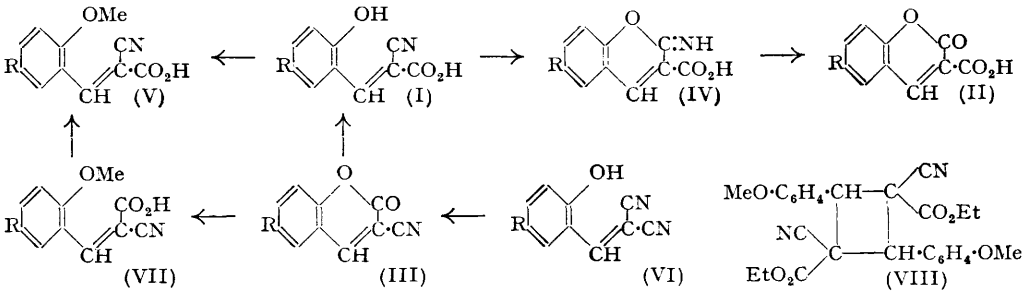
22. *Stereochemistry of Arylidenecyanoacetic Acids and Arylarylideneacetonitriles.*

By Wilson Baker and C. S. Howes.

Aromatic aldehydes react with the sodium salt or the ethyl ester of cyanoacetic acid to give *trans*(with respect to the aryl and carboxyl groups)-arylidenecyanoacetic acids or esters. In the *o*-hydroxyaryl series, the configuration is established by conversion in boiling water into coumarin-3-carboxylic acids (II). *cis*-2-Methoxyarylidenecyanoacetic acids are prepared by methylation in alkaline solution of 3-cyanocoumarins (III) (new preparation). Two stereoisomeric pairs of 2-methoxyarylidenecyanoacetic acids have thus been prepared; the *cis*-acids are converted into the *trans*-acids on melting. In the light of this work the arylarylideneacetonitriles are shown to be the *trans*-isomers.

2-Hydroxybenzylidenecyanoacetic acid (I; R = H), prepared by condensation of salicylaldehyde with aqueous, alkaline sodium cyanoacetate, passes in 1—2 minutes in boiling water into the ammonium salt of coumarin-3-carboxylic acid (II; R = H) (Baker and Lapworth, *J.*, 1925, **127**, 561; see also Clarke and Francis, *Ber.*, 1911, **44**, 275). This cannot be due to hydrolysis of the cyano- to a carboxyl group and lactonisation (Bechert, *J. pr. Chem.*, 1894, **50**, 11), since the arylidenecyanoacetic acids, except those with an *o*-hydroxyl group, are unaffected by prolonged boiling with water or even hydrochloric acid, nor can it be due to lactonisation to 3-cyanocoumarin (III; R = H) and hydrolysis to the acid (II; R = H), since (III; R = H) and the related amide are not hydrolysed by boiling water. The acid (I; R = H) must, therefore, pass into (II; R = H) *via* an imino-lactone (IV; R = H) which is at once hydrolysed to the coumarin, and must consequently possess adjacent hydroxyl and cyano-groups. Hence (I; R = H) is a derivative of *trans*-cinnamic acid, and may be termed *trans*-2-hydroxybenzylidenecyanoacetic acid (*trans*-α-cyano-2-hydroxycinnamic acid).

The conversion of (I; R = H) into (II; R = H) is initiated by attack of the anionoid phenolic oxygen atom on the cationoid carbon of the cyano-group held in a stereochemically favourable position by the olefinic bond. The related saturated acid, 2-hydroxybenzylcyanoacetic acid, is almost unchanged by boiling with water for 30 hours. The time of



conversion of (I; R = H) into (II; R = H) in boiling water is increased by addition of hydrochloric acid (*e.g.*, 3 minutes in N-HCl, 7 minutes in 10N-HCl); the choice between alternative explanations for this behaviour cannot be made.

Evidence that an imino-lactone (IV; R = H) is an intermediate in the conversion of (I; R = H) into (II; R = H) is provided by a new preparation of 3-cyanocoumarin (III; R = H) from *o*-hydroxybenzylidenemalononitrile (VI; R = H), itself prepared from salicylaldehyde and malononitrile. The dinitrile (VI; R = H), which is insoluble in water, dissolves rapidly in cold dilute hydrochloric acid as the salt of the imino-lactone, and, after a few minutes, the neutral 3-cyanocoumarin (III; R = H) separates out. The dicyano-compound (VI; R = H) is a powerful sternutator and irritant, and thus resembles some other αβ-unsaturated malononitriles (Corson and Stoughton, *J. Amer. Chem. Soc.*, 1928, **50**, 2825).

3-Cyanocoumarin (III; R = H) dissolves in N-sodium hydroxide at 30° as the sodium salt of *cis*-2-hydroxybenzylidenecyanoacetic acid; acidification reprecipitates (III; R = H). If, however, the alkaline solution is boiled for five minutes, acidification precipitates the *trans*-acid (I; R = H). Mild treatment with methyl sulphate of the solution of the sodium salt of the *cis*-acid gives *cis*-2-methoxybenzylidenecyanoacetic acid (VII; R = H), which differs from the *trans*-2-methoxybenzylidenecyanoacetic acid (V; R = H) prepared either by methylation of the *trans*-acid (I; R = H) or by condensation of 2-methoxybenzaldehyde with aqueous sodium cyanoacetate. It was hoped that there might be sufficient difference in the ultra-violet absorption spectra of the *cis*- and the *trans*-isomer to enable them to be used as reference compounds in deciding the stereochemistry of other arylidenecyanoacetic acids or related molecules; the curves are, however, so alike (see Table) that this object cannot be achieved.

These stereoisomeric acids (VII; R = H) and (V; R = H) differ markedly in their stability, the *cis*-acid (m. p. 159—160°) being converted into the *trans*-acid (m. p. 211—212°) at its melting point. Again, although the *trans*-acid undergoes normal esterification to the ethyl ester (Dave and Nargund, *J. Univ. Bombay*, 1938, **7**, 196) (also obtained directly from *o*-methoxybenzaldehyde and ethyl cyanoacetate), the *cis*-acid, even under mild conditions in presence of hydrogen chloride or toluene-*p*-sulphonic acid, gives the ethyl ester of the *trans*-acid. The two acids also differ in their behaviour when the solids are irradiated with ultra-violet light (see Experimental).

Crystalline ethyl *trans*-2-methoxybenzylidenecyanoacetate passes extremely slowly in daylight, more rapidly in ultra-violet light, into a higher-melting, saturated dimeride. This is probably one stereoisomer of diethyl 1 : 3-dicyano-2 : 4-di-*o*-methoxyphenyl*cyclo*butane-1 : 3-dicarboxylate (VIII).

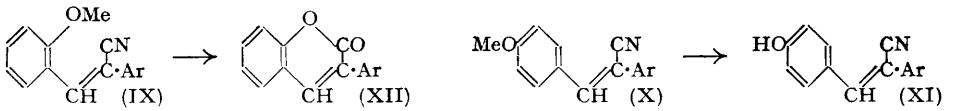
A similar series of reactions has been carried out starting with 5-bromo-2-hydroxybenzaldehyde. With sodium cyanoacetate it gives *trans*-5-bromo-2-hydroxybenzylidenecyanoacetic acid (I; R = Br), which with boiling water gives the ammonium salt of 6-bromocoumarin-3-carboxylic acid (II; R = Br). Methylation of (I; R = Br) gives

trans-5-bromo-2-methoxybenzylidenecyanoacetic acid (V; R = Br), also obtained from 5-bromo-2-methoxybenzaldehyde and sodium cyanoacetate. 5-Bromo-2-methoxybenzaldehyde and malononitrile give 5-bromo-2-hydroxybenzylidenemalononitrile (VI; R = Br), converted by dissolution in dilute hydrochloric acid into 6-bromo-3-cyanocoumarin (III; R = Br). Methylation of this cyanocoumarin in alkaline solution gives *cis*-5-bromo-2-methoxybenzylidenecyanoacetic acid (VII; R = Br). The *cis*-acid crystallises unchanged from benzene but gives the *trans*-acid when crystallised from ethanol or when melted. There were again differences in the behaviour of the solid stereoisomerides towards ultra-violet light; the ultra-violet extinction curves in ethanol were very similar, but as in the case of the stereoisomeric acids (V and VII; R = H) the absorption curve of the *trans*-acid is displaced towards the longer wave-lengths in comparison with the *cis*-acid.

Ethyl *trans*-5-bromo-2-methoxybenzylidenecyanoacetate, obtained either by esterification of the acid (I; R = Br) or, more conveniently, from 5-bromo-2-methoxybenzaldehyde and ethyl cyanoacetate, does not dimerise in ultra-violet light.

In the β-resorcylaldehyde series, 2-hydroxy-4-methoxybenzaldehyde and sodium cyanoacetate give *trans*-2-hydroxy-4-methoxybenzylidenecyanoacetic acid, converted by boiling water into 7-methoxycoumarin-3-carboxylic acid (Baker and Collis, *J.*, 1949, S 12), and by methyl sulphate and alkali into *trans*-2 : 4-dimethoxybenzylidenecyanoacetic acid, also obtained from 2 : 4-dimethoxybenzaldehyde and sodium cyanoacetate. Esterification of *trans*-2 : 4-dimethoxybenzylidenecyanoacetic acid gave the ethyl ester, identical with that obtained from 2 : 4-dimethoxybenzaldehyde and ethyl cyanoacetate (Kauffmann, *Ber.*, 1919, **52**, 1433); this ester is unaltered by ultra-violet light.

The present work explains the "abnormal behaviour" of 2-methoxybenzylidenearylacetonitriles (IX) when demethylated by boiling with pyridine hydrochloride (Buu-Hoï, Hoán, and Lavit, *J.*, 1950, 2130; Buu-Hoï and Hoán, *J.*, 1951, 251; Buu-Hoï, Hoán, and Khenissi, *J.*, 1951, 2307). These authors observed that although demethylation of, *e.g.*, 4-methoxybenzylidenearylacetonitriles (X) gave simply the phenols (XI), yet demethylation of the corresponding 2-methoxybenzylidene derivatives "resulted also in hydrolysis of the nitrile group and lactonisation, with formation of 3-substituted coumarins" (XII).



There is no reason to expect a different order of stability of the CN groups in the *o*- and *p*-methoxy-compounds (IX) and (X), and it is clear that the demethylation of (IX) is followed by reaction of the phenolic group with the adjacent cyano-group to give an imino-lactone which is then hydrolysed to the 3-arylcoumarin (XII). Hence these 2-methoxybenzylidenearylacetonitriles must possess that geometrical configuration in which the aryl radicals are in the *trans*-position as shown in (IX). It is likely that all the arylidenearylacetonitriles are the *trans*-isomers.

Experimental

M. p.s are uncorrected. Analyses are by Drs. Weiler and Strauss, Oxford, and Mr. W. M. Eno, Bristol.

trans-2-*Methoxybenzylidenecyanoacetic* (trans-α-*Cyano*-2-*methoxycinnamic*) *Acid* (V; R = H).—2-Hydroxybenzylidenecyanoacetic acid (7·5 g.; Haarmann and Reimer, D.R.-P., 189,252), suspended in 50% ethanol (40 c.c.), was shaken during portionwise addition of 40% aqueous potassium hydroxide (75 c.c.) and methyl sulphate (50 c.c.) at 40—50° (it is essential to keep the mixture very strongly alkaline, for otherwise the product is coumarin-3-carboxylic acid). The now pale yellow solution was diluted, acidified, and boiled to convert unchanged 2-hydroxybenzylidenecyanoacetic acid into coumarin-3-carboxylic acid, and the solid crystallised twice from ethanol, giving *trans*-2-methoxybenzylidenecyanoacetic acid (5·0 g.) as yellow prisms, m. p. 211—212°, identical (mixed m. p.) with that prepared by condensation of *o*-methoxybenzaldehyde with sodium cyanoacetate (McRae and Hopkins, *Canad. J. Res.*, 1932, **7**, *B*, 248). The crystalline acid shows a blue fluorescence in ultra-violet light, but solutions of the acid do not fluoresce.

Esterification (Fischer–Speier) gave the ethyl ester as greenish-yellow prisms, m. p. 76—77° (Dave and Nargund, *loc. cit.*); this *trans*-ester (mixed m. p.) was also obtained from *o*-methoxybenzaldehyde (20 g.), ethyl cyanoacetate (17 g.), and piperidine (0·5 c.c.) in ethanol (100 c.c.) by boiling for 1 minute and cooling (yield, 29·4 g.).

2-*Hydroxybenzylidenemalononitrile* (VI; R = H).—To a solution of salicylaldehyde (5 g.) and malononitrile (2·6 g.) in ethanol (20 c.c.) was added piperidine (2 drops), heat being evolved. A very pale yellow solid separated from the cooled orange-red solution; after being washed with cold alcohol this product (5·5 g.) had m. p. 167° (decomp.) (Found: C, 69·5; H, 3·4; N, 16·0. $C_{10}H_6ON_2$ requires C, 70·6; H, 3·5; N, 16·4%). This 2-*hydroxybenzylidenemalononitrile* must be handled with care (see p. 120). Like *trans*-2-hydroxybenzylidenecyanoacetic acid (I; R = H) it could not be recrystallised unchanged. It differs from the reddish-yellow substance, m. p. 183—184°, prepared in a similar way by Hinrichsen and Lohse (*Annalen*, 1904, **336**, 344), and claimed, without analytical support, to be the dinitrile (VI; R = H).

3-*Cyanocoumarin* (III; R = H).—2-Hydroxybenzylidenemalononitrile (5 g.) was dissolved, by shaking, in 4N-hydrochloric acid (300 c.c.), and after a few minutes 3-cyanocoumarin began to separate; the reaction is faster at 60°. The washed product (4·6 g., 92%) had m. p. 184—185° before and after crystallisation from ethanol, from which it separated in almost colourless prisms (Found: N, 8·3. Calc. for $C_{10}H_5ON$: N, 8·2%). 3-Cyanocoumarin, m. p. 182°, was prepared by Bechert (*J. pr. Chem.*, 1894, **50**, 23) from salicylidenebismalonic ester and by Sastry and Seshadri (*Proc. Indian Acad. Sci.*, 1942, **16**, *A*, 29) from salicylaldehyde, ethyl cyanoacetate, and piperidine (30% yield).

cis-2-*Methoxybenzylidenecyanoacetic Acid* (VII; R = H).—The conditions necessary to obtain this compound are critical. 3-Cyanocoumarin (3·8 g.) was shaken for 10 minutes with N-sodium hydroxide (120 c.c.) at 30°; most of the solid dissolved to a yellow solution, and then methyl sulphate (4 × 2 c.c.) was added during 45 minutes with continual shaking at 25—30°. After a further ¼ hour, the solution was cooled, acidified with dilute hydrochloric acid, and kept at 0° for 1 hour, and the pale yellow solid was washed and then shaken with dilute aqueous sodium hydrogen carbonate (100 c.c.). Insoluble 3-cyanocoumarin (2·7 g.) was collected, and the chilled filtrate acidified, giving a yellow solid (1·15 g., m. p. 156°). This was crystallised from a solution saturated at 30° in a mixture of methylene chloride and light petroleum (b. p. 60—80°) by slowly cooling to −5°, giving cis-2-*methoxybenzylidenecyanoacetic* (cis-α-*cyano*-2-*methoxycinnamic*) *acid* as bright yellow needles, m. p. 159—160° [Found: C, 65·0; H, 4·5; N, 6·6; OMe, 15·0. $C_{10}H_6O_2N(OMe)$ requires C, 65·1; H, 4·4; N, 6·9; OMe, 15·2%]. After melting at 159—160° it resolidifies at 160° in 30 seconds, and then has m. p. 208° owing to conversion into the *trans*-acid (V; R = H). More vigorous methylation leads to a mixture of *cis*- and *trans*-methylated acids.

Solutions of this acid are not fluorescent. In ultra-violet light the crystals at first appear brown, but in about 5 minutes develop a yellow-green fluorescence. This may be due to change in crystalline form, since solution in, *e.g.*, acetone and evaporation of the solvent gives again the non-fluorescent material with which the changes may be repeated.

Dimerisation of Ethyl trans-2-*Methoxybenzylidenecyanoacetate*.—This ester (2·7 g.; m. p. 76—77°) was finely powdered, enclosed in a slowly rotating (20—30 r.p.m.), clear, silica tube (15 × 3 cm.), and irradiated with ultra-violet light for 9 days; the m. p.s after 1, 5, and 9 days were 75—115°, 84—135°, and 110—140° respectively. The product was spread in a thin, compact layer on porous porcelain and kept at 80—85° for 12 hours, leaving a residue (m. p. 146—152°) which, twice crystallised from ethanol, gave the *dimeride* as a colourless microcrystalline powder (1·51 g.), m. p. 163° (Found: C, 67·5; H, 5·7; N, 6·3%; *M*, ebullioscopic in benzene, 469. $C_{26}H_{26}O_6N_2$ requires C, 67·5; H, 5·6; N, 6·1%; *M*, 462). Unchanged starting material was obtained from the porcelain.

trans-5-*Bromo*-2-*hydroxybenzylidenecyanoacetic* (trans-5-*Bromo*-α-*cyano*-2-*hydroxycinnamic*) *Acid* (I; R = Br).—5-Bromo-2-hydroxybenzaldehyde (4 g.; Auwers and Burger, *Ber.*, 1904, **37**, 3934) was condensed with alkaline, aqueous sodium cyanoacetate according to Lapworth and McRae (*J.*, 1922, **121**, 1700), giving, after washing with water and benzene, the *acid* as a bright yellow powder (4·9 g.), m. p. 167—168° (decomp.) (Found: N, 5·1; Br, 29·9. $C_{10}H_6O_3NBr$ requires N, 5·2; Br, 31·0%). Like other *trans*-*o*-hydroxybenzylidenecyanoacetic acids, this acid cannot be recrystallised unchanged, and its colour fades and the m. p. rises on several weeks' storage.

6-*Bromocoumarin*-3-*carboxylic Acid* (II; R = Br).—The acid (I; R = Br) (325 mg.) was boiled with water (30 c.c.) for a few minutes, and the colourless solution acidified and cooled. The precipitated 6-bromocoumarin-3-carboxylic acid (II; R = Br) (300 mg.) crystallised from

dilute ethanol in needles, m. p. 198° (Found : C, 45·0; H, 1·9; Br, 29·5. Calc. for $C_{10}H_5O_4Br$: C, 44·6; H, 1·9; Br, 29·7%) (Pandya and Pandya, *Proc. Indian Acad. Sci.*, 1943, **18**, *A*, 164, prepared this acid from 5-bromo-2-hydroxybenzaldehyde and malonic acid, and record m. p. 200°).

trans-5-*Bromo*-2-*methoxybenzylidenecyanoacetic Acid* (V; R = Br).—(*a*) Methylation of the phenolic acid (I; R = Br) (4·9 g.) essentially as described in the case of the acid (I; R = H) gave a mixture of (V; R = Br) and 6-bromocoumarin-3-carboxylic acid (II; R = Br). These were separated by 3% aqueous sodium hydrogen carbonate (400 c.c.) in which the latter is very sparingly soluble, filtering, and acidifying the solution slowly; the colourless acid (II; R = Br), first precipitated, is removed, and is followed by the yellow acid (V; R = Br) (1·1 g.). The trans-5-*bromo*-2-*methoxybenzylidenecyanoacetic* (trans-5-*bromo*-α-*cyano*-2-*methoxycinnamic*) *acid* separated from ethanol in prisms, m. p. 240—241° (Found : C, 47·5; H, 2·9; N, 4·8; Br, 28·9. $C_{11}H_8O_3NBr$ requires C, 46·8; H, 2·8; N, 5·0; Br, 28·4%). It shows a pale green fluorescence in ultra-violet light.

(*b*) 5-Bromo-2-methoxybenzaldehyde (Shapiro and Smith, *J.*, 1946, 143) (3 g.) was condensed with warm, alkaline sodium cyanoacetate [see preparation of acid (I; R = Br)], giving the acid (V; R = Br) (2·8 g.), which after crystallisation from ethanol had m. p. and mixed m. p. 241—242°.

6-*Bromo*-3-*cyanocoumarin* (III; R = Br).—5-Bromo-2-hydroxybenzaldehyde (5 g.) was condensed with malononitrile (1·8 g.) as in the case of salicylaldehyde (above), giving crude 5-bromo-2-hydroxybenzylidenemalononitrile (5·1 g.), m. p. 174—175° (decomp.) (Found : N, 13·0. $C_{10}H_5ON_2Br$ requires N, 11·3%), which could not be crystallised unchanged. This substance is a powerful sternutator and irritant. The dinitrile (4 g.) was converted by dilute hydrochloric acid, as in the case of compound (VI; R = H), into 6-*bromo*-3-*cyanocoumarin* (3·5 g.), which crystallised from ethanol (charcoal) in almost colourless prisms, m. p. 200—201° (Found : C, 47·7; H, 1·6; N, 5·4; Br, 33·0. $C_{10}H_4O_2NBr$ requires C, 48·0; H, 1·6; N, 5·6; Br, 32·0%). This cyanocoumarin is precipitated unchanged from a solution in N-sodium hydroxide at 30°, but if the alkaline solution is boiled for 5 minutes acidification gives *trans*-5-bromo-2-hydroxybenzylidenecyanoacetic acid (I; R = Br).

cis-5-*Bromo*-2-*methoxybenzylidenecyanoacetic Acid* (VII; R = Br).—6-Bromo-3-cyanocoumarin (2·25 g.) was methylated in alkaline solution as in the preparation of *cis*-2-methoxybenzylidenecyanoacetic acid (VII; R = H). From the mixed product was isolated unchanged 6-bromo-3-cyanocoumarin (1·4 g.), insoluble in aqueous sodium hydrogen carbonate, and the filtrate yielded a solid (0·85 g.) which was crystallised twice from benzene, giving cis-5-*bromo*-2-*methoxybenzylidenecyanoacetic* (cis-5-*bromo*-α-*cyano*-2-*methoxycinnamic*) *acid* as aggregates of pale yellow, microscopic prisms (Found : C, 47·1; H, 3·0; N, 4·8; Br, 28·7. $C_{11}H_8O_3NBr$ requires C, 46·8; H, 2·8; N, 5·0; Br, 28·4%), m. p. (very rapid heating) 165° followed by immediate resolidification and final melting at 237—239° owing to conversion into the *trans*-acid (V; R = Br). The solid acid shows the same phenomena in ultra-violet light as does *cis*-2-methoxybenzylidenecyanoacetic acid (VII; R = H).

Ethyl trans-5-*Bromo*-2-*methoxybenzylidenecyanoacetate*.—(*a*) 5-Bromo-2-methoxybenzaldeyde (2·5 g.), ethyl cyanoacetate (1·5 g.), ethanol (10 c.c.), and piperidine (2 drops) were warmed and cooled, giving *ethyl* trans-5-*bromo*-2-*methoxybenzylidenecyanoacetate* (3·2 g.) as pale yellow crystals, m. p. 103° (Found : C, 50·6; H, 3·9; N, 4·2; Br, 26·2. $C_{13}H_{12}O_3NBr$ requires C, 50·4; H, 3·9; N, 4·5; Br, 25·8%), from ethanol. (*b*) Esterification (Fischer–Speier) of *trans*-5-bromo-2-methoxybenzylidenecyanoacetic acid (V; R = Br) gave the same ester in 86% yield. This substance is not dimerised when exposed to ultra-violet light.

trans-2 : 4-*Dimethoxybenzylidenecyanoacetic* (trans-α-*Cyano*-2 : 4-*dimethoxycinnamic*) *Acid*.—(*a*) 2 : 4-Dimethoxybenzaldehyde (5 g.), with alkaline, aqueous sodium cyanoacetate as in the previous cases, gave the *acid* (88%) as yellow needles, m. p. 255° (decomp.) (Found : C, 61·8; H, 4·9; N, 5·9. $C_{12}H_{11}O_4N$ requires C, 61·8; H, 4·7; N, 6·0%), from ethanol. It gives a yellow fluorescence in ultra-violet light. (*b*) 2-Hydroxy-4-methoxybenzylidenecyanoacetic acid was treated with methyl sulphate and alkali, and the product crystallised several times from dioxan and finally from ethanol, giving *trans*-2 : 4-dimethoxybenzylidenecyanoacetic acid (*ca.* 20%) identical with that obtained above.

3-*Cyano*-7-*methoxycoumarin*.—2-Hydroxy-4-methoxybenzaldehyde (8 g.) and malononitrile (3·4 g.) gave, as in the cases of the dinitriles (VI; R = H and Br), crude 2-hydroxy-4-methoxybenzylidenemalononitrile (10·3 g.), m. p. 162—165° (decomp.), which could not be crystallised unchanged (Found : N, 15·3. Calc. for $C_{11}H_8O_2N_2$: N, 14·0%). This dinitrile with dilute hydrochloric acid [see preparations of the cyanocoumarins (III; R = H and Br)] yielded

3-*cyano*-7-*methoxycoumarin* (80%), needles, m. p. 221—222° (Found: C, 65·4; H, 3·7; N, 6·7. $C_{11}H_7O_3N$ requires C, 65·7; H, 3·5; N, 7·0%), from ethanol. Dilute solutions of this compound show strong blue-violet fluorescence. Methylation to *cis*-2 : 4-dimethoxybenzylidenecyanoacetic acid could not be achieved.

Ultra-violet absorption spectra characteristics of cis- *and* trans-R·CH:C(CN)·CO_2H *in* EtOH.

R	$\lambda_{max.}$, mμ (log ε)	$\lambda_{min.}$, mμ (log ε)
cis-o-Methoxyphenyl	225(4·02) 279(4·05) 323(3·94)	222(4·01) 247(3·65) 304(3·86)
trans- ,, ...	229(3·95) 284(4·04) 334(3·96)	222(3·92) 249(3·55) 311(3·85)
cis-5-Bromo-2-methoxyphenyl ...	224(4·18) 281(4·03) 341(3·80)	— 258(3·84) 316(3·70)
trans- ,, ,, ...	224(4·18) 282(4·06) 345(3·82)	— 258(3·82) 320(3·70)

Ethyl trans-2 : 5-*Dimethoxybenzylidenecyanoacetate*.—Esterification of *trans*-2 : 4-dimethoxybenzylidenecyanoacetic acid (Fischer–Speier) gave the ethyl ester (80%), pale yellow needles (from ethanol), m. p. 142—143°, identical (mixed m. p.) with that prepared from 2 : 4-dimethoxybenzaldehyde and ethyl cyanoacetate (Kauffmann, *Ber.*, 1919, **52**, 1433). It is not dimerised by ultra-violet light.

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