1 : 2-*Dicarboxylic Acids. Part IV.* Saturated and Unsaturated Dialkyl- and Alkyl-aryl-dinitriles.*

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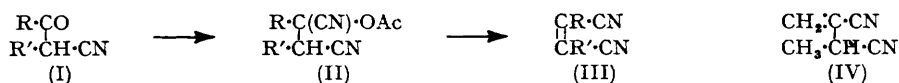
Dialkyl and alkyl-aryl derivatives of maleic and fumaric dinitriles, which are key intermediates for syntheses of metallic tetrazaporphins, have been prepared in excellent yields by pyrolysis of the cyanohydrin acetates of β-keto-nitriles.† The *cis-* and *trans*-stereoisomers have been separated and characterised by measurement of their dipole moments.

A general method for preparing αβ-dialkyl- and β-alkyl-α-phenyl-succinonitriles depending on the thermal instability of *tert.*-butyl α-alkyl-αβ-dicyanobutyrate and α-alkyl-αβ-dicyanophenylpropionate respectively is described. The latter compounds were obtained in good yields by an extension of Higson and Thorpe's method (*J.*, 1906, **89**, 1462).

THE importance of maleinitrile and of alkyl derivatives of this nitrile and fumaronitrile as intermediates for syntheses of metallic tetrazaporphins has recently been demonstrated (Linstead and Whalley, *J.*, 1952, 4839; France, Jones, and Imperial Chemical Industries Limited, B.P. 688,768, 689,387, 689,389), but investigation of the new pigments has hitherto been restricted by inaccessibility of many of the necessary intermediates. Although methods have been described for the preparation of maleinitrile by Linstead and Whalley (*loc. cit.*) and of 3 : 4 : 5 : 6-tetrahydrophthalonitrile by Ficken and Linstead (*J.*, 1952, 4846), yet the simple dialkyl and alkyl-aryl derivatives of fumaric and maleic dinitriles have hitherto proved extremely difficult to obtain, even in small quantities. Analogous succinonitrile derivatives, which are potentially useful intermediates (Elvidge and Linstead, *J.*, 1954, 442), were also inaccessible because the usual methods for making the parent compound failed when applied to its αβ-dialkyl derivatives.

The present investigation has shown, however, that dinitriles of the unsaturated series (III) are best obtained by pyrolysis of the cyanohydrin acetates (II) of β-keto-nitriles. The β-keto-nitriles (I) required for this synthesis were obtained by dimerisation of aliphatic

$$
\begin{array}{cccc}
\text{R·CO} & \text{R·C(CN)·OAc} & \text{CR·CN} & \text{CH}_2\text{:C·CN} \\
\text{R'·CH·CN} \longrightarrow & \text{R'·CH·CN} \longrightarrow & \text{CR'·CN} & \text{CH}_3\text{·CH·CN} \\
\text{(I)} & \text{(II)} & \text{(III)} & \text{(IV)}
\end{array}
$$

nitriles in the presence of sodium, with subsequent alkylation and hydrolysis (Mohr, *J. pr. Chem.*, 1914, **90**, 195), or by the new method described below. Aryl-substituted β-keto-nitriles (I; R' = aryl) were made by condensation of phenylacetonitriles with esters in the presence of sodium ethoxide (*Org. Synth.*, Coll. Vol. II, 1943, p. 487). The cyanohydrins of these keto-nitriles are unstable, even at ordinary temperatures. When treated with a mixture of thionyl chloride and pyridine, they gave very poor yields (*ca.* 10%) of unsaturated dinitriles (III). By pyrolysis of the more stable cyanohydrin acetates (II) at 470—490°, however, the dimethyl (III; R = R' = Me), ethylmethyl (III; R = Me, R' = Et), phenyl (III; R = H, R' = Ph), methylphenyl (III; R = Me, R' = Ph), and benzyl-methyl (III; R = Me, R' = CH₂Ph) derivatives of fumaric and maleic dinitriles were prepared in yields of approximately 90%. The product of pyrolysis usually consisted of a mixture of *cis-* and *trans*-forms of type (III); these were separated by fractional distillation, and characterised by measurement of their dipole moments, the *cis*-forms possessing moments of approx. 6 D, and the *trans*-forms much lower moments, usually well below 2 D. The possibility that some of these compounds might possess the alternative, itacononitrile, type of structure (*e.g.*, IV) appeared from spectrometric results to be unlikely. In particular, the bands in the region 940—950 cm.⁻¹, which would be expected if the structure CH₂:C(CN)·CHR·CN was present (Kitson, *Analyt. Chem.*, 1953, **25**, 1470), were not observed.
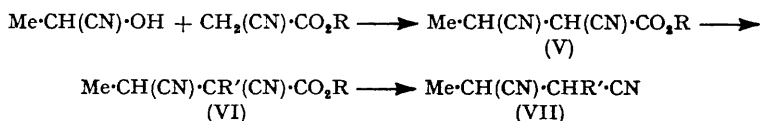
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* Part III, Ficken, France, and Linstead , *J.*, 1954, 3730.   † Patent protection pending.

A by-product obtained from the pyrolysis of 2-acetoxy-2 : 3-dicyanopentane (II ; R = Me, R′ = Et), appeared, however, to be $\alpha\gamma$-dimethylitacononitrile, as it gave the corresponding acid on hydrolysis.

Attempts to prepare $\alpha\beta$-dimethylsuccinonitrile by the methods generally used for making succinonitrile were unsuccessful. Treatment of 2 : 3-dichloro- or 2 : 3-dibromo-butane with metallic cyanides under a variety of conditions afforded none of the required dinitrile ; only tars, unsaturated compounds, and unchanged halogenobutanes were isolated. α-Methylcrotononitrile proved very unreactive towards hydrogen cyanide in the presence of basic catalysts, and gave only traces of $\alpha\beta$-dimethylsuccinonitrile, even under drastic conditions. This was not unexpected in view of the results obtained by Kurtz (*Annalen*, 1951, **572**, 23) when attempting to add hydrogen cyanide to crotononitrile.

The reaction between cyanohydrins and ethyl sodiocyanoacetate, first described by Higson and Thorpe (*loc. cit.*), appeared to provide the basis of a general method for the synthesis of alkyl- and aryl-succinonitriles. Attempts to prepare $\alpha\beta$-dimethylsuccino-nitrile (VII ; R′ = Me) by partial hydrolysis and decarboxylation of ethyl $\alpha\beta$-dicyano-α-methylbutyrate (VI ; R = Et, R′ = Me), however, gave only small yields of the dinitrile (Linstead and Whalley, *J.*, 1954, 3722). As the low yield of dinitrile obtained by Linstead and Whalley appeared to be due, at least in part, to side reactions during the partial

$$\text{Me·CH(CN)·OH} + \text{CH}_2\text{(CN)·CO}_2\text{R} \longrightarrow \text{Me·CH(CN)·CH(CN)·CO}_2\text{R} \longrightarrow$$
$$\text{(V)}$$

$$\text{Me·CH(CN)·CR′(CN)·CO}_2\text{R} \longrightarrow \text{Me·CH(CN)·CHR′·CN}$$
$$\text{(VI)} \qquad\qquad\qquad \text{(VII)}$$

hydrolysis, it seemed desirable to use in place of the ethyl ester one which could be de-alkylated by some method other than hydrolysis. Possibilities included the benzyl ester (Bowman, *J.*, 1950, 325), the tetrahydropyran-2-yl ester (Bowman and Fordham, *J.*, 1952, 3945) and the *tert.*-butyl ester (Breslow, Baumgarten, and Hauser, *J. Amer. Chem. Soc.*, 1944, **66**, 1286 ; Fonken and Johnson, *ibid.*, 1952, **74**, 831) ; in practice, the *tert.*-butyl ester gave excellent results and proved easy to manipulate on account of the convenience of *tert.*-butanol as a solvent. Troublesome ester interchanges which were encountered, for example, when using the benzyl ester in ethanol were thus avoided.
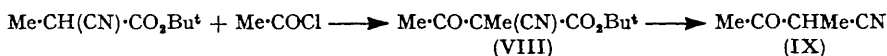
The key intermediate for this synthesis, *tert.*-butyl cyanoacetate, was prepared in good yield by treatment of cyanoacetyl chloride (Schroeter and Seidler, *J. pr. Chem.*, 1922, **105**, 171) with *tert.*-butanol and dimethylaniline. *tert.*-Butyl α-cyanopropionate was prepared similarly from α-cyanopropionic acid.

tert.-Butyl cyanoacetate with acetaldehyde cyanohydrin in the presence of sodium *tert.*-butoxide afforded *tert.*-butyl sodio-$\alpha\beta$-dicyanobutyrate (in almost quantitative yield), which with methyl iodide and with benzyl chloride gave high yields of *tert.*-butyl α-methyl-(VI ; R = Bu^t, R′ = Me) and α-benzyl-$\alpha\beta$-dicyanobutyrate (VI ; R = Bu^t, R′ = CH$_2$Ph), respectively. These esters decomposed when heated, especially under slightly acid conditions, to give $\alpha\beta$-dimethyl- (VII ; R′ = Me) and α-benzyl-β-methyl-succinonitrile (VII ; R′ = CH$_2$Ph), respectively, together with *iso*butylene and carbon dioxide. The best yields (81% and 89%) of dinitriles were obtained by dropping the *tert.*-butyl esters, mixed with some acetic acid, on silica at 200—210°. When *tert.*-butyl $\alpha\beta$-dicyano-α-methyl-butyrate was heated at 180° with 2% of toluene-p-sulphonic acid in a flask, lower yields of dimethylsuccinonitrile were obtained together with a considerable amount of α-cyano-$\alpha\beta$-dimethylsuccinimide formed by interaction of the cyano- and the carboxyl group of the intermediate $\alpha\beta$-dicyano-α-methylbutyric acid (cf. König, *J. pr. Chem.*, 1904, **69**, 1). The formation of this compound explains why poor yields of dimethylsuccinonitrile were obtained by distillation of the acid, *i.e.*, high yields of dinitrile result only when the free acid is liberated at a temperature sufficiently high to effect its rapid decarboxylation. In this connection it is noteworthy that *tert.*-butyl $\alpha\beta$-dicyanobutyrate (VI ; R = Bu^t, R′ = H), which evolves *iso*butylene at much lower temperatures than its α-methyl derivative, gave a very poor yield of methylsuccinonitrile on pyrolysis.

In preparing phenylsuccinonitrile and α-methyl-β-phenylsuccinonitrile, benzaldehyde

was condensed with *tert.*-butyl cyanoacetate in the presence of piperidine, and the product was treated with sodium cyanide.   The resulting *tert.*-butyl αβ-dicyano-β-phenylpropionate decomposed when heated to phenylsuccinonitrile.   Methylation of the sodio-derivative of the former yielded *tert.*-butyl αβ-dicyano-α-methyl-β-phenylpropionate which afforded α-methyl-β-phenylsuccinonitrile on pyrolysis.

In the synthesis just described, two common reactions of ethyl cyanoacetate (Knoevenagel condensation and Higson–Thorpe condensation with cyanohydrins) were applied to the *tert.*-butyl ester.   Several other possibilities were envisaged, but only the synthesis of β-keto-nitriles, of special importance in the present investigation, was examined. Treatment of *tert.*-butyl sodio-α-cyanopropionate with acetyl chloride afforded *tert.*-butyl α-cyano-α-methylacetoacetate (VIII).   Pyrolysis of the latter at 220—230° gave a good yield of α-acetylpropionitrile (IX), thus providing an alternative to the method of Mohr (*loc. cit.*) for making the β-keto-nitriles required as intermediates for alkylmaleic and alkyl-fumaric dinitriles :

$$\text{Me·CH(CN)·CO}_2\text{Bu}^t + \text{Me·COCl} \longrightarrow \underset{\text{(VIII)}}{\text{Me·CO·CMe(CN)·CO}_2\text{Bu}^t} \longrightarrow \underset{\text{(IX)}}{\text{Me·CO·CHMe·CN}}$$

EXPERIMENTAL

Preparation of Cyanohydrin Acetates of β-*Keto-nitriles.*—The ketonitrile (1 mol.) was added gradually with stirring to a mixture of anhydrous hydrogen cyanide (100 c.c.; 2·5 mols.) and potassium hydroxide (10 pellets; *ca.* 1 g.) at 0—5°; after 15—20 hours' stirring, the mixture was kept at 10—15° for 1 hr. and then cooled again to 5°.   Sulphuric acid (25 drops; *d* 1·84) was added, and excess of hydrogen cyanide distilled off under reduced pressure (bath-temp. 50—60°).   The residue, which consisted of the unstable cyanohydrin, was treated immediately with acetic anhydride (210 c.c.) and sulphuric acid (21 drops).   After the mixture had been heated for 2 hr. on the steam-bath, the cyanohydrin acetate (Table 1) was isolated by fractional distillation.   Yields averged 90—95% of theory.

TABLE 1.   *Physical properties and analyses of cyanohydrin acetates of* β-*keto-nitriles.*

	Cyanohydrin acetates			Found, %			Required, %		
Keto-nitrile	B. p./mm.	n_D^{20}	Formula	C	H	N	C	H	N
α-Methylacetoacetonitrile [1]	95°/0·7	1·4362	$C_8H_{10}O_2N_2$	58·0	6·0	16·7	57·85	6·0	16·85
α-Ethylacetoacetonitrile [1]	98—100°/ 0·9	1·4395	$C_9H_{12}O_2N_2$	60·5	6·3	15·5	60·0	6·65	15·55
α-Formyl-α-phenylaceto-nitrile [2]	138—140°/ 0·07 [3]	—	$C_{12}H_{10}O_2N_2$	—	—	13·2	—	—	13·1
α-Phenylacetoacetonitrile [4]	120°/0·03	(m. p. 74—84°) [5]	$C_{13}H_{12}O_2N_2$	68·1	5·5	12·4	68·4	5·25	12·3
α-Benzylacetoacetonitrile [1]	158°/0·04	(m. p. 103—104°)	$C_{14}H_{14}O_2N_2$	69·4	5·8	11·5	69·4	5·8	11·55

[1] Mohr, *J. pr. Chem.*, 1914, **90**, 189.   [2] Ghosh, *J.*, 1916, **109**, 113.   [3] This compound gave some unsaturated dinitrile during prolonged distillation.   [4] *Org. Synth.*, Coll. Vol. II, 1943, p. 487. [5] Mixture of stereoisomers.

TABLE 2.   *Pyrolysis of cyanohydrin acetates of* β-*keto-nitriles.*

Compound pyrolysed	Wt. (g.)	Acetic acid (c.c.)	Yield of mixed dinitriles		Approx. ratio, *trans : cis*
			Wt. (g.)	%	
2-Acetoxy-2 : 3-dicyanobutane	291	333	169	91	3 : 1
2-Acetoxy-2 : 3-dicyanopropane	121·3	130	64·7	80	2 : 1
2-Acetoxy-1 : 2-dicyano-1-phenylethane	36	35	23·2	90	1 : 1
2-Acetoxy-1 : 2-dicyano-1-phenylpropane	100	85	63·8	87	7 : 1
3-Acetoxy-2 : 3-dicyano-1-phenylbutane	72·6	103	45·8	84	20 : 1

Preparation of Substituted Maleic and Fumaric Dinitriles by Pyrolysis of Cyanohydrin Acetates.—A solution (Table 2) of the cyanohydrin acetate in acetic acid was introduced dropwise (2—2·5 c.c./min.) into an inclined pyrolysis tube (90 × 2·5 cm.) packed with pieces of silica and kept at 470—490° (internal thermocouple) by means of an electric tube furnace (1 kw).   The volatile products were condensed in a receiver cooled by ethanol–solid carbon dioxide.   The tube

was afterwards purged of residual products by passage of acetic acid (100 c.c.) and then nitrogen The dinitriles were isolated by fractional distillation. Separation of the *cis-* and the *trans-* forms (and, in some cases, of other isomers) was effected by fractional distillation under reduced pressure of the mixed dinitriles through a column packed with stainless-steel gauze rings. The individual fractions were further purified by crystallisation, usually from methanol or ethanol.

Pyrolysis of 2-acetoxy-2 : 3-dicyanopentane gave in addition to ethylmethyl-fumaro- and -malei-dinitriles (combined yield, 61%) an isomeric compound (19%), b. p. 61—63°/11 mm., which was not obtained quite pure (Found : C, 70·9; H, 6·6; N, 22·8. Calc. for $C_7H_8N_2$: C, 70·0; H, 6·65; N, 23·35%). Alkaline hydrolysis of this product gave an acid, m. p. 195° (decomp.). Fichter and Rudin (*Ber.*, 1904, **37**, 1617) give m. p. 202° (decomp.) for $\alpha\gamma$-dimethyl-itaconic acid.

Pyrolysis of 3-acetoxy-2 : 3-dicyanophenylbutane gave a small amount (<5% of total product) of a *compound* of unknown constitution. After crystallisation from benzene, this had m. p. 80° (Found : C, 40·5, 40·7; H, 8·4, 8·7%).

Hydrolysis of the *nitriles* of phenylmaleic and phenylfumaric acid with hot, concentrated hydrochloric acid gave respectively phenylmaleic anhydride and phenylfumaric acid. The former, after crystallisation from carbon disulphide, had m. p. 119°. Alexander (*Annalen*, 1890, **258**, 77) gives m. p. 119—119·5° (Found : C, 69·0; H, 3·0. Calc. for $C_{10}H_6O_3$: C, 69·0; H, 3·45%). Phenylfumaric acid, after crystallisation from benzene, melted at 125—127°. Almström (*ibid.*, 1916, **411**, 375) gives m. p. 128—129°.

TABLE 3. *Physical properties and analyses of $\alpha\beta$-unsaturated dinitriles.*

Dinitrile	M. p.	B. p./mm.	Dipole moment, D [1]	Formula	Found, % C	H	N	Required, % C	H	N
Dimethylmaleic	48°	136—138°/21	6·0	$C_6H_6N_2$	67·9	5·4	26·3	67·9	5·65	26·4
Dimethylfumaric	81°	101—102°/55	0·7	$C_6H_6N_2$	67·9	5·9	26·1	67·9	5·65	26·4
Ethylmethylmaleic ...	(n_D^{20} 1·4671)	131—132°/12	5·5	$C_7H_8N_2$	69·5	6·3	22·9	70·0	6·65	23·35
Ethylmethylfumaric	(n_D^{20} 1·4613)	72—74°/12	1·4	$C_7H_8N_2$	69·5	6·8	23·2	70·0	6·65	23·35
Phenylmaleic	89—90°	115—118°/0·05	6·1	$C_{10}H_6N_2$	78·1	4·3	18·0	77·9	3·9	18·2
Phenylfumaric	42—43°	82—84°/0·2	1·9	$C_{10}H_6N_2$	77·7	3·8	17·9	77·9	3·9	18·2
Methylphenylmaleic	57°	110°/0·04	6·2	$C_{11}H_8N_2$	78·8	4·8	16·6	78·55	4·75	16·65
Methylphenylfumaric	70°	80—85°/0·05	1·2	$C_{11}H_8N_2$	78·3	5·0	17·1	78·55	4·75	16·65
Benzylmethylmaleic [2]	[Liquid]	137°/0·05	3·7	$C_{12}H_{10}N_2$	79·6	5·8	12·7	79·1	5·5	15·4
Benzylmethylfumaric	40°	90—92°/0·15	0·8	$C_{12}H_{10}N_2$	79·2	5·7	15·3	79·1	5·5	15·4

[1] Approximate values, in benzene solution at 30°. [2] Owing to the small quantity of material, benzylmethylmaleidinitrile was not obtained pure. Its infra-red spectrum showed a strong band at 1720 cm.[-1], indicating the presence of a carbonyl impurity (probably α-benzylacetoacetonitrile); this would explain the anomalous nitrogen analysis and dipole moment.

Acetaldehyde Cyanohydrin.—Acetaldehyde (110 g.) was added to a cooled mixture of anhydrous hydrogen cyanide (97 c.c.) and piperidine (2 g.) at 10—20°. After the mixture had been kept at 25° for 4 hr., it was treated with sulphuric acid (1 c.c.; *d* 1·84). Fractional distillation afforded acetaldehyde cyanohydrin (160 g.; 90%), b. p. 72—76°/7 mm., $n_D^{18·2}$ 1·4041. Brühl (*Z. physikal. Chem.*, 1895, **16**, 214) gives $n_D^{18·4}$ 1·4058.

tert.-*Butyl Cyanoacetate.*—Phosphorus pentachloride (417 g.) was added portionwise to a stirred solution of cyanoacetic acid (170 g.) in anhydrous ether (1 l.). The mixture was cooled occasionally to prevent excessive refluxing, and stirring was continued until the phosphorus pentachloride had dissolved completely. Most of the ether was then distilled from a bath at 50—60°, after which phosphoryl chloride was removed at 10—15 mm. (bath-temp. 50—65°), the receiver being cooled in ice–salt. The residue (205 g.) was added dropwise and without delay to a stirred solution of dry *tert.*-butanol (148 g.) and dimethylaniline (242 g.) in anhydrous ether (300 c.c.); the mixture was cooled occasionally to prevent excessive refluxing. After being boiled under reflux for 2 hr. and stored for 15 hr., the mixture was stirred with water (1 l.), and the ethereal layer separated. The latter was shaken with successive portions of 2N-sulphuric acid (500 c.c.) until free from dimethylaniline after which it was washed with 2N-sodium carbonate and dried (MgSO₄). After removal of the ether by distillation the residue

was treated with potassium carbonate (*ca.* 1 g.; anhyd.) and purified by distillation under reduced pressure (yield, 186 g., 66%; b. p. 90°/10 mm., 54—56°/0·3 mm., n_D^{20} 1·4198) (Found : C, 59·9; H, 7·9; N, 9·6. Calc. for $C_7H_{11}O_2N$: C, 59·6; H, 7·8; N, 9·95%).

tert.-Butyl α-cyanopropionate was prepared from α-cyanopropionic acid in a similar manner (yield 63%; b. p. 55°/0·3 mm., n_D^{20} 1·4138) (Found : C, 62·2; H, 8·6; N, 9·2. $C_8H_{13}O_2N$ requires C, 61·95; H, 8·4; N, 9·05%).

tert.-Butyl αβ-Dicyanobutyrate (V; R = Bu^t).—Sodium (17·3 g.), in small pieces, was boiled under reflux with *tert.*-butanol (750 c.c.) for 18 hr. The resulting suspension of sodium *tert.*-butoxide was cooled to 25° and *tert.*-butyl cyanoacetate (105·8 g.) was added with stirring, followed immediately by acetaldehyde cyanohydrin (53·3 g.). During addition of the latter, the temperature was kept at 35—40°. After the mixture had been stirred for 6 hr. and kept for a further 16 hr., *tert.*-butanol (*ca.* 400 c.c.) was distilled off under reduced pressure (internal temp., *ca.* 30°), and the residue diluted with water (1·5 l.). The solution was acidified (Congored) with hydrochloric acid, and the oily product extracted with ether (750 c.c.). The ethereal solution was washed with aqueous sodium hydrogen carbonate and dried (MgSO₄). After removal of the ether by distillation, the residue (138 g., 93%) set to a crystalline solid, which afforded the pure *ester*, m. p. 57—58° on crystallisation from ether at −70° (Found : C, 62·0; H, 7·4; N, 14·2. $C_{10}H_{14}O_2N_2$ requires C, 61·85; H, 7·2; N, 14·45%). Extensive decomposition occurred on attempted distillation of the substance under reduced pressure.

tert.-Butyl αβ-Dicyano-α-methylbutyrate (VI; R = Bu^t, R' = Me).—*tert.*-Butyl cyanoacetate (105·8 g.) was condensed with acetaldehyde cyanohydrin (53·3 g.) as described above. After 16 hr., the solution was treated with methyl iodide (60 c.c.). The temperature rose spontaneously from 23° to 50°, and the reaction was completed by 1 hour's heating on the steambath. *tert.*-Butanol (*ca.* 500 c.c.) was then distilled off under reduced pressure, and the residue diluted with water (1 l.). The oily product was extracted with ether (450 c.c.), and the extract washed with N-sodium carbonate and dried (MgSO₄). After distillation of the ether, the residue was treated with a trace of potassium carbonate and distilled under reduced pressure (yield, 129 g., 83%; b. p. 92°/0·3 mm., n_D^{20} 1·4328) (Found : C, 63·1; H, 7·6; N, 13·5. $C_{11}H_{16}O_2N_2$ requires C, 63·45; H, 7·7; N, 13·45%).

tert.-Butyl α-Benzyl-αβ-dicyanobutyrate (VI; R = Bu^t, R' = CH₂Ph).—*tert.*-Butyl cyanoacetate (70·5 g.) was condensed with acetaldehyde cyanohydrin (36 g.) in a solution of sodium (11·5 g.) in *tert.*-butanol (500 c.c.) as above. Benzyl chloride (72 c.c.) was then added, and the mixture boiled under reflux for 24 hr. After removal of most of the *tert.*-butanol under reduced pressure, the residue was diluted with water (625 c.c.), and the product extracted with ether (500 c.c.). The ethereal solution was dried (MgSO₄) and, after removal of the ether, the residue was distilled at 0·1 mm. (bath-temp. 140°) to remove excess of benzyl chloride. The residue (121 g., 85%) set to a pasty solid. Crystallisation from *tert.*-butanol afforded the pure *ester*, m. p. 96—97° (Found : C, 71·5; H, 6·7; N, 10·2. $C_{17}H_{20}O_2N_2$ requires C, 71·85; H, 7·05; N, 9·85%).

tert.-Butyl αβ-Dicyano-β-phenylpropionate.—A mixture of benzaldehyde (10·6 g.), *tert.*-butyl cyanoacetate (14·1 g.), and aqueous alcohol (30 c.c.; 60%) was treated with piperidine (35 drops). When the solution was shaken, the temperature rose spontaneously to 45°. The mixture was heated to 60°, cooled to 25°, and treated with water (10 c.c.). Sodium cyanide (4·9 g.) was added portionwise and with shaking during 10 min., the mixture being kept at 30—40°. After a further 0·5 hr., during which the mixture was occasionally shaken, a clear solution resulted. This was acidified (Congo-red) with hydrochloic acid, and the liquor decanted from the oily product, which soon solidified. The product was extracted with benzene (50 c.c.), the solution dried (MgSO₄), and the benzene distilled off under reduced pressure, giving a residue (22·9 g., 89%) which set to a pasty solid. Recrystallisation from benzene–ligroin or from *cyclo*hexane gave the pure *ester*, m. p. 80—81° (Found : C, 70·3; H, 6·2; N, 11·0. $C_{15}H_{16}O_2N_2$ requires C, 70·35; H, 6·25; N, 10·95%).

tert.-Butyl αβ-Dicyano-α-methyl-β-phenylpropionate.—*tert.*-Butyl αβ-dicyano-β-phenylpropionate (89 g.) in *tert.*-butanol (205 c.c.) was added to a solution of sodium (8·1 g.) in *tert.*-butanol (350 c.c.), at 25—30°. Methyl iodide (30 c.c.) was added; the temperature rose spontaneously from 25° to 40°. The mixture was boiled under reflux for 2 hr., after which most of the *tert.*-butanol was removed under reduced pressure. The residue was diluted with water (450 c.c.), and the product extracted with ether (450 c.c.). The extract was dried (MgSO₄), and the ether removed, giving a viscous oil (92·5 g.) which was not obtained pure. On attempted distillation under reduced pressure, it partly decomposed, giving α-methyl-β-phenylsuccinonitrile.

Beech and Piggott :

tert.-*Butyl* α-*Cyano*-α-*methylacetoacetate* (VIII).—Sodium *tert.*-butoxide, prepared by boiling sodium (8 g.) with *tert.*-butanol (350 c.c.) for 17 hr. and subsequently removing *tert.*-butanol by distillation under reduced pressure, was suspended in dry benzene (360 c.c.), and *tert.*-butyl α-cyanopropionate (53·5 g.) added. *tert.*-Butanol was removed as its azeotrope with benzene through a metal-packed column. The residual solution was cooled to 20° and acetyl chloride (50 c.c.) was added with stirring; the temperature rose spontaneously to 55°. The mixture was boiled under reflux for 1 hr., stored for 18 hr., and then shaken with water (500 c.c.) at 0°. The benzene solution was washed with N-sodium carbonate and dried (MgSO₄), and the benzene removed by distillation. Distillation of the residue under reduced pressure afforded tert.-*butyl* α-*cyano*-α-*methylacetoacetate* (41·5 g., 61%), b. p. 108—114°/20 mm., 55—60°/0·1 mm. (Found : C, 60·5; H, 7·7; N, 7·4. $C_{10}H_{15}O_3N$ requires C, 60·9; H, 7·6; N, 7·1%).

Preparation of Nitriles by Dealkylation and Decarboxylation of tert.-*Butyl Esters.*—(*a*) A mixture of the *tert.*-butyl ester and acetic acid (in some cases containing up to 5% of hydrogen chloride) was introduced dropwise into a vertical pyrolysis tube packed with pieces of silica and kept at 200—210° (internal thermocouple) by means of an electric-tube furnace. For small-scale work (*e.g.*, 0·05—0·1 mole), a pyrolysis tube measuring 12 × 2 cm. was suitable; on a larger scale, a tube of 20 × 3·5 cm. was preferred. Complete passage of the solution took 0·5—1·25 hr. according to the scale. The volatile products were collected in a receiver cooled in ethanol–solid carbon dioxide. The pyrolysis tube was purged with a small quantity of acetic acid and finally with nitrogen. The products were isolated and purified by fractional distillation under reduced pressure.

(*b*) The *tert.*-butyl ester was mixed with anhydrous toluene-*p*-sulphonic acid (4 g./mole) in a distillation flask attached to a condenser and receiver. The apparatus was evacuated by a water-pump, and the flask was heated by immersion in an oil-bath at 175—180°. The start of the reaction was marked by a considerable rise of pressure. After a few minutes, when evolution of gas had ceased, the pressure fell to 10—20 mm. and the product was distilled. The yields obtained by this method were usually inferior to those produced by method (*a*).

TABLE 4. *Preparation of nitriles by dealkylation and decarboxylation of* tert.-*butyl cyano-esters.*

tert.-Butyl ester pyrolysed	Wt. (g.)	Method	AcOH (c.c.)	HCl	Toluene-*p*-sulphonic acid (g.)	Product	Yield (%)
αβ-Dicyanobutyrate	23	*a*	12	+	—	Methylsuccinonitrile	12
	19·4	*b*	—	—	0·4	,, ,,	14
αβ-Dicyano-α-methylbutyrate	20·8	*a*	5	—	—	αβ-Dimethylsuccinonitrile	81
,, ,,	20·8	*a*	5	+	—	,, ,,	74
,, ,,	20·8	*b*	—	—	0·4	,, ,,	62
α-Benzyl-αβ-dicyanobutyrate	52·8	*a*	55	—	—	α-Benzyl-β-methylsuccino-nitrile	89
,, ,,	14·2	*a*	14·5	—	—	,, ,,	88
,, ,,	14·2	*a*	14·5	+	—	,, ,,	89
,, ,,	29·3	*b*	—	—	0·4	,, ,,	75
αβ-Dicyano-β-phenylpro-pionate	12·8	*b*	—	—	0·2	Phenylsuccinonitrile	45
αβ-Dicyano-α-methyl-β-phenylpropionate	43	*b*	—	—	0·65	α-Methyl-β-phenylsuccino-nitrile	51
α-Acetyl-α-cyanopropionate	19·2	*a*	5	—	—	(Decomp. incomplete at 200—210°)	—
,, ,,	19·2	*a* Temp. 220—230°	5	+	—	α-Acetylpropionitrile	88
,, ,,	30·3	*b*	—	—	0·6	,, ,,	64

+ Indicates that up to 5% of hydrogen chloride was added.

αβ-Dimethylsuccinonitrile, b. p. 122—135°/15 mm., obtained by any of the above methods, was a mixture of (±)- and *meso*-forms as pasty crystals. After being dried on a porous tile, the substance had m. p. 44—45° (Found : C, 66·5; H, 7·5; N, 26·0. Calc. for $C_6H_8N_2$: C, 66·65; H, 7·5; N, 25·95%). Crystallisation from ethanol–light petroleum afforded the (±)-form, m. p. 58°, described by Linstead and Whalley (*loc. cit.*). By method (*b*), a high-boiling product (b. p. 140°/0·3 mm.) was also obtained. This substance probably consisted of a mixture of stereoisomeric α-*cyano*-αβ-*dimethylsuccinimides* (Found : C, 55·0; H, 5·8;

N. 18·0. $C_7H_8O_2N_2$ requires C, 55·25; H, 5·3; N, 18·4%). Hydrolysis with hot, concentrated hydrochloric acid gave principally *meso*-αβ-dimethylsuccinic acid, m. p. 196° (Found : C, 49·1; H, 6·8%; equiv., 74. Calc. for $C_6H_{10}O_4$: C, 49·3; H, 6·85%; equiv., 73).

Methylsuccinonitrile was obtained in only small yield by pyrolysis of *tert.*-butyl αβ-dicyano-butyrate; the greater part of the product was a viscous oil, b. p. 130—140°/0·2 mm., believed to be a mixture of stereoisomeric α-cyano-β-methylsuccinimides. Both products gave methyl-succinic acid, m. p. 114°, on hydrolysis.

α-Benzyl-β-methylsuccinonitrile was obtained as a viscous oil, b. p. 122—132°/0·1 mm., consisting of a mixture of stereoisomers (Found : C, 78·4; H, 6·4; N, 14·8. $C_{12}H_{12}N_2$ requires C, 78·25, H, 6·5; N, 15·2%). On storage, the oil became semi-solid; the crystalline portion, after recrystallisation from benzene–ligroin, had m. p. 70°.

Phenylsuccinonitrile, after crystallisation from benzene–ligroin, had m. p. 67°, not de-pressed on admixture with an authentic sample. Mowry (*J. Amer. Chem. Soc.*, 1946, **68**, 2108) gives m. p. 68°. *α-Methyl-β-phenylsuccinonitrile* formed a viscous oil, b. p. 118—122°/0·3 mm., which partly crystallised (Found : C, 78·0; H, 6·4. $C_{11}H_{10}N_2$ requires C, 77·65; H, 5·9%). The crystalline portion had m. p. 80—81° after crystallisation from benzene–ligroin (Found : N, 16·95. $C_{11}H_{10}N_2$ requires N, 16·45%).

α-Acetylpropionitrile was isolated from the product of pyrolysis by dilution with water, neutralisation of the solution with sodium hydrogen carbonate, and extraction with ether. After being dried ($MgSO_4$), the extract was fractionally distilled, giving the keto-nitrile, b. p. 74—76°/15 mm., characterised as the semicarbazone, m. p. 162° (Found : C, 47·25; H, 6·8; N, 36·0. Calc. for $C_6H_{10}ON_4$: C, 46·75; H, 6·5; N, 36·35%); Mohr (*loc. cit.*) gives m. p. 153°.

Attempted Preparation of αβ-*Dimethylsuccinonitrile by Other Methods.—From halogeno-compounds and metallic cyanides.* Several attempts were made to prepare αβ-dimethylsuccino-nitrile by heating 2 : 3-dichloro- or -dibromo-butane with metallic (sodium, cuprous, and mercuric) cyanides with and without solvents (2-methoxyethanol, aqueous ethanol, anhydrous pyridine, γ-picoline, and ethylene glycol). Products obtained included unchanged starting material, 3-bromobut-1-ene, other unsaturated compounds, and tar. No αβ-dimethylsuccinonitrile was obtained.

From αβ-*unsaturated nitriles and hydrogen cyanide.* (a) A mixture of angelonitrile and tiglonitrile gave a small yield of *meso*-αβ-dimethylsuccinic acid, m. p. 196°, when boiled with aqueous-alcoholic potassium cyanide for 24 hr.

(b) A mixture of angelonitrile and tiglonitrile (50 g.) was heated with anhydrous hydrogen cyanide (27 c.c.) and potassium cyanide (2 g.) in a steel bomb at 100—110° (bath temp.) for 72 hr. Fractional distillation of the product gave αβ-dimethylsuccinonitrile (2·1 g.; 3%), b. p. 125—135°/15 mm., which yielded on hydrolysis *meso*-αβ-dimethylsuccinic acid, m. p. and mixed m. p. 196°. When a mixture of angelonitrile and tiglonitrile (10 g.) was treated with hydrogen bromide and subsequently with water, a small yield of β-*bromo-α-methylbutyramide* was obtained. After crystallisation from benzene, this had m. p. 111—112° (Found : N, 7·9; Br, 44·0. $C_5H_{10}ONBr$ requires N, 7·8; Br, 44·45%).

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