321. *Reduction by Dissolving Metals. Part VII. The Reactivity of Mesomeric Anions in Relation to the Reduction of Benzene Rings.*

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The equilibrium between 2 : 5- (I) and 2 : 3-dihydroanisole (III), set up through their potassium salt (II), is investigated in liquid ammonia solution, and the conditions are defined for the interconversion of the two isomers. Some reactions of the dipotassium salts derived by the action of potassium amide in ammonia on several 1 : 4-dihydrobenzoic acids, several αβ-unsaturated aliphatic acids, and several arylacetic acids are investigated; in particular methyl iodide is found to introduce one or two methyl groups on to the carbon atom adjacent to the carboxyl group. Several 2 : 5-dihydroanisole derivatives are similarly methylated in the 2-position, and a methyl or a 2-phenylethyl group is introduced into the 2-position of 1 : 3-dimethoxy-2 : 5-dihydrobenzene.

Some generalisations on the reactivity of mesomeric anions are applied to explain the positions taken up by the hydrogen atoms added to substituted benzene rings by means of sodium and alcohols in liquid ammonia.

The hydrogenation of an aromatic system by a dissolving metal proceeds by electron and proton addition in what may be considered as successive or simultaneous stages according to conditions, since a series of equilibria is involved : $M + 2e \rightleftharpoons M^{-*} + e \rightleftharpoons M^{--} \longrightarrow MH_2$ (M = an aromatic molecule throughout this paper), and, under the right pH conditions, $M^{-*} + H^+ \rightleftharpoons MH^*$ (Birch, *Quart. Rev.*, 1950, **4**, 69, *q.v.* for references to any undocumented statements in the present paper).† The rate- or potential-determining stage appears from polarographic and other evidence to be the addition of the first electron. The addition of the second electron appears to be slow by comparison, although chemical evidence is available that this stage is at least chemically reversible. The slowness is understandable, because the reaction is between two negatively charged particles, a radical-anion and a solvated electron. The reduction process can be pictured as the rapid and reversible addition of an electron, the position of equilibrium being governed in the usual manner by the free-energy difference between M and M^{-*}, followed by further reactions which are either irreversible or slow to attain equilibrium. The rate, or the potential at which reduction occurs at any given rate, thus depends chiefly on the concentration of M^{-*}, and hence on the free-energy difference. This difference can be calculated in a semi-quantitative manner from bond-energy and resonance-energy changes which are considered in more detail elsewhere (cf. Birch, *loc. cit.*).

In the reduction of aromatic compounds containing benzene rings the primary reduction product, defined for convenience as the first non-ionic product which can be isolated, contains two added hydrogen atoms and thus corresponds to the addition of two electrons and two protons. With polycyclic compounds, or benzoic acids, these additions can be made to take place in two separate stages, the salt of the di-anion, *e.g.*, $2Na^+M^{--}$, being stable in ammonia at about $-70°$ (*e.g.*, Hückel and Bretschneider, *Annalen*, 1937, **540**, 157). With a molecule containing one isolated benzene ring such successive addition is not possible, and reduction occurs only by the simultaneous action of the metal and an alcohol in ammonia. This must be caused by the addition of protons from the alcohol either to M^{--} or to the less strongly basic M^{-*}, followed in the latter case by the addition of another electron and another proton. The equilibria above are thus caused to proceed in the direction of formation of stable hydrogenation

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† The signs $^-$ and * here represent two and one unshared electrons respectively.

products, even though the instantaneous concentration of ions may be very small because of the small free-energy change in the process of electron-addition.

Whichever route is followed, it is evident that a reduction intermediate is the mesomeric univalent anion MH^-: $M^{--} + H^+ \longrightarrow MH^-$, or $M^{-*} + H^+ \longrightarrow MH^* + e \longrightarrow MH^-$. There are at least two positions in such ions where proton-addition can occur, and in the case of benzene rings (*e.g.*, II) there are three positions. A study of their reactivity is therefore fundamental for an understanding of the relative positions of the hydrogen atoms added to the ring. Reactivity is experimentally found to be in the $\alpha\delta$-positions [*e.g.*, anisole $\longrightarrow$ 2 : 5-dihydroanisole (I)] with sodium–alcohol–ammonia solutions (*e.g.*, Part I, *J.*, 1944, 430), although with calcium hexamminoniate the $\alpha\beta$-dihydro-derivatives appear to be intermediates which are further reduced because they contain conjugated double bonds (*e.g.*, Part V, *J.*, 1947, 1642). An examination has accordingly now been made of the addition of protons to several types of mesomeric anion, such as (II), under conditions where the process is reversible and irreversible, *i.e.*, when the proton-donor is a much stronger acid than the conjugate acid from the ion, and when it is of about the same strength. For the reduction of benzene rings these conditions hold when the proton donor is alcohol (pK about 18) (irreversible addition) and when it is ammonia (pK about 34) (reversible addition).

It has already been briefly pointed out that the constitution of the product depends on whether the addition of protons to an anion is reversible or irreversible (Birch, *Faraday Soc. Discussion*, 1947, **2**, 246; cf. Catchpole, Hughes, and Ingold, *J.*, 1948, 8). Under reversible conditions an equilibrium is set up, such as (i), where A^- and B^- are the canonical forms defining the mesomeric anion :

$$AH \underset{H^+}{\overset{NH_2^-}{\rightleftharpoons}} A^- \; B^- \underset{NH_2^-}{\overset{H^+}{\rightleftharpoons}} BH \; . \; . \; . \; . \; . \; . \; . \; (i)$$
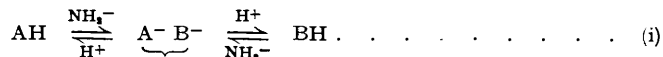
The equilibrium position is determined by the free-energy difference between the two possible conjugate acids AH and BH (Branch and Calvin, " The Theory of Organic Chemistry," N.Y., 1944, p. 289; de la Mare, Hughes, and Ingold, *J.*, 1948, 22). On the other hand, the products of irreversible proton addition are governed·by the relative rates of combination of a proton with the various positions where a free charge appears in $A^- \; B^-$. The expectation is that addition will be most rapid at the point of greatest free-charge density to give the strongest " acid " (*Faraday Soc. Discussion*, *loc. cit.*; Dewar, " The Electronic Theory of Organic Chemistry," Oxford, 1949, p. 103). This expectation is verified experimentally, the charge distribution being qualitatively estimated on the basis of the known electrical effects of substituents, and is confirmed by a study of the acidity of the conjugate acids AH and BH.

Apart from the evidence cited in the references above, the following observations lend further support to the theory. The enol of acetoacetic ester is formed when the sodium salt is treated with acid at a low temperature (Knorr, Rothe, and Averbeck, *Ber.*, 1911, **44**, 1138); the ionisation and the enolisation of ketones proceed at the same rate (Ives and Wilks, *J.*, 1938, 1455) as do their racemisation and deuterium exchange (Hsü, Ingold, and Wilson, *J.*, 1938, 78); $\beta\gamma$-unsaturated nitriles exchange the α-hydrogen for deuterium far more rapidly than they isomerise to the $\alpha\beta$-isomer (Ingold, de Salas, and Wilson, *J.*, 1936, 1328); and the metal salts formed from some $\alpha\beta$-unsaturated malonic esters on careful treatment with acid give the $\beta\gamma$-unsaturated esters (Hugh and Kon, *J.*, 1930, 775). It is apparent that the greatest free-

charge density in the ions of hetero-enoid systems, *e.g.*, $C\dot{=}C\dot{=}C\dot{=}C\dot{=}O$ is on the hetero-atom because of its greater electron-affinity compared with carbon. Accordingly, it might appear on this theory that irreversible addition of a proton should always occur in that position, as with acetoacetic ester. However, it is often difficult or impossible to find conditions where such combination is in fact irreversible for a proton, so attention can usually be confined to the lessmobile carbon system. The hetero-atom in such cases acts as a charge-stabilising influence on the carbon system, the free-charge density being greatest on the carbon β to it.
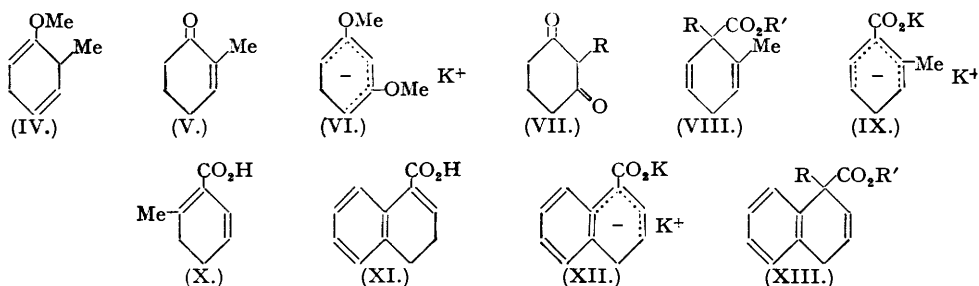
Systems containing only carbon atoms have been little examined because the high energies of the anions result in very low acidities in the conjugate hydrocarbon " acids " (pK of the order 37—40; Morton, *Chem. Reviews*, 1944, **35**, 8). The products of reduction of substituted allyl alcohols, where such ions intervene, accord with the theory (Birch, *J.*, 1945, 809). By using stronger hydrocarbon " acids " such as dihydrobenzenes, it is possible to make the anions by the action of a metal amide in ammonia (pK about 34) (Part V, *loc. cit.*). The following

equilibrium which has now been examined is a direct illustration of equation (i) for a carbon system.†

$$\text{(I.)} \rightleftharpoons \text{(II.)} \; K^+ \rightleftharpoons \text{(III.)} \qquad . \; . \; . \; \text{(ii)}$$
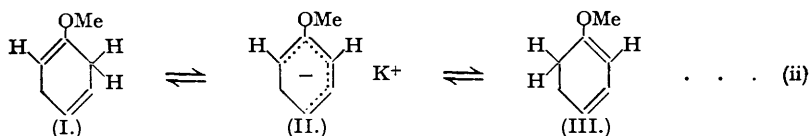
By the use of a small proportion of potassium amide in ammonia, it has already been found possible (Part V, *loc. cit.*) to convert the unconjugated 2 : 5-dihydroanisole (I) into the conjugated 2 : 3-dihydroanisole (III) of lower energy, the potassium salt (II) acting as a " turntable." The proton addition is *reversible*, because the ammonia and carbon " acids " of this type are comparable in strength. When several moles of potassium amide are used, the salt (II) is the major product and can be obtained either from (I) or from (III). If this salt is acted upon by an acid (ammonium chloride or water) strong compared with the carbon " acids," *irreversible* proton addition occurs and the product is chiefly the unconjugated (higher-energy) isomer (I). The absorption spectra and other properties make it quite clear that the conjugated (III) can thus be converted into the unconjugated (I).

The formation of the potassium salt (II) is attested by the deep red colour of the solution, and by the action of methyl iodide which causes addition of a methyl group in the same position as that taken up by the proton, since acid hydrolysis of the product (IV) gives 2-methyl*cyclo*hex-2-enone (V). Similarly, the potassium salt from 3-methyl-2 : 5-dihydroanisole gives rise, though in poor yield, to 2 : 3-dimethyl*cyclo*hex-2-enone. 1 : 3-Dimethoxy-2 : 5-dihydrobenzene gives a salt (VI) very readily, which is converted by the action of methyl iodide or 2-phenylethyl bromide, followed by acid hydrolysis, into 2-methyl*cyclo*hexane-1 : 3-dione (VII ; R = Me) and 2-2′-*phenylethyl*cyclo*hexane*-1 : 3-*dione* (VII ; R = CH₂·CH₂Ph), respectively.

$$\text{(IV.)} \quad \text{(V.)} \quad \text{(VI.)} \quad \text{(VII.)} \quad \text{(VIII.)} \quad \text{(IX.)}$$

$$\text{(X.)} \quad \text{(XI.)} \quad \text{(XII.)} \quad \text{(XIII.)}$$

The equilibrium (i) is also illustrated, though not quite so directly, by the reactions of several derivatives of 1 : 4-dihydrobenzoic acid. The reduction of *o*-toluic acid with sodium and ethanol in ammonia produces 2-*methyl*-1 : 4-*dihydrobenzoic acid* (VIII ; R = R′ = H), which with potassium amide in ammonia forms a deep-red solution evidently containing the dipotassium salt (IX). The action of methyl iodide on the solution leads to 1 : 2-*dimethyl*-1 : 4-*dihydrobenzoic acid* (VIII ; R = Me, R′ = H). The constitution of the last substance is proved by its lack of a light-absorption maximum in the region 2200—2800 A. (unconjugated double bonds) and by its oxidation by lead tetra-acetate to *o*-xylene. The action of ammonium chloride on the dipotassium salt (IX) is to add a proton to the 1-position, regenerating the original acid. However, if the acid is boiled with aqueous sodium hydroxide, an equilibrium is eventually established and the product isolated on acidification is a conjugated isomer ($\lambda_{max.}$ 2780 A.), probably 2-*methyl*-3 : 4-*dihydrobenzoic acid* (X).

An even more interesting case is that of 3 : 4-dihydro-1-naphthoic acid (XI). By the action of potassium amide in ammonia, this gives a dark red solution evidently containing the dipotassium salt (XII) because the action of methyl iodide leads to 1-*methyl*-1 : 4-*dihydro*-1-*naphthoic acid* (XIII ; R = Me, R′ = H). The constitution of this compound is proved by its oxidation by lead tetra-acetate to 1-methylnaphthalene. The salt (XII) by the action of aqueous ammonium chloride gives rise, not to the starting acid, but to the unconjugated 1 : 4-dihydronaphthoic acid (XIII ; R, R′ = H).

The observation that such dipotassium salts are formed quite readily led to an examination of the action of potassium amide in ammonia on several other unsaturated acids which should be

† Only the relevant hydrogen atoms are shown in these and subsequent formulæ.

capable of losing a proton from the unsaturated system. Exhaustive treatment with the reagent and methyl iodide brings about the following transformations : phenylacetic acid to 2-phenylpropane-2-carboxylic acid (CPhMe$_2$·CO$_2$H) ; 1-naphthylacetic acid to 2-1′-*naphthyl-propane-2-carboxylic acid* (C$_{10}$H$_7$·CMe$_2$·CO$_2$H) ; crotonic acid (CHMe:CH·CO$_2$H) to 2-*methylbut-3-ene-2-carboxylic acid* (CH$_2$:CH·CMe$_2$·CO$_2$H) ; and sorbic acid (CHMe:CH·CH:CH·CO$_2$H) to 2-*methylhexa-3* : 5-*diene-2-carboxylic acid* (CH$_2$:CH·CH:CH·CMe$_2$·CO$_2$H). In each case the methyl group has been added to the position in the mesomeric carbon-anion adjacent to the carboxyl group, where the charge density should be greatest. This happens even when, as in the last two examples, the double bonds are moved out of conjugation with the carboxyl by so doing.

It may also be noted that the irreversible addition of a proton, or of a methyl group, to the anion derived from the dihydroanisoles (*e.g.*, I), takes place in the 2-position, *ortho* to the methoxyl group and in the middle of the mesomeric system where the charge density should be greatest (cf. Dewar, *Faraday Soc. Discussion*, 1947, **2**, 261).

The foregoing experimental results thus make it plain that the intervention of mesomeric anions such as in (II) would explain the αδ-positions taken up by the hydrogen atoms in reductions by sodium and alcohols in liquid ammonia. Furthermore, reductions under conditions of reversible proton addition, which undoubtedly exist with calcium hexammoniate, would be expected to lead to the conjugated isomers of lower energy level, such as (II), and hence to further reduction. This agrees with the experimental findings (Part V, *loc. cit.*).

EXPERIMENTAL.

Interconversions of 2 : 5- and 2 : 3-Dihydroanisole.—2 : 5-Dihydroanisole (12 g.), b. p. 151°, n_D^{18} 1·4740 (obtained by the reduction of anisole), was added to potassium amide (from the metal, 0·5 g.) in ammonia (200 c.c.), and the dark red solution left for 20 minutes. It was then decomposed by adding ethanol (1 c.c.) drop by drop, with stirring, during 5 minutes, and then water (150 c.c.). Distillation of the oily product gave 2 : 3-dihydroanisole, b. p. 147—149° (mainly 148°) (8·5 g.), n_D^{18} 1·4830, $\lambda_{max.}$ 2680 A., $\varepsilon_{max.}^{mol.}$ 4270. The reduction of this substance with sodium and ethanol in ammonia gave tetrahydroanisole, detected by acid hydrolysis to *cyclo*hexanone, the 2 : 4-dinitrophenylhydrazone of which formed golden plates, m. p. 155—156°, undepressed by an authentic specimen.

2 : 3-Dihydroanisole (7·5 g.) was added to potassium amide (from the metal, 7·0 g.) in ammonia (200 c.c.). The solution was left for 10 minutes and decomposed by pouring it very cautiously into a solution of ammonium chloride (20 g.) in water (150 c.c.). Extraction and distillation gave an oil (4·6 g.), b. p. 151—152°, n_D^{20} 1·4765 (Found : C, 76·5 ; H, 8·9. Calc. for C$_7$H$_{10}$O : C, 76·4 ; H, 9·1%). That this is chiefly 2 : 5-dihydroanisole was confirmed by the absorption, the only maximum between 2200 and 2800 A. having $\lambda_{max.}$ 2700 A., $\varepsilon_{max.}^{mol.}$ 580, which must be due to 10—15% of either starting material or anisole. The substance was treated with sodium and ethanol in ammonia, and, unlike the starting material, required only a little sodium before a momentary blue colour was obtained throughout the solution. The material recovered from this treatment gave rise to the 2 : 4-dinitrophenylhydrazone of *cyclo*hex-2-enone as orange-red plates, m. p. 165°.

Methylation of 2 : 5-Dihydroanisoles.—2 : 5-Dihydroanisole (5 g.) and potassium amide (from the metal, 4 g.) in ammonia (100 c.c.) were left for 10 minutes, and methyl iodide was added drop by drop as rapidly as the rather violent reaction would allow until the red colour had disappeared. Water (50 c.c.) was then added and the oil collected with ether and refluxed with sulphuric acid (10%) for 15 minutes. The product was taken up in ether (15 c.c.) and shaken twice with water (20 c.c.) to remove most of the *cyclo*hexenone. The product was a colourless oil (1·4 g.), b. p. 169—174°, which gave rise to 2-methyl*cyclo*hexenone 2 : 4-dinitrophenylhydrazone as dark red prisms (from ethyl acetate), m. p. 204—205°, undepressed by an authentic specimen (Found : C, 54·2 ; H, 4·7. Calc. for C$_{13}$H$_{14}$O$_4$N$_4$: C, 53·8 ; H, 4·7%). The semicarbazone crystallised as cream-coloured prisms, m. p. 208°, from ethanol. 3-Methyl-2 : 5-dihydroanisole, treated similarly, gave a ketone, b. p. 85—90°/17 mm. The action on this of cold semicarbazide acetate in methanol for 10 minutes gave 3-methyl*cyclo*hex-2-enone semi-carbazone, m. p. 199—200° (undepressed by an authentic specimen), which corresponds to unchanged starting material. The unreactive oil (0·4 g.), b. p. 93—95°/20 mm., was probably 2 : 3-dimethyl*cyclo*hex-2-enone (Found : C, 77·6 ; H, 9·5. Calc. for C$_8$H$_{12}$O : C, 77·4 ; H, 9·7%). The 2 : 4-*dinitrophenyl-hydrazone* formed dark red needles (from ethyl acetate), m. p. 199—200° (Found : C, 55·5 ; H, 5·1. C$_{14}$H$_{16}$O$_4$N$_4$ requires C, 55·2 ; H, 5·2%) ; the semicarbazone formed colourless prisms, m. p. 227° (decomp.). Dupont (*Bull. Soc. chim. Belg.*, 1937, **46**, 21) gives m. p. 224° (slow heating) and 240° (fast heating).

Alkylation of 1 : 3-Dimethoxy-2 : 5-dihydrobenzene.—1 : 3-Dimethoxy-2 : 5-dihydrobenzene (7 g.) and potassium amide (from the metal, 2 g.) in ammonia (100 c.c.) were left for 10 minutes, and methyl iodide was added slowly with stirring to discharge the red colour. The oil obtained after addition of water (100 c.c.) and ether-extraction was heated on the steam-bath for 5 minutes with 2N-sulphuric acid (15 c.c.). The product was extracted with ether (3 × 25 c.c.) and the ethereal solution shaken with sodium hydroxide solution (5%) in small portions until acidification gave no more product. The crystalline solid so obtained crystallised from ethyl acetate as colourless prisms (2·8 g.), m. p. 206—207° (Found : C, 67·0 ; H, 7·8. Calc. for C$_7$H$_{10}$O$_2$: C, 66·7 ; H, 8·0%). The compound is certainly 2-methyl-*cyclo*hexane-1 : 3-dione, m. p. 210° (Blaise and Maire, *Compt. rend.*, 1907, **144**, 573 ; *Bull. Soc. chim.*, 1908, **3**, 697), this being the only isomer which melts so high. Evaporation of the ether gave an alkali-insoluble oil (1·5 g.), b. p. 93—95°/12 mm.

The same reaction was carried out using 2-phenylethyl bromide (9 g.) instead of methyl iodide, the product being 2-2′-*phenylethyl*cyclo*hexane*-1 : 3-*dione*, crystallising from ethyl acetate as colourless prisms, m. p. 144—145° (Found : C, 77·7; H, 7·4. $C_{14}H_{16}O_2$ requires C, 77·8; H, 7·4%).

2-Methyl-1 : 4-dihydrobenzoic Acid.—o-Toluic acid (10 g.) in ammonia (300 c.c.) and ethanol (12 g.) was reduced by the action of sodium (5 g.). Ammonium sulphate (40 g.) was then added, followed by water (40 c.c.), and the ammonia evaporated off, finally under reduced pressure. Acidification of the residue gave an oil which rapidly solidified. This was taken up in ether (50 c.c.), dried (Na_2SO_4), the solvent removed, and light petroleum (b. p. 40—60°) (10 c.c.) added to the residue. The crystals (9·2 g.) were filtered off and recrystallised from a little light petroleum (b. p. 80—100°). *2-Methyl-1 : 4-dihydrobenzoic acid* formed large colourless prisms (7·3 g.), m. p. 74—75° (Found : C, 69·5; H, 7·2. $C_8H_{10}O_2$ requires C, 69·6; H, 7·2%). Lack of conjugation of the double bonds was confirmed by the absence of a light-absorption maximum in the region 2200—2800 A. The action of potassium amide (3 mols.) in ammonia gave a dark red solution, but addition of ammonium sulphate and water as above led to recovery of the starting material.

2-Methyl-3 : 4(?)-dihydrobenzoic Acid.—The above acid (7 g.) was heated under reflux for 6 hours with sodium hydroxide solution (100 c.c.; 20%). Acidification gave an oil which solidified and crystallised from light petroleum (b. p. 80—100°) as colourless prisms (3·2 g.), m. p. 76—78°, considerably depressed by the starting material (Found : C, 69·6; H, 7·3. $C_8H_{10}O_2$ requires C, 69·6; H, 7·2%). Conjugation is shown by light absorption at $\lambda_{max.}$ 2780 A., $\varepsilon_{max.}^{mol.}$ 3280 (ethanol). The *acid* is probably identical with that obtained, but not fully investigated by Hutchinson (*Ber.*, 1891, **24**, 178), but is not identical with 2-methyl-2 : 3-dihydrobenzoic acid, m. p. 128° (Perkin, *J.*, 1911, **99**, 758), or 2-methyl-4 : 5-dihydrobenzoic acid, m. p. 175° (Mazza and Carlò, *Gazzetta*, 1927, **57**, 315).

1 : 2-Dimethyl-1 : 4-dihydrobenzoic Acid.—2-Methyl-1 : 4-dihydrobenzoic acid (5 g.) was added to potassium amide (from the metal, 3 g.) in ammonia (100 c.c.), and methyl iodide (15 g.) in ether (20 c.c.) was cautiously added. Water (50 c.c.) was added, and the acid isolated by evaporation of the ammonia, acidification, and ether-extraction. Crystallisation from light petroleum (b. p. 40—60°) gave *1 : 2-dimethyl-1 : 4-dihydrobenzoic acid* as large colourless prisms, (3·3 g.), m. p. 73—74°, considerably depressed on admixture with either of the preceding acids (Found : C, 70·8; H, 7·6. $C_9H_{12}O_2$ requires C, 71·0; H, 7·9%). Lack of conjugation is indicated by the absence of a light-absorption maximum between 2200 and 2800 A. The *ethyl* ester was a colourless oil, b. p. 105°/17 mm (Found : C, 73·4; H, 9·1. $C_{11}H_{16}O_2$ requires C, 73·3; H, 8·9%). The acid (3 g.) was added slowly to lead tetra-acetate (15 g.) and acetic acid (40 c.c.) at 50°. Rapid evolution of carbon dioxide took place with rise of temperature. Addition of water and extraction with a little ether gave an oil, b. p. 140—144° (1·4 g.), which, redistilled over sodium, had b. p. 143—144°, n_D^{15} 1·5030. o-Xylene has b. p. 144°, n_D^{23} 1·5046. Oxidation by refluxing nitric acid (25%) for 12 hours gave o-toluic acid, m. p. 103—104°, undepressed by an authentic specimen.

1 : 4-Dihydronaphthoic Acid from 3 : 4-Dihydronaphthoic Acid.—3 : 4-Dihydronaphthoic acid, m. p. 120° (2 g.), was added rapidly to potassium amide (from the metal, 5 g.) in ammonia (100 c.c.), and the dark red solution left for 3 minutes under an atmosphere of nitrogen. The solution was then forced by gas-pressure into a solution of ammonium chloride (25 g.) in water (75 c.c.), most of the ammonia removed under reduced pressure, and the solution acidified. The precipitated solid was dissolved in the minimum amount of dilute ammonia solution, and a concentrated solution of barium chloride added drop by drop until no further precipitate was formed. After filtration, the solution was acidified and the acid crystallised from light petroleum (b. p. 80—100°) with the aid of a little fuller's earth. It formed colourless, elongated prisms, m. p. 82—84°, undepressed by 1 : 4-dihydronaphthoic acid, m. p. 86—87°, but depressed by the starting material. Acidification of the barium salt which had been removed by filtration gave a solid, which was crystallised from acetic acid and identified as 1-naphthoic acid by its m. p. (162°, undepressed by an authentic specimen).

1-Methyl-1 : 4-dihydro-1-naphthoic Acid.—3 : 4-Dihydro-1-naphthoic acid (1·5 g.) was treated with potassium amide (from the metal, 0·8 g.) and methyl iodide to discharge the colour, and worked up as for the dihydrobenzoic acid above. The product was 1-*methyl-1 : 4-dihydro-1-naphthoic acid*, crystallising as small colourless prisms, m. p. 116—117°, from benzene–light petroleum (b. p. 40—60°) (Found : C, 76·9; H, 6·2. $C_{12}H_{12}O_2$ requires C, 76·6; H, 6·4%). On oxidation of the acid with lead tetra-acetate in acetic acid at 50°, carbon dioxide was evolved, and addition of water and ether-extraction gave an oil with an odour of naphthalene. This readily gave rise to 1-methylnaphthalene picrate as yellow needles (from ethanol), m. p. 154° (undepressed by an authentic specimen) (Found : C, 54·5; H, 3·6. Calc. for $C_{17}H_{13}O_7N_3$: C, 54·9; H, 3·5%).

2-Phenylpropane-2-carboxylic Acid.—Phenylacetic acid (10 g.) was added to potassium amide (from the metal, 10 g.) in ammonia (300 c.c.), followed by methyl iodide to discharge the red colour. The resultant acid was only partly crystalline, so the treatment was repeated. The product was then 2-phenylpropane-2-carboxylic acid, which crystallised from light petroleum (b. p. 80—100°) as large colourless elongated prisms, m. p. 80°, undepressed by an authentic specimen.

2-1′-Naphthylpropane-2-carboxylic Acid.—1-Naphthylacetic acid (5 g.) was treated twice, as above, using potassium amide (from the metal, 7 g.). The resulting 2-1′-*naphthylpropane-2-carboxylic acid* formed colourless prisms, m. p. 120—121°, from light petroleum (b. p. 60—80°) (Found : C, 78·6; H, 6·4. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·5%).

2-Methylbut-3-ene-2-carboxylic Acid.—Crotonic acid (5 g.), when added to a solution of potassium amide (from the metal, 7 g.) in ammonia (250 c.c.), gave a deep-red solution and a precipitate. Methyl iodide was added to discharge the colour, and the acid product isolated as above. Owing to the comparative insolubility of the potassium salt it was necessary to repeat the process twice more to obtain a uniform product, the salt in the last run being completely soluble. Distillation of the acid product gave two fractions : (a) (3·3 g.), b. p. 95—98°/15 mm., and (b) (0·6 g.), b. p. 110—117°/15 mm. Fraction (a) was 2-*methylbut-3-ene-2-carboxylic acid* (Found : C, 63·5; H, 9·0. $C_6H_{10}O_2$ requires C, 63·1; H, 8·8%). It gave an *amide* as colourless plates (from ethanol), m. p. 85° (Found : C, 63·7; H, 9·7. $C_6H_{11}ON$ requires C, 63·7; H, 9·7%). Hydrogenation (Pd–C) of the acid gave 1 : 1-dimethylbutyric acid, b. p.

183—185° [amide m. p. 102° (Found : C, 62·5; H, 11·1.   Calc. for $C_6H_{13}ON$: C, 62·6; H, 11·3%)].
Haller and Bauer (*Compt. rend.*, 1909, **148**, 129) give m. p. 103—104° for the amide.   From its analysis
(Found : C, 64·7; H, 9·0.   Calc. for $C_7H_{12}O_2$: C, 65·6; H, 9·4%) fraction (b) appears to be chiefly a
trimethylcrotonic acid, probably 2-methylpent-3-ene-2-carboxylic acid.

2-*Methylhexa*-3 : 5-*diene*-2-*carboxylic Acid.*—Sorbic acid (10 g.) was treated three times as above,
using potassium amide (from the metal, 7 g.) in ammonia (400 c.c.).   The acid product was separated by
distillation into two fractions : (a) (8 g.), b. p. 122—124°/13 mm., and (b) (0·7 g.), b. p. 130—134°/13 mm.
Fraction (a) was 2-*methylhexa*-3 : 5-*diene*-2-*carboxylic acid* (Found : C, 68·7; H, 8·6. $C_8H_{12}O_2$ requires
C, 68·6; H, 8·6%).   It gave rise to the *amide* as colourless plates (from ethanol), m. p. 82° (Found : C,
68·5; H, 9·2. $C_8H_{13}ON$ requires C, 69·0; H, 9·3%).   On hydrogenation (Pd–C) the acid absorbed
2 moles of hydrogen, the first much more readily than the second, to give 2 : 2-dimethylhexanoic acid,
b. p. 123°/16 mm. (Found : C, 66·5; H, 11·0.   Calc. for $C_8H_{16}O_2$: C, 66·7; H, 11·1%).   The amide
crystallised as colourless plates (from ethanol), m. p. 92° (Found : C, 66·7; H, 11·6.   Calc. for $C_8H_{17}ON$:
C, 67·1; H, 11·9%).   Its m. p. was not depressed by an authentic specimen, m. p. 92°, prepared by the
method of Locquin and Leers (*Compt. rend.*, 1924, **178**, 2095).   The diene-acid, after several months in a
sealed tube, had polymerised to a colourless glass, soluble in acetone or aqueous sodium hydroxide.