 or 3 leads to conditions which are favorable for the formation of a double bond, as shown in the following scheme.



The stable end product would be 2,5-dihydrofuran. Abstraction of hydrogen atoms from either the 2 or 4 positions does not lead to a situation which is as favorable for the formation of a double bond. The abstraction of two hydrogen atoms has been observed in the case of cyclopentanol and cyclopentanone.[20]

A test for the actual formation of 2,5-dihydrofuran and also naphthalene was carried out by vapor phase chromatography. Known solutions of different compositions as indicated in Figure 1, along with the solution obtained from the reaction of tris(1-naphthalene)phosphine (TNP) with sodium in THF were prepared and chromatographed under the same conditions. Comparison of the resultant chromatograms of these solutions showed and confirmed the following. (1) The chromatogram from solution e is almost identical

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[17] S. I. Weissman, J. Townsend, D. E. Paul, and S. E. Pake, *J. Chem. Phys.*, 21, 2227 (1953).

[18] (a) A. Streitwieser, Jr., and S. Suzuki, *Tetrahedron*, 16, 153 (1961); (b) A. J. Birch, *Quart. Rev. Chem. Soc.*, 4, 69 (1950).

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[20] W. T. Dixon and R. O. C. Norman, *ibid.*, 4850 (1964).

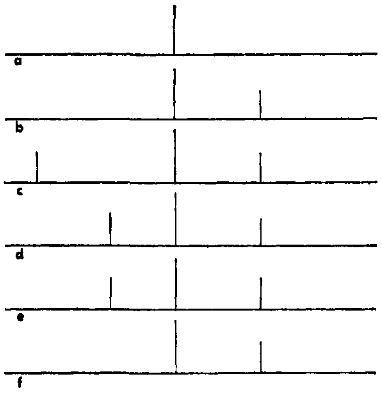


Figure 1. Schematic diagram of chromatograms obtained from (a) a solution of tris(1-naphthalene)phosphine (TNP) in pure THF, $10^{-3}M$, prepared in the same manner as that used for the esr studies; (b) a solution of TNP in THF ($10^{-3}M$) together with naphthalene ($10^{-3}M$); (c) same as (b) plus furan ($10^{-3}M$); (d) same as (b) plus 2,5-dihydrofuran; (e) solution obtained from the reaction of TNP in THF with sodium following generation of the naphthalene free radical anion; (f) a solution of THF plus naphthalene.

with that from the known solution d which contains TNP, 2,5-dihydrofuran, THF, and naphthalene. This means that the reaction solution also contains 2,5-dihydrofuran which resulted from the conversion of THF after hydrogen abstraction. (2) From the comparison of the chromatograph of solution e with that of the known solution b, it appears to be clear that the reaction solution contains naphthalene which resulted from the reaction of TNP with Na in THF. This result supports the observations made from the esr spectra which show the formation of the naphthalene radical anion.

A similar result was obtained when the reaction was run in DME instead of THF. In this case, the solvent, following hydrogen abstraction, was converted to $CH_3O—CH═CH—OCH_3$ according to the equation

$$CH_3O—CH_2—CH_2—OCH_3 \xrightarrow{-H} CH_3O—\dot{C}H—CH_2—OCH_3 \xrightarrow{-H} CH_3O—CH═CH—O—CH_3$$

Vpc chromatographic analysis was used in a manner similar to that described for THF.

The fate of the other cleavage product, $(C_{10}H_7)_2P^-Na^+$, in this reaction, will now be considered. This moiety, because of the presence of the two naphthyl groups, should also be capable of forming a free radical by reduction. Consequently, the esr spectrum would be expected to show the presence of two types of free radicals. However, in the present case this second radical did not give any signal. This is most likely due to the fact that $(C_{10}H_7)_2PNa$ underwent a two-electron reduction when it reacted with an excess of the sodium to form the dianion radical, which is diamagnetic.

B. Reactions with Potassium in THF and DME. In both solvents, the reaction with potassium proceeded in a similar manner. The reduction of the tris(1-naphthalene)phosphine was allowed to proceed at temperatures ranging from −65° up to room temperature. The color, which was light blue at low temperatures, became more intense with an increase in temperature. After the reaction had been permitted to proceed for about 1 hr at room temperature, the color changed to a dark greenish brown.

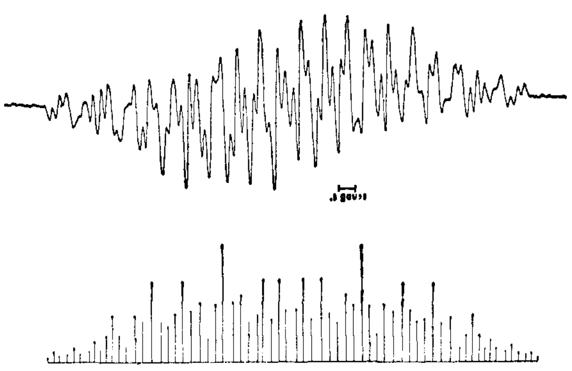
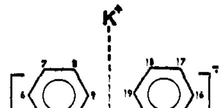


Figure 2. Esr spectrum of the free radical generated by the reaction of TNP with potassium in THF at temperatures between −50 and 0°.

According to the analysis of the esr spectra, as discussed below, each fragment in this reaction which resulted from the cleavage of a C–P bond was reduced at a rate which differs from that with sodium. Consequently the esr spectra were different in both reactions. This is due to the differences in the alkali metal ion size and their reducing ability.

Samples which were measured at temperatures between *ca.* −50 and 0° gave well-resolved spectra, which were identical in both solvents. The spectrum consists of 66 lines (Figure 2). The analysis of this spectrum was carried out from the line intensities (some of which are affected by overlapping) and the electron densities on the carbon atoms in the naphthalene groups. These electron densities were calculated by MO calculations,[21] in which the phosphorus atom is considered as the heteroatom in the molecule. These calculations show that carbon atoms follow the order: (3,5,13,15) > (7,9,17,19) > (4,14) > (8,18) > (6,16). From this analysis, it appears that there are five sets of nuclei which interact with the odd electron of the free radical. Following the assignment of the observed hyperfine splitting constants to each set according to their electron densities,[21] the free-radical anion is that of bis(1-naphthalene)phosphine potassium which has the following structure. Because of the overlap of the



III

spectral lines there occurred some changes in the line intensities and they did not follow the binomial expansion exactly, especially in the middle portions of the spectrum. However, this order of the intensities followed a normal pattern at both ends of the spectrum. This overlapping has also caused the reduction of the number of lines from the theoretical number of 450 to

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(21) M. H. Hnoosh, Ph.D. Dissertation, Texas A&M University, College Station, Texas, Jan 1969. The complete document has been deposited with University Microfilms, Inc., Ann Arbor, Mich. (order No. 69-14,143). The MO calculations are listed in pp 140–149 of this document.

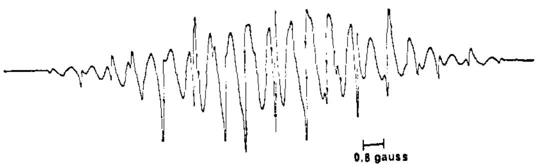


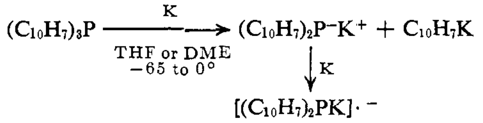
Figure 3. Esr spectrum of the free-radical anion generated by the reaction of TNP with potassium at room temperature.

the observed 66 lines. Table I shows the hyperfine splitting constant of each set of nuclei in radical III along with the number of atoms in each set, their position, and the multiplicity of lines.

Table I. Hyperfine Splitting Constants of the Different Sets of Nuclei in the Esr Spectrum of Bis(1-naphthalene)phosphinepotassium (III)

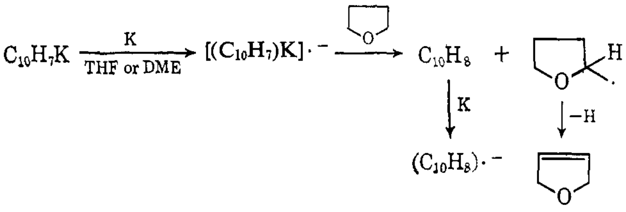
Atom	No. of atoms	Position in III	Multiplicity of lines	Hsc, G
P	1	1	2	7.20
H	4	3,5,13,15	5	3.60
H	4	7,9,17,19	5	2.40
H	2	4,14	3	1.20
H	2	8,18	3	0.40

In the above analysis we observe that: (1) the value of the hyperfine splitting constant for the phosphorus atom attached to a naphthyl group, as expected, is smaller than when attached to a phenyl group[5] (8.4 G). A phosphorus atom bonded to a naphthyl group, which is more electron attracting than a phenyl group, would be expected to reduce the electron density on the phosphorus atom. Accordingly, the interaction of the phosphorus nucleus (spin of $^1/_2$) with an unpaired electron, will be less in the case of the naphthyl derivative, and, consequently, the hyperfine splitting constant will be smaller. (2) Because the electron densities on carbon atoms 6 and 16 are low, there is not observed any hyperfine splitting arising from interaction with the proton in these positions. (3) No splitting was observed for the potassium ion which might be due to the fact that both the radical and the potassium ions are too distant. Consequently, any interaction is very weak. The esr spectrum of the sample, which was taken after the reaction mixture was permitted to stand for ~1 hr at room temperature, is different from that just discussed. This spectrum (Figure 3) is actually due to the presence of two different free-radical anions in the same solution. One of these is obviously the naphthalene-radical anion. The other radical anion gives rise to a spectrum which is ill-defined and has broad lines of lower intensities. This second radical may be $[(C_{10}H_7)_2P^-K^+]\cdot^-$, as was seen in the spectra of the samples discussed previously. The spectral data indicate that both the temperature and time of contact with the alkali metal are important. In general, for this reaction, we can say that there are major steps involved: (1) cleavage of the carbon–phosphorus bond and production of two kinds of molecules as follows



$$\begin{tikzcd}(C_{10}H_7)_3P \arrow[r, "K", "\text{THF or DME}\ -65\text{ to }0°"'] & (C_{10}H_7)_2P^-K^+ + C_{10}H_7K \arrow[d, "K"] \\ & {[(C_{10}H_7)_2PK]\cdot^-}\end{tikzcd}$$

(2) $C_{10}H_7K$ will be reduced and then it abstracts hydrogen from THF or DME and is converted to the naphthalene molecule which is reduced to the naphthalene anion radical



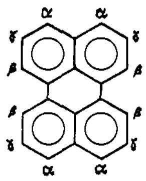
While the naphthalene is forming and is reduced to the anion, the slow second reduction of $[(C_{10}H_7)_2PK]\cdot^-$ to the diamagnetic dianion is taking place. Therefore, the concentration of the $[(C_{10}H_7)_2PK]\cdot^-$ free radical is decreasing and its esr signal becomes weak when it is compared with that of the naphthalene radical anion.

C. Reactions with Na-K Alloy in THF and DME. When the reaction products were taken from liquid nitrogen temperature up to the point where they liquefied, the formation of a blue solution was observed. The blue color continued to intensify as the solution was warmed to room temperature. The esr spectra of samples taken at −65 to 0° in THF and at −55 to 0° in DME were identical. These spectra were also identical with those obtained with potassium which have been described in section B (Figure 2). Therefore, this spectrum is of the free-radical anion $(C_{10}H_7)_2P\cdot^-\cdots M^+$ (where M is Na or K). According to the observed spectrum, we believe that the reaction proceeded exactly the same way as with potassium, *i.e.*

$$(C_{10}H_7)_3P \xrightarrow[\text{THF or DME}]{\text{NaK}} [(C_{10}H_7)_2P\cdots M]\cdot^- + C_{10}H_7M$$

D. Reactions with Lithium in THF. Lithium metal was heated to its melting point and the heating was continued in an attempt to carry vapors of the metal into the reaction bulb. A vigorous reaction was observed to take place between the glass surface and the molten metal with which it was in contact. Some of the hot-lithium-glass reaction product sputtered into the dry TNP. THF was condensed into the reaction bulb and the solution was allowed to come in contact with the lithium metal and the lithium-glass reaction product. At −65° the formation of a greenish blue solution was noted. The solution was taken to room temperature and it remained in contact with the metal for about 1 hr. The solution formed was deep violet in color. Samples of this solution were taken and their esr spectra were measured in the temperature range −65 to −40°.

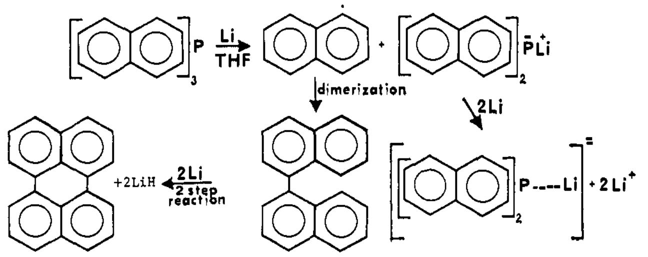
A well-resolved spectrum was obtained consisting of 59 lines. The analysis of this spectrum shows that there are three quintets of lines belonging to three different sets of equivalent protons. When this spectrum is compared with that of the perylene[14] radical anion, it is found to be identical. Therefore the three quintets of lines were assigned to the three sets of protons, α, β, and γ (as in IV) with hyperfine splitting constants 3.53, 3.09, and 0.46 G, respectively. Each quintet displays line intensities having ratios of 1:4:6:4:1.



IV

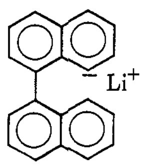
According to the analysis of the observed spectrum, it appears that this reaction produces the perylene radical anion under the conditions described.

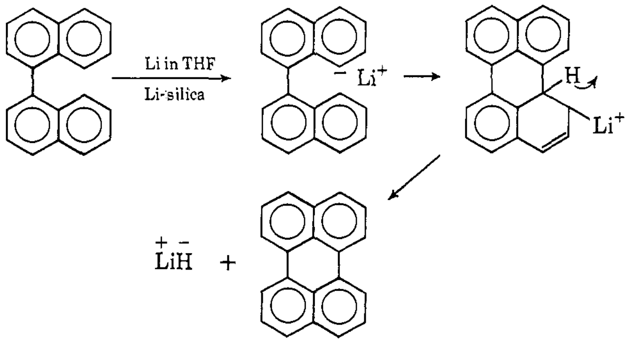
The formation of the perylene radical anion in this reaction probably arises in the manner described.

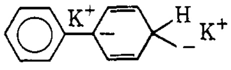


Cleavage of the C–P bond is expected because of the similarity of the reaction of this compound with Na and K as in the case of the reaction of TPP and its oxide.[5,9] Dimerization of naphthyl groups to form binaphthyl is quite reasonable. A similar reaction[9] has been observed when TPPO reacts with Na in THF. In this case the dimerization of two phenyl groups to form biphenyl has been reported. It has also been shown[11] that the action of Raney nickel on organo-P, -As, -Sb, and -Hg derivatives brings about the hydrogenolysis of the C–P, C–As, C–Sb, and C–Hg bonds, and dimerization of the aromatic radicals. Thus, 1,1′-binaphthyl is obtained from $(1\text{-}C_{10}H_7)_3As$. The dimerization observed in the current work happens quite rapidly. The purple color which forms and then changes to violet may well indicate the formation of 1,1′-binaphthyl.

Conversion of binaphthyl to perylene has been shown to take place in several ways. Rooney and Pink[12] reported that when a concentrated solution of 1,1′-binaphthyl in carbon disulfide was added to a catalyst (sodium-exchanged silica–alumina) a pink color was developed. When the carbon disulfide was removed and the system heated to 200° *in vacuo*, a deep violet color developed and the esr spectrum was identical with that of the perylene cation. Binaphthyl was converted to perylene by cyclodehydrogenation[22] when it was passed over a palladium catalyst at 490°. Binaphthyl, which resulted from a series of conversions in the pyrolysis of tetralin, underwent cyclohydrogenation and was converted to the perylene.[23] This pyrolysis was carried out by passing tetralin vapor with nitrogen through a silica tube filled with porcelain chips, at 700°. In the conversion on the activated silica–alumina catalyst this catalyst served as an acid catalyst. Consequently, the final product was the perylene carbonium ion. In the present case it is quite possible that the catalyst consists of lithium on silica, a result of the reaction of the hot lithium with the silicate in the glass. This catalyst would be basic in character and it would result in the formation of the carbanion.[24] This catalyst would assist in the dehydrogenation of the 1,1′-binaphthyl and in the formation of the lithium salt. Then this carbanion will add to the other ring forming a bond between the two carbon atoms facing each other followed by the loss of a hydride ion. A similar mechanism for the formation of biphenyl from the reaction of the benzene carbanion $(C_6H_5)^-$ with benzene has been reported.[25] The addition of phenylpotassium to benzene has also been reported.[26] A mechanism has been proposed which shows the formation of biphenyldipotassium.







This idea is supported by the fact that when the same reaction was run under the same conditions except that lithium was not allowed to react with glass material, only the binaphthyl radical anion was identified from its esr spectrum. This means that in the absence of a catalyst, such as lithium on silica, the reaction stops with the formation of 1,1′-binaphthyl and does not proceed through a cyclodehydrogenation step which produces perylene.

In order to corroborate the formation of the 1,1′-binaphthyl radical anion in the reaction referred to just above, the reduction of 1,1′-binaphthyl with alkali metals and the resultant esr spectra were investigated. It was found that the esr spectrum of the 1,1′-binaphthyl radical anion and the spectrum just mentioned are identical.

Reduction of 1,1′-Binaphthyl with Li, Na, and K in THF and DME and the Resulting Esr Spectra. The reaction of 1,1′-binaphthyl with Li, Na, K, and Na–K alloy in THF and DME took place even at temperatures as low as −65°. In the case of lithium, however, the reaction started at about −50°. The resultant solutions were light purple. The color intensified with time and increase in temperature. At room temperature the solutions were very dark purple.

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[25] H. Pines and V. Mark, *J. Amer. Chem. Soc.*, **78**, 4316 (1956).

[26] A. A. Morton and E. L. Lanpher, *J. Org. Chem.*, **23**, 1639 (1958).

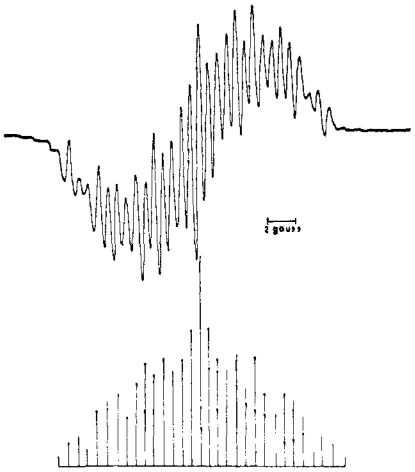
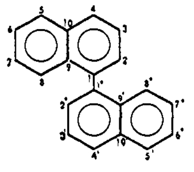


Figure 4. Esr spectrum of the 1,1′-binaphthyl free-radical anion in THF at temperatures between −65 and −25°.

The esr spectra of the radical anions formed were found to be temperature dependent. At low recording temperatures, −65 to −25°, well-resolved spectra were obtained. As the recording temperature rose above −10° spectral lines broadened and the resolution diminished. At room temperature a sample prepared from the reaction with lithium or sodium gave spectra having a fewer number of broadened lines. The samples obtained from the reaction with potassium or sodium–potassium alloy gave one broad and poorly defined line.

The well-resolved spectrum (Figure 4) recorded at temperatures between −65 and −25° consists of 31 lines. The analysis of this spectrum was carried out with the use of the electron densities calculated by Fukui, *et al.*,[27] for the α-substituted naphthalenes, where the substituent is an electron-withdrawing group (such as the naphthyl group in this case of 1,1′-binaphthyl). Their calculations[27] show that the carbon atoms in 1,1′-binaphthyl (V) have electron densities: 8,8′ > 5,5′ > 4,4′ > 3,3′ ≈ 6,6′ > 2,2′.



V

The assignments of the hyperfine splitting constants for each set of equivalent protons in the radical according to their positions in V are reported in Table II.

Table II. Hyperfine Splitting Constants from the Esr Spectrum of 1,1′-Binaphthyl (V)

Atom	No. of atoms	Position	No. of lines	Hsc, G
H	2	8,8′	3	4.30
H	2	5,5′	3	2.92
H	2	4,4′	3	2.20
H	4	3,3′,6,6′	5	0.73
H	2	2,2′	3	0.40

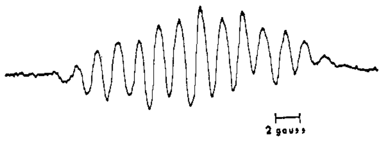


Figure 5. Esr spectrum of the 1,1′-binaphthyl free-radical anion at room temperature.

Because of the low electron densities on carbon atoms in positions 2 and 2′ the interaction of each proton attached to them is weak and, consequently, their spectral lines are not observed in most of the spectra. However, the triplet splitting with a hyperfine splitting constant of 0.40 G is observed in some of the spectra, especially at the extreme ends of the spectrum.

The esr spectrum (Figure 5) recorded at room temperature, obtained from the reactions with lithium and sodium separately, consisted of 15 broad lines. This may be due to ion-pair phenomena and the state of the association of the alkali metal cation with the radical. At room temperature the thermal motion of the metal cation changes its location with respect to the molecule anion. This, in turn, produces great variations in the proton line widths as is observed in the spectrum.

Chinese workers, Fu, *et al.*,[28] reported the esr spectrum of the 1,1′-binaphthyl radical anion at room temperature. They reported a 23-line spectrum which they interpreted as arising from the interaction of three distinct sets of equivalent protons with the unpaired electron. They reported that only 21 lines could be seen because of the weakness of the two lines at the ends of the spectrum. They assigned those sets as two (positions 4,4′), two (2,2′), and another four (5,5′;8,8′). Their coupling constants are 7.14, 3.57, and 1.19 G, respectively.

The spectrum at low temperature which we obtained and discussed previously is different from that reported.[28] The spectrum recorded in the present study has greater resolution and sharper peaks. It has also been observed that spectral resolution is lost as the temperature is raised. In addition, the assignments of the hyperfine splitting constants in the spectrum reported by Fu, *et al.*,[28] do not follow the order of the electron densities.[27] It is known that position 8 in the α-substituted naphthalene with electron-attracting group has the highest electron density and it is the most reactive site toward electrophilic substitution in the molecule.[27] Therefore, the proton in position 8 should have the higher hyperfine splitting constant and not the lowest, as they reported. Finally, it appears that their spectrum has lower resolution because of the temperature at which it was obtained.

The Reactions of Tris(1-naphthalene)phosphine Oxide, Sulfide, and Selenide with Na, K, and Na–K Alloy in THF and DME. Tris(1-naphthalene)phosphine oxide, sulfide, and selenide all behaved similarly in their reactions with sodium, potassium, and Na–K alloy in either THF or DME. Greenish blue solutions were formed at the initiation of these reactions. This green color intensified as the temperature was increased and the reaction mixture remained in contact with the alkali metal. At room temperature the blue color was gone and only the

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[27] K. Fukui, T. Yonezawa, C. Nagata, and H. Shingu, *J. Chem. Phys.*, 22, 1433 (1954).

[28] K. H. Fu, H. Y. Sheng, and C. L. P'an, *K'o Hsueh T'ung Pao*, 6, 540 (1965).

green was observed. Samples were collected at different temperatures during the period of contact with the alkali metal. The esr spectra of all samples collected at temperatures from −65 to 0° in THF and −55 to 0° in DME were identical. Each spectrum indicated the presence of two different radicals in the solution. One of these radicals was easily identified as the naphthalene radical anion from the values of the hyperfine splitting constants and the relative line intensities. The other radical is difficult to analyze because of the broad lines and the overlap of some of them with those due to the naphthalene radical anion. The second radical is believed to be the di(1-naphthyl)phosphine oxide, sulfide, or selenide–alkali metal adduct.

The esr spectrum of the sample at room temperature was typical of that of the naphthalene radical anion. The expected lines were very well characterized. In addition, there were present other broad lines of very low intensities compared to those observed in the spectra of the samples taken at lower temperatures. This suggests that the concentration of the second radical present together with the naphthalene radical anion is lower at room temperature than at low temperature. This occurs because of the conversion of the second radical to the dinegative anion at the higher temperature. Also, the radical has been permitted to remain in contact with the alkali metal for a longer time.

Reactions of Tris(1-naphthalene)phosphine Oxide, Sulfide, and Selenide with Lithium in THF and DME. It has been mentioned that lithium behaves differently than the other alkali metals in its reactions with some phosphine compounds. The reaction of the three tris(1-naphthyl)phosphine chalcogenides with lithium in both THF and DME proceeded similarly. The color of the reaction solution was purple throughout the temperature range studied, from −65° in THF and in DME from −55° to room temperature. The esr spectra of all samples taken from this reaction were identical. This spectrum was identified as that of the 1,1′-binaphthyl radical anion. This means that a carbon–phosphorus bond was cleaved to produce the naphthyl radical which then undergoes dimerization to binaphthyl. This, in turn, is reduced with lithium to produce the 1,1′-binaphthyl radical anion. No other radical was observed in the spectra.

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Pair Production and Cage Reactions of Alkyl Radicals in Solution

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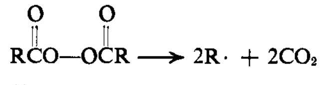
Abstract: Aliphatic diacyl peroxides undergo homolysis on ultraviolet irradiation at 30° to a pair of alkyl radicals and 2 mol of carbon dioxide. The quantum yield for carbon dioxide formation is 2 (2537 Å) and independent of the structure of the alkyl groups. The alkyl radicals are generated in sufficiently high steady state concentrations to enable the esr spectra of a variety of transient alkyl species to be recorded with excellent signal-to-noise ratios. The disproportionation and combination of alkyl–alkyl radical pairs formed in this manner are studied in various solvents and the results compared to those obtained in the gas phase. The cage processes of alkyl–alkyl radical pairs are delineated. The esr study of the rearrangement of cyclopropylmethyl and ω-hexenyl radicals indicates that the cage combination is fast and only those alkyl radicals which diffuse from the solvent cage are observed. In contrast to the thermolytic decomposition of diacyl peroxides, little or no esters are formed in the photolytic process.

Homolytic decomposition of diacyl peroxides has been used extensively as a source of alkyl and aryl radicals.[1] In most cases the decomposition has been induced thermally. However, diacyl peroxides



$$\mathrm{R\overset{O}{\overset{\|}{C}}O{-}O\overset{O}{\overset{\|}{C}}R} \longrightarrow 2\mathrm{R}\cdot + 2\mathrm{CO_2}$$

in which the alkyl group can readily sustain a cationic charge are prone to undergo ionic decomposition *via* carboxy inversion, especially in polar solvents.[2]

We recently showed that photolysis of a diacyl peroxide at low temperatures constitutes a convenient and versatile method of generating a specific alkyl radical in solution for electron spin resonance studies.[3]

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(2) (a) F. D. Greene, H. S. Stein, C. C. Chu, and F. M. Vane, *J. Amer. Chem. Soc.*, **86**, 2081 (1964); (b) C. Walling, H. N. Moulden, J. H. Waters, and R. C. Neuman, *ibid.*, 87, 518 (1965); (c) H. Hart and D. Wyman, *ibid.*, 81, 4891 (1959); (d) J. K. Kochi, *ibid.*, **85**, 1958 (1963); (e) R. C. Lamb and J. R. Sanderson, *ibid.*, **91**, 5034 (1969); (f) S. Oae, T. Kashiwagi, and S. Kozuka, *Chem. Ind.* (London), 1964 (1965); (g) D. B. Denney and N. Sherman, *J. Org. Chem.*, 30, 3760 (1965); (h) D. S. Tarbell, *Accounts Chem. Res.*, 2, 296 (1969).

(3) J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **91**, 3940 (1969); R. O. C. Norman, *Chem. Soc., Spec. Publ.*, No. **24** (1970).