493. *Naphthaquinone Chemistry. Part V.*[1] *The Reactions of Azidonaphthaquinones with Phosphite Esters*

By W. L. MOSBY and M. L. SILVA

The reactions of 2,3-bisazido-1,4-naphthaquinone and related azides with phosphite esters are discussed. A novel mode of decomposition of the azide group is considered.

IN Part IV [1] we discussed the reactions of certain vicinal bisazides with phosphines, and we now report on their reactions with phosphite esters (cf. Kabachnik and his co-workers [2-7]). No examples of the phosphazene intermediates (I) have been isolated, although they are undoubtedly formed on the way to (II).

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[1] Part IV, W. L. Mosby and M. L. Silva, *J.*, 1965, 1003.

[2] M. I. Kabachnik and V. A. Gilyarov *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1956, 790.

[3] V. A. Gilyarov, *Khim. i Primenenie Fosfororgan. Soedin., Akad. Nauk S.S.S.R. Kazansk. Filial, Tr.* 1 *Konf.*, 1955, 275 (*Chem. Abs.*, 1958, **52**, 243).

[4] M. I. Kabachnik, V. A. Gilyarov, and E. N. Tsvetkov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1959, 2135.

[5] M. I. Kabachnik and V. A. Gilyarov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1961, 816.

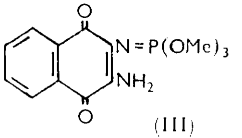
[6] M. I. Kabachnik, V. A. Gilyarov, and E. M. Popov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1961, 1022.

[7] M. I. Kabachnik, V. A. Gilyarov, and E. M. Popov, *Zhur. obshchei Khim.*, 1962, **32**, 1598.

$$(RO)_3P + N_3R' \longrightarrow [(RO)_3P{=}N{-}N{=}N{-}R'] \xrightarrow{-N_2} (RO)_3P{=}N{-}R'$$
$$\qquad\qquad\qquad\qquad\text{(I)}\qquad\qquad\qquad\qquad\text{(II)}$$

It is apparent that, in going down a series of diminishing nucleophilicity: $(R_2N)_3P > R_3P > Ar_3P > (RO)_3P$, we are reaching the lower limits of reactivity in the case of the phosphite esters. Many of the reactions which we attempted between azides and trimethyl phosphite gave intractable oily mixtures. The reaction of 2,3-bisazidonaphthaquinone with dimethyl phenylphosphonite, $PhP(OMe)_2$, gave evidence of a colour change and gas evolution, but the only isolable product was 2-amino-3-azidonaphthaquinone (in very low yield). A similar reaction with triphenyl phosphite gave no visible evidence of reaction, and only traces of unidentified materials could be isolated. Similar results were obtained using $PhP(SPh)_2$, while $P(SEt)_3$, $P(SPh)_3$ or $HOP(OEt)_2$ gave no reaction at all.

When 2,3-bisazidonaphthaquinone was reacted with two molar equivalents of trimethyl phosphite, only traces of product (III) and unidentified materials were isolated.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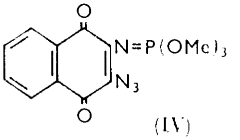
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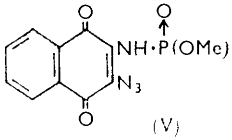
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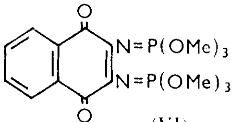
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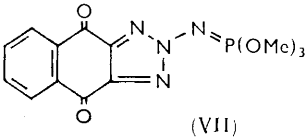
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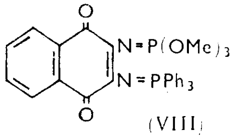
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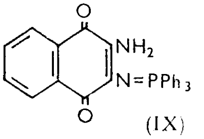
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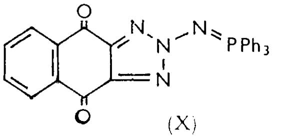
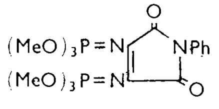

(X)


(XI)

The use of triethyl phosphite gave the ethyl homologue of (III) in very low yield, together with traces of the ethyl homologue of (V) and of 2,3-diaminonaphthaquinone. Perchloro-2,3-bisazidonaphthoquinone,[8] behaved similarly. It is of interest that no evidence could be found for the formation of compounds (VI) and (VII), analogues of the products customarily formed [1] from phosphines (or aminophosphines) and the bisazide. Also, whilst compound (IV) did not react with a second mole of trimethyl phosphite to give (VI), it reacted readily with triphenylphosphine to give (VIII) and (IX),[1] together with traces of (X).[2] Curiously, however, bisazidomaleanil afforded, as the sole product isolated, a substance evidently of structure (XI), possibly as a result of the stabilisation offered by a variety of forms such as (XIa).

By contrast, the reaction of bisazidonaphthaquinone with a single equivalent of trimethyl phosphite gave compound (IV) in high yield. Similar results were obtained with perchlorobisazidonaphthaquinone. Acid hydrolysis of (IV) readily cleaved one of the methyl groups, affording (V). The infrared spectrum (a small sharp band at 3·18 μ) supports the tautomeric structure shown (with the proton on nitrogen rather than oxygen), as Kabachnik *et al.* have reported [4,6] for related products. A similar hydrolysis attempted on compound (VIII), gave only compound (IX). Alkaline hydrolysis of compound (V) readily afforded a good yield of 2-amino-3-azidonaphthaquinone.

When compound (V) reacted with one equivalent of trimethyl phosphite, a 33% yield of compound (XII) (identified by comparison with an authentic [9] specimen) was obtained as the sole recognisable product. One can postulate mechanisms for the formation of

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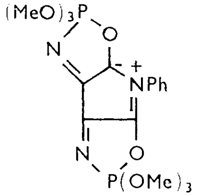
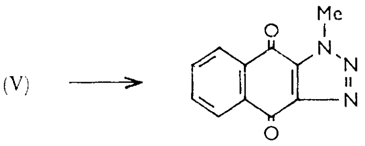
[8] W. L. Mosby and M. L. Silva, *J.*, 1964, 3990.

[9] L. F. Fieser and E. L. Martin, *J. Amer. Chem. Soc.*, 1935, **57**, 1844.

(XII), but we have little evidence to support them, and no information as to the fate of the phosphorus moieties eliminated.



(XIa)



(XII)

Further anomalous behaviour of (V) was encountered when it was treated with triphenylphosphine. A 60—70% yield was obtained of a pale yellow substance for which microanalyses suggested the formula $C_{28}H_{21}N_4O_2P$. It was stable, could be crystallised repeatedly from different solvents, and it even could be vacuum sublimed without change. Infrared and nuclear magnetic resonance spectra confirmed the presence of two NH groups. The ultraviolet spectrum closely resembled that [1] of triazolonaphthaquinone, and indeed, acidic or basic hydrolysis of the substance yielded the latter compound. Treatment with acetic anhydride yielded *N*-acetyltriazolonaphthaquinone, and by using benzoyl chloride in pyridine, we were able to isolate *N*-triphenylphosphoranylidenebenzamide.[10] Methylation with either diazomethane or with methyl sulphate gave compound (XII). Professor Fausto Ramirez suggested that the substance might actually be a molecular complex of triazolonaphthaquinone and triphenylphosphoranylidenimine, analogous to the stable phenol–phosphine oxide complexes which he had encountered.[11] The accuracy of this hypothesis was demonstrated by a synthesis of the same complex from the two components. The unusual stability of this complex is probably related to its salt-like character, as a similar complex formed from triazolonaphthaquinone and triphenylphosphine oxide (much more weakly basic than the imine) dissociates when recrystallised from cylohexane.

The conversion of compound (V) into triazolonaphthaquinone and its *N*-methyl derivative (XII) presents a most interesting possibility. In each case, the azido-group appears to have suffered the loss of a *single* nitrogen atom. As far as we are aware, all reported scissions of azides involve the loss of two nitrogen atoms. The isolation of *N*-triphenylphosphoranylidenebenzamide further suggests that it is specifically the terminal nitrogen of the azido-group which is eliminated.

EXPERIMENTAL

Melting points were measured in Pyrex capillaries in a Hershberg melting-point apparatus, using Anschütz thermometers.

Trimethyl 3-*Azido*-1,4-*dihydro*-1,4-*dioxonaphthalene*-2-*phosphorimidate* (IV).—To a solution of 2,3-bisazidonaphthaquinone (2·40 g.) in methylene chloride (200 ml.) was added a solution of redistilled trimethyl phosphite (1·35 g.) in methylene chloride (5—10 ml.). The magenta solution was stirred for 1 hr. at room temperature, and the solvent removed *in vacuo*. The resulting solid was washed well with cyclohexane and dried, giving 2·91 g. (87%) of red product. Crystallisation from cyclohexane gave the *triester*, m. p. 99·5—100·5° (decomp.) (Found: C, 46·3; H, 4·55; N, 16·4; O, 23·4; P, 9·15. $C_{13}H_{13}N_4O_5P$ requires C, 46·5; H, 3·85; N, 16·7; O, 23·8; P, 9·25%).

Trimethyl 3-*Azido*-5,6,7,8-*tetrachloro*-1,4-*dihydro*-1,4-*dioxonaphthalene*-2-*phosphorimidate*.—A slurry of 2,3-bisazido-5,6,7,8-tetrachloronaphthaquinone [8] (7·17 g.) in methylene chloride (250 ml.) was stirred and heated under reflux, while a solution of trimethyl phosphite (2·57 g.) in a little methylene chloride was added dropwise during 1 hr. The mixture was stirred and boiled for 1 hr., then filtered hot from unchanged bisazide (1·10 g.). Concentration of the dark red-brown filtrate gave the red-brown *product* (7·27 g.), m. p. 109—113° (decomp.). It

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[10] H. Staudinger and E. Hauser, *Helv. Chim. Acta*, 1921, **4**, 861.

[11] F. Ramirez and S. Dershowitz, *J. Amer. Chem. Soc.*, 1956, **78**, 5614.

could not be crystallised satisfactorily (Found: C, 31·4; H, 1·85; Cl, 30·5; N, 10·0; P, 6·8. $C_{13}H_9Cl_4N_4O_5P$ requires C, 32·9; H, 1·9; Cl, 30·0; N, 11·9; P, 6·55%).

Trimethyl 3-*Amino*-1,4-*dihydro*-1,4-*dioxonaphthalene*-2-*phosphorimidate* (III).—To a solution of 2,3-bisazidonaphthaquinone (2·40 g.) in methylene chloride (200 ml.) was added trimethyl phosphite (2·73 g.) and the mixture refluxed for 1 hr. The solvent was removed *in vacuo*, and the purplish-red residue was taken up in a small volume of benzene and put on to a column of acid-washed alumina (Merck). Development with benzene gave several unidentified gummy fractions, and finally a red-brown component was eluted. Trituration with benzene gave the brick-red *product* (0·60 g.), m. p. 158·5—161° (decomp.) (Found: C, 49·7; H, 5·1; N, 9·1; P, 10·1. $C_{13}H_{15}N_2O_5P$ requires C, 50·4; H, 4·85; N, 9·05; P, 10·0%).

Reaction of 2,3-*Bisazidonaphthaquinone with Two Equivalents of Triethyl Phosphite*.—Triethyl phosphite (2·80 g.) was added to a solution of the bisazide (2·00 g.) in benzene (300 ml.) and the mixture was boiled down to a small volume and put on to a column of acid-washed alumina. Development with 1 : 1 ethyl acetate–benzene produced a leading red band (0·16 g. of unidentified red oily material), a yellow band (0·09 g. orange solid) and a second red band (1·90 g. red solid). The yellow band proved to be *diethyl* 3-*azido*-1,4-*dihydro*-1,4-*dioxonaphthalene*-2-*phosphoramidate*, an orange solid, m. p. 130—131° (decomp.) (Found: C, 47·5; H, 4·1; N, 15·7; P, 8·6. $C_{14}H_{16}N_4O_5P$ requires C, 47·9; H, 4·55; N, 15·9; P, 8·85%).

The second red band was *triethyl* 3-*amino*-1,4-*dihydro*-1,4-*dioxonaphthalene*-2-*phosphorimidate*, m. p. 136—137° (decomp.) (from ethyl acetate) (Found: C, 53·4; H, 5·25; N, 7·85; P, 8·95. $C_{16}H_{21}N_2O_5P$ requires C, 54·5; H, 5·95; N, 7·95; P, 8·8%).

Trimethyl 1,4-*Dihydro*-1,4-*dioxo*-3-*triphenylphosphoranylideneaminonaphthalene*-2-*phosphorimidate* (VIII).—Triphenylphosphine (3·00 g.) was added to a stirred solution of compound (IV) (3·36 g.) in methylene chloride (25 ml.). The initially red solution turned blue, and gas was evolved. After about an hour the solvent was removed and the residue was dissolved in a little benzene and put on to a column of regular alumina. Development with cyclohexane removed the excess of triphenylphosphine, and benzene removed a broad blue band which gave compound (IX) (2·03 g.). Further development with 5 : 1 benzene–ethyl acetate removed a yellow band [compound (X) (0·20 g.)], and finally ethyl acetate removed the *product* (VIII) (1·78 g.). Crystallisation from methylcyclohexane gave a pure sample, m. p. 201—202° (decomp.) (Found: C, 64·7; H, 4·65; N, 5·15; P, 10·9. $C_{31}H_{28}N_2O_5P_2$ requires C, 65·3; H, 4·9; N, 4·9; P, 10·9%).

Dimethyl 3-*Azido*-1,4-*dihydro*-1,4-*dioxonaphthalene*-2-*phosphoramidate* (V).—The trimethyl ester (IV) (0·20 g.) was dissolved in acetic acid (1 ml.) and concentrated hydrochloric acid (4 drops) and water (2 drops) were added. The solution was warmed until the initial red colour has faded to a dark orange. Dilution with water and filtration gave an orange product (0·16 g., 84%), which yielded the azide as needles (0·13 g.), m. p. 129—131° (decomp.) (from ethyl acetate) (Found: C, 44·9; H, 3·6; N, 17·4; P, 9·8. $C_{12}H_{10}N_4O_5P$ requires C, 44·7; H, 3·4; N, 17·4; P, 9·65%).

2-*Amino*-3-*azido*-1,4-*naphthaquinone*.—A dilute (10%) solution of sodium hydroxide was added dropwise to a slurry of compound (V) (1·00 g.) in water (15 ml.) until a deep blue violet solution resulted. A violet precipitate of the product rapidly formed, and was filtered, washed and dried (0·59 g., 89%). It crystallised from nitromethane as chocolate-brown rosettes. When put into the melting-point bath at 110°, it shrank at 117° and darkened slowly up to 150°, but if put into the bath at 125° it decomposed vigorously (Found: C, 56·2; H, 2·75; N, 25·8; O, 15·2. $C_{10}H_6N_4O_2$ requires C, 56·0; H, 2·8; N, 26·2; O, 15·0%).

Reaction of Compound (V) *with Trimethyl Phosphite*.—A solution of trimethyl phosphite (1·35 g.) in a little methylene chloride was added to a stirred solution of compound (V) (3·21 g.) in methylene chloride (150 ml.). The initial orange colour changed to dark red, and after $\frac{1}{2}$ hr. the solvent was removed *in vacuo*. The resulting oil was triturated with light petroleum and then with methanol and filtered, giving 1-methyl-1*H*-naphtho[2,3-*d*]triazole-4,9-dione (0·72 g., 33%), m. p. 242—243°, identified by comparison of the melting point and infrared spectrum with those of an authentic specimen.[9]

Reaction of Compound (V) *with Triphenylphosphine*.—A solution of triphenylphosphine (6·00 g.) in methylene chloride (30 ml.) was added dropwise to a solution of compound (V) (6·63 g.) in methylene chloride (110 ml.). The orange solution turned purple, and a precipitate formed. After concentration to about half its volume, the reaction mixture was filtered, giving a cream-coloured *complex* (5·67 g., 58%). Crystallisation from nitromethane or pyridine gave yellow needles, m. p. 250—251° (decomp.) (Found: C, 70·5; H, 4·5; N, 11·8; P, 6·4. $C_{28}H_{21}N_4O_2P$ requires C, 70·6; H, 4·4; N, 11·8; P, 6·5%). The product was shown by synthesis to be a very stable, 1 : 1 complex of naphtho[2,3-*d*]triazoledione and triphenylphosphoranylideneimine.

Synthesis of the Complex from its Components.—A mixture of naphtho[2,3-*d*]triazoledione [9] (0·05 g.), triphenylphosphoranylideneimine hydrochloride [12] (0·16 g.), dry pyridine (3 ml.), and dry triethylamine (15 ml.) was boiled and triturated well for 5 min. The solvents were evaporated in an air stream, the residue was triturated with water, and the solid was filtered and washed with water, methanol, and light petroleum. When dry it weighed 0·08 g. Crystallisation from nitromethane gave yellow needles, m. p. 249·5—251° (decomp.) having an infrared spectrum identical with that of the complex obtained above.

Hexamethyl 2,5-*Dioxo*-1-*phenyl*-Δ^3-*pyrroline*-3,4-*diphosphorimidate* (XI).—A solution of trimethyl phosphite (2·75 g.) in methylene chloride (25 ml.) was added dropwise to a stirred solution of bisazidomaleanilide [13] (2·55 g.) in methylene chloride (150 ml.). The solution turned orange, and heat and gas were evolved. After 1 hr. the solvent was removed *in vacuo*, leaving an orange oil, which was dissolved in benzene and chromatographed on a column of alumina. The product was removed with ethyl acetate, and evaporation of the solvent gave an orange-yellow resin which slowly solidified. Trituration with light petroleum gave 2·10 g. of yellow powder, m. p. 75—85°, which could not be crystallised (Found: C, 42·7; H, 5·3; N, 9·2; P, 13·6. $C_{16}H_{23}N_3O_8P_2$ requires C, 43·0; H, 5·15; N, 9·4; P, 13·9%).

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Bound Brook, New Jersey, U.S.A.

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[12] H. H. Sisler, A. Sarkis, H. S. Ahuja, R. J. Drago, and N. L. Smith, *J. Amer. Chem. Soc.*, 1959, **81**, 2982; R. Appel and A. Nauss, *Chem. Ber.*, 1960, **93**, 405.

[13] A. Mustafa, S. Zayed, and S. Khatab, *J. Amer. Chem. Soc.*, 1956, **78**, 145.