316. *The Oxidation of Toluene by Sodium Dichromate.*

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Oxidation of toluene by sodium dichromate and sulphuric acid gives, besides benzoic acid and benzaldehyde, mainly phenyl *o*-, *m*-, and *p*-tolyl ketone and phenyl-*o*-, -*m*-, and -*p*-tolylmethane (these two sets of products in the ratio 2 : 1), and very small amounts of benzyl alcohol, dibenzyl, diphenylmethane, and anthraquinone.

This paper records an investigation of the products, other than acids, formed when toluene is oxidised by sodium dichromate and sulphuric acid. The general procedure was to use a relatively small amount of oxidising agent so that the excess of toluene acted as solvent for the oxidation products, then to remove the aqueous layer, extract the organic acids with aqueous alkali, and to submit the organic layer to further oxidation after it had been made up to its original volume with more toluene. In this way a toluene solution containing 35—40% of neutral oxidation products was obtained.

The neutral products were found to consist mainly of phenyl *o*-, *m*-, and *p*-tolyl ketones, phenyl-*o*-, -*m*-, and -*p*-tolylmethanes, benzyl alcohol, benzaldehyde, a very small amount of dibenzyl, and traces of diphenylmethane and anthraquinone. Of these, the three ketones and phenyl-*m*-tolylmethane appear not to have been recorded previously among the oxidation products of toluene (cf. Beilstein, " Handbuch der Organischen Chemie," 4th edn., Vol. V, p. 284). After removal of benzyl alcohol, benzaldehyde, and benzoic acid, fractionation of the crude product between light petroleum and sulphuric acid separates the hydrocarbons from the ketones and gives the following composition: ketones 60%; hydrocarbons 30%; unidentified substances 10% (of which 6% is separable as being soluble in ether but insoluble in light petroleum).

Substantial amounts of phenyl *p*-tolyl ketone are readily obtained crystalline. The other ketones were obtained as mixtures of isomers; they were identified by analysis of the mixture and by its oxidation to benzoylbenzoic acids which were separated and identified. The diarylmethanes were also obtained as mixed isomers, which were recognised by analysis and oxidation to the mixed ketones (from which some of the *p*-compound was obtained crystalline) and then to the benzoylbenzoic acids which were again separated and identified.

It seems probable that the diphenylmethane owes its origin to a little benzene present in the commercial toluene used.

Experimental.

(Light petroleum used in this work had b. p. 40—60°.)

The starting material was produced in a commercial process for the preparation of benzoic acid by oxidation of toluene by aqueous sodium dichromate and sulphuric acid in a 2000-gallon lead-lined vat, with vigorous stirring. When all the dichromate had been reduced, the aqueous layer was run off, and the organic layer extracted with sodium hydroxide solution, which was then heated, acidified with hydrochloric acid, cooled, and filtered. The precipitate was washed until acid-free, dried, sublimed, and identified as benzoic acid (m. p. and mixed m. p. 121°). The residual toluene solution was made up to its original volume with more toluene and again treated as above, this process being repeated until the toluene contained *ca.* 40% of oxidation products. 1·5 Gallons of this solution were worked up as recorded below with overall loss of only a few grams.

Initial Fractionation.—(*a*) Most of the unchanged toluene was removed by distillation and the resulting " toluene residues " were treated by one of the following procedures.

(i) The residues were distilled in steam from a bath at 100—110°, benzyl alcohol, benzaldehyde, and a small amount of anthraquinone being thus removed as well as residual benzoic acid. Distillation in superheated steam, from a bath at 250°, then gave a clear yellow oil and a dark friable residue (*ca.* 4%). The former was dried ($CaCl_2$) and fractionated *in vacuo* [see (*b*) below].

(ii) Alternatively, the " toluene residues " were distilled in steam as above at 100—110°, and the involatile material dried and directly fractionated *in vacuo* as in (*b*) below.

(iii) In a third method, the " toluene residues " were diluted with toluene, ether, or light petroleum, extracted successively with aqueous sodium hydroxide, aqueous sodium hydrogen sulphite (which removed benzaldehyde), aqueous sodium hydroxide, and water, and dried ($CaCl_2$), filtered, and fractionated as in (*b*) below.

(*b*) The yellow oil from (i) or the residue from (ii) or (iii) above was fractionally distilled (b. p. range 90—195°/18 mm.); fractions of b. p. 180—187°/18 mm. and 187—195°/18 mm. partly solidified, the former only on cooling, to yield phenyl *p*-tolyl ketone (see below), m. p. 54°, which was removed. Repeated fractional distillation concentrated the material into a fraction (*A*), b. p. 143—145°/10 mm. and a portion (*B*), b. p. 165—185°/10 mm., with small intermediate fractions of intermediate composition. The difference in b. p.s permitted almost complete separation of fractions (*A*) and (*B*). These fractions could, however, not be satisfactorily sub-divided, although partial concentration of the *p*-ketone was effected. Substantial amounts of crystalline phenyl *p*-tolyl ketone, obtained from various fractions, particularly those of higher b. p., were separated as far as possible, and identified (see below).

Fraction (A). *Diarylmethanes.*—This purely hydrocarbon fraction (Found: C, 92·0; H, 8·0%) consisted mainly of phenyltolylmethanes (Calc. for $C_{14}H_{14}$: C, 92·3; H, 7·7%), but analysis does not exclude the presence of the isomeric dibenzyl, and an orange-like odour indicated the presence of some diphenylmethane. Treatment of fraction (*A*) (50 g.) with chromium trioxide (40 g., equiv. to *ca.* 2·2 atoms of O) gave neutral products (*C*) (46·5 g.), that had lost the orange-like odour, and a very small quantity of acids (benzoic, which arises from dibenzyl, with a little *o*-benzoylbenzoic acid). Oxidation of fraction (*A*) (50 g.) with potassium permanganate (65 g., equiv. to *ca.* 2·2 atoms of O) gave neutral products (*C'*) (50 g.) and a similar mixture of acids (3·5 g.). As under these conditions phenyltolylmethanes give ketones and only traces of benzoylbenzoic acids, dibenzyl gives benzoic acid, and diphenylmethane gives benzophenone, the results of the above oxidations indicate that fraction (*A*) contained very approximately 5% of dibenzyl and 2% of diphenylmethane (which was responsible for the orange-like odour).

From its analysis (Found: C, 85·9, 86·0; H, 7·2, 7·1%) the oil (*C* or *C'*) seemed to contain phenyl tolyl ketones (Calc. for $C_{14}H_{12}O$: C, 85·7; H, 6·1%) and some unchanged hydrocarbon. In agreement therewith it boiled over a range (mainly 145—175°/10 mm.). Fractions obtained in such distillations yielded, on oxidation with chromium trioxide, mixed benzoylbenzoic acids in which the *o*-acid predominated.

The Portion (B). *Diaryl Ketones.*—That the fraction of b. p. 165—168°/10 mm. is composed of phenyl tolyl ketones is indicated by analysis before (Found: C, 85·4; H, 6·4%) and after (Found: C, 85·5; H, 6·4%) the usual oxidation procedure. Treatment of this fraction of the material (*B*) (20 g.) with chromium trioxide (40 g.) in boiling acetic acid (150 c.c.) for 120 hours gave 10 g. of (mainly *o*-) benzoylbenzoic acid and 4 g. of unchanged ketone. Similarly, from 20 g. of the same fraction (*B*) potassium permanganate (32 g.) in water (1 l.) gave, after 2 months at room temperature, 10·0 g. of unchanged ketone, 9 g. of the three benzoylbenzoic acids, and a small amount of benzoic acid.

Two fractions contiguous to the above-mentioned fraction contained substantially only phenyl tolyl ketones [Found (fraction of b. p. 168—172°/10 mm.): C, 85·5; H, 6·3; (fraction of b. p. 172—180°/10 mm.): C, 85·5; H, 6·4%]. Each was oxidised by chromium trioxide or potassium permanganate, giving the three benzoylbenzoic acids; the highest-boiling fraction gave the largest proportion of *p*-isomer.

Other Fractions.—Three small fractions, intermediate between (*A*) and (*B*) and boiling between 145° and 160° at 10 mm., were united (total, 23 g.) and heated with chromium trioxide (23 g.) in acetic acid (100 c.c.) for 9 hours, yielding mainly ketones (19·5 g.) with only 1 g. of benzoylbenzoic acids (*o*- and *p*-isomers identified). These fractions thus contained mainly phenyltolylmethanes.

A fourth and larger intermediate fraction, b. p. 160—165°/10 mm., contained a large proportion of phenyl-*o*-tolylmethane, for on prolonged oxidation (30 g. of fraction; 75 g. of chromium trioxide in 200 c.c. of acetic acid; 100 hours' boiling) it afforded 2·5 g. of neutral material and 29·5 g. of the three benzoylbenzoic acids in which the *o*-isomer predominated

Distillation Residues.—A residue was obtained at each distillation. Each was extracted with light petroleum which removed an oil which was added to another appropriate fraction. Treatment of the remainder with ether yielded, usually, a small amount of anthraquinone (m. p. and mixed m. p. 273°) and, in all cases, a high-boiling oil, of which altogether 52 g. were accumulated. This oil (52 g.) was boiled with chromium trioxide (40 g.) in acetic acid, giving a brown amorphous acid (3·6 g.) but no benzoylbenzoic acid, so that none of the phenyl tolyl ketones was present; much (30 g.) of the oil was recovered after the oxidation.

Phenyl p-*Tolyl Ketone.*—This ketone was identified by its m. p. and mixed m. p. (both 54°), by analysis (Found: C, 85·55; H, 6·2%), and by oxidation by chromium trioxide to *p*-benzoylbenzoic acid only (m. p. and mixed m. p. 193—194°).

Separation of Benzoylbenzoic Acids.—Separation of the acids formed on oxidation was always tedious and varied somewhat according to the composition of the mixture under examination. The following is a typical example. It should be added that no fraction was neglected and that acids other than benzoic and the benzoylbenzoic acids were definitely absent.

The mixed acids (10—15 g.) were shaken with successive amounts (each 600 c.c.) of water at 80—85° to give saturated solutions which were then filtered. Gradual separation occurred, to yield first *p*-benzoylbenzoic acid as the least soluble portion, m. p. 175—190°, which crystallised from methyl alcohol in plates, m. p. 194° alone or mixed with an authentic specimen (Found: C, 74·25; H, 4·3. Calc. for $C_{14}H_{10}O_3$: C, 74·3; H, 4·4%). The aqueous filtrates, on slow cooling, deposited (*a*) woolly flocks, m. p. 140—145°, (*b*) large transparent flattened prisms, m. p. 90—94°, and (*c*) globules of oil which crystallised when cold. The flocks were separated by decantation, and the solidified globules by hand-picking. The cold filtrates from these three materials deposited during 2 days small glistening prisms, identified by their m. p. and mixed m. p. (both 93—94°) as *o*-benzoylbenzoic acid hydrate. The woolly flocks (*a*) and the large prisms (*b*) were further fractionally crystallised from water until only one type of crystal was obtained in each fraction.

On extraction of the flocks with carbon disulphide there remained *m*-benzoylbenzoic acid as small glistening needles, m. p. and mixed m. p. 160—161° (Found: C, 74·2; H, 4·5%). When the prisms (*b*) were extracted with cold carbon disulphide there remained *o*-benzoylbenzoic acid hydrate, m. p. and mixed m. p. 93—94° (Found: C, 68·6; H, 5·1. Calc. for $C_{14}H_{10}O_3,H_2O$: C, 68·8; H, 5·0%), which at 100—115° afforded the anhydrous acid, m. p. and mixed m. p. 126—127°. The solidified globules (*c*), when ground and extracted with cold carbon disulphide, gave the insoluble *o*-benzoylbenzoic acid (does not readily sublime) and the much more soluble benzoic acid (sublimes readily), m. p. and mixed m. p. 121°.

In some cases, for *o* + *p*-mixtures, the difference in the solubilities of the barium and the calcium salts in water and alcohol was also utilised for separations; in others, fractional precipitation of the acids from aqueous solutions of the sodium salts was an aid.

Over-all Composition.—0·5 Kg. of the oil remaining after the initial distillation of the crude " toluene residues " was dissolved in light petroleum (2·5 l.), kept for several days, and decanted from a small amount of dark sludge (5 g.). The solution was then shaken cautiously with successive portions (150, 100, and 50 c.c.) of concentrated sulphuric acid; the third extraction removed little, for no heat was generated and the acid became green and not brown

The petroleum solution, now much lighter, was washed free from acid, dried, and evaporated, giving a pale oil (145 g.), which afforded fractions of b. p. 140—150° (mainly 143—145°)/10 mm. (120 g.) and 150—160°/10 mm. (25 g.) and a small, dark, foul-smelling residue. The b. p.s and oxidation to the benzoylbenzoic and benzoic acids indicate the composition as diarylmethanes (plus dibenzyl).

The sulphuric acid solution was poured into water (2 l.) and shaken with a large volume of light petroleum. The whole was filtered through a fluted paper which retained a dark viscid oil (30 g.), almost completely soluble in ether. The aqueous acid was discarded. The petroleum solution gave, on evaporation, an oil (320 g.) which, when dried and distilled, gave three fractions, b. p. 160—168°/10 mm., 168—175°/10 mm., and 175—185°/10 mm., and a residue (which behaved like, and was treated as, the residues described above). The second and the third fraction partly crystallised, the third prolifically. All three fractions were cooled and filtered; the crystals, washed with light petroleum, had m. p. 54° (38·0 g.). Three repetitions of the distillation and crystallisations afforded more of this phenyl *p*-tolyl ketone, and 80·0 g. in all were collected. This isolation, the b. p.s, and oxidation to benzoylbenzoic acids show the sulphuric acid-soluble material to contain essentially only ketones.

The separations are clear-cut and lead to the over-all composition given on p. 1379.

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