

**1095.** *The Conditions Determining the Quaternisation of Tertiary Phosphines by Methyl 2,4-Dinitrobenzenesulphonate.*

By K. B. MALLION and FREDERICK G. MANN.

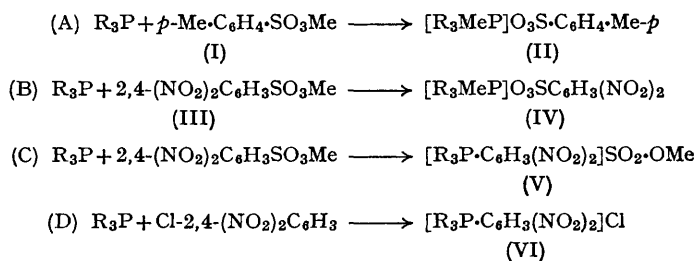
Tertiary phosphines are quaternised with methyl toluene-*p*-sulphonate to give the methylphosphonium cation. This cation is also formed when some tertiary phosphines are treated with methyl 2,4-dinitrobenzenesulphonate, but other phosphines with this reagent give the 2,4-dinitrophenylphosphonium cation, which can usually also be prepared from such phosphines by direct union with 1-chloro-2,4-dinitrobenzene.

The factors which determine which type of quaternisation a particular phosphine undergoes, and the probable mechanism of the formation of the 2,4-dinitrophenylphosphonium cation, are discussed.

WE have investigated the conversion of a series of tertiary phosphines into their methyl quaternary salts using various quaternising reagents and have observed in certain cases

marked and significant differences. Most of these phosphines reacted readily with methyl iodide and, when treated in toluene solution with methyl toluene-*p*-sulphonate (I), gave the colourless methylphosphonium toluene-*p*-sulphonate (II) (reaction A); the identity of the latter salts was confirmed by their conversion in solution by sodium iodide into the methiodide or (in most cases) by the similar conversion into the methopicrate, identical with that obtained from the methiodide.

Certain phosphines when treated in cold toluene with methyl 2,4-dinitrobenzenesulphonate (III) reacted similarly, giving the colourless methylphosphonium 2,4-dinitrobenzenesulphonates (IV), (reaction B), which could be converted similarly into the methylphosphonium iodide or picrate [as (II)]. Other phosphines, however, when thus treated with the



sulphonate (III), gave a deep purple colour followed usually by deposition of a viscous purple syrup. These syrups were of varying stability, and in some cases the purple colour faded to a buff or yellow colour; apart from a few unstable members, all, in solution, furnished the 2,4-dinitrophenylphosphonium salts (V) (reaction C). The identification of these salts is based on the evidence: (a) solutions of these salts with sodium picrate gave the crystalline 2,4-dinitrophenylphosphonium picrates [as (V)]; (b) the phosphines giving reaction (C) also combined in toluene solution with chloro-2,4-dinitrobenzene to give the corresponding phosphonium chlorides (VI) (reaction D), and these salts of unambiguous structure gave in each case the same crystalline picrates as those from the salts (V).

Since the coloured products from reactions (C and D), and also some of the colourless products from reaction (A), were viscous syrups, they were converted into their distinctive crystalline picrates for identification throughout this investigation.

The purple solids from reaction (C) were usually freely soluble in cold methanol, ethanol, and acetone, but almost insoluble in ether, toluene, or petroleum. Cold ethanolic solutions of the purple solids were instantly decolorised by the addition of dilute sulphuric or hydrochloric acid, but the subsequent addition of dilute aqueous sodium hydroxide restored the purple colour. The initial purple solution and the colourless acidified solution gave with sodium picrate, however, the same picrate [as (V)]. It follows that the cation in the salts (V) and (VI) is colourless, and that the purple solids were either intermediate compounds or mixtures.

The phosphines studied could therefore be divided into two groups.

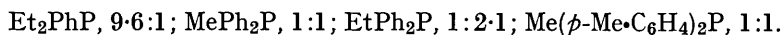
*Phosphines giving reaction (B).* Me(*o*-Me·C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>P; (*o*-MeO·C<sub>6</sub>H<sub>4</sub>)MePhP; (*o*-MeO·C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>MeP; Et(*o*-ClC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>P; Et(2-Cl-5-Me·C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>P; Ph<sub>3</sub>P; (*p*-Me·C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P; (NC·C<sub>2</sub>H<sub>4</sub>)<sub>3</sub>P.

*Phosphines giving reaction (C).* Me<sub>2</sub>PhP; Et<sub>2</sub>PhP; MePh<sub>2</sub>P; EtPh<sub>2</sub>P; Me(*p*-Me·C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>P; (*p*-MeO·C<sub>6</sub>H<sub>4</sub>)MePhP.

Two phosphines showed reaction (C) with rapid conversion of the product into that produced by reaction (B). A toluene solution of (*p*-MeO·C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P treated with the methyl ester (III) gave initially a yellow-orange colour, but after 3—4 seconds the solution became turbid, then reddish-purple in colour, and deposited a purple gum. This material changed in colour to cream-yellow during 1.25 hours, and when then dissolved in ethanol still gave the 'normal' picrate [as (IV)]. The phosphine (*o*-MeO·C<sub>6</sub>H<sub>4</sub>)MePhP behaved similarly.

Of the six phosphines listed as giving reaction (C), the purple derivative of the first

(Me<sub>2</sub>PhP) was solely of type (V), for it furnished only the corresponding picrate. The next four phosphines gave purple derivatives which were mixtures of salts of the types (IV) and (V); the purple product in each case gave a mixture of two picrates, which showed no apparent tendency to interconversion, and which could usually be completely separated by careful fractional recrystallisation, a method which proved superior to other physical methods investigated. The ratios of picrate of type (IV) to that of type (V) were:



It is noteworthy that when the reaction mixture from methyldiphenylphosphine was set aside at room temperature with occasional stirring, the purple gum changed completely to a cream-coloured solid during two weeks; this solid, when collected and washed, still gave the "abnormal" picrate [as (V)]. The similar reaction mixture from ethyldiphenylphosphine gave a purple gum changing within 4 hours to a yellow solid which gave the two picrates [as (IV) and (V)].

The above results indicate that the main factor which determines whether the phosphorus atom attacks the C(Me) atom of the ester (III) (reaction B) or the C(1) atom of the benzene ring (reaction C) is the steric effect. For example, the phosphine EtPh<sub>2</sub>P gave considerable attack at the C(1) atom, whereas the phosphines Et(*o*-ClC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>P and Et(2-Cl-5-Me·C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>P attacked solely at the C(Me) atom. It might be urged that the *o*-chloro-groups of these phosphines reduce the electron density at the phosphorus atom by the *-I* effect, but the phosphine Me(*o*-Me·C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>P, in which the *+I* effect of the *o*-methyl groups would increase this electron density, also attacks solely at the C(Me) atom. Furthermore, the phosphine Me(*p*-Me·C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>P, in which the *p*-methyl groups would similarly increase this density but where no steric effect exists, reacts (like methyldiphenylphosphine) at the C(Me) and C(1) atoms to approximately the same extent.

These steric results are in harmony with those of Brady and Cropper,<sup>1</sup> who found that a set of primary and secondary amines attacked the 1-position in 1-chloro-2,4-dinitrobenzene at differing rates, which were unrelated to their basicities but were closely correlated with front-side interference by *N*-alkyl groups or adjacent *C*-alkyl groups of the amines.

The effect of electron density at the phosphorus atom was shown by tris-2-cyanoethylphosphine, which although free from steric hindrance, reacted solely at C(Me); triphenylphosphine did also, but tri-*p*-methoxyphenylphosphine, for which steric hindrance to attack at C(1) must be at least as great as that of triphenylphosphine, gave the purple colour of reaction (C). This difference must be attributed to the *p*-methoxyl groups increasing the electron density at the phosphorus atom, for tri-*m*-methoxyphenylphosphine reacted precisely as triphenylphosphine. Similarly, *o*-methoxyphenylmethylphenylphosphine gave a purple deposit changing in 2–3 hours to the colourless salt of type (IV), but the *p*-methoxy-isomer gave a purple deposit sufficiently stable for isolation. It is probable that the steric factor is stronger than that of the electron density.

The relative quantities of the salts (IV) and (V) given by a phosphine would depend on the relative rates of reaction at the C(Me) and C(1) atoms, respectively, the second reaction, being very sensitive to steric hindrance, often exerting the major influence. An increase in the nucleophilic power of the phosphorus might increase both these rates of attack, although not necessarily in proportion. The ester (III) is known to be about sixty times more reactive than methyl sulphate in methylating benzothiazoles;<sup>2</sup> consequently the C(Me) atom of the ester should be more susceptible to nucleophilic attack than the C(1) atom. This is supported by the very rapid hydrolysis of the ester by damp air to the free sulphonic acid, and not to 2,4-dinitrophenol.<sup>3</sup>

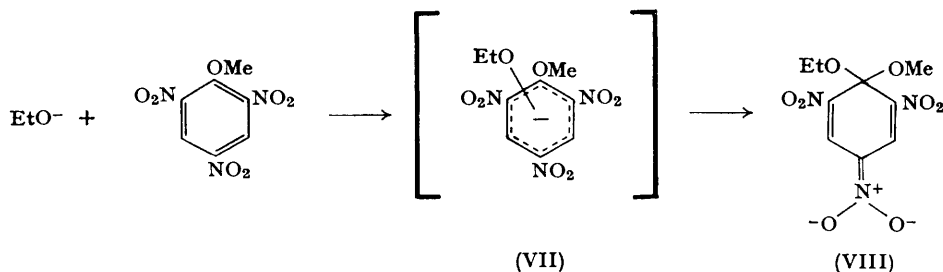
Since all the phosphines could therefore react most readily at the C(Me) atom, *direct* attack at the C(1) atom to give the purple products is very improbable. When the cold

<sup>1</sup> O. L. Brady and F. R. Cropper, *J.*, 1950, 507.

<sup>2</sup> G. I. Kipriyanov and A. I. Tolmatshev, *Zhur. obshchei Khim.*, 1957, 27, 142.

<sup>3</sup> Personal communication from Professor F. G. Holliman.

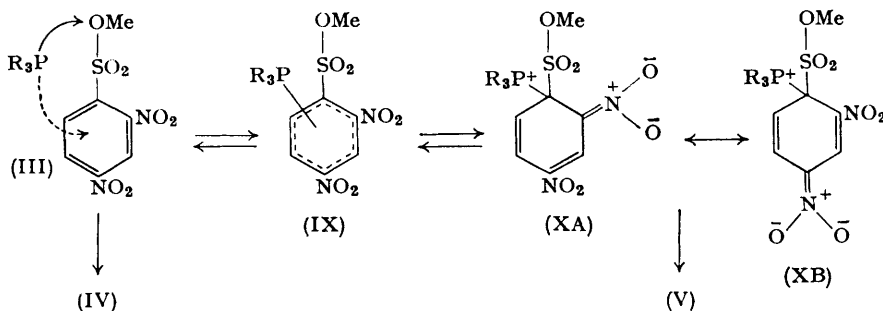
toluene solutions of each phosphine and the ester (III) were mixed, a yellow colour of varying depth instantly appeared; this colour faded rapidly when the salt (IV) alone was ultimately isolated, but in the other cases it darkened and the purple product separated. This process of darkening and precipitation was sometimes very rapid; when it occurred more slowly, it bore a very striking resemblance to the two-step colour reaction between the ethoxide ion and 2,4,6-trinitroanisole studied by Ainscough and Caldin.<sup>4</sup> These workers observed the very fast initial formation of a yellow colour, followed by the slower formation of the deep-red Meisenheimer complex (VIII), and kinetic studies of the two distinct stages at low temperatures indicated that the yellow colour was that of a charge-transfer complex denoted as (VII).



Meisenheimer had earlier established the structure of this red complex, of which (VIII) is one canonical form, by preparing it by the action of the ethoxide ion on 2,4,6-trinitroanisole and by that of the methoxide ion on 2,4,6-trinitrophenetole.<sup>5</sup> Later studies have confirmed the structure.<sup>6</sup>

The main characteristics of a charge-transfer complex are that it is formed very rapidly by the 1:1 association of an electron-deficient and an electron-rich molecule through a "one-electron-bond," and that it exists in solution in equilibrium with its component donor and acceptor molecules.<sup>7</sup>

We suggest therefore that the most probable mechanism of our reactions is that shown below. When the solutions of the phosphine and the ester (III) are mixed, the phosphine may attack the C(Me) atom apparently almost exclusively, with formation of the "normal"



salt (IV). In all cases however the immediate development of a yellow colour indicates the initial formation in equilibrium of the yellow charge-transfer complex, denoted as (IX), by the association of the electron-rich phosphorus atom and the electron-deficient  $\pi$ -system of the aromatic ring in the ester. This process brings the phosphine into close contact with the

<sup>4</sup> J. B. Ainscough and E. F. Caldin, *J.*, 1956, 2528.

<sup>5</sup> J. Meisenheimer, *Annalen*, 1902, **323**, 205.

<sup>6</sup> L. K. Dyal, *J.*, 1960, 5160; R. Foster and D. Ll. Hammick, *J.*, 1954, 2153; S. Nagakura, Technical Report of the I.S.S.P., Tokyo, 1962, Series A, No. 35.

<sup>7</sup> R. S. Mulliken, *J. Chem. Phys.*, 1951, **514**, 19; *J. Amer. Chem. Soc.*, 1950, **72**, 600; *J. Phys. Chem.*, 1952, **56**, 801.

aromatic ring, and away from the influence of the reactive methyl group. The phosphine, provided it is (a) not sterically hindered and (b) sufficiently nucleophilic, then attacks the C(1) atom of the ring to give the purple Meisenheimer complex having the canonical forms (XA) and (XB). This complex then spontaneously (and often slowly) rearranges to give the colourless "abnormal" salt (V).

In other cases, the competing rapid reaction at the C(Me) atom will cause the complex to revert to its components and thus give the salt (IV) almost exclusively; alternatively, the nature of the phosphine, and therefore the relative speed of the two reactions of the complex, may produce a mixture of the salts (IV) and (V).

Two points provide support for this mechanism. Dimethylphenylphosphine reacted under standard conditions with the ester (III) by ultimate exclusive attack on the C(1) atom to give the salt (V). When the phosphine was similarly treated with methyl 3,5-dinitrobenzenesulphonate, the solution immediately became yellow but furnished exclusively the "normal" salt analogous to (IV). In this case, the charge-transfer complex [as (IX)] was apparently formed; the C(1) atom would not be activated towards nucleophilic attack as in the 2,4-dinitro-isomer, and in addition a true Meisenheimer complex could not be formed.

The importance of the relative rates of attack at C(Me) and C(1) in determining the final proportions of the salts of type (IV) and (V), respectively, was shown by the reaction of tri-*p*-tolylphosphine with the methyl ester (III) and with phenyl 2,4-dinitrobenzenesulphonate. This phosphine reacted under the standard conditions with the methyl ester (III) to give the yellow charge-transfer complex (IX) but reaction at C(1) to form the Meisenheimer complex (X A—B) was so slow compared with that at C(Me) that no purple product was observed and the phosphine was ultimately completely converted into the normal salt (IV). When this experiment was repeated using the phenyl ester, in which the rate of attack at the phenyl group would be drastically reduced, the mixture gave an immediate brownish-yellow colour which changed to purple within 6 minutes with deposition of the purple complex (X A—B), which in turn gave the picrate of type (V).

It is noteworthy that Foster,<sup>8</sup> when studying the two-step colour reaction between amines and 1,3,5-trinitrobenzene, also attributed these stages to the formation of a charge-transfer complex and a Meisenheimer complex, but neither he nor Ainscough and Caldin<sup>4</sup> in their work noted above obtained decisive evidence that the formation of the two complexes was competitive or consecutive. The formation of the two complexes in our work certainly appeared to be consecutive.

Even the most stable of our purple products could not be recrystallised, but in three cases precipitation from a cold acetone solution by ether furnished a fine purple powder which approached "analytical" purity, but which may have been still contaminated with the isomeric salts of types (IV) and (V).

Triethylphosphine, the only aliphatic phosphine that we have examined, when treated with the ester (III) gave an intense purple gum which slowly became brown even under nitrogen; this gum did not give a picrate and appeared to be covalent. The phosphine reacted with chloro-2,4-dinitrobenzene to give a reddish-brown gum which could not be crystallised, did not give a picrate, and in ethanolic solution was not decolourised by dilute hydrochloric acid. The nature of these products remains uncertain.

Trimethylarsine, diethylphenylarsine, and triphenylarsine were similarly treated with the methyl ester (III). Only trimethylarsine gave a purple derivative, which faded rapidly in colour and then consisted of the normal salt of type (IV). The other arsines gave salts of this type directly. Apparently the arsines are too bulky or insufficiently nucleophilic to give the "abnormal" quaternisation to stable salts of type (V).

#### EXPERIMENTAL

Certain compounds gave consistent m. p.s only when determined in sealed evacuated tubes, denoted as (E.T.).

<sup>8</sup> R. Foster, *J.*, 1959, 3508.

The tertiary phosphines were usually prepared by the action of the appropriate Grignard reagent on phosphorus trichloride or on methyl-, ethyl-, or phenyl-phosphonous chloride.

The methiodides were prepared by the slow addition of an excess of methyl iodide to a stirred toluene solution of the phosphine. Usually the mixture rapidly became cloudy and the methiodide was deposited; occasionally the mixture required gentle warming. The methopicrates were obtained by the action of saturated aqueous sodium picrate on the aqueous or ethanolic methiodides.

For the other reactions, a cold stirred toluene solution of the phosphine under nitrogen was treated with the ester (I) (1.1—1.5 mol.), the ester (III) (1.1 mol.), or with 1-chloro-2,4-dinitrobenzene (1.1—1.5 mol.), all in (usually) cold toluene. The toluene-*p*-sulphonates (II) often crystallised readily; others separated as gums which were not obtained solid. The toluene solutions of the ester (III) were always filtered directly into the phosphine solution to remove traces of the insoluble 2,4-dinitrobenzenesulphonic acid. The reaction with the ester (I) was not always investigated if the phosphine gave a decisive reaction (B) with the ester (III). Whenever the cation in a non-crystalline product was converted into the methopicrate, the latter was identified by mixed m. p. determinations with the authentic methopicrate. When a phosphine gave reaction (C), the product was identified as the quaternary picrate, identical with that obtained from the chloro-2,4-dinitrobenzene reaction mixture.

The phosphines are taken in the order given under reactions (B and C), respectively (p. 5717), and further details are noted only when reaction (C) was given.

The term "petroleum" refers throughout to light petroleum, b. p. 60—80°.

*Methyldi-o-tolylphosphine*, m. p. 54—54.5° (E.T.),<sup>9</sup> gave a *methiodide*, m. p. 226.5—228.5° (ethanol) (Found: C, 51.9; H, 5.5. C<sub>16</sub>H<sub>20</sub>IP requires C, 51.8; H, 5.4%) and a *methopicrate*, m. p. 179—181.5° (ethanol) (Found: C, 56.2; H, 4.7; N, 8.9. C<sub>22</sub>H<sub>22</sub>N<sub>3</sub>O<sub>7</sub>P requires C, 56.15; H, 4.7; N, 8.9%). The ester (III) added to the phosphine solution gave an immediate greenish-yellow colour which faded as the *dimethyldi-o-tolylphosphonium 2,4-dinitrobenzenesulphonate*, m. p. 171.5—173° (ethanol) separated (Found: C, 53.5; H, 4.65; N, 5.8. C<sub>22</sub>H<sub>23</sub>N<sub>2</sub>O<sub>7</sub>PS requires C, 53.8; H, 4.7; N, 5.7%); it gave the above iodide and picrate.

*o-Methoxyphenylmethylphenylphosphine*, m. p. 45—46°,<sup>10</sup> gave a *methiodide*, m. p. 198—199.5° (ethanol) (Found: C, 48.6; H, 4.8. C<sub>15</sub>H<sub>15</sub>IOP requires C, 48.4; H, 4.9%) and a *methopicrate*, m. p. 156—157° (ethanol-acetone) (Found: C, 53.15; H, 4.3; N, 8.95. C<sub>21</sub>H<sub>20</sub>N<sub>3</sub>O<sub>8</sub>P requires C, 53.3; H, 4.3; N, 8.9%). The addition of the ester (III) caused the phosphine solution to become brownish-yellow, then turbid, and after *ca.* 3 sec. suddenly purple, with deposition of a purple gum, which when stirred under the solution for 2.5 hr. crystallised to the almost white *o-methoxyphenyldimethylphenylphosphonium 2,4-dinitrobenzenesulphonate*, m. p. 98—100° (water) (Found: C, 51.2; H, 4.4; N, 6.1. C<sub>21</sub>H<sub>21</sub>N<sub>2</sub>O<sub>8</sub>PS requires C, 51.25; H, 4.3; N, 5.8%). The methopicrate was fractionally precipitated from the purple gum before solidification, but gave solely the above methopicrate, m. p. and mixed m. p. 156—157°.

*Di(o-methoxyphenyl)methylphosphine*, m. p. 121—123° (E.T.) (ethanol) (Found: C, 68.9; H, 7.0. C<sub>15</sub>H<sub>17</sub>O<sub>2</sub>P requires C, 69.2; H, 6.6%), gave a *methiodide*, m. p. 217.5—219.5° (water) (Found: C, 47.6; H, 5.1. C<sub>16</sub>H<sub>20</sub>IO<sub>2</sub>P requires C, 47.8; H, 5.0%) and a *methopicrate*, m. p. 164—166° (aqueous ethanol) (Found: C, 52.85; H, 4.4; N, 8.4. C<sub>22</sub>H<sub>22</sub>N<sub>3</sub>O<sub>9</sub>P requires C, 52.5; H, 4.4; N, 8.3%). The addition of the ester (III) gave a very weak green colour, immediately followed by a white turbidity and deposition of *di-o-methoxyphenyldimethylphosphonium 2,4-dinitrobenzenesulphonate*, m. p. 162—164.5° (water) (Found: C, 50.4; H, 4.2; N, 5.3. C<sub>22</sub>H<sub>23</sub>N<sub>2</sub>O<sub>9</sub>PS requires C, 50.6; H, 4.2; N, 5.4%).

*Di(o-chlorophenyl)ethylphosphine*<sup>11</sup> gave a methiodide which was converted directly into the *methopicrate*, m. p. 126—127° (ethanol) (Found: C, 47.8; H, 3.2; N, 8.0. C<sub>21</sub>H<sub>18</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>7</sub>P requires C, 47.9; H, 3.45; N, 8.0%). Addition of the ester (III) caused rapid separation of the crystalline *di(o-chlorophenyl)ethylmethylphosphonium 2,4-dinitrobenzenesulphonate*, m. p. 165—167° (ethanol) (Found: C, 46.6; H, 3.5; N, 5.25. C<sub>21</sub>H<sub>19</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>7</sub>PS requires C, 46.25; H, 3.5; N, 5.1%); it gave the above methopicrate.

*Di(2-chloro-5-methylphenyl)ethylphosphine*<sup>11</sup> gave a methiodide, m. p. 203—205°, and a *methopicrate*, m. p. 142—144° (ethanol) (Found: C, 50.2; H, 4.1; N, 7.6. C<sub>23</sub>H<sub>22</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>7</sub>P requires C, 49.8; H, 4.0; N, 7.6%). No reaction apparently occurred with the ester (I) in cold solution, but boiling for 15 min. gave *di(2-chloro-5-methylphenyl)ethylmethylphosphonium toluene-*

<sup>9</sup> K. B. Mallion, F. G. Mann, B. P. Tong, and V. P. Wystrach, *J.*, 1963, 1327.

<sup>10</sup> F. G. Mann, B. P. Tong, and V. P. Wystrach, *J.*, 1963, 1155.

<sup>11</sup> M. Davis and F. G. Mann, *J.*, 1964, 3786.



*p*-sulphonate, m. p. 223.5—225° (acetone) (Found: C, 58.3; H, 5.4.  $C_{24}H_{27}Cl_2O_3PS$  requires C, 57.9; H, 5.5%). Addition of the ester (III) gave an immediate green colour and slow deposition of the corresponding 2,4-dinitrobenzenesulphonate, m. p. 218—220° (ethanol) (Found: C, 48.2; H, 4.3; N, 5.0.  $C_{23}H_{23}Cl_2N_2O_7PS$  requires C, 48.2; H, 4.0; N, 4.9%). Both salts gave the above methopicate. When a methanol-toluene solution of the phosphine and chloro-2,4-dinitrobenzene was boiled for 4 hr. and cooled, the unchanged phosphine crystallised.

*Triphenylphosphine* was converted into the methiodide and the methopicate, m. p. 134—134.5° (ethanol) (Found: C, 59.55; H, 4.2; N, 8.2.  $C_{25}H_{20}N_3O_7P$  requires C, 59.35; H, 4.0; N, 8.3%). The phosphine, boiled with the ester (I) in toluene for 10 min. and cooled, deposited the colourless gummy quaternary salt, which did not solidify. The phosphine, treated with the ester (III) in cold solution, gave a faint green colour and deposited *methyltriphenylphosphonium* 2,4-dinitrobenzenesulphonate, m. p. 182.5—183.5° (ethanol) (Found: C, 56.8; H, 4.2; N, 5.3.  $C_{25}H_{21}N_2O_7PS$  requires C, 57.25; H, 4.0; N, 5.3%). Both salts gave the methopicate.

*Tri-*o*-tolylphosphine* gave a methiodide, m. p. 233—234°,<sup>9</sup> and a methopicate, m. p. 170—171° (ethanol) (Found: C, 61.1; H, 4.8; N, 7.9.  $C_{28}H_{28}N_3O_7P$  requires C, 61.4; H, 4.8; N, 7.7%). It gave a very weak yellow-green colour with the ester (III), and the solution, when boiled for 30 min. and cooled, deposited a colourless gum which did not solidify, but was converted into the methopicate.

*Tri-*p*-tolylphosphine*, m. p. 145—146° (lit.,<sup>12</sup> 146°) gave a methiodide, m. p. 191—192°,<sup>9</sup> and a methopicate, m. p. 134—135° (ethanol) (Found: C, 61.2; H, 4.7; N, 7.9.  $C_{28}H_{28}N_3O_7P$  requires C, 61.4; H, 4.8; N, 7.7%). The phosphine did not apparently react with the ester (I) in cold toluene, but the solution, after being boiled for 15 min., deposited an oil, which after trituration with ether gave the toluene-*p*-sulphonate [as (II)], a white amorphous powder, m. p. 98—103°; this could not be crystallised, but gave the methopicate. The phosphine solution with the ester (III) gave a dark-yellow colour and deposited a pale-brown oil, which hardened to a stiff white gum which was not obtained crystalline; it was the salt of type (IV) and also gave the methopicate.

The phosphine solution with 1-chloro-2,4-dinitrobenzene became immediately yellow, then orange, and after 2 min. ruby-red, and after 10 min. started to deposit a dark oil, which when set aside overnight formed a yellow-brown powder. This could not be crystallised, but was the salt of type (VI), for it furnished 2,4-dinitrophenyltri-*p*-tolylphosphonium picrate, m. p. 190.5—191.5°, after crystallisation from ethanol-acetone-petroleum (charcoal) (Found: C, 56.95; H, 3.6; N, 10.1.  $C_{33}H_{26}N_5O_{11}P$  requires C, 56.7; H, 3.75; N, 10.0%).

The phosphine solution, treated with phenyl 2,4-dinitrobenzenesulphonate, gave an immediate brownish-yellow colour changing to intense purple over *ca.* 6 min., and deposited a purple oil. Next day, the separated oil hardened when treated with petroleum but could not be crystallised. Its identity as the phenyl analogue of the salt of type (V) was shown by its conversion in ethanolic solution into the above picrate, m. p. and mixed m. p. 190—191.5°; the two picrates had identical infrared spectra.

*Tri-*m*-methoxyphenylphosphine*<sup>12</sup> reacted with the ester (III) to give a white gummy deposit without any purple coloration.

*Tri-*p*-methoxyphenylphosphine*, m. p. 129—131° (lit.,<sup>12</sup> 131°) gave a methiodide, m. p. 224.5—226° (water) (Found: C, 53.7; H, 5.1.  $C_{22}H_{24}IO_3P$  requires C, 53.4; H, 4.9%) and a methopicate, m. p. 108—109° (aqueous ethanol) (Found: C, 56.8; H, 4.6; N, 7.1.  $C_{28}H_{28}N_3O_{10}P$  requires C, 56.5; H, 4.4; N, 7.1%).

The phosphine with the ester (I) precipitated a white gum of type (II), which could not be recrystallised but gave the methopicate. The phosphine solution with the ester (III) gave an immediate yellow-orange colour which within 5 sec. changed to purple with deposition of a purple gum, which became cream-yellow within 1.25 hr. It could not be obtained solid, but also gave only the above methopicate.

The phosphine solution, when treated with 1-chloro-2,4-dinitrobenzene, became orange-yellow and then rapidly reddish-brown with separation of a fluffy solid. After 12 hr. the purplish-brown solid was collected. The deep-brown colour of its ethanolic solution was changed to pale yellow by a few drops of 2*N*-hydrochloric acid, and the solution then gave *tri-*p*-methoxyphenyl*-2,4-dinitrophenylphosphonium picrate, m. p., 179—181°, after trituration with petroleum and recrystallisation from ethanol-petroleum (charcoal) (Found: C, 53.3; H, 3.8; N, 9.2.  $C_{33}H_{26}N_5O_{14}P$  requires C, 53.0; H, 3.5; N, 9.4%).

<sup>12</sup> F. G. Mann and E. J. Chaplin, *J.*, 1937, 527.

*Tri-2-cyanoethylphosphine*<sup>13</sup> gave a methiodide, m. p. 243—244° (lit.,<sup>13</sup> 238—239°) (aqueous ethanol), very slowly in toluene but rapidly in acetone (Found: C, 36.3; H, 4.45; N, 12.5. Calc. for C<sub>10</sub>H<sub>15</sub>IN<sub>3</sub>P: C, 35.8; H, 4.5; N, 12.55%) and a *methopicrate*, m. p. 136.5—138° (aqueous ethanol) (Found: C, 44.2; H, 4.4; N, 19.2. C<sub>16</sub>H<sub>17</sub>N<sub>6</sub>O<sub>7</sub>P requires C, 44.1; H, 3.9; N, 19.3%).

The phosphine in methanol-toluene, treated with the ester (III), gave a very pale green colour and after *ca.* 30 sec. deposited a green oil which hardened to the white *tri-2-cyanoethyl-methylphosphonium 2,4-dinitrobenzenesulphonate* [as (IV)], m. p. 144—146° (water) (Found: C, 42.4; H, 4.2; N, 15.25. C<sub>16</sub>H<sub>18</sub>N<sub>5</sub>O<sub>7</sub>PS requires C, 42.2; H, 4.0; N, 15.4%). It gave the methopicrate.

*Dimethylphenylphosphine*<sup>12</sup> gave the methiodide (crude, m. p. 233—236°) (lit.,<sup>14</sup> 236°) and methopicrate, m. p. 133—135° (ethanol) (lit.,<sup>15</sup> 132—133°) (Found: C, 47.4; H, 4.3; N, 11.0. Calc. for C<sub>15</sub>H<sub>18</sub>N<sub>3</sub>O<sub>7</sub>P: C, 47.2; H, 4.2; N, 11.0%). With the ester (I), it gave *trimethylphenylphosphonium toluene-p-sulphonate*, m. p. 160.5—162° (acetone) (Found: C, 59.3; H, 6.6. C<sub>16</sub>H<sub>21</sub>O<sub>3</sub>PS requires C, 59.25; H, 6.5%). The phosphine, treated with 1-chloro-2,4-dinitrobenzene, gave an almost immediate deep-purple colour and a yellowish-orange precipitate, which when collected gave dark-brown solutions in ethanol and in aqueous acetone, both giving a positive test for chloride ion. The precipitate gave *dimethyl-2,4-dinitrophenylphenylphosphonium picrate* [as (V)], m. p. 235—236° (aqueous ethanol; charcoal) (Found: C, 45.0; H, 3.3; N, 13.1. C<sub>20</sub>H<sub>16</sub>N<sub>5</sub>O<sub>11</sub>P requires C, 45.05; H, 3.0; N, 13.1%).

The phosphine (0.70 g.) in toluene (10 ml.), when treated with the ester (III) (1.46 g., 1.1 mol.) in toluene (20 ml.), gave an immediate deep-purple colour and precipitate (1.9 g., 94%). The purple deposit gave deep-purple solutions in ethanol or aqueous acetone the colour of which was discharged by dilute acid and restored by dilute alkali. The deposit, when partly purified by precipitation from cold acetone with ether, formed a purple powder, m. p. 105—109° (decomp.) (E.T.) (Found: C, 46.3; H, 4.8; N, 7.3. C<sub>15</sub>H<sub>17</sub>N<sub>2</sub>O<sub>7</sub>PS requires C, 45.0; H, 4.3; N, 7.0%).<sup>16</sup> It gave a picrate, m. p. 235—237° (aqueous ethanol), which before and after crystallisation had an infrared spectrum identical with that of the above picrate but distinct from that of the methopicrate. All attempts to detect the latter in the crude precipitated picrate failed.

The phosphine (0.32 g.), when treated with phenyl 2,4-dinitrobenzenesulphonate (0.83 g., 1.1 mol.), gave a similar immediate colour and deposit (0.86 g.); the latter in turn gave the picrate, m. p. 233.5—236.5°.

The phosphine, treated with methyl 3,5-dinitrobenzenesulphonate, gave a faint yellow colour and a white crystalline deposit of *trimethylphenylphosphonium 3,5-dinitrobenzenesulphonate*, m. p. 205—206° (ethanol) (Found: C, 45.3; H, 4.3; N, 7.2. C<sub>15</sub>H<sub>17</sub>N<sub>2</sub>O<sub>7</sub>PS requires C, 44.9; H, 4.3; N, 7.0%), which gave the methopicrate.

*Diethylphenylphosphine* gave a methiodide, m. p. 110—112° (lit.,<sup>17</sup> 108—109°) and a *methopicrate*, m. p. 73.5—74.5° (ethanol) (Found: C, 49.9; H, 5.0; N, 10.15. C<sub>17</sub>H<sub>20</sub>N<sub>3</sub>O<sub>7</sub>P requires C, 49.8; H, 4.9; N, 10.3%). The phosphine with the ester (I) gave a colourless oil which did not solidify but gave the methopicrate.

The phosphine with 1-chloro-2,4-dinitrobenzene gave a sticky purple deposit, which in aqueous acetone gave *diethyl-2,4-dinitrophenylphenylphosphonium picrate*, m. p. 205—208° (aqueous ethanol with a trace of acetone) (Found: C, 47.1; H, 3.75; N, 12.7. C<sub>22</sub>H<sub>20</sub>N<sub>5</sub>O<sub>11</sub>P requires C, 47.15; H, 3.6; N, 12.5%).

The phosphine (0.59 g.) when treated with the ester (III) (1.05 g., 1.1 mol.) deposited a purple gum, which when collected and rubbed in turn with ether and petroleum gave a purple powder (1.39 g., 91%). This powder (800 mg.) gave a crude picrate (633 mg.), m. p. 197—203°, which when recrystallised gave the above picrate (528 mg.), m. p. 206.5—208°. Concentration of the first mother-liquors and fractionation (ethanol) gave the normal methopicrate (55 mg.), m. p. 72.5—74.5°.

*Methyldiphenylphosphine*, b. p. 108—110°/0.5 mm. (lit.,<sup>17</sup> 161°/14 mm.) gave a methiodide, m. p. 253—254° (lit.,<sup>18</sup> 241°,<sup>19</sup> 245—247°) (ethanol) and a *methopicrate*, m. p. 116.5—118° (ethanol)

<sup>13</sup> M. M. Rauhut, I. Hechenbleikner, H. A. Currier, F. C. Schaefer, and V. P. Wystrach, *J. Amer. Chem. Soc.*, 1959, **81**, 1103. We are indebted to Dr. Rauhut for a sample of this phosphine.

<sup>14</sup> G. W. Fenton and C. K. Ingold, *J.*, 1929, 2342.

<sup>15</sup> C. K. Ingold, F. R. Shaw, and I. S. Wilson, *J.*, 1928, 1280.

<sup>16</sup> We are indebted to Dr. R. C. Hinton for the isolation of this product.

<sup>17</sup> J. Meisenheimer, J. Caspar, M. Höring, W. Lauter, L. Lichtenstadt, and W. Samuel, *Annalen*, 1926, **449**, 213.

<sup>18</sup> A. Michaelis and A. Link, *Annalen*, 1881, **207**, 193.

<sup>19</sup> M. Epstein and S. A. Buckler, *Tetrahedron*, 1962, **18**, 1231.



(Found: C, 54.2; H, 4.5; N, 9.7.  $C_{20}H_{18}N_3O_7P$  requires C, 54.2; H, 4.2; N, 9.5%). It gave with the ester (I) the crystalline *methotoluene-p-sulphonate*, m. p. 166—168° (acetone-ethanol) (Found: C, 65.3; H, 6.2.  $C_{21}H_{23}O_3PS$  requires C, 65.3; H, 6.0%).

The phosphine, with 1-chloro-2,4-dinitrobenzene, gave a faint purple colour which became more intense as a faintly purple precipitate separated. The latter changed during 2 hr. to a hygroscopic brown powder, which gave *methyl-2,4-dinitrophenyldiphenylphosphonium picrate*, m. p. 181.5—182° (acetone-ethanol) (Found: C, 50.25; H, 3.1; N, 11.9.  $C_{25}H_{18}N_5O_{11}P$  requires C, 50.35; H, 3.05; N, 11.8%).

The phosphine with the ester (III) gave an almost immediate purple colour and a gummy deposit which was mainly yellow with reddish-purple striations; the deposit, left in contact with the reaction mixture for 2 weeks, formed a hard cream-coloured solid. The deposit, before or after this change, readily afforded the above picrate, m. p. 181—182°. Investigations of the mother-liquors revealed the presence of the much more soluble methopicrate, m. p. 115—117°, which after careful fractional crystallisation was obtained in almost the same quantity as the "abnormal" picrate.

The initial gummy deposit, purified by precipitation as before, gave a hygroscopic purple powder, m. p. 96° (blackening from 78°) (E.T.) (Found: C, 51.7; H, 4.6; N, 5.8.  $C_{20}H_{19}N_2O_7PS$  requires C, 51.95; H, 4.1; N, 6.1%).<sup>16</sup>

*Ethyldiphenylphosphine*, b. p. 108—111°/0.3 mm. (lit.,<sup>17</sup> 184°/22 mm.) gave a methiodide, m. p. 186—187° (lit.,<sup>20</sup> 182—183°) (ethanol-ether), and a methopicrate, m. p. 100.5—102° (ethanol) (lit.,<sup>18</sup> 86°) (Found: C, 55.2; H, 4.4; N, 9.4. Calc. for  $C_{21}H_{20}N_3O_7P$ : C, 55.15; H, 4.4; N, 9.2%). With the ester (I) it gave an oil, hardened to a white gum by rubbing with petroleum; this *methotoluene-p-sulphonate* could not be obtained solid, but readily gave the methopicrate, m. p. 101—102°.

The phosphine with 1-chloro-2,4-dinitrobenzene developed a purple colour during *ca.* 5 min. and set aside overnight deposited a brown deliquescent solid. The conversion of this solid into a picrate gave considerable difficulty, but the addition of a filtered aqueous solution to an excess of saturated aqueous sodium picrate very slowly deposited *ethy-2,4-dinitrophenyldiphenylphosphonium picrate*, m. p. 136—137° (ethanol-acetone-petroleum) (Found: C, 51.55; H, 3.6; N, 11.8.  $C_{26}H_{20}N_5O_{11}P$  requires C, 51.2; H, 3.3; N, 11.5%).

Addition of the ester (III) to the phosphine solution gave an immediate yellow colour and a white turbidity, followed after about 5 sec. by the sudden development of the purple colour and deposition of a purple gum, which after about 4 hr. had become yellow. The gum gave a crude picrate which, recrystallised as before, gave the same picrate, m. p. 137.5—138.5°. Concentration and fractional crystallisation then yielded the far more soluble methopicrate, m. p. 97—99°.

*Methyl-di-p-tolylphosphine*,<sup>9</sup> b. p. 125—127°/0.45 mm. (lit.,<sup>21</sup> 345°), gave a methiodide, m. p. 159.5—161° (ethanol), and a *methopicrate*, m. p. 134—135° (ethanol) (Found: C, 56.2; H, 4.9; N, 8.65.  $C_{22}H_{22}N_3O_7P$  requires C, 56.15; H, 4.7; N, 8.9%). The phosphine solution with 1-chloro-2,4-dinitrobenzene gave a reddish-purple coloration and deposit, but after 20 min. both the solution and the deposit were dark brown. The latter, when rubbed with ether, formed a deliquescent powder; this gave a picrate, which after repeated recrystallisations from aqueous ethanol softened at *ca.* 110° with m. p. 180—190° (decomp.).

The phosphine with the ester (III) gave the usual purple gum, which in contact with the reaction mixture became yellow after 5 days. It afforded a picrate, initially a black sticky gum, which after considerable purification, followed by slow crystallisation from aqueous ethanol, softened at 78° and ultimately melted at 140° (decomp.): this *methyl-2,4-dinitrophenyldi-p-tolylphosphonium picrate* (Found: C, 51.3; H, 3.7; N, 11.0.  $C_{27}H_{22}N_5O_{11}P$  requires C, 52.0; H, 3.6; N, 11.25%) had an infrared spectrum which was identical with that of the previous picrate. Concentration of the picrate mother-liquors followed by fractional crystallisation from ethanol gave the methopicrate, m. p. 124—127.5°; its infrared spectrum was identical with that of the authentic methopicrate.

*p-Methoxyphenylmethylphenylphosphine*, which with the ester (I) gave the colourless salt (II),<sup>22</sup> with the ester (III) gave a purple deposit which, after precipitation as before, afforded a purple powder, m. p. 106° (decomp., blackening from 80°) (E.T.) (Found: C, 51.8; H, 4.1; N, 5.9.  $C_{21}H_{21}N_2O_8PS$  requires C, 51.2; H, 4.3; N, 5.7%).<sup>16</sup>

<sup>20</sup> S. T. D. Gough and S. Trippett, *J.*, 1961, 4263.

<sup>21</sup> A. Michaelis, *Annalen*, 1901, 315, 43.

<sup>22</sup> R. C. Hinton and F. G. Mann, *J.*, 1959, 2835.

Trimethylarsine methiodide was converted into the *methopicrate*, m. p. 308—309° (ethanol with 5% acetone) (Found: C, 33.25; H, 3.7; N, 11.75.  $C_{10}H_{14}AsN_3O_7$  requires C, 33.1; H, 3.9; N, 11.6%). The arsine in toluene with the ester (III) gave a purple colour and a crystalline reddish-purple deposit which when set aside overnight became pink. Crystallisation from ethanol rapidly discharged the colour and gave *tetramethylarsonium 2,4-dinitrobenzenesulphonate*, m. p. 186.5—188° (Found: C, 32.0; H, 3.8; N, 7.5.  $C_{10}H_{15}AsN_2O_7S$  requires C, 31.85; H, 4.0; N, 7.3%); it gave the *methopicrate*. The arsine with 1-chloro-2,4-dinitrobenzene gave no significant colour changes but deposited a cream-coloured solid, which in turn afforded *trimethyl-2,4-dinitrophenylarsonium picrate*, m. p. 191—191.5° (ethanol) (Found: C, 35.1; H, 3.0; N, 13.9.  $C_{15}H_{14}AsN_5O_{11}$  requires C, 34.9; H, 2.7; N, 13.6%).

Diethylphenylarsine gave a *methopicrate*, m. p. 85—87° (ethanol) (Found: C, 44.8; H, 4.4; N, 9.4.  $C_{17}H_{20}AsN_3O_7$  requires C, 45.1; H, 4.45; N, 9.3%). The arsine with the ester (III) gave no colour change but deposited *diethylmethylphenylarsonium 2,4-dinitrobenzenesulphonate*, m. p. 124—125° (ethanol) (Found: C, 43.0; H, 4.65; N, 6.0;  $C_{17}H_{21}AsN_2O_7S$  requires C, 43.2; H, 4.5; N, 6.0%); it gave the *methopicrate*. The arsine solution with 1-chloro-2,4-dinitrobenzene became brown and a dark gum separated during 1 week, when the reaction was completed by boiling for 1.5 hr. The gum gave a picrate, m. p. 131—132° (ethanol); unsatisfactory analyses were obtained for two preparations but the product was probably the "abnormal" picrate.

Triphenylarsine gave a methiodide, m. p. 176—177° (lit.,<sup>23</sup> 176°) (ethanol), and a *methopicrate*, m. p. 145.5—146.5° (ethanol) (Found: C, 54.7; H, 3.6; N, 7.7.  $C_{25}H_{20}AsN_3O_7$  requires C, 54.65; H, 3.7; N, 7.6%). The arsine, when boiled in toluene with the ester (I), gave an oily metho-toluene-*p*-sulphonate which could not be crystallised but gave the *methopicrate*. The arsine in toluene, when warmed with the ester (III), readily gave the crystalline *methyltriphenylarsonium 2,4-dinitrobenzenesulphonate*, m. p. 191—192.5° (ethanol) (Found: C, 52.9; H, 3.9; N, 5.0.  $C_{25}H_{21}AsN_2O_7S$  requires C, 52.8; H, 3.6; N, 4.9%); it gave the *methopicrate*. The arsine, boiled in toluene with 1-chloro-2,4-dinitrobenzene for 2.5 hr., gave only the impure oily unchanged arsine.

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<sup>23</sup> A. Michaelis, *Annalen*, 1902, **321**, 166.

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