The Preparation of Benzotrifurazan and of Some Complexes which it Forms with Organic Molecules †

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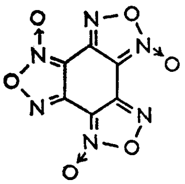
Reduction of benzotrifuroxan with trimethyl, triethyl, or tri-isopropyl phosphite yields a complex of benzotrifurazan with the corresponding trialkyl phosphate. Benzotrifurazan has a complexing ability similar to that of 1,3,5-trinitrobenzene.

BENZOTRIFUROXAN (I) forms[1,2] charge-transfer complexes with a variety of aromatic compounds and it was of interest to examine the properties of the related compound benzotrifurazan (II). The formation of furazans by reduction of furoxans is well known,[3] and recently[4] it has been reported that triphenyl phosphine and triethyl phosphite reduce benzofuroxan to benzofurazan. We observed that the reduction of benzofuroxan with triethyl phosphite with benzene as solvent was complete in 30 min., in contrast to the 12 hr. required with ethanol,[4] and it was decided to examine the reduction of benzotrifuroxan with phosphite esters in benzene.

On adding triethyl phosphite to a hot solution of benzotrifuroxan in benzene a red coloration was observed which had faded after 5 min. A similar change is observed when chloranil is reduced by triethyl phosphite and may be due to the formation of a charge-transfer complex.[5] A crystalline solid (m. p. 67—68°) which was not the expected furazan (II) and which gave analytical results in agreement with the formula $C_{12}H_{15}N_6O_7P$ was isolated. By using trimethyl or tri-isopropyl phosphite, solids of formulae $C_9H_9N_6O_7P$ and $C_{15}H_{21}N_6O_7P$, respectively, were obtained. The yield with trimethyl phosphite was smaller than that with the other esters. This may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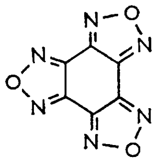
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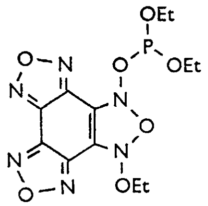
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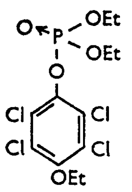
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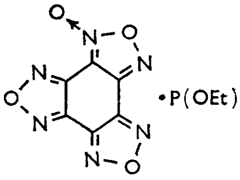

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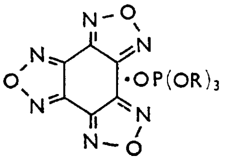

(VI)

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† A preliminary account of this work has been published; *Chem. and Ind.*, 1964, 1424.

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be owing to isomerisation of the ester to dimethyl methylphosphonate.[6]

We considered three possible structures for the compounds: (*a*) an adduct (III) similar to those formed by the addition of trialkyl phosphite to quinones, for example (IV);[5] (*b*) a complex of benzodifurazanfuroxan with triethyl phosphite (V); charge-transfer complexes of this type have been suggested[5] as intermediates in the reduction of chloranil by phosphite esters; and (*c*) a complex of benzotrifurazan with triethyl phosphate (VI; R = Et). The nuclear magnetic resonance (n.m.r.) (^{1}H) spectra of the methyl and ethyl ester adducts were measured in carbon tetrachloride (Table 1). All the alkyl groups are equivalent and the signals are split by the phosphorus atom, which makes structure (III) impossible. It is also clear that the alkyl groups are contained in phosphate rather than phosphite esters.[7] From the association constants (see below) it may be calculated that the complexes are highly associated at the concentrations used (0·6M) for the n.m.r. measurements. The observed shifts towards higher field may be due to changes in the diamagnetic susceptibility of the medium[8] or to charge-transfer complex formation;[9] the protons of the parent heterocycle, furazan, are highly deshielded (τ = 1·81 in carbon tetrachloride).[10] The ^{31}P n.m.r. spectrum (carbon tetrachloride) showed shifts summarised in Table 2.

TABLE 1

	$\tau(CH_3)$	$\tau(CH_2)$	$J_{\alpha H-P}$	$J_{\beta H-P}$	$J_{\beta H-\alpha H}$
Trimethyl phosphate	6·26		10·5		
$(MeO)_3PO$–benzotrifurazan	6·56		10·5		
Triethyl phosphate	8·66	5·95	8·0	~1	7·0
$(EtO)_3PO$–benzotrifurazan	8·81	6·32	8·0	~1	7·0

TABLE 2

	C./sec. from P_4O_6	P.p.m. from 85% phosphoric acid
Triethyl phosphate	+2833·6	+0·9
Triethyl phosphite	−633·6	−137·8
$(EtO)_3PO$–benzotrifurazan...	+2873·3	+2·4

These results rule out structure (V) in which the phosphorus is trivalent. The mass spectra of the trimethyl and triethyl phosphate complexes contain no signal for the intact complex (*m/e* 344 and 386), but show intense peaks due to the trifurazan (II) (*m/e* 204) and the two phosphate esters (*m/e* 140 and 182); this confirms structure (VI).

The apparent molecular weights of the trimethyl and the triethyl phosphate complexes were determined in carbon tetrachloride solution and the degrees of association calculated (see Experimental section). The association constant for the ethyl compound is lower than that for the methyl one, a fact that may be due to steric repulsions either amongst the rotating alkyl groups or between them and the benzotrifurazan ring. The basicity of tertiary amines towards trimethylboron follows a similar pattern,[11] trimethylamine being a stronger base than triethylamine. The apparent molecular weight of the trimethyl phosphate complex was determined in ethyl methyl ketone (at one concentration only), giving $K_{\text{assn.}}$ 44; the triethyl phosphate compound was completely dissociated in this solvent. Further evidence that the phosphate ester is not covalently bonded to the heterocycle was obtained by adding various aromatic compounds (see later) to solutions of the complexes; coloured charge-transfer complexes of the aromatic compound with benzotrifurazan were obtained, the phosphate ester being displaced. The trimethyl phosphate and the triethyl phosphate complex each gave the same adduct with pyrene; by decomposing the dimethylaniline complex with mineral acid, benzotrifurazan (II) was isolated. By adding triethyl phosphate to a solution of (II) in light petroleum, the complex (VI; R = Et) was re-formed.

The ultraviolet spectrum of (II) in ethanol showed $\lambda_{\text{max.}}$ 209, 243, 250, 258, and 267 mμ (log ε 4·203, 3·776, 3·798, 3·750, and 3·540); furazan shows only end absorption.[10] The ultraviolet spectrum of (VI; R = Et) was identical with that of (II) and no charge-transfer band could be observed in either ethanol or chloroform solution. No such band was found for iodine–trifluoromethylbenzene[12] and only tail absorption at 220 mμ for iodine–tributyl phosphate,[13] but charge-transfer bands have been observed for other π-*n* complexes.[12,14,25]

The infrared spectrum of benzotrifurazan contained only 8 strong bands, at 1675, 1535, 1450, 1350, 1175, 1000, 995, and 875 cm.$^{-1}$. The spectrum is similar to that of furazan;[10] the band at 1675 cm.$^{-1}$ is probably due to a C=N stretching vibration.[4,15] The infrared spectra of the phosphate ester complexes showed peaks at 1250—1300 cm.$^{-1}$, assigned to P=O stretching,[16] this band sometimes appearing as a doublet; the bands at 1160 (triethyl ester) and 1189 cm.$^{-1}$ (trimethyl ester) are assigned to P–O–C stretching.[17] Shifts of the P=O

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stretch to lower frequency have been observed in solutions of phosphate ester complexes with electron acceptors.[18,19] The P=O frequency shift was measured using a technique to compensate for uncomplexed ester [18] and shifts of 14 and 21 cm.$^{-1}$ were observed. In the presence of iodine the shift is 36 cm.$^{-1}$ suggesting that the interaction of phosphate esters with iodine [18] is greater than with (II). A similar shift in the P=O bond frequency is observed when phosphate esters are hydrogen-bonded, and the ability of triethyl phosphate to form hydrogen-bonds has been related to its ability to associate with iodine.[18] This correlation and studies on the systems phosphate ester–boron halide and tributyl phosphate–nitric acid–water [19] have led to the view that the P=O oxygen atom is the donor site; this idea is supported by bond refraction [20] and dipole moment [21] studies. Parallel shifts of the frequency of the C=O band in carbonyl compounds in the presence of iodine or phenol have been observed and it has been suggested that here the C=O oxygen atom acts as the donor site.[22] The trialkyl phosphate–benzotrifurazan complexes are thus n-π complexes, the phosphate acting as an n-donor through the P=O oxygen atom. Similar complexes have been observed [14a,23] with polynitro-aromatic compounds and ethoxide ion or amines. π-n Complexes of aromatic hydrocarbons (donor) with halogens or sulphur dioxide are well known.[12,14b,24,25]

The spectrophotometric association constants of benzotrifurazan with dimethylaniline and with pyrene were measured in chloroform solution. For comparison the association constant of benzotrifuroxan (I) with dimethylaniline was measured; it was impossible to determine K for benzotrifuroxan–pyrene since the complex is insoluble in chloroform. The values obtained are given in Table 3 along with values of K for some other complexing agents.

TABLE 3

Acceptor	K (l. mole^{-1})	Temp.
With pyrene:		
Tetracyanobenzene [26]	12·4	22·5°
s-Trinitrobenzene [26]	8·1	22·5
Tetrachlorophthalonitrile [26]	5·7	24
Benzotrifurazan	4·3	24
With dimethylaniline:		
Benzotrifuroxan	3·4	24
Tetracyanobenzene [26]	2·5	18·5
Benzotrifurazan	1·5	24
s-Trinitrobenzene [27]	1·3	21
Tetrachlorophthalonitrile [26]	0·8	24

This method of measuring K has been widely used; it has recently been shown by Foster [28] to be rather inaccurate and small differences in the values of K may not be used to give an order of complexing ability. However, the figures do indicate that the complexing ability of benzotrifurazan is about the same as that of trinitrobenzene, smaller than that of benzotrifuroxan, and much smaller than those of tetracyanoethylene [1] and $\alpha\alpha\alpha'\alpha'$-tetracyanoquinodimethane.[29] For all the compounds listed in the Table K for pyrene is greater than K for dimethylaniline, the ratio varying between 2·8 and 7·1. A series of solid complexes with aromatic compounds was prepared; the melting points of the benzotrifurazan complexes were lower than those of the benzotrifuroxan complexes, except for the complexes of indole and hexamethylbenzene. The complexes from stilbene, 1,4-diphenylbutadiene, and diphenylacetylene contained 2 moles of benzotrifurazan per mole of hydrocarbon. Unlike benzotrifuroxan, the furazan failed to complex with tetralin, benzene, and diphenylmethane; the complexes with 8-hydroxyquinoline and with bis-8-hydroxyquinolinatocopper(II) have already been described.[2]

Benzotrifuroxan (I) crystallised from trimethyl phosphate as a rather unstable 1 : 1 complex which could not be recrystallised; p-benzoquinone, chloranil, and s-trinitrobenzene recrystallised from trimethyl phosphate without solvent, and tetracyanoethylene was decomposed by the ester.

Unlike other complexing agents, benzotrifurazan (II) is low-melting and soluble in non-polar solvents such as light petroleum; the formation of a solid complex is controlled by the solubilities of the components and complex in the solvent used.[30] The crystal structures of (II), (VI), and of benzotrifurazan–bis-8-hydroxyquinolinatocopper(II) are being examined.

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus, ultraviolet spectra on a Cary 14M spectrometer (the solvent being ethanol unless otherwise stated), and infrared spectra on a Perkin-Elmer 237 spectrometer. ^{1}H n.m.r. spectra were measured by Mrs. R. E. Richards on a Perkin-Elmer 60 Mc. spectrometer. The phosphite esters were distilled immediately before use.

Benzofurazan.—(*a*) Trimethyl phosphite (1 ml.) was added to a solution of benzofuroxan [31] (2 g.) in benzene (20 ml.), and the solution heated in an open flask on a

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water-bath at 70—80° for 15 min. More trimethyl phosphite (1 ml.) was added and the heating continued for a further 15 min. Benzene was removed under reduced pressure, and the residue taken up in a little methanol. This solution when poured into water gave a solid which was collected, washed, dried, and sublimed (70°/0·5 mm.), m. p. 50° (85%). Recrystallisation gave needles, m. p. and mixed m. p. 52° (lit.,[4] 52°). (*b*) Triethyl phosphite gave a 70% yield of the same compound when used in place of the trimethyl ester.

Benzotrifurazan–Trimethyl Phosphate Complex (VI; R = Me).—Trimethyl phosphite (2 ml.) was added carefully to a hot solution of benzotrifuroxan (2 g.) in benzene (50 ml.). The pale yellow solution turned red immediately and then the colour faded to orange. The solution was heated in an open flask on a water-bath for 15 min., more trimethyl phosphite (2 ml.) added and the solution heated for a further 15 min. Benzene was removed under reduced pressure and the red liquid washed with water to remove trimethyl phosphate. The material was crystallised by scratching and seeding, dried on a porous plate (24 hr.), and sublimed. At first a little trimethyl phosphate distilled over and then the *complex* sublimed at 100°/0·1 mm. (yield 30—40%), m. p. 92—93°. Recrystallisation [light petroleum (b. p. 60—80°)] gave needles, m. p. 93° (Found: C, 31·6; H, 2·5; P, 8·6. $C_9H_9N_6O_7P$ requires C, 31·4; H, 2·6; P, 9·0%).

After sublimation the similarly prepared *triethyl phosphate complex* (VI; R = Et) had m. p. 63—65° (51—55%). Recrystallisation [light petroleum (b. p. 40—60°)] gave needles, m. p. 67—68° (Found: C, 37·4; H, 3·8; N, 21·7. $C_{12}H_{15}N_6O_7P$ requires C, 37·4; H, 3·9; N, 21·8%). The following modifications were made in an attempt to improve the yield: (*a*) toluene as solvent (30%); (*b*) ethanol, product difficult to crystallise (15%); (*c*) excess of triethyl phosphite, mixture exploded and ignited; (*d*) old peroxidised dioxan [4c] at room temperature for 2 weeks (starting material recovered); (*e*) carefully dried benzene (heated under reflux, yield unchanged); (*f*) original conditions but benzotrifuroxan purified via its benzene complex [1] (no change in yield); (*g*) use of only 2 ml. of triethyl phosphite gave mixtures containing benzotrifuroxan. Passage of either oxygen or nitrogen through the solution did not affect the yield. Benzotrifuroxan was not reduced by phosphorus trichloride in chloroform.

A slight excess of triethyl phosphate was added to a solution of benzotrifurazan (II) (see below) in hot light petroleum (b. p. 60—80°). From the cooled solution, needles of the triethyl phosphate complex, identical (m. p., mixed m. p., and infrared) with the material obtained by reduction of benzotrifuroxan with triethyl phosphite, separated.

The product obtained by reducing (II) with tri-isopropyl phosphite was washed with water several times before crystallisation occurred (tri-isopropyl phosphate is less soluble in water than the ethyl ester). The *complex* (VI; R = Pr^i) sublimed at 100°/0·1 mm. (75%). Recrystallisation [light petroleum (b. p. 60—80°)] gave needles, m. p. 86° (Found: N, 20·0; P, 7·7. $C_{15}H_{21}N_6O_7P$ requires N, 20·6; P, 7·7%).

Benzotrifurazan (II).—To a solution of benzotrifurazan–triethyl phosphate in either warm light petroleum (b. p 40—60°) or hot aqueous methanol was added a slight excess of *NN*-dimethylaniline. The complex formed crimson needles, m. p. 102° (yield from light petroleum 65%, from aqueous methanol 90%) (Found: C, 50·6; H, 3·5; N, 29·7. $C_{14}H_{11}N_7O_3$ requires C, 51·1; H, 3·4; N, 30·2%). Hydrochloric acid (20 ml.; 4N) was added to a solution of the complex (1 g.) in ether (20 ml.), and the mixture was shaken thoroughly; the red colour of the ether layer disappeared. The ether was washed with hydrochloric acid and water and dried ($MgSO_4$). The solvent was removed and the residue sublimed at 90°/0·1 mm. (yield 95%). The material was resublimed at 60° and appeared to be polymorphic, softening at 50°, and melting at 62°. When a molten sample was supercooled and solidified, it had m. p. 48—50°; seeding with the higher m. p. material then gave a product, m. p. 62—63°. Recrystallisation [light petroleum (b. p. 60—80°)] gave needles, m. p. 62°; from carbon tetrachloride prisms were obtained m. p. 62—63° (Found: C, 35·3, 35·2; H, 0·0, 0·0; N, 41·2. $C_6N_6O_3$ requires C, 35·3; N, 41·2%). The free furazan was also isolated by decomposing the *p*-dimethylaminobenzoic acid complex with hydrochloric acid, followed by chromatography on silica.

Molecular Complexes.—The complexes (Table 4) were

TABLE 4

Donor	Solvent	Complex	M. p.	Ratio of acceptor : donor
Durene	A	Colourless [a]	149—152°	1 : 1
Hexamethylbenzene	B	Pale yellow [b]	226	1 : 1
Naphthalene	B	Cream-coloured [c]	172	1 : 1
1,7-Diphenylnaphthalene	C	Yellow [d]	113—116	1 : 1
Azulene	A	Dark green [e]	168—170	1 : 1
Phenanthrene	B	Cream-coloured [f]	204—206	1 : 1
Pyrene	B	Yellow [g]	256	1 : 1
Perylene	D	Red [h]	267—270	1 : 1
Stilbene	D	Yellow	153	2 : 1
1,4-Diphenylbutadiene	E	Yellow plates [j]	193—194	2 : 1
Diphenylacetylene	E	Yellow [k]	128	2 : 1
Biphenyl	B [r]	Colourless [l]	115—116	1 : 1
m-Xylylene	D	Colourless [m]	172	1 : 1
Benzo[*b*]thiophen	B [r]	Cream-coloured [n]	150	1 : 1
Indole	B [r]	Yellow [o]	200	1 : 1
2,3-Diphenylindole	B [r]	Red [p]	147	1 : 1
p-Dimethylaminobenzoic acid	B [r]	Orange prisms [q]	190—192	1 : 2

A, methanol; B, ethanol; C, hexane; D, chloroform; E, carbon tetrachloride. [a] Found: C, 56·3; H, 3·9; N, 25·1. $C_{16}H_{14}N_6O_3$ requires C, 56·8; H, 4·1; N, 24·8%. [b] Found: C, 59·4; H, 4·7; N, 23·2. $C_{18}H_{18}N_6O_3$ requires C, 59·0; H, 4·9; N, 23·0%. [c] Found: C, 57·8; H, 2·5. $C_{16}H_8N_6O_3$ requires C, 57·8; H, 2·4%. [d] Found: N, 17·4. $C_{28}H_{16}N_6O_3$ requires N, 17·4%. [e] Found: C, 57·8; H, 2·4; N, 25·4. $C_{16}H_8N_6O_3$ requires C, 57·8; H, 2·4; N, 25·3%. [f] Found: N, 22·4. $C_{20}H_{10}N_6O_3$ requires N, 22·0%. [g] Found: C, 65·2; H, 2·8. $C_{22}H_{10}N_6O_3$ requires C, 65·0; H, 2·9%. [h] Found: N, 18·3; $C_{26}H_{12}N_6O_3$ requires N, 18·4%. [i] Found: C, 52·7; H, 2·1; N, 28·6%. $C_{26}H_{12}N_{12}O_6$ requires C, 53·1; H, 2·0; N, 28·6%. [j] Found: C, 54·2; H, 2·3; N, 27·4. $C_{28}H_{14}N_{12}O_6$ requires C, 54·7; H, 2·3; N, 27·4%. [k] Found: C, 52·5; H, 1·9; N, 27·8. $C_{26}H_{10}N_{12}O_6$ requires C, 53·2; H, 1·7; N, 28·7%. [l] Found: C, 60·0; H, 2·9. $C_{18}H_{10}N_6O_3$ requires C, 60·3; H, 2·8%. [m] Found: C, 64·2; H, 4·1. $C_{22}H_{16}N_6O_3$ requires C, 64·2; H, 3·9%. [n] Found: N, 25·2; S, 9·4. $C_{14}H_6N_6O_3S$ requires N, 24·7; S, 9·4%. [o] Found: N, 30·2. $C_{14}H_7N_7O_3$ requires N, 30·5%. [p] Found: N, 20·6. $C_{26}H_{15}N_7O_3$ requires N, 20·7%. [q] Found: C, 53·8; H, 4·4; N, 20·3. $C_{24}H_{22}N_8O_7$ requires C, 53·9; H, 4·1; N, 20·9%. [r] Aqueous ethanol.

prepared by adding a slight excess of triethyl phosphate–benzotrifurazan to a solution of the donor, heating the mixture to boiling, and allowing the solution to cool slowly (crystals always needle-shaped unless otherwise stated).

Treatment of an ethanolic solution of the trimethyl phosphate–benzotrifurazan complex with pyrene gave the pyrene complex (m. p. 256°) identical with the compound obtained using the triethyl phosphate complex. Chrysene (chloroform solution) gave an orange-coloured complex, m. p. 219—220° (Found: C, 65·3; H, 2·8; N, 20·2. $C_{24}H_{12}N_6O_3$ requires C, 66·7; H, 2·8; N, 19·5%). The analytical figures suggest that a small quantity of the 2 : 1 complex is also formed. The following compounds failed to form adducts (solvent in parentheses): benzene (light petroleum or an excess of benzene), diphenylmethane (aqueous ethanol or carbon tetrachloride), trimethylamine (light petroleum).

Benzotrifuroxan was recrystallised from trimethyl phosphate. Pale yellow needles of the *complex* separated, m. p. 73—75°. On further heating the melt resolidified, m. p. 195° (m. p. of benzotrifuroxan 195°) (Found: C, 27·9; H, 2·2; P, 8·1, 7·6. $C_9H_9N_6O_{10}P$ requires C, 27·6; H, 2·3; P, 7·9%). Attempted recrystallisation from light petroleum yielded benzotrifuroxan.

Association Constants of the Phosphate Complexes (Table 5).—Association constants were determined at 37° using a Mechrolab vapour pressure osmometer.[32] Carbon tetrachloride was dried ($MgSO_4$) and distilled, benzil was twice recrystallised from ethanol (m. p. 96°), and pyrene recrystallised four times from ethanol (m. p. 152°). The phosphate ester complexes were resublimed and crystallised from light petroleum. The calibration curve for the instrument was determined with benzil as standard. Solutions of the complexes were made up in grade A flasks, the apparent molecular weight determined, and hence the degree of dissociation. For each run one of the syringes on the instrument contained a freshly made standard solution of pyrene and the accuracy of the instrument was checked before and after each set of determinations.

TABLE 5

Dissociation constant of triethyl phosphate–benzotrifurazan complex

Molarity	$M_{\text{app.}}$	α	α^2	$1-\alpha$	$10^2K_{\text{dissn.}}$
0·01610	240·0	0·608	0·370	0·392	1·5
0·02495	256·9	0·503	0·253	0·497	1·3
0·03265	260·4	0·482	0·232	0·518	1·5
0·03987	267·4	0·449	0·202	0·551	1·4
0·05396	271·8	0·420	0·176	0·580	1·6
0·06521	285·7	0·351	0·123	0·649	1·2

Average $K_{\text{dissn.}}$ 1·4 × 10^{-2} mole l.$^{-1}$; $K_{\text{assn.}}$ 71 l. mole^{-1}.

Trimethyl phosphate complex $K_{\text{dissn.}}$ 4·7 × 10^{-3} mole l.$^{-1}$; $K_{\text{assn.}}$ 210 l. mole^{-1}. The apparent molecular weight of the trimethyl phosphate complex was measured in ethyl methyl ketone at one concentration (0·0340M); $M_{\text{app.}} = 221·6$; $K_{\text{assn.}}$ 44. The triethyl phosphate complex was completely dissociated in this solvent. Spectrophotometric association constants were determined by the method previously described.[1,26] Chloroform was washed with water six times, dried ($CaCl_2$), and distilled; dimethylaniline was distilled with 1% of acetic anhydride; benzotrifuroxan was recrystallised from acetic acid–water; benzotrifurazan was twice sublimed; $\lambda_{\text{max.}}$ for the determinations (benzotrifurazan–pyrene) 420; (benzotrifurazan–dimethylaniline) 450; (benzotrifuroxan–dimethylaniline) 410 mμ. The shifts of P=O stretching frequency on complex formation were measured on a Perkin-Elmer 21 spectrometer in carbon tetrachloride solution using the technique[18] described to compensate for uncomplexed ester.

The authors thank Messrs. Albright and Wilson for gifts of phosphite esters and for the determination of the ^{31}P n.m.r. spectra, Dr. A. F. Thomas and Dr. B. Willhalm, Firmenich et Cie, Geneva, for determination of the mass spectra, and the East Suffolk Education Committee for financial assistance (J. M. E.). The manuscript was completed during the tenure of a Visiting Professorship at the University of Oregon (A. S. B.).

[6/1444 *Received, November 14th*, 1966]

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