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

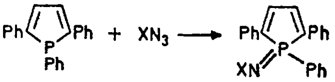
(*Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh* EH9 3JJ)

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, $ArSO_2$, $MeSO_2$, EtO_2C, Ph_2PO) 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 [$Ph_3P{=}NAr$ or $(EtO)_3P{=}NAr$].

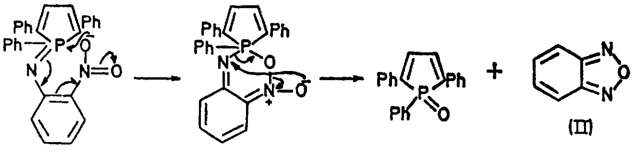
WE describe a new class of organophosphorus compounds, the phospholimines (I), and also report a new synthesis of benzofurazan (II) *via* thermolytic rearrangement and fission of *N*-(*o*-nitrophenyl)-1,2,5-triphenylphospholimine (III).

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*-$Me{\cdot}C_6H_4$, *p*-$NO_2{\cdot}C_6H_4$, *o*-$NO_2{\cdot}C_6H_4$, *p*-$I{\cdot}C_6H_4$, *p*-$CO_2Et{\cdot}C_6H_4$, *p*-$Me{\cdot}C_6H_4$, 2-NO_2-4-$Me{\cdot}C_6H_3$, 2-NO_2-4-$MeO{\cdot}C_6H_3$, *etc.*, *p*-$Me{\cdot}C_6H_4{\cdot}SO_2$, *p*-$NO_2{\cdot}C_6H_4{\cdot}SO_2$, $Ph_2P(O)$, $MeSO_2$, EtO_2C] as crystalline solids in good yields† (usually 40—95%). *N*-Toluene-*p*-sulphonyl-1,2,5-triphenylphospholimine (I; X = *p*-$Me{\cdot}C_6H_4SO_2$) 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)-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.



(I)



(III)

(II)

Reaction as shown in the Scheme is therefore indicated. That the corresponding triethyl *N*-*o*-nitrophenylphosphorimidate [$(EtO)_3P{=}NAr$] and triphenyl-*N*-*o*-nitrophenylphosphinimine ($Ph_3P{=}NAr$) do not undergo this type of reaction indicates that the phospholimine ylide function is relatively more polarised ($\equiv \overset{+}{P}{-}\overset{-}{N}{-}$). In accord with this *N*-*o*-nitrophenyl phosphoramidic trichloride ($Cl_3P{=}NAr$) 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.