TABLE I

ELECTRON-TRANSFER REACTIONS OF DEHYDROINDIGO (**6**), INDIGO (**8**), LEUCOINDIGO (**10**), 2,2′-BIBENZIMIDAZOLE (**13**), AND $\Delta^{2,2'}$-BIISOBENZIMIDAZOLYLIDENE (**11**)

Donor (M)	Acceptor (M)	Base (M)	Solvent[a]	R·⁻	Concn of R·⁻ (M)	Time[b] (min)	Color
$C_6H_5COCH_2CH_3$ (0.05)	**6** (0.004)	KOBu (0.25)	DMSO	**7**	2.3×10^{-3}	10 or 32	Green
.....	**6** (0.005)	KOBu (0.25)	DMSO	**7**	1×10^{-4}	32	Green
8 (0.005)	**6** (0.005)	KOBu (0.25)	DMSO	**7**	3×10^{-4}	60	Green
.....	**8** (0.005)	KOBu (0.25)	DMSO	**9**	2×10^{-5}	22	Blue
$C_6H_5COCH_2CH_3$ (0.05)	**8** (0.005)	KOBu (0.25)	DMSO	**9**	4.5×10^{-4}	165	Blue
10 (0.0025)	**8** (0.0025)	KOBu (0.25)	DMSO	**9**	3.5×10^{-3}	10	Blue
.....	**8** (0.0025)	KOH (2.0)	EtOH	**9**	1.1×10^{-4} 5×10^{-4}	160 11 hr	Brown Red
$C_6H_5COCH_2CH_3$ (0.05)	**8** (0.005)	KOH (1.0)	EtOH	**9**	1.5×10^{-4}	60	Brown
10 (0.0025)	**8** (0.0025)	KOH (2.0)	EtOH	**9**	7×10^{-4}	11	Brown
$C_6H_5COCH_2CH_3$ (0.05)	**6** (0.004)	KOH (1.0)	EtOH	**9**	4.5×10^{-4} 11×10^{-4}	10 10 hr	Red-brown Red-brown
.....	**6** (0.001)	KOH (0.5)	EtOH	Asymmetric spectrum	3×10^{-4}	8	Brown
8 (0.005)	**6** (0.005)	KOH (2.0)	EtOH	Asymmetric spectrum	4×10^{-4}	10	Brown
13 (0.0025)	**11** (0.0025)	KOBu (0.05)	DMSO	**12**	8×10^{-4}	240	Green
.....	**11** (0.0025)	KOBu (0.005)	DMSO	**12**	1.5×10^{-3}	50	Green
13 (0.005)	...	KOBu (0.05)	DMSO	**12**	5×10^{-2}		Orange
13 (0.005)	...	KOBu (0.25)	DMSO	**12**	1.5×10^{-4}[c]		Green
13 (0.0005)	**11** (0.0005)	KOH (0.05)	CH_3OH	**12**	1.4×10^{-4}	170	Olive green
.....	**11** (0.0005)	KOH (0.05)	CH_3OH	**12**	8×10^{-5}	90	Olive green
13 (0.001)	...	KOH (0.05)	CH_3OH	...	None detected[d]		Orange

[a] DMSO = DMSO (80 vol. %)–t-butyl alcohol (20 vol. %). [b] Time for maximum concentration of radical anion to be formed. Concentration measurements by comparison with standard solutions of diphenylpicrylhydrazyl in same solvent and similar instrument settings. Radical anions did not decay appreciably with time. [c] Trace of oxygen added. [d] In presence or absence of a trace of oxygen.

$\Delta^{2,2'}$-Biisobenzimidazolylidene.—According to the procedure of Hill,[8] 2,2′-bibenzimidazole was oxidized with lead dioxide to yield coppery crimson crystals (from benzene), mp 220–250° dec (lit.[8] decomposition above 200°). The infrared spectrum was identical with that reported by Hill.[8] The ultraviolet spectrum in ethanol showed λ_{max} 262 mμ (lit.[8] λ_{max} 262 mμ in ethanol). The ultraviolet spectrum in chloroform clearly showed the compound not to be the isomeric 5,6,11,12-tetraazanaphthacene.[9]

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[9] G. M. Badger and I. S. Walker, *J. Chem. Soc.*, 122 (1956).

Organophosphorus Thio Esters from Disulfides and Primary and Secondary Phosphines

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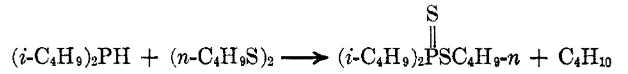
We have found that primary and secondary phosphines react with disulfides in the presence of radical inhibitors to give phosphonodithioites (I) and phosphinothioites (II), respectively, in high yield. With

$$RPH_2 + 2R'SSR' \longrightarrow \underset{\text{I}}{RP(SR')_2} + 2R'SH$$

$$R_2PH + R'SSR' \longrightarrow \underset{\text{II}}{R_2PSR'} + R'SH$$

alkyl disulfides, in the absence of radical inhibitors, further abstraction of sulfur occurs to give phosphonotrithioates, $RP(S)(SR')_2$, and phosphinodithioates, $R_2P(S)SR'$, respectively. At the reactant ratios used and with the yields obtained, the additional thiono sulfur must be derived from the product mercaptan. Furthermore, butane was isolated and identified by mass spectrometry from the reaction of n-butyl disulfide and diisobutylphosphine in refluxing benzene. Walling and



$$(i\text{-}C_4H_9)_2PH + (n\text{-}C_4H_9S)_2 \longrightarrow (i\text{-}C_4H_9)_2\overset{\overset{\displaystyle S}{\|}}{P}SC_4H_9\text{-}n + C_4H_{10}$$

Rabinowitz[1] have shown that the formation of phosphorothionate and alkane from alkyl mercaptan and phosphite first described by Hoffman, Ess, Simmons, and Hanzel[2] is a chain process involving thiyl radicals.

$$RS\cdot + (R'O)_3P \longrightarrow (R'O)_3\dot{P}SR \longrightarrow (R'O)_3P{=}S + R\cdot \xrightarrow{RSH} RH + RS\cdot$$

With a disulfide instead of mercaptan, attack by the alkyl radical gave a sulfide and regenerated thiyl radical to carry the chain.[1] These reactions also occur with trialkylphosphines.[3]

The formation of I and II presumably occurs by ionic displacement (SN2) at the disulfide bond as with tertiary phosphines[4] and trialkyl phosphites[5] which give tertiary phosphine sulfides and phosphorothiolate esters, respectively, as well as sulfides. Although radical processes may occur in these reactions to give the same products, the ionic mechanism appears to be favored in

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[1] C. Walling and R. Rabinowitz, *J. Am. Chem. Soc.*, **81**, 1243 (1959).

[2] F. W. Hoffman, R. J. Ess, T. C. Simmons, and R. S. Hanzel, *ibid.*, **78**, 6414 (1956).

[3] C. Walling, O. H. Basedow, and E. J. Savas, *ibid.*, **82**, 2181 (1960).

[4] L. Maier, "Topics in Phosphorus Chemistry," Vol. 2, M. Grayson and E. J. Griffith, Ed., John Wiley and Sons, Inc., New York, N. Y., 1965, p 43.

[5] R. G. Harvey and E. R. DeSombre, "Topics in Phosphorus Chemistry," Vol 1, M. Grayson and E. J. Griffith, Ed., John Wiley and Sons, Inc., New York, N. Y., 1964, p 82.

TABLE I

PHOSPHINOTHIOITE ESTERS

$R_2PH + R'SSR' \longrightarrow R_2PSR' + R'SH$

R	R′	Bp (mm), °C	Yield, %	Anal, %							
				Calcd				Found			
				C	H	P	S	C	H	P	S
i-C_4H_9	n-C_4H_9	156–166(0.17)	91	61.42	11.60	13.11	13.67	61.28	12.20	13.07	13.34
c-C_6H_{11}	n-C_4H_9	126–133(0.15)	52[a]	67.03	10.90	10.82	11.18	66.87	10.86	10.53	11.48
i-C_4H_9	p-$CH_3C_6H_4$	110–115(0.17)	81	67.16	9.38	11.53	11.93	67.28	9.42	11.67	12.02
i-C_4H_9	C_6H_5	94–98(0.12)	93	66.11	9.11	12.17	12.61	66.14	9.19	12.07	12.97
i-C_4H_9	$C_2H_5O_2CCH_2CH_2$	123–128(0.18)	87	56.08	9.78	11.12	11.52	56.27	9.52	10.21	11.67

[a] A small amount of higher boiling material containing P=S was observed.

the presence of inhibitors. Aside from thiolate ester formation with trialkyl phosphites or related compounds[6] owing to the special driving force of the Michaelis–Arbuzov type of valence expansion,[5] and the reaction of disulfides with elemental phosphorus,[7] this type of reaction with disulfides appears to be unknown with other trivalent phosphorus compounds.

A further interesting variation of this process is the preparation of phosphorothiolate esters by reaction of the appropriate phosphine and excess disulfide in aqueous media such as 80:20 t-butyl alcohol–water.

$$(c\text{-}C_6H_{11})_2PH + 2(C_6H_5S)_2 + H_2O \xrightarrow{t\text{-BuOH}} (c\text{-}C_6H_{11})_2P(O)SC_6H_5 + 3C_6H_5SH$$

The intermediate formation of phosphinothioite ester was demonstrated by synthesis in high yield in the aqueous medium with an equivalent amount of disulfide and by treating this compound separately with more phenyl disulfide under the same conditions to give the same product in high yield. The rapid hydrolysis of

$$(c\text{-}C_6H_{11})_2PSC_6H_5 + (C_6H_5S)_2 + H_2O \xrightarrow{t\text{-BuOH}} (c\text{-}C_6H_{11})_2P(O)SC_6H_5 + C_6H_5SH$$

tertiary phosphine aryl disulfide adducts to give a tertiary phosphine oxide and thiophenol was first reported by Schonberg[8] and has been suggested as an analytical technique for aromatic disulfides.[9] The early work of Hantzsch and Hibbert with hydrolysis of the pseudo-phosphonium salts obtained by alkylation of tertiary phosphine sulfides[10] strongly suggests direct attack of water on the analogous structure in the case of disulfides, $R_3P^+SR{\cdot}RS^-$. From the latter work one would also conclude that the reaction should be applicable to alkyl disulfides as well. However, a preliminary experiment with di-n-butyl disulfide and diisobutylphosphine in aqueous t-butyl alcohol in the presence of hydroquinone gave both P=S- and P=O-containing products in roughly equal amounts. The mixture was not separated. It is likely that a more effective inhibitor would facilitate the formation of phosphinothiolate ester by preventing the radical sulfur abstraction from by-product mercaptan.

Experimental Section

All melting and boiling points are uncorrected. Mono- and dialkylphosphines were prepared by the radical addition of phosphine to the appropriate olefin.[11] Disulfides were commercial reagent grade materials except for bis(2-carbethoxyethyl) disulfide which was prepared by iodine oxidation of ethyl 2-mercaptopropanoate. Volatile products were checked routinely for purity by gas–liquid partition chromatography.

Phenyl Dicyclohexylphosphinothioite.—Phenyl disulfide (11.0 g, 0.050 mole), dicyclohexylphosphine (10.0 g, 0.050 mole), and 0.05 g of hydroquinone were refluxed for 2.25 hr in 100 ml of benzene under an atmosphere of argon. Vacuum distillation gave 14.3 g (92%) of product, bp 175–179° (0.1 mm). The infrared spectrum was consistent with the proposed structure (PS at 512 cm^{-1}). *Anal.* Calcd for $C_{18}H_{27}PS$: C, 70.62; H, 8.87; P, 10.09; S, 10.42. Found: C, 70.54; H, 9.19; P, 10.24; S, 10.70.

Other phosphinothioites were prepared similarly (Table I) except that longer reaction times were allowed for alkyl disulfides (*e.g.*, 12 hr or longer). This compound was also prepared in 83% yield in 80:20 t-butyl alcohol–water.

Diphenyl Cyclohexylphosphonodithioite.—Phenyl disulfide (53.2 g, 0.245 mole) and cyclohexylphosphine (14.0 g, 0.121 mole) were refluxed for 20 hr in 125 ml of benzene under argon. Vacuum distillation gave 36.0 g (90%) of product, bp 183–189° (0.15 mm). The infrared spectrum was consistent with the proposed structure (PS at 503 cm^{-1}). *Anal.* Calcd for $C_{18}H_{21}PS_2$: C, 65.28; H, 6.37; P, 9.32; S, 19.29. Found: C, 65.14; H, 6.43; P, 9.27; S, 18.97.

Diphenyl *n*-Butylphosphonodithioite.—Phenyl disulfide (96.0 g, 0.44 mole) and n-butylphosphine (20.0 g, 0.22 mole) were refluxed for 16 hr in 125 ml of benzene under argon. Vacuum distillation gave 63.1 g (93%) of product, bp 175–180° (0.30 mm). *Anal.* Calcd for $C_{16}H_{19}PS_2$: C, 62.68; H, 6.24; P, 10.11; S, 20.94. Found: C, 62.85; H, 6.27; P, 10.11; S, 20.13.

Di-*n*-butyl *n*-Butylphosphonodithioite.—n-Butyl disulfide (48.0 g, 0.27 mole), n-butylphosphine (13.5 g, 0.15 mole), and 1.1 g of hydroquinone were refluxed for 30 hr in 70 ml of benzene under argon. Vacuum distillation gave 8.2 g (23%) of product, bp 96–110° (0.25 mm). The absorption band for PS[12] in the infrared was present at 497 cm^{-1}. *Anal.* Calcd for $C_{12}H_{27}PS_2$: C, 54.08; H, 10.20; P, 11.62; S, 24.10. Found: C, 52.72; H, 9.90; P, 11.59; S, 24.74.

A 3.8-g fraction of slightly higher boiling point was also obtained which contained some trithioate ester (P=S 678 cm^{-1}, 27.36% S).

***n*-Butyl Dicyclohexylphosphinodithioate.**—n-Butyl disulfide (12.5 g, 0.070 mole) and dicyclohexylphosphine (13.2 g, 0.067 mole) were refluxed for 20 hr in 50 ml of benzene under argon. Vacuum distillation gave 19.0 g (90%) of product, bp 167–175° (0.15 mm). The infrared spectrum was consistent with the proposed structure (PS at 521[12] and P=S at 638 cm^{-1}). *Anal.* Calcd for $C_{16}H_{31}PS_2$: C, 60.30; H, 9.81; P, 9.74; S, 20.11. Found: C, 61.02; H, 10.07; P, 9.75; S, 19.78.

***n*-Butyl Diisobutylphosphinodithioate.**—n-Butyl disulfide (26.7 g, 0.15 mole) and diisobutylphosphine (17.2 g, 0.12 mole) were refluxed for 16 hr in 150 ml of benzene under argon. The gases evolved during reaction were collected over water. Mass spectrometry indicated over 95% butane was present. Vacuum distillation gave 30.4 g (97%) of product, bp 97–103° (0.05 mm). *Anal.* Calcd for $C_{12}H_{27}PS_2$: C, 54.10; H, 10.42;

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(6) K. Pilgrim, D. D. Phillips, and F. Korte, *J. Org. Chem.*, **29**, 1844 (1964).

(7) D. R. Stevens and R. S. Spindt (to Gulf Research and Development Co.), U. S. Patent 2,542,370 (1948); *Chem. Abstr.*, **45**, 5712 (1951).

(8) A. Schonberg, *Ber.*, **68B**, 163 (1935).

(9) R. E. Humphrey and J. M. Hawkins, *Anal. Chem.*, **36**, 1812 (1964).

(10) A. Hantzsch and H. Hibbert, *Ber.*, **40**, 1508 (1907).

(11) A. R. Stiles, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **74**, 3282 (1952); M. M. Rauhut, H. A. Currier, A. M. Semsel, and V. P. Wystrach, *J. Org. Chem.*, **26**, 5138 (1961).

(12) Single-bond P–S assignment was by N. Colthup, private communication.

P, 11.63; S, 24.02. Found: C, 54.71; H, 10.30; P, 11.71; S, 22.84.

2-Carbethoxyethyl Diisobutylphosphinodithioate.—2-Carbethoxyethyl disulfide (24.0 g, 0.09 mole), diisobutylphosphine (14.6 g, 0.10 mole), and 0.2 g of azobisisobutyronitrile (AlBN) were refluxed for 62 hr in 100 ml of benzene under argon. An additional 0.2 g of AlBN was added and reflux was continued for another 5 hr. Vacuum distillation gave 18.6 g (67%) of product, bp 152–157° (0.20 mm). *Anal.* Calcd for $C_{13}H_{27}PS_2O_2$: C, 50.26; H, 8.76; P, 9.98; S, 20.64. Found: C, 51.59; H, 8.80; P, 10.24; S, 18.35.

Di-*n*-butyl *n*-Butylphosphonotrithioate.—*n*-Butyl disulfide (37.1 g, 0.21 mole) and *n*-butylphosphine (9.9 g, 0.11 mole) were refluxed for 67 hr in 75 ml of benzene under argon. AlBN was added at 2, 35, and 65 hr in 0.1-g portions. Vacuum distillation gave 24.3 g (87%) of product, bp 138–144° (0.17 mm). The infrared spectrum was consistent with the proposed structure (PS at 527 and P=S at 638 cm^{-1}). *Anal.* Calcd for $C_{12}H_{27}PS_3$: C, 48.30; H, 9.12; P, 10.38; S, 32.20. Found: C, 47.88; H, 8.76; P, 10.36; S, 31.37.

Phenyl Dicyclohexylphosphinothiolate.—Phenyl disulfide (22.0 g, 0.10 mole), dicyclohexylphosphine (10.0 g, 0.05 mole), and 0.2 g of hydroquinone were refluxed for 64 hr in 600 ml of 80:20 *t*-butyl alcohol–water. The solvent was removed by vacuum distillation and the residue was crystallized from petroleum ether (bp 30–60°). The yield of white solid was 14.4 g (90%), mp 84–90.5°. A second crystallization gave mp 91–93° (lit.[13] mp 91–93.5°). A mixture melting point with an independently prepared sample[12] gave no depression. *Anal.* Calcd for $C_{18}H_{27}POS$: P, 9.61; S, 9.94. Found: P, 9.56; S, 9.91.

The compound was also prepared in 92% yield by direct reaction of phenyl disulfide and phenyl dicyclohexylphosphinothioite under the same conditions, mp 91.5–93°.

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[13] M. Grayson, C. E. Farley, and C. A. Streuli, *Tetrahedron*, in press.

1,4,9,10-Tetrahydroanthracene from the Stepwise Reduction of 9,10-Dihydroanthracene by Lithium in Ammonia[1]

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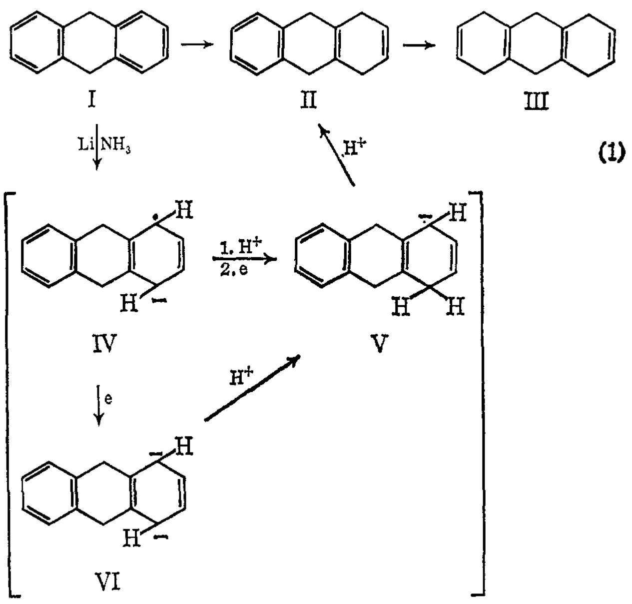
Partially reduced polycyclic aromatic hydrocarbons having an internal tetrasubstituted olefinic bond are a relatively unknown class of compounds. With few exceptions, compounds of this type (*e.g.*, 1,2,3,4,9,10-hexahydrophenanthrene[2] and 5,6,11,12-tetrahydrochrysene[3]) have arisen *via* cyclization of precursors with fewer rings.

In the present study we have explored metal–ammonia reduction for the preparation of 1,4,9,10-tetrahydroanthracene (II), the synthesis of which typifies one of the essential problems to achieving controlled step-by-step reduction of higher aromatic systems. Thus, 9,10-dihydroanthracene (I), presumably the initial product from Birch reduction of anthracene, possesses two isolated and equivalent benzenoid rings so that selective, two-stage reduction (*i.e.*, synthesis of II in preference to III) (eq 1 of Chart I) is improbable by conventional techniques. Treatment of anthracene with sodium and alcohol in liquid ammonia is reported to furnish its hexahydro derivative (III),[4,5] while similar reaction in the absence of alcohol provided only the dihydro compound (I).[6] Reduction of I with lithium in methylamine[7] also provides III.

CHART I



An efficient synthesis of II from I has now been achieved. Optimum conditions are as follows. A stirred solution prepared from I (900 mg, 5 mmoles), lithium (2.5 equiv), and 75 ml of dry THF in 150 ml of purified ammonia was maintained at reflux for 2 hr. Reaction was quenched by addition first of alcohol, then of water. The pure substances, I, II, and III (15, 76, and 9%, respectively), were conveniently isolated by *charge-transfer chromatography*[8,9] on a column of silica gel impregnated with 1,3,5-trinitrobenzene. The nmr spectrum of I exhibited aromatic proton resonance at τ 2.80 and a sharp methylene singlet at 6.10; II showed absorptions at τ 2.92, 4.27, 6.77, and 7.30 for aromatic, vinylic, and inner and outer ring methylene protons, respectively; for III vinyl protons were unaltered at τ 4.27, while central and outer methylene protons underwent downfield shift to 7.52 and 7.42, respectively.

The foregoing synthetic procedure, based upon an empirical study of this reduction (Table I), contains several significant features. Firstly, purity of the ammonia is essential,[10] since reduction failed to occur in this solvent taken directly from a commercial cylinder. Iron compounds are apparently responsible, since ferric salts had a similar inhibitory effect. Secondly, maximum yield of II relative to III is favored by the omission of alcohol or other added proton source during the formal reaction period. Thirdly, while a small excess of lithium is necessary to maintain the concentration of

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[1] This investigation was supported in part by Public Health Service Research Grant 1-RO1-CA-08674 from the National Cancer Institute.

[2] B. Belleau, *J. Am. Chem. Soc.*, **75**, 1159 (1953).

[3] E. Cahana, G. Schmidt, and K. Shah, *J. Org. Chem.*, **24**, 556 (1959).

[4] A. J. Birch, P. Fitton, D. C. C. Smith, D. E. Steere, and A. R. Stelfox, *J. Chem. Soc.*, 2209 (1963).

[5] J. Runge, *Z. Chem.*, **2**, 374 (1962).

[6] P. Le Beau, *Compt. Rend.*, **159**, 70 (1914); H. F. Miller and G. B. Bachman, *J. Am. Chem. Soc.*, **57**, 768 (1935).

[7] E. Vogel, *et al.*, *Angew. Chem.*, **78**, 642 (1966).

[8] R. G. Harvey and M. Halonen, *J. Chromatog.*, in press.

[9] This technique has proved invaluable for the efficient separation of closely related hydroaromatic molecules, often virtually impossible to obtain free of one another by recrystallization or conventional chromatography.

[10] Despite reports[6] that in the absence of a proton source anthracene is reduced only as far as I, we have found that reduction beyond this stage proceeds readily, providing that the ammonia is free of metallic impurities. These and related experiments will be published shortly.