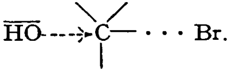
429. *Experiments on the Interaction of Hydroxy-compounds and Phosphorus and Thionyl Halides in the Absence and in the Presence of Tertiary Bases. Part VIII.*

By W. GERRARD, A. NECHVATAL, and BARBARA M. WILSON.

tert.-Butylcarbinol (*neo*pentyl alcohol) interacts readily with thionyl and phosphorus chlorides, thereby forming the chloro-esters, RO·SOCl and $RO{\cdot}PCl_2$. In an ethereal solution containing pyridine, thionyl chloride effects an almost quantitative precipitation of pyridine hydrochloride and the formation of the sulphite, $(RO)_2SO$. In a similar way, the phosphite, $(RO)_2PHO$, was isolated in the phosphorus trichloride system, and corresponding experiments with phosphorus tribromide and with the oxyhalides of phosphorus are described.

Halogen and the hydrogen phosphite afforded the halogenophosphates, $(RO)_2POCl$, $(RO)_2POBr$, and, although chlorine reacted with the sulphite, definite information as to the consequences have not yet been obtained.

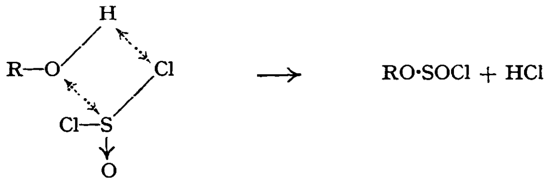
Therefore, although these experiments provide further evidence of the reluctance which *tert.*-butylcarbinol shows towards replacement of the hydroxyl group by halogen, presumably because this involves a sterically hindered " end-on " approach to the alcoholic carbon atom, they demonstrate a ready response to four-centre " broadside " reactions concerning the oxygen–hydrogen bond.

A REMARKABLE observation was made by Dostrovsky, Hughes, and Ingold (*J.*, 1946, 173) that *tert.*-butylcarbinyl bromide (*neo*pentyl bromide) showed little response to the S_N1 ethoxylation mechanism, in accordance with its constitution as a primary bromide but nevertheless demonstrating a rapid damping of the influence of the three methyl groups attached to the carbon atom adjacent to the reactive one. More remarkable, indeed, was the observation that the rate constant for the S_N2 mechanism was extremely small, the activation energy being abnormally large. This reluctance has been explained in terms of steric hindrance to end-on approach of the entering group,  $\overline{\mathrm{HO}}\dashrightarrow\mathrm{C}{-}\cdots\mathrm{Br}$.

Whitmore and Rothrock (*J. Amer. Chem. Soc.*, 1932, **54**, 3431) had previously drawn attention to the resistance which *tert.*-butylcarbinol shows to replacement of its hydroxyl group by a halogen atom through the agency of, *e.g.*, thionyl chloride and phosphorus tribromide.

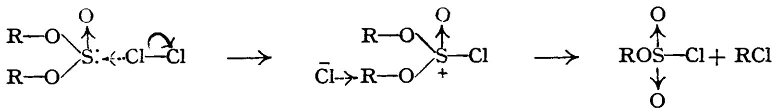
Therefore it appeared of interest to study what we term the " broadside " (four-centre) reactions of *tert.*-butylcarbinol with inorganic halides, such reactions being concerned with the link between the oxygen and the hydrogen atom of the hydroxyl group.

By the addition of the alcohol to thionyl chloride, *tert.*-butylcarbinyl chlorosulphinate, RO·SOCl, was readily formed. Addition of either this product (1 mol.) or thionyl chloride (0·5 mol.) to an ethereal solution of the alcohol (1 mol.) and pyridine (1 mol.) gave rise immediately to di-*tert.*-butylcarbinyl sulphite, $(RO)_2SO$, and pyridine hydrochloride. Further-more, interaction between the sulphite and thionyl chloride occurred, and the chlorosulphinate was formed. These reactions are depicted as " broadside " reactions, and for this type *tert.*-butylcarbinol behaves as does, *e.g.*, butan-1-ol (Gerrard, *J.*, 1939, 99; 1940, 218) :



Gerrard suggested that pyridine facilitates this process by formation of the hydrogen bond, $ROH{:}NC_5H_5$, and Cleverdon and Smith (*Chem. and Ind.*, 1948, 29) have obtained dipole-moment evidence of the formation of this bond.

The behaviour of the chlorosulphinate on being heated with a small amount of pyridine hydrochloride was very different from that of a number of chlorosulphinates examined by French and Gerrard (*J.*, 1949, 3326). Instead of a clean and smooth conversion into the chloride, RCl, and sulphur dioxide at a relatively low temperature (60—70°), the chlorosulphinate showed a reluctance to decompose even at 110°. The products obtained were thionyl chloride, the sulphite $(RO)_2SO$, and what was most likely a mixture of *tert.*-amyl chloride and *tert.*-butylcarbinyl chloride. Although the sulphite readily absorbed a molecular proportion of chlorine (cf. Cross and Gerrard, *J.*, 1949, 2686) there was no definite evidence available to indicate that the reaction had proceeded by the sequence :



Tri-*tert.*-butylcarbinyl phosphite was the main distilled product of the interaction of the alcohol (1 mol.) and the trihalide (0·33 mol.) in the presence of pyridine (1 mol.), although it was contaminated by a little of the hydrogen phosphite. The precipitation of the pyridine hydrohalide was rapid in ethereal solution, and the behaviour of the system was similar to that of the butan-1-ol system (Gerrard, *J.*, 1940, 464).

There is evidence (Gerrard, *loc. cit.*; *J.*, 1944, 85; 1945, 848) for believing that in the examples of such alcohols as butan-1-ol and octan-2-ol, the chloride RCl is formed by the rapid interaction of hydrogen chloride and the tri-ester which are formed during the primary reactions occurring between the alcohol (1 mol.) and the trichloride (0·33 mol.). This rapid attack very probably follows the course: $(RO)_3P{:} + HCl \dashrightarrow Cl^- + (RO)_3\overset{+}{P}{:}H \dashrightarrow ClR + (RO)_2PHO$. Subsequent dealkylation of the phosphite is slow at room temperature, presumably because the " lone-pair " mechanism is no longer available. It is interesting to find that, in the example of *tert.*-butylcarbinol, the interaction with phosphorus trichloride or tribromide (0·33 mol.) leads to the isolation of the phosphite as the main product, no halide RX being found.

When the alcohol was added to excess of trichloride, *tert.*-butylcarbinyl dichlorophosphinite, $RO{\cdot}PCl_2$, was isolated in 80% yield.

The phosphate, $(RO)_3PO$, was obtained by means of phosphorus oxychloride or oxybromide, in the presence of pyridine.

Interaction of chlorine and the tri-*n*-butyl phosphite was studied by Gerrard (*loc. cit.*), and McCombie, Saunders, and Stacey (*J.*, 1945, 380) have shown that halogens readily react with hydrogen phosphites to give the halogenophosphate $(RO)_2POX$ and hydrogen halide (cf. Gerrard and Philip, *Research*, 1948, **1**, 477). End-on approach to the carbon atom is not involved, and we readily obtained di-*tert.*-butylcarbinyl dichloro- and dibromo-phosphonate. These afforded the phosphate, $(RO)_3PO$, by interaction with alcohol and pyridine.

As Dostrovsky, Hughes, and Ingold (*Nature*, 1947, **160**, 901) felt that Gerrard and Nechvatal (*ibid.*, 1947, **159**, 812) had not given the right emphasis in their interpretation of statements by Whitmore and Rothrock (*loc. cit.*), we deem it desirable to elucidate this matter now for future reference.

Whitmore and Rothrock described, in some detail, evidence of interaction with sulphuric acid involving the replacement of the hydrogen atom of the hydroxyl group. Their evidence concerning thionyl chloride was presented in such a way as to compel a reader to infer that neither the hydroxyl group as a whole, nor the hydrogen atom of the hydroxyl group had undergone reaction : the authors specifically declared that the alcohol (80%) had been recovered. According to our experiments, those authors had the sulphite $(RO)_2SO$ (0·5 mol., from 1 mol. each of alcohol and pyridine) and thionyl chloride (about 0·5 mol.) in the ethereal solution after the initial mixing. Either the temperature of the reaction mixture was sufficiently high, during the period of storage, to convert a considerable amount of the sulphite into the chlorosulphinate, which water would hydrolyse to the alcohol, or the treatment with water (presumably given) was so unusually vigorous as to hydrolyse a considerable amount of the sulphite itself. In their phosphorus tribromide experiment, they obtained a yield of 14% of the bromide RBr; but apart from this, they claim recovery of the alcohol.

Therefore their statement " the inactivity of *neo*pentyl alcohol to heat and reagents has been demonstrated " applied precisely to their experiment with thionyl chloride (as their evidence was presented) with respect both to the hydroxyl group as a whole and to the hydrogen atom of the hydroxyl group considered separately. To their experiment with phosphorus tribromide their statement applied qualitatively (inactivity replaced by low activity) to the replacement of the hydroxyl group, since a yield of 14% of the bromide was isolated, but again applied precisely to the replacement of hydrogen separately.

EXPERIMENTAL.

Notes on Procedure.—Dry ether, kept over sodium, was used throughout. Precipitates obtained when pyridine was used in an experiment were separated by filtration and kept in a vacuum for 1—2 hours before being weighed and analysed, without further treatment. Unless otherwise stated, "aqueous treatment" refers to washing first with water, then with a dilute solution of sodium carbonate, followed by drying (K_2CO_3) and storage over sodium sulphate. When pyridine had been used, washing with a dilute solution of sulphuric acid was carried out before treatment with the solution of carbonate.

Interaction of tert.*-Butylcarbinol and Thionyl Chloride in the Presence of Pyridine.*—Thionyl chloride (2·97 g., 0·5 mol.) in 15 c.c. of ether was added dropwise to a well-shaken solution of the alcohol (4·4 g., 1 mol.) and pyridine (3·95 g., 1 mol.) in ether (20 c.c.) at −15°. Separation of pyridine hydrochloride (5·31 g., 92·1%) commenced immediately (Found : Cl, 30·2; C_5H_5N, 68·0. Calc. for C_5H_5N,HCl : Cl, 30·8; C_5H_5N, 68·4%), and from the washed ethereal solution *di-*tert.*-butylcarbinyl sulphite* (85%), b. p. 103°/12 mm., n_D^{16} 1·4263 (Found : SO_2, 28·6. $C_{10}H_{22}O_3S$ requires SO_2, 28·8%), was obtained.

When 1·2 mols. of thionyl chloride were used instead of 0·5 mol. and the primary reaction mixture was set aside for 12 hours in order to follow Whitmore and Rothrock's procedure in that detail, the products isolated were *tert.*-butylcarbinol (0·3 g.), b. p. 30°/15 mm., and the sulphite (3·5 g.), b. p. 105—106°/15 mm. (from 5·0 g. of alcohol).

*Interaction of Di-*tert.*-butylcarbinyl Sulphite and Thionyl Chloride.*—Thionyl chloride (1·63 g., 1·1 mols.) was added dropwise to the sulphite (2·77 g., 1 mol.) at −15° and agitated by a stream of dry nitrogen, and the resulting mixture was then kept for 1 hour at 17° and for 30 minutes at 70—80°. On distillation without aqueous treatment, tert.*-butylcarbinyl chlorosulphinate* (2·78 g.), b. p. 64—67°/12 mm. (Found : Cl, 19·4. $C_5H_{11}O_2ClS$ requires Cl, 20·8%, see later), and di-*tert.*-butylcarbinyl sulphite (0·725 g.), b. p. 102°/12 mm. (Found : SO_2, 28·6%), were obtained. The chlorosulphinate fumed in moist air and reacted vigorously with water.

Interaction of tert.*-Butylcarbinol and Thionyl Chloride.*—The alcohol (4·4 g., 1 mol.) in ether (15 c.c.) was added dropwise to thionyl chloride (9·31 g.) at −15°. After the mixture had been gradually (1 hour) warmed to 70°, it was distilled, whereupon *tert.*-butylcarbinyl chlorosulphinate (6·9 g.), b. p. 58·5°/11 mm., n_D^{14} 1·4515 (Found : Cl, 20·7; SO_2, 36·1. Calc. for $C_5H_{11}O_2ClS$: Cl, 20·8; SO_2, 37·6%, see previous experiment), and di-*tert.*-butylcarbinyl sulphite (0·55 g.), b. p. 102°/12 mm., n_D^{14} 1·4268, were obtained.

Interaction of tert.*-Butylcarbinol and* tert.*-Butylcarbinyl Chlorosulphinate in the Presence of Pyridine.*—The chlorosulphinate (2·55 g., 1 mol.) was added dropwise to a shaken mixture of alcohol (1·32 g., 1 mol.) and pyridine (1·19 g., 1 mol.) in ether (15 c.c.) at −15°. Pyridine hydrochloride (1·50 g.) (Found : Cl, 30·05; C_5H_5N, 68·3%) began to form immediately, and after 1 hour at 15° filtration and aqueous treatment of the ethereal solution led to isolation of di-*tert.*-butylcarbinyl sulphite (3·0 g., 91%), b. p. 99—100°/10 mm., $n_D^{15·5}$ 1·4268 (Found : SO_2, 28·6%).

Decomposition of the Chlorosulphinate.—The chlorosulphinate (5·35 g.) was heated at 70° for one hour with 0·03 g. (0·01 mol., approx.) of pyridine hydrochloride. On distillation of the reaction mixture, the chlorosulphinate (4·78 g.) was recovered. The temperature of the recovered material (again in presence of pyridine hydrochloride, 0·03 g.) was raised from 70° to 110° during 1 hour. A colourless liquid (0·25 g.) distilled. Distillation of the reaction mixture at 12 mm. then resulted in the recovery of 3·0 g. of the chlorosulphinate, the sulphite R_2SO_3 (0·3 g.) also being obtained.

The chlorosulphinate (6·0 g.) and hydrochloride (0·04 g.) were heated for 2 hours at 110°, and then the temperature was raised to 150° during 1 hour. The colourless distillate (3·25 g.), b. p. 76—81°, fumed in air, and from behaviour on re-distillation and analysis appeared to be a mixture of thionyl chloride (1·41 g.), *tert.*-amyl chloride, and *tert.*-butylcarbinyl chloride (total chloride, RCl, 1·66 g.). The chloride (RCl) distillate was dissolved in ether and given aqueous treatment. A distillate (1·5 g.), b. p. 83—84° (Found : C, 56·6; H, 10·4; Cl, 31·7. Calc. for $C_5H_{11}Cl$: C, 56·3; H, 10·3; Cl, 33·3%), was obtained.

From hydrolytic behaviour of this material in the presence of water we believe it to be a mixture of the two chlorides just referred to, these having very nearly the same b. p.

The residue (1·0 g.) from the primary heat treatment had b. p. 100—101°/15 mm. (Found : SO_2, 27·6%) and was identified as the sulphite $(RO)_2SO$.

When pyridine hydrochloride was omitted for the heat treatment, there was no distillate whilst the chlorosulphinate was kept at 110° for 2 hours. On the temperature being slowly raised (4 hours) to 160° a distillate (1·3 g.), b. p. 74°, of a similar character to that of the previous experiment, was obtained. 0·5 G. of chlorosulphinate was recovered, and 0·7 g. of sulphite was obtained.

*Interaction of Chlorine and Di-*tert.*-butylcarbinyl Sulphite.*—After chlorine had been passed through the sulphite (6·6 g.) for 1 hour at −10°, the liquid became yellow, indicating excess of (unchanged) chlorine. When attempts were made to isolate a chloride RCl, the material decomposed (oil-bath, 110°), hydrogen chloride and sulphur dioxide being evolved. Continuing the process under reduced pressure we obtained the sulphite (1·0 g.) and a thick tar (4·5 g.). Treatment with water and a solution of sodium carbonate, followed by drying before distillation, led to no improvement.

Interaction of tert.*-Butylcarbinol and the Halides and Oxyhalides of Phosphorus in the Presence of Pyridine.*—(1) *Trichloride.* Phosphorus trichloride (2·29 g., 0·33 mol.) in ether (15 c.c.) was added to a well-shaken mixture of the alcohol (4·4 g., 1 mol.) and pyridine (3·95 g., 1 mol.) in ether (15 c.c.) at −15°. Pyridine hydrochloride (5·29 g., 92%) (Found: Cl, 30·4; C_5H_5N, 68·5%) was formed immediately, and evaporation of the ethereal solution, after aqueous treatment, left a residue (4·4 g. Calc. for the tri-ester, 4·8 g.) (Found : P, 10·0; no chlorine. The *tri-ester* $C_{15}H_{33}O_3P$ requires P, 10·6%). From this was obtained *di-*tert.*-butylcarbinyl hydrogen phosphite* (3·84 g.), b. p. 116—119°/13 mm., n_D^{13} 1·4200 (Found: P, 14·0. $C_{10}H_{23}O_3P$ requires P, 13·95%). When the filtrate from the reaction mixture was distilled without treatment with water, a white solid, b. p. 71°/1 mm. (Found : P, 11·3%), accounted for nearly all the alcohol used. From its behaviour with hydrogen halides, we conclude that this product was the tri-ester mixed with a little hydrogen phosphite.

(2) *Tribromide.* Pyridine hydrobromide (7·86 g., 98·3%) (Found : Br, 48·9; C_5H_5N, 48·0. Calc. for C_5H_5N,HBr : Br, 50·0; C_5H_5N, 49·4%) and, from the washed ethereal solution, a residue (4·12 g.) (Found : P, 10·3; Br, 0%) were obtained. Distillation afforded *di-tert.*-butylcarbinyl hydrogen phosphite (3·6 g.), b. p. 115—117°/12 mm. (Found : P, 14·0%). The weight of alcohol used was the same as in the previous experiment.

(3) *Oxychloride.* Phosphorus oxychloride (2·56 g., 0·33 mol.) in ether (15 c.c.) was added to the alcohol (4·4 g., 1 mol.) and pyridine (3·95 g., 1 mol.) in ether (20 c.c.) at −15°. Although precipitation of the hydrochloride commenced immediately, it was incomplete even after 16 hours at 15°. The precipitate (3·95 g., 68·5%) (Found : Cl, 30·7; C_5H_5N, 68·6%) was separated, and from the washed ethereal solution a residue (4·35 g.) (Found : P, 12·0; Cl, 0%) was obtained which afforded a white sublimate (0·3 g.), b. p. 30—40°/20 mm., a waxy solid (*tri-*tert.*-butylcarbinyl phosphate*) (2·3 g.), b. p. 149—152°/14 mm., m. p. 80° (Found : P, 10·9. $C_{15}H_{33}O_4P$ requires P, 10·05%), and a brown residue.

(4) *Oxybromide.* Phosphorus oxybromide, prepared as described by Gerrard, Nechvatal, and Wyvill (*Chem. and Ind.*, 1947, 437) (4·90 g., 0·33 mol.), in ether (20 c.c.) was added to the alcohol (4·52 g., 1 mol.) and pyridine (4·06 g., 1 mol.) in ether (20 c.c.) at −15°. Precipitation of pyridine hydrobromide (7·65 g., 93·4%) (Found : Br, 49·9; C_5H_5N, 49·5%) commenced immediately and proceeded much more rapidly than with the oxychloride. The mixture was filtered after 2 days, and on evaporation of the washed ethereal solution there was left a white solid (4·7 g.) (Calc. for the tri-ester, 5·1 g.) (Found : P, 10·1; Br, 0%), which on distillation afforded a white waxy solid, b. p. 152°/11 mm., m. p. 84—85° (Found : P, 10·0%), and a residue, 0·2 g.

Interaction of Phosphorus Trichloride and tert.*-Butylcarbinol.*—(1) The trichloride (2·29 g., 0·33 mol.) was added dropwise to the alcohol (4·4 g., 1 mol.) at −15°, nitrogen being passed through the reaction vessel and thence to absorption tubes containing pellets of potassium hydroxide. Hydrogen chloride (0·034 g.) was evolved during mixing, a further 0·96 g. whilst the mixture warmed to 15°, and a further 0·165 g. whilst it was warmed to 50—60° for 15 minutes, the total weight being equivalent to 0·66 mol. The product then yielded a sublimate of *tert.*-butylcarbinol (0·37 g.), b. p. 30—35°/10 mm., m. p. 45°, and the hydrogen phosphite $(RO)_2P\cdot OH$ (3·32 g.), b. p. 109°/10 mm., n_D^9 1·4200 (Found : P, 13·9%).

(2) The alcohol (1·76 g., 1 mol.) in ether (10 c.c.) was added to the trichloride (4·4 g.) at −15°, whilst nitrogen was passed through the reaction liquid. Hydrogen chloride (1 mol.) was evolved when the reaction mixture was set aside for 3 hours at 15°, and for 30 minutes whilst it was warmed to 70°. Trichloride carried over was allowed for in this estimation. tert.*-Butylcarbinyl dichlorophosphinite* was obtained as a colourless fuming liquid (3·03 g., 80%), b. p. 47·5—48°/10 mm., without residue (Found : Cl, 37·6; P, 16·4. $C_5H_{11}OCl_2P$ requires : Cl, 37·6; P, 16·4%).

Interaction of Phosphorus Tribromide and tert.*-Butylcarbinol.*—(1) The tribromide (4·52 g., 0·33 mol.) was added dropwise to the alcohol (4·4 g., 1 mol.) at −15°, a stream of nitrogen being passed through as in the experiment with the trichloride. After the reaction mixture had been kept at 15° for 1·5 hours and gradually warmed (30 minutes) to 80°, the alcohol (0·5 g.), b. p. 30—35°/9 mm., m. p. 43°, the hydrogen phosphite (2·06 g.), b. p. 106—108°/9 mm., n_D^9 1·4240 (Found: P, 14·4%), and a residue of tar (0·64 g.) were obtained. In a second experiment the primary mixture, obtained by addition of the tribromide (4·5 g., 0·33 mol.) dropwise to the alcohol (4·4 g., 1 mol.) without solvent at −10°, was set aside for 12 hours at 15°. It was then mixed with ice (wash-water contained 0·0064 g. of P), and the dried ethereal extract was evaporated at low pressure, the temperature being slowly raised to 100°. A liquid (0·3 g.) which appeared to be a mixture of the two halides, RBr, was collected. The residue (3·04 g.) (Found : P, 12·8%) had b. p. 120°/20 mm. and distilled completely.

Interaction of Halogens and Hydrogen Halides and the Phosphorous Ester.—Passage of hydrogen chloride into the solid tri-ester, obtained as described, resulted in the rapid formation of the hydrogen phosphite, but it was not clear whether chloride RCl was formed.

Passage of hydrogen bromide and of hydrogen iodide through the "phosphite" product (4·4 g.) obtained by distillation after water treatment led to *tert.*-amyl bromide (0·3 g.), b. p. 110—115° (decomp.), and *tert.*-amyl iodide (0·1 g.), b. p. 122°, but the bulk of the original material was recovered as hydrogen phosphite. When hydrogen bromide was passed through the recovered hydrogen phosphite at 15°, no *tert.*-amyl bromide was isolated, the bulk of the hydrogen phosphite being recovered.

Chlorine was passed into the hydrogen phosphite (4·04 g.) at room temperature for 15 minutes, after which the liquid became yellow. During this period, the liquid became warm, and hydrogen chloride was copiously evolved. From the residue, *di*-tert.*-butylcarbinyl chlorophosphonate*, $(RO)_2POCl$ (3·9 g.), b. p. 115—120°/12 mm., 90°/2 mm., m. p. 42·5°, was obtained as a white solid (Found: Cl, 13·4. $C_{10}H_{22}O_3ClP$ requires Cl, 13·8%).

This ester (2·5 g., 1 mol.) in ether (10 c.c.) was added to ethyl alcohol (0·8 g.) and pyridine (1·5 g.) in ether (10 c.c.) at −10°. Precipitation of pyridine hydrochloride commenced during the dropwise mixing and appeared to be well advanced after a few minutes. The mixture was set aside for 2 days, however, before filtration. Pyridine hydrochloride (0·78 g.) (Found: Cl, 30·3; C_5H_5N, 67·5%) was separated, and from the filtrate a liquid (1·8 g.), b. p. 83·5°/1 mm., and a residue (0·3 g.) were obtained. When *tert.*-butylcarbinol was used instead of ethyl alcohol, the rate of precipitation of pyridine hydrochloride was much slower, and was incomplete after 2 days. Unchanged alcohol (0·4 g.), b. p. 38°/12 mm., unchanged chlorophosphonate (0·46 g.), b. p. 115—116°/12 mm., and the tri-ester, $(RO)_3PO$ (0·94 g.), m. p. 84° (Found: P, 9·6%), were obtained.

Bromine vapour (3·6 g., 1·2 mols.) was passed into the hydrogen phosphite (4·4 g.) at room temperature. The mixture became warm and was cooled, and hydrogen bromide was copiously evolved. Distillation afforded *di*-tert.*-butylcarbinyl bromophosphonate* as a white solid (2·0 g.), b. p. 90°/1 mm. (Found: Br, 25·4. $C_{10}H_{22}O_3BrP$ requires Br, 26·6%), and a second white solid (1·0 g.), b. p. 160°/1 mm. (Found: Br, 3·0; P, 15·3%). Addition of the bromophosphonate (1·58 g.) to an ethereal solution of pyridine and ethanol caused pyridine hydrobromide (0·73 g.) to be precipitated much more readily than the hydrochloride was precipitated by the chlorophosphonate.

THE NORTHERN POLYTECHNIC, LONDON, N.7.

[*Received, May 11th,* 1950.]