54. *The Chemistry of the Three-carbon System. Part XXVIII. Nitriles of Butenoic and Hexenoic Acids. A Note on the Analysis of Unsaturated Nitriles by Halogen Addition.*

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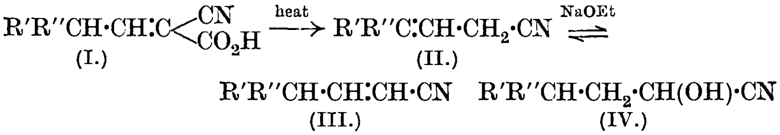
IN a previous investigation (Kandiah and Linstead, J., 1929, 2139) it was shown that the purity of αβ- and βγ-unsaturated nitriles and the composition of mixtures of such isomerides could be estimated with some accuracy by iodometric analysis, and by applying this method the following general relationships were found to hold: (1) Dehydration of the amides of αβ- and βγ-unsaturated acids yields the corresponding nitriles without migration of the double bond (compare von Auwers, *Annalen*, 1923, **432**, 46), (2) decarboxylation of αβ-unsaturated cyano-acids (I) yields pure βγ-nitriles (II), in agreement with previous workers (references in the earlier paper), (3) αβ- and βγ-nitriles (III and II) are smoothly interconverted by cold alcoholic sodium ethoxide with the formation of an equilibrium mixture, and the reactions (preparation, alkylation. addition) involving the use of this medium are readily understandable in the light of this fact.



$$R'R''CH\cdot CH{:}C<\genfrac{}{}{0pt}{}{CN}{CO_2H} \xrightarrow{\text{heat}} R'R''C{:}CH\cdot CH_2\cdot CN \overset{\text{NaOEt}}{\rightleftharpoons}$$

(I.) (II.)

$$R'R''CH\cdot CH{:}CH\cdot CN \qquad R'R''CH\cdot CH_2\cdot CH(OH)\cdot CN$$

(III.) (IV.)

This early work was carried out exclusively with β-alkylated nitriles and in some cases with those with an additional α-substituent. A study has now been made of the effect of γ-alkylation, which has been shown (J., 1929, 2498, *et seq.*) to have a striking influence on three-carbon equilibria. For this purpose the butenonitriles (III and II; R′, R″ = H, H), the *n*-hexenonitriles (R′ = Et, R″ = H), and the *iso*hexenonitriles (R′, R″ = Me, Me) were examined. The standard preparative methods were again used and a comparative study was made of the products obtained by dehydration of the corresponding cyanohydrins (IV), a reaction which has been extensively used in recent years by Bruylants and his school. The properties of the products are given in detail in the experimental section and in summary in Tables I, II, and III.

TABLE I.

n-Hexenonitriles ($[R_L]_D$ calc., 29·26).

Method.	*n*.*	*d*.*	$[R_L]_D$.	*J*.†	Product.	Observer.‡
Dehydration						
of αβ-amide	1·4379	0·8274	30·16	0·4	αβ	L.L.
of *n*-valeraldehyde cyanohydrin	1·4323	0·8271	29·82	23·2	Mixture	L.L.
of βγ-amide	1·4301	0·8381	29·28	47·0	βγ	L.L.
of hydrosorbamide	1·4322	0·841	—	—	βγ + γδ	A.
Decarboxylation						
of cyano-acid	1·4296	0·8364	29·30	45·0	βγ	L.L.

* $n_D^{20°}$, $d_{4°}^{20°}$ throughout this paper, unless otherwise stated.

† *J*, % Iodine addition under the conditions given on p. 448.

‡ Full references at foot of Table III.

The amide used for the preparation of the βγ-nitrile was obtained from the pure Δ^{β}-*n*-hexenoic acid of Boxer and Linstead (J., 1931, 740) through the acid chloride, and melted at 86°. The amide of m. p. 60° used by von Auwers (*loc. cit.*) for the same purpose had been prepared from hydrosorbic acid and undoubtedly contained some Δ^{γ}-hexenoamide (compare Eccott and Linstead, J., 1929, 2153). Philippi and Galter (*Monatsh.*, 1929, **51**, 253) state that methyl hydrosorbate is converted by ammonia into an amide of m. p. 75°. In general, their work indicates that γδ-esters are much less readily converted into amides than are βγ-esters and it is therefore quite possible that their amide was largely βγ.

TABLE II.

*iso*Hexenonitriles ($[R_L]_D$ calc., 29·26).

Method.	*n*.	*d*.	$[R_L]_D$.	*J*.	Product.	Observer.
Dehydration						
of *iso*valeraldehyde cyanohydrin	—	$0{\cdot}8268^{16°}$	—	—	Mixture	H.
of αβ-amide	$1{\cdot}4342^{20°}_{\mathrm{He}}$	0·823	—	—	αβ	A.
of αβ-amide	1·4337	0·8179	30·24	1·3	αβ	L.L.
of βγ-amide	1·4354	0·8547	29·26	74·0	βγ	L.L.
Decarboxylation						
of cyano-acid	1·4374	0·855	—	—	βγ	A.
of cyano-acid	1·4352	0·8511	29·16	78·0	βγ	L.L.

Dehydration of *iso*valeraldehyde cyanohydrin gave a product of indefinite boiling point, a typical fraction of which had the following properties: *n* 1·4314, *d* 0·8215, *J* 13·6%. While this work was in progress, Bruylants and Minetti (*Bull. Acad. roy. Belg.*, 1930, **16**, 1116) described a study of the same reaction, which yielded very similar results (*e.g.*, their main upper fraction had *n* 1·4362, *d* 0·8249, *J* 8·3%), and it is clear that the bulk of the product is a mixture of *trans*-αβ-, and some βγ-nitrile. Bruylants and Minetti isolated a low-boiling *cis*-form of the αβ-nitrile and the existence of this was also indicated by the physical properties of our low-boiling fractions.

TABLE III.

Butenonitriles ($[R_L]_D$ calc., 20·02).

Method.	*n*.	*d*.	$[R_L]_D$.	*J*.	Product.	Observer.
CuCN and						
allyl bromide	1·4060	0·8341	—	—	βγ	B.
allyl bromide	1·406	0·836	—	—	,,	A.
allyl bromide	1·4048	0·8351	19·96	61·9	,,	L.L.
allyl alcohol	$1{\cdot}4073^{15°}$	$0{\cdot}8418^{15°}$	19·91	$63{\cdot}8^{15°}$	,,	L.L.
Dehydration						
of αβ-amide	$1{\cdot}4249^{14°}$	0·824	—	—	αβ	A.
of αβ-amide	1·4217	0·8242	20·64	0·6	,,	L.L.
of cyanohydrin	1·4169	—	—	—	Mixture	B.
of cyanohydrin	1·4170	—	—	12·0	,,	L.L.
Decarboxylation						
of cyano-acid	1·4156	0·822	—	—	Mixture	A.
of cyano-acid	—	—	—	1·7	Mainly αβ	L.L.

References: A., von Auwers, *loc. cit.* and *Ber.*, 1923, **56**, 1172. B., Bruylants, *Bull. Soc. chim. Belg.*, 1922, **31**, 175. H., Henry, *Bull. Acad. roy. Belg.*, 1898, **36**, 22. L.L., present work.

The iodometric analysis of the butenonitriles fully confirms the structures assigned to them on the chemical evidence of Bruylants and the spectrochemical work of von Auwers. The properties of crotononitrile prepared by us from (*trans*-)crotonamide are in almost exact agreement with those given by Bruylants for the pure *trans*-

nitrile (*n* 1·4216, *d* 0·8239). In our hands the method of Breckpot (*Bull. Soc. chim. Belg.*, 1930, **39**, 462) gave Δ^{β}-butenonitrile of slightly greater purity than did the original Henry–Bruylants reaction.

This examination of the usual methods available for the preparation of unsaturated nitriles confirms the correctness of the views already expressed as to their usefulness. A not unexpected exception to the rule that decarboxylation of αβ-cyano-acids occurs with quantitative displacement of the double bond to the βγ-position is provided by α-cyanocrotonic acid (I; R′R″ = HH), which gives a largely αβ-product. It is of interest that dehydration of *trans*-αβ-amides yields in all cases homogeneous nitriles, whereas dehydration of cyanohydrins yields mixtures of the βγ- and stereoisomeric forms of the corresponding αβ-nitriles and is unsuited for the preparation of pure material. Clearly, this is connected with the fact that in the former reaction only the functional group participates, whereas in the latter the double bond is formed under conditions tending to lability.

Tautomeric Changes.—(1) *Alkali.* Both the *n*- and the *iso*-hexenonitrile very readily underwent interconversion when treated with alcoholic sodium ethoxide at 25°. Prolonged treatment with the reagent yielded additive compounds (compare Bruylants, *Bull. Soc. chim. Belg.*, 1922, **31**, 225). The mobility and position of equilibrium, determined for each series by Kon and Linstead's method (J., 1929, 1269), are given below :

Nitriles.	Equilibrium, % αβ.	Mobility, $(k_1 + k_2) \times 10^4$.	Half-change period (approx.), mins.
n-Hexenoic	86	930	7
*iso*Hexenoic	21	170	33

Treatment of Δ^{β}-butenonitrile with sodium ethoxide either in equivalent or in " catalytic " amount, on the other hand, led to its complete conversion into β-ethoxy-nitrile, presumably by instantaneous isomeric change followed by addition to the αβ-phase. The extremely high mobility of the system is also indicated by the isomerisation of the βγ-form by caustic alkali, demonstrated by von Auwers (*loc. cit.*, *Ber.*) and Bruylants (*Bull. Soc. chim. Belg.*, 1924, **33**, 331). Reinvestigation of this change showed that 12 hours' treatment of the βγ-nitrile with *N*-caustic soda solution reduced its iodine addition to 2·4%—a value which could not be lowered by further treatment with alkali. On the other hand, crotononitrile showed no increase in iodine addition after 2 days' similar treatment. This is in entire agreement with the results of von Auwers, except that the βγ-content at " equilibrium " cannot exceed 4% and is probably negligible. The persistence of iodine addition in the equilibrated βγ-nitrile is difficult to explain, but may be connected with the formation of some slightly additive *cis*-αβ-nitrile.

An inspection of the equilibrium values shows that the effect of γ-alkylation in nitriles is almost the same as in acids :

	γ-Substituents	H, H	H, Et	Me, Me
% αβ at equilibrium in	acids	*ca.* 100	75	22
	nitriles.........	96—100	86	21

It has previously been shown that β-alkyl groups, which to some extent stabilise the βγ-forms of unsaturated acids, have no such effect on the corresponding nitriles, which are all largely αβ- at equilibrium (Kandiah and Linstead, *loc. cit.*), and it was assumed that the position of equilibrium was controlled predominantly by the nitrile group. The new results show, however, that the influence of γ-groups is considerably more powerful than that of β-groups, presumably because their polar effects act directly on one of the carbon atoms concerned in the tautomeric change.

(2) *Heat.* In view of the comparatively ready equilibration of pure unsaturated acids at high temperatures (J., 1930, 1603) it became of importance to examine the stability of the corresponding nitriles under the same conditions. If the change in acids can be attributed to the polar nature of the functional group, it would be expected that the nitriles would show little or no tendency to tautomerise at high temperatures. Further interest was lent to this question by the publication of Bruylants and Minetti's investigation of the distillation of the *iso*hexenonitriles produced by dehydrating *iso*valeraldehyde cyanohydrin. In this it is claimed that a purified αβ-nitrile was partly isomerised to the βγ-form. On the other hand, von Auwers (*loc. cit.*, *Ber.*) has reported that Δ^{α}-*iso*heptenonitrile was unchanged by 3 hours' boiling.

In the present work, the materials were heated in carefully cleaned apparatus in an atmosphere of carbon dioxide. *trans*-Δ^{α}-*iso*Hexenonitrile was unchanged on distillation, and even after being boiled under reflux for 8 hours, the iodine addition then having increased by only 0·7%. The same result was obtained by carrying out the latter experiment without special precautions, although the absence of carbon dioxide led to considerable charring. It is to be supposed that Bruylants and Minetti's results are due to a concentration by fractionation of βγ-nitrile *already present*, or possibly to an isomerising action of some alkaline catalyst. Actually, all the pure nitriles prepared in this work were remarkably stable to heat, even Δ^{β}-butenonitrile being almost unaffected by 8 hours' heating under pressure at 200°. Spontaneous tautomeric change in pure compounds of this type must therefore occur very slowly, if at all.

Analysis of Unsaturated Nitriles by Halogen Addition.—Heim (*Bull. Soc. chim. Belg.*, 1930, **39**, 458) states that, whereas Kandiah and Linstead find iodine additions of approximately 3 and 56% for αβ- and βγ-nitriles respectively, he obtains additions of only 1·4 and 7% to *trans*-crotononitrile and Δ^{β}-butenonitrile. Hence he concludes that "the method fails." Furthermore, Bruylants and Minetti (*loc. cit.*) and Colmant (*Bull. Soc. chim. Belg.*, 1930, **39**, 568) estimate the βγ-content of isomeric mixtures from iodine additions when no specific reference data are available. It therefore becomes necessary to comment on the use of the analytical method in this connexion, as its principle has obviously been misunderstood by the Belgian school.

As it is difficult to obtain a set of conditions under which reaction with halogens occurs completely at βγ-double bonds and not at all at αβ-double bonds, it is necessary to find for *every pair* of isomerides conditions of reagent, solvent and concentration such that a *convenient difference in reactivity* is obtained. Reference data for each particular pair of isomerides are obtained and the composition of mixtures can then be estimated by comparison. Fortunately, most systems can be examined under one or other of the standard conditions already described (Linstead, J., 1927, 355; Linstead and May, *ibid.*, p. 2565). It has, however, been frequently pointed out that the multiplication of unsaturated substituents, or the absence of alkyl groups in the vicinity of the double bond, leads to a diminution in reactivity of the βγ-form such that more vigorous conditions of reaction become necessary. The low affinity of Δ^{β}-butenonitrile for iodine chloride is quite to be expected, but by a suitable increase in the concentration of the reagents (see experimental portion) it is a simple matter to obtain the necessary degree of reaction in a convenient time.

The bromometric method of Heim (*loc. cit.*) is a modification differing only in detail from those referred to above. In agreement with Heim we find that this method gives concordant results for the butenonitriles. It is, however, unsatisfactory for higher nitriles, because, as a two-phase system (chloroform–water) is involved in the reacting mixture, it follows that when addition to the βγ-form is not very rapid it is considerably affected by uncontrollable variations in the extent of shaking.

EXPERIMENTAL.

Iodine Additions (J).—The hexenonitriles in *M*/15-solution in chloroform and the iodine chloride in the concentration used by Kandiah and Linstead (*loc. cit.*) were allowed to react for 2 hours at

20°. Under these conditions Δ^β-butenonitrile added only 25·6% of iodine. After further trials, solutions of the following concentrations were used for the butenonitriles : *M*/15-nitrile in chloroform, and iodine chloride obtained from solutions of 34 g. of iodine and 50·7 g. of mercuric chloride each in 250 c.c. of rectified spirit. Equivalent amounts of Δ^β-butenonitrile and the reagent then gave a 63·8% addition in 2 hours at 20°.

n-*Hexenonitriles* (compare Table I).

(1) *From Amides.*—A solution of Δ^α-*n*-hexenoyl chloride, prepared from the solid acid, in sodium-dried ether (5 vols.) was treated with an excess of dry ammonia gas, and the product washed with very dilute hydrochloric acid and freed from solvent. Δ^α-n-*Hexenoamide*, obtained in 96% yield, crystallised from chloroform or benzene in shining leaflets, m. p. 122° (Found : N, 12·3. $C_6H_{11}ON$ requires N, 12·4%). When ammonia solution (*d* 0·880) was used, the yield was 90%. The purity of the acid chloride was checked by conversion of a small quantity into the *p*-toluidide of m. p. 125° (Fichter and Pfister, *Ber.*, 1904, **37**, 1997).

Treatment of the amide with phosphorus pentachloride and phosphorus oxychloride yielded only mixtures containing partially chlorinated products. This method of dehydration therefore appears to be applicable only to ββ-substituted amides (Kandiah and Linstead, *loc. cit.*). The chlorine could be removed by distillation from dry caustic soda but not by treatment with sodium ethoxide. Dehydration with phosphoric oxide was more successful : A mixture of the amide (20 g.) and the pentoxide (30 g.) was cautiously heated in a flask fitted with an efficient condenser. When the amide melted, a vigorous reaction set in, and at its close the mixture was diluted and distilled in steam. The nitrile was extracted from the first litre of the distillate with ether, dried, and freed from solvent. Δ^α-n-*Hexenonitrile* (III; $R' = Et$, $R'' = H$) was thus obtained in about 60% yield as a colourless oil, b. p. 50°/10 mm., having the properties already recorded (Found : C, 75·5; H, 9·5. C_6H_9N requires C, 75·8; H, 9·5%). Dehydration in a diluent (dry benzene) was rather less satisfactory.

Δ^β-*n*-Hexenoyl chloride, yielding the *p*-toluidide, m. p. 95°, of Eccott and Linstead (*loc. cit.*), gave a 95% yield (from the acid) of Δ^β-n-*hexenoamide*, which crystallised from benzene and light petroleum in leaflets, m. p. 86° (Found : C, 64·0; H, 9·8. $C_6H_{11}ON$ requires C, 63·7; H, 9·7%).

When the amide was treated with phosphorus pentachloride and oxychloride, chlorination again occurred, but by using phosphoric oxide under the conditions given for the αβ-amide, a 40% yield of Δ^{β}-n-*hexenonitrile* (II; R′ = Et, R″ = H) was obtained, b. p. 58°/15 mm. (Found : C, 75·4; H, 9·4%).

(2) *From the Cyano-acid.*—Cyanoacetic acid was conveniently prepared in quantity by the method of Phelps and Tillotson (*Amer. J. Sci.*, 1908, **26**, 275), with the modifications given for the preparation of the ethyl ester by Kohler and Allen (" Organic Syntheses," III, 53). The product was left for a week over sulphuric acid and was then frozen to a solid of m. p. 68° (yield, 68%).

For the preparation of the unsaturated cyano-acid, the following application of von Auwers's method gave good results : Molecular quantities of cyanoacetic acid and redistilled *n*-butaldehyde were heated on the steam-bath for 4 hours with piperidine (*M*/50). The acid product after extraction in the usual manner in sodium bicarbonate solution was obtained as a viscous brown oil, which was heated at 70—80° in a vacuum for some time and dissolved in dry ether, and the solution allowed to evaporate slowly. The coarse white powder obtained (75%) yielded pure *α-cyano-*Δ^{α}-n-*hexenoic acid* (I; R′ = Et, R″ = H), on vacuum sublimation or crystallisation from benzene and light petroleum, as needles, m. p. 102° (Found : C, 60·0; H, 6·6; equiv., 141. $C_7H_9O_2N$ requires C, 60·4; H, 6·5%; equiv., 139). The acid resisted fission when treated with ozonised oxygen in ethyl acetate solution for a week, but the position of the double bond was proved by its oxidation (5 g.) with potassium permanganate (10 g.) in sodium bicarbonate solution. After a week the solution was filtered, acidified, and extracted continuously with ether for a day. The acid, isolated by cautious evaporation of the dried extract, was identified as *n*-butyric acid by conversion into the amide, m. p. and mixed m. p. 113°.

Condensation occurred to only a slight extent between cyanoacetic acid and *n*-butaldehyde in the presence of pyridine, the product being the same α-cyano-acid. This presents an interesting contrast to the condensation of malonic acid in the ordinary Doebner reaction.

Only small quantities of nitrile could be obtained by heating the cyano-acid (i) under pressure at 100°, 180°, and 240°, or (ii) rapidly under reduced pressure, which led to sublimation. Decomposition was best effected by heating small quantities of the acid, mixed with an equal quantity of fine sand, at atmospheric pressure. The product was dried in ethereal solution and distilled at 57—58°/11 mm. It had the properties already given. The yields varied widely and did not exceed 40%.

(3) *From the Cyanohydrin.*—*n*-Valeraldehyde was prepared from *n*-butyl bromide by the method used by Bodroux for the preparation of *iso*valeraldehyde (*Compt. rend.*, 1904, **138**, 700) but modified

along the lines indicated by Linstead and Mann (J., 1930, 2070). Consistent yields were obtained only by the following procedure: The Grignard compound of the bromide was treated with orthoformic ester (2/3 mol.) in an equal volume of ether, addition being rapid so that the ether was kept boiling (about 15 mins.). The mixture was left over-night and then boiled and shaken for an hour. After removal of the ether, the product was worked up in the usual manner, the acetal being hydrolysed with 20% sulphuric acid for ½ hour, and the aldehyde converted into the bisulphite compound (yield, 50% calculated on the orthoformate used).

The aldehyde failed to give the cyanohydrin by Ultée's method (*Rec. trav. chim.*, 1909, **28**, 1, 248). A modification of the alternative method of Albert (*Ber.*, 1916, **49**, 1382) was tested with the more readily available butaldehyde and found satisfactory (see below). It was therefore applied to the valeraldehyde bisulphite compound, 47 g. of which were suspended in water (16 c.c.) and treated slowly and with cooling with potassium cyanide (16 g.; 1 mol.) in 22 c.c. of water. A reproducible yield of 12 g. (43%) of *α-hydroxy-*n*-hexonitrile* (IV; $R' = Et, R'' = H$) was thus obtained, b. p. 116°/14 mm., d 0·9217, n 1·4265, $[R_L]_D$ 31·39 (calc., 31·45) (Found: C, 63·7; H, 10·3. $C_6H_{11}ON$ requires C, 63·7; H, 9·7%).

By the same method, n-butaldehyde (44 c.c.; ½ mol.) was added to a cooled, freshly prepared bisulphite solution (¾ mol.) and, after standing over-night, the mixture was cooled in a freezing mixture and cautiously treated with small quantities of a concentrated aqueous solution of potassium cyanide (33 g.). After a further hour's standing, the precipitated salts were filtered off, the cyanohydrin was extracted with ether, the solution dried over-night with sodium sulphate, and the solvent removed. The cyanohydrin was stabilised with a few drops of concentrated sulphuric acid and distilled at 103°/14 mm., 106°/20 mm. The yield was 35 g. (70%), but fell to 60% when a 15% excess of potassium cyanide was used. The pure substance had d 0·9397, n 1·4211, $[R_L]_D$ 26·72 (calc., 26·83) (Found: C, 60·0; H, 9·2. Calc.: C, 60·6; H, 9·1%) (compare Henry, *Bull. Acad. roy. Belg.*, 1898, **36**, 241).

For the dehydration, n-valeraldehyde cyanohydrin (5 g.) was added to a mixture of phosphoric oxide (10 g.) and dry sand; 55% of mixed nitriles were obtained, b. p. 62—70°/25 mm.

Reference Curve.—The iodine additions of the various preparations are in Table I. The reference curve was constructed with mixtures of the αβ-nitrile (from the amide) and the βγ-nitrile (from the cyano-acid):

Composition, % αβ ...	0	10	20	40	60	80	90	100
J, %	45	41·7	38·7	31·8	23·9	13·8	8·0	0

The variation in addition of the βγ-nitrile with temperature is given below :

Temperature	18·5°	19·5°	20°	27°
J, %	43·1	44·6	45·0	48·9

Equilibrations.—(1) Those with sodium ethoxide were carried out at 25° by the method of Kon and Linstead (*loc. cit.*). Reaction for more than 20 minutes yielded some β-ethoxy-nitrile. In these cases the distillate of b. p. 58—70°/15 mm. was refractionated and the fraction boiling below 65°/15 mm. was taken as unsaturated nitrile. In other experiments the fraction of the first distillation boiling below 65°/15 mm. was used. The physical properties of these low fractions show that they are free from the ethoxy-nitrile. The recovery of nitrile averaged 75%. The results are given in Table IV.

TABLE IV.

Equilibration of *n*-Hexenonitriles.

Material.	Time of equil. (mins.).	Unsaturated nitrile obtained.				Ethoxy-nitrile.
		d.	*n*.	*J*.	Comp., % αβ.	
βγ	5	0·8328	1·4323	31·4	41	nil
,,	5	0·8318	1·4315	30·4	43	,,
,,	10	0·8335	1·4316	27·5	49·5	trace
,,	15	0·8316	1·4327	19·6	67	some
,,	20	0·8322	1·4327	17·7	71	*ca.* 40%
,,	30	0·8351	—	11·6	84	*ca.* 65%
αβ	5	0·8273	1·4362	5·0	94·5	trace
,,	20	0·8275	1·4353	9·3	88·5	>50%
88·5% αβ	10	0·8308	1·4348	11·0	85	trace
,,	30	—	1·4347	10·8	85	>50%

With one equivalent of *N*/10-sodium ethoxide the βγ-nitrile yielded 35% of the αβ-nitrile in 30 minutes.

For the isolation of the ethoxy-compound the βγ-nitrile (4 g.) was treated with *N*-sodium ethoxide (1 mol.) for 4 hours. The reaction product yielded pure β-*ethoxy*-n-*hexonitrile*, b. p. 82°/11 mm., *d* 0·8818, *n* 1·4219, $[R_L]_D$ 40·7 (calc., 40·61) (Found : C, 68·2 ; H, 10·6. $C_8H_{15}ON$ requires C, 68·1 ; H, 10·6%).

(2) For equilibrations with heat, all apparatus was carefully cleaned with chromic acid mixture, distilled water, alcohol, and redistilled sodium-dried ether. (*a*) The nitriles were distilled under reduced pressure into a small Claisen flask, which was then filled with pure carbon dioxide. From this they were slowly distilled in a current of carbon dioxide at atmospheric pressure into a sealed-on condensing apparatus and receiver. (*b*) The nitriles were heated in a Geisler flask fitted with a ground-in air condenser, an atmosphere

of carbon dioxide being maintained. The properties of the products are given below :

Product.	*d.*	*n.*	*J.*	B. p./mm.
Δ^{α}-*n*-Hexenonitrile, distilled at 162°	0·8271	1·4373	1·2	57°/17
Δ^{α}-*n*-Hexenonitrile, refluxed for 7½ hours	0·8273	1·4369	1·3	57/17
Δ^{β}-*n*-Hexenonitrile, distilled at 157°	0·8412	1·4287	41·1	56/17
Δ^{β}-*n*-Hexenonitrile, refluxed for 8½ hours	0·8418	1·4289	40·2	56/17

iso*Hexenonitriles* (compare Table II).

[Except where stated, the procedure was that used above.]

Δ^{α}-*iso*Hexenoamide, m. p. 84°, prepared in 70% yield from the acid (von Auwers *et al.*, *Annalen*, 1923, **432**, 46), was dehydrated with phosphoric oxide and dry sand (not alone) in small quantities to Δ^{α}-*iso*hexenonitrile (III; R′, R″ = Me, Me). Yield 40%, b. p. 61°/16 mm. (Found : C, 75·7; H, 9·4. Calc. : C, 75·8; H, 9·5%).

Δ^{β}-*iso*Hexenoic acid (Linstead, J., 1929, 2498; this vol., p. 125), prepared from the αβ-acid and purified by partial esterification and hydrolysis, was converted by the action of thionyl chloride into its own acid chloride, b. p. 63°/25 mm., and that of the γ-chloro-acid, which were separated by fractionation. Treatment of the low-boiling fraction in ether with ammonia, evaporation to dryness, and extraction with benzene yielded the βγ-amide (30%), which was very soluble in water and crystallised in white leaflets, melting at 81—82° alone and at 65—70° when mixed with the αβ-amide. This amide could not be made from the βγ-ester and ammonia under a variety of conditions. Dehydrated in the usual way, it yielded Δ^{β}-*iso*hexenonitrile (Braun, *Monatsh.*, 1896, **17**, 207), b. p. 56—57°/16 mm. (Found : C, 75·3; H, 9·5. Calc. : C, 75·8; H, 9·5%).

*iso*Butaldehyde readily yielded solid α-cyano-Δ^{α}-*iso*hexenoic acid (60%), small needles from benzene and petroleum, m. p. 89° (Braun, *loc. cit.*, gives m. p. 87—88°). When distilled with sand, this gave a variable (*ca.* 60%) yield of the βγ-nitrile, b. p. 66°/24 mm., this being the simplest method for making this substance.

*iso*Valeraldehyde cyanohydrin (compare Bruylants and Minetti, *loc. cit.*) was made from the bisulphite compound and potassium cyanide and dehydrated with phosphoric oxide and sand. The product is described on p. 445.

Reference Curve.—The βγ-nitrile was obtained from the cyano-acid, and the αβ-nitrile from the amide.

Composition, % *αβ*	0	10	20	40	60	80	90	100
J, %	78·0	74·0	68·2	54·1	37·0	21·0	10·1	1·3

Equilibration.—(1) *Alkali*.

TABLE V.

*iso*Hexenonitriles with 1 Equiv. of *N*-Sodium Ethoxide at 25°.

		Unsaturated nitrile obtained.			
Material.	Time (mins.).	*d*.	*n*.	*J*.	Composition (% $\alpha\beta$).
$\beta\gamma$	5	0·8474	1·4347	77·0	2
,,	15	0·8509	1·4334	76·6	3
,,	20	0·8511	1·4345	75·0	7
,,	30	0·8498	1·4336	74·5	9
,,	60	0·8494	1·4344	74·0	11
,,	120	0·8496	1·4337	68·6	19·5*
$\alpha\beta$	5	0·8202	1·4333	8·5	92·5
,,	15	0·8283	1·4340	11·5	88·5
,,	20	0·8362	1·4340	28·4	71·0
,,	30	0·8303	1·4313	34·0	65·0
,,	65	0·8469	1·4332	54·9	39·0
,,	180	0·8461	1·4331	63·5	27·0
57·5% $\alpha\beta$	120	0·8482	1·4327	63·5	27·0
27% $\alpha\beta$	120	0·8525	1·4336	66·2	22·5*
Mixed products*	120	—	—	67·4	21·5

(2) *Heat*. The αβ-nitrile was distilled at 152° under " aseptic " conditions and then had *d* 0·8204, *n* 1·4337, *J* 1·8%. After 8 hours' boiling in carbon dioxide it had *d* 0·8185, *n* 1·4330, *J* 2·0%. When it was heated for 8 hours in the same flask, which had been exposed to the dust of the laboratory, and with no special precautions, there was a good deal of charring, but no change in the properties of the nitrile, which after distillation had *d* 0·8185, *n* 1·4332, *J* 2·0%.

Butenonitriles (compare Table III).

Δ^{β}-Butenonitrile was prepared from allyl bromide by Bruylants's method (*loc. cit.*; compare " Organic Syntheses," VIII, 4), a yield of 80% being obtained by distillation of the reaction product from the stirred solution without reduction in pressure, and from allyl alcohol by Breckpot's method (*loc. cit.*), which was somewhat more convenient, as it did not necessitate the drying of the cuprous cyanide. The nitrile boiled at 116—121° and was obtained in 64% yield.

trans-Crotonic acid was prepared by Staudinger's method (Henle, " Org. Chem. Praktikum," 1927, 188), with the following modifications which considerably increased the yield. Paraldehyde (50 g.) was slowly run into a few drops of concentrated sulphuric acid, heated on the steam-bath, and the acetaldehyde evolved was collected in dry ether in the apparatus described by Henle. The ethereal solution was treated with dry malonic acid (26 g.) and pyridine (20 g.), and the mixture left for 2 days in ice and for 1 day at room temperature; the ether was then removed, and the residue warmed until no more carbon dioxide was evolved. It was dissolved in a little ice and water and acidified with concentrated hydrochloric acid. The pure crotonic acid which separated, m. p. 72° without crystallisation, was filtered off and a small additional amount was extracted from the filtrate with ether. Yield, 18·5 g. (86%) calculated on the malonic acid. Through the acid chloride, the anilide, m. p. 115°, and amide, m. p. 157° (50%), were prepared in the usual manner. The amide was best separated from ammonium chloride by fractional crystallisation from water. Dehydrated with phosphoric oxide and sand (compare von Auwers, *loc. cit.*), it gave *trans*-crotononitrile, b. p. 118—119°, in 40% yield.

Propaldehyde cyanohydrin was prepared by the method described for the butaldehyde compound. It distilled at 98°/20 mm., had d 0·9260, n 1·4081, $[R_L]_D$ 22·7 (calc., 23·0), and on dehydration in the usual manner gave a 50% yield of mixed butenonitriles, b. p. 117—120°.

α-Cyanocrotonic acid (von Auwers, *loc. cit.*, *Ber.*) could not be induced to crystallise by the methods successful with the higher homologues. Distilled with sand, it gave a poor yield of nitrile.

Equilibrations.—(1) *Alkali.* With sodium ethoxide or alcoholic caustic soda under a variety of conditions, Δ^β-butenonitrile yielded almost exclusively the β-ethoxy-nitrile, b. p. 170°, d 0·8945, n 1·4107, whence $[R_L]_D$ 31·35 (calc., 31·37) (compare Bruylants, *loc. cit.*, 1922). With aqueous alkali the following results were obtained :

(1) Δ^β-Butenonitrile (from the bromide) in 5 volumes of ether was allowed to stand with N-aqueous caustic soda (10 vols.) for 4 days. The product had d 0·8277, n 1·4147, J 32·6%. (2) As in (1) but without ether : The product had d 0·8262, n 1·4177, J 2·4%. (3) As (2) for 12 hours : The product had d 0·8235, n 1·4201, J 2·3%. (4) Δ^β-Butenonitrile (from the alcohol) was shaken with 10 vols. of $N/2$-aqueous caustic soda for 4 days. The product was almost identical in properties with that obtained in experiment (2) (J 2·5%). (5) In an attempt to remove the βγ-isomeride, if any, the product of (4) was treated with bromine and redistilled; it then had b. p. 118—120°, d 0·8262, n 1·4197, J 2·0% (determinations at 15°). (6) The product of (5) was shaken with caustic soda for 4 days, and then had d 0·8266, n 1·4210, J 2·5% (at 15°). (7) *trans*-Crotononitrile (from the amide) was shaken for 2 days with caustic soda solution; it then had n 1·4210, J 0·5% (at 15°).

In all these equilibrations the product was fractionated to remove traces of low- and high-boiling material. A wide fraction (108—124°) was collected in each case to include the *cis*-crotononitrile (b. p. 108°), which was always formed to some extent.

(2) *Heat.* (1) Δ^{β}-Butenonitrile (J 61·9%) was refluxed under aseptic conditions for 8 hours; it then had J 60·0%, n 1·4063. (2) The nitrile (J 63·8%) was heated under pressure in a sealed tube for 8 hours at 200°. The product had d 0·8347, n 1·4097, J 57·4% (at 15°).

Bromometric Estimations (Heim, *loc. cit.*).—

	% Addition of bromine.		
Nitrile.	Mean.	Maximum.	Minimum.
Δ^{β}-Buteno-	100·4	100·6	100
Δ^{α}-*n*-Hexeno-	3·6	3·6	3·6
Δ^{β}-*n*-Hexeno-	56	64	50
Δ^{α}-*iso*Hexeno-	3·6	3·6	3·5
Δ^{β}-*iso*Hexeno-	65	75	60

We are indebted to the Chemical Society for a grant to one of us (R. A. L.) which has partly defrayed the cost of this work.

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[*Received, December* 14*th*, 1931.]