

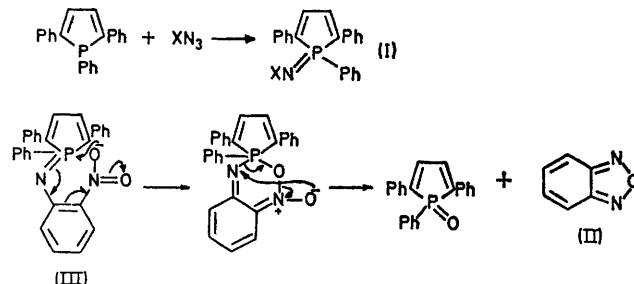
Formation of Phospholimine and Novel Preparation of Benzofurazans by Thermolytic Rearrangement of *N*-(*o*-Nitroaryl)-1,2,5-triphenylphospholimines

By J. I. G. CADOGAN,* R. GEE, and R. J. SCOTT

(Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ)

Summary Reactions of 1,2,5-triphenylphosphole with aryl-, arylsulphonyl-, methylsulphonyl-, ethoxycarbonyl-, and diphenylphosphinyl-azides readily give the novel 1,2,5-triphenylphospholimines (I; X = Ar, ArSO₂, MeSO₂, EtO₂C, Ph₂PO) which are thermally stable except for *N*-*o*-nitroaryl derivatives, *e.g.* (III), which give benzofurazans and 1,2,5-triphenylphosphole oxide, a reaction which does not occur with the corresponding *P*-triphenyl- or *P*-triethoxy-derivatives [Ph₃P=NAr or (EtO)₃P=NAr].

1,2,5-triphenylphospholimine (III) which readily gives 1,2,5-triphenylphosphole oxide (95%) and benzofurazan (60%) on thermolysis in boiling mesitylene. The 4-methyl-2-nitrophenyl- and 4-methoxy-2-nitrophenyl-derivatives also give the corresponding benzofurazans.



We describe a new class of organophosphorus compounds, the phospholimines (I), and also report a new synthesis of benzofurazan (II) *via* thermolytic rearrangement and fission of *N*-(*o*-nitrophenyl)-1,2,5-triphenylphospholimine (III).

Reactions of 1,2,5-triphenylphosphole (1 mol) with aryl-, arylsulphonyl-, diphenylphosphinyl-, methylsulphonyl-, and ethoxycarbonyl-azides (1.5 mol), in boiling dioxan or toluene at 100°, readily give the corresponding 1,2,5-triphenylphospholimines [I; X = Ph, *p*-Me·C₆H₄, *p*-NO₂·C₆H₄, *o*-NO₂·C₆H₄, *p*-I·C₆H₄, *p*-CO₂Et·C₆H₄, *p*-Me·C₆H₄, 2-NO₂-4-Me·C₆H₃, 2-NO₂-4-MeO·C₆H₃, *etc.*, *p*-Me·C₆H₄·SO₂, *p*-NO₂·C₆H₄·SO₂, Ph₂P(O), MeSO₂, EtO₂C] as crystalline solids in good yields† (usually 40–95%). *N*-Toluene-*p*-sulphonyl-1,2,5-triphenylphospholimine (I; X = *p*-Me·C₆H₄SO₂) was also obtained by reaction of chloramine-T with 1,2,5-triphenylphosphole.

These phospholimines are thermally stable, under normal conditions, with the exception of *N*-(*o*-nitrophenyl)-

Reaction as shown in the Scheme is therefore indicated. That the corresponding triethyl *N*-*o*-nitrophenylphosphorimidate [(EtO)₃P=NAr] and triphenyl-*N*-*o*-nitrophenylphosphinimine (Ph₃P=NAr) do not undergo this type of reaction indicates that the phospholimine ylide function is relatively more polarised (≡ P⁺–N[–]). In accord with this *N*-*o*-nitrophenyl phosphoramidic trichloride (Cl₃P=NAr) also undergoes thermolytic rearrangement to benzofurazan.

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† Satisfactory analytical, mass- and/or n.m.r.-spectral data were obtained for all compounds described in this communication.