

The Decarboxylation of Some α -Ethoxycarbonyloxybenzyl Cyanides. Part 2.¹ 1,2-Dicyano-1,2-bis(3,4-dimethoxyphenyl)ethane, a Minor Product Formed from 3,4-Dimethoxy- α -ethoxycarbonyloxybenzyl Cyanide by a Free-radical Process

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3,4-Dimethoxy- α -ethoxycarbonyloxybenzyl cyanide was heated in boiling toluene with chloroacetic acid or phosphoryl chloride and gave 1,2-dicyano-1,2-bis(3,4-dimethoxyphenyl)ethane in 2–3% yield; two interconvertible stereoisomers have been isolated. Formation of this substance requires electron transfer to two carbocations to yield a pair of free radicals. The same 1,2-dicyano-1,2-diarylethane was formed in 70% yield by reaction of 3,4-dimethoxyphenylacetonitrile with di-*t*-butyl peroxide in refluxing *t*-butylbenzene. The (*E*)- and (*Z*)-isomers of the corresponding stilbene have been characterised. Decomposition of the nitrilo-ester with concentrated sulphuric acid gave a trace of 9,10-dicyano-2,3,6,7-tetramethoxyanthracene.

Compounds of the type $\text{ArCH}(\text{OCO}_2\text{Et})\text{CN}$ (Ar = some aryl residues) lose CO_2 when heated in an inert solvent with a catalytic quantity of sulphuric acid; if the residue Ar carries an alkoxy group in the *ortho*- or *para*-position then the corresponding ether, $\text{ArCH}(\text{OEt})\text{CN}$, is formed. The mechanism has been given earlier,¹ and, for the specific case Ar = 3,4-dimethoxyphenyl, is summarised in the sequence: (1) \rightarrow benzylic cation (2) \rightarrow ether (3).

Generally, the ethers were colourless. However, the specific product (3) was coloured by an unidentified material whose yellow colour, intense blue fluorescence and (unpublished) u.v. spectrum suggested an anthracene, plausibly the then unknown 9,10-dicyano-2,3,6,7-tetramethoxyanthracene (4). This could result from reaction of the cation (2) with either the ester (1) or the ether (3), *via* the ion (5), followed by loss of the two hydrogen atoms from the intermediate dihydroanthracene.

We studied the reaction further, hoping for an easy path to the anthracene (4) that has been made by another route.² We were disappointed. Changing the solvent showed that the lower the temperature the better the yield of crude anthracene, but in boiling benzene, the lowest temperature used, the yield did not exceed 0.6%. Using refluxing toluene we varied the catalyst. Iodine alone, a mild oxidising agent and Lewis acid, was ineffective and the starting ester was recovered in part. Sulphuric acid and iodine together gave little more crude anthracene than sulphuric acid alone. An excess of either chloroacetic acid or phosphoryl chloride gave the ether (3) but only traces of the anthracene.

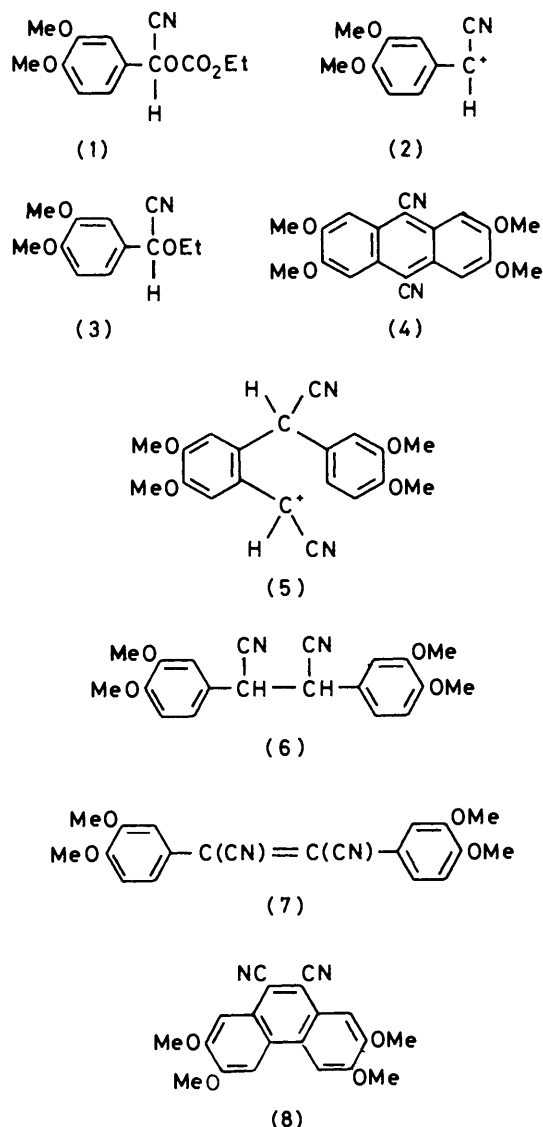
Column chromatography of the products from the last two runs showed that other C_{20} -compounds present were 1,2-dicyano-1,2-bis(3,4-dimethoxyphenyl)ethane (6), and the corresponding stilbene (7). The former cannot plausibly arise by a process involving the cation (2); however, gain of one electron would give the corresponding radical, which dimerises to compound (6). The mechanism involves the redox change from ion-pair to radical-pair, whose components then separate. The redox transfer may be relatively easy owing to the ambivalent nature of the nitrile group which inductively destabilises an adjacent carbenium ion, while providing resonance stabilisation.³ The former effect disappears as one electron is gained. Support for this free-radical mechanism is given by the finding that compound (6) is formed in 70% yield when 3,4-dimethoxyphenylacetonitrile is refluxed with one half a molar quantity of di-*t*-butyl peroxide in *t*-butylbenzene.

Two interconvertible stereoisomers of the ethane (6) have been isolated. A dimorphic one of lower m.p. that changed in

part into the higher-melting isomer when heated above its m.p.; and a higher-melting isomer that, when heated under nitrogen above its m.p. and the melt quenched, afforded some of the lower-melting material. Clearly, one is a racemate, and the other the *meso*-form, interconverted (probably) by a prototropic change; however we make no stereochemical assignment. In principle, reaction of a chiral shift reagent at the nitrile groups could provide a distinction, the singlet for the benzylic protons changing into a doublet for the racemate and into a quartet for the *meso*-form.⁴ The higher-melting isomer was sparingly soluble in all solvents tried; use of tris[3-(trifluoromethyl)hydroxymethylene]-(+)-camphorato]europium(III) with the lower-melting isomer changed only the signals due to the aryl protons, showing preferential complexation at the oxygen atoms.

We have also isolated the (*E*)- and (*Z*)-isomers of the stilbene (7). Generally, for stilbenes and similar systems, the following apply: the (*Z*)-isomer has the lower melting-point; ^{5a} thermal rearrangement occurs in the sense (*Z*) \rightarrow (*E*); ^{5a} the u.v. spectrum of the (*E*)-isomer shows the larger values of λ_{max} and ϵ for the longwave band; ^{5b} and in the ¹H n.m.r. spectra the signals for the aryl protons of the (*E*)-isomer are further downfield than those for the (*Z*)-isomer.^{5c} Our assignments meet all these criteria. It is possible to ascribe the formation of the stilbenes either to a reaction between the cation (2) and the ester (1) giving a proton and a derivative of 1,2-diphenylethane containing the system $\text{>HCC}(\text{OCO}_2\text{Et})\text{<}$, followed by loss of ethyl hydrogen carbonate [alternatively, with ether (3) in place of (1), then loss of ethanol], or to hydrogen transfer between the 1,2-diarylethane (6) and the radical corresponding to (2). However, solutions of the diarylethane are easily oxidised by air, and we believe that the stilbenes are artefacts of the processes of isolation, rather than primary products. The (*Z*)-stilbene and one crystalline form of the diarylethane have the same m.p.s, and the crystals of the latter often retained yellow material. Much time was spent in establishing that two different compounds were involved, using only the material from the run with chloroacetic acid as catalyst. Ultimately, the products from this run showed more stilbene than diarylethane; contrariwise for the run when phosphoryl chloride was used, and the work of separation was faster. In both cases the total yields of C_{20} -compounds were similar.

The materials that moved fastest on chromatography showed a strong blue fluorescence in daylight. The bulked materials from all runs, after extensive recrystallisation, gave



2 mg of material, apparently homogeneous, whose properties are consistent with those of 9,10-dicyano-2,3,6,7-tetramethoxyanthracene (4),² though the mass spectrum showed the presence of an ion for $C_{20}H_{15}NO_6$; another minor product is an isomer of the anthracene (4), probably 5,6-dicyano-2,3,8,9-tetramethoxyphenanthrene (8).

Experimental

Unless otherwise stated, m.p.s were determined on a K fler block, i.r. spectra were taken on Perkin-Elmer models 257 or 397, u.v. spectra on a Perkin-Elmer model 402, and 1H n.m.r. spectra on a Perkin-Elmer model R32 instrument at 90 MHz in $CDCl_3$, chemical shifts being given as p.p.m. downfield from tetramethylsilane as internal standard (coupling constants in Hz) and mass spectra on an AEI MS9 instrument.

3,4-Dimethoxy- α -ethoxycarbonyloxybenzyl Cyanide (1).—Prepared as described earlier,¹ the substance previously reported as an oil formed crystals, m.p. 32 °C; ν_{max} . (Nujol) 1752 cm^{-1} (CO) (Found: C, 59.0; H, 5.7; N, 5.6. Calc. for $C_{13}H_{15}NO_5$: C, 58.8; H, 5.7; N, 5.3%).

Decarboxylation Experiments. Isolation of the Ether (3) and of Crude 9,10-Dicyano-2,3,6,7-tetramethoxyanthracene (4).—A solution of the ester (1) in an inert solvent, at a concentration of 1 g to 5 ml, together with the catalyst was boiled under reflux until evolution of CO_2 ceased, or for 5 h, whichever was the shorter. The solvent was removed and the ether (3) distilled under reduced pressure. The dark residue was then sublimed under reduced pressure (bath temp. 150–180 °C at 0.3 mmHg). Any sublimate was washed with diethyl ether to remove traces of the nitrilo-ether (3). Using a catalytic quantity of sulphuric acid with different solvents, the yields of the ether (3) and of the crude anthracene (4) were, respectively: xylene, not recorded, none; toluene, 66% \pm 9, 0.1%; benzene, 65% \pm 5, 0.6%. Using toluene as solvent and varying the catalyst gave the results: iodine (0.8M), no decarboxylation, some starting ester recovered; iodine (0.8M) and a catalytic quantity of sulphuric acid, 57%, 0.3%; chloroacetic acid (>1.0M), 51%, trace; phosphoryl chloride (>1.0M), 57%, trace.

Isolation of the Minor Products from the Decarboxylation Experiments.—The tarry products from the last three runs were separately treated with about the same volume of methanol and allowed to stand; any of the high-melting isomer of the diarylethane (6) separated. The methanol was evaporated off and the residue chromatographed in chloroform over silica gel. The sequence of elution was: a pale yellow oil (apparently polymeric, not examined), the anthracene (4) and an isomer (see below) and the isomers of the stilbene (7) as overlapping bands, and then the low-melting isomer of the diarylethane (6). Of the fast-running materials, the stilbenes were relatively soluble; their isomers were separated by hand-picking. The yields using chloroacetic acid and phosphoryl chloride were, respectively: diarylethanes, 23 and 43 mg; stilbenes, 58 and 20 mg; totals of these dimeric compounds, 3 and 2%.

The Isomers of 1,2-Dicyano-1,2-bis(3,4-dimethoxyphenyl)ethane (6).—The low-melting isomer formed needles from methanol, m.p. 197 °C or, metastable form, 178 °C; the melt resolidified as rhombs. On repeated melting and resolidification the m.p. fell to 173 °C, then rose to 252 °C {Found: m/e 352.1439 (11%, M^+); 176.0711 [100%, ($M/2$)⁺]; C, 68.6; H, 5.8; N, 8.3. $C_{20}H_{20}N_2O_4$ requires m/e 352.1423; C, 68.2; H, 5.7; N, 8.0%}; δ 3.81, 3.88 (each 6 H, s, CH_3O), 4.21 (2 H, s, ArCH), 6.71 (2 H, m, 6-H), and 6.82 (4 H, m, 2-H and 5-H).

The high-melting isomer formed needles from hot pyridine or, less usefully, from hot chloroform, m.p. 262–263 °C, the melt yellow; above ca. 180 °C the material sublimed as narrow plates {Found: m/e 352.1427, (19%, M^+); 176.0648 [100%, ($M/2$)⁺]; C, 67.9; H, 5.8; N, 7.8%}; δ (on a Bruker WM 250 instrument at 250 MHz) 3.824, 3.895 (each 6 H, s, CH_3O), 4.185 (2 H, s, ArCH), 6.665 (2 H, d, J 2 Hz, 2-H), 6.770 (2 H, dd, J 8, 2 Hz, 6-H), and 6.848 (2 H, d, J 8 Hz, 5-H).

The isomers were interconvertible. Thus, heating the lower-melting isomer above its m.p. gave the higher-melting form, as shown by the rise in m.p., and the change in the appearance of the crystals. Also, solutions in methanol or ethanol of the lower-melting isomer deposited crystals of the higher-melting form during long storage at room temperature. The change was also made in the reverse direction. The high-melting isomer (495 mg) was heated at 270 °C under nitrogen for 8 min, then the material quenched with cold chloroform, leaving chloroform-insoluble material (172 mg). Recrystallisation of the chloroform-soluble material from ethyl acetate gave the crude low-melting isomer (151 mg), m.p. 189–196 °C. A second recrystallisation gave the pure material, m.p. 195–

197 °C, capillary m.p. 193 °C, undepressed when mixed with the low-melting isomer described above.

The Isomers of 1,2-Dicyano-1,2-bis(3,4-dimethoxyphenyl)ethene (7).—From ethyl acetate the (*E*)-*stilbene* formed yellow needles, m.p. 207 °C; the melt resolidified as blades and needles [Found: *m/e* 350.1275 (100%, *M*⁺); C, 68.4; H, 5.1; N, 7.7. C₂₀H₁₈N₂O₄ requires *m/e* 350.1266; C, 68.6; H, 5.2; N, 7.8%]; λ_{max.} (log ε) (methanol) 237 (4.16), 267 (4.05), and 402 nm (4.20); δ 3.95 (12 H, s, CH₃O), 6.95 (2 H, d, *J* 9 Hz, 5-H), 7.36 (2 H, d, *J* 2 Hz, 2-H), and 7.44 (2 H, dd, *J* 9, 2 Hz, 6-H).

The (*Z*)-*stilbene* separated as tablets and prisms from cold ethyl acetate, or as rectangular plates from hot, changing into prisms on long contact with the cold solvent. When heated, the tablets broke up below 100 °C; thereafter, both forms showed a phase change at ca. 184 °C; m.p. 197 °C, not sharp. Repeated melting and resolidification caused the m.p. to fall to 178 °C, then rise; heating above 250 °C then resolidification gave blades, m.p. 201 °C [Found: *m/e* 350.1232 (100%, *M*⁺); C, 68.7; H, 5.0; N, 7.6%]; λ_{max.} (log ε) (methanol), 260 (4.16) and 392 nm (4.08); δ 3.65, 3.88 (each 6 H, s, CH₃O), 6.77 (2 H, d, *J* 2 Hz, 2-H), 6.80 (2 H, d, *J* 8 Hz, 5-H), and 7.04 (2 H, dd, *J* 8, 2 Hz, 6-H).

9,10-Dicyano-2,3,6,7-tetramethoxyanthracene (4) and an Isomer.—The anthracene was one component of the sublimates mentioned earlier, and also of the sparingly soluble material from the fast-moving fractions of the chromatograms. Repeated crystallisation of material from all runs gave yellow needles (2 mg) from hot pyridine, subliming but unmelted at 340 °C (lit.,² subliming but unmelted at 360 °C) [Found: *m/e* 348.1097 (100%, *M*⁺); C, 68.8; H, 4.7. Calc. for C₂₀H₁₆N₂O₄: *m/e* 348.1110; C, 69.0; H, 4.6%]; ν_{max.} (KBr disk) 2 251 cm⁻¹ (CN); λ_{max.} (log ε) (chloroform) 252 (4.71), 283 (5.05), 407 (4.23), and 425 nm (4.40); δ (on a Bruker WM 250 instrument at 250 MHz) 4.134 (12 H, s, CH₃O) and 7.477 (4 H, s, ArH). The material was sparingly soluble in all solvents, its solutions having an intense blue fluorescence; although it was apparently homogeneous, every sample examined showed peaks in the mass spectrum at *m/e* 365.0866 (*M*⁺) and 182.5462, [(*M*/2)⁺] (for the sample described above, their intensities were, respectively, 17 and 0.3% of the base peak).

The anthracene was accompanied by an isomer [*m/e* 348.1095 (100%, *M*⁺), m.p. 330 °C (resolidified, 327 °C), whose solutions were not fluorescent. The u.v. spectrum, λ_{max.} (log ε) (chloroform) 262 (4.54), 276 (4.65), 287 (4.61), 298 (4.59), 368 (4.23), and 416 nm (3.74), suggested a phenanthrene, plausibly 5,6-dicyano-2,3,8,9-tetramethoxyphenanthrene.

*Reaction Between 3,4-Dimethoxyphenylacetonitrile and Di-*t*-butyl Peroxide.*—A solution of di-*t*-butyl peroxide (0.41 g, 2.8 mmol) in *t*-butyl benzene (10 ml) was added in portions during 30 min to a refluxing solution of 3,4-dimethoxyphenylacetonitrile (1.0 g, 5.6 mmol) in *t*-butylbenzene (50 ml). Reflux was continued during 3½ h, and the mixture left another 24 h, during which time a pale brown solid (0.36 g), m.p. 248–255 °C separated. Volatile materials in the mother liquor were removed by steam distillation; washing the dried residue with cold ethyl acetate left a white solid (0.27 g), m.p. 253–259 °C. The ethyl acetate later deposited a yellow solid (46 mg), m.p. 196–202 °C. Repetition of the reaction using the nitrile (10.1 g) in *t*-butylbenzene (110 ml) with di-*t*-butyl peroxide (4.14 g) in *t*-butylbenzene (20 ml) gave crude product (5.10 g) directly. The combined mother-liquors from these two runs contained unchanged 3,4-dimethoxyphenylacetonitrile (2.86 g). The conversion yields were thus 63 and 51%; overall, allowing for recovered starting material, 70%. Recrystallisation from pyridine gave the high-melting isomer of 1,2-dicyano-1,2-bis(3,4-dimethoxyphenyl)ethane (6), m.p. 263 °C, capillary m.p. 255 °C, not depressed by mixture with material obtained from the ester (1) [Found: *m/e* 352.1390 (41%, *M*⁺); 176.0659 [100%, (*M*/2)⁺]; C, 68.2; H, 5.8; N, 8.2%]; ν_{max.} (KCl disk) 2 240 cm⁻¹ (CN); δ (on a Bruker WM 250 instrument at 250 MHz) 3.826 and 3.898 (each 6 H, s, CH₃O), 4.189 (2 H, s, ArCH), 6.664 (2 H, d, *J* 2 Hz, 2-H), 6.777 (2 H, dd, *J* 8, 2 Hz, 6-H), and 6.849 (2 H, d, *J* 8 Hz, 5-H).

Minor products included two solids, both yellow, whose appearance and m.p.s, 189–197 and 198–205 °C, were consistent with their being, respectively, the (*Z*)- and (*E*)-*stilbenes* described above.

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