396. *Reactions of Unsaturated Compounds. Part I. Addition of Arylamines to* cyclo*Hexene and* 1 : 4-*Dihydronaphthalene.*

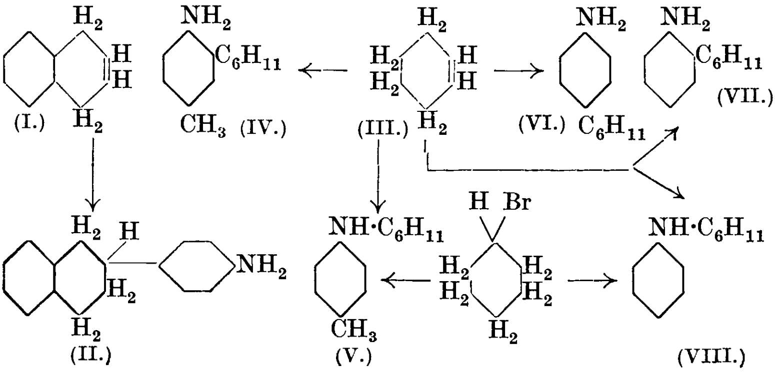
By Wilfred J. Hickinbottom.

It has been shown (this vol., p. 2396) that trimethylethylene reacts with aniline cobaltochloride, cobaltobromide, or hydrobromide to yield the corresponding salts of *p*-amino-*tert.*-amylbenzene. Since this appears to be the first recorded instance of an olefin combining additively with the nucleus of an aromatic amine, this reaction has been examined further, the behaviour of *cyclo*hexene and of 1 : 4-dihydronaphthalene with aniline and *p*-toluidine having been studied.

1 : 4-Dihydronaphthalene (I) when heated with a mixture of aniline and its hydrochloride or cobaltobromide at 200—300° gives principally 2-p-*aminophenyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (II), together with another primary and a secondary amine (not identified). It being assumed that there is no migration of the double bond, there is no ambiguity about the position occupied by the entering group. It was then only necessary to determine the orientation of the amino-group. This was done by converting the amine into the corresponding bromo-compound and subsequently oxidising it with chromic acid; *p*-bromobenzoic acid was obtained, thereby establishing the formula (II).

*cyclo*Hexene (III), when heated at 200—270° in sealed tubes with aniline and its hydrochloride, gave two isomeric primary amines: one was identified as 4-aminophenyl*cyclo*hexane (VI) by comparison with a specimen prepared from *cyclo*hexylbenzene; the other is presumably the corresponding ortho-compound (VII). The product also contained appreciable amounts of *cyclo*hexylaniline (VIII), identified by means of its p-*toluenesulphonyl* derivative (m. p., mixed m. p., and crystallographically).

The reaction between *p*-toluidine and *cyclo*hexene was then investigated. It was expected that the product would be less complex than that from aniline and that the secondary amine would be present in greater amount and more easily isolated. Actually, the product consisted of a mixture from which 4-*amino*-3-cyclo*hexyl*-*toluene* (IV) and cyclo*hexyl*-p-*toluidine* (V) were isolated in a pure state. The latter is crystalline at room temperature and was



identified by comparison of the free amine, its *nitrosoamine*, and its p-*toluenesulphonyl* and m-*nitrobenzenesulphonyl* derivatives with specimens derived from another source.

The formation of secondary amines by this reaction can be considered in effect to result from the addition of $R{\cdot}NH_2$ to the double bond, and is the first record of such an addition to an unsaturated hydrocarbon, the only known examples of combination of this group with the double bond being confined to the αβ-unsaturated acids and αβ-unsaturated ketones. As compounds containing the $-\dot{C}{:}C{\cdot}CO$ group have an unusual facility for additive reactions with many classes of substance which are indifferent to unsaturated hydrocarbons (cf. Lapworth and McRae, J., 1922, **121**, 2741; Kolker and Lapworth, J., 1925, **127**, 307), the addition of $R{\cdot}NH_2$ to *cyclo*hexene is unexpected. Discussion of the nature of this reaction is deferred until it has been possible to examine experimentally some of the hypotheses which might be advanced to account for it.

During the course of these investigations it became necessary to prepare *cyclo*hexylaniline and *cyclo*hexyl-*p*-toluidine. These were readily obtained by heating *cyclo*hexyl bromide with a moderate excess of the arylamine; 25—30% of the *cyclo*hexyl bromide was converted into *cyclo*hexene.

EXPERIMENTAL.

Reaction between cyclo*Hexene, Aniline, and Aniline Hydrochloride : Formation of* cyclo*Hexylaniline,* 2- *and* 4-*Aminophenyl*cyclo*hexanes.*

*cyclo*Hexene (12·15 g.), NH_2Ph (12 g.), and dry NH_2Ph,HCl (21 g.) were heated in a sealed tube at 230—250° for 6 hrs. After cooling, the reaction mixture was acidified with HCl and steam distilled. whereby unchanged *cyclo*hexene (3·65 g.; b. p. 80—85°) and a small amount (0·1 g.) of a higher-boiling Cl-containing substance were removed. The residue was rendered alkaline, and the amine taken up in Et_2O and fractionally distilled under 35 mm. press. After excess of NH_2Ph had passed over, almost all the amine (10·5 g.) was obtained between 165° and 178°. The small residue was not further examined. By systematic fractionation of the main and intermediate fractions, the reaction product was collected at 158—165°/26·5 mm. (10·56 g.; 62% of theo. after allowing for recovered *cyclo*hexene). After unsuccessful attempts to separate the components by fractional crystallisation of their salts, combined with fractional distillation, two primary amines and one secondary amine or their derivatives were isolated by the following process.

Isolation of 2-*Aminophenyl*cyclo*hexane* (VII) *and* cyclo*Hexylaniline* (VIII).—The mixture of amines (10·56 g.), diluted with C_6H_6, was warmed with insufficient picric acid (10 g.) to combine with all the base present. The ppt. was collected, and this, together with a further amount obtained by concn. of the filtrate, was washed several times with cold Et_2O and reserved (A). The combined mother-liquors and washings were dark red and showed no sign of depositing further cryst. picrate. They were accordingly decomposed by NH_3 aq., and the liberated amines taken up in Et_2O, the extract being washed, dried (Na_2SO_4), and fractionated. The amine distilled almost completely (3·67 g.) at 171—174°/35 mm., and was found to be a mixture of a primary and a secondary amine which were subsequently identified as 2-aminophenyl*cyclo*hexane and *cyclo*hexylaniline.

The former was purified by fractional crystn. of the mixed nitrates, first from H_2O and then from EtOH. 2-Aminophenyl*cyclo*hexane is a colourless oil; its *hydrochloride* crystallises from H_2O in needles (sometimes 1″ long) containing $1H_2O$, which is lost at 80° (Found, for the anhydrous salt: HCl, 17·3. $C_{12}H_{17}N,HCl$ requires HCl, 17·25%). The nitrate separates from EtOH in well-formed transparent tablets or plates, often 2 or 3 mm. broad. The p-*toluenesulphonyl* derivative, prep. in C_5H_5N solution, separates from EtOH in small white crystals, m. p. 156—157° (Found : N, 4·7. $C_{19}H_{23}O_2NS$ requires N, 4·2%); and the acetyl derivative forms a felted mass of slender needles from aq. EtOH, m. p. 102—103°.

The mother-liquors from the fractionation of the nitrates contained a considerable proportion of a secondary amine (shown by nitrosoamine test); as it could not be freed completely from primary amine, it was converted into its *p*-toluenesulphonyl derivative by reaction in C_5H_5N, and this was dissolved in Et_2O. Repeated extraction of this solution by aq. alc. NaOH removed the derivative of the primary amine, and evaporation of the ethereal solution yielded that of the secondary amine. It separated from EtOH in well-formed tablets, m. p. 141—142° (Found : N, 4·6. $C_{19}H_{23}O_2NS$ requires N, 4·2%), and was identified as the p-*toluenesulphonyl* derivative of *cyclo*hexylaniline by comparison (and mixed m. p.) with a specimen prepared from another source (p. 2651). This identity was confirmed crystallographically by Mr. E. G. Cox of this Department, who reports as follows : "A crystallographic examination of the two samples of *p*-toluenesulphonyl derivative of *cyclo*hexylaniline showed them to be identical in cryst. form. The crystals (Fig. 1) are monoclinic combinations of the forms $a\{100\}$, $c\{001\}$, and $o\{11\bar{1}\}$, usually tabular on a, but sometimes with a and o equally developed, c being always small. The single face (210) was observed on one crystal only; apart from this, the class appears to be prismatic. The elements are $a : b : c = 1·279 : 1 : 1·1090$; $\beta = 93° 47'$, whilst the classification angles (according to the system proposed by T. V. Barker) are $cr(001):(101) = 38° 49'$, $ra(101):(100) = 47° 24'$, $am(100):(110) = 51° 56'$, and $bq(010):(011) = 42° 26'$. The birefringence is high ($>0·1$), the direction of the maximum index being apparently parallel to the b-axis."

Isolation of 4-*Aminophenyl*cyclo*hexane* (VI).—The amine liberated from the crude picrate (A; p. 2648) by treatment with NH_3 aq. was not pure and could not be purified by further crystn. of the picrate. It was converted into the sulphate, which was fractionally crystallised from H_2O and then from EtOH. The most sparingly sol. fractions yielded an amine, b. p. 157—158°/16 mm., which did not solidify at −16° and still contained an isomeride, but acetylation afforded a mixture from which the pure acetyl derivative was isolated (as nacreous leaflets, m. p. 130—131°, from EtOH) by crystn. from HOAc aq. Hydrolysis of the purified acetyl compound (hot 20% HCl) yielded the hydrochloride of 4-aminophenyl*cyclo*hexane, from which the pure amine was isolated; flat needles or prisms, m. p. 54—55° (Found : C, 82·3; H, 10·3; N, 8·1. Calc. for $C_{12}H_{17}N$: C, 82·2; H, 9·8; N, 8·0%), from light petroleum. The phenylthiourea derivative forms small glistening crystals from EtOH, m. p. 163—164° (Kursanoff, *Annalen*, 1901, **318**, 309, gives m. p.'s 54—56°, 128—129·5°, and 157—158° for the amine, acetyl derivative, and phenylthiourea derivative respectively). m-*Nitrobenzenesulphonyl* derivative, slender white needles from EtOH, m. p. 160—161° (Found : N, 8·0. $C_{18}H_{20}O_4N_2S$ requires N, 7·8%).

For confirmation, 4-aminophenyl*cyclo*hexane was prepared from *cyclo*hexyl bromide as follows.

cyclo*Hexylbenzene.* Freshly-distilled *cyclo*hexyl bromide (54 g.) was added gradually to 250 g. of C_6H_6 and 10 g. of anhyd. $AlCl_3$, the mixture being kept at 35° and the addition regulated so that a steady evolution of HBr was maintained. The whole was then kept at 50° for 3—4 hrs., and after the usual treatment with ice-cold HCl aq., the product was fractionated. The main fraction (235—250°) solidified in a freezing mixture; m. p. 2—6° (Kursanoff gives m. p. 7°) (yield 33·2 g.). It was purified by fractionation under reduced pressure, b. p. 110°/20 mm.

FIG. 1.

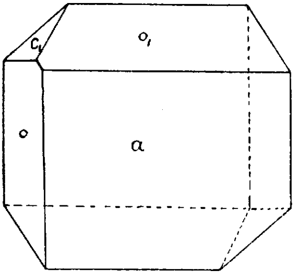
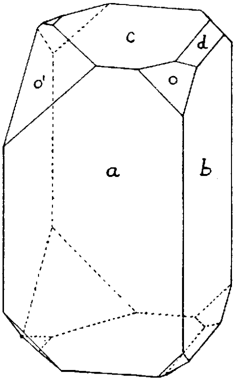


FIG. 2.



4-*Nitrophenyl*cyclo*hexane.* Fuming HNO_3 (110 g.) was added gradually to *cyclo*hexylbenzene (18·9 g.) cooled in ice-water and well stirred. The mixture was kept in ice for 1 hr., and the upper layer was separated, washed with ice-water, diluted with Et_2O, and added to a further ethereal solution obtained from the aq. layer and the washings. After the usual procedure, distillation under 17 mm. gave a fraction at 170—190°, followed at 190° by 4-nitrophenyl*cyclo*hexane, which solidified on cooling. The pure nitro-compound separates from EtOH in thin plates, m. p. 56—58° (Kursanoff, *loc. cit.*, gives m. p. 57—58°, b. p. 200—205°/26 mm.; Mayes and Turner, J., 1929, 500, give m. p. 58·5°, b. p. 198°/16 mm.).

Reduction of the nitro-compound by Sn and aq. alc. HCl gave 4-aminophenyl*cyclo*hexane, m. p. 54—55°, unaltered on admixture with the product described on p. 2649. The acetyl derivatives from both sources were similarly shown to be identical.

Preparation of cyclo*Hexylaniline from* cyclo*Hexyl Bromide.*—NH_2Ph (60 g.) and *cyclo*hexyl bromide (32·5 g.) were heated together in an oil-bath at 120° for 4 hrs., and then the temp. was gradually raised to 150° during 8 hrs. On cooling, the product deposited crystals, and had a strong odour of *cyclo*-

hexene. It was strongly acidified, and steam distilled to remove *cyclo*hexene (4·17 g., b. p. 81—84°; 0·35 g. of higher b. p. containing unchanged *cyclo*hexyl bromide). The amine liberated from the acid solution was taken up in Et_2O and distilled first at ordinary press. to remove NH_2Ph and then under reduced press. *cyclo*Hexylaniline was collected at 162°/34 mm. or 146—147°/16 mm.; it solidified in a freezing mixture, and then melted at 8° (yield 19·6 g.; 73% of theo. after allowing for recovered *cyclo*hexene) (Sabatier and Senderens, *Compt. rend.*, 1904, **138**, 457, give m. p. about 10°, b. p. 171°/30 mm.; Fouque, *ibid.*, 1917, **165**, 1062, gives m. p. 16°, b. p. 157°/20 mm.; I. G. Farbenind., E.P. 261,764/1926, give b. p. 142°/15 mm.).

The *hydrochloride* crystallises well from its conc. aq. solution (Found: HCl, 17·25. $C_{12}H_{17}N,HCl$ requires HCl, 17·25%). The amine was further characterised by its picrate, m. p. 164—165°; acetyl derivative, m. p. 69—70°; benzoyl derivative, m. p. 101—102° (Fouque, *loc. cit.*, gives m. p.'s 164°, 66°, and 102° respectively). The p-*toluenesulphonyl* derivative separates from EtOH in stout glistening tablets, m. p. 141—142° (Found: N, 4·6. $C_{19}H_{23}O_2NS$ requires N, 4·2%).

Reaction between cyclo*Hexene,* p-*Toluidine, and* p-*Toluidine Hydrochloride: Formation of* cyclo*Hexyl*-p-*toluidine and* 4-*Amino*-3-cyclo*hexyltoluene.*

A mixture of *p*-toluidine (4 g.), its hydrochloride (20 g.), and *cyclo*hexene (8·1 g.) was heated in sealed tubes at 270—280° for 6 hrs. The product was acidified with HCl aq., steam-distilled to remove unchanged *cyclo*hexene (2 g.), then diluted and partially neutralised. The suspended tarry matter was collected and extracted twice or thrice with small amounts of boiling H_2O. The combined washings and filtrate were made alkaline and the liberated amine taken up in Et_2O. After removal of Et_2O and most of the *p*-toluidine at ordinary press., fractionation under 20 mm. gave 7·61 g., b. p. 150—170°, and left no appreciable residue. Further fractionation gave 6·11 g. at 160—170°/20 mm., principally at 165—170°. This fraction was a mixture of a primary with a secondary amine; separation was effected by crystn. of the oxalates alternately from hot EtOH and hot H_2O.

Isolation of 4-*Amino*-3-cyclo*hexyltoluene* (IV).—The most sparingly sol. oxalate fractions melted at 175—178° (efferv.) and yielded by treatment with aq. alkali 4-amino-3-*cyclo*hexyltoluene (1·65 g.), b. p. 167—168°/21 mm.; a further 0·21 g. was obtained boiling outside this range. From the other fraction of the oxalates, another 1·57 g. of the pure oxalate of the primary amine was fractionally crystallised.

4-*Amino*-3-cyclo*hexyltoluene* is a viscous, very pale yellow liquid, which slowly darkens on keeping (Found: N, 7·7. $C_{13}H_{19}N$ requires N, 7·4%); *hydrochloride*, long needles, generally grouped in radiating masses (Found: HCl, 15·9. $C_{13}H_{19}N,HCl$ requires HCl, 16·15%), from aq. EtOH; sulphate, sparingly sol. in cold H_2O, separating in radiating clusters of hair-like needles; the *acetyl* derivative, clusters of slender needles, m. p. 136—137° (Found: C, 77·5; H, 9·1. $C_{15}H_{21}ON$ requires C, 77·8; H, 9·1%), from aq. EtOH, is hydrolysed comparatively slowly by hot HCl aq.

Isolation of cyclo*Hexyl*-p-*toluidine* (V).—The most sol. fractions (from the separation of the product as oxalates) were made alkaline, and the amine which separated was taken up in Et_2O and fractionated under reduced press. The principal fraction (0·68 g.), b. p. 179—181°/33 mm., was a secondary amine containing traces of a primary; other fractions (total 0·49 g.) contained relatively less secondary amine.

The main fraction solidified on keeping. After draining on porous earthenware, it melted at 42°. It was identified as *cyclo*hexyl-*p*-toluidine by its nitrosoamine, m. p. 56—57°; *p*-toluenesulphonyl derivative, m. p. 133—134°; and *m*-nitrobenzenesulphonyl derivative, m. p. 143—144°. These were identical with corresponding specimens prepared in the following manner.

cyclo*Hexyl*-p-*toluidine*. *p*-Toluidine (64 g.) and *cyclo*hexyl bromide (38 g.) were heated together under reflux in an oil-bath at 130°. After 4 hrs., the semi-solid product was cooled, acidified with HCl aq., and steam distilled. The distillate yielded *cyclo*hexene (5·4 g.; b. p. 81—84°) and 1 g. of a mixture of the unchanged bromide and *cyclo*hexene. The residue was rendered alkaline, the liberated amines taken up in Et_2O, dried, and fractionated. After removal of the bulk of the *p*-toluidine at ordinary press., the residue (18·6 g.) distilled at 163—171°/22 mm. It solidified on cooling and after a further fractionation was obtained pure; m. p. 42—42·5°, b. p. 161—161·5°/20 mm. (Found: C, 82·6, 82·4; H, 10·4, 10·6; N, 7·6, 7·7. $C_{13}H_{19}N$ requires C, 82·5; H, 10·1; N, 7·4%). cyclo*Hexyl*-p-*toluidine* is fairly easily sol. in most of the common org. solvents; it separates from light petroleum (b. p. 40—60°) as thin transparent plates. The *hydrochloride* separates from warm H_2O in groups of small prismatic needles (Found: HCl, 16·05. $C_{13}H_{19}N,HCl$ requires HCl 16·15%). The *acetyl* derivative, transparent tablets from light petroleum (b. p. 40—60°), m. p. 87—88° (Found: N, 6·4. $C_{15}H_{21}ON$ requires N, 6·1%), is easily sol. in the usual org. solvents; its crystals have the following properties (E. G. Cox): "This substance (Fig. 2) occurs in colourless monoclinic crystals, exhibiting the forms $a\{100\}$, $b\{010\}$, $c\{001\}$, $d\{012\}$, $d'\{0\bar{1}2\}$, and $o\{111\}$, $o'\{1\bar{1}1\}$, $p\{11\bar{1}\}$, and $p'\{1\bar{1}\bar{1}\}$, a usually predominating, d and d' very small. The development of the crystals indicates sphenoidal symmetry. The elements are $a : b : c = 1·304 : 1 : 0·926$, $\beta = 100° 24'$; the classification angles are $cr(001) : (101) = 31° 45'$, $ra(101) : (100) = 47° 51'$, $am(100) : (110) = 52° 04'$, and $bq(010) : (011) = 47° 40'$. The birefringence is high ($>0·12$)."

Gradual addition of $NaNO_2$ aq. to a solution of the amine in ice-cold 20% HOAc yielded the *nitrosoamine*; after being washed and dried on porous earthenware, this was recryst. from light petroleum (b. p. 40—60°), separating as very pale yellow prismatic needles, m. p. 57—58° (Found: N, 13·2. $C_{13}H_{18}ON_2$ requires N, 12·85%).

The p-*toluenesulphonyl* derivative crystallises from EtOH in prismatic needles, m. p. 133—134° (Found: N, 4·3. $C_{20}H_{25}O_2NS$ requires N, 4·1%); and the m-*nitrobenzenesulphonyl* derivative forms a white mass of slender needles, m. p. 143—144° (Found: N, 7·6. $C_{19}H_{22}O_4N_2S$ requires N, 7·5%).

The Reaction between 1 : 4-*Dihydronaphthalene, Aniline, and Aniline Salts: Formation of* 2-p-*Aminophenyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene.*

1 : 4-Dihydronaphthalene was prepared by Bamberger and Lodter's method (*Annalen*, 1895, **288**, 75), precautions being taken to minimise isomerisation to 1 : 2-dihydronaphthalene (cf. Straus and Lemmel, *Ber.*, 1921, **54**, 25); it contained unchanged naphthalene, but as this took no part in the subsequent reaction, it was not removed.

NH_2Ph (6 g.), dry NH_2Ph,HCl (3 g.), and 1 : 4-dihydronaphthalene (6 g.) were heated slowly (4½ hrs.) in a sealed tube to 300°, and kept at that temp. for 4½ hrs. After cooling, the contents were solid and cryst.; they were made strongly acid with HCl and steam distilled, naphthalene and dihydronaphthalene (1·5 g.) passing over. The residue was largely diluted with H_2O and partially neutralised. It was then filtered, and the tarry matter extracted repeatedly with hot H_2O and very dil. HCl. The combined filtrate and extracts were made alkaline, the liberated amines taken up in Et_2O, dried (K_2CO_3), and the solvent evaporated; distillation up to 200° then removed aniline, leaving a dark viscous mass consisting largely of aminophenyltetrahydronaphthalene (yield 5·3 g.). This was purified by conversion into sulphate, which was cryst. from EtOH and then extracted once with H_2O (yield 4·17 g.). The purified sulphate, by treatment with conc. NH_3 aq. in presence of Et_2O, yielded the free amine, which solidified on evaporation of the solvent.

Some other preparations are summarised in the following table :

NH_2Ph, g.	* Dihydronaphthalene, g.	Aniline salt used, and wt., g.	Exptl. conditions.	Yield of dry sulphate, g.
6·0	4·3	Cobaltobromide, 4·0	4½ hrs. at 300°	3·1
8·0	3·64	Cadmibromide, 10·0	9 hrs. at 300—320°	4·8
8·0	6·4	Hydrobromide, 4·0	4 hrs. at 260—300°	4·75
7·2	9·9	,, 13·3	6 hrs. at 220°	(9·8 crude amine)

* In this wt., allowance is made for the material recovered after the reaction.

2-p-*Aminophenyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* was purified by crystn. from rectified spirit, from which it separates in thick tablets, m. p. 89—90° [Found : C, 86·2; H, 7·6; N, 6·2; *M*, 242 (Rast). $C_{16}H_{17}N$ requires C, 86·05; H, 7·7; N, 6·3%; *M*, 223]. It is readily sol. in Et_2O and C_6H_6, less sol. in cold EtOH or light petroleum.

The *hydrochloride* crystallises from H_2O in small nodular clusters of flattened needles (Found : HCl, 14·1. $C_{16}H_{17}N,HCl$ requires HCl, 14·05%); it is readily sol. in EtOH, less sol. in cold H_2O, and is pptd. from aq. solution by excess of HCl. The *hydrobromide* was recryst. from hot H_2O (Found : HBr, 26·4. $C_{16}H_{17}N,HBr$ requires HBr, 26·6%). The *sulphate* is very sparingly sol. in cold H_2O, somewhat more readily in boiling H_2O or EtOH [Found : H_2SO_4, 18·4. $(C_{16}H_{17}N)_2,H_2SO_4$ requires H_2SO_4, 18·0%]. The *picrate* is sparingly sol. in C_6H_6 and in Et_2O, easily sol. in acetone. It separates from hot C_6H_6 containing EtOH in groups of radiating yellow needles, m. p. 186—188° (decomp.) (Found : N, 12·3. $C_{16}H_{17}N,C_6H_3O_7N_3$ requires N, 12·4%). The *acetyl* derivative separates from EtOH in thin platelets, m. p. 184—185° (Found : N, 5·4. $C_{18}H_{19}ON$ requires N, 5·3%); and the m-*nitrobenzenesulphonyl* derivative crystallises from glac. HOAc or aq. acetone in stout, cream-coloured prisms or tablets, m. p. 168—169° (Found : N, 6·9. $C_{22}H_{20}O_4N_2S$ requires N, 6·9%), sparingly sol. in EtOH, more readily in acetone, and sol. in dil. NaOH aq.

a-Phenyl-β-(p-*tetrahydronaphthylphenyl*)*thiourea* was prepared by warming the amine in C_6H_6–light petroleum (b. p. 60—80°) with a slight excess of PhNCS. The oil which separated solidified on keeping, and was purified by extraction with small amounts of C_6H_6 and EtOH, followed by crystn. from acetone; nodules of small needles, m. p. 154—155° (Found : N, 7·9. $C_{23}H_{22}N_2S$ requires N, 7·8%).

2 p-*Hydroxyphenyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*.—A warm solution of the amine in a large excess of dil. H_2SO_4 was chilled rapidly and diazotised by addition of slight excess of $NaNO_2$ aq. Excess of HNO_2 was removed by addition of urea, and the solution poured into moderately conc. H_2SO_4 and

then heated under reflux on a steam-bath for 2 hrs. Steam distillation removed the phenol as a crystalline solid, which was collected, and purified by solution in dil. NaOH aq. and repptn. by acid. It separates from light petroleum or aq. EtOH in slender needles, m. p. 130—131° (softening at 129°) (Koenigs, *Ber.*, 1891, **24**, 179, gives m. p. 129—130°).

Preparation and Oxidation of 2-p-*Bromophenyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene.*—The finely divided hydrobromide of *p*-aminophenyltetrahydronaphthalene, suspended in excess of HBr aq., was diazotised, and excess HNO_2 removed, as above. The solution was then poured into CuBr in HBr and steam distilled. The very pale yellow dense oil which passed over was washed in ethereal solution by dil. NaOH aq., the solvent evaporated, and the residual oil oxidised without further purification.

After several preliminary experiments the following process was adopted. A solution of the bromo-compound in HOAc was warmed with excess of CrO_3 in 50% HOAc. When the slow oxidation had ceased, the solution was cooled and conc. H_2SO_4 added. After the vigorous reaction had moderated, oxidation was completed by heating on a steam-bath for 2 hrs. After cooling, the resulting cryst. solid was collected, dissolved in Na_2CO_3 aq., filtered, and repptd. by dil. HCl. The organic acid thus pptd. had m. p. 243—244° after crystn. from aq. EtOH, and was proved (mixed m. p.) (Found : equiv., 200. Calc. : 201) to be *p*-bromobenzoic acid.

The author thanks Mr. E. G. Cox for the crystallographic measurements.

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