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# **117.** *Reduction by Dissolving Metals. Part I.*

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Sodium in liquid ammonia in presence or absence of available hydrogen from alcohols shows very different reducing properties. The former combination is capable of reducing sodium $\alpha$- and $\beta$-naphthoxides and a number of methoxyalkylbenzenes and alkylbenzenes to the $\alpha\delta$-dihydro-derivatives shown in Tables I, II, and III. It appears to be anionoid in character, and rules governing the effect of methoxy-groups, alkyl groups, and saturated rings on the positions of reduction are given.

In many cases of reduction by dissolving metals it is clear that the initial stage consists of electron addition; in other cases " nascent " (possibly atomic) hydrogen may be added directly (cf. Campbell and Campbell, *Chem. Rev.*, 1942, **31**, 78). Since sodium in liquid ammonia behaves as a solution of metal kations and solvated electrons in equilibrium with metal atoms (Kraus, *J. Amer. Chem. Soc.*, 1921, **43**, 764), it might be expected to reduce by " electron addition," but the addition of a ready proton source, such as an alcohol, to the reagent renders reduction by " nascent " hydrogen a possibility. The action of sodium in liquid ammonia on a number of naphthalene and benzene derivatives in presence and in absence of an alcohol has now been examined in order to determine whether the presence of the latter alters the course of the reaction.

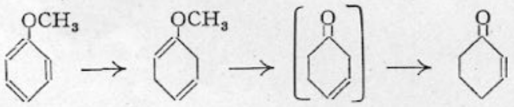
Preliminary experiments on sodium α- and β-naphthoxides (Table I) definitely indicated that a considerable change was produced by addition of *tert.*-amyl alcohol (chosen as a proton source unlikely to displace any of the phenol from its sodium salt), since sodium alone produced little reduction, but in presence of the alcohol good yields of dihydro-derivatives were obtained. Sodium α-naphthoate, however, was reduced readily in absence of alcohol, probably because the carboxyl ion is capable of taking up electrons by an electromeric mechanism, despite its negative charge. As a preparative method for 5 : 8-dihydro-α-naphthol and β-tetralone it is not necessary to employ the sodium salt, the free phenol acting as a partial source of hydrogen for its own reduction.

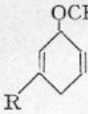
TABLE I.

| Substance reduced (2 atoms of sodium). | Product. |
|---|---|
| Sodium α-naphthoxide | 5 : 8-Dihydro-α-naphthol (trace) |
| α-Naphthol and *tert.*-$C_5H_{11}{\cdot}OH$ (1 mol.) | 5 : 8-Dihydro-α-naphthol (65%) |
| Sodium α-naphthoxide and *tert.*-$C_5H_{11}{\cdot}OH$ (2 mols.) | 5 : 8-Dihydro-α-naphthol (85%) |
| Sodium β-naphthoxide | (? 5 : 8)-Dihydro-β-naphthol (trace) and β-tetralone (trace) |
| β-Naphthol and *tert.*-$C_5H_{11}{\cdot}OH$ (1 mol.) | β-Tetralone (65%) |
| Sodium β-naphthoxide and *tert.*-$C_5H_{11}{\cdot}OH$ (2 mols.) | β-Tetralone (55%) |

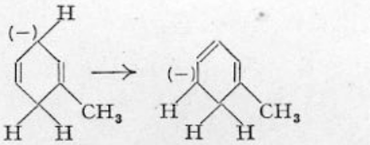
Freudenberg, Lautsch, and Piazolo (*Ber.*, 1941, **74**, 1886) found that potassium in liquid ammonia acts on methoxybenzene derivatives merely as a demethylating agent, and this was found to be true also for sodium, no appreciable reduction occurring. Wooster (U.S.P., 1938, 2,182,242) reduced a number of compounds containing an isolated benzene ring, including anisole, by sodium and methyl alcohol in liquid ammonia, and concluded that dihydro-derivatives were formed, although this was proved definitely only for benzene itself. This work has been confirmed and extended by reduction of the methoxyalkyl- and alkyl-benzenes shown in Tables II and III, ethyl being substituted for methyl alcohol in some cases.

The methoxyalkylbenzenes gave about 10% of the phenol formed by demethylation, and a mixture of starting material and reduction product which was difficult to separate into its pure components owing to their similar physical properties. The presence of the dihydro-derivatives was proved by treatment with hot dilute mineral acid, the products being αβ-unsaturated ketones; 3-methylanisole, for instance, gave 3-methyl-$\Delta^2$-*cyclo*hexenone. There is no doubt that the ketones are αβ-unsaturated from the agreement in properties between their derivatives and those of the latter, when known, and from the formation of semicarbazido-semicarbazones in a number of cases, but it is clear that the initial dihydro-derivatives do not contain the conjugated bonds this evidence may appear to indicate. This follows from the fact that such bond systems are reduced more readily than the benzene rings under the conditions used, and from the fact that the product from 3-methylanisole (3-*methyl*-2 : 5-*dihydroanisole*) shows no light absorption in the region 2400—2800 A. The course of the series of reactions is as follows :





(I.)



(IV.) (V.)

$CH_2{:}C(CH_3){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2R'$.

(II.) $R' = C(CH_3){:}CH{\cdot}CH_2{\cdot}OCH_3$.
(III.) $R' = C(CH_3){:}CH{\cdot}CH_3$.
(VI.) $R' = C(CH_3)(OH){\cdot}CH{:}CH_2$.
(VII.) $R' = C(CH_3){:}CH{\cdot}CH_2OH$.

It is, in general, unlikely that any appreciable amount of a dihydro-derivative of type (I) is produced, since this would give a benzene, rather than a *cyclo*hexenone derivative by the action of acid, and would, in any case, lose the methoxyl by further reduction. This was shown by reducing geranyl methyl ether (II) to geraniolene (III) under the same conditions, although the methoxyl is activated by only one double bond. In the unique case of 3-methylanisole, the formation of a small proportion of hydrocarbon giving derivatives of 1-methyl-$\Delta^1$-*cyclo*hexene can be explained by reduction of (I, R = $CH_3$). That the hydrocarbon is a tetrahydro-, rather than a dihydro-benzene seems to indicate the intermediate formation and further reduction of a conjugated diene, probably by way of the electromeric change (IV) ⟶ (V). A similar rearrangement of an anion must be postulated in the reduction by this process of linalol (VI) to give a hydrocarbon (III) identical with that obtained from geraniol (VII) (Chablay, *Ann. Chim.*, 1917, **8**, 192; Dupont, Dulou, and Desreux, *Bull. Soc. chim.*, 1939, **6**, 83).

The initial dihydro-derivatives were converted directly into the unsaturated ketones, and these estimated as derivatives, usually with semicarbazide, but in the cases of (A), (K), and (P) (see Table II) with 2 : 4-dinitrophenylhydrazine. The yields shown represent the proportion of ketone in the crude product, calculated on the derivative, and the product shown is the principal one; in the case of (B) some of the alternative αβ-unsaturated ketone (2-methyl-$\Delta^2$-*cyclo*hexenone) was probably present.

On the reasonable assumption that the αβ-unsaturated ketones are formed from the βγ- by bond shift by the shortest route the positions of addition of the hydrogen atoms to the anisole are given in the last column.

Reduction of several benzenoid hydrocarbons under similar conditions gave the products shown in Table III.

Owing to the similarity in boiling point it was difficult to separate the dihydro-derivatives from starting material, but the product from *m*-xylene was shown to contain only about 21% of benzenoid material by means of its ultra-violet absorption spectrum. The transparency of the compound in the region 2300—2800 A.,

TABLE II.

| | Compound. | Product. | Yield, %. | Atoms of H per mol. | Positions of added H atoms. |
|---|---|---|---|---|---|
| A. | Anisole | $\Delta^2$-*cyclo*Hexenone | 20 | 2·4 (EtOH) | 2 : 5 |
| B. | 2-Methylanisole | 6-Methyl-$\Delta^2$-*cyclo*hexenone | 12 | 2·4 (EtOH) | 3 : 6 |
| C. | 3-Methylanisole | 3-Methyl-$\Delta^2$-*cyclo*hexenone | 42 | 4·0 (EtOH) | 2 : 5 |
| D. | 4-Methylanisole | 4-Methyl-$\Delta^2$-*cyclo*hexenone | 33 | 4·0 (MeOH) | 2 : 5 |
| E. | 2 : 6-Dimethylanisole | 2 : 6-Dimethyl-$\Delta^2$-*cyclo*hexenone | 10 | 2·4 (EtOH) | 2 : 5 |
| F. | 2 : 5-Dimethylanisole | (? 3 : 6)-Dimethyl-$\Delta^2$-*cyclo*hexenone | 15 | 2·4 (EtOH) | 3 : 6 ? |
| G. | 2 : 4-Dimethylanisole | 4 : 6-Dimethyl-$\Delta^2$-*cyclo*hexenone | 22 | 2·4 (MeOH) | 3 : 6 |
| H. | 3 : 4-Dimethylanisole | (? 3 : 4)-Dimethyl-$\Delta^2$-*cyclo*hexenone | 35 | 2·4 (MeOH) | 2 · 5 ? |
| J. | 3 : 5-Dimethylanisole | 3 : 5-Dimethyl-$\Delta^2$-*cyclo*hexenone | 16 | 4·0 (EtOH) | 2 : 5 |
| K. | 5-Methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene | 1-Keto-$\Delta^{9:10}$-octalin | trace | 8·0 (EtOH) | 7 : 10 |
| L. | 6-Methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene | 2-Keto-$\Delta^{1:9}$-octalin | 44 | 2·5 (MeOH) | 5 : 8 |
| M. | 6-Methoxy-5-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene | No ketonic product | | | |
| N. | 5-Methoxyhydrindene | 5-Keto-$\Delta^{4:9}$-tetrahydrohydrindene | 30 | 4·0 (EtOH) | 4 : 8 |
| P. | 5-Methyl-2-*iso*propylanisole | 3-Methyl-6-*iso*propyl-$\Delta^2$-*cyclo*hexenone (piperitone) | small | 4·0 (MeOH) | 3 : 6 |

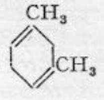
TABLE III.

| | Compound. | Product. |
|---|---|---|
| Q. | 1 : 2 : 3 : 4-Tetrahydronaphthalene | 1 : 2 : 3 : 4 : 5 : 8-Hexahydronaphthalene (IX) |
| R. | *m*-Xylene | 2 : 5-Dihydro-*m*-xylene (VIII) |
| S. | *p*-Xylene | (? 2 : 5)-Dihydro-*p*-xylene |
| T. | *p*-Cymene | $\gamma$-Terpinene (X) |

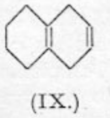
except for bands definitely due to *m*-xylene, demonstrates the absence of a conjugated bond system. The constitution was proved to be (VIII) by ozonolysis, a considerable proportion of acetylacetone being isolated from the product as its copper salt. The hydrocarbon also gave a crystalline *nitrosochloride* and *nitrolpiperidine*. Removal of hydrogen chloride from the former by means of aqueous-alcoholic sodium hydroxide gave 2 : 4 : 2′ : 4′-tetramethylazoxybenzene, doubtless by way of the phenylhydroxylamine (cf. Richter and Wolff, *Ber.*, 1930, **63**, 1714). This confirms the structure, since it locates the nitroso-group in the nitrosochloride on $C_4$ and therefore indicates the presence of a double bond between $C_3$ and $C_4$ in the original hydrocarbon. The alternative 1 : 4-dihydro-*m*-xylene would give 2 : 6 : 2′ : 6′-tetramethylazoxybenzene, since the 2 : 3-double bond would react preferentially with nitrosyl chloride.

The reduced tetralin gave a blue, very soluble *nitrosochloride*. Since derivatives of this type are only produced from substances having a double bond between quaternary carbon atoms, this indicates the presence of a 9 : 10-double bond, and if the other bond is not conjugated, as seems very likely, the constitution of the hydrocarbon must be (IX).

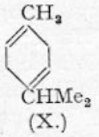
The presence of $\gamma$-terpinene (X) in the *p*-cymene product was proved by the formation of the characteristic nitrosochloride and nitrolpiperidine. This constitutes a synthesis of the terpene. The ready formation of a *nitrosochloride* from the *p*-xylene compound appears to favour the constitution given, which would also be expected by analogy with *p*-cymene.



(VIII.)



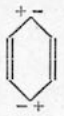
(IX.)



(X.)

It is clear that electron addition must be an anionoid process, and this appears to be the case with the nascent hydrogen reduction also, since the sodium phenoxides are not reduced—the naphthoxides are so probably by virtue of the greater polarisability of the naphthalene ring—and there is no evidence of reduction being initiated in the position occupied by, or para to the methoxyl group, with the minor exception of (C). Sachs (*Ber.*, 1906, **39**, 3006) found that sodamide, a typically anionoid reagent, reacts with sodium $\alpha$- and $\beta$-naphthoxide to give sodium 5-amino-$\alpha$- and -$\beta$-naphthoxide, thus leading to the expectation that an anionoid reduction should take place in the unsubstituted ring in both cases. This is not fulfilled for sodium $\beta$-naphthoxide, which is probably first reduced to sodium 1 : 4-dihydro-$\beta$-naphthoxide, and the reagent appears to be kationoid. Since free radicals behave amphoterically according to the type of activation in the substrate molecule (Hey and Waters, *Chem. Rev.*, 1937, **21**, 187), the intervention of hydrogen atoms may explain this result, the anionoid activation of the 1-position of sodium $\beta$-naphthoxide being particularly high.

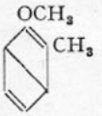
On the assumption of anionoid reduction it should be possible to correlate the orientation influences of methoxyl and alkyl groups with those observed for other anionoid reagents. Data are scarce, but Sartoretto and Sowa (*J. Amer. Chem. Soc.*, 1937, **59**, 603), by a comparison of the effect of substituents on the direction of cleavage of diphenyl ethers by sodium in liquid ammonia, showed that deactivation (increasing order of intensity) was produced by *o*-$CH_3$, *p*-$CH_3$, and *p*-$OCH_3$, and activation by *o*-$OCH_3$. Since the reductions are αδ, the benzene ring must tend to polarise for reaction as in (XI), initial addition occurring at the positive pole; for convenience these activated forms may be written as the Dewar formula (XII). It is evident from the results of Sartoretto and Sowa, and from the known inductive effect of alkyl groups, that these will tend to prevent addition of an anionoid reagent in the substituted position, or para to it, so that the bridge of the Dewar formula corresponding to the principal reduction product will end on the least number of alkyl groups. This is obviously true for the hydrocarbons (Q), (R), and (T) (Table III). In the methoxyalkylbenzene series no reduction is initiated in the position occupied by, or para to a methoxyl except to a small extent with (C), and the rule can therefore be extended to cover these compounds by omitting from consideration the Dewar formula having a methoxyl at the bridge head. This result, which also agrees with those of Sartoretto and Sowa, shows that the unshared electrons of the oxygen atom must strongly repress reaction of both the occupied and the para-position towards an anionoid reagent, and oppose the inductive effect of the methoxyl which would be expected to assist the process. The rule may be stated so as to cover all the cases as follows. If a benzene ring bearing methoxyl and alkyl groups (or the ends of a saturated ring) is written in the Dewar formulæ in which the bridge head is not occupied by a methoxyl group, the chief reduction product will correspond to the formula having the least number of substituents at the bridge heads. The formulæ corresponding to the products definitely identified in Table II are given below, and the rule is easily verified.



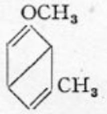
(XI.)


(XII.)

(A.)

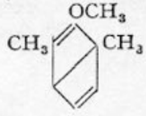


(B.)

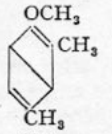


(C.)

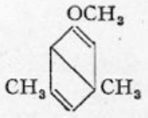
(D.)



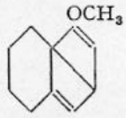
(E.)



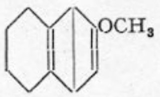
(G.)



(J.)

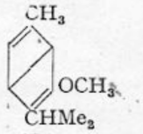


(K.)



(L.)

(N.)



(P.)

2 : 3-Disubstituted anisoles, such as (K), give two possible formulæ between which the rule does not distinguish, and it is necessary to restate it somewhat differently. Reduction will tend to be initiated (*a*) in an unoccupied position and (*b*) *o*- or *m*- rather than *p*- to an alkyl or methoxyl group, the latter having the greater deactivating effect in both cases. With (K) it is impossible for both these rules to be obeyed, and from the nature of the product (*a*) or (*b*) must have preponderance according to whether reduction is initiated *m*- or *o*- to the methoxyl group. The latter is the more probable position from the results of Sartoretto and Sowa (*loc. cit.*), but since the addendum is symmetrical it is impossible to decide at present.

The mechanism of the " nascent hydrogen " reduction is still in doubt. It must differ from that of " electron addition " in which bivalent anions are produced from polycyclic compounds as the initial stage (Hückel and Bretschneider, *Annalen*, 1939, **540**, 157; Wawzonek and Laitinen, *J. Amer. Chem. Soc.*, 1942, **64**, 2365), evidently because the greater resonance in an isolated benzene ring renders the production of such anions difficult. It is also evident that univalent anions such as (IV) cannot be intermediates, since, as already seen, these would give tetrahydro- rather than dihydro-derivatives. It is possible that in presence of available protons the formation of a charged ring is avoided. An alternative hypothesis is that reduction is due to hydrogen atoms, since Geib and Harteck (*Ber.*, 1933, **66**, 1815) have shown that these, in the gaseous state, are capable of reducing benzene. Metallic iron catalyses the combination of hydrogen atoms to molecules, and it was found that 6-methoxytetralin (L) and sodium β-naphthoxide were not reduced in presence of a little of the finely divided metal. This may be due merely to removal of the sodium by reaction with ammonia, also catalysed by iron, but this process also produces " nascent " hydrogen, so the state of the latter must be important.

The practical application of this type of reduction is limited by the low solubility of many compounds in liquid ammonia, since reduction is in competition with hydrogen evolution.

## EXPERIMENTAL.

*Naphthalene Derivatives.*—The apparatus and conditions used in the following experiments were the same, the anhydrous liquid ammonia being drawn from a cylinder into a 350-c.c. Dewar flask, and the reaction carried out with stirring.

*Reduction of α-naphthol.* (i) α-Naphthol (5·5 g.) was treated with finely powdered sodamide (1·5 g.) in liquid ammonia (60 c.c.), and sodium (1·8 g.) added in small pieces during an hour. When the blue colour had disappeared, the ammonia was evaporated, and the residue decomposed with ice and dilute hydrochloric acid. Extraction of the product with ether and fractionation from benzene–light petroleum showed it to consist mainly of starting material, m. p. 94°, but the more soluble fraction, after removal of the naphthol as its picrate by treatment with alcoholic picric acid, gave 5 : 8-dihydro-α-naphthol (0·3 g.) as colourless prisms, m. p. and mixed m. p. 74° (Rowe and Levin, J., 1921, **119**, 2023, give m. p. 75°).

(ii) As above, but the sodamide being omitted and *tert.*-amyl alcohol added (2·9 g.) with the naphthol. The 5 : 8-dihydro-α-naphthol crystallised from benzene–light petroleum as massive colourless prisms (3·2 g.), m. p. and mixed m. p. 74°. This method of preparation is superior to that of Rowe and Levin (*loc. cit.*).

(iii) To α-naphthol (10 g.) and powdered sodamide (2·7 g.) in ammonia (100 c.c.) was added *tert.*-amyl alcohol (12·5 g.) and then sodium (3·2 g.) in small pieces. Most of the ammonia was evaporated, water (100 c.c.) added, and the solution extracted several times with ether. It was then acidified, and the precipitated oil, which rapidly solidified, recrystallised from light petroleum (b. p. 80—100°). 5 : 8-Dihydro-α-naphthol (8·5 g.) was obtained as massive colourless prisms, m. p. 71—74°, undepressed by an authentic specimen. A further 0·6 g. of less pure material was obtained from the mother-liquor.

*Reduction of β-naphthol.* (i) β-Naphthol (15 g.) and sodamide (4·0 g.) in liquid ammonia (140 c.c.) were treated with sodium (4·6 g.) in small pieces. After the blue colour had disappeared the ammonia was evaporated, and the residue decomposed with ice. This, like all alkaline solutions of the reduction products of β-naphthol, had to be protected as far as possible from the air, and worked up quickly to avoid the formation of tetralone-blue. Immediate extraction with ether gave only a trace of β-tetralone, but after acidification and exhaustion of the ethereal extract with 10% sodium hydroxide the ether contained 2·2 g. of neutral oil, which gave a crystalline derivative with sodium bisulphite. Decomposition of this with dilute sulphuric acid gave β-tetralone (1·2 g.), b. p. 140°/14 mm. ; semicarbazone, m. p. and mixed m. p. with an authentic specimen kindly presented by Dr. J. W. Cornforth, 193°. The above alkaline solution was treated with methyl sulphate, and the resulting solid recrystallised from alcohol, giving 2-methoxynaphthalene (8 g.). The mother-liquor from the crystallisation was treated with alcoholic picric acid; the picrate removed, and the alcohol evaporated. The residual oil was taken up in ether, washed with 10% sodium hydroxide solution, dried, and distilled, yielding a colourless oil with a phenolic odour (0·9 g.), b. p. 145—150°/14 mm. It seemed to be mainly an ar-*dihydro-2-methoxynaphthalene* (Found : C, 82·0 ; H, 7·7. $C_{11}H_{12}O$ requires C, 82·5 ; H, 7·5%).

(ii) As above, but with *tert.*-amyl alcohol (8·5 g.) instead of sodamide. The neutral product (10·5 g.), b. p. 138—140°/14 mm., was purified through the bisulphite compound, giving β-tetralone (9·8 g.), b. p. 140°/13 mm. ; semicarbazone, m. p. 193°.

(iii) β-Naphthol (5 g.) and sodamide (1·3 g.) were brought into reaction in liquid ammonia (50 c.c.), and *tert.*-amyl alcohol (5·6 g.) added, followed by sodium (1·5 g.) in small pieces, and the ketonic product worked up as above, giving β-tetralone (2·6 g.), semicarbazone, m. p. 193°.

*Reduction of α-naphthoic acid.* α-Naphthoic acid (4·4 g.), sodamide (1 g.), and liquid ammonia (25 c.c.) were treated with sodium (1·2 g.) in small pieces, reaction being rapid. A small portion of the acid product recrystallised from benzene as colourless prisms, m. p. 75°, undepressed by an authentic sample of 1 : 4-dihydro-α-naphthoic acid prepared by Sowinski's method (*Ber.*, 1891, **24**, 2355). The remainder of the product was heated on the steam-bath for 30 mins. with an excess of 20% sodium hydroxide solution, and then acidified with dilute sulphuric acid. The product crystallised from aqueous acetic acid as colourless prisms (2·8 g.), m. p. 112°. Sowinski (*loc. cit.*) gives m. p. 112° for 3 : 4-dihydro-α-naphthoic acid.

*Methoxybenzene Derivatives.—Materials.* The anisole, *o*-, *m*-, and *p*-tolyl methyl ethers were from stock, the 5-methoxyhydrindene was made by the method of Cook and Linstead (J., 1934, 952), and 5-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene from the phenol obtained by reduction of α-naphthol in presence of Raney nickel at 125°/100 atm. The dimethylanisoles were obtained by methylation of the phenols : 3 : 4- from "1 : 2 : 4-xylenol," m. p. 61° (Kahlbaum) ; 2 : 5- from "*p*-xylenol," m. p. 74° (Schuchardt) ; 2 : 6- from "1 : 2 : 6-xylenol," m. p. 45—46° (I.C.I.) ; 2 : 4- from "1 : 3 : 4-xylenol," b. p. 210—212° (Kahlbaum) ; 3 : 5- from "1 : 3 : 5-xylenol," m. p. 65° (I.C.I.) ; and 5-methyl-2-*iso*propylanisole from thymol. 6-Methoxy-5-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene was kindly presented by Dr. R. H. Martin.

3-*Methyl*-2 : 5-*dihydroanisole*. A mixture of 3-methylanisole (20 g.) and methyl alcohol (28 g.) was dropped into a solution of sodium (20 g.) in liquid ammonia (500 c.c.) with stirring during an hour. The mixture was cautiously decomposed with ice and then with water, the organic layer collected with ether, and fractionated into two portions : (I) b. p. 105—120° (2·5 g.), (II) b. p. 165—173° (9·8 g.). Redistillation gave the fractions (A) b. p. 108—115° (2 g.), (B) b. p. 170—171° (9 g.). Fraction (A) gave a nitrosochloride, m. p. 92—93° (Found : C, 52·6 ; H, 7·6. Calc. for $C_7H_{12}ONCl$ : C, 52·0 ; H, 7·4%), undepressed by an authentic sample of 1-methyl-$\Delta^1$-*cyclo*hexene nitrosochloride, and it gave a nitrolpiperidine, m. p. 146—147°, undepressed by an authentic specimen of 1-methyl-$\Delta^1$-*cyclo*hexene nitrolpiperidine, m. p. 146—147°.

Fraction (B) consisted essentially of 3-*methyl*-2 : 5-*dihydroanisole* (Found : C, 77·2 ; H, 9·4. $C_8H_{12}O$ requires C, 77·4 ; H, 9·7%). The ultra-violet absorption spectrum showed no appreciable band in the region of 2400—2800 A., where conjugated double bonds would be expected to absorb, except a band at $\lambda_{max.}$ 2740 A. ; $\epsilon_{max.}$ 410, corresponding to about 20% of starting material. An end absorption rising to $\epsilon = 3100$ at $\lambda$ 2300 A. probably corresponds to the absorption of the enol ether double bond. (Measurements by Dr. F. B. Strauss, Oxford.)

A small portion of the fraction was refluxed with 10% aqueous sulphuric acid for an hour, the oil collected in ether, and heated on the steam-bath with excess of aqueous-alcoholic semicarbazide acetate. After addition of a little petrol, the solid was removed and extracted several times with small portions of boiling alcohol, leaving a white residue (*A*). Addition of a little water to the alcoholic extract gave colourless prisms (*B*). Fraction (*A*) recrystallised from a large volume of water as colourless needles, m. p. 210° (decomp.) (Found : C, 44·2 ; H, 7·3. $C_9H_{18}O_2N_6$ requires C, 43·7 ; H, 7·65%), apparently 3-*methyl*-$\Delta^2$-cyclo*hexenonesemicarbazido-semicarbazone*. Fraction (*B*) recrystallised from a little alcohol as flat colourless prisms, m. p. 199—200°. Vorländer and Gärtner (*Annalen*, 1899, **304**, 23) give m. p. 199—201° for the semicarbazone of 3-methyl-$\Delta^2$-*cyclo*hexenone. Treatment of the semicarbazone with alcoholic 2 : 4-dinitrophenylhydrazine sulphate in alcohol gave the 2 : 4-*dinitrophenylhydrazone* as dark red plates (from benzene–alcohol), m. p. 173° (Found : C, 53·4 ; H, 4·7. $C_{13}H_{14}O_4N_4$ requires C, 53·7 ; H, 4·8%).

If in the above reduction of 3-methylanisole the methyl alcohol was omitted, the disappearance of the sodium was slow, and about half the material was converted into the water-soluble sodium salt of *m*-cresol, identified by formation of the *m*-tolyloxyacetic acid, m. p. 102°, by treatment with sodium chloroacetate. The water-insoluble portion was nearly pure starting material, and after refluxing with dilute acid gave no derivative with 2 : 4-dinitrophenylhydrazine sulphate.

*Reductions shown in Table* II.—All the reductions were carried out in a similar manner in a 350-c.c. Dewar flask without external cooling. Continuous stirring was necessary, the mixture assuming a very pasty consistency towards the end. The example given below is typical, except that ether was added only in the cases of the methoxytetralins and methoxyhydrindene.

2-*Keto*-$\Delta^{1:9}$-*octalin*. 6-Methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene (8·1 g.) and methyl alcohol (4 g.) were added to liquid ammonia (100 c.c.) and ether (30 c.c.), and sodium (3 g.) slowly added in pieces of about 0·2 g., the colour being allowed to disappear between additions. The ammonia was then mostly evaporated, the residue decomposed with ice and water, and the organic layer removed. Distillation gave a homogeneous fraction with practically the same b. p. as the starting material (235°) (6·8 g.). This was then refluxed with 10% sulphuric acid for an hour, extracted with ether, washed with sodium carbonate solution, the solvent evaporated, and the residual pleasant-smelling oil heated on the steam-bath for 30 minutes with an excess of aqueous-alcoholic semicarbazide acetate. After cooling, light petroleum (25 c.c.) was added, the solid filtered off, washed with petrol and a little alcohol and then water, and dried (3·85 g.). It was practically pure 2-keto-$\Delta^{1:9}$-octalin semicarbazone; a little was recrystallised from dioxan–alcohol, being obtained as cream-coloured prisms, m. p. and mixed m. p. with an authentic specimen obtained by the method of du Feu, McQuillin, and Robinson (J., 1937, 53), 215°. The ketone was also characterised by addition of methylmagnesium iodide in the presence of cuprous bromide (Birch and Robinson, J., 1943, 501), the semicarbazone of *cis*-2-keto-9-methyldecalin being obtained from the product, m. p. and mixed m. p. 212—213°.

If the ammonia contained finely divided iron (1% by weight of the phenol ether) produced by the reduction of ferric nitrate by sodium, *in situ*, no ketonic product could be isolated, the substance being unchanged apart from a little demethylation.

The following substances were obtained from the other phenol ethers shown in Table II.

(A) *cyclo*Hexenone-2 : 4-dinitrophenylhydrazone as orange, flat needles from benzene–alcohol, m. p. 163°, undepressed by an authentic specimen.

(B) The semicarbazone of the product, crystallised from alcohol, had m. p. 164—165° (Found: C, 57·3; H, 7·8. Calc. for $C_8H_{13}ON_3$: C, 57·5; H, 7·8%). Kötz and Steinhorst (*Annalen*, 1911, **379**, 17) give m. p. 177—178° for the semicarbazone of 6-methyl-$\Delta^2$-*cyclo*hexenone, and Wallach (*Annalen*, 1908, **369**, 303) m. p. 207—208° for that of the alternative 2-methyl-$\Delta^2$-*cyclo*hexenone. Repeated crystallisation from methyl alcohol of the product from (B) slowly raised the m. p. to about 170°, and it appears to be derived mainly from the 6-methyl compound, since admixture with the 2-methyl derivative produced a depression in m. p. The original ketone gave a 2 : 4-*dinitrophenylhydrazone* as bright orange needles from benzene–alcohol, m. p. 122—126° (Found: C, 52·6; H, 4·75. $C_{13}H_{14}O_4N_4$ requires C, 53·7; H, 4·8%).

(D) 4-Methyl-$\Delta^2$-*cyclo*hexenonesemicarbazone was obtained as colourless prisms from alcohol, m. p. 188—189° (Found: C, 57·2; H, 7·95. Calc. for $C_8H_{13}ON_3$: C, 57·5; H, 7·8%): Kötz and Steinhorst (*loc. cit.*) give m. p. 184—185°. The ketone also gave a derivative with 2 : 4-dinitrophenylhydrazine as bright red prisms from benzene–alcohol, m. p. 158—159°.

(E) 2 : 6-*Dimethyl*-$\Delta^2$-cyclo*hexenonesemicarbazone* was obtained as cream-coloured prisms from alcohol–dioxan, m. p. 210—211° (Found: C, 59·7; H, 8·5. $C_9H_{15}ON_3$ requires C, 59·7; H, 8·3%). The 2 : 4-dinitrophenylhydrazone consisted of flat, red needles (benzene–alcohol), m. p. 153°.

(F) 3 : 6(?)-*Dimethyl*-$\Delta^2$-cyclo*hexenonesemicarbazido-semicarbazone* unaccompanied by any semicarbazone was obtained as small, colourless needles from a large volume of water, m. p. 214° (decomp.) (Found: C, 46·6; H, 7·9. $C_{10}H_{20}O_2N_6$ requires C, 46·9; H, 7·8%). The 2 : 4-*dinitrophenylhydrazone* crystallised from benzene–alcohol as orange-red needles, m. p. 134° (Found: C, 55·2; H, 5·3. $C_{14}H_{16}O_4N_4$ requires C, 55·3; H, 5·3%).

(G) 4 : 6-*Dimethyl*-$\Delta^2$-cyclo*hexenonesemicarbazone* was obtained as cream-coloured prisms from alcohol, m. p. 175° (Found: C, 59·2; H, 8·2. $C_9H_{15}ON_3$ requires C, 59·7; H, 8·3%). Wallach (*Annalen*, 1913, **397**, 198) gives m. p. 194—195° for the alternative 2 : 4-dimethyl derivative. The 2 : 4-dinitrophenylhydrazone crystallised as flat, red needles from benzene–alcohol, m. p. 152°.

(H) 3 : 4-*Dimethyl*-$\Delta^2$-cyclo*hexenone* (?) *semicarbazone* was obtained as cream-coloured prisms from alcohol, m. p. 193° (Found: C, 60·0; H, 8·5. $C_9H_{15}ON_3$ requires C, 59·7; H, 8·3%). The 2 : 4-dinitrophenylhydrazone crystallised from benzene–alcohol as red prisms, m. p. 146°.

(J) 3 : 5-Dimethyl-$\Delta^2$-*cyclo*hexenonesemicarbazone was obtained as colourless prisms from alcohol, m. p. 177° (Found: C, 59·3; H, 8·65. Calc. for $C_9H_{15}ON_3$: C, 59·7; H, 8·3%): Knoevenagel (*Annalen*, 1897, **297**, 165) gives m. p. 179—180°. A small amount of white, insoluble material, m. p. 199° (decomp.), which accompanied the semicarbazone is probably the semicarbazido-semicarbazone.

(K) The 2 : 4-dinitrophenylhydrazone was obtained as dark red, flat needles, m. p. 263° (decomp.), undepressed by an authentic specimen of 1-keto-$\Delta^{9:10}$-octalin-2 : 4-dinitrophenylhydrazone, m. p. 264°, derived from the ketone prepared in poor yield by oxidation of $\Delta^{9:10}$-octalin with selenium dioxide. Cook and Lawrence (J., 1937, 817) give m. p. 266·5—267° (decomp.).

(N) 5-*Keto*-$\Delta^{4:9}$-*tetrahydrohydrindenesemicarbazone* was obtained as cream-coloured prisms from dioxan–alcohol, m. p. 228—230° (Found: C, 61·9; H, 7·6. $C_{10}H_{15}ON_3$ requires C, 62·15; H, 7·8%). The 2 : 4-*dinitrophenylhydrazone* crystallised as red plates from dioxan–alcohol, m. p. 197—198° (Found: C, 57·2; H, 5·15. $C_{15}H_{16}O_4N_4$ requires C, 57·0; H, 5·1%).

For comparison, these substances were synthesised as follows. 2-Diethylaminomethyl*cyclo*pentanone (10 g.) and methyl iodide (10 g.) were mixed in ether (20 c.c.) and left overnight in the refrigerator. The ether was then decanted, the residual quaternary salt dissolved in alcohol and added to a cold solution of acetoacetic ester (15 g.) and sodium (3·2 g.) in alcohol (30 c.c.). After 3 hours it was heated on the steam-bath for a few minutes. Worked up in the usual manner, the product was a colourless, pleasant-smelling oil, b. p. 125°/10 mm. (3 g.), which gave derivatives shown to be identical with those above by mixed m. p.

(P) *dl*-Piperitone-2 : 4-dinitrophenylhydrazone was obtained from alcohol as orange needles, m. p. 117—118°, undepressed by an authentic specimen kindly supplied by Professor John Read, F.R.S.

*Reduction of Geranyl Methyl Ether.*—Geranyl methyl ether (b. p. 205—207°, 5 g.) and ethyl alcohol (6 g.) were added to liquid ammonia (40 c.c.), followed by sodium (3 g.) in small pieces over 45 minutes. Worked up as usual, the product was a colourless oil, b. p. 165—170° (Found: C, 86·7; H, 12·7. Calc. for $C_{10}H_{18}$: C, 87·0; H, 13·0%).

*Absence of Compounds of Type* (I).—In the cases of (B), (C), and (D), after removal of the semicarbazone the residue was distilled, and refluxed with a mixture of equal volumes of hydrobromic acid (*d* 1·5) and acetic acid for an hour. In all cases the product was almost completely soluble in dilute sodium hydroxide solution.

*Alkylbenzenes.*—The reductions were carried out in a similar manner to that used by Wooster (*loc. cit.*), except that no external cooling was used. The sodium was dissolved in liquid ammonia in a Dewar flask, and a mixture of the hydrocarbon and ethyl alcohol equivalent to the sodium used was slowly dropped in with stirring.

*Reduction of* m-*xylene.* Hydrocarbon (18 g.) and alcohol (25 c.c.) were added to a solution of sodium (10 g.) in liquid ammonia (150 c.c.). The product was a colourless oil, b. p. 142—144° (15 g.) (Found: C, 89·1; H, 10·8. $C_8H_{12}$ requires C, 88·9; H, 11·1%). It gave the following absorption bands corresponding to *m*-xylene, the proportion of the latter being calculated from the values of $\epsilon$ given for the pure substance by Wolf and Herold (*Z. physikal. Chem.*, 1931, *B*, **13**, 213) (data by Dr. F. B. Strauss, Oxford):

| $\gamma_{max.}$, A. | <2290 | 2657 | 2687 | 2726 |
|---|---|---|---|---|
| $\epsilon_{max.}$ | — | 59·4 | 41·1 | 54·8 |
| *m*-Xylene, % | — | 21·6 | 18·0 | 21·8 |

Treatment with amyl nitrite and hydrochloric acid in acetic acid in the usual manner (Wallach, *Annalen*, 1906, **343**, 49) gave the *nitrosochloride* as colourless needles, m. p. 123° (decomp.) (Found: C, 55·8; H, 7·1. $C_8H_{12}ONCl$ requires C, 55·3; H, 6·9%). This on heating with a few drops of piperidine in alcohol gave the *nitrolpiperidine* as prismatic needles, m. p. 137° (Found: C, 70·1; H, 9·3. $C_{13}H_{22}ON_2$ requires C, 70·3; H, 9·0%).

The nitrosochloride (1 g.) was heated on the steam-bath for 15 minutes with 10 c.c. of a mixture of equal volumes of alcohol and 20% aqueous sodium hydroxide, and the mixture then added to 30% aqueous sulphuric acid (10 c.c.). The solid precipitate was recrystallised first from a little alcohol and then from a little light petroleum (b. p. 40—60°). It consisted of pale yellow prisms, m. p. 75° (Found : C, 75·3; H, 7·3. Calc. for $C_{16}H_{18}ON_2$ : C, 75·6; H, 7·1%). Bamberger and Brady (*Ber.*, 1900, **33**, 3644) give m. p. 76—76·5° for 2 : 2′ : 4 : 4′-tetramethylazoxybenzene, and Bamberger and Rising (*Annalen*, 1901, **316**, 265) give m. p. 88·5—89° for the alternative 2 : 2′ : 6 : 6′-tetramethylazoxybenzene.

Reduced hydrocarbon (3·2 g.) in chloroform (25 c.c.) was ozonised, the ozonide being decomposed with water and zinc dust. The chloroform solution was filtered, and well shaken with a solution of copper acetate (10 g.) in warm water (100 c.c.). The chloroform layer was separated, dried, and evaporated, leaving a copper compound which recrystallised from chloroform–ether as blue needles (0·7 g.); this did not melt below 300° (Found : C, 45·6; H, 5·5. Calc. for $C_{10}H_{14}O_4Cu$ : C, 45·8; H, 5·3%). It was, therefore, the copper salt of acetylacetone.

*Reduction of tetralin.* Addition of tetralin (13·2 g.) and ethyl alcohol (18 g.) to a solution of sodium (9·2 g.) in liquid ammonia (250 c.c.) gave a colourless oil (12 g.), b. p. 204—208°. Treatment with amyl nitrite and hydrochloric acid in acetic acid solution gave a bright blue colour, but no precipitate. After evaporation at room temperature in a vacuum a blue solid was obtained, which recrystallised from a little light petroleum as bright blue prisms, resembling copper sulphate, m. p. 91° (Found : C, 59·9; H, 7·1. $C_{10}H_{14}ONCl$ requires C, 60·0; H, 7·0%), doubtless the *nitrosochloride* of 1 : 2 : 3 : 4 : 5 : 8-hexahydronaphthalene.

*Reduction of* p-*cymene.* *p*-Cymene (10 g.) and alcohol (20 g.) were added to sodium (10 g.) in liquid ammonia (200 c.c.). The product (9·5 g.) was a colourless oil with a slight lemon odour, b. p. 175—180° (1 G. absorbed 98 c.c. of hydrogen in the presence of Raney nickel, corresponding to 15% of substance with two double bonds). Fractionation gave a fraction, b. p. 179—180° (Found : C, 89·2; H, 11·0. Calc. for $C_{10}H_{14}$ : C, 89·6; H, 10·4%. Calc. for $C_{10}H_{16}$ : C, 88·2; H, 11·8%). From the analysis this fraction contained about 25—30% of a dihydro-*p*-cymene, consisting at least partly of $\gamma$-terpinene, since the nitrosochloride, m. p. 110°, and nitrolpiperidine, m. p. and mixed m. p. with an authentic specimen 144°, were obtained from it.

*Reduction of* p-*xylene.* *p*-Xylene (10·6 g.) was reduced with sodium (9·2 g.) and alcohol (24 c.c.) in ammonia (150 c.c.), giving a product (9 g.), b. p. 140—142°. This gave a nitrosochloride (2·2 g.) as colourless needles, m. p. 98°, a little of which was converted into the nitrolpiperidine, m. p. 133°. The nitrosochloride, after being heated with 20 c.c. of a mixture of equal volumes of alcohol and 20% sodium hydroxide on the steam-bath for 15 minutes, and then diluted with 20 c.c. of 30% sulphuric acid, gave a yellow solid which recrystallised as sulphur-yellow needles from methyl alcohol, m. p. 110° (Found : C, 75·3; H, 7·3. Calc. for $C_{16}H_{18}ON_2$ : C, 75·6; H, 7·1%). Bamberger and Rising (*Annalen*, 1901, **316**, 290) give m. p. 110—110·5° for 2 : 2′ : 5 : 5′-tetramethylazoxybenzene.

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