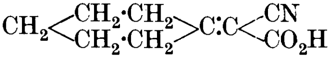
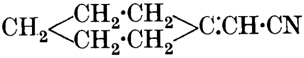
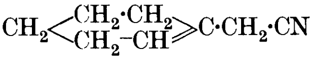
CCLXXVI.—*The Chemistry of the Three-carbon System. Part XXII. The Preparation and Interconversion of Isomeric Unsaturated Nitriles.*

By ARUPILLAI KANDIAH and REGINALD PATRICK LINSTEAD.

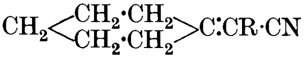
IN the course of the general determination of the effect of substituent groups on the mobility and equilibrium of three-carbon systems, we deemed it desirable, in view of certain anomalies, to reinvestigate the tautomerism of unsaturated nitriles observed by Birch and Kon (J., 1923, **123**, 2440), whose results may be summarised as follows: Pyrogenic decomposition of αβ-unsaturated cyano-acids such as (I) produced unsaturated nitriles capable of reacting in the αβ-phase, but having the βγ-structure (III). On the other

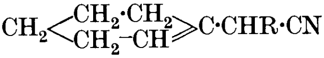
(I.) 
$CH_2<\begin{smallmatrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{smallmatrix}>C{:}C<\begin{smallmatrix}CN\\ CO_2H\end{smallmatrix}$

 (II.)
$CH_2<\begin{smallmatrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{smallmatrix}>C{:}CH\cdot CN$

 (III.)
$CH_2<\begin{smallmatrix}CH_2\cdot CH_2\\ CH_2-CH\end{smallmatrix}\gg C\cdot CH_2\cdot CN$

hand, the homologues with an alkyl group attached to the same carbon atom as the cyano-group, produced by the action of sodium ethoxide on the corresponding alkylated cyano-esters, were invariably obtained in the αβ-phase (IV).

(IV.) 
$CH_2<\begin{smallmatrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{smallmatrix}>C{:}CR\cdot CN$

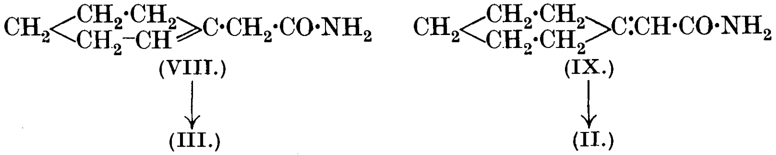
 (V.)
$CH_2<\begin{smallmatrix}CH_2\cdot CH_2\\ CH_2-CH\end{smallmatrix}\gg C\cdot CHR\cdot CN$

One of the immediate objects of this work was, therefore, to account for this discrepancy, and for this purpose it was decided to effect the synthesis of the individual isomerides of the types (II), (III), (IV), and (V), and to study their controlled interconversion (Kon and Linstead, this vol., p. 1269).

A ready solution of the preparative problem was fortunately available. It had been observed by one of us (R. P. L.) that styrylacetamide (VI), although not cleanly dehydrated by the conventional reagent, phosphoric oxide, was smoothly converted into a crystalline nitrile, m. p. 59—60°, on treatment with a solution of phosphorus pentachloride in phosphorus oxychloride:

(VI.) $CHPh{:}CH\cdot CH_2\cdot CO\cdot NH_2 \longrightarrow CHPh{:}CH\cdot CH_2\cdot CN$ (VII.)

This product appeared to be in every way identical with that (m. p. 59—60°) prepared by Thiele and Sulzberger (*Annalen*, 1901, **319**, 209) who used a complex synthesis affording no clue as to the position of the double bond. This nitrile gives benzaldehyde on oxidation and has undoubtedly the βγ-structure (VII). The fact that the process yielded the unsaturated nitrile in a state of purity and did not cause an undue amount of resinification led us to apply it to the two individual amides, (VIII) and (IX), of the *cyclo*hexane series, and we obtained the isomeric nitriles (III) and (II) in good yield. That prepared from *cyclo*hexylideneacetamide (IX)



$$CH_2{<}\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH_2-CH}{\geqslant}C\cdot CH_2\cdot CO\cdot NH_2 \qquad CH_2{<}\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH_2\cdot CH_2}{>}C{:}CH\cdot CO\cdot NH_2$$

(VIII.) → (III.)   (IX.) → (II.)

had the higher boiling point, as expected, and showed considerable exaltation in its molecular refraction. The αβ-position of the double bond was confirmed by oxidation to *cyclo*hexanone. The nitrile obtained from the isomeric amide on the other hand undoubtedly had the βγ-structure (III), and was in every way identical with Birch and Kon's product (*loc. cit.*).

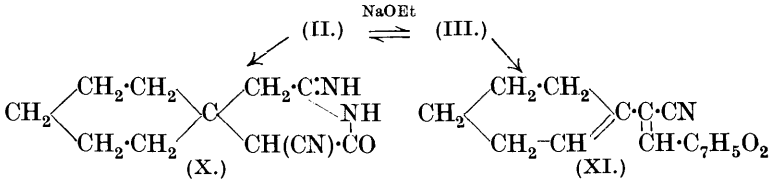
For the further examination of these compounds and for the study of their interconversion, the iodometric method was applied. It was necessary, however, to modify the usual conditions owing to the comparatively low reactivity of these substances. Satisfactory results were obtained by using the reagents in double the usual concentration (Linstead and May, J., 1927, 2565) and prolonging the time of reaction to one hour. Under these conditions the βγ-nitrile gave an iodine addition of 56%, and the αβ- of 3%.

Apart from the fact that von Auwers (*Ber.*, 1923, **56**, 1172) has observed that the unstable allyl cyanide is converted into crotononitrile when its ethereal solution is shaken with dilute alkali, the tautomeric changes of unsaturated nitriles have not been directly investigated. It is now found that αβ- and βγ-unsaturated nitriles pass rapidly into an equilibrium mixture on treatment with sodium ethoxide at room temperature. Eight pairs of isomerides have been examined and the reaction appears to be general. For example, when the two *cyclo*hexane nitriles (II) and (III) were treated for 24 hours with sodium ethoxide (1 mol.) under the standard conditions of Kon and Linstead (*loc. cit.*), the product in each case was composed almost exclusively of the αβ-nitrile. The iodine additions of the two products were 10·7% from the βγ-side and 10·0% from the αβ-, corresponding to an αβ-content of 94·5 and 95% respectively.

The equilibration was remarkably free from side reaction, and about 85% of material could be recovered. The principal change βγ- ⟶ αβ-nitrile was confirmed by hydrolysis of the equilibrated nitrile, prepared from the βγ-side, with 100% sulphuric acid (compare Macq, *Bull. Acad. roy. Belg.*, 1926, **12**, 753). The pure αβ-amide was isolated by fractional crystallisation of the mixture of amides obtained. Under the same conditions the pure βγ-nitrile yielded only the βγ-amide without movement of the double bond. This result indicates the exceptional stability of the unsaturated system to acid catalysts and thus serves to confirm the value of the method used in the preparation of the nitriles. The reactions of the equilibrated nitrile with condensing agents (see below) also confirm the composition found iodometrically.

The mobility of the nitriles of the *cyclo*hexane series was investigated along the usual lines and was found to be unexpectedly high, interconversion being virtually complete in an hour. The half-change period is about 7·5 mins., and the mobility is of the order of 920, *i.e.*, slightly higher than that of the corresponding ketones (Kon and Linstead, *loc. cit.*).

It is now possible to review Birch and Kon's results. The preparation of their nitrile by distillation of the αβ-cyano-acid (I) has been repeated and gave a product identical with our pure βγ-nitrile (the movement of the double bond in this reaction is discussed later), and having an iodine addition of 55%. It is, therefore, clear that Birch and Kon's product contains no αβ-nitrile as such and that tautomeric change is only effected by alkaline catalysts, in the general manner of the substances investigated in this series. This is confirmed by the reactions of the isomeric nitriles. Thus, Birch and Kon obtained a 30% yield of the imino-compound (X) on condensing their (βγ-) nitrile with cyanoacetamide, and a 70% yield of the piperonylidene compound (XI), both reactions being carried out in the presence of sodium ethoxide :

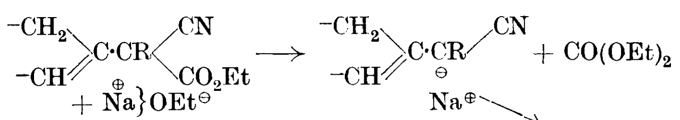


Under identical conditions it is now found that the αβ-nitrile gives a 63% yield of the imino-compound (X), and the yield from the βγ-nitrile is confirmed as 30%. If, however, the βγ-nitrile is *first equilibrated* with sodium ethoxide and then treated with sodio-cyanoacetamide the yield is increased to 51%. The same piperonylidene compound (XI) is given by both the isomeric nitriles, the yields being 70% from the βγ- and 45% from the αβ-isomeride. It is clear that the effectiveness of the ethoxide as a catalyst in the three-carbon change is diminished by the presence of condensing reagents, presumably by a process of partition.

The production of the βγ-nitrile from the cyano-acid (I) is of some interest. There is no doubt that condensation of *cyclo*hexanone with ethyl cyanoacetate yields a substantially αβ-product—the ethyl ester of (I) (Lapworth and McRae, J., 1922, **121**, 2741; Birch, Kon, and Norris, J., 1923, **123**, 1361). The position of the double bond in the corresponding cyano-acid has, however, not been proved, for although Lapworth and McRae were of the opinion that this substance had the αβ-structure, they were unable to obtain it in the state of purity necessary for examination. We have been able to confirm their view of the structure of this acid both by oxidising the purified material (m. p. 109°; Harding, Haworth, and Perkin, J., 1908, **93**, 1947, give 109—110°) with permanganate, whereby *cyclo*hexanone was obtained, and by esterification, which yielded an ester identical in properties with the well-known ethyl α-cyano*cyclo*hexylideneacetate. The movement of the double bond in the pyrogenic formation of this nitrile, anticipated by Lapworth and McRae (*loc. cit.*), is thus proved, the result being in agreement with previous work (Braun, *Monatsh.*, 1896, **17**, 218; Strassmann, *ibid.*, 1897, **18**, 722; von Auwers, *loc. cit.*).

α-Alkyl Series.—The isomeric nitriles in both the α-methyl and the α-ethyl series (IV and V, R = Me and Et) were readily prepared from the corresponding amides by the standard procedure. In each series, two distinct isomerides were obtained, with the properties to be expected from their method of preparation, and on treatment with sodium ethoxide they gave an equilibrium mixture which in each case had the expected preponderance of αβ-form. Interconversion was somewhat slower than in the unsubstituted series, and, of the alkyl derivatives, the ethyl were appreciably less mobile than the methyl (see table, p. 2144).

It is clear that the " abrupt contrast " between the substituted and unsubstituted series is non-existent, and that the differences previously observed were due purely to the fact that the substances were not examined under comparable conditions. Kon and Narayanan's explanation (J., 1927, 1536) of the formation of α-alkylated nitriles from alkylated cyano-esters (XII), in which the double bond must be βγ-, now becomes unnecessary in view of the proved high mobility of these substances in the presence of sodium ethoxide. We would attribute the first stage of this decomposition to the formation of the active ion (XIII), which can then undergo the necessary tautomeric change :



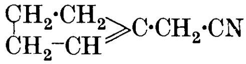
(XII.) (XIII.) (IV.)

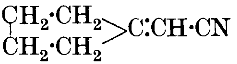
The present work has other repercussions on that of Kon and Narayanan, and Dr. Kon has dealt with these in a note (p. 2144).

Other Series.—The new methods of preparation, analysis, and equilibration were successfully applied in the cases briefly described below.

(i) cyclo*Pentane series.* The two isomeric nitriles (XIV, XV) underwent extremely rapid interconversion in the presence of sodium ethoxide, the equilibrium being far on the αβ-side (93·5%). The βγ-nitrile (XIV) was apparently identical with that prepared by Harding and Haworth (J., 1910, **97**, 486) and by Birch and Kon (*loc. cit.*) from the corresponding cyano-acid. These investigators correctly assigned the βγ-structure to this substance. The

(XIV.)





(XV.)

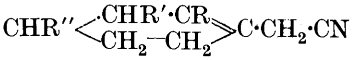
structure of the new αβ-nitrile was confirmed by its oxidation to *cyclo*pentanone.

(ii) β-*Methylpentenoic series.* The isomeric nitriles derived from methyl ethyl ketone, *viz.*,

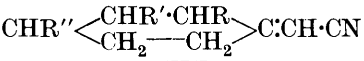
(XVI.) $CHMe{:}CMe{\cdot}CH_2{\cdot}CN$ and $CH_2Me{\cdot}CMe{:}CH{\cdot}CN$ (XVII.)

closely resembled their *cyclo*pentane analogues. Equilibrium was rapidly reached, and in this series its position was so far on the αβ-side that the analytical method was incapable of detecting the presence of the βγ-isomeride. Gardner and Haworth (J., 1909, **95**, 1955) describe the preparation of a β-methyl-Δ^{α}-pentenonitrile by the distillation of an impure α-cyano-β-methyl-Δ^{α}-pentenoic acid, having determined the position of the double bond by hydrolysis of the nitrile through the ethyl ester to an acid, which was considered to be β-methyl-β-ethylacrylic acid as it gave methyl ethyl ketone on oxidation. To fall into line with other substances, a nitrile prepared in this manner would be expected to have the βγ-structure, and it appears probable that in Gardner and Haworth's work, at some stage of the hydrolysis, appreciable interconversion occurred with the final production of an acid containing sufficient of the αβ-form to give the appropriate oxidation product. This view is supported by the fact that Gardner and Haworth's acid is described as a mobile liquid, whereas pure β-methyl-β-ethylacrylic acid is a solid, m. p. 45° (Fichter and Gisiger, *Ber.*, 1909, **42**, 4707; Kon and Linstead, *loc. cit.*; but see p. 2151).

(iii) *Methyl*cyclo*hexane series.* In addition to the foregoing experiments, we have examined the effect of substitution of a methyl group in the 2-, 3-, and 4-positions in the *cyclo*hexane ring. In this work, however, the preparation and dehydration of the six amides was not undertaken on account of the considerable expense involved. The βγ-nitrile (XVIII; or with double bond in 1 : 6- instead of 1 : 2-position) in each series was prepared from the corresponding cyano-acid, the general method of Harding, Haworth, and Perkin (*loc. cit.*) being used. The double bond in all these cyano-acids is presumably αβ-, and the original formulæ need adjustment in this respect.


$CHR''<\begin{matrix}CHR'\cdot CR\\CH_2-CH_2\end{matrix}>C\cdot CH_2\cdot CN$

(XVIII.)


$CHR''<\begin{matrix}CHR'\cdot CHR\\CH_2-CH_2\end{matrix}>C{:}CH\cdot CN$

(XIX.)

All three nitriles gave iodine additions of about 50%, which fell on equilibration to steady values of about 7%. This is attributed to the formation of at least 90% of the αβ-isomerides (XIX), the iodine additions of the pure αβ-nitriles being assumed to be of the same order as those already determined. The βγ-nitriles prepared from the cyano-acids give the usual reactions characteristic of both phases. All three condense with piperonal to give the higher homologues of (XI), but with sodiocyanoacetamide only the 3-methyl and 4-methyl compounds condense. The 2-methyl nitrile reacts neither at once nor after preliminary equilibration, abnormality of a 2-methyl*cyclo*hexanone derivative being not without precedent (compare Kon and Thorpe, J., 1919, **115**, 686). The structures of the condensation products from the 3- and 4-methyl nitriles were controlled by hydrolysis to the corresponding diacetic acids.

Summary.—The mobility and position of equilibrium of these nitriles determined under standard conditions are given in the following table :

Series.	Half-change period (mins.).	Mobility, $(k_1 + k_2) \times 10^4$.	Ratio αβ-/βγ- at equilibrium.	αβ-, %.
*cyclo*Hexane	*ca.* 7·5	*ca.* 920	19	95
α-Methyl*cyclo*hexane	20	360	16	94
α-Ethyl*cyclo*hexane	93	74	9	90
*cyclo*Pentane	—	>1000	14	93·5
β-Methylpentenoic	—	>1000	Very high	99
2-Methyl*cyclo*hexane	—	—	*ca.* 9	*ca.* 90
3-Methyl*cyclo*hexane	—	—	*ca.* 9	*ca.* 90
4-Methyl*cyclo*hexane	—	—	*ca.* 9	*ca.* 90

Two definite generalisations may be drawn : (1) the cyano-group is among the most powerful single activating groups known; (2) the position of equilibrium is almost independent of the alkyl substituents, and may be assumed to be controlled predominantly by the cyano-group. In addition, the α-alkylated nitriles supply a well-marked example of the fall in mobility with the increasing size of the α-group : $H>CH_3>C_2H_5$.

Note (By G. A. R. KON).—The experiments described above definitely establish the great mobility conferred on the three-carbon system by a terminal nitrile group, and provide a ready explanation of the contradictions formerly observed in the chemistry of these substances. It is clear that Kon and Narayanan's interpretation of their results (*loc. cit.*) was incorrect, and that it is the $\beta\gamma$-form of the nitriles which is the less stable. The production of this form in the pyrogenic decomposition of an $\alpha\beta$-unsaturated cyano-acid is remarkable; it is analogous to the formation of *cyclo*hexylideneacetone from Δ^1-*cyclo*hexenylacetoacetic acid (Jupp, Kon, and Lockton, J., 1928, 1638; compare Dickins, Hugh, and Kon, this vol., p. 572).

EXPERIMENTAL.

General Methods.—(1) *Preparation of nitriles from amides.* Powdered phosphorus pentachloride (30 g.) was warmed with phosphorus oxychloride (30 c.c.) in a wide-mouthed flask under reflux until the most part had dissolved. The flask was then removed from the source of heat and the amide (20 g.) added gradually from a wide tube. The mixture was well shaken after each addition, hydrogen chloride being copiously evolved, and was finally heated on the steam-bath until evolution of the gas ceased (about 2 hours). The dark brown liquid was cooled and slowly poured into water, care being taken to prevent the accumulation of undecomposed phosphorus chlorides. The nitrile was extracted with ether, the extract washed with water, and the residue after removal of the solvent was distilled in steam. The nitrile passed over in the first litre of distillate, and was extracted twice with ether, dried, and the solvent removed, the residue being purified by distillation under reduced pressure. All the nitriles prepared in this work (except styrylacetonitrile) were colourless mobile oils with strong characteristic odours.

(2) *Iodometric estimations.* With the usual solutions (Linstead and May, *loc. cit.*), trial experiments showed that the addition even to $\beta\gamma$-nitriles was small in an hour. After various trials, convenient results were obtained by using solutions containing 10·14 g. of mercuric chloride and 6·76 g. of iodine each in 100 c.c. of rectified spirit, equal volumes of these solutions being mixed and kept in the dark for 24 hours before use. In an analysis, $\frac{1}{150}$ g.-mol. of nitrile was dissolved in 50 c.c. of chloroform. The procedure otherwise followed the usual lines (*loc. cit.*), a reaction period of one hour being used throughout. The method gave very concordant results and there was no back reaction after titration.

(3) *Equilibration.* The general procedure of Kon and Linstead

(*loc. cit.*) was followed. At the end of the required time, an amount of the equilibrated solution equivalent to about 2 g. of nitrile was pipetted into water and exactly neutralised with dilute sulphuric acid. The nitrile was isolated in the usual way and distilled under reduced pressure.

Styrylacetic Series.—Styrylacetyl chloride (Linstead and Williams, J., 1926, 2735) (35 g.) on treatment with aqueous ammonia (*d* 0·880) gave a solid product which after trituration with ether, in which the amide is insoluble, and one crystallisation from dilute alcohol, yielded styrylacetamide (VI) as small shining plates with a slight brown colour, m. p. 128°. Kohl (*Ber.*, 1903, **36**, 174) found m. p. 130° for the amide prepared from the corresponding ethyl ester. On being heated with phosphoric oxide in a glycerol-bath at 140°, the amide gave only resinous products, but treatment with phosphorus pentachloride in phosphorus oxychloride in the manner already described yielded the pure nitrile in 62% yield. The steam distillation may be dispensed with in this preparation.

Styrylacetonitrile (VII) forms beautiful white shining leaflets from light petroleum, m. p. 59—60° (compare Thiele and Sulzberger, *loc. cit.*). It is insoluble in water or cold petroleum, sparingly soluble in cold ether, and readily soluble in alcohol, hot ether, and hot petroleum (Found : C, 83·6; H, 6·4. Calc. for $C_{10}H_9N$: C, 83·9; H, 6·2%).

On treatment of the nitrile with excess of neutral permanganate the smell of benzaldehyde soon became perceptible. When oxidation had apparently ceased, the organic material was extracted with ether, and the benzaldehyde was identified in the residue after removal of the solvent, by means of the semicarbazone (m. p. 218—219°; mixed m. p.).

cyclo*Hexane Series.*—40 G. of Δ^1-*cyclo*hexenylacetamide (VIII), m. p. 152° (Wallach, *Annalen*, 1907, **353**, 284) were obtained from 50 g. of the corresponding acid. On dehydration, 20 g. yielded 10 g. of the nitrile (III), b. p. 105°/22 mm., $d_{4^\circ}^{19^\circ}$ 0·9533, $n_D^{19^\circ}$ 1·4843, whence $[R_L]_D$ 36·30 (Calc. 36·30) (Birch and Kon, *loc. cit.*, give $d_{4^\circ}^{21 \cdot 1^\circ}$ 0·9473, $n_D^{21 \cdot 1^\circ}$ 1·4787 (Found : C, 79·2; H, 9·2. Calc. : C, 79·3; H, 9·1%).

25 G. of *cyclo*hexylideneacetamide (IX) (m. p. 147°, mixed m. p. with the βγ-isomeride, 115—120°) (Wallach, *Annalen*, 1909, **368**, 262) were obtained from 30 g. of the acid. The amide (20 g.) yielded 58% of the corresponding cyclo*hexylideneacetonitrile* (II), b. p. 107—108°/22 mm., $d_{4^\circ}^{15^\circ}$ 0·9483, $n_D^{15^\circ}$ 1·4928, whence $[R_L]_D$ 37·1 (Found : C, 79·5; H, 9·2. $C_8H_{11}N$ requires C, 79·3; H, 9·1%).

A suspension of the nitrile in water was left with a slight excess of 3% aqueous potassium permanganate for 12 hours. The filtrate from this mixture was extracted with ether, and evaporation of the solvent gave a mixture of unchanged nitrile and *cyclo*hexanone, identified as its semicarbazone, m. p. 165—166°, alone or when admixed with an authentic sample.

Mixtures of the two nitriles reacted with iodine chloride, under the conditions already defined, as follows :

αβ-Nitrile, %	100	80	70	50	30	10	0 (βγ-)
Addition, %	3·0	25·0	31·5	43·0	50·0	54·0	56·3

Equilibrium. The βγ-nitrile (4·8 g.) was equilibrated with an excess of *N*/1-sodium ethoxide for 24 hours at 25°. From the resulting solution, 4·2 g. of nitrile were isolated having b. p. 106°/20 mm., $d_{4^\circ}^{16^\circ}$ 0·9493, $n_D^{16^\circ}$ 1·4892 (Found : C, 79·0; H, 9·2%). The boiling point was steady and there was no high fraction. The iodine addition of the product was 10·7%, corresponding to 94·5% αβ-nitrile. A similar experiment with the αβ-nitrile gave a product with the same properties and an iodine addition of 10·0%, corresponding to 95% αβ-nitrile.

Mobility. The conversion of the βγ-nitrile into the equilibrium mixture under standard conditions is shown by the following figures :

Time of treatment (mins.)	15	50	75	105
Iodine addition, %	24·8	15·6	12·6	11·6
αβ-Nitrile formed, %	80·5	90·5	93	94

Hydrolysis to amides. The βγ-nitrile was resinified by treatment with warm 2*N*-sulphuric acid and with 50% sulphuric acid. The following procedure was satisfactory, however. The nitrile (4 g.) was cautiously treated with an equimolecular amount of ice-cold 100% sulphuric acid, prepared by adding the requisite amount of fuming acid to the concentrated acid (Macq, *loc. cit.*). The thick brown liquid, which evolved sulphur dioxide freely, was heated on the steam-bath for 10 hours and then cooled. The hard mass was shaken with ice and repeatedly extracted with ether. The extract was washed with sodium carbonate solution and water, dried, and evaporated. A white crystalline solid was obtained (crude m. p. 142°), which, after two crystallisations from dilute alcohol, had m. p. 152°. Its identity with the βγ-amide was confirmed by a mixed melting-point determination. On similar treatment, a sample of the equilibrated nitrile prepared from the βγ-isomeride gave a crude amide, m. p. 115°. From the less soluble fraction, the αβ-amide was isolated by crystallisation from dilute alcohol; m. p. 146·5°, mixed m. p. 146°. The more soluble fraction yielded a small amount of the βγ-amide, m. p. 152°.

Treated under the conditions of Birch and Kon (*loc. cit.*) for

24 hours, the βγ-nitrile (1·9 g.) gave 2·8 g. of the piperonylidene compound (XI), m. p. 127°. The αβ-nitrile (1·9 g.) gave 1·8 g. of the same compound under these conditions, the identity of the products being confirmed by a mixed melting-point determination. On treatment with sodiocyanoacetamide under the conditions of Birch and Kon for 2 hours, the αβ-nitrile gave the imino-compound (X), which decomposed indefinitely at about 276°. The yield of the product dried at 100° was 63%. A control experiment with the βγ-nitrile gave a 30% yield. The βγ-nitrile, equilibrated in the manner already stated and then treated under identical conditions, gave a yield of 51%. The products were hydrolysed in the usual manner through the ω-imide of α-cyano*cyclo*hexane-1 : 1-diacetic acid, m. p. 213—214°, to *cyclo*hexanediacetic acid, m. p. 181°. The identity of the material was in each case checked by a mixed melting-point determination.

Experiments with cyclo*hexylidenecyanoacetic acid* (I). The cyano-acid, prepared by Harding, Haworth, and Perkin's method using sodium ethoxide as condensing agent (*loc. cit.*), had m. p. 109°. A solution of 5 g. in 30 c.c. of absolute alcohol was saturated with hydrogen chloride at 0° and kept over-night. The ester isolated in the usual way was distilled under reduced pressure; it had b. p. 154—155°/23 mm., $d_{4°}^{17·5°}$ 1·0560, $n_{D}^{17·5°}$ 1·4975, whence $[R_L]_D$ 53·58. The ester prepared from *cyclo*hexanone and cyanoacetic ester by direct condensation has b. p. 151°/10 mm., $d_{4°}^{19·5°}$ 1·0539, $n_{D}^{19·5°}$ 1·4967. The cyano-acid (1 g.) was dissolved in sodium carbonate solution and treated with a cold 3% solution of potassium permanganate. *cyclo*Hexanone was isolated from the product in the usual way, and identified as its semicarbazone, m. p. 165—166°.

When the cyano-acid was heated, a nitrile distilled at 120—135°/50 mm., and after purification (Birch and Kon, *loc. cit.*) had b. p. 105°/22 mm., iodine addition 55%.

*α-Methyl*cyclo*hexane Series*.—Crude *cyclo*hexanolpropionic acid (von Auwers and Ellinger, *Annalen*, 1912, **387**, 200) (70 g.) was dehydrated in the usual manner with acetic anhydride. In this and similar preparations, the yield was considerably improved if the acetic acid and acetic anhydride were removed under reduced pressure before the reaction product was steam-distilled. Solid α-*cyclo*hexylidenepropionic acid began to separate after the first two litres of steam-distillate had passed over. In all, 10 litres were collected and kept over-night. The solution was filtered, extracted with ether, the solvent removed, the residue digested with sodium carbonate, and the acid recovered from the alkaline layer in the usual way. The acid obtained by extraction was always contaminated with an oily impurity. The total yield of αβ-acid was 65%. It distilled at 160°/17 mm., and crystallised in thick plates from light petroleum, m. p. 83° (Found : C, 69·9; H, 9·3. Calc. for $C_9H_{14}O_2$: C, 70·1; H, 9·1%) : von Auwers and Ellinger (*loc. cit.*) give m. p. 79°, but do not appear to have analysed this acid. Thionyl chloride gave a rather poor yield of the acid chloride, b. p. 115—116°/12 mm., which with gaseous ammonia yielded the amide, crystallising from dilute alcohol in lustrous plates, m. p. 120°. On dehydration this gave a good yield of α-*cyclo*hexylidenepropionitrile (IV; R=Me), b. p. 102—103°/13 mm., $d_{4^\circ}^{17^\circ}$ 0·9366, $n_D^{17^\circ}$ 1·4941, $[R_L]_D$ 42·0 (Calc., 40·9) (Found : C, 79·8; H, 9·6. Calc. for $C_9H_{13}N$: C, 80·0; H, 9·6%).

Ethyl α-Δ¹-*cyclo*hexenylpropionate, prepared from the β-hydroxy-ester by using phosphorus oxychloride as dehydrating agent, boiled at 105—110°/26 mm., and on cautious hydrolysis (Linstead, J., 1927, 2585) yielded α-Δ¹-*cyclo*hexenylpropionic acid,* b. p. 144°/14 mm. (Wallach and Evans, *Annalen*, 1908, **360**, 26, give b. p. 148—150°/13 mm.). The pure ethyl ester, prepared by esterification of the acid by dry, ice-cold alcoholic hydrogen chloride has b. p. 97—98°/12 mm. The acid chloride, prepared in the usual way, yielded the *anilide*, needles from dilute alcohol, m. p. 56° (Found : C, 78·5; H, 8·5. $C_{15}H_{19}ON$ requires C, 78·6; H, 8·3%). The amide, also prepared from the acid chloride, crystallised from aqueous alcohol in fine needles, m. p. 90°, and on dehydration (23 g.) gave the nitrile (15 g.). α-Δ¹-*cyclo*Hexenylpropionitrile (V; R = Me) boils at 113°/13 mm., and has $d_{4^\circ}^{16^\circ}$ 0·9382, $n_D^{16^\circ}$ 1·4761; $[R_L]_D$ 40·7 (Calc., 40·9) (Found : C, 79·9; H, 9·8. Calc. for $C_9H_{13}N$: C, 80·0; H, 9·6%). Harding, Haworth, and Perkin's nitrile, b. p. 150°/90 mm., is probably identical with this (*loc. cit.*).

Mixtures of the isomeric nitriles reacted with iodine chloride as follows :

αβ-Nitrile, % ……	100	80	65	50	35	20	0 (βγ-)
Addition, % ……	2·2	13·2	19·8	27·0	31·0	36·0	40·5

Equilibration of the βγ-nitrile under standard conditions yielded products with the following properties :

Time of treatment (hrs.) …	0·5	1·0	1·5	2·5	4	24
Iodine addition, % ………	16·5	10·2	6·9	6·0	5·4	5·5
αβ-Nitrile formed, % ………	72·5	85·5	91·5	93	94	94

Similar treatment of the αβ-nitrile for 24 hours gave a product with iodine addition 5·2%, whence αβ-nitrile = 94·5%.

A sample of *cyclo*hexylidenepropionitrile prepared from ethyl α-cyano-α-Δ¹-*cyclo*hexenylpropionate (Birch and Kon, *loc. cit.*) had

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* This acid has subsequently been obtained as a solid, m. p. 38°, by Mr. R. S. Thakur of this College.

b. p. 106°/14 mm., iodine addition 3%, and hence was the almost pure αβ-isomeride.

α-*Ethyl*cyclo*hexane Series.*—Ethyl α-*cyclo*hexanolbutyrate (Kon and Narayanan, *loc. cit.*) was hydrolysed with cold 10% aqueous potassium hydroxide. The acid was isolated in the usual way in a yield (75%) much better than that obtained in the work quoted. A small quantity of the acid was distilled without decomposition at 164°/24 mm. The crude hydroxy-acid was dehydrated with acetic anhydride and worked up in the usual manner. After 7 litres of steam-distillate had passed over, the unsaturated acid began to solidify; 16 litres in all were collected, the acid being worked up in the same way as for the lower homologue. The product boiled at 152—153°/10 mm., and partially solidified on cooling. The solid acid was filtered off, drained on porous earthenware, and recrystallised from dilute alcohol.

α-*cyclo*Hexylidenebutyric acid forms prisms, m. p. 62° (Found: C, 71·6; H, 9·6. Calc. for $C_{10}H_{16}O_2$: C, 71·4; H, 9·4%). Kon and Narayanan's liquid acid (b. p. 165°/20 mm.) presumably contained isomeric impurity. The acid chloride boiled at 110—111°/10 mm., and yielded the amide, crystallising from dilute alcohol in long silky needles, m. p. 108—109° (compare Kon and Narayanan). On dehydration this yielded α-*cyclo*hexylidenebutyronitrile (IV; R = Et), b. p. 114°/11 mm., $d_{4^\circ}^{17\cdot4^\circ}$ 0·9225, $n_D^{17\cdot4^\circ}$ 1·4887; $[R_L]_D$ 46·53 (Calc., 45·53) (Found: C, 80·2; H, 10·3. Calc. for $C_{10}H_{15}N$: C, 80·5; H, 10·1%). A sample of the nitrile prepared by Farrow and Kon's method (J., 1926, 3124) had b. p. 112—113°/12 mm., $d_{4^\circ}^{17^\circ}$ 0·9228, $n_D^{17^\circ}$ 1·4887. The substance does not appear to have been previously analysed.

α-Δ¹-*cyclo*Hexenylbutyramide, prepared by Kon and Narayanan's method (*loc. cit.*), had m. p. 115—116°. On dehydration it gave α-Δ¹-cyclo*hexenylbutyronitrile* (V; R = Et), b. p. 112°/12 mm., $d_{4^\circ}^{17\cdot4^\circ}$ 0·9263, $n_D^{17\cdot4^\circ}$ 1·4794, $[R_L]_D$ 45·68 (Found: C, 80·3; H, 10·2. $C_{10}H_{15}N$ requires C, 80·5; H, 10·1%).

Mixtures of the isomeric nitriles had the following iodine additions:

αβ-Nitrile, %	100	80	65	50	35	20	0 (βγ-)
Iodine addition, %	2·5	9·1	13·3	19·5	24·4	26·8	30·3

Standard equilibration of the βγ-nitrile gave the following results:

Time of treatment (hrs.)	0·5	1·0	2·0	3·0	6·0	8·0	24·0
Iodine addition, %	27·5	24·2	18·0	13·7	8·0	6·8	5·7
αβ-Nitrile formed, %	18·5	32·5	53·5	65·0	83·5	86·5	89·5

The αβ-nitrile on similar treatment gave a product with an iodine addition of 5·2%, whence αβ = 90%.

cyclo*Pentane Series.*—*cyclo*Pentylideneacetyl chloride (Kon and

Linstead, J., 1925, **127**, 820) was converted into the amide, m. p. 138°, 20 g. of which yielded 55% of nitrile on dehydration. *cyclo*-*Pentylideneacetonitrile* (XV) has b. p. 97—98°/24 mm., $d_{4^\circ}^{18\cdot4^\circ}$ 0·9427, $n_{\mathrm{D}}^{18\cdot4^\circ}$ 1·4805, $[R_L]_{\mathrm{D}}$ 32·30 (Calc., 31·68) (Found : C, 78·3; H, 8·2. C_7H_9N requires C, 78·5; H, 8·4%), and on oxidation in the manner described for the analogous *cyclo*hexane compound, it yielded *cyclo*-pentanone, identified as the semicarbazone (m. p. 204°, mixed m. p.).

Δ^1-*cyclo*Pentenylacetamide, m. p. 144° (Wallach and Speransky, *Annalen*, 1902, **323**, 159) (25 g.) yielded 62% of the corresponding nitrile (XIV). This had b. p. 91—92°/19 mm., $d_{4^\circ}^{18\cdot4^\circ}$ 0·9395, $n_{\mathrm{D}}^{18\cdot4^\circ}$ 1·4683, $[R_L]_{\mathrm{D}}$ 31·7 (Found : C, 78·2; H, 8·2. Calc. : C, 78·5; H, 8·4%). Birch and Kon's figures for the nitrile prepared from the cyano-acid are b. p. 99°/33 mm., $d_{4^\circ}^{20\cdot5^\circ}$ 0·9394, $n_{\mathrm{D}}^{20\cdot5^\circ}$ 1·4681 (*loc. cit.*, p. 2446).

Mixtures of the isomeric nitriles had the following iodine additions :

αβ-Nitrile, %	100	80	70	50	30	0 (βγ-)
Iodine addition, %	4·0	18·4	23·1	32·0	40·8	49·3

On equilibration under standard conditions for 24 hours the products from the αβ- and βγ-nitriles had iodine additions of 8·7 and 9·3%, corresponding to αβ-contents of 94 and 93% respectively. The mobility could not be determined, for after 5 minutes' treatment of the βγ-nitrile, the product was almost indistinguishable from the equilibrium mixture.

β-*Methylpentenoic Series.*—β-Methyl-β-ethylacrylic acid (Kon and Linstead, J., 1925, **127**, 623) distilled at 122—123°/22—23 mm. The last fraction of the acid solidified in the condenser, and the bulk of the distillate on cooling. The solid acid, m. p. 45°, was identical with that previously obtained, but there was a considerable amount of liquid product. The solid acid gave an amide, m. p. 99° (Kon and Linstead give 92—93°), and the same product was obtained in a state of purity from the liquid acid. It would appear that these represent geometrically isomeric forms of β-methyl-β-ethylacrylic acid, yielding a common acid chloride and amide (compare Newbery, J., 1925, **127**, 295).* On dehydration, the amide (19 g.) yielded β-methyl-Δ^α-pentenonitrile (XVII) (6 g.), b. p. 63°/20 mm., $d_{4^\circ}^{20\cdot3^\circ}$ 0·8432, $n_{\mathrm{D}}^{20\cdot3^\circ}$ 1·4447, $[R_L]_{\mathrm{D}}$ 30·0 (Calc., 29·36).

β-Methyl-Δ^β-pentenamide (15 g.), m. p. 124—125° (Kon and Linstead, *loc. cit.*), yielded 10 g. of the corresponding nitrile. β-*Methyl*-Δ^β-*pentenonitrile* (XVI) has b. p. 60°/19 mm., $d_{4^\circ}^{20\cdot5^\circ}$ 0·8478,

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* These acids are being further investigated. If the existence of the liquid isomeride is confirmed, the fact that Gardner and Haworth's acid was liquid (see p. 2143) can no longer be taken as providing evidence as to its lack of homogeneity.

$n_D^{20\cdot5°}$ 1·4367, $[R_L]_D$ 29·36 (Found : C, 75·5; H, 9·7. C_6H_9N requires C, 75·8; H, 9·5%).

Mixtures of these nitriles had the following iodine additions :

αβ-Nitrile, %	100	80	50	20	0 (βγ-)
Iodine addition, %	2·0	15·7	33·3	46·0	51·5

On equilibration, the αβ- and βγ-nitriles gave products with iodine additions (2·0%) exactly agreeing with that of the pure αβ-nitrile. After 5 minutes' treatment, the addition of the βγ-nitrile falls to 5% and the system is therefore too mobile for accurate measurement.

o-, m-, *and* p-*Methyl*cyclo*hexane Series.*—*α-Cyano-*1-*methyl*cyclo*hexylidene-*2-*acetic acid* (formula I with Me in position 1) was prepared from 2-methyl*cyclo*hexanone (Deutsche Hydrierwerke A.-G.) by the general method of Harding, Haworth, and Perkin. The crude acid solidified after standing in a vacuum desiccator for several days, and was drained on porous earthenware; it separated from benzene in short needles, m. p. 106—107° (Found : C, 67·3; H, 7·3. $C_{10}H_{13}O_2N$ requires C, 67·0; H, 7·3%). On distillation it yielded 2-*methyl*-$\Delta^{1\,(\text{or }6)}$-cyclo*hexenyl*-1-*acetonitrile* (XVIII; R = Me, R′ = R″ = H), b. p. 101°/14 mm., $d_{4°}^{21°}$ 0·9384, $n_D^{21°}$ 1·4762, $[R_L]_D$ 40·4 (Calc., 40·9) (Found : C, 79·9; H, 9·8. $C_9H_{13}N$ requires C, 80·0; H, 9·6%). The iodine addition was 51·6%, falling after equilibration to 5·2%, corresponding with the production of the αβ-isomeride.

3-Methyl-Δ^1-*cyclo*hexenyl-1-acetonitrile (XVIII; R′ = Me, R = R″ = H) (Wallach and Beschke, *Annalen*, 1906, **347**, 341; Harding and Haworth, *loc. cit.*), prepared from the cyano-acid, had b. p. 113°/20 mm., $d_{4°}^{21°}$ 0·9239, $n_D^{21°}$ 1·4732, $[R_L]_D$ 41·3. Its iodine addition was 47·3%, and after equilibration, 7·2%.

4-Methyl-Δ^1-*cyclo*hexenyl-1-acetonitrile (XVIII; R″ = Me, R = R′ =H) (Harding, Haworth, and Perkin, *loc. cit.*) boiled at 109°/16 mm., and had $d_{4°}^{21°}$ 0·9232, $n_D^{21°}$ 1·4726, $[R_L]_D$ 41·0. The iodine addition of 55·2% fell on equilibration to 8·8%.

Condensation with cyanoacetamide. Each of the nitriles (2 c.c.) was allowed to react with 2·1 g. of cyanoacetamide as before. The *m*- and *p*-methyl compounds each yielded 0·8 g. of the imino-compounds (as X), but the *o*-methyl compound did not react either before or after equilibration. The two imino-compounds were hydrolysed to the corresponding *ω-imides* of *α-cyano-*3- and -4-*methyl*cyclo*hexane*-1 : 1-*diacetic acids*, which melted at 235° and 230° respectively (Found, for the 3-methyl compound : C, 65·3; H, 7·4; for the 4-methyl compound : C, 65·5; H, 7·3. $C_{12}H_{16}O_2N_2$ requires C, 65·5; H, 7·3%). Hydrolysis with concentrated sulphuric acid gave quantitative yields of the corresponding diacetic acids, m. p. 143° and 158° respectively (Thorpe and Wood, J., 1913, **103**, 1586). Mixed melting points with authentic specimens showed no depression.

Condensation products with piperonal. These were obtained from the three nitriles in very good yield by the method of Birch and Kon (*loc. cit.*). The *piperonylidene* derivative of the *p*-methyl nitrile formed colourless lustrous needles m. p. 132° (Found : C, 76·0 ; H, 6·3%) ; that of the *m*-methyl nitrile first separated as an orange powder which, after two crystallisations from aqueous alcohol, formed clusters of yellow needles, m. p. 84° (Found : C, 76·2 ; H, 6·5%) ; and that of the *o*-methyl nitrile separated as a gelatinous mass, but after being drained on porous earthenware could be crystallised from alcohol, separating as yellow needles, m. p. 122° (Found : C, 76·2 ; H, 6·5. $C_{17}H_{17}O_2N$ requires C, 76·4 ; H, 6·4%).

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