

267. *Oxidation by Persulphate. Part II.* Oxidation Effects with a Methyl Group and Some Substituted Methyl Groups on a Benzene Nucleus.*

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Reaction with aqueous persulphate may result in oxygenation, coupling, or fission of C-C bonds in methyl or substituted-methyl groups attached to a benzene nucleus. Catalytic amounts of silver ion greatly increase the oxidising power of the reagent: toluene thus gives benzaldehyde (50%), together with coupled products which include bibenzyl; benzyl alcohol is rapidly oxidised to benzaldehyde and the latter is relatively slowly oxidised to benzoic acid; phenylacetic acid is quantitatively decarboxylated, and gives benzaldehyde and bibenzyl. Silver catalysis is ineffective for benzyl chloride, but uncatalysed oxidation gives products which include 2,4-dichlorophenol. A mixture of chloride ion and persulphate is a chlorinating agent; this is demonstrated in chlorinations of toluene and of acetanilide.

OXIDATION of phenols by aqueous persulphate solution containing catalytic amounts of silver ions † was described in Part I.* A radical mechanism was suggested, the first step being an electron-transfer, giving bivalent silver: $\text{Ag}^+ + \text{S}_2\text{O}_8^{2-} \longrightarrow \text{Ag}^{2+} + \text{SO}_4^{\cdot-} + \text{SO}_4^{2-}$. Evidence in favour of this step has since been published.¹ We now describe

* Part I, *J.*, 1954, 2275 (under the title of "Oxidation Studies").

† The reagent is symbolised throughout this paper as $\text{S}_2\text{O}_8^{2-}\text{Ag}^+$.

¹ Bawn and Margerison, *Trans. Faraday Soc.*, 1955, **51**, 925.

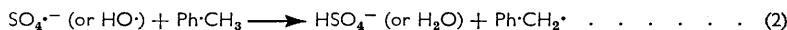
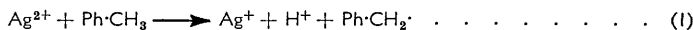
oxidations involving a methyl group or substituted-methyl group attached to a benzene nucleus. The results, which raise several mechanistic problems, provide examples of oxygenation, coupling, and cleavage of the substituent groups.

Toluene and its Oxidation Products.—In reactions of toluene with common liquid-phase oxidants, such as aqueous permanganate,² the step $\text{Ph}\cdot\text{CHO} \longrightarrow \text{Ph}\cdot\text{CO}_2\text{H}$ occurs more rapidly than earlier steps, making benzoic acid the chief product. Chromyl chloride, or chromium trioxide in the presence of acetic anhydride, gives benzaldehyde through hydrolysable intermediates. Direct production of the aldehyde has, however, been reported³ for oxidations in the liquid phase with Mn^{IV} , Mn^{III} , and Ce^{IV} , and the effect of $\text{S}_2\text{O}_8^{2-}\text{-Ag}^+$ proved similar to these multivalent-metal reagents. It rapidly oxidised a stirred suspension of toluene at 60° , giving a complex product with a marked predominance of benzaldehyde ($\sim 50\%$) over benzoic acid ($\sim 10\%$), even though air was present. Formation of benzaldehyde by the reagent had been noted by Austin,⁴ though Law and Perkin⁵ had stated that the process required a strongly acid medium and gave variable results. We found no need for addition of acid and found results reproducible. At the acid concentration advocated by Law and Perkin (4*N*) a complicating factor would be the conversion of perdisulphate into permonosulphate (Caro's acid).⁶ This possibility is also present whenever high concentrations of aqueous persulphate are used, for the oxidant develops acidity owing to the overall change:



About 20% of the oxidation product consisted of bibenzyl, from oxidative coupling between methyl groups, mixed with other hydrocarbons, which have not yet been identified. Results reported for toluene with other oxidants suggest the possible presence of (a) the isomeric phenyltolylmethanes (benzyltoluenes), $\text{Ph}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\text{Me}$, from oxidative coupling between a methyl group and an aromatic nucleus; (b) trimers, tetramers, etc., resulting from further coupling reactions. The former have been observed in oxidations of toluene under acidic conditions with manganese dioxide,⁷ ceric oxide,⁸ and dichromate.⁹ Bibenzyl was reported¹⁰ when toluene was oxidised with boiling aqueous persulphate without addition of metal-ion catalyst. On re-examining oxidation under these conditions we found that attack on toluene was slow; some of the persulphate solution decomposed to oxygen, and the ratio of dimers and other polymers to oxygenated products was higher than it was in the catalysed oxidations.

Benzyl radicals could be formed as intermediates by reaction (1), in which the catalyst Ag^+ is regenerated. Alternatively, they could result from reaction (2):



(Hydroxyl radicals have been suggested as products of reaction of $\text{SO}_4^{\cdot -}$ or Ag^{2+} with water.)

Reaction (1) is similar to those postulated by Waters¹¹ and by Cullis and Ladbury² for oxidations of toluene by CrO_3 or Mn^{3+} respectively. The benzyl radicals may be consumed (a) by coupling, (b) by substitution reactions in a nucleus or methyl group,

² Cullis and Ladbury, *J.*, 1955, 555.

³ Ferguson, *Chem. Rev.*, 1946, **38**, 227; Bayer, "Methoden der Organischen Chemie" (Houben-Weyl), G. Thieme, Stuttgart, 4th edn., 1954, Vol. VII, Pt. 1, p. 135.

⁴ Austin, *J.*, 1911, **99**, 262.

⁵ Law and Perkin, *J.*, 1907, **91**, 258.

⁶ Kolthoff and Miller, *J. Amer. Chem. Soc.*, 1951, **73**, 3055; Bacon and Hill, unpublished data.

⁷ Weiler, *Ber.*, 1900, **33**, 464.

⁸ Meister, Lucius, and Bruning, G.P. 158,609/1902.

⁹ Abell, *J.*, 1951, 1379.

¹⁰ Moritz and Wolfenstein, *Ber.*, 1899, **32**, 432, 2531.

¹¹ Waters, *J.*, 1946, 1151.

(c) by oxygenation processes, of uncertain mechanism but presumably involving water as the source of oxygen: $\text{Ph}\cdot\text{CH}_2\cdot \longrightarrow \text{Ph}\cdot\text{CH}_2\cdot\text{OH} \longrightarrow \text{Ph}\cdot\text{CHO} \longrightarrow \text{Ph}\cdot\text{CO}_2\text{H}$.

The coupling reactions of toluene in aqueous-phase oxidations find parallels in homolytic reactions of toluene in non-aqueous systems. Thus, toluene gives bibenzyl by pyrolysis¹² and, along with higher polymers, by reaction with radicals during decomposition of some peroxides.¹³ Side-chain coupling, however, is easier in the case of ethylbenzene or isopropylbenzene.^{14,15} Attack on toluene by phenyl radicals, formed from benzoyl peroxide, produces little or no bibenzyl, but produces the methylbiphenyl isomers, $\text{C}_6\text{H}_4\text{Me}\cdot\text{Ph}$. By analogy, the formation of phenyltolylmethanes in aqueous-phase oxidations may be due to nuclear substitution by benzyl radicals.

In the absence of other oxidisable compounds, Ag^{2+} and water give oxygen, possibly through intermediate hydroxyl radicals,¹ but otherwise oxygen may be transferred to organic compounds present in the system. Above, we have suggested the successive formation of alcohol, aldehyde, and acid, though benzyl alcohol is so easily oxidised that its isolation from toluene is exceptional and never occurs in good yield. We have not isolated it when using $\text{S}_2\text{O}_8^{2-}\text{-Ag}^+$ but we have observed the step $-\text{CH}_3 \longrightarrow -\text{CH}_2\cdot\text{OH}$, under similar conditions of oxidation, in the case of 2,4,6-trimethylphenol (Part III, following paper).

Observations on rates of oxidation of benzyl alcohol and of benzaldehyde by $\text{S}_2\text{O}_8^{2-}\text{-Ag}^+$ confirmed that the step $-\text{CH}_2\cdot\text{OH} \longrightarrow -\text{CHO}$ is considerably faster than $-\text{CHO} \longrightarrow -\text{CO}_2\text{H}$. For example, benzaldehyde was obtained from the alcohol in yields of 80% or more at 20–30°, even when excess of oxidant was present, while conversion of aldehyde into benzoic acid and resins was only about half complete under similar conditions at 60° and was accompanied by evolution of oxygen. Benzoic acid was slowly oxidised to resins. We have obtained aldehydes and ketones in good yield (unpublished work) from several alcohols of types $\text{Ar}\cdot\text{CH}_2\cdot\text{OH}$ and $\text{Ar}\cdot\text{CHR}\cdot\text{OH}$, in which respect the reagent provides an alternative to others recently advocated, such as manganese dioxide¹⁶ or dinitrogen tetroxide.¹⁷

Bibenzyl or benzyl sulphate ion might be considered as possible intermediates in the formation of oxygenated products from toluene. Bibenzyl must be excluded because it proved to be inert under the conditions we employed. The sulphate might be formed in the steps: $\text{SO}_4^{-} + \text{Ph}\cdot\text{CH}_2\cdot \longrightarrow \text{Ph}\cdot\text{CH}_2\cdot\text{SO}_4^{-}$ or $\text{S}_2\text{O}_8^{2-} + \text{Ph}\cdot\text{CH}_2\cdot \longrightarrow \text{Ph}\cdot\text{CH}_2\cdot\text{SO}_4^{-} + \text{SO}_4^{-}$, and its formation is plausible in view of the known¹⁸ conversion $\text{CHMe}_2\cdot\text{CO}_2\text{H} \longrightarrow \text{CHMe}_2\cdot\text{SO}_4^{-}$, effected by $\text{S}_2\text{O}_8^{2-}\text{-Ag}^+$. However, under the usual oxidation conditions, the slowness of conversion of sodium benzyl sulphate into benzaldehyde indicated that this is unlikely to be the main route from toluene to aldehyde. Under the same conditions sodium toluene- ω -sulphonate showed little change; this failure may be associated with precipitation of the silver.

S-Benzylthiuronium persulphate, briefly reported earlier,¹⁹ was incidentally examined. Like some other persulphates of organic bases,²⁰ it is sparingly soluble in water and when heated in water it decomposes to S-benzylthiuronium sulphate.

Oxidation of Phenylacetic Acid.—When oxidised under similar conditions to toluene, this acid underwent rapid and almost quantitative decarboxylation. Oxygenation, giving mainly benzaldehyde, occurred to about the same extent (~50%) as with toluene, but the

¹² Szwarc, *J. Chem. Phys.*, 1948, **16**, 128.

¹³ Farmer and Moore, *J.*, 1951, 131; Ford and Mackay, *J.*, 1957, 4620; cf. Rust, Seubold, and Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 95.

¹⁴ Hey, Pengilly, and Williams, *J.*, 1955, 6; 1956, 1463.

¹⁵ Kharasch, McBay, and Urry, *J. Org. Chem.*, 1945, **10**, 401.

¹⁶ Turner, *J. Amer. Chem. Soc.*, 1954, **76**, 5175; Highet and Wildman, *ibid.*, 1955, **77**, 4399.

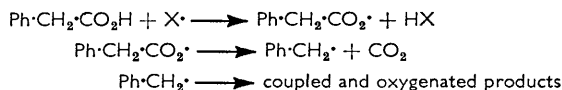
¹⁷ Field and Grundy, *J.*, 1955, 1110.

¹⁸ Bacon and Bott, *Chem. and Ind.*, 1953, 1285.

¹⁹ Chabrier, *Bull. Soc. chim. France*, 1947, **14**, 797.

²⁰ Vitali, *Boll. Chim.-farm.*, 1903, **42**, 273; Wolfenstein and Wolff, *Ber.*, 1908, **41**, 717.

yield of bibenzyl (up to 25%) was much greater. If hydrogen abstraction occurs in the carboxyl group, possible steps are:



Attack by X· on the α -methylene group seems less likely, since diphenylsuccinic acid would be expected* from the intermediate radical HO₂C·CHPh·.

Electrolytic oxidation of carboxylate ions²¹ also involves decarboxylation, formation of both coupled and oxygenated products, and probable participation of radicals as intermediates. Electrolysis of alkali-metal salts of phenylacetic acid²² thus gives mainly bibenzyl (Kolbe coupling reaction), with a little benzyl alcohol (Hofer-Moest hydroxylation). The results of the non-catalysed oxidation of many carboxylic acids by aqueous persulphate show striking similarities to the results of electrolytic oxidations, as is known from the work of Fichter and his co-workers.²³ They do not appear to have used metal-ion catalysts or to have examined the non-catalysed oxidation of phenylacetic acid by persulphate.

Oxidation of Benzyl Chloride. Chlorinations with Mixtures of Chloride and Persulphate Ions.—Precipitation as chloride destroys the catalytic effect of silver ions on persulphate oxidations. Benzyl chloride, readily yielding chloride ion, was therefore not responsive to catalysis, but with aqueous persulphate at 90°, in the absence of silver, a complicated reaction occurred, giving chlorine, oxygenated products (mainly benzoic acid), and a substantial phenolic fraction from which 2,4-dichlorophenol was isolated. Although the yield of the purified dichlorophenol was only about 3%, experience suggests that even this small quantity might not have been isolated if the nucleus had not been protected from further oxidation by the entry of chlorine. In the formation of this product a carbon side-chain has been replaced by a phenolic hydroxyl group. Many such cleavage reactions are known, brought about by other peroxidic oxidants, and they have generally been interpreted by ionic mechanisms.²⁴

The nuclear chlorination accompanying the formation of phenol is due to chlorine molecules (or possibly chlorine atoms) from the oxidation of chloride ions: $2\text{Cl}^- + \text{S}_2\text{O}_8^{2-} \longrightarrow \text{Cl}_2 + 2\text{SO}_4^{2-}$. Substitutions by "nascent halogen" have long been known for various other halide-oxidant mixtures.²⁵ We tested chloride-persulphate mixtures in chlorinations of acetanilide and of toluene. The process, at least for acetanilide, was favoured by high concentration of acid and, by variation in acidity, could be regulated to produce *p*-chloro- or 2,4-dichloro-acetanilide. The only conditions examined for toluene involved persulphate and dilute hydrochloric acid at 90°, *i.e.*, at the temperature used in oxidation of benzyl chloride. The resulting chlorinated hydrocarbons contained comparable amounts of chlorine in the methyl group and the nucleus.

EXPERIMENTAL

Procedure for Oxidations.—Aqueous sodium persulphate, the organic compound, and aqueous silver nitrate were added in that order to the reaction flask. The mixture was efficiently

* Later work (with R. W. Bott) has shown that persulphate readily converts ethyl phenylacetate or benzyl cyanide into ethyl diphenylsuccinate or diphenylsuccinonitrile.

²¹ Weedon, *Quart. Rev.*, 1952, **6**, 380.

²² Fichter and Stenzl, *Helv. Chim. Acta*, 1939, **22**, 970; Linstead, Shephard, and Weedon, *J.*, 1952, 3624.

²³ Fichter *et al.*, *Helv. Chim. Acta*, 1929, **12**, 993; 1932, **15**, 885, 996; 1933, **16**, 338; 1935, **18**, 704, 1276; 1936, **19**, 149.

²⁴ Leffler, *Chem. Rev.*, 1949, **45**, 385; Waters, Gilman's "Organic Chemistry," Wiley and Sons, New York, 1953, Vol. IV, p. 1120; Hassall, *Org. Reactions*, 1957, **9**, 73.

²⁵ Kempf, Houben's "Methoden der Organischen Chemie," G. Thieme, Leipzig, 3rd edn., 1930, Vol. III, p. 1084.

stirred, and approximate constancy of temperature was maintained by preheating of reagents and adjustment of bath-temperature during reaction. Evolution of oxygen was measured in an attached gas-burette. Typical titration data (ferrous and permanganate method) in absence of an organic compound were:

Residual persulphate (initially 1.25M-Na ₂ S ₂ O ₈ , 0.01M-AgNO ₃).						
Min.	30	60	120	180	240	300
At 50° (%)	89	80	67	55	45	37
At 60° (%)	79	62	36	20	10	3

After an oxidation the product was extracted into benzene or ether and separated into alkali-soluble and alkali-insoluble fractions. When benzaldehyde was present it was estimated,²⁶ in benzene solution, by mixing aliquot parts with ~100% excess of freshly prepared 2N-ethanolic hydroxylamine hydrochloride, leaving the mixture for at least 3 hr. at ~20°, and determining hydrochloric acid by potentiometric titration with ethanolic potassium hydroxide. Results obtained with known amounts of benzaldehyde were correct to within 1% of theory and were not significantly affected by the presence of benzoic acid in substantial concentration.

Oxidation of Toluene.—(a) In a typical experiment, toluene (69 g., 0.75 mole) was vigorously stirred for 2 hr. at 60° with sodium persulphate (360 g., 1.5 moles) in aqueous 0.01M-silver nitrate (600 ml.). Most of the reaction occurred during the first 30 min. No oxygen was evolved, and practically all the persulphate was consumed. Except for 0.5 g. of resin, the product dissolved in benzene to give a brown solution, the alkaline extract of which yielded, on acidification, benzoic acid (8.3 g., 9%) and resin (8.2 g.). The neutral fraction contained 40.6 g. (51%) of benzaldehyde by analysis, and when distilled yielded unchanged toluene (2 g.), benzaldehyde (40 g.), a series of oils, b. p. 150—230°/20 mm. (9 g.), and resin (4.5 g.). The lower-boiling of the oily fractions deposited bibenzyl (2 g., 3%), m. p. and mixed m. p. 52—53° after recrystallisation from ethanol. Only traces of crystals were obtained from the other fractions; benzoic acid was the only identified product when these fractions were oxidised by permanganate.

Inadequate stirring led to low conversions of toluene. With efficient stirring, conversion was practically complete with 2 mol. of persulphate, but was only ~50% with 1 mol. and ~33% with 0.5 mol. Addition of an equivalent amount of sodium chloride destroyed the catalytic effect of the silver and resulted, *e.g.*, in 92% of the persulphate being unchanged after 2 hr. at 60°.

(b) Oxidation in absence of silver catalyst was typically carried out by stirring toluene (11.5 g., 0.125 mole) and sodium persulphate (0.25 mole) in water (100 ml.) for 2 hr. at 90°. Consumption of persulphate was 95%, of which 21% gave oxygen. The product contained unchanged toluene (8.1 g., 70%), benzaldehyde (2% by titration), benzoic acid (1.8 g., 12%), bibenzyl and accompanying neutral products (1.6 g., 14%), benzene-insoluble resin (0.5 g.), and a trace of a phenol.

Stability of Bibenzyl.—Treatment of bibenzyl with S₂O₈²⁻-Ag⁺ under the conditions described for toluene resulted in decomposition of 80% of the persulphate, continuous evolution of oxygen, and recovery of unchanged bibenzyl (98%).

Oxidation of Benzyl Alcohol.—Oxidation was rapid at 20—40° and very vigorous at 60°. Typically, benzyl alcohol (13.5 g., 0.125 mole) was stirred for 2 hr. at 30° with sodium persulphate (60 g., 0.25 mole) and silver nitrate (0.17 g., 0.001 mole) in water (100 ml.). No oxygen was evolved, 64% of the persulphate was decomposed, and the products were benzaldehyde (83% by analysis, 75% when isolated by distillation), benzoic acid (1.2 g., 8%), and resin (1.2 g.).

Oxidation of Benzaldehyde.—With S₂O₈²⁻-Ag⁺, under the conditions used for benzyl alcohol, stirring for 2 hr. at 60° resulted in 82% consumption of persulphate, of which 35% gave oxygen. The product contained unchanged aldehyde (42%), benzoic acid (4.4 g., 29%), and resin (24% of initial weight of aldehyde). The resin was not readily soluble in benzene but soluble in acetone, ethanol, and aqueous sodium hydroxide; analyses of fractions indicated compositions (C₇H_{4.8-6.6}O_{2.6-3.8})_n.

Oxidation of Benzoic Acid.—Stirring benzoic acid (15.3 g., 0.125 mole) for 2 hr. at 60° with sodium persulphate (0.5 mole) and silver nitrate (0.001 mole) in water (500 ml.) resulted in 63%

²⁶ Cf. Wild, "Estimation of Organic Compounds," Cambridge Univ. Press, 1953.

consumption of persulphate, of which 26% gave oxygen. Resulting resin (4.4 g.), soluble in acetone, had the approximate composition $(C_7H_5O_{2.5})_n$. Unchanged benzoic acid (9.5 g.) was recovered by extraction of the solution with ether.

Oxidation of Phenylacetic Acid.—Phenylacetic acid (34 g., 0.25 mole) was similarly oxidised with sodium persulphate (0.5 mole) and silver nitrate (0.002 mole) in water (200 ml.). Consumption of persulphate was 96%, carbon dioxide was evolved in 97% of the theoretical volume, and analysis of the resulting red-brown oil showed a 48% yield of benzaldehyde. From the combined products of three such oxidations, 14 g. of acidic material, comprising benzoic acid (4% yield) and resin, were extracted. Distillation of the neutral fraction yielded benzaldehyde (32 g., 40%), bibenzyl (14 g., 24%), m. p. and mixed m. p. 50–52° after one recrystallisation from ethanol (Found: C, 92.3; H, 7.6. Calc. for $C_{14}H_{14}$: C, 92.3; H, 7.7%), and resins (9 g.).

Oxidation of Sodium Benzyl Sulphate.—Chlorosulphonic acid (0.5 mole) was added dropwise to a stirred and ice-cooled mixture of benzyl alcohol (0.5 mole) and triethylamine (1 mole) diluted with chloroform. Neutralisation with concentrated aqueous sodium hydroxide precipitated leaflets of sodium benzyl sulphate, m. p. 183.5–184.5° from aqueous ethanol. This salt (10.5 g., 0.05 mole) was treated for 2 hr. at 60° with sodium persulphate (0.1 mole) in 60 ml. of 0.007M-aqueous silver nitrate; 62% of the persulphate was unchanged and benzaldehyde (17%), benzoic acid (3%), and resin (1.6 g.) resulted.

Oxidation of Sodium Toluene- ω -sulphonate.—When this salt²⁷ was treated under the same conditions as the preceding one, a white precipitate, apparently the silver sulphonate, immediately appeared. Only 8% of the persulphate was decomposed and only 1.5% of benzaldehyde was found on analysis. Oxidation for 2 hr. at 90° in the absence of silver afforded only benzoic acid (3%).

Oxidation of Benzyl Chloride.—This oxidation by persulphate, in presence of silver nitrate, during 2 hr. at 60°, led to 87% decomposition of persulphate and a 4% yield of benzaldehyde, corresponding figures in the absence of silver nitrate being 92% and 3%. At 90° in absence of silver, decomposition of persulphate was 91%, of which 33% led to evolution of oxygen. In 2 hr. at 90° in 2N-sulphuric acid, benzyl chloride gave chloride ion (determined potentiometrically), corresponding with 47% hydrolysis.

Benzyl chloride (95 g., 0.75 mole) was stirred at 90° with sodium persulphate (1.5 moles) in water (600 ml.), the reagent being added in portions during 0.5 hr., and stirring was continued for 1.5 hr. longer. The evolved oxygen contained chlorine; residual chloride ion in the aqueous phase was equivalent to 2% of the benzyl chloride. Nearly all the red-brown organic layer dissolved in benzene, and extraction of this solution with 2N-sodium hydroxide, followed by treatment of the extract with carbon dioxide and then with acid, yielded a brown, partly crystalline phenolic fraction (9.7 g.), benzoic acid (16.8 g., 20%), and resin (2.6 g.). Distillation of the phenolic fraction at 16 mm. yielded colourless needles of 2,4-dichlorophenol (3.4 g., 3%), m. p. 42–43° (Found: C, 44.3; H, 2.5; Cl, 43.5. Calc. for $C_6H_4OCl_2$: C, 44.2; H, 2.5; Cl, 43.5%). This was characterised as 2,4-dichlorophenoxyacetic acid, m. p. 137–138° (Found: C, 43.8; H, 2.6; Cl, 32.4. Calc. for $C_8H_6O_3Cl_2$: C, 43.5; H, 2.7; Cl, 32.1%), and as the benzoate, m. p. and mixed m. p. 93–94° (Found: C, 58.3; H, 3.1. Calc. for $C_{13}H_8O_2Cl_2$: C, 58.4; H, 3.0%). Distillation of the neutral fraction (45 g.) yielded unchanged benzyl chloride (35%), benzaldehyde (6%), and higher-boiling products (5 g.), which, when oxidised with aqueous permanganate, yielded benzoic acid and a little *p*-chlorobenzoic acid.

Chlorination of Toluene.—Toluene (11.5 g., 0.125 mole) was stirred with sodium persulphate (0.25 mole) in water (100 ml.) for 2 hr. at 90°, and concentrated hydrochloric acid (0.5 mole) was added during the first 15 min. The product contained unchanged toluene, chlorinated hydrocarbons (8–9 g.), b. p. mainly 50–110°/16 mm., benzaldehyde (2–4% by analysis), a trace of phenolic material, and an acid fraction (0.2 g.) which was essentially *p*-chlorobenzoic acid. When concentrated aqueous sodium chloride (0.5 mole) replaced the hydrochloric acid, 10–12 g. of chlorinated hydrocarbon were obtained. Benzyl chloride underwent chlorination about as readily as toluene. Benzaldehyde gave only a little benzoic acid.

The mixture of chlorinated hydrocarbons obtained from toluene was shown by the following tests to contain both nuclear and side-chain chlorine. (a) Boiling ethanolic silver nitrate gave silver chloride equivalent to a 55% content of benzyl chloride or a 70% content of chlorobenzyl chlorides. (b) Treatment with thiourea, followed by picric acid, gave a mixture of thiuronium picrates containing 5% of combined (nuclear-bound) chlorine. Recrystallisation yielded a

²⁷ Johnson and Ambler, *J. Amer. Chem. Soc.*, 1914, **36**, 372.

fraction, m. p. 209—210° (decomp.), which corresponded in analysis with a chlorobenzylthiuronium picrate. (c) Conversion into quaternary salts with hexamethylenetetramine likewise gave a mixture, analysis of which indicated the presence of about equal parts by weight of the benzyl chloride derivative and chlorobenzyl chloride derivatives. (d) Fractions obtained by distillation of the crude chlorinated hydrocarbons yielded *o*- and *p*-chlorobenzoic acids, in approximately equal quantities, after oxidation by aqueous permanganate.

Chlorination of Acetanilide.—(a) A solution of acetanilide (81 g., 0.6 mole) in concentrated hydrochloric acid (4 l.) was stirred at ~10° while sodium persulphate (1.25 moles) in water (800 ml.) was added during 40 min. The crystalline precipitate which had then appeared increased in bulk while the solution was stirred for 2 hr. at 20° and left overnight. Filtration gave 2,4-dichloroacetanilide (89 g., 73%) as prisms, m. p. 143° (lit., 145°), raised to 144° in one recrystallisation from ethanol; hydrolysis gave 2,4-dichloroaniline (93%), m. p. 63° (lit., 63°). An identical result was obtained when the persulphate was replaced by an equivalent amount of hydrogen peroxide.

(b) A solution of acetanilide (13.5 g., 0.1 mole) in 5.5*N*-hydrochloric acid (500 ml.) was stirred at 35—40° while sodium persulphate (0.21 mole) in water (150 ml.) was added during 15 min. The precipitate, isolated after stirring had been continued for 1 hr. longer, was impure *p*-chloroacetanilide (48%) and yielded the pure compound in needles, m. p. 178° (lit., 179°), by one recrystallisation from ethanol. An identical result was obtained when the persulphate was replaced by an equivalent amount of hydrogen peroxide.²⁸ After a longer period of reaction a less pure product was obtained in greater quantity.

(c) When reaction was attempted under the conditions described in (b), except that 5.5*N*-sodium chloride replaced the hydrochloric acid, the acetanilide was largely undissolved and was recovered practically unchanged after 4 hr. at 40—60°.

Benzylthiuronium Persulphate.—A mixture of equal volumes of aqueous 0.5*M*-benzylthiuronium chloride and 0.25*M*-sodium persulphate gave a precipitate of benzylthiuronium persulphate, (C₈H₁₁N₂S)₂S₂O₈, in 86—88% yield, as leaflets, m. p. 166—168°; other samples varied in the range 165—170° (decomp.). Chabrier¹⁹ recorded m. p. 180° (decomp.) and 200°. The salt gave the usual colour reactions of persulphates with aromatic amines and phenols, and reacted with potassium iodide in warm aqueous ethanol, yielding iodine equivalent to an S₂O₈ content of 35.3% (Calc.: 36.5%). It recrystallised unchanged in m. p. from aqueous acetone below 40°, but a solution in boiling aqueous ethanol deposited needles of benzylthiuronium sulphate,²⁹ (C₈H₁₁N₂S)₂SO₄, m. p. 185—187° (decomp.), identical with the salt precipitated from aqueous solutions of benzylthiuronium chloride with sodium sulphate or sodium hydrogen sulphate; the chloride and 10*M*-sulphuric acid gave the hydrogen sulphate, C₈H₁₁N₂S.HSO₄, m. p. 140—144° (decomp.). When the persulphate was decomposed in boiling aqueous ethanol the solution yielded barium sulphate equivalent to an S₂O₈ content of 35.8%.

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²⁸ Cf. Leulier, *Bull. Soc. chim. France*, 1924, **35**, 1325.

²⁹ Lecher *et al.*, *Annalen*, 1925, **445**, 35; Bolliger, *Helv. Chim. Acta*, 1951, **34**, 916.