548. *Homolytic Substitution at a Saturated Carbon Atom. Part I. Products of the Gaseous Nitration of t-Butylbenzene.*

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Existing evidence is equivocal as to whether alkyl radicals intervene in aliphatic nitration in the liquid or the gas phase by aqueous nitric acid or by nitrogen dioxide. This question is tested by a study of the gas-phase nitration of t-butylbenzene by these reagents, because the alkyl radical of that hydrocarbon, the 2-methyl-2-phenylpropyl (neophyl) radical, is one of the few alkyl radicals known to be capable of an internal rearrangement, by which, we hoped, it might disclose itself. Products of its rearrangement were found.

Although the classification of bonding electrons as σ and π is often criticised as inadequate, it is striking that the most typical and powerful electrophilic substituting agents, such as the chlorine molecule, the chlorinium ion, and the nitronium ion, which characteristically substitute at aromatic and other π-electron centres, make no headway at all against carbon σ-electrons. In order to chlorinate or nitrate an alkane we must employ materials containing or producing other substituting agents, *e.g.*, for chlorination, partly atomised chlorine, and for nitration, nitrogen dioxide or dilute nitric acid.

Among these reactions, chlorination is especially well investigated as to mechanism. It is amenable to kinetic study, and, with guidance from prior work on the chlorine–hydrogen reaction, finally interpreted by the chain mechanism of Nernst, the chlorine–alkane reaction has kinetically been established as an analogous radical-propagated chain-process. However, as regards the substitutions which put into alkanes those groups which the typical electrophilic substitutions so easily introduce at aromatic centres, the kind of certainty about mechanism that can be secured by kinetic investigation ends with halogenation.

The nitration of alkanes is in a very different position. It has not yet been found possible to investigate it kinetically, mainly because of difficulties arising from concurrent oxidation with degradation. The only observations available to serve as evidence of mechanism relate to the nature of the products. Therefore, present ideas on mechanism are either vague or not agreed. It is widely thought that the reaction probably involves radicals, but views vary as to how these arise, what they all are, what happens to them, and, in particular, whether or not they carry forward a chain process.

In studying the mechanism of aliphatic nitration, our approach is to seek unequivocal answers to certain very limited questions first, in the hope that several such answers will make clear enough what is waiting to be proved to enable a confirmatory investigation to be designed. In this paper we investigate the validity of the idea that the mechanism depends on the extraction of a hydrogen atom from the alkane to give an alkyl radical. We must explain how the historical situation leads to this first question.

The nitration of alkanes (including cycloalkanes) with concurrent oxidation by dilute nitric acid at its boiling point or at higher temperatures under pressure (concentrated acid effecting only oxidation under such conditions) has been known since 1880.[1] A more modern phase of investigation of alkane nitration was initiated by Hass and his co-workers in 1936,[2] who used vapour flow at temperatures above, sometimes very much above, 150°, and concluded that reaction took place in the vapour, because silica gel exerted no catalysis. They employed two nitrating agents, namely, somewhat concentrated aqueous nitric acid and dinitrogen tetroxide, and claimed the same products from both, but better conversions from the former. The products consisted of a mixture of all the mononitro-compounds that could be formed by introducing a nitro-group in place of any hydrogen atom or any lower alkyl radical, in the original alkane; also of all the aldehydes or ketones that could result from oxygen uptake where a lower alkyl radical had been split off, together with various products of their further oxidation. The ease of replacement of the different types of hydrogen was in the order tertiary > secondary > primary at lower temperatures, with a shift towards equality at higher temperatures. No rearrangement of a carbon skeleton was observed; Hass was so impressed by this that he made it the first of the thirteen " rules " in which he summarised his findings.

One of the theories [3] considered during this work was that free radicals, thermally produced from the reagent, extracted hydrogen from the alkane to leave an alkyl radical, which then picked up a nitro-radical from the reagent. It was subsequently noticed [4] that added nitric oxide reduced conversion, whilst added oxygen and, as Bachman and his co-workers,

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[1] Beilstein and Kurbatov, *Ber.*, 1880, **13**, 1818, 2028. Cf. Ellis, " The Chemistry of Petroleum Derivatives," Chemical Catalog Co., Inc., New York, 1937, vol. 2, p. 1087.

[2] Hass, Hodge, and Vanderbilt, *Ind. Eng. Chem.*, 1936, **28**, 339; Hass and Paterson, *ibid.*, 1938, **30**, 67; Seigl and Hass, *ibid.*, 1939, **31**, 648; Hibsham, Pierson, and Hass, *ibid.*, 1940, **32**, 427; Hass, Dorsky, and Hodge, *ibid.*, 1941, **33**, 1138; Hass and Riley, *Chem. Rev.*, 1943, **32**, 376; Hass, *Ind. Eng. Chem.*, 1943, **35**, 1146; Hass and Howe, *ibid.*, 1946, **38**, 251; Hass and Shechter, *ibid.*, 1947, **39**, 817.

[3] McCleary and Degering, *Ind. Eng. Chem.*, 1938, **30**, 64; Hass and Paterson, *ibid.*, p. 67.

[4] Hass and Alexander, *Ind. Eng. Chem.*, 1949, **41**, 2266.

showed,[5] added chlorine increased it. It was inferred that nitric oxide retards by destroying radicals, and that oxygen and chlorine accelerate either by creating them, or at least by destroying the nitric oxide formed in the oxidation which accompanies nitration. Thus the more definite picture emerged that nitrogen dioxide molecules from dinitrogen tetroxide, or nitrogen dioxide and a free hydroxyl radical, formed by the homolysis of nitric acid, $HNO_3 \longrightarrow OH + NO_2$, extract alkane hydrogen; and that the alkyl radical thus formed either combines with preformed nitrogen dioxide or extracts it from the reagent, leaving, if this is nitric acid, a hydroxyl radical, which, in collaboration with the alkyl radical, carries forward the propagation steps of the chain reaction:

$$RH + OH \longrightarrow R + H_2O$$
$$HNO_3 + R \longrightarrow OH + RNO_2$$

The obvious chain-terminating step is the radical combination,

$$R + NO_2 \longrightarrow RNO_2$$

Bachman added the suggestion that some of the nitrogen dioxide combines through oxygen to form an alkyl nitrite, which, by pyrolysis in the accepted way[6] to nitric oxide, a carbonyl compound, and a lower alkyl radical,

$$R'_3C{\cdot}ONO \longrightarrow R' + R'_2CO + NO$$

leads to the oxidation products and the lower nitro-compounds.

Plausible as these suggestions seem, they have been attacked at two vital points. Stevens and Schiessler[7] nitrated optically active 3-methyloctane by heating it with dilute nitric acid under pressure; they obtained an optically active 3-methyl-3-nitro-octane. They therefore preferred to assume a bimolecular exchange of radicals in a synchronous homolytic process, rather than any step-wise mechanism involving the intermediate production of a free alkyl radical. Fréjacques[8] showed that the pyrolysis of nitric acid vapour at 280—380° is of second order, and is therefore not rate-controlled by the assumed unimolecular homolysis to hydroxyl and nitroxyl radicals, but might be by a bimolecular dehydration to water and dinitrogen pentoxide, the latter being instantly converted, as it would be at the temperatures used, into the other final products of the pyrolysis, namely, nitrogen dioxide and oxygen. Fréjacques also showed that, in a mixture of nitric acid and methane, pyrolysis of the former was concluded long before nitration of the latter was, and hence that the nitration could not depend on nitric acid molecules, as the hypothetical chain-reaction made it, but must be effected by some product of the pyrolysis of nitric acid. Thus the most widely considered concept of aliphatic nitration, the chain mechanism, has been doubly undermined, inasmuch as both the short-lived radicals on which it relies, alkyl and hydroxyl, have been questioned. This paper is concerned with the alkyl radical.

The test we have employed for the validity of this intermediate is equally one of the predictive power of Hass's rule that in aliphatic nitration the carbon skeleton is not rearranged. A necessary condition[9] for rearrangement in a reaction of a saturated carbon system is the formation of an intermediate with an incomplete electron shell, and therefore of either a carbonium ion or a neutral carbon radical. This mechanistic condition, though necessary, is not sufficient, for the thermodynamic condition, that the free-energy change must be in the right direction, has also to be satisfied; so has the kinetic condition that the intermediate must live long enough to allow for the group migration. Only if all three conditions are fulfilled shall we observe rearrangement. Therefore, if we do not observe it, we can conclude nothing about mechanism; if we do, then we shall have established the formation of an intermediate with an electron-deficient centre.

[5] Bachman, Addison, Hewett, Kohn, and Millikan, *J. Org. Chem.*, 1952, **17**, 906.

[6] Rice and Radovskas, *J. Amer. Chem. Soc.*, 1935, **57**, 350.

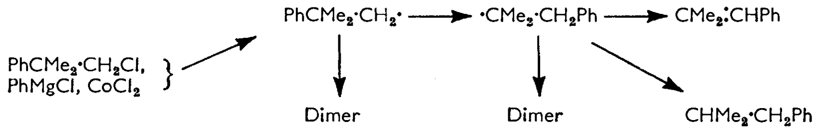
[7] Stevens and Schiessler, *J. Amer. Chem. Soc.*, 1940, **62**, 2885.

[8] Fréjacques, *Mém. Poudres*, 1953, 35, appendix.

[9] Ingold, " Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, New York, 1953, Chap. 9.

Rearrangements by way of a carbonium ion have a very large literature, and are obviously much easier to realise than rearrangements by way of a carbon radical, which have a very small one. Probably the kinetic condition, that the life of the intermediate must be longer than the time required for rearrangement, is much more easily satisfied in carbonium ions than it is in radicals.[10] The idea that alkyl radicals are intermediates in alkane nitrations could probably be reconciled with Hass's non-rearrangement rule on the basis that rearranging radicals are sufficiently uncommon to make it likely that none of the hydrocarbons which he nitrated would have produced one. However, radicals can be produced which can gain such stability by the internal migration of a sufficiently mobile group that an observable amount of rearrangement occurs during their lifetime. We therefore sought a hydrocarbon which by hydrogen loss would yield such a radical, planning to nitrate it under such conditions that, if formed, the alkyl radical could live long enough to permit observable rearrangement, and would therefore disclose itself by the formation of rearrangement products.

The simplest well-authenticated radical of the required kind is the 2-methyl-2-phenylpropyl (neophyl) radical, which Urry and Kharasch produced by reduction of the chloride with a Grignard reagent and cobaltous chloride.[11] They showed that they had made the radical by isolating its dimer, and that part of it is rearranged in their conditions to the presumably more stable 1-benzyl-1-methylethyl radical by isolating the dimer of that also. The non-dimerised reaction products were simple redox derivatives, ωω-dimethylstyrene and 2-benzylpropane, of the rearranged radical:



Our choice of a hydrocarbon for this study of aliphatic nitration therefore fell upon t-butylbenzene, which, by loss of an alkyl hydrogen atom, can only give the 2-methyl-2-phenylpropyl radical. Using the vapour-flow method, we have examined its reaction with aqueous nitric acid and with nitrogen dioxide in the gas phase between 200° and 350°, particularly at and near 325°.

At the outset there was doubt as to whether our plan would be frustrated by nuclear nitration. Ordinary electrophilic nitration in the ring of t-butylbenzene is nearly as fast as in that of toluene, whereas any homolytic replacement of side-chain hydrogen in t-butylbenzene is expected to be considerably slower than in toluene, and hence more easily masked by a competing nuclear nitration. Reports on the gas-phase nitration of toluene with aqueous nitric acid were equivocal, Bullock and Mitchell [12] having claimed the production of nitrotoluenes in this way, whereas Hass and Riley [13] reported a number of products of attack on the side-chain, including nitrobenzene, but no nitrotoluene. As to liquid-phase nitration, Titov [14] heated toluene with dinitrogen tetroxide under pressure, and obtained both nuclear and side-chain nitration products. The only related prior report on t-butylbenzene is one by Konovalov,[15] who heated it with with dilute nitric acid under pressure, and obtained only a side-chain nitro-derivative.

In the course of our experiments by the vapour-flow method with t-butylbenzene and nitric acid, we did observe nuclear nitration, the main product of which was *p*-nitro-t-butylbenzene, but only under such conditions as to indicate that this product was being formed, not in the gas phase, but by ordinary electrophilic nitration, presumably by

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[10] Seubold, *J. Amer. Chem. Soc.*, 1953, **75**, 2532.

[11] Urry and Kharasch, *J. Amer. Chem. Soc.*, 1944, **66**, 1438.

[12] Bullock and Mitchell, *J. Amer. Chem. Soc.*, 1941, **63**, 3230.

[13] Hass and Riley, *Chem. Rev.*, 1943, **32**, 383.

[14] Titov, *J. Gen. Chem. U.S.S.R.*, 1940, **62**, 1855.

[15] Konovalov, *Jahresber.*, 1895, p. 1538.

nitronium ion, in the liquid condensate formed by the gases emerging from the hot space. Thus nuclear nitration was observed if the nitric acid supplying the vapour feed were so concentrated, *e.g.*, 95%, that it would, as liquid, rapidly nitrate t-butylbenzene. Further, the extent of nuclear nitration in the products of vapour-flow experiments increased in proportion as, by keeping the vapour flow-rate up or the temperature of the hot space down, unchanged nitric acid and t-butylbenzene both emerged therefrom to be condensed together. Nuclear nitration was not observed when the nitric acid supplying the vapour feed was so dilute (68% or less) that it could not, as liquid, nitrate t-butylbenzene in the time available to the condensate; this remained true independently of the flow-rates and temperatures employed for the gas reaction. These results allow us to disregard Bullock and Mitchell's report of the gaseous nuclear nitration of toluene, for the nitric acid supplying their vapour feed was always of concentration above 70% and their hot space was at only 150°. Probably little happened until their materials, emerging from the hot space, were recondensed, when ordinary electrophilic substitution took place in the condensate.

We did not observe any nuclear nitration by nitrogen dioxide when t-butylbenzene was treated with it by the vapour-flow method, but we did observe it, with the production, particularly, of *p*-nitro-t-butylbenzene, during experiments in which liquid t-butylbenzene and dinitrogen tetroxide were heated together under pressure. However, we only then observed it in experiments in which a visible acid layer appeared, either before heating owing to insufficient care to exclude moisture when loading the tubes, or after heating because the nitration and oxidation had been allowed to go so far as to produce enough water to make a visible layer. In those experiments in which no acid layer was formed, no *p*-nitro-t-butylbenzene appeared. Since any formed acid layer must consist largely of nitric acid, it seems clear that nuclear nitration, when observed, results from ordinary electrophilic substitution presumably by nitronium ion, in an aqueous-acid phase. We therefore conclude that in Titov's experiments, in which toluene and dinitrogen tetroxide were heated together under pressure, the nitrotoluenes arose by nitration in an acid layer whose presence was not noticed.

In all the experiments now to be summarised on the gaseous nitration of t-butylbenzene, conditions were avoided in which the hydrocarbon could be nitrated by nitric acid in a liquid phase.

A large number of experiments in which the vapours of t-butylbenzene and aqueous nitric acid were injected to produce gas mixtures of the composition 0·5—2·0 mol. of hydrocarbon, plus 1 mol. of nitric acid, plus 1·65 mol. of water into a reaction space at temperatures from 200° to 350°, at rates allowing reaction times from many minutes at the lower temperatures to a few seconds at the upper, gave closely similar products. In all cases, apart from unchanged hydrocarbon recovered, the main product was ω-nitro-t-butylbenzene. The chief by-product was nitrobenzene. Next in order of importance came acetophenone and benzoic acid, then *o*-nitrophenol and 2,4-dinitrophenol. Acetic, oxalic, and formic acids and carbon dioxide were also isolated as such or as derivatives. Tars, and also traces of many unidentified chromatographically distinct products, were formed. A typical weight distribution of identified aromatic products, based on 100 g. of t-butylbenzene used but not recovered and assumed converted, was as follows: 48 g. of ω-nitro-t-butylbenzene, 17 g. of nitrobenzene, 14 g. of an acid fraction whose chief components were benzoic acid > *o*-nitrophenyl > 2,4-dinitrophenol, and 4 g. of acetophenone. About 12 g. of partly acidic and partly non-acidic tar were obtained. An assay of the identified aliphatic acids was not attempted.

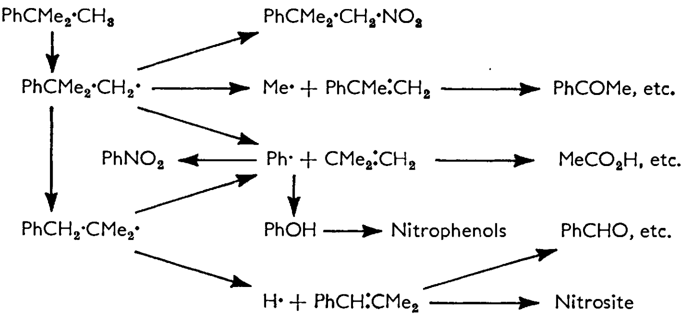
A further series of experiments was conducted in which t-butylbenzene vapour and nitrogen dioxide, in the proportions of 0·5—8·5 mol. of the former to 1 mol. of the latter, were injected into a reaction space at 325°, at a rate which allowed 30—40 sec. for the reaction. The identified products were as before, and in very similar proportions, together with unidentified chromatographically distinguishable traces of other products and tar, but with less of the latter than in the previous series of experiments.

None of these products has to be attributed to rearrangement in a 2-methyl-2-phenylpropyl radical, for none has either a hydrogen atom bound to the α-carbon atom, or a methyl group bound to the β-carbon atom of an aromatic side-chain. Now this might occur, either because the 2-methyl-2-phenylpropyl radical is never formed, or because it is, when formed, too closely surrounded by species eager to react with it to be allowed to survive the length of time required for its rearrangement. We therefore investigated the effect of considerable dilution of the reactants with water vapour. In contrast to liquid-phase nitration, in which water has a specific significance as a base and as a medium controlling the electrolytic situation, the rôle of water vapour in gas-phase nitration, as Bachman has concluded, is only the relatively non-specific one of a carrier gas.

Experiments were therefore conducted in which vapours of t-butylbenzene and dilute aqueous nitric acid, in proportions to produce gas mixtures of the composition 2—5 mol. of hydrocarbon plus 1 mol. of nitric acid plus 40—90 mol. of water, were supplied to the reaction space at 325—350°, with rates allowing reaction times of 10—40 sec. All the identified products previously mentioned were again obtained, and also benzaldehyde and $\omega\omega$-dimethylstyrene nitrosite, both of which must have arisen from a rearrangement of the 2-methyl-2-phenylpropyl radical. It is possible that dimethylstyrene emerges as such from the hot space, and is converted into its nitrosite only in the condensate, for this conversion is very easily done by oxides of nitrogen at room temperature, a reaction that affords a convenient means of separating and characterising the hydrocarbon. Typical yields, per 100 g. of t-butylbenzene used but not recovered and assumed converted, were 40 g. of ω-nitro-t-butylbenzene, 12 g. of nitrobenzene, 28 g. of total aromatic acids, 5 g. of $\omega\omega$-dimethylstyrene nitrosite, and 1·5 g. of benzaldehyde, along with other products.

With the identification of rearrangement products, our main aim was accomplished, for we could conclude that alkyl radicals certainly arise in gas-phase nitration.

The scheme set out below should be considered as no more than a plausible way of understanding the formation of the products. The assumption of the scheme is that the 2-methyl-2-phenylpropyl radical is first produced, that then it either combines with nitrogen dioxide, or is degraded to olefins, or rearranges, and that the rearranged radical is mainly degraded. Many variants of the scheme would be as plausible. For example, the only reason why we make no use of Bachman's idea that alkyl nitrites might be intermediates in oxidations is the inconclusive one that, whilst we were unable to prepare 2-methyl-2-phenylpropyl nitrite, we did make the nitrite of the rearranged radical, and found it to be thermally stable under the conditions of our nitrations.



EXPERIMENTAL

Preparations.—t-Butylbenzene, either fractionated commercial material, or prepared from benzene, t-butyl chloride, and ferric chloride, had b. p. 168·5—169°, n_D^{25} 1·4905.

Attempts were made to prepare and discover the properties of some of the products that might arise in the gas-phase nitration of t-butylbenzene. 1-Benzyl-1-methylethanol, b. p.

88·5—89°/7·0 mm., n_D^{25} 1·5138, prepared from benzylmagnesium chloride and acetone, was converted by hydrogen bromide into the bromide, b. p. 88—89°/5·3 mm., n_D^{25} 1·5382, and this was treated with silver nitrite to give the nitrite, b. p. 88—89°/7·5 mm., n_D^{25} 1·5139, which could be reduced with zinc and aqueous ammonium chloride to restore the alcohol (3,5-dinitrobenzoate, m. p. 97°). The nitrite on passage as vapour through the gaseous nitration tube with the hot space at 300° was unchanged. An attempt to make the isomeric nitro-compound by reaction between benzyl bromide and the sodium salt of 2-nitropropane failed, benzaldehyde and acetoxime being obtained. An attempt to prepare 2-methyl-2-phenylpropyl nitrite from the corresponding chloride and silver nitrite failed, because rearrangement occurred to give the isomeric nitrite. A by-product of this reaction was ωω-dimethylstyrene, which was prepared in larger amount, as described in the literature, by pyrolysis of 1-benzyl-1-methylethyl bromide, and, more conveniently, by refluxing 1-benzyl-1-methylethanol with a crystal of iodine for several hours. The hydrocarbon had b. p. 71—72°/13 mm., 78—79°/20 mm., n_D^{25} 1·5322; on treatment in ether with the gases from acetic acid–sodium nitrite, it at once gave crystals of its nitrosite which, crystallised from chloroform, had m. p. 116° (Found: C, 57·9; H, 5·93; N, 13·9. Calc. for $C_{10}H_{12}O_3N_2$; C, 57·7; H, 5·81; N, 13·5%). The isomeric hydrocarbon, 2-methyl-3-phenylprop-1-ene, prepared by pyrolysis of 2-methyl-2-phenylpropyl chloride, does not give a crystalline nitrosite in these conditions. From a cursory study, we gained the impression that pyrolysis of ω-nitro-t-butylbenzene too slow to be important in determining the products of the vapour-phase nitrations here described; it was ascertained that no nitrobenzenes arises in this way. The ω-nitro-compound had b. p. 127°/7 mm., n_D^{25} 1·5240, and was converted by aqueous sodium hydroxide into a crystalline sodium salt, from which it could be recovered by acidification. Hot alkaline permanganate oxidised it to α-phenylisobutyric acid, m. p. 77°, convertible through the chloride to the amide, m. p. 160—161°. In order to simplify characterisation, the ω-nitro-compound was nitrated with fuming nitric acid to pω-*dinitro-t-butylbenzene*, which, crystallised from aqueous ethanol, had m. p. 64—65° (Found: C, 67·2; H, 7·5; N, 8·1. $C_{10}H_{12}O_4N_2$ requires C, 67·0; H, 7·3; N, 7·8%). *p*-Nitro-t-butylbenzene, prepared by nitration of *t*-butylbenzene with fuming nitric acid in the liquid phase, had b. p. 126°/7 mm., m. p. 28—29°, n_D^{25} 1·5300; it was insoluble in alkali. It was further characterised by conversion into *p*-acetamido-t-butylbenzene, m. p. 172—172·5°.

Apparatus.—Liquid t-butylbenzene was delivered from a constant-head burette, through an internally sealed nozzle, the drops from which could be counted, into the top of a vertical capillary tube, the rate of flow of liquid through which, and hence the dropping rate, could be adjusted by pushing a Nichrome wire into it. The capillary descended, made a U-turn, and immediately on the other side of this the rising tube was joined to a vertical length of wider tubing, which was surrounded by an electric furnace. This was the " vaporiser "; from it the vapour passed into the inner of two concentric horizontal tubes, which were surrounded by another electric furnace. This was the " preheater," in which the separate vapours were brought to the reaction temperature, before being mixed. The vapour of aqueous nitric acid was delivered through a second such arrangement into the outer tube of the preheater. In some experiments in which nitrogen dioxide was the nitrating agent, water vapour was delivered through this second system. The nitrogen dioxide was delivered from a glass container, through a screw-valve and a flow-meter, also into the outer tube of the preheater. Both tubes of the preheater were constricted just where the inner one ended, and the preheated gases became mixed, thus to pass on through the " reaction vessel," which was a 1-metre length of 2·5 cm. diam. tube in its own electric furnace. To the outlet of this tube was sealed a 15-cm. length of downward-sloping air-condenser, which delivered into a receiver, surmounted by a water-condenser, to the top of which solid-carbon-dioxide-cooled and liquid-air-cooled traps could be attached.

Method.—The dropping rates or flow-meter readings of the different delivery systems were calibrated for actual rate of a passage of the substances by trapping and weighing. Before an experiment, each delivery system used was set to deliver at the required rate. Then, the temperatures of the vaporisers, preheater, and reaction vessel having been set, and the collecting apparatus assembled, the delivery systems were connected to the preheater. The delivery rates were usually set on the basis of a preconceived delivery-rate ratio, and a reaction time which settled itself as a result of a preliminary experiment, as follows. The reactants were fed through in the required rate-ratio, but at individual rates which were gradually diminished together until brown fumes ceased to emerge from the reaction vessel. The rates of flow, the volume of the vessel, and the temperature and pressure (atmospheric) being known, the period of time available for the gas reaction could be calculated.

Separation of Products.—Carbon dioxide was identified in the liquid-air-cooled trap. In the solid-carbon-dioxide-cooled trap, after evaporation of the nitric oxide an oily and an aqueous layer remained, from which non-volatile oxalic acid was isolated. The volatile components were added to the contents of the main receiver, where also there had collected an aqueous and an oily layer. The aqueous solution was basified, concentrated, acidified with sulphuric acid, and distilled, to give a first fraction of water and formic acid, in which the latter was identified as its *p*-bromophenacyl ester, m. p. and mixed m. p. 133—133·5°. The oily layer from the receiver was stripped of acids with aqueous sodium carbonate, when some tar separated; and the alkaline aqueous solution was acidified, and extracted with ether. The residue left on evaporation of the ether was distilled to give a first fraction consisting mainly of acetic acid, characterised as its *p*-bromophenacyl ester, m. p. and mixed m. p. 84—85°. The residue after removal of acetic acid was distilled in steam, to give a yellow oil followed by less coloured substances; all these materials were collected in ether and chromatographed on alumina. The lowest band was yellow; from it *o*-nitrophenol was eluted (m. p., mixed m. p., and benzoyl derivative). The next band was of benzoic acid (m. p. and mixed m. p.). The next one, rather firmly held, had to be washed out with sodium hydroxide as a red soluble salt, which, on acidification, gave 2,4-dinitrophenol (m. p., mixed m. p., and benzoyl derivative). The residue from the steam-distillation was similarly chromatographed, to yield 2,4-dinitrophenol, and a very elaborate chromatogram which, having no outstanding bands, was not further examined. The oily layer from which acids had been stripped was distilled under reduced pressure. The first distillate consisted of unchanged t-butylbenzene. As a routine, this material was extracted with sodium hydrogen sulphite solution before being redistilled, and the extract was examined for carbonyl compounds, though with no result, except as described later. After the hydrocarbon had passed over, there followed a combined fraction of acetophenone and nitrobenzene which, by redistillation, could be approximately separated. The former was identified as its 2,4-dinitrophenylhydrazone, and the latter by conversion into acetanilide and benzanilide. The main product, ω-nitro-t-butylbenzene, came over as the last distillable fraction, to leave a pitch-like residue. This fraction was usually collected at 126—129°/7 mm., and on redistillation had a sharper b. p., *e.g.*, 126·8—127·2°/7·1 mm. (Found: C, 67·2; H, 7·56; N, 8·1. Calc. for $C_{10}H_{13}O_2N$: C, 67·0; H, 7·31; N, 7·8%). It had to be carefully distinguished from isomers, *e.g.*, *p*-nitro-t-butylbenzene, which has almost the same b. p., and the unknown but conceivable 2-benzyl-2-nitropropane. That our ω-nitro-compound did not contain either of these isomers was shown by the fact that it was completely converted by aqueous sodium hydroxide into a white crystalline sodium salt, which, on extraction with ether, gave no product, unless it was first acidified, when it regenerated the original nitro-compound. Further confirmation of the identity of the nitro-compound was secured by oxidising it with hot alkaline permanganate to α-phenylisobutyric acid (cf. p. 2740), a product not obtainable by oxidation of any other isomer. For routine characterisation, the nitro-compound was converted by liquid-phase nitration with fuming nitric acid into *p*ω-dinitro-t-butylbenzene, m. p. 64—65° (cf. p. 2740).

In nitrations with vapour from highly aqueous nitric acid, two additional products appeared. First, crystals found in the main receiver were collected, preferably as soon as their separation appeared to be complete, as they slowly redissolved if left. This substance, crystallised from chloroform–ethanol, had m. p. 116° (Found: C, 56·0; H, 5·9; N, 13·8%). ωω-Dimethylstyrene nitrosite has been recorded as having m. p. 112° and 156°, but not 116°. However, made (cf. p. 2740) from authentic ωω-dimethylstyrene, it has m. p. 121°, and was identical with the substance from the vapour-phase nitration. The second additional substance was benzaldehyde. During the distillation of the non-acidic product, it came over mainly in the tail of the hydrocarbon fraction. It was extracted therefrom with aqueous sodium hydrogen sulphite, recovered, and converted into its 2,4-dinitrophenylhydrazone. All experiments which yielded ωω-dimethylstyrene nitrosite yielded benzaldehyde. If, through delay in the collection of the nitrosite crystals, the yield of that substance was lower than usual, then the yield of benzaldehyde was comparably higher, as if the former product became converted into the latter when left in the receiver with the other products of the vapour-phase nitration.

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[*Received, March* 18*th*, 1959.]