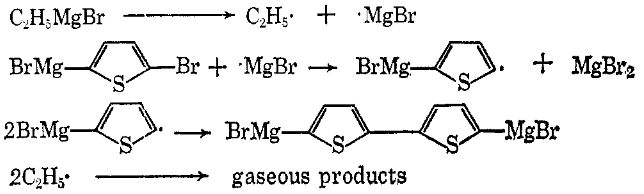
preparation of II. Coupling occurred only on use of ethyl bromide.

A suggested mechanism for the formation of III is *via* the formation of the Grignard of 5,5′-dibromo-2,2′-bithiophene by a thermal, free-radical reaction involving ethylmagnesium bromide,[11] followed by its subsequent reaction with heptafluorobutyryl chloride.



Experimental Section[19]

2-Pentafluoropropionylthiophene (IVb).—An ether solution of 1.0 mole of 2-thienylmagnesium bromide was added over a period of 2 hr to an ether solution of 1.2 moles of pentafluoropropionyl chloride maintained at a temperature of −30°. The mixture was stirred for 2 hr during which time the temperature was allowed to rise to 25°. The mixture was then refluxed for 6 hr and worked up in a manner previously described.[15] Distillation through a 12-in. Vigreux column gave a 17% yield, bp 66.5–67.2° (21 mm), $n^{20}\text{D}$ 1.4515.

Anal. Calcd for $C_7H_3F_5OS$: C, 36.53; H, 1.31; F, 41.27. Found: C, 36.98; H, 1.40; F, 40.96.

The 2,4-dinitrophenylhydrazone, recrystallized from an alcohol-water mixture, melted at 107–108°.

2-Pentadecafluorocaprylylthiophene (IVc).—The reaction was performed in the same manner as above, employing 2-pentadecafluorocaprylyl chloride as the fluorinated intermediate. After addition of the Grignard to the ether solution of the acid chloride (room temperature), the mixture was refluxed for 6 hr. Distillation through a 12-in. Vigreux column gave a 19% yield, bp 64.4–65.8° (0.32 mm), $n^{20}\text{D}$ 1.3914.

Anal. Calcd for $C_{12}H_3F_{15}OS$: C, 30.01; H, 0.63; F, 59.35. Found: C, 30.34; H, 0.91; F, 56.75.

Several recrystallizations of the 2,4-dinitrophenylhydrazone from an alcohol–water mixture afforded pure product, mp 92.0–93.6°.

5-Bromo-2-heptafluorobutyrylthiophene (II).—In an attempt to synthesize I, a two-to-one ratio of magnesium turnings to halide was used in order to prepare the di-Grignard of 2,5-dibromothiophene. Iodine crystals and heat were found necessary to initiate the reaction. The Grignard was refluxed for 10 hr, filtered under nitrogen through glass wool,[20] and added over a period of 4 hr to an ether solution of the acid chloride. The mixture was then refluxed for 18 hr and worked up by the usual procedure. The crude, orange product was separated from tars by distillation at 5 mm,[21] collecting the fraction from 75–85°. Distillation through a 3-in. Vigreux column gave a purple forecut and a light yellow middle cut, bp 91–92 (7.5 mm). Fractionation of the middle cut through a 3-in. column containing $^1/_8$ in. helices gave a 17% yield, bp 145.0–145.3 (93 mm), $n^{20}\text{D}$ 1.4733. Infrared bands (neat) appeared at 3100 (vw–b),[22] 1678 (vs), 1663 (sh), 1512 (w), 1403 (vs), 1351 (s), 1326 (s), 1116 (vs),[23] 1066 (m), 987 (s), 962 (s), 930 (m), 865 (vw–b), 841 (sh), 823 (s–b), 802 (s–b), 748 (s), 728 (m–b), 715 (m–b), and 687 (m) cm^{-1}.

Anal. Calcd for $C_8H_2BrF_7OS$: C, 26.76; H, 0.56; Br, 22.26; F, 37.04; S, 8.93. Found: C, 27.03; H, 0.62; Br, 22.03; F, 36.89; S, 9.04.

5,5′-Diheptafluorobutyryl-2,2′-bithiophene (III).—The reaction was performed initially in the same manner as that for II, employing 0.7 g-atom of magnesium turnings and 0.1 mole of 2,5-dibromothiophene. The mixture was refluxed for 3 hr and cooled to room temperature; 0.5 mole of ethyl bromide in ether was added in 1 hr. The ether solution of the Grignard compounds was refluxed for 17 hr, filtered under nitrogen through glass wool (1.7 g of magnesium recovered), and added over a 45-min period to 0.7 mole of heptafluorobutyryl chloride in ether. The mixture was refluxed for 10 hr and worked up in the usual manner. Distillation removed the liquid portion boiling from 28 to 113° (22 mm)[24] and left a tarry residue. Extraction of the residue with hot petroleum ether (bp 30–60°) gave the orange, crude product. Crystallization from petroleum ether and recrystallization from heptane gave yellow platelets, mp 152.6–153.8°, 26% yield. Infrared bands (Nujol mull) appeared at 3100 (w), 1670 (vs), 1510 (w), 1440 (s), 1360 (m), 1317 (m), 1290 (m), 1262 (m), 1230 (s), 1212 (s), 1190 (m), 1176 (m), 1149 (m), 1122 (vs), 1088 (m), 970 (w), 940 (m), 917 (vw), 893 (w), 828 (m), 811 (m), 754 (m), and 733 (vw–b) cm^{-1}.

Anal. Calcd for $C_{16}H_4F_{14}O_2S_2$: C, 34.42; H, 0.72; F, 47.64; S, 11.49. Found: C, 34.29; H, 0.97; F, 47.32; S, 11.06.

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[19] All melting and boiling points are uncorrected; analyses were by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Infrared spectra were obtained on a Perkin-Elmer Model 21 spectrophotometer.

[20] Almost one-half the magnesium charge was recovered.

[21] Distillation was stopped upon appearance of decomposition vapors.

[22] b = broad, vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder.

[23] A strong, broad band appears in the C–F absorption regon, 1290–1130 cm^{-1}.

[24] At 80°, a small quantity of orange product crystallized on the condenser wall.

Radical Anions Derived from Indigo and 2,2′-Bibenzimidazole[1]

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We have previously discussed radical anions and cations derived from 2,2′-biindan-1,1′,3,3′-tetraone (**3**) and particularly the very stable diprotonated form of **4**.[2] We now report an investigation of various aza derivatives of 2,2′-biindan including dehydroindigo (**6**), indigo (**8**), leucoindigo (**10**), $\Delta^{2,2'}$-biisobenzimidazolylidene (**11**), and 2,2′-bibenzimidazole (**13**). We find that whereas both **7** and **9** can be prepared, apparently only **12** is readily prepared in the bibenzimidazole series. There appears to be a trend in stability from the more highly reduced structure in series A (**4** is stable) to the more highly oxidized structure in series C (**12** is stable). Series B is intermediate, (**7** and **9** both stable). We have been unable to detect the oxidized radical anion in series A (**2**) or the reduced radical anion in series C (**14**) (see Chart I).

Two radical anions were detected in series B which we attribute to the dehydroindigo radical anion (**7**) and the indigo radical ion (**9**). Reduction of **6** yielded a poorly resolved esr spectrum which is consistent with hyperfine splitting by two equivalent nitrogen atoms, $a^N \sim 2$ gauss. Reduction of **8** or oxidation of **10** gave a more highly resolved spectrum previously observed by Bruin, Heineken, and Bruin.[3] The previous workers assigned this radical structure **7** but the method of synthesis in the present work strongly suggests structures **9**. The concentration of **9** formed from equimolar mixtures of **8** and **10** in dimethyl sulfoxide (80%)–*t*-butyl alcohol (20%) solution containing potassium *t*-

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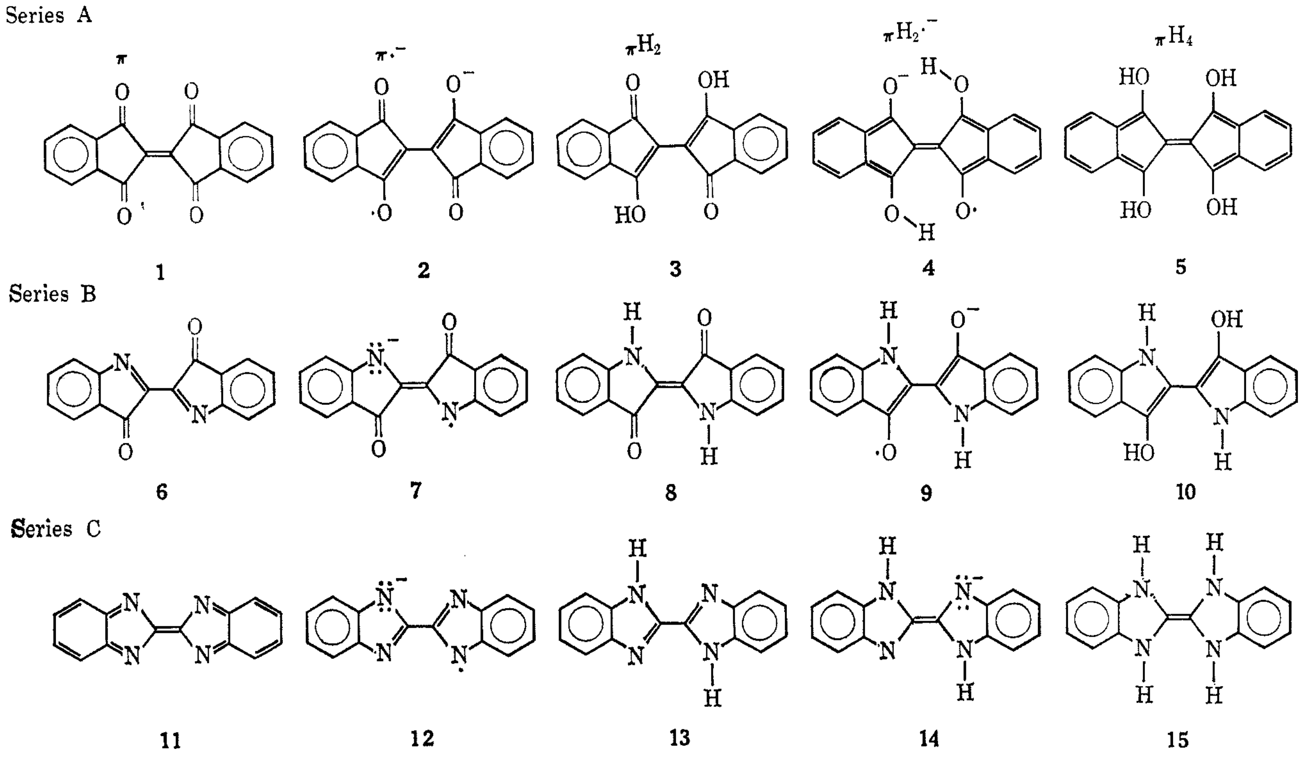
[1] Part IV. Electron Transfer Processes. For part III, see O. W. Maender and G. A. Russell, *J. Org. Chem.*, **31**, 442 (1966). This work was supported by a grant from the National Science Foundation.

[2] G. A Russell and M. C. Young, *J. Am. Chem. Soc.*, **88**, 2007 (1966).

[3] F. Bruin, F. W. Heineken, and M. Bruin, *J. Org. Chem.*, **28**, 562 (1963). These workers report a somewhat better spectrum (below room temperature) than we have observed at 25°. Both spectra have 19 sets of lines.

CHART I



butoxide or potassium hydroxide in ethanol is quite large, namely 70 and 14%, respectively. Apparently we are observing the equilibrium that follows.

$$\pi_{H_4}(\mathbf{10}) \rightleftarrows \rightleftarrows \pi_{H_2}{}^{2-}(\mathbf{10}^{2-})$$

$$\pi_{H_2}(\mathbf{8}) + \pi_{H_2}{}^{2-}(\mathbf{10}^{2-}) \rightleftarrows 2\pi_{H_2}\cdot^{-}(\mathbf{9})$$

Numerous other examples of this type of electronic disproportionation are recognized.[4] Table I summarizes the conditions used to prepare **7** and **9**. The use of propiophenone enolate anion as a reducing agent for nitroaromatics and other unsaturated systems has been discussed previously.[4b]

The reduction of **6** to **7** by propiophenone anion proceeds in quite high yield; the first entry in the table corresponds to a 57% yield of **7** while the tenth entry corresponds to a 28% yield in 10 hr. On the other hand the reduction of indigo by propiophenone enolate yielded only small concentrations of **9**, ~3-10% in both solvent systems. We conclude that leucoindigo is a very efficient donor and dehydroindigo a very efficient acceptor.

Table I also summarizes our results with compounds **11** and **13**. Only a single paramagnetic species was found and it corresponded with **12** prepared by Geske[5] by the electrolytic reduction of **11**. A study of the table does not provide evidence for the disproportionation shown below. In fact, **11** gives rise to a higher con-

$$\pi(\mathbf{11}) + \pi^{2-}(\mathbf{13}^{2-}) \rightleftarrows 2\pi\cdot^{-}(\mathbf{12})$$

centration of **12** spontaneously in basic solution (60%, entry 14; 15%, entry 18) than in the presence of an equivalent amount of **13**. Moreover, **13** is not readily oxidized to **12** by air in basic solutions (entries 16 and 19). We conclude that **11** is a very good acceptor while **13** is not too efficient as a donor. The rate of the electron-transfer processes given in the table were very slow and **12** once formed was exceedingly stable.

The spontaneous formation of **12** from **11** in basic solution may well involve the addition of an anion (OH^-, OR^-, $CH_3SOCH_2^-$) to **11** to form a new anion capable of donating an electron to another molecule of **11** to give **12** and a free radical that would dimerize or otherwise react.

Experimental Section

Esr spectra were obtained using an inverted U cell and a deoxygenation chamber described previously.[4b] The spectra were obtained on a Varian V-4500 epr spectrometer at ~9.5 kMcps with 100-kcps field modulation and a 6-in. magnet. Spectra were calibrated in field relative to *p*-benzosemiquinone.

Dehydroindigo.—Indigo (5 g) and lead dioxide (25 g) were suspended in 500 ml of benzene at 60° for 50 min with mechanical stirring. The benzene filtrate was evaporated to give a residue that crystallized. Recrystallization from chloroform gave dark red-brown crystals, mp 215–218° dec (lit.[6] mp 210–215° dec). The product contained no NH groups by infrared or nmr spectroscopy.

Dihydroindigo (Leucoindigo).—Indigo (0.5 g) was added to 10 ml of 5% aqueous sodium hydroxide under a nitrogen atmosphere and 1 g of sodium dithionite was added. After 30 min the solution became yellow-brown. Treatment with 10% hydrochloric acid gave a precipitate that was quickly filtered and stored under nitrogen until used. The crystals were yellow and became blue on the surface when exposed to air.

2,2′-Bibenzimidazole.—Following the procedure of Lane[7] ammonium oxalate monohydrate (7.2 g), *o*-phenylenediamine (11 g), and glycerol (20 g) were refluxed for 3 hr and poured into 200 ml of water, and the resulting solid was removed by filtration. Recrystallization from ethylene glycol gave fine, yellow crystals (3 g), mp 392–396° dec (lit.[7,8] mp 395–400° dec, 350°). The product had λ_{max} at 315, 325, and 340 mμ in ethanol (lit.[8] λ_{max} at 316, 325, and 342 in ethanol).

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[4] (a) G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, **84**, 4155 (1962); (b) G. A. Russell, E. G. Janzen, and E. T. Strom, *ibid.*, **86**, 1807 (1964).

[5] D. Geske and G. R. Padmanabhan [*ibid.*, **87**, 1651 (1965)] report $a^N = 2.97$, $a^H = 1.40$ and 0.83 gauss in acetronitrile solution. We found in DMSO (80%)–*t*-BuOH (20%) a^N (4 equiv) = 2.88, a^H (4 equiv) = 1.44 and 0.72 gauss.

[6] L. Kalb, *Ber.*, **42**, 3643 (1909).

[7] E. S. Lane, *J. Chem. Soc.*, 2238 (1953).

[8] J. H. M. Hill, *J. Org. Chem.*, **28**, 1932 (1963).

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}	160	Brown
					5×10^{-4}	11 hr	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}	10	Red-brown
					11×10^{-4}	10 hr	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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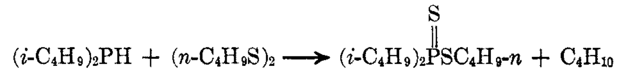
We have found that primary and secondary phosphines react with disulfides in the presence of radical inhibitors to give phosphonodithioites (I) and phosphinothioites (II), respectively, in high yield. With

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

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

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 (S_N2) 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.