Reduction of Aromatic Ketones or Thioketones with Phenylphosphine

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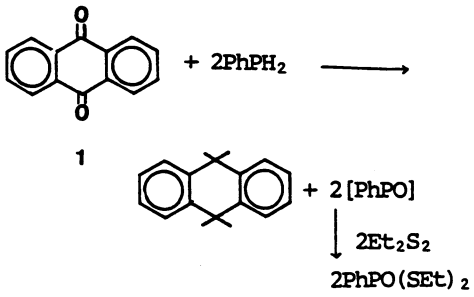
Reactions of certain aromatic ketones or thioketones with phenylphosphine and subsequent addition of diethyl disulfide gave the reduction products of the ketones and *S,S*-diethyl phenylphosphonodithioate or *S,S*-diethyl phenylphosphonotrithioate. A possible intermediate of the phosphine moiety was suggested to be phenylphosphinylidene [PhP=O] or phenylphosphinothioylidene [PhP=S]. The reduction of 10,10′-bianthrone and $\Delta^{10,10'}$-bianthrone resulted in the cleavage of the carbon-carbon single and double bonds and the reduction of the carbonyl groups, respectively.

The reducing properties of the compounds which contain a trivalent phosphorus atom have attracted little attention so far. Because of the affinity of a phosphorus atom for a oxygen atom and its ability to donate hydrogen atoms, primary phosphine is expected to behave as a reducing reagent.

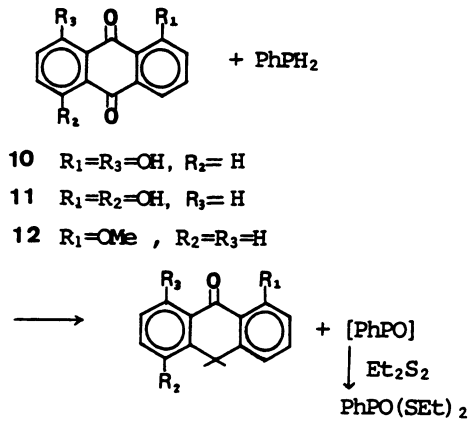
The successful reductions of *N*-chloro-*p*-toluenesulfonamide to *p*-toluenesulfonamide,[1] 1-naphthol to naphthalene,[2] arenesulfonyl chloride to disulfide,[3] and nitro compounds with phosphine to azoxy derivatives[3] and amines[4] have been reported. However, there is no report concerning the reduction of carbonyl or thiocarbonyl compounds with phosphine. The reductions of the carbonyl compounds to alcohols can be achieved by using various reducing reagents such as metal hydrides and dissolving metals, and by catalytic hydrogenations.[5] The complete removal of the oxygen atom from a carbonyl group to give methylene group can be accomplished by well-known Wolf-Kishner[6] and Clemmensen reductions.[7] These methods involve alkaline (Wolf-Kishner) or acidic (Clemmensen) conditions and need drastic heating. The thiocarbonyl groups are also readily reduced with various reducing reagents.[8] Especially, diaryl thioketones are known to be reduced with Zn/HCl to give diarylmethylene.[9] This paper describes our finding about the reduction of aromatic ketones or thioketones with phenylphosphine under mild and neutral conditions.

Results and Discussion

Reduction of anthraquinone (**1**) with $LiAlH_4$[10,11] or $NaBH_4$[12] gives 9,10-dihydro-9,10-anthracenediol, and reduction with Sn/HCl[13] or $SnCl_2$/HCl[14] gives mainly anthrone. Also anthracene was obtained by the reduction of anthraquinone with triphenylsilane,[15] zinc dust/HCl,[16] and HI/AcOH.[17] The conversion of anthraquinone to 9,10-dihydroanthracene was realized by Clemmensen reduction,[18] and reduction with hydriodic acid-phosphorus-iodine[19] and reduction with tetralin in molten $SbCl_3$.[20] Reaction of anthraquinone with two equivalents of phenylphosphine in a sealed ampoule at 140 °C for 3 d and subsequent addition of excess amount of diethyl disulfide gave 91% yield of 9,10-dihydroanthracene and 65% yield of *S,S*-diethyl phenylphosphonodithioate.

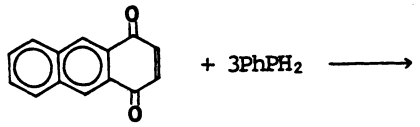


The reduction of this type was carried out successfully with a number of aryl ketones such as 5,12-naphthacenequinone (**2**) and 6,13-pentacenequinone (**3**). By the reaction with equimolar amounts of phenylphosphine, the carbonyl groups of fluorenone (**4**), xanthone (**5**), thioxanthone (**6**), acridinone (**7**), 10-methyl-9(10*H*)-acridone (**8**), and 7*H*-benz[*de*]-anthracen-7-one (**9**) were easily converted to the methylene groups in high yields. Chrysazin(1,8-dihydroxyanthraquinone) (**10**) and anthrarufin(1,5-dihydroxyanthraquinone) (**11**) gave the corresponding anthrones, *i.e.*, 1,8-dihydroxy-9(10*H*)-anthracenone and 1,5-dihydroxy-9(10*H*)-anthracenone, respectively, upon reduction with excess amounts of phenylphosphine.



Also, 1-methoxyanthraquinone (**12**) gave 1-methoxy-9(10*H*)-anthracenone. These anthraquinones, in which one or both of the carbonyl groups were protected by hydrogen bonding or by steric hindrance, show strong resistance to the complete removal of the oxygen atoms.

The reduction of 1,4-anthraquinone (**13**) with three molar excess of phenylphosphine and subsequent treatment with excess amounts of diethyl disulfide gave 1,2,3,4-tetrahydroanthracene. *S,S*-Diethyl phenylphosphonodithioate and *S,S*-diethyl phenylphosphonodithioite were separated from the phosphine moiety in 2:1 molar ratio.



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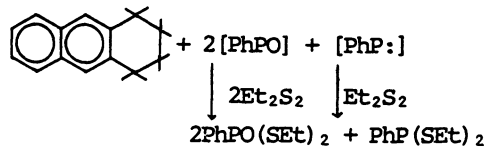
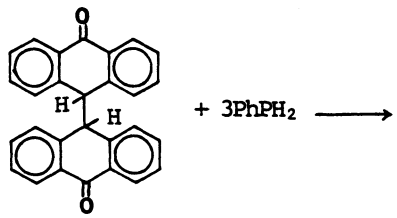


10,10′-Bianthrone (**14**) and $\Delta^{10,10'}$-bianthrone (**15**) were reduced with three and four molar amounts of phenylphosphine to gave 9,10-dihydroanthracene. Also, *S,S*-diethyl phenylphosphonodithioate and *S,S*-diethyl phenylphosphonodithioite were obtained in 2:1 and 1:1 molar ratios, respectively.



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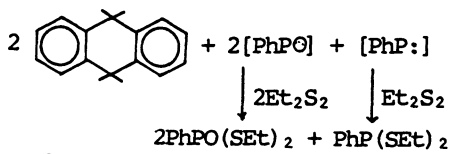

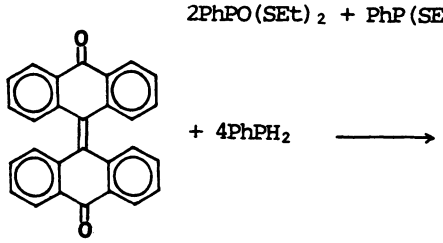

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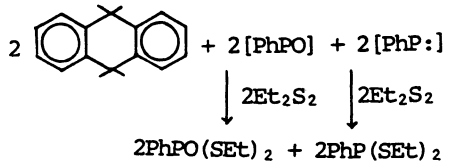

In these reductions, the carbon–carbon single and double bonds were cleaved in addition to the removal of the oxygen atoms from the carbonyl groups.

The reduction of benzophenone (**16**) and acetophenone (**17**) with phenylphosphine gave diphenylmethane and ethylbenzene, respectively. However, the yield of the reduction of acetophenone was very low, and aliphatic ketones could not be reduced with this reagent. Therefore, the intermediate of this reduction must have two aryl rings for stabilization.

Thiocarbonyl groups of 9*H*-xanthenethione (**18**), 9*H*-thioxanthenethione (**19**), 9(10*H*)-acridinethione (**20**), and 10-methyl-9(10*H*)-acridinethione (**21**) were rapidly converted to the methylene groups to give 9*H*-xanthene, 9*H*-thioxanthene, 9,10-dihydroacridine, and 10-methyl-9,10-dihydroacridine, respectively.

With regard to the mechanism of this reduction, a carbonyl or thiocarbonyl group will undergo insertion into the P–H bond of the phenylphosphine to form >CH–XPHPh (X=O or S) as an intermediate. The C–X bond in this intermediate would be cleaved and the hydrogen atom on the phosphorus atom would migrate to the carbonyl carbon atom. Therefore, phenylphosphine would accept an oxygen or a sulfur atom and donate two hydrogen atoms suggesting the intermediary of phenylphosphinylidene [PhP=O] or phenylphosphinothioylidene [PhP=S].

$$>C{=}X + PhPH_2 \longrightarrow >CH\text{-}XPHPh \longrightarrow >CH_2 + PhP{=}X \quad (X{=}O \text{ or } S)$$

By subsequent addition of diethyl disulfide, these phosphine moieties were trapped as *S,S*-diethyl phenylphosphonodithioate and *S,S*-diethyl phenylphosphonotrithioate.

In the cases of the reduction of 1,4-anthraquinone, 10,10′-bianthrone and $\Delta^{10,10'}$-bianthrone, some part of phenylphosphine acts as a hydrogen donor only and gives phenylphosphinidene [PhP:] as an intermediate, which is converted to *S,S*-diethyl phenylphosphonodithioite by the reaction with diethyl disulfide.

Experimental

General. All the reactions were carried out under an argon atmosphere. Melting points determined with a Yanagimoto micro-melting point apparatus were uncorrected. IR spectra were taken with a Shimadzu IR-430 spectrometer, UV spectra on a Hitachi 200-10 spectrophotometer, ^1H and ^{13}C NMR spectra on a JEOL JNM-FX 60 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. MS spectra were recorded on a Hitachi RMU-6L spectrometer. Commercially available carbonyl compounds were used without further purification. 1-Methoxyanthraquinone was prepared from 1-chloroanthra-

quinone according to the method as that reported by Cook and Pauson.[21] 1,4-Anthraquinone was obtained by the reduction of quinizarin with $NaBH_4$ and purified by sublimation.[22] 9*H*-Xanthenethione, 9*H*-thioxanthene-9-thione, 9(10*H*)-aoacridinethione, and 10-methyl-9(10*H*)-acridinethione were prepared by treatment of the corresponding carbonyl compounds with phosphorus pentasulfide.[8] Phenylphosphine was obtained by the reduction of dichlorophenylphosphine with $LiAlH_4$ according to the method described by Pass and Schindlbauer.[23]

Reduction Procedure. A mixture of an aromatic ketone (10 mmol) with phenylphosphine (molar amount used is specified in Table 1) was placed in a sealed ampoule under argon atmosphere, and heated at 140 °C for periods shown in Table 1. The reaction mixture turned into homogeneous pale orange paste. Subsequently, an excess amount (50 mmol) of diethyl disulfide was added to the ampoule, which was resealed and heated at 140 °C for another 24 h. After removal of excess diethyl disulfide, the reduction products were obtained by sublimation under reduced pressure (13.33 Pa/120 °C). From the sublimation residue, *S,S*-diethyl phenylphosphonodithioate or *S,S*-diethyl phenylphosphonotrithioate were distilled. In the reduction of 1,4-anthraquinone, 10,10′-bianthrone, and $\Delta^{10,10'}$-bianthrone. *S,S*-diethyl phenylphosphonodithioate and *S,S*-diethyl phenylphosphonodithioite were separated by column chromatography (silica gel–$CHCl_3$ as eluent) of the distillation mixture. The structures of the reduction products were deduced based on the following analytical and spectroscopic data.

9,10-Dihydroanthracene: White crystals; mp 70—72 °C (lit,[19] 108—110 °C). Spectra data(IR,[24] ^1H,[25] and ^{13}C[26] NMR) matched with the reported data.

5,12-Dihydronaphthacene: Pale yellow needles; mp 210—211 °C; IR (KBr-disk) 3030(w), 2880(w), 1501(w), 1492(w), 1477(m), 1438(w), 767(vs), and 755(vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.24—7.72 (m, 10H), and 4.06 (s, 2H); ^{13}C NMR δ=137.16, 135.73, 132.48, 127.28, 126.31, 125.33, 125.20, and 36.84; UV_{max} (C_2H_5OH) 228 (ε 56200), 260 (ε 2300), 271 (ε 3200), 280 (ε 3020), and 291 nm (ε 2290); MS (70 eV), *m/z* (rel intensity), 230 (M^+, 100), 229 (94), 228 (26), 110 (26), and 109 (90). Found: C, 93.51; H, 6.50%. Calcd for $C_{18}H_{14}$: C, 93.87; H, 6.13%.

6,13-Dihydropentacene: White needles; mp 265—268 °C; IR (KBr-disk) 3055—2750(w), 1595(w), 1485(w), 1440(w), 750(vs), and 740(vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.16—7.78 (m, 12H) and 4.24 (s, 2H); ^{13}C NMR δ=135.93, 133.72, 127.28, 125.33, 125.14, and 37.36; UV_{max} (C_2H_5OH) 234 (ε 105000), 260 (ε 8900), 272 (ε 10200), 281 (ε 9330), and 292 nm (ε 6300); MS (70 eV), *m/z* (rel intensity), 280 (M^+, 100), 270 (72), 278 (56), 140 (33), 79 (39), and 78 (28). Found: C, 93.88; H, 5.62%. Calcd for $C_{22}H_{16}$: C, 94.25; H, 5.75%.

Fluorene: White plate; mp 117—118 °C. All spectroscopic data were identical with those of commercially available sample.

Xanthene: White crystals; mp 98—100 °C (lit,[27] 100.5 °C). All spectroscopic data were identical with those of commercially available sample.

Thioxanthene: White crystals; mp 126—127 °C (lit,[15] 128 °C). IR and ^1H NMR spectra data matched with reported data (IR; Aldrich 627F, ^1H NMR; Aldrich 5, 533 A).

9,10-Dihydroacridine: White crystals; mp 165—167 °C; IR Aldrich 695E.

10-Methyl-9,10-dihydroacridine: White crystals; mp 85—88 °C; IR (KBr-disk) 2960(w), 1585(s), 1460(s), 1152(m), 1110(m), 1032(m), and 742(vs) cm^{-1}; ^1H NMR δ=7.19—6.58

Table 1. Reduction conditions and yields of products

Compd	$PhPH_2$ Equiv	Reaction period	Product from ketone(A)	Yields/% (A)	Yields/% $PhPX(SEt)_2$[a]	Yields/% $PhP(SEt)_2$
(1)	2	3 d	9,10-Dihydroanthracene	91	65	—
(2)	2	3 d	5,12-Dihydronaphthacene	46	36	—
(3)	2	3 d	6,13-Dihydropentacene	32	28	—
(4)	1	3 d	Fluorene	100	76	—
(5)	1	1 d	Xanthene	88	73	—
(6)	1	12 h	Thioxanthene	100	81	—
(7)	1	1 d	9,10-Dihydroacridine	95	79	—
(8)	1	1 d	10-Methyl-9,10-dihydroacridine	81	67	—
(9)	1	3 d	7*H*-benz[*de*]anthracene	56	43	—
(10)	2	3 d	1,8-Dihydroxy-9(10*H*)-anthracenone	13	8	—
(11)	2	3 d	1,5-Dihydroxy-9(10*H*)-anthracenone	17	10	—
(12)	2	3 d	1-Methoxy-9(10*H*)-anthracenone	12	8	—
(13)	3	3 d	1,2,3,4-Tetrahydroanthracene	51	45	22
(14)	3	3 d	9,10-Dihydroanthracene	61	52	31
(15)	4	3 d	9,10-Dihydroanthracene	18	10	8
(16)	1	1 d	Diphenylmethane	96	75	—
(17)	1	5 d	Ethylbenzene	7	trace	—
(18)	1	10 h	Xanthene	93	63	—
(19)	1	10 h	Thioxanthene	90	59	—
(20)	1	10 h	9,10-Dihydroacridine	99	70	—
(21)	1	10 h	10-Methyl-9,10-dihydroacridine	89	52	—

a) X=O for compds 1—17 and X=S for compds 18—21.

(m, 8H), 3.71 (s, 3H), and 3.05 (s, 2H); ^{13}C NMR δ=125.19 (C-1), 118.24 (C-2), 124.54 (C-3), 109.54 (C-4), 121.81 (C-9a), 141.22 (C-4a), 30.65 (C-9), and 30.91 (N-Me); UV_{max} (C_2H_5OH) 210 (ε 10200), 249 (ε 2500), 282 (ε 1120), 355 (ε 1380), and 380 nm (ε 1380); MS (70 eV), *m/z* (rel intensity) 196 (21), 195 (M^+, 100), 194 (28), 181 (35), 180 (81), 166 (26), and 152 (31). Found: C, 86.31; H, 6.68%. Calcd for $C_{14}H_{13}N$: C, 86.12; H, 6.71%.

7H-Benz[de]anthracene: White crystals; mp 70—72 °C; IR (KBr-disk) 3030(m), 2940(w), 2900(w), 1603(m), 1497(s), 1455(m), 1440(s), 765(m), and 752 (s) cm^{-1}; ^{1}H NMR δ=7.29—8.77 (m, 10H) and 4.54 (s. 2H); ^{13}C NMR δ=134.37, 133.33, 131.18, 128.91, 126.67, 126.83, 126.44, 126.18, 125.92, 125.46, 124.42, 123.71, 123.32, 122.73, 120.72, 118.57, and 34.44; UV_{max} (C_2H_5OH) 206 (ε 12300), 223 (ε 14100), 227 (ε 14100), 250 (ε 8500), 256 (ε 8300), 304 (ε 3000), 316 (ε 3700), 330 (ε 4900), and 345 nm (ε 4200); MS (70 eV), *m/z* (rel intensity) 216 (M^+, 53), 215 (100), 213 (21), 107 (15), and 94 (15). Found: C, 94.06; H, 5.51%. Calcd for $C_{17}H_{12}$: C, 94.41; H, 5.59%.

1,8-Dihydroxy-9(10H)-anthracenone: All physical and spectroscopic data were identical with those of an authentic sample.[28]

1,5-Dihydroxy-9(10H)-anthracenone: All physical and spectroscopic data were identical with those of an authentic sample.[28]

1-Methoxy-9(10H)-anthracenone: Reddish orange needles; mp 125—126 °C; IR (KBr-disk) 3050(w), 1660(vs), 1606(vs), 1591(vs), 1454(m), 1438(m), 1305(vs), 1260(s), 1241(m), 1063(s), 731(vs), and 711(vs) cm^{-1}; ^{1}H NMR δ=6.99—8.39 (m, 7H), 4.15 (s, 3H), and 3.92 (s, 2H); ^{13}C NMR δ=156.85 (C-1), 113.38 (C-2), 132.68 (C-3), 119.42 (C-4), 128.91 (C-5), 127.54 (C-6), 126.97 (C-7), 127.41 (C-8), 184.33 (C-9), 27.42 (C-10), 129.88 (C-9a), 140.66 (C-4a), 133.13 (C-8a), and 131.96 (C-10a); UV_{max} (C_2H_5OH) 213 (ε 51300), 256 (ε 57500), 330 (ε 5750), 367 (ε 2880), and 381 nm (ε 1860); MS (70 eV), *m/z*(rel intensity) 224 (M^+, 100), 208 (75), 179 (65), 163 (50), 151 (25), 150 (70), 149 (20), 85 (25), 76 (35), 75 (20), and 63 (29). Found: C, 80.20; H, 5.48%. Calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39%.

1,2,3,4-Tetrahydroanthracene: White lieflets; mp 105—106 °C (lit, 96—105 °C,[29] 103—105 °C[30]); IR(KBr-disk) 3040(w), 2920(s), 2845(m), 2825(w), 1500(m), 1490(w), 1441(w), 970(w), 946(m), and 742(vs) cm^{-1}; ^{1}H NMR δ=7.39—7.60 (m, 6H), 2.92 (s, 4H), and 1.83 (s, 4H); ^{13}C NMR δ=29.83 (C-1), 23.46 (C-2), 127.05 (C-5), 124.88 (C-6), 126.63 (C-9), 136.32 (C-4a), and 132.42 (C-10a); UV_{max} (C_2H_5OH) 228 (ε 33900), 257 (ε7240), 265 (ε 7940), 277 (ε 7940), 285 (ε 7080), and 298 nm (ε3700); MS (70 eV), *m/z* (rel intensity), 182 (M^+, 100), 166 (33), 165 (21), 164 (36), 153 (88), 152 (36), 151 (33), 140 (46), and 114 (21). Found: C, 92.56; H, 7.92%. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74%.

Diphenylmethane and Ethylbenzene: All physical and spectroscopic data were identical with those of commercially available materials.

S,S-*Diethyl Phenylphosphonodithioate*: Colorless liquid; bp 106—108 °C/26.66 Pa. Spectra data matched with the reported data.[31]

S,S-*Diethyl Phenylphosphonodithioite*: All physical and spectroscopic data were identical with those of an authentic sample prepared by a standard method.[32]

S,S-*Diethyl Phenylphosphonotrithioate*: Orange liquid; bp 117—120 °C/26.66 Pa. Spectra data matched with the reported data.[33]

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