327. *Reduction by Dissolving Metals. Part V.*

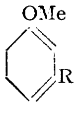
By ARTHUR J. BIRCH.

Potassium amide in liquid ammonia conjugates the double bonds of 2 : 5-dihydroanisoles with formation of 2 : 3-dihydroanisoles, which give adducts with maleic anhydride and are reduced by sodium in ammonia chiefly to alkyl*cyclo*hexenes, but by sodium and alcohol in ammonia chiefly to alkyltetrahydroanisoles. With alkyl-2 : 5-dihydrobenzenes, instead of the conjugated dienes, the products are chiefly the alkylbenzenes, and the conjugated compound 4 : 5-dihydro-*m*-xylene gives *m*-xylene under the same conditions. Also observed are the transformations : 2 : 4-dimethylhexa-1 : 5-diene ⟶ 2 : 4-dimethylhexa-2 : 4-diene; oct-1-ene ⟶ oct-2-ene; 4-phenylbut-1-ene ⟶ 4-phenylbut-2-ene; 3-butoxy-2-methylpropene ⟶ 1-*butoxy-2-methylpropene*; 3-methoxy*cyclo*hexene ⟶ a mixture of *cyclo*hexene and benzene; a number of hydrocarbons are unchanged.

The bond migrations are postulated as taking place through anions formed by loss of a proton from an allyl position. The theory is related to the effects of alkyl substitution on the ease of the process, and applied to a consideration of some reduction phenomena with sodium in ammonia and with calcium hexammine.

In Part III (*J.*, **1946**, 593) it was found that the αδ-dihydro-derivatives obtained by the reduction with sodium and alcohol in liquid ammonia of methoxyalkyl-, dimethylaminoalkyl-, and alkyl-benzenes were further reduced by sodium and ammonia or by calcium hexammine. Intermediate conjugation of the double bonds was postulated as taking place through a mesomeric anion formed by loss of a proton to the anionoid reagent (either sodium, or calcium hexammine, or the sodium or calcium amide formed in increasing amount as the reaction proceeds). Farmer, Koch, and Sutton (*J.*, **1943**, 545) have postulated a similar intervention of mesomeric allylic radicals to explain the formation of conjugated peroxides from non-conjugated dienes in oxidation reactions.

Conjugated compounds have now been produced from the methoxyalkyl-αδ-dihydrobenzenes by the action of the amides of sodium or potassium in liquid ammonia (the latter preferred because of its solubility); the deep red-brown colour of the solution confirms the formation of a mesomeric carbanion in the process. The products (*e.g.*, I) were identified as conjugated by the formation of crystalline maleic anhydride adducts, by their light absorption at $\lambda_{max.}$ *ca.* 2700 A., and by their ready reduction with sodium and alcohol in ammonia. They must have a disposition of double bonds relative to the methoxyl group of type (I) rather than (II) or (III, R = OMe). Acid hydrolysis produced unsaturated ketones, rather than hydrocarbons, thus eliminating (II), and the maleic anhydride adducts did not behave as the enol ethers of ketones, and were therefore of type (IV) corresponding to (I) rather than of type (V) corresponding to (III, R = OMe). Also, the product from 2 : 5-dihydro-*p*-tolyl methyl ether must be 2 : 3-*dihydro*-p-*tolyl methyl ether* since it gave rise to the 2 : 4-dinitrophenylhydrazone of 4-methyl*cyclo*hex-3- rather than -2-enone.



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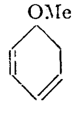

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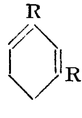

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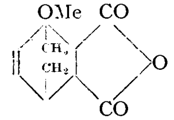

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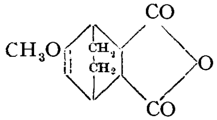

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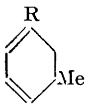

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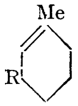

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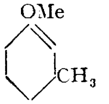

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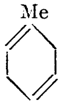

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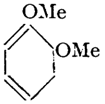
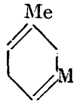


(X.)



(XI.)

The conjugated compound from 2 : 5-dihydro-*m*-tolyl methyl ether is formulated as (I, R = Me) since acid hydrolysis gave 3-methyl*cyclo*hex-2-enone, not the alternative 5-methyl*cyclo*hex-2-enone to be expected from (VI, R = OMe). Further confirmation came from its reduction products. Sodium and alcohol in ammonia gave a little 1-methyl*cyclo*hexene (VII, R = H) and preponderantly 1-methoxy-3-methyl*cyclo*hexene (VIII), acid hydrolysis of which produced 3-methyl*cyclo*hexanone, and permanganate oxidation α-methyladipic acid. Sodium in ammonia gave mainly (VII, R = H) and a little (VIII). The hydrocarbons similarly obtained from the dihydro-*o*- and -*p*-tolyl methyl ethers were identified by their infra-red absorption spectra as mixtures of methyl*cyclo*hexenes : ortho-, the 4-methyl- two parts, and the 1- and 3-methyl one part each; para-, one part each of the 1-, 3-, and 4-methyl. The 2 : 5-dihydro-derivatives from 3 : 5-dimethyl- and 2 : 6-dimethyl-anisole gave by the prolonged action of sodium in ammonia (doubtless with intermediate conjugation) small amounts of 1-methoxy-3 : 5- and -2 : 6-dimethyl*cyclo*hexene (hydrolysed by acid to 3 : 5-dimethyl- and 2 : 6-dimethyl-*cyclo*hexanone) together with the same hydrocarbon, identified as 2 : 4-dimethyl*cyclo*hexene by comparison of its derivatives with those obtained from an authentic specimen. 1 : 2-Dimethoxy-3 : 6-dihydrobenzene gave anisole by the action of potassium amide in ammonia, probably by way of the intermediate (X).

The formation of conjugated derivatives of type (I) can be explained by assuming that a proton is removed from the CH_2 adjacent to the methoxyl group, and that the anion then adds a proton with the final result of pivoting the enol double bond about this group. This is particularly clearly shown by the formation of (I, R = Me) rather than (VI, R = OMe) from dihydro-*m*-tolyl methyl ether. Some dehydrogenation which accompanies the isomerisation may be explained by loss of a hydrogen anion from the intermediate salt (compare the hydrocarbons on p. 1644).

Addition of the alkyldihydrobenzenes such as 2 : 5-dihydrotoluene (IX) or 2 : 5-dihydro-*m*-xylene (XI) to potassium or sodium amide in liquid ammonia gave a red colour, but the recovered product contained little, if any, of the conjugated diene, the chief constituent being the aromatic hydrocarbon together with a little of the alkyltetrahydrobenzene and polymeric material. The product obtained by acting on 2 : 5-dihydrotoluene with sodium amide for a short time gave rise to a trace of a maleic anhydride *adduct*, probably derived from 1-methyl*cyclo*hexa-1 : 3-diene, since it was not identical with that obtained from 1-methyl*cyclo*hexa-1 : 5-diene. That *cyclo*hexa-1 : 3-dienes themselves can be dehydrogenated by the reagent was shown by the production of *m*-xylene from 4 : 5-dihydro-*m*-xylene, the red colour of the intermediate ion being visible in this case also. These ions must be similar in type to those from the unconjugated dienes, and both can assume the stable aromatic configuration by the expulsion of a hydrogen anion. The dehydrogenation may be compared with the formation of naphthalene and lithium hydride by the action of phenyl lithium on 1 : 4-dihydronaphthalene (Gilman and Bradley, *J. Amer. Chem. Soc.*, 1938, **60**, 2333). The source of the small amount of tetrahydrobenzene derivative in the aromatic product is not certain, but in view of the small reducing power of sodium hydride (Swamer and Hauser, *J. Amer. Chem. Soc.*, 1946, **68**, 2647) it may have been present in the starting material.

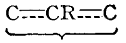
The formation of a considerable proportion of tetrahydrobenzene derivative by the action of sodium in ammonia or of calcium hexammine on the unconjugated compound must have been due to reduction of the conjugated compound as it was produced; this also agrees with the fact that less polymeric material was formed. Even here, however, some aromatic material appeared (see 2 : 5-dihydrotoluene). It is noteworthy that the same ratio of 1- to 3-methyl*cyclo*hexene was obtained from toluene or 2 : 5-dihydrotoluene, irrespective of which reduction process was employed, and that reduction of 4 : 5-dihydro-*m*-xylene (III; R, R′ = Me) gave 1 : 3-dimethyl*cyclo*hexene (VII, R = Me) already obtained from *m*-xylene and 2 : 5-dihydro-*m*-xylene (Part III, *loc. cit.*). The fact that alkyl*cyclo*hexenes are unaltered by the reagents makes it possible to draw conclusions about the reduction intermediates from the position of the double bond in these products.

The reason for the observed difference in the rate of dehydrogenation of the dihydroanisole and dihydrobenzene derivatives may be due to the higher energy of the anions with the latter due to the inductive effect of the alkyl groups; this may be correlated with the fact that, although some conjugated material was detected in the case of dihydrotoluene, none was observed with the more highly alkylated dihydro-*m*-xylene. That methoxyl groups have a stabilising effect on anions except when the charge is forced to reside on the occupied or para-carbon atoms is clear from a number of results obtained in Part IV (this vol., p. 102) and from the fact that 2-methoxynaphthalene is reduced mainly in the occupied ring.

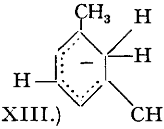
Hydrocarbon.	Reagent.	Product.
2 : 5-Dihydrotoluene	KNH_2,NH_3	Toluene; methyl*cyclo*hexene (tr.)
2 : 5-Dihydro-*m*-xylene	KNH_2,NH_3	*m*-Xylene
4 : 5-Dihydro-*m*-xylene	KNH_2,NH_3	*m*-Xylene
Oct-1-ene	KNH_2,NH_3	Oct-1-ene, 80%; oct-2-ene, 20%
2 : 5-Dimethylhexa-1: 5-diene	KNH_2,NH_3	2 : 5-Dimethylhexa-2 : 4-diene
4-Phenylbut-1-ene	KNH_2,NH_3	4-Phenylbut-2-ene(?); polymer
3-Methyl-, 1 : 3-dimethyl-, 2 : 4-dimethyl-*cyclo*hexene; *d*-limonene, *d*-sylvestrene, methylgeraniolene, 1 : 2 : 3 : 4 : 1′ : 2′ : 3′ : 4′-octahydrodiphenyl	KNH_2,NH_3 or $Ca(NH_3)_6$	Unchanged
2 : 5-Dihydrotoluene	Na,NH_3	1-Methyl*cyclo*hexene, 50%; toluene, 40%; 3-methyl*cyclo*hexene, 10%
2 : 5-Dihydrotoluene	$Ca(NH_3)_6$	1-Methyl*cyclo*hexene, 80%; 3-methyl*cyclo*hexene, 10%
2 : 5-Dihydro-*m*-xylene	Na,NH_3; $Ca(NH_3)_6$	1 : 3-Dimethyl*cyclo*hexene *
4 : 5-Dihydro-*m*-xylene	$Na,EtOH,NH_3$	1 : 3-Dimethyl*cyclo*hexene
Toluene	$Ca(NH_3)_6$	1-Methyl*cyclo*hexene, 80%; 3-methyl*cyclo*hexene, 20%
4-Phenylbut-1-ene	Na,NH_3	Phenylbutane

* Part III, *loc. cit.*; the constitution of the product is proved in the present paper.

The ability to conjugate depends on the ability to form the alkali-metal salts and therefore on the presence of a relatively acidic hydrogen atom, which, with the *cyclo*hexadienes, is due to stabilisation of the anion resulting from proton removal by resonance of the charge with the ends of the two double bonds. The production of the conjugated compound on addition of a proton to this ion is, of course, due to the lower energy of the double bonds in conjugation. It has already been pointed out (Part II, *J.*, 1945, 809) that the lower the degree of alkylation of the end carbon atoms of a mesomeric anion of type (XII) the more readily it is formed, *i.e.*, the more acidic the proton whose removal produces it. This is further confirmed by the work of Morton, Brown, Holden, Letsinger, and Margat (*J. Amer. Chem. Soc.*, 1945, **67**, 2224) on the direct metallation of alkylethylenes. These ideas may be applied to predict that the conjugation of 1 : 3-dimethyl-2 : 5-dihydrobenzene (XI), which might proceed through (XIII) or (XIV), should take place through the latter, since the negative charges would reside on less alkylated carbon atoms at the ends of the mesomeric system. This is confirmed by the production of 1 : 3-dimethyl*cyclo*hexene (VII, R = Me) by sodium in ammonia reduction, since this could hardly be derived from (XIII) through (VI, R = Me), and is given by (III; R = R′ = Me) derivable from (XIV).


$\underbrace{C \cdots CR \cdots C}_{-}$

(XII.)



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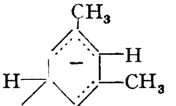


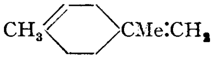
(XIV.)

$CH_2{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH_2$ (XV.)

$CMe_2{:}CH{\cdot}CH{:}CMe_2$ (XVI.)

$Ph{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2$ (XVII.)

$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CHMe$ (XVIII.)



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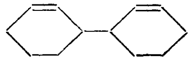
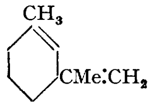


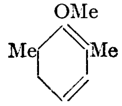
(XX.)



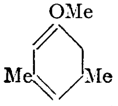
(XXI.)

$CH_2{:}CMe{\cdot}CH_2{\cdot}O{\cdot}C_4H_9$ (XXII.)

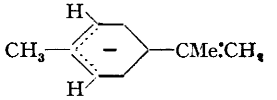
$CMe_2{:}CH{\cdot}O{\cdot}C_4H_9$ (XXIII.)



(XXIV.)



(XXV.)



(XXVI.)

With compounds having double bonds insulated from one another by two saturated carbon atoms the conditions for migration are less favourable, since removal of a proton in the allyl position gives an anion in which the charge can resonate with only one double bond. The double bond in oct-1-ene was moved in part to the 2-position, and in this case the mesomeric anion has a low degree of alkylation, having at its ends CH_2 and CHR. This is also true of the initial stage of isomerisation of 2 : 5-dimethylhexa-1 : 5-diene (XV) to 2 : 5-dimethylhexa-2 : 4-diene (XVI) (the compound has also been reduced by means of calcium hexammine; Kazanskii and Glushnev, *Bull. Acad. Sci. U.R.S.S.*, 1938, 1065) and of the isomerisation of 4-phenylbut-1-ene (XVII) to 1-phenylbut-2-ene and a polymer, probably derived from 1-phenylbut-1-ene; (XVII) was also reduced to phenylbutane by the prolonged action of sodium in ammonia. The second unsaturated centre must have some influence, however, since isomerisation in these cases is much readier than with oct-1-ene. Substitution of the hexa-1 : 5-diene with saturated carbon atoms at the ends of the potential resonating ion, *e.g.*, in methylgeraniolene (XVIII), *d*-limonene (XIX), and 1 : 2 : 3 : 4 : 1′ : 2′ : 3′ : 4′-octahydrodiphenyl (XX), prevented isomerisation with potassium amide in ammonia or reduction by calcium hexammine; more surprisingly, sylvestrene (XXI) was also unaffected. Several of these compounds should have relatively acidic hydrogen atoms present in methyl groups, but the anion formed by loss of a proton should merely regenerate the starting material. Production of the anion (XXVI) from *d*-limonene would result in re-formation of the starting material in the racemic form; in fact, the rotation was unaltered. This agrees with the observation that the double bond in alkyl*cyclo*hexenes was not moved.

3-Butoxy-2-methylpropene (XXII), the resonating anion from which would contain CH_2 and CHR, was isomerised to 1-butoxy-2-methylpropene (XXIII), but no 1-methoxy*cyclo*hexene was obtained from 3-methoxy*cyclo*hexene, loss of methyl alcohol producing a hydrocarbon analysing for *cyclo*hexadiene. It gave no reaction with maleic anhydride, and its physical properties indicated a mixture of benzene and *cyclo*hexene.*

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* *Added in Proof.*—For a further discussion of the relationship between structure and acidity see Birch, Faraday Society Discussion, 1947, "Labile Molecules" (in the press).

Reduction of the conjugated *cyclo*hexadienes can be explained by the initial addition of two electrons to the system. With the hydrocarbons the bivalent anions so formed then abstract two protons from the alcohol or ammonia; in the case of the methoxy-compounds this may occur, and is naturally favoured by the presence of more readily available protons from alcohol, or a methoxyl anion may be expelled with addition of another electron and finally two protons to give an alkyl*cyclo*hexene. This seems to be confirmed by the fact that 2-ethoxy-3 : 4-dihydronaphthalene gave with sodium in ammonia, with or without alcohol, tetrahydronaphthalene as the first recognisable product. It also explains the formation of the same dimethyl*cyclo*hexene from the dihydro-derivatives of 2 : 6- and 3 : 5-dimethylanisole by way of the conjugated (XXIV) and (XXV), which would give the same anion after expulsion of the methoxyl. It is noteworthy that dimethyl-2 : 5-dihydro-*m*-toluidine did not give rise to any hydrocarbon, the product containing the tetrahydroamine, and this may be correlated with the greater energy of formation of the dimethylamino- than of the methoxy-anion.

It is necessary to determine the positions of addition of nascent hydrogen to asymmetrical alkyl*cyclo*hexadienes before further conclusions can be drawn; evidence is already available that it may occur in both the αβ- and the αδ-positions.

EXPERIMENTAL.

Alkyl-2 : 3-dihydroanisoles.—The alkyl-2 : 5-dihydroanisoles were prepared from the alkylanisoles by reduction with sodium and alcohol in liquid ammonia as described in Part III (*loc. cit.*) under the preparation of the derived ketones. The compounds (10 g.) were conjugated by dissolving them in a solution of potassium amide (from the metal, 2 g.) in ammonia (100 c.c.) and stirring for 1½ hours. Water was then added very cautiously to the dark red solution, the oil taken up in ether, dried (K_2CO_3), and distilled. It is unlikely that conjugation is brought about by the caustic alkali formed during working up, since it could not be accomplished with boiling 15% alcoholic potassium ethoxide. The maleic anhydride adducts were prepared by addition to excess of the anhydride in benzene and 6 hours' standing. Material boiling up to 120°/10 mm. was then removed, the product extracted from polymeric material in the residue with ether and crystallised from benzene–light petroleum with the aid of a little fuller's earth.

The reduction of the conjugated compounds was carried by two methods. (*A*) A solution of the substance (5 g.) and sodium (4 g.) in ammonia (70 c.c.) was left for 30 minutes, excess of ammonium chloride added, then water (70 c.c.), and the oil separated with the aid of a centrifuge if necessary; owing to the volatility of the methyl*cyclo*hexenes in boiling ammonia only 2—2·5 g. of product were obtained. (*B*) The substance (10 g.) in ammonia (100 c.c.) and alcohol (10 g.) was gradually reduced by the addition of sodium (6 g.) over 3 hours with stirring, and the product worked up as above.

2 : 5-Dihydroanisole (b. p. 148—150°) gave 2 : 3-*dihydroanisole* (6·2 g.), b. p. 145°, $n_D^{18°}$ 1·4902, $\lambda_{max.}$ 2690 A., $\epsilon_{max.}$ 4560 (Found : C, 76·1; H, 9·2. $C_7H_{10}O$ requires C, 76·4; H, 9·1%). Cold 2 : 4-dinitrophenylhydrazine sulphate in alcohol indicated a 91% content of dihydro-compound, and the derivative formed, m. p. 140—146°, appeared to be a mixture of the *cyclo*hex-3-enone derivative, m. p. 134°, and the Δ^2-derivative, m. p. 167°. Brief refluxing with alcoholic sulphuric acid gave the latter. The maleic anhydride *adduct* had m. p. 91° (Found : C, 63·3; H, 5·8. $C_{11}H_{12}O_4$ requires C, 63·4; H, 5·8%). This was unaffected by Brady's reagent.

Reduced by method (*B*), 2 : 3-dihydroanisole gave 1-methoxy*cyclo*hexene, b. p. 140—145°, which readily gave rise to *cyclo*hexanone 2 : 4-dinitrophenylhydrazone, m. p. 156—157°.

The mixture of 3 : 6- and 2 : 5-dihydro-*o*-tolyl methyl ether obtained by reduction of *o*-tolyl methyl ether (Parts I and III, *loc. cit.*) gave a *compound* (chiefly 2 : 3-dihydro-*o*-tolyl methyl ether ?), b. p. 155—160° (Found : C, 77·3; H, 9·3. $C_8H_{12}O$ requires C, 77·4; H, 9·7%). Continuation of the reaction for 5½ hours gave a product, b. p. 165—167°, which appeared to be mainly *o*-tolyl methyl ether (Found : C, 79·1; H, 8·3. Calc. for $C_8H_{10}O$: C, 78·7; H, 8·2%). Reduction of the conjugated diene mixture by method (*A*) gave a fraction, b. p. 100—104°, shown by its infra-red absorption to contain a mixture of methyl*cyclo*hexenes : Δ^3- two parts, Δ^1- and Δ^2- one part each.

2 : 5-Dihydro-*m*-tolyl methyl ether gave 5 : 6-*dihydro*-m-*tolyl methyl ether*, b. p. 165—167° (Found : C, 77·6; H, 9·7. $C_8H_{12}O$ requires C, 77·4; H, 9·7%). The maleic anhydride *adduct* crystallised from benzene–light petroleum in prisms, m. p. 77° (Found : C, 65·2; H, 6·3. $C_{12}H_{14}O_4$ requires C, 64·9; H, 6·3%). Treatment with 2 : 4-dinitrophenylhydrazine sulphate in hot alcohol gave the derivative of 3-methyl*cyclo*hex-2-enone, m. p. 174—175°. Reduction by method (*A*) gave chiefly a fraction, b. p. 106—110°, $n_D^{18°}$ 1·4500 (Found : C, 87·4; H, 12·5. Calc. for C_7H_{12} : C, 87·5; H, 12·5%). The nitrolpiperidine, m. p. 146—147°, and its infra-red absorption spectrum showed this hydrocarbon to be 1-methyl*cyclo*hexene. A small fraction, b. p. 155—162°, gave rise to the 2 : 4-dinitrophenylhydrazone of 3-methyl*cyclo*hexanone, m. p. 154°, and a few drops of material, b. p. 162—172°, appeared to contain *m*-tolyl methyl ether. Reduction by method (*B*) gave a trace of a fraction (i) b. p. 110—115°, and mainly 1-methoxy-3-methyl*cyclo*hexene (ii), b. p. 156—160°, $n_D^{14°}$ 1·4660. Hydrolysis of this by boiling with 10% sulphuric acid for an hour, conversion of the oil into a solid bisulphite compound, and regeneration gave 3-methyl*cyclo*hexanone, b. p. 165°; 2 : 4-dinitrophenylhydrazone m. p. 155°, semicarbazone m. p. 180°. Oxidation of (ii) with potassium permanganate in acetone gave an acid which did not crystallise, but readily formed the dianilide of α-methyladipic acid, m. p. 173° (Found : C, 73·7; H, 7·4. Calc. for $C_{19}H_{22}O_2N_2$: C, 73·5; H, 7·1%). Bouveault and Locquin (*Bull. Soc. chim.*, 1908, **3**, 451) give m. p. 174—175°.

2 : 5-Dihydro-*p*-tolyl methyl ether (b. p. 168—170°) gave 2 : 3-*dihydro*-p-*tolyl methyl ether*, b. p. 165—167°, $\lambda_{max.}$ 2720, $\epsilon_{max.}$ 4060 (Found : C, 77·6; H, 9·7. $C_8H_{12}O$ requires C, 77·4; H, 9·7%), giving

with cold Brady's reagent the 2 : 4-dinitrophenylhydrazone of 4-methyl*cyclo*hex-3-enone, m. p. 122°, converted by hot dilute alcoholic sulphuric acid into the derivative of 4-methyl*cyclo*hex-2-enone, m. p. 174°. The maleic anhydride *adduct* had m. p. 85—86° (Found : C, 64·8; H, 6·3. $C_{12}H_{14}O_4$ requires C, 64·9; H, 6·3%). Reduction by method (*A*) gave a hydrocarbon fraction, b. p. 103—105° (Found : C, 87·3; H, 12·7. Calc. for C_7H_{12} : C, 87·5; H, 12·5%). This was shown by its infra-red absorption to contain about one part each of 1-, 3-, and 4-methyl*cyclo*hexene. Reduction by method (*B*) gave chiefly a fraction (1-*methoxy*-4-*methyl*cyclo*hexene*), b. p. 157—162° (Found : C, 76·0; H, 10·6. $C_8H_{14}O$ requires C, 76·2; H, 11·1%), which on acid hydrolysis and bisulphite purification gave 4-methyl*cyclo*hexanone, b. p. 165—167°, semicarbazone m. p. 196°.

In order to investigate the ease of dehydrogenation in this case the conjugation reaction was continued for (i) 2½ hours and (ii) 5½ hours, giving as the products : (i), b. p. 165—167° (Found : C, 77·4; H, 9·8. Calc. for $C_8H_{12}O$: C, 77·4; H, 9·7%), $\lambda_{max.}$ 2720, $\epsilon_{max.}$ 3640; and (ii), b. p. 165—170° (Found : C, 77·9; H, 9·3. Calc. for $C_8H_{12}O$: C, 77·4; H, 9·7%). The latter by estimation with Brady's reagent showed only about a 50% content of methyldihydroanisole. Dehydrogenation had thus taken place, although to a smaller extent than with the dihydro-*o*-tolyl methyl ether.

2 : 6-Dihydroveratrole (Part IV, *loc. cit.*) gave rise to anisole, b. p. 145—150°, unaffected by Brady's reagent and demethylated to phenol.

Reduction of 3 : 5- *and* 2 : 6-*Dimethylanisole*.—These compounds (10 g.) were reduced in ammonia (100 c.c.) with sodium (5 g.) and alcohol (5 g.), a further amount of sodium (5 g.) added, and the mixture left for 10 hours and worked up as usual.

3 : 5-Dimethylanisole gave (i), b. p. 125—130° (2·4 g.), and (ii), b. p. 185—195°. Fraction (i) gave a good yield of a *nitrolpiperidine* as colourless prisms from methyl alcohol, m. p. 146—147° (Found : C, 69·4; H, 10·6. $C_{13}H_{24}ON_2$ requires C, 69·6; H, 10·7%), undepressed by the derivative of 2 : 4-dimethyl*cyclo*hexene. Fraction (ii) seemed to be largely starting material, but reacted with Brady's reagent to give the 2 : 4-*dinitrophenylhydrazone* of 3 : 5-dimethyl*cyclo*hexanone, m. p. 155—157° (Found : C, 54·2; H, 6·0. $C_{14}H_{18}O_4N_4$ requires C, 54·7; H, 6·1%). Two stereoisomers are possible, and there is no evidence as to whether one or a mixture was present.

2 : 6-Dimethylanisole gave (i), b. p. 125—130° (1·1 g.), and (ii), b. p. 160—170° (0·5 g.), together with a higher fraction of starting material. Fraction (i) gave the nitrolpiperidine, m. p. 146—147°, of 2 : 4-dimethyl*cyclo*hexene. Fraction (ii) gave the 2 : 4-*dinitrophenylhydrazone* of 2 : 6-dimethyl*cyclo*hexanone, m. p. 149—150°, also possibly a mixture of stereoisomers (Found : C, 55·0; H, 5·9. $C_{14}H_{18}O_4N_4$ requires C, 54·7; H, 6·1%).

The 2 : 4-dimethyl*cyclo*hexene required for comparison was synthesised by reducing *m*-4-xylenol with Raney nickel and hydrogen at 150°/100 atm., esterifying the resulting 2 : 4-dimethyl*cyclo*hexanol with palmitic acid, and distillation of the ester at 340—350°. It had b. p. 124—125° (Found : C, 87·1; H, 12·7. Calc. for C_8H_{14} : C, 87·3; H, 12·7%). In order to ensure that no movement of the double bond had taken place, the hydrocarbon was oxidised with potassium permanganate in acetone, and the resulting acid gave β-methyladipic dianilide, m. p. 198° (Found : C, 73·0; H, 7·2. Calc. for $C_{19}H_{22}O_2N_2$: C, 73·5; H, 7·1%). Markownikoff (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 226) gives m. p. 197—198°. Addition of nitrosyl chloride gave a solid which was refluxed with sodium acetate in acetic acid and hydrolysed with dilute mineral acid to a ketone, b. p. 93—96°/16 mm. (cf. Wallach, *Annalen*, 1913, **395**, 275; **397**, 198). This gave rise to a 2 : 4-*dinitrophenylhydrazone* as bright red needles (from ethyl acetate–alcohol), m. p. 183—184° (Found : C, 55·0; H, 5·4. $C_{14}H_{16}O_4N_4$ requires C, 55·3; H, 5·3%), which must be derived from 2 : 4-dimethyl*cyclo*hex-2-enone, since it is not identical with the derivatives from 2 : 6-dimethyl-, m. p. 153°, from 3 : 5-dimethyl-, m. p. 165°, or from 4 : 6-dimethyl-*cyclo*hex-2-enone, m. p. 164—165°. The semicarbazone had m. p. 167—168° (Found : C, 59·5; H, 8·3. Calc. for $C_9H_{15}ON_3$: C, 59·7; H, 8·3%). This examination was necessary, since Wallach (*loc. cit.*) gives m. p. 130—131° for the nitrolpiperidine and m. p. 194—195° for the semicarbazone obtained as above.

Methallyl butyl ether, obtained from sodium *n*-butoxide and methallyl chloride, b. p. 135—137°, $n_D^{20°}$ 1·3942, gave 1-*butoxy*-2-*methylpropene*, b. p. 138—140°, $n_D^{20°}$ 1·4230 (Found : C, 75·0; H, 12·6. $C_8H_{16}O$ requires C, 75·0; H, 12·5%), which, unlike the starting material, gave the 2 : 4-dinitrophenylhydrazone of *iso*butaldehyde on boiling with Brady's reagent, m. p. 182° (Found : C, 47·6; H, 4·8. Calc. for $C_{10}H_{12}O_4N_4$: C, 47·4; H, 5·1%). Mathiesssen and Hagedorn (*Mikrochem.*, 1941, **29**, 58) give m. p. 183·5—185°.

3-Methoxy*cyclo*hexene (Berlande, *Bull. Soc. chim.*, 1942, **9**, 653) gave a hydrocarbon, b. p. 78—82°, $n_D^{14°}$ 1·4720 (Found : C, 89·6; H, 10·4. Calc. for C_6H_8 : C, 90·0; H, 10·0%). It was unsaturated, but did not react with maleic anhydride and was probably a mixture of *cyclo*hexene and benzene. A small higher-boiling fraction contained no 1-methoxy*cyclo*hexene since it failed to react with Brady's reagent.

Action of Sodium or Potassium Amide on Unsaturated Hydrocarbons.—The metal (2 g.) in ammonia (100 c.c.) was converted into the amide by the catalytic action of ferric nitrate, the hydrocarbon (10 g.) added, and the mixture stirred for 6 hours with exclusion of air. The product was worked up by addition of ice and ether extraction; in many cases considerable loss of material occurred by volatilisation.

2 : 5-*Dihydrotoluene* was obtained by reduction of toluene with sodium and alcohol in liquid ammonia (cf. dihydro-*m*-xylene, Part III); b. p. 114—115°, $n_D^{18°}$ 1·4695 (Found : C, 89·2; H, 10·7. C_7H_{10} requires C, 89·4; H, 10·6%), nitrolpiperidine m. p. 122—123°. It gave rise to a product, b. p. 108—110°, $n_D^{18°}$ 1·4890 (Found : C, 90·4; H, 9·3. Calc. for C_7H_8 : C, 91·3; H, 8·7%. Calc. for C_7H_{12} : C, 87·5; H, 12·5%). This gave a small yield of the nitrolpiperidine, m. p. 146—147°, of 1-methyl*cyclo*hexene, and must consist of an admixture of a trace of this with toluene. After treatment of 2 : 5-dihydrotoluene with sodium amide in ammonia for one hour the product (b. p. 108—112°) was left with maleic anhydride in cold acetone for 5 hours and then steam-distilled. The small residue crystallised and the *adduct* was recrystallised from aqueous methanol; m. p. 62—63° (Found : C, 68·5; H, 6·2. $C_{11}H_{12}O_3$ requires C, 68·8; H, 6·2%). Brief heating on the steam-bath with *p*-toluidine gave a *derivative*, m. p. 182° (from alcohol) (Found : C, 77·2; H, 6·7. $C_{18}H_{19}O_2N$ requires C, 76·8; H, 6·7%). For comparison the derivative of 1-methyl*cyclo*hexa-1 : 5-diene was synthesised from *cyclo*hex-2-enone by the action of methylmagnesium iodide, dehydration of the carbinol by distillation with a trace of iodine, and treatment

of the product (b. p. 110°) with maleic anhydride in cold acetone. The *adduct*, b. p. 180°/16 mm., solidified in ice and melted at about 14° (Found : C, 68·8; H, 6·0. $C_{11}H_{12}O_3$ requires C, 68·7; H, 6·2%). The *derivative* obtained with *p*-toluidine had m. p. 175° (from alcohol), depressed by the above (Found : C, 76·4; H, 6·9. $C_{18}H_{19}O_2N$ requires C, 76·8; H, 6·7%).

2 : 5-Dihydro-*m*-xylene (Part I) gave *m*-xylene, b. p. 136—138°, $n_D^{18°}$ 1·4960, and no conjugated material could be detected.

4 : 5-Dihydro-*m*-xylene, b. p. 135°, was obtained by the action of methylmagnesium iodide on 3-methyl*cyclo*hex-2-enone followed by dehydration of the carbinol by distillation with a trace of iodine. It gave rise to a colourless oil, b. p. 135—137° (Found : C, 90·2; H, 9·7. Calc. for C_8H_{10} : C, 90·5; H, 9·5%). The ultra-violet absorption of this was consistent with its being a mixture of 80% of *m*-xylene and 20% of starting material.

Oct-1-ene was prepared by the action of amylmagnesium bromide on allyl bromide (cf. Henne, Chanan, and Turk, *J. Amer. Chem. Soc.*, 1941, **63**, 3474); b. p. 119°. It gave rise to a product, b. p. 119—122°, which was shown by its infra-red absorption spectrum to contain 80% of oct-1-ene and 20% of an isomer, probably oct-2-ene.

2 : 5-Dimethylhexa-1 : 5-diene (*idem, ibid.*), b. p. 114°, $n_D^{19°}$ 1·4360, gave rise to 2 : 5-dimethylhexa-2 : 4-diene, b. p. 133—135°, $n_D^{19°}$ 1·4780, m. p. 13°. Henne and Turk (*J. Amer. Chem. Soc.*, 1942, **64**, 826) give for this substance b. p. 134·5°, $n_D^{20°}$ 1·4781, m. p. 14°.

4-Phenylbut-1-ene (obtained by the action of benzylmagnesium chloride on allyl bromide) when treated as above gave the red colour but the product was largely high-boiling, probably produced by the polymerisation of phenylbut-1-ene. By limiting the reaction time to 2 hours some polymer was formed together with a product, b. p. 175—182° (Found : *C*-Me, 7·3. Calc. for $C_9H_9{\cdot}CH_3$: *C*-Me, 11·4%). From the b. p. it was probably a mixture containing a considerable proportion of phenylbut-2-ene.

Methylgeraniolene, b. p. 167°; *d*-limonene, b. p. 175°, $\alpha_D + 73·5°$; *d*-sylvestrene, b. p. 173·5°, $\alpha_D + 17°$; and 1 : 2 : 3 : 4 : 1′ : 2′ : 3′ : 4′-octahydrodiphenyl (Berlande, *loc. cit.*), b. p. 232—235° (used in ether, 50 c.c., because of its low solubility in ammonia), were all recovered unchanged, the product from the last substance failing to show any reaction with maleic anhydride, and the optical rotations of the active compounds were unchanged. 1 : 3- and 2 : 4-Dimethyl*cyclo*hexene gave their characteristic nitrolpiperidines after treatment, and 4-methyl*cyclo*hexene showed unaltered infra-red absorption.

Reduction of Hydrocarbons.—2 : 5-Dihydrotoluene (10 g.) and sodium (5 g.) in ammonia (100 c.c.) after 4 hours gave a product, b. p. 105—110°, $n_D^{18°}$ 1·4731 (Found : C, 89·4; 10·4%), shown by its infra-red absorption to contain 40% of toluene, 50% of 1-methyl*cyclo*hexene, and 10% of 3-methyl*cyclo*hexene.

2 : 5-Dihydrotoluene (10 g.) with calcium hexammine (from the metal, 10 g.) over 48 hours gave a product, b. p. 104—108°, $n_D^{20°}$ 1·4470 (Found : C, 87·3; H, 12·3. Calc. for C_7H_{12} : C, 87·5; H, 12·5%), which contained about 80% of 1- and 20% of 3-methyl*cyclo*hexene (infra-red absorption). Reduction of toluene by the same method gave a product still containing aromatic material, and the process was repeated on this using the hexammine from calcium (5 g.) and a mixture identical with the above obtained (infra-red absorption).

4 : 5-Dihydro-*m*-xylene (3·5 g.) was reduced with sodium (2 g.) and alcohol (4 g.) in ammonia (45 c.c.), giving a product, b. p. 124—126° (Found : C, 86·8; H, 12·3. Calc. for C_8H_{14} : C, 87·3; H, 12·7%). That it was chiefly 1 : 3-dimethyl*cyclo*hexene was shown by the preparation of the nitrolpiperidine, m. p. 156—157°. For comparison, the hydrocarbon was prepared by distilling the palmitate of 2 : 6-dimethyl*cyclo*hexanol at 330—350°; b. p. 125—126° (Found : C, 87·2; H, 12·7. Calc. for C_8H_{14} : C, 87·3; H, 12·7%). This gave the nitrolpiperidine, m. p. 156—157°, also obtained from the reduction products of *m*-xylene and 2 : 5-dihydro-*m*-xylene (Part III, *loc. cit.*). Removal of hydrogen chloride from the nitrosochloride by means of sodium acetate in boiling acetic acid (cf. Wallach, *loc. cit.*) and treatment of the resulting oxime with Brady's reagent gave the derivative of 2 : 6-dimethyl*cyclo*hex-2-enone, m. p. 153°, already obtained from the reduction product of 2 : 6-dimethylanisole (Part I, *loc. cit.*), thus confirming the position of the double bond in the hydrocarbon. Dehydration of 2 : 6-dimethyl*cyclo*hexanol with acid reagents such as phosphoric oxide produced considerable isomerisation to give 2 : 4-dimethyl*cyclo*hexene.

4-Phenylbut-1-ene (10 g.) and sodium (5 g.) in liquid ammonia (100 c.c.) were left for 5 hours, excess of sodium destroyed with ammonium chloride, and the product worked up as usual. Distillation gave an oil, b. p. 177—182°, which was shaken with ice-cold aqueous potassium permanganate until a permanent colour was obtained. The distilled oil (4 g.) was phenylbutane, b. p. 179—181° (Found : C, 90·3; H, 10·1. Calc. for $C_{10}H_{14}$: C, 89·6; H, 10·4%).

1 : 3-Dimethyl- and 2 : 4-dimethyl-*cyclo*hexene, *d*-limonene, and *d*-sylvestrene were unchanged by sodium in ammonia or by calcium hexammine, as shown by unchanged physical constants, in particular the optical rotations of the last two substances. Methylgeraniolene and 4-methyl*cyclo*hexene were also shown by means of their infra-red absorption to be unchanged.

2-Ethoxy-3 : 4-dihydronaphthalene (kindly presented by Mr. C. T. Beer), reduced with sodium (4 equivs.) and ammonia either in presence or in absence of alcohol (5 equivs.), gave a hydrocarbon as the product. Obtained in presence of alcohol, this showed slight unsaturation to bromine, but with sodium alone it was 1 : 2 : 3 : 4-tetrahydronaphthalene, b. p. 202—208° (Found : C, 90·6; H, 9·3. Calc. for $C_{10}H_{12}$: C, 90·9; H, 9·1%). When only 2 equivs. of sodium were employed the product was a mixture of about equal parts of tetralin and starting material.

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