

765. *Acylation and Allied Reactions catalysed by Strong Acids.
Part XV.* Some Reactions of Simple Alkyl Perchlorates.*

By H. BURTON, D. A. MUNDAY, and P. F. G. PRAILL.

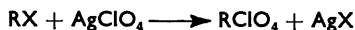
Alkylation of anisole and benzene by methyl, ethyl, *n*-propyl, and the four butyl perchlorates has been studied. Two types of reaction appear to be taking place: (1) nuclear alkylation occurring almost simultaneously with the formation of the alkyl perchlorate in solution, (2) subsequent alkylation by the alkyl perchlorate in certain cases. Detailed mechanisms have not been determined. The possible importance of these types of reaction in the more conventional Friedel-Crafts reactions is discussed.

ALTHOUGH acylation and alkylation by the Friedel-Crafts reaction are considered to be similar, it is also recognised that alkylation processes are more difficult to study because of the numerous side reactions that may occur. In our previous work with acyl and aralkyl perchlorates we have observed that nuclear alkylation and acylation do not seem to be completely analogous and we have made reference to this from time to time.¹ Some further indications of this difference are now presented.

* Part XIV, *J.*, 1955, 3089.

¹ Burton and Prail, (a) *J.*, 1951, 522; (b) *J.*, 1953, 827.

A preliminary account of the reaction between silver perchlorate and methyl iodide in benzene and in anisole has been reported,² and this work has now been extended to incorporate some other simple alkyl compounds. When an alkyl halide is added to a solution of silver perchlorate in an aromatic solvent, metathesis takes place:



If the aromatic component is suitably constituted, nuclear alkylation occurs. We found, for example, that methyl, ethyl, *n*-propyl, *n*-butyl, *isobutyl*, *sec.*-butyl, and *tert.*-butyl iodide all gave alkylphenyl methyl ethers when they were added to a solution of silver perchlorate in anisole. Although we were unable to determine the distribution of isomers in the products, it would seem that alkylation occurred predominantly in the *para*-position, since, although the products do not behave as pure substances, we have been unable to isolate any other than *para*-derivatives. However, we do not wish to overemphasize this since prolonged treatment with strong acid in the demethylation of the ethers was a prerequisite to their identification, and it is well known that such conditions might lead to rearrangement of alkyl substituents. With benzene as solvent the *n*-alkyl halides gave extremely small amounts of alkylated derivatives, but, as might be expected, *tert.*-butyl halides gave *tert.*-butylbenzene (0.5 mole per mole of perchlorate) and polyalkyl derivatives, as well as some unsaturated materials. The alkylation of toluene by *tert.*-butyl perchlorate has been reported³ and it has been stated that *n*-butyl perchlorate does not attack aromatic hydrocarbons in the presence of excess of silver perchlorate.

It will be seen from the Table that for a given time the yield of alkylated anisole increases in the series, Bu^t > Bu^s > Buⁿ > Prⁿ > Et > Me. Further, although the yield of alkylated product increases with time in the case of Bu^t and Bu^s, those for the Buⁿ and Me derivatives undergo no increase after 4 hours. The significance of these observations will be referred to below.

Addition of nitromethane in any of the above experiments led to the formation of high-boiling intractable materials and resulted in a decreased yield of the monoalkylated derivatives. In some cases it was found that the products contained nitrogen and thus some attack on the solvent must have taken place. In our work on acylation⁴ nitromethane was found to be a very suitable polar medium and little or no attack on the solvent was observed, a marked contrast to our present experience. In general, the use of nitromethane was avoided as far as possible.

The alkyl perchlorates are violent explosives,^{5,6} so we carried out our experiments under the mildest conditions and did not heat any of the mixtures. Further, it was found necessary to take special precautions in working up the reaction mixtures. We found it extremely difficult to remove all traces of organic perchlorate by the usual washing techniques. This was especially true if the benzene used contained traces of sulphur compounds; in such cases a black amorphous solid separated during the distillation of the product. This undesirable material, which was found to be explosive, could be avoided if the benzene was previously refluxed with Raney nickel. However, we found that the safest procedure was to wash the reaction mixture free from water-soluble perchlorate and then to treat the organic phase with an excess of alcoholic potassium hydroxide. The precipitated potassium perchlorate could then be readily removed. The amount of potassium salt obtained in this way can be taken as a rough measure of unchanged alkyl perchlorate but we do not wish to overestimate the importance of this because the relative rates of hydrolysis of the alkyl perchlorates during the initial washing with water, were not determined.

Whilst our present results are not sufficiently conclusive to attribute them to any particular mechanism it is of interest to see how well they can be explained by available information.

The reaction between alkyl halides and silver salts in hydroxylic solvents has been

² Burton and Prail, *Chem. and Ind.*, 1951, 939.

³ Cauquil, Barrera, and Barrera, *Bull. Soc. chim. France*, 1953, 1111.

⁴ Burton and Prail, *J.*, 1950, 2034; 1951, 529.

⁵ Meyer and Spormann, *Z. anorg. Chem.*, 1936, 228, 341.

⁶ Burton and Prail, *Analyst*, 1955, 80, 4.

studied extensively⁷⁻¹¹ and the overall reactions may be represented by the following two simultaneous processes :



where R = alkyl, R' = H or alkyl, X = halide, Y = NO₃⁻, OAc⁻, etc. It has been shown that the substitution process is autocatalytic with respect to the silver halide formed and that the heterogeneous reaction is very similar to a homogeneous unimolecular hydrolysis (S_N1). Our results with the *n*-alkyl halides indicate that a similar process may be occurring here. The fact that the yield of *n*-butylanisole does not increase with time can be explained in this way. The only other reasonable explanation would be that a state of equilibrium had been reached, thus :



That this is unlikely is shown by an experiment in which a pre-formed solution of *n*-butyl perchlorate in nitromethane was found not to have alkylating properties towards anisole under the conditions employed. Now it has been shown that addition of nitromethane, or benzene, to reaction mixtures resulted in a marked decrease in the yield of alkylated product, yet if an equilibrium such as the above was involved we should have expected to detect the formation of some butylanisole. We wish to emphasise the point about the conditions under which these experiments were carried out because alkylation might be brought about under more drastic conditions but we have not yet examined this possibility, owing to the hazardous nature of the experiments.

Our results are probably best explained in terms of reactions (1) and (2) with the aromatic component in place of the hydroxylic compound. Whether the alkylation follows an S_N1 or an S_N2 mechanism cannot be determined from our present information. Lack of rearrangement of the *n*-alkyl group is no criterion, since nuclear alkylation may be faster than the rearrangement. This is not unlikely, for *n*-alkyl carbonium ions would be much more reactive than tertiary alkyl cations, and reactions where the latter occur are known to be fast. On the other hand, proof of an S_N1 mechanism in hydroxylic solvents does not mean that the same mechanism holds for aromatic solvents.

Reactions of the type (1) and (2) undoubtedly hold for secondary and tertiary derivatives also. However, we found that in the case of *sec.*-butyl the yield of butylanisole increased with time; further, a pre-formed solution of *sec.*-butyl perchlorate alkylated anisole in good yield, a reaction analogous to acylation with acyl perchlorates in the absence of silver salts. The yield of *tert.*-butylanisole also increased with time, indicating that *tert.*-butyl perchlorate has some stability in anisole. However, in the presence of nitromethane *tert.*-butyl perchlorate underwent preferential self-condensation with the formation of unsaturated derivatives, behaviour which has also been observed for some allyl¹² and benzyl^{1,13} perchlorates. It has not been possible, therefore, to pre-form a solution of *tert.*-butyl perchlorate. Evidence that *tert.*-butyl perchlorate is itself an alkylating agent is quite clear from the formation of polyalkylbenzenes in our experiments with benzene. *tert.*-Butylbenzene would be expected to be alkylated more readily than benzene in spite of the lower concentration of the former. Again, it has been shown¹⁴ that phenol may be converted in good yield into *p-tert.*-butylphenol and 2 : 4-di-*tert.*-butylphenol by mixtures of aqueous perchloric acid and *tert.*-butyl alcohol. The occurrence of carbonium ions in the reactions of some alkyl perchlorates is shown by our results with *isobutyl* perchlorate which gave some tertiary butyl derivatives. It has been reported¹⁵ that optically active 2-bromopentane is nearly completely racemised when it reacts with silver perchlorate in toluene.

⁷ Burke and Donnan, *J.*, 1904, **75**, 555.

⁸ *Idem*, *Z. phys. Chem.*, 1909, **69**, 148.

⁹ Baker, *J.*, 1934, 987.

¹⁰ Hughes, Ingold, *et al.*, *J.*, 1937, 1236, 1243.

¹¹ Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell & Sons, London, 1953, p. 357.

¹² Burton and Munday, *J.*, 1954, 1456.

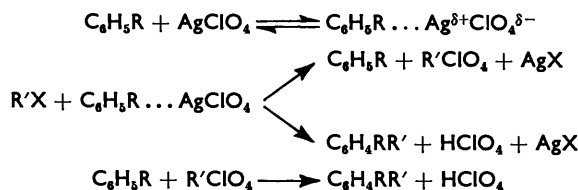
¹³ Praill, Ph.D. Thesis, London, 1954.

¹⁴ Sears, *J. Org. Chem.*, 1948, **13**, 120.

¹⁵ Work by Ingold, Hughes, and Berger, quoted in ref. 3.

Our results indicate that the degree of alkylation which results from the reaction of alkyl halides with silver perchlorate in solution is a function both of the electrophilic activity of the alkyl group and of the nucleophilic activity of the solvent. However, in the absence of more detailed information it would be unjustified to attempt an explanation for the obvious variation in yields in the series Me, Et, Prⁿ, Buⁿ. The initial reaction doubtlessly occurs between the alkyl halide and the solvent-AgClO₄ complex, with a transition state involving a certain proportion of energised molecules which may be sufficiently active to overcome the energy barrier involved in nuclear alkylation. This is a reaction in which adsorption to the silver halide probably plays an essential part (cf. Dostrovsky and Hughes¹⁶). We suggest that similar reactions may also play a rôle in other Friedel-Crafts alkylations, as, for example, attack of an alkyl halide on a solvent-metal halide complex. If this be so, the nature of the ternary systems, alkyl halide-aromatic component-metal halide, becomes of increasing importance and interest. The work of Brown and his co-workers¹⁷ shows that some Friedel-Crafts alkylations exhibit a kinetic dependence of first order in each of the three reactants. The reaction we are suggesting would also conform to this, as does the probable simultaneous reaction of the alkyl halide-metal halide complex with the solvent.

Our results show that the ternary reaction may be accompanied by, and then superseded by, a slower reaction of the alkyl perchlorate with the solvent. The latter reaction might follow an S_N1 or an S_N2 mechanism. These results are summarised by the following equations:



EXPERIMENTAL

Materials.—Silver perchlorate was treated as described previously.¹⁸ Nitromethane and anisole were dried (CaCl₂) and redistilled. Methyl, ethyl, *n*-propyl, and *tert.*-butyl iodide and *tert.*-butyl chloride were redistilled laboratory reagents. *n*-Butyl, *sec.*-butyl, and *isobutyl* iodide were prepared from the corresponding alcohols which were carefully fractionated through a 100-cm. Fenske column with a variable take-off. Benzene was an "AnalaR" reagent which was treated with Raney nickel, dried (Na), and redistilled.

Experiments with anisole.

The alkyl halide (0.05 mole) was either added from a dropping funnel or distilled by using a vacuum-manifold technique, into a cold (<10°) solution of silver perchlorate (0.05 mole) in anisole (0.25 mole). The mixture was stirred by a magnet during the addition. The temperature of the mixture rose slowly to that of the room (20–22°) and was left for the time stated in the Table. Silver halide was filtered off on a weighed, sintered-glass crucible and was washed with ether and with water; the filtrate dropped directly into cold water (250–300 ml.). The ethereal solution was separated and washed with water. A concentrated alcoholic solution of potassium hydroxide (4 g.) was added to the ethereal solution and sufficient ethanol was added to ensure homogeneity. After several hours, any potassium perchlorate which had separated was filtered off and washed with ethanol and aqueous ethanol. The filtrate was diluted with 2–3 vol. of water and extracted thrice with ether. After the combined extracts had been washed with water, the dried (Na₂SO₄) solution was evaporated. The residue was then fractionally distilled. In all cases recovery of silver halide was 95–100%.

Reaction with Methyl Perchlorate.—The yield of the methyl tolyl ether was not high enough

¹⁶ Dostrovsky and Hughes, *J.*, 1946, 169.

¹⁷ Brown and Grayson, *J. Amer. Chem. Soc.*, 1953, **75**, 6285; cf. papers immediately preceding this; Brown and Jungk, *ibid.*, 1955, **77**, 5584.

¹⁸ Burton and Prail, *J.*, 1950, 2034.

for isolation as such, so the bulk of the unchanged anisole was distilled carefully until the temperature began to rise above 151°. The residue (about 4 g.) was oxidised with alkaline potassium

Results

(All quantities are in moles, unless stated otherwise, and to simplify comparison all experimental values have been corrected to correspond to 0.05 mole of alkyl halide.)

Expt. no.	Alkyl halide	Reaction time (hr.)	Yield of monosubst. product	Amt. of KClO ₄ obtained	Expt. no.	Alkyl halide	Reaction time (hr.)	Yield of monosubst. product	Amt. of KClO ₄ obtained
1	MeI	4	0.001	—	9	Bu ^s I	3½	0.015	0.023
2	"	18	0.001	0.036	10	"	18½	0.030	—
3	EtI	21	0.006	0.033	11	"†	22	0.017	—
4	Pr ⁿ I	18	0.008	0.030	12	Bu ^t I	3	0.038	—
5	Bu ⁿ I	18	0.012	0.024	13	Bu ^t Cl	0.8	0.037	—
6	"	4	0.013	0.025	14	"	16	0.042	—
7	"*	18	0.006	0.002	15	"†	—	—	—
8	Bu ⁿ I†	18	—	0.012	16	Bu ^t I	3	0.033	—

Nearly all the yields quoted are minimal and correspond to the monoalkyl-anisole fraction; usually small amounts of low-boiling material and residue were also obtained.

* Nitromethane as solvent.

† Pre-formed perchlorate.

permanganate. The acid produced was isolated in the usual way and identified as *p*-methoxybenzoic acid (m. p. and mixed m. p.).

Reaction with Ethyl Perchlorate.—The fraction, b. p. 160—182° (mostly 180—182°) (0.79 g.), was collected. After demethylation with hydrogen bromide in acetic acid, the phenol was isolated as the 3 : 5-dinitrobenzoate, light brown needles (from methanol), m. p. 131—132° (Vogel¹⁹ gives m. p. 132° for *p*-ethylphenyl 3 : 5-dinitrobenzoate).

Reaction with n-Propyl Perchlorate.—A low-boiling fraction (0.5 g.), b. p. mainly 175—180°, was not identified. The fraction, b. p. 206—214° (mainly 212°), was demethylated with hydrogen bromide in acetic acid. The resulting phenol was converted into its 3 : 5-dinitrobenzoate, m. p. 113—114°, mixed m. p. with 4-*n*-propylphenyl 3 : 5-dinitrobenzoate, 115—116° (below).

4-*n*-Propylphenyl 3 : 5-Dinitrobenzoate.—4-*n*-Propylanisole, obtained by reduction of anethole with sodium and ethanol, was demethylated with hydriodic acid and red phosphorus (Klages²⁰). The phenol was converted into the 3 : 5-dinitrobenzoate which crystallised from methanol as pale yellow needles, m. p. 118° (Found : C, 58.2; H, 4.3; N, 8.5. C₁₆H₁₄O₆N₂ requires C, 58.2; H, 4.2; N, 8.5%).

Reactions with n-Butyl Perchlorate.—A low-boiling fraction, b. p. 160—200° (0.6—0.7 g.), was not identified. The fraction, b. p. 200—234° (mainly 226—234°)/760 mm., or 116—118°/28 mm., was collected as a colourless oil, n_D^{21} 1.5014 (Found : C, 80.5; H, 9.6; Calc. for C₁₁H₁₆O : C, 80.5; H, 9.8%). Heilbron and Bunbury²¹ give b. p. 120°/19 mm., n_D^{15} 1.5027, for 4-*n*-butylanisole.

Demethylation with hydriodic acid (*d* 1.7) was followed by conversion of the phenol into the aryloxyacetic acid, which crystallised as colourless, fine needles from light petroleum (b. p. 40—60°), m. p. 80—81° (Found : C, 69.5; H, 7.7. Calc. for C₁₂H₁₆O₃ : C, 69.2; H, 7.7%). Rosenwald *et al.*²² give m. p. 80—81° for 4-*n*-butylphenoxyacetic acid.

A reaction carried out in nitromethane (52.5 g.) gave a much reduced yield of butylanisole (cf. Table, Expt. 7), but there was more non-distillable residue (1.35 g.).

A solution of *n*-butyl perchlorate in nitromethane (160 g.) was filtered from precipitated silver halide, by use of our alternative technique.^{1a} Anisole (37 g.) was added, and the mixture left for 18 hr. (cf. Table, Expt. 8). When the mixture was worked up as before it gave no fraction corresponding to butylanisole and only 1.0 g. of high-boiling residue.

Reaction with isoButyl Perchlorate.—The fraction, b. p. 90—105° (mainly 102—104°)/25 mm., was redistilled at ordinary pressure, having b. p. 215—220° (mainly 216—219°), $n_D^{19.5}$ 1.5040 (Found : C, 80.4; H, 9.5%). Demethylation with hydriodic acid gave a phenol which solidified; crystallisation of this from light petroleum (b. p. 40—60°) gave colourless needles which, although obviously impure, did not melt completely below 95°. The m. p. of 4-*tert.*-butylphenol was not depressed on admixture with this material.

¹⁹ Vogel, "Practical Organic Chemistry," Longmans Green & Co., London, 1948, p. 657.

²⁰ Klages, *Ber.*, 1899, **32**, 1438.

²¹ Heilbron and Bunbury, "Dictionary of Organic Compounds," Eyre and Spottiswoode, London, 1946, p. 367.

²² Rosenwald, Hoatson, and Chenicek, *Ind. Eng. Chem.*, 1950, **42**, 162.

Reactions with sec.-Butyl Perchlorate.—Some material (0.4 g.), b. p. 180—200°, was obtained, but it still contained some anisole after repeated distillation. Demethylation gave phenol from which the only aryloxyacetic acid that could be obtained was phenoxyacetic acid, colourless flakes [from light petroleum (b. p. 60—80°)] or prisms (from water), m. p. 97° (Found : C, 62.9; H, 5.2. Calc. for $C_8H_8O_3$: C, 63.2; H, 5.3%). The m. p. of this acid is variously reported as 96°, 97°, and 98—99° (cf. Beilstein's "Handbuch der Organischen Chemie," Vol. VI, p. 161).

Two further fractions were collected : (A) b. p. 200—215° (mainly 212—214°), n_D^{19} 1.5056 (Found : C, 80.8; H, 9.8%); (B) b. p. 215—220° (mainly 216—218°), n_D^{19} 1.5044 (Found : C, 80.7; H, 10.0%). Heilbron and Bunbury²¹ give b. p. 106—108°/16 mm., n_D^{20} 1.5062, for 4-*sec.*-butylanisole.

Demethylation of the above materials gave oily or waxy products from which the solid phenol, m. p. 54—55°, was obtained as colourless needles. Heilbron and Bunbury²¹ give m. p. 53—54° for 4-*sec.*-butylphenol.

Attempts to obtain pure aryloxyacetic acids from the demethylated materials were unsuccessful. Some evidence for the presence of 2-*sec.*-butylphenoxyacetic acid was obtained by separating a small amount of crystalline material, m. p. 110—111° (Found : C, 69.0; H, 7.7. Calc. for $C_{12}H_{16}O_3$: C, 69.2; H, 7.7%). Rosenwald *et al.*²² give m. p. 111° for 2-*sec.*-butylphenoxyacetic acid and 61.5—62.5° for the 4-derivative.

Reactions with tert.-Butyl-Perchlorate.—The fraction, b. p. 100—110°/22—23 mm. or 210—220°/760 mm., was collected as a colourless, sweet-smelling oil, $n_D^{17.5}$ 1.5050 (Found : C, 80.7; H, 9.7%). Heilbron and Bunbury²¹ give b. p. 215—216° for 4-*tert.*-butylanisole.

Demethylation with hydriodic acid gave a solid phenol that crystallised from light petroleum (b. p. 40—60°) as colourless needles, m. p. 98—98.5° (Found : C, 80.1; H, 9.4. Calc. for $C_{10}H_{14}O$: C, 80.0; H, 9.3%). The m. p. was not depressed by admixture with 4-*tert.*-butylphenol.

When anisole was added to a pre-formed solution of "tert.-butyl perchlorate" in nitromethane, no *tert.*-butylanisole was obtained. The nitromethane fraction showed some evidence of unsaturation. There was an intractable high-boiling residue (2.6 g.).

A solution of "tert.-butyl perchlorate" was prepared on the vacuum line; no evidence for the formation of free *isobutene* was obtained. When the mixture was worked up in the usual way, a small amount of a yellow unsaturated oil (0.6 g.), b. p. 96—150°/2—3 mm., was obtained. The non-distillable residue (2.3 g.) was a dark brown tar which contained a little nitrogen (Lassaigne).

Reactions with benzene.

Reaction with Methyl Perchlorate.—Methyl iodide (0.05 mole) was added dropwise to silver perchlorate (0.05 mole) in benzene (0.2 mole) and nitromethane (50.0 g.) at room temperature (*ca.* 20°). The initial separation of silver iodide was fairly rapid and appeared to cease after about 2 hr. The mixture was kept at room temperature for 20 hr. before being worked up in the usual way. The silver halide that had separated was 96% of the theoretical amount.* The dried (Na_2SO_4) ethereal extracts were fractionated through a 30-cm. Fenske column. Distillation was discontinued when the temperature at the top of the column had reached 75°, because the residue was then becoming very dark. The residue was diluted with water (50 ml.) and then oxidised by the addition of solid potassium permanganate (15 g.) to the boiling mixture. A few drops of ethyl alcohol were added to remove the last traces of permanganate. The mixture was filtered, and the filtrate concentrated to small bulk; acidification with sulphuric acid caused the separation of solid which was largely inorganic. The mixture was extracted thrice with ether and the ethereal solution was evaporated. Sublimation of the residue gave a few mg. of benzoic acid (m. p. and mixed m. p.).

When the reaction was carried out in benzene alone (230 g.) there was no indication of the formation of benzoic acid.

Reaction with n-Butyl Perchlorate.—A similar reaction in benzene and with *n*-butyl iodide gave very little evidence for the formation of butylbenzene.

Reaction with sec.-Butyl Perchlorate.—Here again, there was little evidence of nuclear alkylation in benzene solutions which were left for 5½ or 20 hr. Small quantities (0.6 g.) of orange oil with a b. p. higher than that of benzene were obtained. Attempts to oxidise these materials to identifiable ketonic products with chromic acid were not successful but evidence for the formation of traces of benzoic acid was obtained.

* Under similar conditions, but with methyl cyanide in place of nitromethane, little or no separation of silver halide occurred after 24 hours.

Reaction with isoButyl Perchlorate.—After 17 hr., a reaction between freshly distilled *isobutyl* iodide (b. p. 118—120°/769 mm.) (0.1 mole) and an equivalent amount of silver perchlorate yielded material, b. p. 100—180° (mainly 150—180°/760 mm. (5.7 g.), and a fraction, b. p. 75—120°/20 mm. (3.4 g.). The residue (0.3 g.) was a brown oil.

Redistillation of the first fraction gave 3.5 g. of a colourless oil, b. p. 163—170° (mainly 167°). On nitration by the method of Biekart *et al.*²³, 2 : 4-dinitro-*tert.*-butylbenzene was obtained (m. p. and mixed m. p. 58—60°).

Redistillation of the second fraction gave a considerable amount of material, b. p. 170—228°, and a smaller fraction (1.0 g.), b. p. 228—236°. The latter partially crystallised and eventually gave 81 mg. of crystalline material, m. p. 76°, identical with the solid obtained from similar experiments with *tert.*-butyl perchlorate.

Reaction with tert.-Butyl Perchlorate.—With use of silver perchlorate (0.05 mole) and an equivalent amount of *tert.*-butyl chloride, the reaction was carried out in benzene (230 g.) at room temperature for 30 min. After the benzene was filtered into ice-water it was separated and washed with water, then, without drying, it was evaporated in a vacuum (water-pump) at > 40° (bath). When the solution had been reduced to about 60 ml., alcoholic potassium hydroxide (4 g.) was added. Only a little potassium perchlorate was precipitated and this was filtered off. The filtrate was diluted with water and worked up as before.

Distillation of the product gave a fraction, b. p. 68—70°/28 mm., or 160—164°/760 mm. (3.1 g.), a colourless oil, n_D^{21} 1.4830 (*tert.*-butylbenzene has n_D^{21} 1.4920). The product contained some unsaturated material which could not be removed by distillation. This was probably triisobutene, b. p. 174—176°, n_D^{21} 1.4300.

The residue (1.2—1.3 g.) from different experiments frequently solidified to give some crystalline material, colourless prisms (from ether), m. p. 76°; *p*-di-*tert.*-butylbenzene²⁴ has m. p. 76°.

Nitration of the *tert.*-butylbenzene fraction by the method of Biekart *et al.*²³ gave 2 : 4-dinitro-*tert.*-butylbenzene, colourless prisms (from ethanol), m. p. and mixed m. p. 60—61°.

When the reaction was carried out with benzene (0.2 mole) in nitromethane (60.6 g.) the yield of *tert.*-butylbenzene was only 0.003 mole. Some material (0.6 g.), b. p. 95—100°/9 mm., crystallised to colourless needles, m. p. 73—75°. The viscous orange residue weighed 2.1 g.

We thank Imperial Chemical Industries Limited for a grant toward the cost of this investigation.

QUEEN ELIZABETH COLLEGE (UNIVERSITY OF LONDON), W.8.

[Received, May 16th, 1956.]

²³ Biekart, Dessens, Verkade, and Wepster, *Rec. Trav. chim.*, 1952, **71**, 321.

²⁴ Baur, *Ber.*, 1894, **27**, 1608.