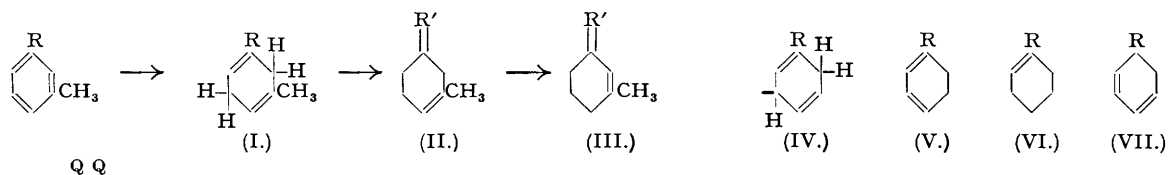


119. Reduction by Dissolving Metals. Part III.

By ARTHUR J. BIRCH.

The reduction by sodium and alcohol in liquid ammonia of methoxyalkylbenzenes (Part I, *J.*, 1944, 430) has been further examined, and the reaction extended to dimethylaminoalkylbenzenes. Confirmation of the initial formation of $\alpha\delta$ -dihydro-derivatives has been obtained by preparation of derivatives of the $\beta\gamma$ -unsaturated ketones produced in the first stage of acid hydrolysis, and in several cases by isolation of the ketones themselves. Further action of sodium in liquid ammonia on the dihydro-compounds gave in many cases small yields of tetrahydro-compounds, hydrolysed by acid to alkylcyclohexanones. The dihydrotolyl methyl ethers gave in addition a hydrocarbon fraction containing methyl- Δ^1 -cyclohexene. The combined processes gave results similar to, but not always identical with, those obtained by the action of calcium hexamine on the aromatic compounds (see table) and the mechanisms are probably similar. The latter reagent produced the same dimethylcyclohexene from *m*-xylene and 2 : 5-dihydro-*m*-xylene, and reduced *o*-chloro- and *p*-bromo-anisole to a mixture of anisole and 2 : 5-dihydroanisole.

In Part I (*loc. cit.*) the reduction of methoxyalkylbenzenes with sodium and alcohol in liquid ammonia was assumed to give the $\alpha\delta$ -dihydro-derivatives (*e.g.*, I, R = OMe) by analogy with the alkylbenzenes and because of the small ultra-violet absorption in the region 2300—2700 Å. of dihydro-*m*-tolyl methyl ether, despite the formation of $\alpha\beta$ -unsaturated ketones (*e.g.*, III, R' = O) by refluxing with dilute mineral acid.



This is confirmed by the preparation of the initial $\beta\gamma$ -unsaturated ketones (*e.g.*, II, $R' = O$) and their derivatives formed from the reduction products of both dimethylamino- and methoxy-alkylbenzenes. The latter (*e.g.*, I, $R = OMe$) on treatment with cold aqueous sodium bisulphite gave solid derivatives which were decomposed with sodium carbonate to give the ketones themselves; *e.g.*, dihydro-*m*-tolyl methyl ether (I, $R = OMe$) gave 3-methyl- Δ^3 -cyclohexenone (II, $R' = O$). The $\beta\gamma$ -unsaturated 2 : 4-dinitrophenylhydrazones [*e.g.*, II, $R' = N \cdot NH \cdot C_6H_3(NO_2)_2$] were obtained by the action of 2 : 4-dinitrophenylhydrazine sulphate in cold alcohol on the ketones or the dihydro-compounds. Their constitution was confirmed by their light absorption (λ_{max} , *ca.* 3680 Å.) which resembles that of the saturated (λ_{max} , *ca.* 3660 Å.) rather than the $\alpha\beta$ -unsaturated ketone derivatives (λ_{max} , 3830 Å.) (cf. Braude and Jones, *J.*, 1945, 498). Similarly, the $\beta\gamma$ -unsaturated semicarbazones, obtained by the action of semicarbazide acetate on the ketones or the dihydro-amines, resemble in their absorption (λ_{max} , *ca.* 2280 Å.) the derivatives of the saturated ketones (λ_{max} , *ca.* 2290 Å.) rather than those of the $\alpha\beta$ -unsaturated ketones (λ_{max} , *ca.* 2670 Å.) (cf. Evans and Gillam, *J.*, 1943, 568).

It is probable that several of the ketones prepared in Part I contained some of the $\beta\gamma$ -unsaturated compounds, since their 2 : 4-dinitrophenylhydrazones melted somewhat below the values now found, and in the case of *p*-tolyl methyl ether it appears from the absorption of the semicarbazone (λ_{max} , 2300 Å.) that the ketone was the relatively acid-stable 4-methyl- Δ^3 -cyclohexenone despite the formation of the $\alpha\beta$ -unsaturated 2 : 4-dinitrophenylhydrazone, since the latter was prepared in hot acid solution.

The dimethylaminoalkylbenzenes showed the same orientation for hydrogen addition as the corresponding methoxy-compounds since they gave rise to the same derivatives on hydrolysis, and from the dimethyltoluidines the process represents a practical method of obtaining the ketones ($\alpha\beta$ -unsaturated with the *ortho*- and *meta*-, $\beta\gamma$ -unsaturated with the *para*-) in 55–65% yield free from the acid-soluble starting material. Dimethylamine was also produced in the hydrolysis.

Further reduction of some of the methoxy- and dimethylamino-dihydroalkylbenzenes to the enol derivatives of the alkylcyclohexanones (*e.g.*, VI, $R = OMe, NMe_2$) was produced by the action of sodium in liquid ammonia, since, after acid hydrolysis of the product, derivatives of these ketones could be prepared in small yield. Other products of the reaction have not yet been fully investigated, but the tolyl methyl ethers gave considerable amounts of hydrocarbon containing methyl- Δ^1 -cyclohexene. Even after the extended reduction, ketonic derivatives corresponding only to the dihydro-derivatives were obtained from a number of compounds (see table). There appear to be two possible explanations of this extended reduction process. The dihydro-derivatives may be isomerised by the sodium through an anion such as (IV) to a conjugated diene (V) which is then reduced to (VI). Double-bond shift in the alternative direction with formation of cyclohexadiene derivatives (VII) may explain the formation of hydrocarbons, since such compounds may well undergo hydrogenolysis and further reduction (cf. Part I, *loc. cit.*; Part II, *J.*, 1945, 809). Alternatively, the tetrahydro-derivatives may actually have been formed in small quantity during the reduction to dihydro-derivatives, the latter then being removed preferentially by further action of sodium with formation of hydrocarbons; however, no derivatives of the saturated ketones have yet been prepared from the dihydro-derivatives.

It is evident that in the preparation of dihydro-derivatives an excess of sodium over the hydrogen donor must be avoided, and by the method now employed it is possible to obtain about 70% yield of product with the tolyl methyl ethers, containing about 95% of dihydro-derivative with the *meta*- and *para*- and 45% with the *ortho*-. The hydrocarbon obtained from *m*-tolyl methyl ether in Part I was undoubtedly due to the method of adding the substance and alcohol to excess of sodium in ammonia, and was not, as at first thought, a primary reduction product.

Kazanskii *et al.* (*J. Gen. Chem. U.S.S.R.*, 1938, 8, 642; *Bull. Acad. Sci., U.R.S.S.*, 1938, 1061, 1065) explained the reduction of benzenoid hydrocarbons to tetrahydro-derivatives with calcium hexamine by assuming the formation of $\alpha\delta$ -dihydro-derivatives, isomerisation of these to conjugated compounds, and further reduction. Since this represents a combination of the two processes outlined above, the products from the second sodium reduction were compared with those obtained by the action of calcium hexamine on the aromatic compounds. The ketonic products obtained on acid hydrolysis were in many cases the same (see table) and any difference can be explained by assuming that the isomerising action of the reagent on the dihydro-derivatives is less powerful than that of sodium. This seems confirmed by the fact that these, when formed, have unconjugated double bonds, since $\beta\gamma$ -unsaturated ketonic derivatives could be obtained. Owing to losses of volatile hydrocarbons in the ammonia evolved and the ether used as a solvent, it has been possible to confirm their presence only in the case of *m*-tolyl methyl ether, where methyl- Δ^1 -cyclohexene was obtained. As additional evidence for the correctness of Kazanskii's theory it was found that 2 : 5-dihydro-*m*-xylene, obtained by sodium reduction, was further reduced by calcium hexamine to a 1 : 3-dimethylcyclohexene identical with that obtained by direct reduction of *m*-xylene.

The frequent isolation of tetrahydro- rather than dihydro-derivatives with calcium hexamine is undoubtedly due to the slowness in these cases of the initial addition of two hydrogen atoms compared with the rate of the subsequent isomerisation and further reduction. Einhorn and Ehret (*Annalen*, 1897, 295, 175) showed that the presence of bromine in a benzene ring facilitated its reduction with sodium and amyl alcohol, the halogen being removed in the process; the action of calcium hexamine on *p*-bromo- and *o*-chloro-anisole was accordingly examined in the hope of increasing the relative rate of the first stage of the reduction. This was realised, since the very rapid reaction gave rise to a mixture of anisole and 2 : 5-dihydroanisole, the presence of the latter being demonstrated by the preparation of Δ^3 -cyclohexenone 2 : 4-dinitrophenylhydrazone.

With anisole itself reduction was slow, and only derivatives of cyclohexanone could be obtained from the product.

In the following table the number of hydrogen atoms added refers only to products of type (I) and (VI), since they are based on an examination of the ketonic products of hydrolysis.

Compound.	Number of hydrogen atoms added.			Compound.	Number of hydrogen atoms added.		
	A.	B.	C.		A.	B.	C.
Anisole	2	4	4	Dimethylaniline	2	4	4, 2
<i>o</i> -Tolyl methyl ether	2	4	2	Dimethyl- <i>o</i> -toluidine	2	4, 2	4, 2
<i>m</i> -Tolyl methyl ether	2	4, 2	2	Dimethyl- <i>m</i> -toluidine	2	2	2
<i>p</i> -Tolyl methyl ether	2	4	4	Dimethyl- <i>p</i> -toluidine	2	4	4
2:4-Dimethylanisole	2	2	2	Dimethyl- <i>p</i> -cumidine	2	—	—
6-Methoxy-1:2:3:4-tetrahydronaphthalene	2	2	2				

EXPERIMENTAL.

Method A.—The substance (7 g.) and ethyl alcohol (15 g.) were dissolved in liquid ammonia (130 c.c.) in a Dewar flask (350 c.c.), and sodium (7 g.) added in small pieces with good stirring as rapidly as possible without the reaction becoming uncontrollable (about 45 minutes). When the blue colour had disappeared, the pasty mass was decomposed by cautious addition of water (100 c.c.), and the oil collected with ether. With the methoxy-compounds this product, consisting chiefly of the dihydro-derivative, could be distilled; with the amines some decomposition occurred in presence of water, but the dihydro-derivative could be isolated if necessary by direct extraction of the reaction mixture with dry ether. Hydrolysis to the acid-stable form of the ketone was accomplished by refluxing the dihydro-derivative with a mixture of concentrated sulphuric acid (6 c.c.) and water (25 c.c.) for 25 minutes, followed by saturation with ammonium sulphate and extraction with ether. Hydrolysis of the methoxyalkyldihydrobenzenes to the $\beta\gamma$ -unsaturated ketones was carried out by shaking with a saturated aqueous solution of sodium hydrogen sulphite (10 g.) for 12 hours. The solid derivative was filtered off, and decomposed by addition to a solution of sodium carbonate (5 g.) in water (15 c.c.), and the ketone extracted with ether and distilled under reduced pressure. The $\beta\gamma$ -unsaturated 2:4-dinitrophenylhydrazones were prepared by adding the dihydro-derivative or the $\beta\gamma$ -unsaturated ketone to excess of 2:4-dinitrophenylhydrazine in cold alcoholic sulphuric acid (5%), the derivative being filtered off and washed with aqueous sodium carbonate and then water to remove any acid which might isomerise it on recrystallisation. They were converted into the $\alpha\beta$ -unsaturated derivatives by refluxing for 3 minutes with a drop of sulphuric acid in alcohol, with addition of benzene in the case of the less soluble ones. The $\beta\gamma$ -unsaturated semicarbazones were obtained in the usual manner from the ketones, or from the dihydro-amines by shaking with aqueous semicarbazide hydrochloride until they dissolved, and then adding sodium acetate.

Method B.—The dihydro-derivatives were obtained by method A, and further treated with a solution of sodium (7 g.) in ammonia (150 c.c.) for 6–8 hours. In some cases the dihydro-derivatives were not isolated from the initial reduction, the extra sodium being added directly. Control experiments showed that identical results were obtained by either method. The products were worked up and hydrolysed as under method A, the ketonic fraction alone being examined, except with the tolyl methyl ethers where the product was distilled before hydrolysis, and the lower-boiling hydrocarbon fraction separated.

Method C.—Calcium (15 g.) was dissolved in ammonia (100 c.c.) in small portions, most of the ammonia evaporated until the golden metallic oil was on the point of solidification, and dry ether (75 c.c.) added with vigorous swirling to obtain the calcium hexamine as a golden sand. To this was added the compound (20 g.) in ether (75 c.c.), and the mixture left for 36–72 hours according to the rate of reaction. It was then very cautiously added to crushed ice under nitrogen, and the product extracted with ether by the aid of a centrifuge. After drying and removal of the solvent, the oil was refluxed for 30 minutes with a mixture of concentrated sulphuric acid (10 c.c.) and water (35 c.c.). The ketones (from the amines) or their derivatives (from the methoxy-compounds) were isolated as under method A.

Dimethylaniline.—Method A gave Δ^2 -cyclohexenone (3.2 g.), b. p. 163–167° (Found: C, 74.5; H, 8.7. Calc. for C_6H_8O : C, 75.0; H, 8.3%), λ_{max} . 2245 Å.; ϵ_{max} . 8440; 2:4-dinitrophenylhydrazone, m. p. 165–166°, undepressed by an authentic specimen; semicarbazone (from water), m. p. 161–162° (Found: C, 54.6; H, 7.5. Calc. for $C_7H_{11}ON_3$: C, 54.8; H, 7.2%); λ_{max} . 2627 Å.; ϵ_{max} . 16,460. Kötze and Grethe (*J. pr. Chem.*, 1909, **80**, 499) give m. p. 161° for Δ^2 -cyclohexenone semicarbazone. Δ^2 -cyclohexenone 2:4-dinitrophenylhydrazone formed orange-yellow plates from alcohol, m. p. 131–132°; λ_{max} . 3690 Å.; ϵ_{max} . 18,700 (Found: C, 52.5; H, 4.4. $C_{12}H_{12}O_4N_4$ requires C, 52.2; H, 4.3%). Treatment with acid converted it into the above derivative, m. p. 165–166°. Δ^2 -cyclohexenone semicarbazone formed colourless needles from water, m. p. 146–147°, λ_{max} . 2288 Å.; ϵ_{max} . 12,350 (Found: C, 54.5; H, 7.2. $C_7H_{11}ON_3$ requires C, 54.8; H, 7.2%).

Method B gave cyclohexanone (2.9 g.), b. p. 150–152° (Found: C, 73.1; H, 10.4. Calc. for $C_6H_{10}O$: C, 73.5; H, 10.2%); 2:4-dinitrophenylhydrazone, orange-yellow plates, m. p. 155–156°, undepressed by an authentic specimen, m. p. 157–158°.

Method C gave in small yield cyclohexanone 2:4-dinitrophenylhydrazone, m. p. and mixed m. p. 157–158°.

Anisole.—Dihydroanisole (method A) gave Δ^2 -cyclohexenone 2:4-dinitrophenylhydrazone, m. p. 132–133°, undepressed by a specimen obtained as above. Methods B and C gave cyclohexanone 2:4-dinitrophenylhydrazone, m. p. and mixed m. p. 157–158°.

*Dimethyl-*o*-toluidine.*—Method A gave the dihydro-derivative containing a little starting material, b. p. 75–78°/14 mm. (Found: C, 79.2; H, 10.6. $C_9H_{12}N$ requires C, 78.9; H, 10.9%). The ketone obtained on hydrolysis (3.25 g.) had b. p. 60–75°/15 mm., λ_{max} . 2263 Å.; ϵ_{max} . 4490 (Found: C, 75.9; H, 9.3. Calc. for $C_9H_{10}O$: C, 76.35; H, 9.1%). The position of the absorption maximum corresponds to a β -alkyl $\alpha\beta$ -unsaturated ketone (Woodward, *J. Amer. Chem. Soc.*, 1942, **64**, 716) and the major constituent is therefore probably 6-methyl- Δ^2 -cyclohexenone. Redistillation gave two fractions, b. p. 164–167° (2.6 g.), and b. p. 167–174° (0.2 g.). The former gave a semicarbazone, m. p. 172°, and the latter a semicarbazone, m. p. 198–200°. Since Kötze and Steinhorst (*Annalen*, 1911, **379**, 17) give m. p. 177–178° for 6-methyl- Δ^2 -cyclohexenone semicarbazone, and Wallach (*Annalen*, 1908, **369**, 303) gives m. p. 207–208° for 2-methyl- Δ^2 -cyclohexenone semicarbazone the above are probably these compounds in a slightly impure form. On treatment

with alcoholic 2:4-dinitrophenylhydrazine sulphate they gave 2:4-dinitrophenylhydrazones respectively as orange-red elongated prisms, m. p. 156—157° (Found: C, 53.8; H, 4.6. $C_{13}H_{14}O_4N_4$ requires C, 53.8; H, 4.8%), and as dark red plates, m. p. 198—199°, undepressed by the derivative of 2-methyl- Δ^2 -cyclohexenone, m. p. 203° (Found: C, 54.2; H, 4.8. $C_{13}H_{14}O_4N_4$ requires C, 53.8; H, 4.8%). The latter derivatives were obtained directly from the crude ketone by crystallising the 2:4-dinitrophenylhydrazone repeatedly from benzene-alcohol, the second being less soluble and present in smaller amount. Treatment of the ketone with excess of 2:4-dinitrophenylhydrazine sulphate in hot alcohol gave an orange, rather insoluble substance; recrystallised from pyridine, this had m. p. 176—177° (Found: C, 46.8; H, 4.1. $C_{19}H_{20}O_6N_8$ requires C, 46.7; H, 4.1%). Since it could not be obtained from 2-methyl- Δ^2 -cyclohexenone it is probably 6-methyl- Δ^2 -cyclohexenone 2:4-dinitrophenylhydrazino-2:4-dinitrophenylhydrazone.

Method B produced a ketone (0.5 g.), b. p. 160—180°, which gave rise to a little of the last substance, m. p. 176—177°, but chiefly 2-methylcyclohexanone 2:4-dinitrophenylhydrazone, m. p. 131—132°, undepressed by an authentic specimen, m. p. 134—135°.

Method C gave a ketone (3.2 g.), b. p. 60—66°/18 mm., which was separated into two fractions: b. p. 162—164° (2.3 g.) and b. p. 166—169° (0.4 g.). The former was chiefly 2-methylcyclohexanone (Found: C, 75.0; H, 10.7. Calc. for $C_7H_{12}O$: C, 75.0; H, 10.7%), and gave the 2:4-dinitrophenylhydrazone as orange plates, m. p. 132—133°, after several crystallisations from alcohol, undepressed by an authentic specimen, m. p. 134—135°. The absorption (λ_{max} , 2263 Å.; ϵ_{max} , 2085) indicated the presence of some of the cyclohexenone. The second fraction contained more of this (λ_{max} , 2263 Å.; ϵ_{max} , 3810) and gave a red 2:4-dinitrophenylhydrazone, m. p. 135—139°, undepressed by the derivative above, m. p. 156—157°, but depressed by that of 2-methylcyclohexanone, m. p. 134—135°.

o-Tolyl Methyl Ether.—The product obtained by method A contained about 45% of dihydro-derivative, since 1.0 g., treated with 2:4-dinitrophenylhydrazine (2.0 g.) in 5% alcoholic sulphuric acid in the cold, gave a 2:4-dinitrophenylhydrazone as orange prisms, m. p. 135—137° (1.0 g.) (Found: C, 53.8; H, 4.6. $C_{13}H_{14}O_4N_4$ requires C, 53.8; H, 4.8%). The ketone obtained after acid hydrolysis must consist of the same mixture of substances as in the case of dimethyl-*o*-toluidine since it gave the two 2:4-dinitrophenylhydrazones, m. p. 155—156° and m. p. 198—199°.

Method B gave the 2:4-dinitrophenylhydrazone of 2-methylcyclohexanone, m. p. 133—134°, in small yield. In addition, a small amount of hydrocarbon, b. p. 105—110°, was obtained, which gave methyl- Δ^1 -cyclohexene nitrolpiperidine, m. p. 146—147°, undepressed by an authentic specimen, m. p. 146—147°.

Method C gave a mixed 2:4-dinitrophenylhydrazone from which a little of the 2-methyl- Δ^2 -cyclohexenone derivative, m. p. 199—200°, was obtained. The main bulk formed orange-red, elongated prisms from benzene-alcohol, m. p. 130—136°, which appeared to consist mainly of the 6-methyl- Δ^2 -cyclohexenone derivative, since on refluxing with 2:4-dinitrophenylhydrazine in alcoholic sulphuric acid it gave the insoluble 2:4-dinitrophenylhydrazino-2:4-dinitrophenylhydrazone, m. p. 175—176°.

Dimethyl-m-toluidine.—Method A gave 3-methyl- Δ^2 -cyclohexenone as a colourless oil (3.1 g.), b. p. 190—195° (Found: C, 75.8; H, 9.1. Calc. for $C_7H_{10}O$: C, 76.35; H, 9.1%); λ_{max} , 2320 Å.; ϵ_{max} , 11,290; Evans and Gillam (*J.*, 1941, 815) give λ_{max} , 2350 Å.; ϵ_{max} , 12,930. The 2:4-dinitrophenylhydrazones formed dark red plates from benzene-alcohol, m. p. 173—174°, and the semicarbazone colourless prisms from alcohol, m. p. 200—201°, λ_{max} , 2640 Å.; ϵ_{max} , 24,500. Treatment of the crude dihydro-derivative with semicarbazide hydrochloride followed by sodium acetate gave 3-methyl- Δ^3 -cyclohexenone semicarbazone as colourless plates from alcohol, m. p. 158—159°; λ_{max} , 2283 Å.; ϵ_{max} , 11,410 (Found: C, 57.3; H, 7.8. $C_8H_{13}ON_3$ requires C, 57.5; H, 7.8%). It was isomerised by refluxing with 5% aqueous-alcoholic semicarbazide hydrochloride for 30 minutes to the above $\alpha\beta$ -unsaturated semicarbazone, m. p. 200—201°.

Method B gave a product which still gave rise to the 2:4-dinitrophenylhydrazone of 3-methyl- Δ^2 -cyclohexenone, m. p. 173—174°, but on addition of further sodium (5 g.) and ammonia (100 c.c.) and standing for 12 hours, the product then gave a very small yield of 3-methylcyclohexanone 2:4-dinitrophenylhydrazone as orange elongated prisms from benzene-alcohol, m. p. 156—157° (Found: C, 53.3; H, 5.4. Calc. for $C_{13}H_{16}O_4N_4$: C, 53.4; H, 5.5%). Allen and Richmond (*J. Org. Chem.*, 1937, 2, 226) give m. p. 155°. The semicarbazone formed colourless prisms from alcohol, m. p. 181—182°.

Method C gave the ketonic hydrolysis product as an oil, b. p. 185—195° (0.8 g.), which gave the 2:4-dinitrophenylhydrazone, m. p. 173—174°, and semicarbazido-semicarbazone, m. p. 214°, of 3-methyl- Δ^2 -cyclohexenone.

m-Tolyl Methyl Ether.—Method A gave the dihydro-derivative as a colourless oil, b. p. 168—170° (cf. Part I). This substance (1.00 g.) gave with a hot solution of 2:4-dinitrophenylhydrazine (2.0 g.) in alcoholic sulphuric acid the 2:4-dinitrophenylhydrazone (2.0 g.) of 3-methyl- Δ^2 -cyclohexenone, m. p. 173—174° (2.15 g.), corresponding to a 94% content of dihydro-derivative. Hydrolysis of the latter (5 g.) with a saturated solution of sodium hydrogen sulphite (10 g.) gave a solid bisulphite compound (4 g.), which was decomposed with a solution of sodium carbonate (5 g.) in water (12 c.c.). Extraction with ether gave 3-methyl- Δ^3 -cyclohexenone as a colourless oil with a marked odour, b. p. 70°/18 mm. (Found: C, 76.1; H, 9.3. $C_7H_{10}O$ requires C, 76.35; H, 9.1%). From the presence of absorption at λ_{max} , 2330 Å.; ϵ_{max} , 2050, it appears to contain some 16% of the isomeric 3-methyl- Δ^2 -cyclohexenone, into which it is very readily converted by the action of acids. The R band at λ_{max} , 2800 Å.; ϵ_{max} , 19, is at a considerably shorter wave-length than the value λ_{max} , 3100 Å.; ϵ_{max} , 48 given for the latter ketone by Evans and Gillam (*loc. cit.*). It gave the semicarbazone as colourless plates, m. p. 159—160°.

Method B gave two fractions: b. p. 105—111° (2.2 g.) and b. p. 160—165° (0.6 g.). The former was a methylcyclohexene, n_D^{16} 1.4526 (Found: C, 87.2; H, 12.8. Calc. for C_7H_{12} : C, 87.5; H, 12.5%). It contained methyl- Δ^1 -cyclohexene, since it gave a solid nitroschloride from which was obtained the nitrolpiperidine, m. p. 147—148°, undepressed by an authentic specimen (Found: C, 68.6; H, 10.4. Calc. for $C_{17}H_{22}ON_2$: C, 68.6; H, 10.5%). Treatment of the second fraction with 2:4-dinitrophenylhydrazine gave a mixed product, but after further treatment with sodium in ammonia it gave a small yield of 3-methylcyclohexanone 2:4-dinitrophenylhydrazone, m. p. 156—157° (Found: C, 53.3; H, 5.4. Calc. for $C_{13}H_{16}O_4N_4$: C, 53.4; H, 5.4%).

Method C, but with omission of the ether ordinarily used as a solvent, gave two fractions: b. p. 100—110° (0.8 g.) and b. p. 167—175° (16 g.). The former gave the nitrolpiperidine of methyl- Δ^1 -cyclohexene, m. p. 145—146°, the latter a small yield of 3-methyl- Δ^2 -cyclohexenone 2:4-dinitrophenylhydrazone, m. p. 173—174°.

Dimethyl-p-toluidine.—Method A gave 4-methyl- Δ^3 -cyclohexenone (4.1 g.), b. p. 74°/17 mm. or 169—172°/755 mm. (Found: C, 75.9; H, 9.6. Calc. for $C_7H_{10}O$: C, 76.35; H, 9.1%). The absence of a maximum at 2260 Å. (ϵ_{mol} , 870) confirmed its formulation as the $\beta\gamma$ -unsaturated ketone. It was also obtained readily by the bisulphite method. The 2:4-dinitrophenylhydrazone formed orange prisms, m. p. 120—121°, λ_{max} , 3680 Å.; ϵ_{max} , 20,200 (Found: C, 53.8; H, 4.8. $C_{13}H_{14}O_4N_4$ requires C, 53.8; H, 4.8%). This was converted by refluxing with alcoholic sulphuric acid for a minute into 4-methyl- Δ^2 -cyclohexenone 2:4-dinitrophenylhydrazone, dark red prisms from benzene-alcohol, m. p. 173—174°, λ_{max} , 3830 Å.; ϵ_{max} , 22,150 (Found: C, 53.8; H, 4.7. $C_{13}H_{14}O_4N_4$ requires C, 53.8; H, 4.8%). The absorption of 4-methylcyclohexanone 2:4-dinitrophenylhydrazone (λ_{max} , 3685 Å.; ϵ_{max} , 19,100) was almost identical with that of the former derivative. 4-Methyl- Δ^3 -cyclohexenone semicarbazone formed colourless prisms, m. p. 188—189°, λ_{max} , 2330 Å.; ϵ_{max} , 11,300.

After the ketone (3 g.) had been refluxed with 3% aqueous sulphuric acid for 6 hours it was redistilled: (i), b. p.

170—173°; (ii), b. p. 173—178°. The former gave the same derivatives as the starting material; the latter (λ_{\max} . 2280 Å.; ϵ_{\max} . 6780) contained some 4-methyl- Δ^2 -cyclohexenone, and gave in the cold a mixture of the 2 : 4-dinitrophenylhydrazones, m. p. 120—121° and 173—174°, the latter being separated by its lower solubility in alcohol. It appears, therefore, that the $\beta\gamma$ -unsaturated ketone is only isomerised to a small extent by acid.

Method B gave a ketone (1.3 g.), b. p. 165—172°, from which the 2 : 4-dinitrophenylhydrazone of 4-methylcyclohexanone, m. p. and mixed m. p. 133—134°, could be obtained (Found : C, 53.0; H, 5.5. Calc. for $C_{13}H_{16}O_4N_4$: C, 53.4; H, 5.5%). The semicarbazone crystallised as prisms from alcohol, m. p. and mixed m. p. 196° (Found : C, 56.8; H, 8.9. Calc. for $C_8H_{15}ON_3$: C, 56.8; H, 8.9%).

Method C also gave a small yield of 4-methylcyclohexanone, identified by the above derivatives, m. p. 133—134° and 196°.

p-Tolyl Methyl Ether.—Method A gave the dihydro-derivative (5 g.), b. p. 167—170°, shown by the action of 2 : 4-dinitrophenylhydrazine sulphate to be 94% pure (cf. *m*-tolyl methyl ether). The 2 : 4-dinitrophenylhydrazone, m. p. 120—121°, was identical with that obtained from dimethyl-*p*-toluidine.

Further reduction of the dihydro-derivative by method B gave (i), b. p. 105—110° (0.7 g.), and (ii), b. p. 155—165° (0.3 g.). The former gave the nitropiperidine of methyl- Δ^1 -cyclohexene, m. p. 146—147°, and the latter the 2 : 4-dinitrophenylhydrazone of 4-methylcyclohexanone, m. p. 132—133°. This derivative was also obtained from the product of reduction by method C.

Dimethyl-p-cumidine.—Method A gave a ketonic product (3.5 g.), b. p. 97—98°/16 mm. It gave in the cold 4-isopropyl- Δ^3 -cyclohexenone 2 : 4-dinitrophenylhydrazone as golden plates (from alcohol), m. p. 107—108° (Found : C, 56.3; H, 5.5. $C_{15}H_{18}O_4N_4$ requires C, 56.6; H, 5.7%). On refluxing with dilute alcoholic sulphuric acid this gave the derivative of 4-isopropyl- Δ^2 -cyclohexenone as orange-red elongated prisms from benzene-alcohol, m. p. 135—136° (Found : C, 56.6; H, 5.8. Calc. for $C_{15}H_{18}O_4N_4$: C, 56.6; H, 5.7%). Berry, Macbeth, and Swanson (*J.*, 1937, 987) give m. p. 138° for the derivative obtained from the optically active ketone.

2 : 4-Dimethylanisole. —Method A gave rise to a 2 : 4-dinitrophenylhydrazone, prepared in hot solution, as orange-red prisms, m. p. 164—165° (Found : C, 55.2; H, 5.2. $C_{14}H_{16}O_4N_4$ requires C, 55.2; H, 5.3%). Since the product from method B gave the same derivative, no further reduction had taken place. Method C proceeded very slowly, and after 14 days the small amount of neutral material gave the above derivative, m. p. 164—165°. The chief product (70% yield) was *m*-4-xyleneol, identified as 2 : 4-dimethylphenoxyacetic acid, m. p. and mixed m. p. 138—139°.

6-Methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene. —The dihydro-derivative prepared by method A was hydrolysed with sodium hydrogen sulphite, and the solid adduct steam-distilled from 10% aqueous sodium carbonate. The 2-keto-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydronaphthalene so obtained was a colourless oil with a marked odour, b. p. 117°/12 mm. (Found : C, 79.6; H, 9.2. $C_{10}H_{14}O$ requires C, 80.0; H, 9.3%). The 2 : 4-dinitrophenylhydrazone, also obtained directly in the cold from the dihydro-compound, formed orange-red elongated plates from benzene-alcohol, m. p. 176—177° (Found : C, 58.3; H, 5.4. $C_{16}H_{18}O_4N_4$ requires C, 58.2; H, 5.45%). On being refluxed with alcoholic sulphuric acid for a minute this was converted into 2-keto-2 : 3 : 4 : 5 : 6 : 7 : 8 : 10-octahydronaphthalene 2 : 4-dinitrophenylhydrazone, which formed dark red plates from benzene-alcohol, m. p. 171—172° (Found : C, 58.2; H, 5.4. $C_{16}H_{18}O_4N_4$ requires C, 58.2; H, 5.45%).

2 : 5-Dihydro-*m*-xylene. —Prepared as in Part I, the hydrocarbon, b. p. 141—142°, contained 8% of *m*-xylene as estimated by the intensity of its ultra-violet absorption bands. Hydrocarbon (12 g.) in ether (40 c.c.) was left with calcium hexamine (from calcium, 10 g.) for 36 hours. The greyish mass was then added carefully to crushed ice under nitrogen, slightly acidified with dilute hydrochloric acid, and the oil distilled. The product (6.8 g.) was a dimethylcyclohexene, b. p. 124—129°, n_D^{20} 1.4530 (Found : C, 87.4; H, 12.5. Calc. for C_8H_{14} : C, 87.3; H, 12.7%). Treatment with amyl nitrite and hydrogen chloride at -15° gave no solid nitrosochloride, but addition of petrol to the blue oil gave a white solid. A portion of this was crystallised from benzene, forming colourless prisms, m. p. 137—138°. The bulk was converted into a mixture of nitropiperidines, the principal constituent of which was obtained as colourless prisms, m. p. 157—158°, by several crystallisations from alcohol (Found : C, 69.4; H, 10.7. $C_{13}H_{24}ON_2$ requires C, 69.6; H, 10.7%). Since two stereoisomers are possible the production of a mixture is not unexpected.

m-Xylene. —Carried out as above, the reduction gave a product still containing a considerable amount of *m*-xylene, and was repeated. The product was a colourless oil, b. p. 124—129°, n_D^{20} 1.4530 (Found : C, 87.6; H, 12.4. Calc. for C_8H_{14} : C, 87.3; H, 12.7%). The intensity of its ultra-violet absorption bands indicated the presence of about 8% of *m*-xylene; the analytical figures calculated for this mixture are : C, 87.6; H, 12.4%. The nitrosochloride, obtained as above, had m. p. 123—126° (crude), m. p. 137—138° after recrystallisation from benzene. Kazanskii (*loc. cit.*) gives m. p. 117—118° for this nitrosochloride. It gave a nitropiperidine, m. p. 157—158°, undepressed by the derivative obtained above.

p-Bromoanisole and *o*-Chloroanisole. —Reduction was by method C, and the reaction was controlled by ice-cooling. The product was separated into two fractions : (i), b. p. 150—160° (5 g.), and (ii), b. p. 160—170° (1.1 g.). The former was shown by demethylation with hydrobromic acid to consist chiefly of anisole; the latter gave the 2 : 4-dinitrophenylhydrazone of Δ^3 -cyclohexenone, m. p. and mixed m. p. 132—133°, converted by acid into the derivative of Δ^2 -cyclohexenone, m. p. 165—166°. 4-Chloro-2-methoxytoluene gave a quantitative yield of *o*-tolyl methyl ether, identified by demethylation and conversion into 2-methylphenoxyacetic acid, m. p. 150°.

The ultra-violet absorption measurements were carried out by Dr. F. B. Strauss, in ethyl alcoholic solution, except with the 2 : 4-dinitrophenylhydrazones which were dissolved in chloroform.

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