179. *Naphthaquinone Chemistry. Part IV.*[1] *The Reactions of Phosphines with Vicinal Bisazides.*

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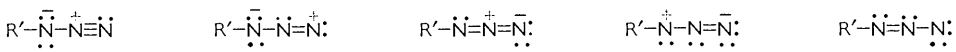
Evidence for a linear structure of phosphazenes ($R'{-}N{=}N{-}N{=}PR_3$) is presented. Novel aminotriazole derivatives are obtained from the reaction of phosphines with 2,3-bisazido-1,4-quinones. A number of new quinone derivatives and their ultraviolet spectra are reported.

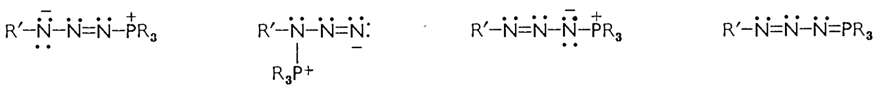
The original studies on the reactions of organic azides with organophosphines were performed by Staudinger and his co-workers,[2] and in recent years renewed interest in this area has been shown by other workers.[3-8] The reaction is perhaps more unusual than one might initially suppose. Phosphines are commonly regarded as nucleophiles, and azides may behave similarly (*e.g.*, in the Schmidt reaction). As one proceeds down a series of diminishing nucleophilic character, $(C_5H_{10}N)_3P > Ph_3P > (MeO)_3P > (PhO_3)P > PCl_3$, the reaction with azides becomes slower, and does not occur at all (at $\leqslant 35°$, as Staudinger showed) with phosphorus trichloride. Similarly, no reaction was detected between azides and weaker nucleophiles such as triphenylarsine, triphenylbismuthine, or 1,1′-thiodipiperidine.

In addition to the two commonly written forms (A) and (C), the azide molecule may enjoy contributions to the resonance hybrid from forms such as (B), (D), and (E), although



(A) (B) (C) (D) (E)

the charge separation in (B) and (D) renders them less probable contributors. Nucleophilic attack by phosphorus (with its electron pair) can occur only upon structures (B), (D), or (E), giving (IB), (ID), or (IE):



(IB) (ID) (IE) (IF)

(IB) and (IE) are merely resonance forms of the equivalent structure (IF) used by Staudinger to depict phosphazenes (which he calls " phosphazides "). Structure (ID) was used[4] without comment, although (IE) was considered[6] recently. We prefer structure (IF) [with contributors (IB) and (IE)] for phosphazenes in general, and will present evidence (*v.i.*) that, at least in the reactions of phosphines with 2,3-bisazido-1,4-quinones, this structure is correct.

Phosphazenes are sometimes isolable and stable, but usually they lose nitrogen forming phosphine imides (II). In the cases studied, Horner and Gross[4] showed that the rate of decomposition of the phosphazene to the imide is faster than its rate of formation. However, stable phosphazenes (IF) * have been reported in which R′ is electron-withdrawing[4,7] or R is electron-releasing,[8] or in which R′ = triphenylmethyl or 9-phenyl-9-fluorenyl and

* Some further examples will be discussed in a subsequent publication.

[1] Part III, Mosby and Silva, *J.*, 1964, 3990.

[2] Staudinger and Meyer, *Helv. Chim. Acta*, 1919, **2**, 635; Staudinger and Hauser, *ibid.*, 1921, **4**, 861.

[3] Horner and Oediger, *Annalen*, 1959, **627**, 142.

[4] Horner and Gross, *Annalen*, 1955, **591**, 117.

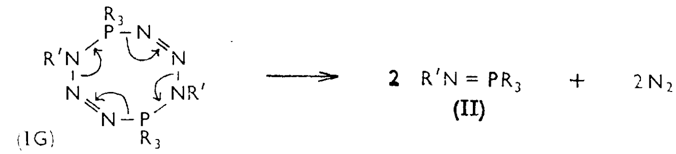
[5] Herring, *J. Org. Chem.*, 1961, **26**, 3998; Baldwin and Washburn, *J. Amer. Chem. Soc.*, 1961, **83**, 4456; Franz and Osuch, *Tetrahedron Letters*, 1963, 841; Cookson and Hughes, *J.*, 1963, 6061; Shaw, Fitzsimmons, and Smith, *Chem. Rev.*, 1962, **62**, 247; Bock and Wiegräbe, *Angew. Chem. Internat. Ed.*, 1962, **1**, 265; 1963, **2**, 484.

[6] Leffler, Honsberg, Tsuno, and Forsblad, *J. Org. Chem.*, 1961, **26**, 4810.

[7] Wittig and Schwarzenbach, *Annalen*, 1961, **650**, 1.

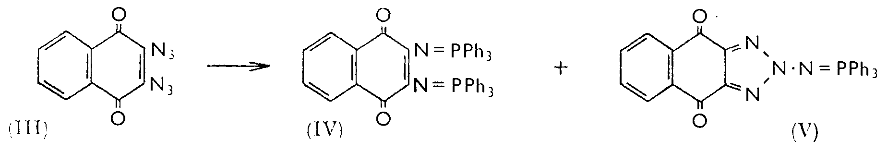
[8] Malz, G.P. 1,104,958; B.P. 919,868.

R = phenyl.[6] The stability of these last two compounds may arise from steric factors. If the decomposition of phosphazenes to phosphine imides is a unimolecular reaction, it could involve the collapse of (ID), or the concerted rearrangement of (IB) by way of a four-membered ring. However, steric considerations would seem unfavourable to this latter mechanism. A bimolecular decomposition could involve the dimerization of two molecules of (IB) to (IG), followed by a concerted collapse to (II). We are studying the decomposition of certain phosphazenes to verify the second-order kinetics reported by Horner.[4]



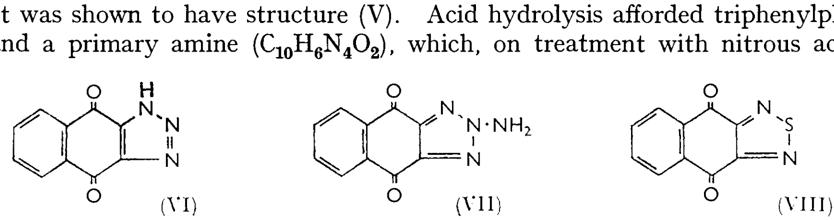
A number of the compounds in Table 1 (Nos. 1, 2, 4, 5, 13, and 14) were obtained from monoazides. However, until recently,[1] only two or three vicinal bisazido-compounds had been reported. We became interested in examining the reactions of this class of compounds with various reagents, because of the possibility of interaction between the azido-groups to give abnormal products.

When two molar equivalents of triphenylphosphine were added to solutions of 2,3-bisazidonaphthaquinone[9] (III), a deep blue colour developed and two products were isolated. The more soluble, deep blue substance was the expected product (IV), as was demonstrated



by its alternative preparation from 2,3-diaminonaphthaquinone and triphenylphosphine dibromide. Compound (IV), in common[4] with other negatively substituted phosphine imides, was highly resistant to hydrolysis. Only one of the two imido-groups was hydrolysed when it was boiled with hydrochloric acid in acetic acid solution, giving compound (XXVII; R = NH_2, R′ = H). However, both this partial hydrolysis product and compound (IV) itself reacted with acetic anhydride and a (necessary) trace of mineral acid to yield the known[10] 2-methyl-1*H*-naphth[2,3-*d*]imidazole-4,9-dione. This substance could also be obtained by heating 2,3-bisacetamidonaphthaquinone in glycol diacetate with a trace of mineral acid.

A number of formulations were considered for the second, golden-yellow product before it was shown to have structure (V). Acid hydrolysis afforded triphenylphosphine oxide and a primary amine ($C_{10}H_6N_4O_2$), which, on treatment with nitrous acid, gave



the known[11] naphtho[2,3-*d*]triazoledione (VI). Also, treatment of the primary amine with triphenylphosphine dibromide reformed the original yellow product, effectively eliminating the possibility of ring rearrangement during the acid hydrolysis. Thus, the

[9] Fries and Ochwat, *Ber.*, 1923, **56**, 1291.
[10] Hoover and Day, *J. Amer. Chem. Soc.*, 1954, **76**, 4148.
[11] Fieser and Martin, *J. Amer. Chem. Soc.*, 1935, **57**, 1844.

amine must be either a 1- or 2-aminonaphtho[2,3-*d*]triazoledione. Two considerations favour the choice of the 2-isomer (VII). First is the evidence provided by the ultraviolet spectra, and second is the probable mechanism of the reaction. Fig. 1 shows the spectrum of compound (VI) presumably the tautomeric form having the proton in the 1-position, as does benzotriazole.[12] Also shown is the spectrum of the above-mentioned primary amine, and that of the known [13] quinone (VIII). The latter two curves are rather similar, and differ from that of compound (VI). On reductive acetylation, quinones (VI)—(VIII) readily afforded the hydroquinone acetates (IX)—(XI), with concomitant *N*-acetylation of (VI) and (VII). The spectra of these three materials are shown in Fig. 2. The resemblance between the curves of compounds (X) and (XI), and the differences between

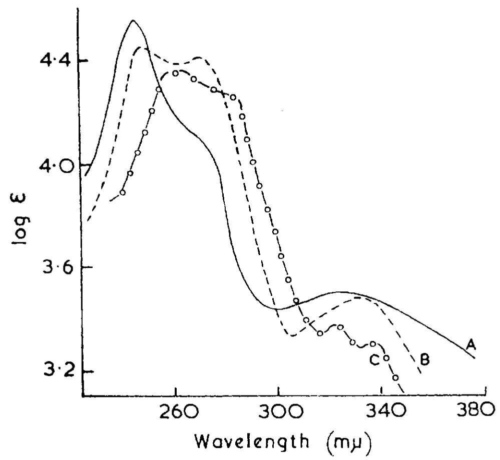


FIG. 1. Ultraviolet spectra of (A), compound (VI); (B), compound (VII); (C), compound (VIII).

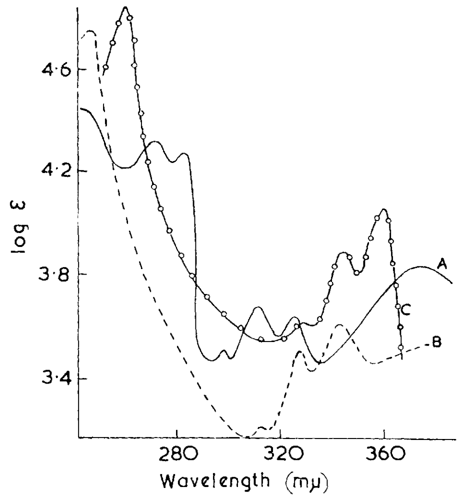
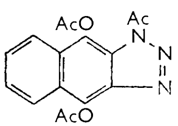


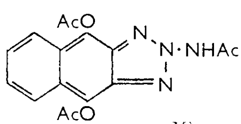
FIG. 2. Ultraviolet spectra of (A), compound (IX); (B), compound (X); (C), compound (XI).

these and the curve of compound (IX) are even more striking than in the case of the quinones (VI)—(VIII) (Fig. 1).

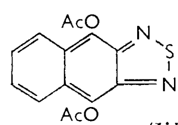
These data suggest that the bond structure of the triazole ring in the primary amine resembles that of (VIII) rather than (VI), and that the amino-group is therefore in the 2-position. Thus, the amine would seem to have structure (VII), and its phosphine imide



(IX)



(X)

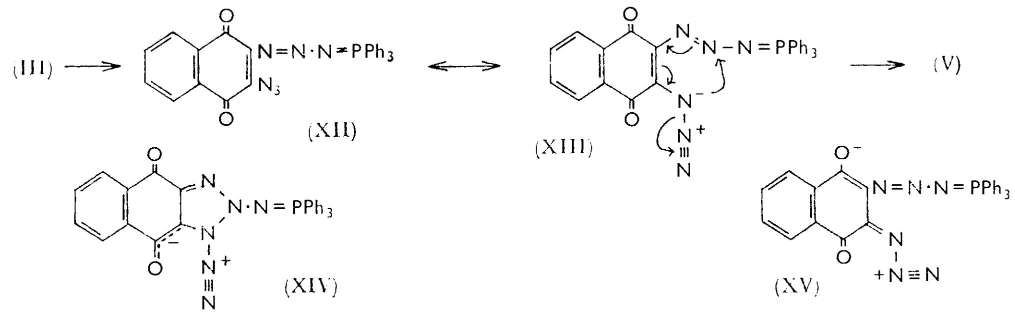


(XI)

precursor structure (V). Further support of structure (V) may be adduced from consideration of its probable mode of formation. Whilst no serious studies of the reaction mechanism have been conducted, the scheme shown seems the most likely. The first step is envisaged as the addition of a molecule of the phosphine to one of the azide groups, producing (XII). Compound (V) may then be formed by the route shown in (XIII), in

[12] Roberts, *J.*, 1963, 5556.
[13] Neeff and Bayer, *Chem. Ber.*, 1957, **90**, 1137.

which (XIV) may be one resonance form of the transition state.* Resonance forms such as (XV), in which delocalization of the nitrogen electron pair occurs, may explain why (V) is accompanied by varying amounts (*v.i.*) of (IV). A similar reasonable mechanism



placing the imido-group in the 1-position of the triazole ring cannot be formulated. It is interesting to note, also, that the intermediate phosphazene [*e.g.*, (XII)] must have the linear structure shown [corresponding to structure (IF)] and cannot have a structure corresponding to (ID), as the latter structure could not produce the final product (V). The other phosphoranylideneaminotriazoles must also be formed by way of linear phosphazene intermediates.

An experiment in which the order of admixture of the reactants was inverted, *i.e.*, a solution of (III) was added to a solution of triphenylphosphine, showed no difference in the nature or ratio of the products formed. However, when a single molar equivalent of triphenylphosphine was added to a solution of (III), a 65% yield of (V) and a 7% yield of 2-azido-3-triphenylphosphoranylideneaminonaphthaquinone (XXVII; $R = N_3$, $R' = H$) resulted. None of the blue compound (IV) was isolated. The monoazide was readily distinguished from the isomeric imido-triazole by its appearance, melting point, and the presence of a strong band at 4·75 μ in the infrared spectrum.

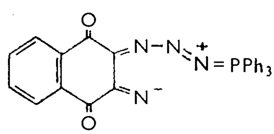
When triphenylphosphine was added to solutions of a group of 5-substituted 2,3-bis-azidonaphthaquinones,[1] the products were of types (IV) and (V), and the ratios of yields, (IV)/(V), were fairly constant. This indicates the relative insignificance of a group in the 5-position of the naphthaquinone molecule. Additional support for the assignment of the triphenylphosphoranylideneamino-group to the 2- rather than the 1-position of the triazole ring may be adduced from these reactions [and also the preparation of compound (XX), *v.i.*]. Were the group in the 1-position, one would expect to obtain, from each reaction, a pair of isomeric triazoles. However, in each case, a single pure compound resulted.

Of considerably more importance appears to be the nature of the solvent in which the reaction is run. The percentage yields of (crude) (IV) and (V), obtained from (III), as the solvent was varied, were as follows:

Solvent	C_6H_6	$CH_3{\cdot}CO_2Et$	PhCl	Pyridine	CH_2Cl_2
Yield of (IV) (%)	43	28	30	14	7
Yield of (V) (%)	36	48	63	68	73

In most cases, any by-products were produced in quantities too small to isolate

* *Note added in proof:* Other forms such as

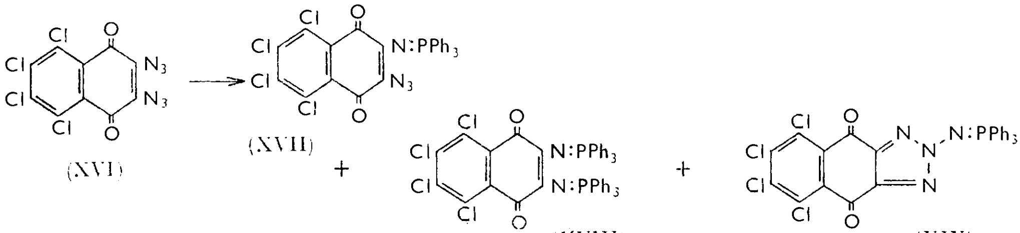


may be involved, analogous to the triazole derivatives recently described by Smith *et al.*[13]

[13a] Smith, Krbechek, and Resemann, *J. Amer. Chem. Soc.*, 1964, **66**, 2025.

and identify. However, in methylene chloride, a 4% yield of 2-amino-3-triphenylphosphoranylideneaminonaphthaquinone (XXVII; R = NH_2, R′ = H) was obtained, and this material was also isolated in 30% yield, together with a 60% yield of (V), when the solvent was dimethylacetamide. Presumably the solvent influences the stability and collpase of the transition state intermediate, *e.g.*, (XIII).

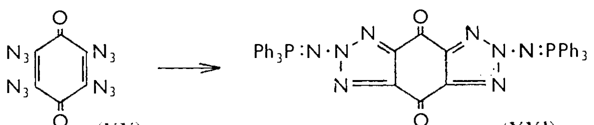
The effect of the solvent was even more pronounced in the reactions of the perchloroquinone [1] (XVI). In toluene, products (XVII) and (XVIII) were obtained in the approximate ratio of 6 : 1; whilst methylene chloride yielded (XVIII) and (XIX) in the approximate ratio of 1 : 4. None of compound (XIX) appeared to form in the first



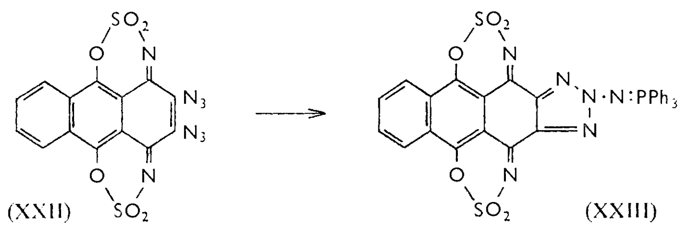
(XVI) (XVII) (XVIII) (XIX)

instance, nor any of compound (XVII) in the latter reaction. It is of interest that (XVII) showed no inclination to isomerize to (XIX) when heated in either chlorobenzene or dimethylacetamide, suggesting that it is not an intermediate in the formation of (XIX).

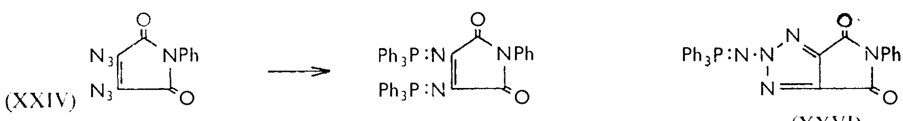
It is evident that the tendency to form the triazole ring is strong, both from the data thus far presented, and from the evidence that, under the conditions employed, the triazole compounds (XXIX) were the only isolable products of the reaction of (III) with tributylphosphine, trispiperidinophosphine, and phenyldipiperidinophosphine. Also, compounds (XX) [14] and (XXII) [15] gave the triazoles (XXI) and (XXIII) in very good yield as the sole identifiable products.



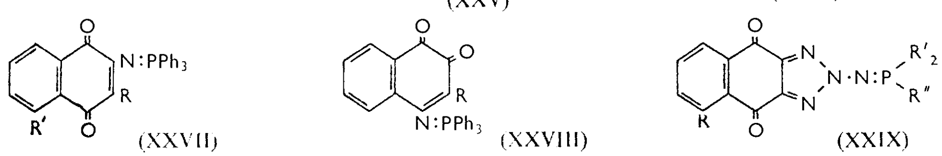
(XX) (XXI)



(XXII) (XXIII)



(XXIV) (XXV) (XXVI)



(XXVII) (XXVIII) (XXIX)

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[14] Korczynski, *Bull. Soc. chim. France*, 1924, **35**, 1196.
[15] Schwechten, Neeff, and Bayer, *Chem. Ber.*, 1957, **90**, 1129.

By contrast, the bisazide (XXIV)[16] afforded chiefly (XXV) at low (~10°) temperatures, but gave almost entirely the triazole (XXVI) at room temperature or above.

It is significant that *o*-bisazidobenzene (prepared by a diazonium displacement reaction upon the known[17] *o*-azidoaniline) reacted with triphenylphosphine in a completely "normal" fashion to give both the mono- and bis-triphenylphosphoranylideneamino-compounds, with no evidence of triazole formation. Thus, it is evident that the adjacent carbonyl (or quinonimine) groups play a key role in the selective formation of triazole compounds by stabilizing the initial adduct, *e.g.*, (XII).

Experimental

Melting points were measured in Pyrex capillaries in a Hershberg melting-point apparatus using Anschütz thermometers. Anlyses of individual elements in a few of the phosphorus compounds are rather unsatisfactory, despite evidence (constant m. p., spectra, etc.) that the compounds are pure. Similar difficulties were encountered by three commercial microanalytical laboratories to which some of these compounds were sent. Under the circumstances, we feel that the analyses reported are about as good as could be obtained on compounds of these types. The ultraviolet spectra were measured with a Cary automatic recording spectrophotometer (model 10).

General Procedure for the Reaction of Bisazides with Phosphines.—The azide was dissolved in a suitable solvent (see Tables) and to this stirred solution was added, either as a solid or in solution, the appropriate phosphine (2·2 ml.). A deep colour invariably developed. With or without an initial period of heating, the solvent was usually evaporated *in vacuo*. In certain cases the naphthotriazoledione (generally less soluble than the di-imide) crystallized out in substantially pure form before the solvent was removed. Chromatography in a solvent such as benzene or chlorobenzene on acid-washed alumina usually gave the pure quinone. The more tighly-held band of the di-imide was conveniently eluted from the column with pyridine. This method was used to prepare the *triphenylphosphoranylideneaminonaphthaquinones* (Table 1) and *naphtho*[2,3-d]*triazolediones* (Table 2). Ultraviolet absorption data are given in Table 3.

N-(4,9-*Diacetoxy*-2H-*naphtho*[2,3-d]*triazol-2-yl*)*triphenylphosphine Imide.*—Standard reductive acetylation of (V) afforded the *diacetoxy-compound*, yellow granules, m. p. 204·5—206·0° (decomp.) (from benzene) (Found: C, 68·9; H, 4·6; N, 10·0; O, 10·7. $C_{32}H_{25}N_4O_4P$ requires C, 68·6; H, 4·6; N, 10·0; O, 11·4%).

2-*Amino*-2H-*naphtho*[2,3-d]*triazole*-4,9-*dione* (VII).—A solution of compound (V) (0·10 g.) in glacial acetic acid (4 ml.), concentrated hydrochloric acid (7 drops), and water (7 drops) was boiled for 5 min., then diluted with water. The *amino-compound*, filtered, washed with methanol, and dried, was a yellow solid (0·41 g., 91%), m. p. 313—314° decomp. (unimproved by crystallization from pyridine), giving a magenta solution when vatted (Found: C, 56·0; H, 2·9; N, 26·0; O, 14·3. $C_{10}H_6N_4O_2$ requires C, 56·0; H, 2·8; N, 26·2; O, 14·9%). The N-*acetyl derivative*, obtained by acetylation of (VII) at room temperature, formed ivory microneedles, m. p. 298—300° (decomp.), $\nu_{max.}$ 5·91 and 5·98 μ (C:O) (Found: C, 56·0; H, 2·95; N, 21·8. $C_{12}H_8N_4O_3$ requires C, 56·3; H, 3·1; N, 21·9%). The NN-*diacetyl derivative*, obtained by boiling either the amine (VII) or the imide (V) with acetic anhydride and a drop of sulphuric acid, was an off-white solid, m. p. ~250—260° (decomp.), $\nu_{max.}$ 5·70 and 5·90 μ (C:O) (Found: C, 56·6; H, 3·75; N, 18·9. $C_{14}H_{10}N_4O_4$ requires C, 56·4; H, 3·35; N, 18·8%).

1H-*Naphtho*[2,3-d]*triazole*-4,9-*dione* (VI).—Solution of compound (VII) in nitrosylsulphuric acid was accompanied by gas evolution, and, after dilution with water, a solid was obtained. The infrared spectrum and m. p. [243·5—245·5° (decomp.)] were identical with those of an authentic specimen[11] of the triazole obtained by treating 2,3-diaminonaphthoquinone in acetic acid solution with sodium nitrite. The N-*acetyl derivative*, obtained by treating the triazole (VI) in acetic anhydride with a drop of pyridine, formed pale beige needles, m. p. 190—191° (decomp.), $\nu_{max.}$ 5·60 and 5·92 μ (C:O) (Found: C, 59·6; H, 2·95; N, 17·4; O, 19·9. $C_{12}H_7N_3O_3$ requires C, 59·6; H, 2·9; N, 17·4; O, 19·9%).

1-*Acetyl*-1H-*naphtho*[2,3-d]*triazole*-4,9-*diol Diacetate* (IX).—Reductive acetylation of compound (VI) gave this *diacetate*, yellow needles, m. p. 171·0—172·0° (from methylcyclohexane).

[16] Mustafa, Zayed, and Khatab, *J. Amer. Chem. Soc.*, 1956, **78**, 145; Awad, Omran, and Nagieb, *Tetrahedron*, 1963, **19**, 1591.
[17] Smith, Hall, and Kan, *J. Amer. Chem. Soc.*, 1962, **84**, 485.

TABLE 1.

Triphenylphosphoranylideneaminonaphthaquinones.

No.	Compound	Colour	Yield (%) Crude	Pure	Reaction solvent	M. p.	Cryst. from
1	(XXVII; R = R′ = H) [a]	Garnet red	99	85	CH_3CO_2Et	176·5—177°	Ethyl acetate–cyclohexane
2	(XXVII; R = OMe, R′ = H) [a,b]	Red-brown	—	56	C_6H_5Me	~185	Ethyl acetate–light petroleum
3	(XXVII; R = NH_2, R′ = H) [c]	Blue	—	~50	—	188—190	Cyclohexane
4	(XXVII; R = NHAc, R′ = H) [d]	Red	—	5	CH_2Cl_2	173—174	Nitroethane
5	(XXVII; R = NAc_2, R′ = H)	Orange	95	66	CH_2Cl_2	208—208·6	Ethyl acetate
6	(XXVII; R = N_3, R′ = H) [e]	Purple	—	7	CH_2Cl_2	122·5—123·5	
7	(IV) [f]	Blue	48	33	C_6H_6	244—245	Pyridine
8	(XXVII; R = N:PPh_3, R′ = NO_2) [g]	Green	14	3	C_6H_6	287—289	Nitromethane
9	(XXVII; R = N:PPh_3, R′ = NH_2) [h]	Green	9	2	CH_2Cl_2	243—245	Nitromethane
10	(XXVII; R = N:PPh_3, R′ = NHAc) [i]	Green	16	4	CH_2Cl_2	284—286	Chlorobenzene
11	(XVII) [j]	Yellow	46	35	C_6H_5Me	131·5—133·5	Chlorobenzene
12	(XVIII)	Red-brown	—	10	C_6H_5Me	251·5—252·5	Benzene
13	(XXVIII; R = H) [k]	Red	80	60	CH_2Cl_2	259—260	Ethyl acetate
14	(XXVIII; R = Cl) [l]	Maroon	75	40	CH_2Cl_2	220—221	Ethyl acetate

No.	Found (%) C	H	N	P	O	Formula	Required (%) C	H	N	P	O
1	77·6	4·4	3·45	6·9	7·05	$C_{28}H_{20}NO_2P$	77·6	4·65	3·25	7·15	7·4
2	74·8	4·85	3·0	6·1	—	$C_{29}H_{22}NO_3P$	75·2	4·75	3·05	6·5	—
3	75·8	5·35	5·65	6·2	—	$C_{28}H_{21}N_2O_2P$	75·0	4·7	6·25	6·9	—
4	73·4	5·05	6·0	6·0	—	$C_{30}H_{23}N_2O_3P$	73·5	4·7	5·7	6·35	—
5	72·2	5·4	5·45	5·7	12·2	$C_{32}H_{25}N_2O_4P$	72·2	4·7	5·25	5·85	12·0
6	71·6	4·55	6·1	10·8	6·25	$C_{28}H_{19}N_4O_2P$	71·0	4·0	6·75	11·8	6·55
7	76·8	5·15	3·15	8·0	—	$C_{46}H_{34}N_2O_2P_2$	77·9	4·8	3·95	8·75	—
8	73·0	4·45	5·9	8·25	8·55	$C_{46}H_{33}N_3O_4P_2$	73·3	4·4	5·6	8·25	8·5
9	—	—	—	7·7	—	$C_{46}H_{35}N_3O_2P_2$	—	—	—	8·6	—
10	71·8	5·05	5·1	7·95	—	$C_{48}H_{37}N_3O_3P_2$	73·3	4·85	5·5	8·1	—
11	56·1	2·75	7·7	5·2	—	$C_{28}H_{15}Cl_4N_4O_2P$ [m]	54·9	2·45	9·15	5·05	—
12	65·6	3·75	2·9	6·4	—	$C_{46}H_{30}Cl_4N_2O_2P_2$ [n]	65·2	3·55	3·3	7·2	—
13	77·5	4·6	3·15	6·8	—	$C_{28}H_{20}NO_2P$	77·6	4·65	3·25	7·15	—
14	72·0	3·8	3·1	6·4	7·05	$C_{28}H_{19}ClNO_2P$	71·9	4·05	3·0	6·65	6·85

[a] Purified by chromatography on Merck's acid-washed alumina. [b] Melted erratically, even after recrystallization. [c] Obtained by acid hydrolysis of compound (IV). [d] At least two other products. were formed. [e] Isolated as the minor product from the 1 : 1 reaction of the azide and the phosphine. [f] Mixture of (IV) and (V) separated by chromatography on acid-washed alumina, (IV) being eluted last with pyridine. [g] Minor, more soluble product. Major product was the triazole (XXIX; R = NO_2, R′ = R″ = Ph). [h] Minor, more soluble product, purified by chromatography in benzene on Fisher's alumina and elution with ethyl acetate. Major product was the triazole (XXIX; R = NH_2, R′ = R″ = Ph). [i] Minor, more soluble product. Major product was the triazole (XXIX; R = NHAc, R′ = R″ = Ph). [j] Major product from the bisazide when toluene was the solvent. Compound (XVIII) was the minor, more soluble product. [k] Purified by chromatography in benzene on acid-washed alumina and elution with ethyl acetate. [l] Purified by chromatography in benzene on Fisher's alumina and elution with ethyl acetate. [m] Found: Cl, 24·3; required Cl, 23·2%. [n] Found: Cl, 16·4; requires Cl, 16·8%).

The infrared spectrum exhibited no absorption in the 3 μ region, but showed carbonyl bands at 5·70 and 5·80 μ (Found: C, 59·0; H, 4·15; N, 12·8; O, 24·3. $C_{16}H_{13}N_3O_5$ requires C, 58·8; H, 4·0; N, 12·9; O, 24·4%).

2-*Acetylamino*-2H-*naphtho*[2,3-d]*triazole*-4,9-*diol Diacetate* (X).—Reductive acetylation of the amine (VII) gave this *diacetate*, yellow microcrystals, m. p. 229·5—231·5° (decomp.) (from ethyl acetate) $\nu_{max.}$ 5·68 and 5·75 (shoulder) μ (C:O) (Found: C, 56·1; H, 4·25; N, 16·3; O, 23·4. $C_{16}H_{14}N_4O_5$ requires C, 56·2; H, 4·1; N, 16·4; O, 23·4%).

TABLE 2.

Naphtho[2,3-*d*]triazolediones.

No.	Compound	Colour	Yield (%) Crude	Yield (%) Pure	Reaction solvent	M. p.	Cryst. from
1	(XXIX; R = H, R′ = R″ = Ph)	Orange	73	64	CH_2Cl_2	252—253°	Nitromethane
2	(XXIX; R = NO_2, R′ = R″ = Ph)	Red	69	53	C_6H_6	248·5—249·5	Nitromethane
3	(XXIX; R = NH_2, R′ = R″ = Ph)	Red-orange	70	37	CH_2Cl_2	253·5—254·5	Nitromethane
4	(XXIX; R = NHAc, R′ = R″ = Ph)	Red	84	57	CH_2Cl_2	264·5—265	Nitromethane
5	(XIX) [b]	Scarlet	71	51	CH_2Cl_2	294—295	Chlorobenzene
6	(XXIX; R = H, R′ = R″ = Bu^n) [c]	Dark red	30	21	CH_2Cl_2	76·5—78	Hexane
7	(XXIX; R = H, R′ = piperidyl, R″ = Ph)	Orange	82	50	CH_2Cl_2	212·5—213·5	Benzene then ethyl acetate
8	(XXIX; R = H, R′ = R″ = piperidyl) [d]	Red	85	49	CH_2Cl_2	169·5—170·2	Methylcyclohexane

No.	Found (%) C	H	N	P	O	Formula	Required (%) C	H	N	P	O
1	70·2	4·1	11·8	6·55	6·7	$C_{28}H_{19}N_4O_2P$	70·9	4·0	11·8	6·55	6·75
2	64·4	3·55	13·6	5·9	12·3	$C_{28}H_{18}N_5O_4P$	64·8	3·45	13·5	6·0	12·3
3	67·5	4·35	13·9	6·1	—	$C_{28}H_{20}N_5O_2P$	68·7	4·1	14·3	6·35	—
4	67·2	4·25	12·2	5·85	—	$C_{30}H_{22}N_5O_3P$	67·8	4·15	13·2	5·85	—
5	54·7	2·55	9·25	4·95	—	$C_{28}H_{15}Cl_4N_4O_2P$ [e]	54·9	2·45	9·15	5·05	—
6	65·7	7·3	13·8	7·45	—	$C_{22}H_{31}N_4O_2P$	63·8	7·5	13·5	7·5	—
7	64·0	6·05	17·2	6·4	—	$C_{26}H_{29}N_6O_2P$	64·0	5·95	17·2	6·35	—
8	60·9	8·0	20·1	6·65	—	$C_{25}H_{34}N_7O_2P$	60·7	6·85	19·8	6·25	—

[a] Yield varied with solvent, highest in CH_2Cl_2. Product purified by chromatography in chlorobenzene on acid-washed alumina. [b] Purified by chromatography on acid-washed alumina and elution with methylene chloride–ethyl acetate (95 : 5). [c] Purified by chromatography in benzene on Fisher's alumina. [d] Purified by chromatography on acid-washed alumina. [e] Found: Cl, 22·7; requires Cl, 23·2%.

Naphtho[2,3-c][1,2,5]*thiadiazole*-4,9-*diol Diacetate* (XI).—Reductive acetylation of the quinone [13] gave the *diacetate*, orange prisms, m. p. 230·5—231·7° (from nitromethane), $\nu_{max.}$ 5·70 μ (ester) (Found: C, 55·7; H, 3·2; N, 8·95; O, 20·75; S, 10·7. $C_{14}H_{10}N_2O_4S$ requires C, 55·6; H, 3·3; N, 9·25; O, 21·2; S, 10·6%).

2,4,6,8-*Tetrahydro*-4,8-*dioxo*-2,6-*bis*(*triphenylphosphoranylideneamino*)*benzo*[1,2-d:4,5-d′]*bistriazole* (XXI).—To a stirred solution of chloranil (2·46 g.) in dimethylformamide (80 ml.), kept below 10° in an ice-bath, was added dropwise a solution of sodium azide (3·0 g.) in water (10 ml.) and dimethylformamide (20 ml.). The mixture was stirred for 1 hr., diluted with ice–water (400 ml.), and filtered. While still damp, the brown filter-cake was dissolved in methylene chloride and the resulting purple solution was dried ($MgSO_4$). To this stirred solution was added, in portions, triphenylphosphine (10·48 g.). Nitrogen was evolved vigorously, the solution became warm, and the colour changed from purple to blood-red to green. The solvent was removed *in vacuo*, and the solid was washed with a little methylene chloride, giving the light brown *product* (6·24 g., 83%) m. p. >360° (Found: C, 68·2; H, 4·35; N, 15·1; O, 4·2; P, 8·25. $C_{42}H_{30}N_8O_2P_2$ requires C, 68·1; H, 4·05; N, 15·1; O, 4·35; P, 8·35%).

2,6-*Diamino*-2H,6H-*benzo*[1,2-d:4,5-d′]*bistriazole*-4,8-*dione*.—A slurry of compound (XXI) (5·75 g.) in boiling glacial acetic acid (35 ml.) was treated with concentrated hydrochloric acid (2 ml.) and water (3 ml.). After 10 min. the mixture was cooled and filtered, and the solid was washed well with water, then with methanol, and dried, giving the ochre *diamine* (1·39 g., 81%), m. p. >360° (Found: C, 32·2; H, 2·0; N, 50·5. $C_6H_4N_8O_2$ requires C, 32·7; H, 1·8; N, 50·9%). It dissolved in aqueous alkali giving a yellow colour, and gave a purple vat solution, aeration of which discharged the colour and precipitated a blue solid, which slowly redissolved to a yellow solution upon continued aeration.

4,5-*Bisazidoanthra*[1,9-de:4,10-d′e′]*bis*[1,2,3]*oxathiazine* 2,2,7,7-*Tetroxide* (XXII).—A slurry of the dichloro-tetroxide [15] (2·31 g.) and sodium azide (1·0 g.) in dry acetonitrile (25 ml.) was stirred and boiled under reflux for 1 hr., cooled to 25°, filtered, and the solid was washed with

TABLE 3.

Ultraviolet absorption data.

Compound	Solvent	$\lambda_{max.}$ (mμ) (ε)
(XXVII; R = R′ = H)	Ethanol	280 (31,950)
(XXVII; R = OMe, R′ = H)	Cyclohexane	285 (29,010)
(XXVII; R = NH_2, R′ = H)	Cyclohexane	262 (24,780); 303 * (17,440); 315 (18,320); 350 * (6930); 582 (2620)
(XXVII; R = NHAc, R′ = H)	Chloroform	290 (28,800)
(XXVII; R = NAc_2, R′ = H)	Chloroform	282 (31,300)
(IV)	Chloroform	269 * (22,600); 273 (22,900); 314 (16,560); 367 (8760)
(XXVII; R = N:PPh_3, R′ = NO_2)	Chloroform	267—275 * (31,200)
(XXVII; R = N:PPh_3, R′ = NHAc)	Chloroform	261 (29,600); 274 * (22,000); 360 (20,500)
(XVII)	Chloroform	263 * (9480); 267 (9680); 274 (10,730); 286 (14,860); 298 (20,900); 319 (1420); 334 (1930); 347 (1760)
(XVIII)	Chloroform	252 (41,800); 305 (28,550); 318 (25,000)
(XXVIII; R = H)	Chloroform	278 (20,300); 340 * (6050)
(XXVIII; R = Cl)	Chloroform	282 (29,000); 339 * (5580)
(XXIX; R = H, R′ = R″ = Ph)	Chloroform	270 * (15,180); 276 (16,380); 318 (28,300)
(XXIX; R = NO_2, R′ = R″ = Ph)	Chloroform	269 (13,730); 276 (14,100); 322 (27,900)
(XXIX; R = NH_2, R′ = R″ = Ph)	Chloroform	269 * (17,300); 278 * (19,250); 306 (25,550); 321 (24,850)
(XXIX; R = NHAc, R′ = R″ = Ph)	Chloroform	269 * (21,800); 276 (22,350); 321 (32,200)
(XIX)	Chloroform	261 (31,400); 335 (36,850)
(XXIX; R = H, R′ = piperidyl, R″ = Ph)	Chloroform	269 * (16,480); 276 * (17,520); 317 (33,810)
(XXIX; R = H, R′ = R″ = piperidyl)	Chloroform	317 (32,000)
(VI)	Ethanol	245 (37,100); 265 * (14,600); 327 (3150)
(VII)	Ethanol	247 (28,700); 270 (25,790); 331 (2980)
(VIII)	Cyclohexane	257 * (22,480); 263 (23,170); 284 * (18,440); 322 (2392); 337 (2024)
(IX)	Chloroform	245 (27,750); 272 (21,350); 282 (19,300); 298 (3280); 312 (4910); 326 (4480); 374 (7120)
(X)	Chloroform	246 (56,600); 313 (1645); 327 (3190); 343 (4140)
(XI)	Chloroform	259 (68,000); 329 (4260); 344 (8060); 360 (11,500)
(XXI)	Chloroform	267 (22,550); 337 (52,250); 274 * (21,500)
(XXIII)	Chloroform	256—264 * (26,250); 270 * (27,300); 278 * (29,250); 290 (32,800); 369 (28,000)
(XXV)	Chloroform	Does not appear to obey Beer's law
(XXVI)	Chloroform	270 * (15,150); 276 (17,150); 303 (23,500)
(VI; 1-Ac for 1-H)	Chloroform	245 (37,700); 266 * (18,850); 329 (3475)
(VII; NHAc for NH_2)	Chloroform	252 (17,620); 328 (1565)
(VII; NAc_2 for NH_2)	Chloroform	257 (38,000); 328 (3370)
(X; N:PPh_3 for NHAc)	Chloroform	289 (32,600); 299 (32,750); 363 (34,100)

* Inflection.

water and with methanol and dried, giving the dark red *product* (2·82 g.) (Found: C, 39·3; H, 1·15; N, 23·6; O, 21·0; S, 14·0. $C_{14}H_4N_8S_2O_6$ requires C, 37·9; H, 0·9; N, 25·2; O, 21·6; S, 14·4%).

5-*Triphenylphosphoranylideneamino*-5H-*triazolo*[4′,5′:2,3]*anthra*[1,9-de:4,10-d′e′]*bis*[1,2,3]-*oxathiazine* 2,2,8,8-*Tetroxide* (XXIII).—Triphenylphosphine (2·00 g.) was added portionwise with stirring to a solution of compound (XXII) (2·60 g.) in 1,2-dichloroethane (200 ml.). The dark solution was concentrated to about 75 ml., whereupon it deposited the brown *imide* (2·96 g.), m. p. 275—277° (decomp.). Two crystallizations from chlorobenzene gave brown needles, m. p. 312—314° (decomp.). The m. p. appeared to depend to some extent upon the temperature of the bath when the sample was inserted (Found: C, 57·5; H, 3·0; N, 11·4; P, 4·05. $C_{32}H_{19}N_6O_6S_2P$ requires C, 56·7; H, 2·8; N, 12·4; P, 4·55%).

5-*Amino*-5H-*triazolo*[4′,5′:2,3]*anthra*[1,9-de:4,10-d′e′]*bis*[1,2,3]*oxathiazine* 2,2,8,8-*Tetroxide*.—A slurry of compound (XXIII) (0·92 g.) in glacial acetic acid (12 ml.) and concentrated hydrochloric acid (2·0 ml.) was boiled for a few minutes until the initial puce colour changed to orange, cooled, filtered, and the solid washed well with methanol and dried, giving the dull orange *amine* (0·45 g.). Crystallization from nitromethane gave light brown crystals (0·26 g.), decomposing above 300° (Found: C, 40·1; H, 1·65; N, 20·3; O, 23·1; S, 15·2. $C_{14}H_6N_6O_6S_2$ requires C, 40·2; H, 1·45; N, 20·1; O, 22·9; S, 15·3%).

o-*Bisazidobenzene.*—A solution of *o*-azidoaniline [17] (5·50 g.) in water (150 ml.) and concentrated hydrochloric acid (20 ml.) was diazotized at 0° by adding an aqueous solution of sodium nitrite (3·0 g.). To this stirred diazo-solution, kept at 0°, was added dropwise an aqueous solution of sodium azide (2·90 g.). The flocculent precipitate was filtered and washed with cold water. The *bisazide* melted at ~23—25° to a tan oil. It was analysed and used without further purification (Found: C, 45·1; H, 2·75; N, 52·4. $C_6H_4N_6$ requires C, 45·0; H, 2·5; N, 52·5%).

N-o-*Azidophenyltriphenylphosphine Imide.*—This *product* was isoated (74% together with 22·5% of the di-imide) when *o*-bisazidobenzene was reacted in methylene chloride with triphenylphosphine. Crystallization from methanol and then from cyclohexane gave greenish-tan flat needles, m. p. 113·0—114·0° (decomp.) (Found: C, 73·1; H, 4·75; N, 14·0; P, 7·85. $C_{24}H_{19}N_4P$ requires C, 73·1; H, 4·75; N, 14·2; P, 7·9%).

o-*Bis(triphenylphosphoranylideneamino)benzene.*—Triphenylphosphine (15·32 g.) was added portionwise to a solution of *o*-bisazidobenzene (4·67 g.) in dry toluene (80 ml.). When the gas evolution had subsided, the mixture was stirred and boiled under reflux for 20 min., cooled, and filtered. The yellow *di-imide* (14·83 g., 81%), m. p. 247·8—249·6° (lit.,[3] 206°), was not purified further as it appeared to decompose upon recrystallization (Found: C, 80·5; H, 5·25; N, 4·5; P, 9·7. $C_{42}H_{34}N_2P_2$ requires C, 80·2; H, 5·4; N, 4·45; P, 9·9%).

N-*Phenylbis(triphenylphosphoranylideneamino)maleimide* (XXV).—A solution of triphenylphosphine (2·63 g.) in methylene chloride (20 ml.) was added dropwise to a chilled (ice-bath) solution of *N*-phenylbisazidomaleimide [16] (1·27 g.) in methylene chloride (30 ml.). The solvent was removed and the residue was washed with methanol and then with benzene, giving the *product* (1·77 g.) red prisms, with an instantaneous m. p. of 257—258° (from benzene) (Found: C, 76·0; H, 4·95; N, 5·8; O,4·15. $C_{46}H_{35}N_3O_2P_2$ requires C, 76·4; H, 4·85; N, 5·8; O, 4·4%).

N-*Phenyl*-2-(*triphenylphosphoranylideneamino*)-2H-1,2,3-*triazoledicarboximide* (XXVI).—A solution of *N*-phenylbisazidomaleimide [16] (2·00 g.) in methylene chloride (30 ml.) was stirred at reflux, while a solution of triphenylphosphine (4·20 g.) in methylene chloride (20 ml.) was added slowly. The solution turned deep red and nitrogen was evolved. The solvent was removed and the orange-brown residue was washed with benzene, giving the *triazole* (1·93 g.), m. p. 213—214·5° (from nitromethane) (Found: C, 68·1; H, 4·1; N, 13·95; O, 6·4; P, 5·8. $C_{28}H_{20}N_5O_2P$ requires C, 68·8; H, 4·1; N, 14·3; O, 6·55; P, 6·35%).

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