88. *The Preparation of Diarylmaleonitriles.*

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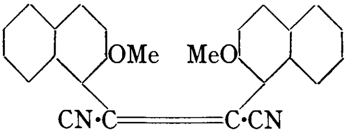
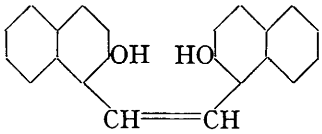
The direct linkage of 1-naphthylacetonitrile residues to give a dinaphthylmaleonitrile proved impracticable, although such linkage proceeds readily with phenylacetonitrile. The difficulty was surmounted by converting 2-methoxy-1-naphthylchloroacetonitrile into a pyridinium salt and thence into an enimine-betaine; the latter decomposed on heating into the desired maleonitrile. The behaviour of other halogenoacetonitriles is described, but the reaction only takes the above course when arylhalogenoacetonitriles are used.

So far the only substituted maleonitriles to have been prepared and converted into pigments of the phthalocyanine type have been diphenylmaleonitrile and its *pp'*-dinitro-derivative (Cook and Linstead, J., 1937, 931). The present work was directed towards the preparation of other such dinitriles.

Attempts were first made to apply the satisfactory method of preparing diphenylmaleonitrile, *i.e.*, by the action of iodine and alkali on phenylacetonitrile, to other acetonitriles. In view of the comparative inaccessibility of 1-naphthylacetonitrile attention was turned to the preparation of 2 : 2'-dimethoxy-1 : 1'-dinaphthylmaleonitrile (I) from the hitherto unknown 2-methoxy-1-naphthylacetonitrile.

(I.)





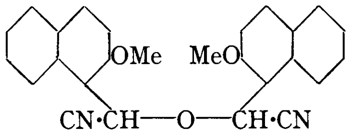
(II.)

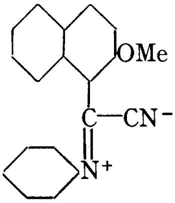
2-Hydroxy-1-naphthaldehyde was reduced by amalgamated aluminium to 2-hydroxy-1-naphthylcarbinol, 2 : 2'-dihydroxy-1 : 1'-dinaphthylmethane, and a small amount of a highly crystalline solid to which structure (II) was assigned; the last was characterised as its *dimethyl* ether. The production of a dinaphthylmethane is noteworthy, though the formation of the same compound by a similar reduction of 2-hydroxy-1-naphthaldehyde has been reported earlier (Betti and Mundici, *Gazzetta*, 1906, **36**, II, 659). 2-Hydroxy-1-naphthylcarbinol could not be converted into 2-hydroxy-1-naphthylmethyl bromide or iodide and we turned therefore to a similar series of reactions with methoxynaphthalene derivatives.

2-Methoxynaphthalene, trioxymethylene and hydrogen chloride in glacial acetic acid at 20° afforded an excellent yield of 2-*methoxy*-1-*chloromethylnaphthalene.* As was expected, the chloromethyl group entered the 1-position, as hydrolysis afforded the known 2-methoxy-1-naphthylcarbinol. At higher temperatures an amorphous, apparently polymeric material was formed, and a similar material was obtained by heating the monomeric chloromethyl compound to 120°, hydrogen chloride being evolved. Hydrogen chloride was also removed by alcoholic silver nitrate at 30° to yield s.-2 : 2'-*dimethoxy*-1 : 1'-*dinaphthylethylene.* This was not identical with the dimethyl ether of (II), but its absorption spectrum was practically superposable on that of (II) and of the dimethyl ether of (II); the two ethers are probably *cis*- and *trans*-isomerides with relative stabilities not infrequently encountered among isomeric stilbenes. The reactivity of the chlorine atom in 2-methoxy-1-chloromethylnaphthalene was in other ways remarkable. Manske and Ledingham (*Canadian J. Res.*, 1939, **17**, *B*, 14; see also Cambron, *ibid.*, p. 10) observed that the action of methyl-alcoholic potassium cyanide on 1-chloromethylnaphthalene afforded not only the corresponding nitrile but also 1-naphthylmethyl methyl ether; moreover the nitrile yielded a bimolecular product on saponification. Similarly treatment of 2-methoxy-1-chloromethylnaphthalene at 30° with sodium bicarbonate in acetone solution yielded 2-methoxy-1-naphthylcarbinol, and the action of alcoholic alkali at 40° yielded the corresponding *ethyl* ether. This recalls the facile preparation of 1-naphthylmethyl ethyl ether from 1-chloromethylnaphthalene, alcohol, and calcium carbonate (D.R.-P. 516,280). 2-*Methoxy*-1-*naphthylacetonitrile* was obtained by the action of potassium cyanide in aqueous acetone at room temperature on the chloride. It was hardly surprising in view of the reactivity mentioned above that this nitrile failed to yield the desired diarylmaleonitrile on treatment with bromine or iodine and bases under the most diverse conditions. Bromination in chloroform in presence of calcium carbonate yielded a homogeneous *monobromo*-compound; this was, however, not the potentially useful methoxynaphthylbromoacetonitrile, for it failed to react with pyridine as did the authentic chloroacetonitrile described below. The original route had therefore to be abandoned and we next attempted the preparation of 2-methoxy-1-naphthylchloroacetonitrile with the object of removing the elements of hydrogen chloride (compare the conversion of phenylchloroacetonitrile into diphenylmaleonitrile).

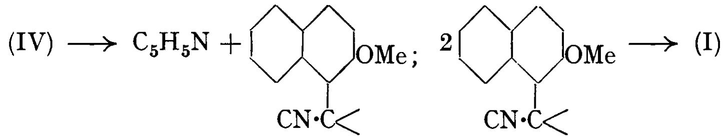
2-Methoxy-1-naphthaldehyde readily formed a cyanohydrin. Treatment of the latter with thionyl chloride in benzene at room temperature gave a bimolecular product which was free from chlorine and was formulated as *di-2-methoxy-1-naphthylcyanomethyl ether* (III). At higher temperatures the action of thionyl chloride in benzene either on the cyanohydrin itself or on (III) led to *2-methoxy-1-naphthylchloroacetonitrile.* This chloro-compound was very sensitive and little success attended attempts to convert it into the maleonitrile until it was found that it reacted readily with pyridine to give a crystalline *quaternary* salt. The latter underwent no noticeable change on boiling with pyridine, nor did it provide any well-defined product on dry distillation. On addition of alkali to its aqueous solution, however, a stable orange solid was obtained, which was reconverted into colourless salts by treatment with acids. This solid was free from halogen and analysis showed that it was not the base with the pyridine ring opened as in Zincke's anils. On the contrary, it was readily soluble in organic solvents and gave intense violet-red colours with picric acid, trinitrobenzene, trinitrotoluene, and styphnic acid; it was formulated, therefore, as the enimine-betaine (IV), like similar compounds prepared by Kröhnke (*Ber.*, 1939, **72**, 83). This betaine, on distilling in a high vacuum at 150°, decomposed into pyridine and the required dinitrile. Some 2-methoxy-1-naphthylacetonitrile was produced possibly by dehydrogenation of part of the reacting melt by the intermediate radical (V):

(III.)





(IV.)



(V.)

Chromatographic examination of the crude dinitrile revealed at least two distinct components. Analysis showed these to be isomeric and there is little doubt that they are stereoisomeric forms of *2 : 2′-dimethoxy-1 : 1′-dinaphthylmaleonitrile.* Both on heating with copper or copper salts gave products of intense green colour in pyridine solution with strong absorption of light at 6250 A. The octanaphthylporphyrazines so formed await detailed examination.

This behaviour of an enimine-betaine led us to enquire whether other similar compounds would undergo analogous decomposition. The betaine from pyridine and ω-bromoacetophenone (Kröhnke, *Ber.*, 1935, **68**, 1184), sublimed at 150°/0·001 mm., readily afforded *s.*-dibenzoylethylene and we therefore attempted analogous preparations of other maleonitriles.

Cyanomethylpyridinium chloride gave on treatment with alkali an unstable yellow-red betaine, which was characterised by the formation of an orange *benzoyl* derivative. Neither the betaine, which was so unstable as to make thorough trial impossible, nor its benzoyl compound decomposed to give a dinitrile. Further, neither cyanomethylpyridinium chloride nor *acetamidopyridinium chloride* afforded any dimeric product on heating. α-Chloropropionitrile also gave a *pyridinium* salt and thence an unstable *betaine*, but this also could not be decomposed in the desired way. On the other hand, phenylchloroacetonitrile reacted with pyridine to give a crystalline *salt* and thence with alkali a moderately stable product possessing enimine-betaine properties (cf. Kröhnke, *Ber.*, 1939, **72**, 88). On dry distillation this gave a good yield of diphenylmaleonitrile. It appeared, therefore, that dimerisation proceeds only with arylhalogenoacetonitriles. This was confirmed in that the *betaine* from α-chloro-β-phenylpropionitrile afforded an almost theoretical yield of cinnamonitrile. Again, cinnamaldehyde cyanohydrin was converted into a chloronitrile, from which a characteristic pyridinium salt or betaine was not obtained. On standing, however, the chloronitrile gave a chlorine-free dimeric product agreeing in analysis with a dinitrile. This had no colour or fluorescence, as would be expected of a dicinnamylmaleonitrile, and as it yielded no porphyrazine pigment it was regarded as a cyclised dimeride, 2 : 5-*diphenyldihydroterephthalonitrile*. On reverting to the arylacetonitrile type a substituted maleonitrile was again obtained. Anisaldehyde cyanohydrin gave a *chloronitrile*, and this at a low temperature a pyridinium salt. Although the last afforded an insoluble enimine-betaine with aqueous alkali and this decomposed to pp′-*dimethoxydiphenylmaleonitrile*, it was unnecessary to prepare the betaine, for the pyridinium salt decomposed in the desired manner equally readily. Qualitative experiments showed that *pp*′-dimethoxydiphenylmaleonitrile also gives a porphyrazine on heating with iron to 280—300°.

EXPERIMENTAL.

2-Hydroxy-1-naphthaldehyde (29 g.) was boiled overnight in moist ether (300 c.c.) with amalgamated aluminium (15 g.) (Vogel, J., 1927, 597), and the product treated with hydrochloric acid. The ethereal solution on slight concentration deposited needles of 2 : 2′-*dihydroxy*-1 : 1′-*dinaphthylethylene*, m. p. 252° after recrystallisation from carbon tetrachloride (yield, 310 mg.) (Found : C, 84·9; H, 5·0. $C_{22}H_{16}O_2$ requires C, 84·7; H, 5·1%). Methylation of this compound with caustic soda and methyl sulphate afforded 2 : 2′-*dimethoxy*-1 : 1′-*dinaphthylethylene*, which formed needles, m. p. 222°, from ethanol (Found : C, 84·7; H, 5·9. $C_{24}H_{20}O_2$ requires C, 84·8; H, 5·9%). It was more soluble in chloroform, carbon tetrachloride, benzene, and ether than the parent compound, but both dissolved in concentrated sulphuric acid, giving deep orange colorations. Light absorption in light petroleum : Maxima, 3420, 2910 A.; inflexion, 2800; $E^{1\%}_{1\,\mathrm{cm.}} = 185, 217, 303$ respectively. The ethereal solution obtained after separation of the dihydroxydinaphthylethylene deposited, on further concentration, first, 2 : 2′-dihydroxy-1 : 1′-dinaphthylmethane and then 2-hydroxy-1-naphthylcarbinol (24 g.).

Trioxymethylene (10 g.), suspended in glacial acetic acid (150 c.c.), was treated with dry hydrogen chloride until a clear solution was obtained. 2-Methoxynaphthalene (25 g.) in acetic acid (250 c.c.) was then added, and a rapid stream of hydrogen chloride again introduced, the temperature being kept below 15° throughout. On standing overnight, pure 2-*methoxy*-1-*chloromethylnaphthalene* (21 g.) separated; it was washed with water and crystallised from alcohol (Found : Cl, 17·0. $C_{12}H_{11}OCl$ requires Cl, 17·2%). It decomposed with elimination of hydrogen chloride at 120°. It was treated in acetone solution for some hours with warm aqueous sodium bicarbonate, and the whole then concentrated under reduced pressure and diluted with cold water. After standing, the crystalline deposit was extracted with alcohol, and the extract evaporated; the residue crystallised from water to give 2-methoxy-1-naphthylcarbinol, m. p. 100°, identical with the product of Jacobs and Heidelberger (*J. Biol. Chem.*, 1915, **20**, 674).

When 2-methoxy-1-chloromethylnaphthalene was warmed with dilute alcoholic alkali at 40° for several hours, it was converted into 2-*methoxy*-1-*naphthylcarbinyl ethyl ether*, an oil, b. p. 173—175°/12 mm. (Found : C, 77·3; H, 7·6. $C_{14}H_{16}O_2$ requires C, 77·8; H, 7·4%).

2-Methoxy-1-chloromethylnaphthalene (18 g.), dissolved in acetone (600 c.c.), was kept for 1 hour with potassium cyanide (12 g.) in water (300 c.c.) at 30—35°. The solution was concentrated under reduced pressure to one third of its volume and diluted with water. 2-*Methoxy*-1-*naphthylacetonitrile* (16 g.) was filtered off after 1 hour and recrystallised from acetone–water; it had m. p. 111° (Found : N, 7·3. $C_{13}H_{11}ON$ requires N, 7·1%).

2-Methoxy-1-chloromethylnaphthalene (1 g.) in acetone (10 c.c.) was added to silver nitrate

(1·4 g.) in alcohol (240 c.c.) and kept for 24 hours at 30°. The bulk of the alcohol was removed in a vacuum, and the product filtered off and extracted with ether. The solid residue from the ethereal extract was recrystallised from light petroleum. The β-form of 2 : 2'-*dimethoxy*-1 : 1'-*dinaphthylethylene* had m. p. 145° (Found : C, 85·0; H, 6·0; *M*, cryoscopic in camphor, 310. $C_{24}H_{20}O_2$ requires C, 84·8; H, 5·9%; *M*, 340). Light absorption in light petroleum : Maxima, 3380, 2960 A.; inflexion, 2830; $E^{1\%}_{1\,\text{cm.}}$ = 180, 270, 300 respectively. Like the α-form, this also gave an orange coloration with concentrated sulphuric acid. Both forms were unsaturated towards tetranitromethane, but neither was appreciably changed by exposure to ultra-violet light in benzene solution.

2-Methoxy-1-naphthylacetonitrile was treated with bromine (1 mol.) in chloroform solution in presence of suspended calcium carbonate. The bromine quickly disappeared at room temperature; the chloroform solution yielded an oil which rapidly solidified and was recrystallised from chloroform. *Bromo*-2-*methoxy*-1-*naphthylacetonitrile* had m. p. 145—146° (Found : Br, 29·4. $C_{13}H_{10}ONBr$ requires Br, 29·1%).

2-Methyl-1-chloromethylnaphthalene (5 g.) was added to a saturated solution of potassium cyanide in 85% alcohol (500 c.c.), and the whole boiled overnight. The product was concentrated under reduced pressure to 100 c.c., and water (400 c.c.) and sodium chloride added. The 2-*methyl*-1-*naphthylacetonitrile* that separated had m. p. 78° after crystallising from light petroleum (Found : N, 7·5. $C_{13}H_{11}N$ requires N, 7·7%). When much water was used in the cyanisation step, the corresponding alcohol, 2-*methyl*-1-*naphthylcarbinol*, was formed, m. p. 137—138° after crystallisation from benzene (Found : C, 83·6; H, 7·3; *M*, cryoscopic in camphor, 160. $C_{12}H_{12}O$ requires C, 83·7; H, 7·0%; *M*, 172). This substance lost water at 100° in a vacuum, but could be reconverted into the chloride by alcoholic hydrogen chloride at room temperature.

2-Methoxy-1-naphthaldehyde (10 g.) in alcohol at 50° was treated with almost saturated sodium bisulphite solution (100 c.c.). After 1—2 hours the bisulphite compound was filtered off and added with stirring to a concentrated solution of potassium cyanide (20 g.) in water. After 1 hour the solid cyanohydrin was separated and crystallised from benzene; it had m. p. 111° (lit., 112°).

The cyanohydrin (1·1 g.) in benzene (30 c.c.) was treated with thionyl chloride (3 c.c.) at room temperature and after 30 mins. light petroleum (40 c.c.) was added. The precipitate, recrystallised from benzene, had m. p. 121°; it was free from chlorine and was formulated as *di*-2-*methoxy*-1-*naphthylcyanomethyl ether* (III) (Found : N, 6·6; *M*, cryoscopic in camphor, 391, 361, 389. $C_{26}H_{20}O_3N_2$ requires N, 6·85%; *M*, 408). When this compound or the original cyanohydrin was boiled with excess of thionyl chloride for 20 mins., and the solution then evaporated, 2-*methoxy*-1-*naphthylchloroacetonitrile* was obtained (yield, 50% of the theoretical); crystallised from benzene, it had m. p. 130° (Found : N, 6·1. $C_{13}H_{10}ONCl$ requires N, 6·2%). This chloronitrile (1·7 g.) was dissolved with slight warming in pyridine (6 c.c.); 2-*methoxy*-1-*naphthylcyanomethylpyridinium chloride*, which slowly separated, had m. p. 165° (slight decomp.) and crystallised from a large volume of benzene or benzene containing a little alcohol (Found : Cl, 11·3. $C_{18}H_{15}ON_2Cl$ requires Cl, 11·3%). This chloride (1 g.) was dissolved in water (20 c.c.) and added to a well-stirred 10% solution of sodium carbonate (50 c.c.). The orange precipitate of 2-*methoxy*-1-*naphthylcyanomethylpyridinium enimine-betaine*, crystallised from benzene–alcohol, had m. p. 150° (decomp.) (Found : N, 10·2. $C_{18}H_{14}ON_2$ requires N, 10·2%). The enimine-betaine was heated at 200°/0·001 mm. Pyridine was liberated and two sublimate fractions were collected. The more volatile fraction was 2-methoxy-1-naphthylacetonitrile identical (m. p. and mixed m. p.) with the nitrile described above; the less volatile sublimate in benzene solution was filtered through an aluminium oxide chromatographic column. The topmost band was resinous and was not further examined; the middle zone gave the α-form of 2 : 2'-*dimethoxy*-1 : 1'-*dinaphthylmaleonitrile*, which formed pale yellow needles, m. p. 255°, from benzene (Found : N, 7·3. $C_{26}H_{18}O_2N_2$ requires N, 7·2%). The lower adsorption band afforded the β-form, which separated from benzene in pale yellow needles, m. p. 290° (mixed m. p. with the α-compound, 230—235°) (Found : N, 7·2%). The yield of these nitriles was 5% of each. They were produced in very much smaller yield by heating the above pyridinium chloride. The nature of these products was confirmed by heating with ferric chloride to 300°. Solutions of the melts in pyridine showed a very intense absorption band at 6250 A. characteristic of iron porphyrazine pigments.

Chloroacetonitrile (25 g.) was kept with pyridine (33 c.c.) overnight. The crystalline deposit was filtered off (more was obtained by allowing the filtrate to stand), washed with ether, and recrystallised from alcohol and benzene, forming long colourless rods, m. p. 178°.

Cyanomethylpyridinium chloride was exceedingly deliquescent, this fact almost certainly accounting for the low nitrogen content (Found : N, 17·4. $C_7H_7N_2Cl$ requires N, 18·1%). On addition of potassium hydroxide or carbonate to a solution of the chloride in water the yellow betaine was precipitated. It was moderately easily soluble in organic solvents, but easily resinified and could not be crystallised. Cyanomethylpyridinium chloride (2·4 g.) and benzoic anhydride (3·6 g.) in chloroform (25 c.c.) were shaken with a solution of potassium carbonate (10 g.) in water (30 c.c.). The clear red chloroform solution was washed with water and evaporated. The product, identical with Kröhnke's ω-cyanophenacylpyridinium benzoate (*Ber.*, 1939, **72**, 83), was obtained as a bright yellow solid; crystallised from ethyl acetate, it had m. p. 145° (Found : N, 12·4. Calc. for $C_{14}H_{10}ON_2$: N, 12·5%).

Chloroacetamide (11 g.) was heated to boiling with pyridine (20 c.c.) and allowed to cool. The resulting *acetamidopyridinium chloride*, recrystallised from benzene–methanol, formed white needles, m. p. 202—203° (Found : N, 16·3. $C_7H_9ON_2Cl$ requires N, 16·3%). It gave no betaine with alkali.

Phenylchloroacetonitrile was treated with pyridine (1·5 equivs.) and kept for 2 days. The clear viscous liquid was stirred with benzene, and the crystalline salt recrystallised from chloroform, forming fine white needles. *α-Cyanobenzylpyridinium chloride* separated in a solvated condition. On drying at 95°, the solvate melted and then resolidified. The free compound had m. p. 159° (Found : N, 11·9. $C_{13}H_{11}N_2Cl$ requires N, 12·1%). The red enimine-betaine (cf. Kröhnke, *loc. cit.*) was sublimed at 120° in a vacuum. The major and less volatile part of the sublimate consisted of diphenylmaleonitrile (yield, ~50%). A smaller yield (10%) was obtained by distilling cyanobenzylpyridinium chloride in a vacuum.

Phenylacetaldehyde cyanohydrin (10 g.) (best obtained by allowing redistilled phenylacetaldehyde to stand with *dry* hydrogen cyanide overnight in presence of piperidine; the solid product may then be used directly), dissolved in benzene, was added slowly to phosphorus pentachloride (18 g.) covered by benzene and cooled in ice. The temperature was slowly raised until all phosphorus halide had dissolved. The mixture was poured on ice, and the benzene solution washed with sodium carbonate solution, dried, and fractionated. *α-Chloro-β-phenylpropionitrile* was obtained as a colourless oil, b. p. 128—130°/13 mm. (yield, 62%) (Found : N, 8·1. C_9H_8NCl requires N, 8·4%). When the nitrile was boiled with quinoline (10 g.), and the red viscous product stirred into benzene, a quantitative yield of quinoline hydrochloride was obtained. The filtrate was washed with dilute sulphuric acid and fractionated, giving a practically quantitative yield of cinnamonitrile, b. p. 120—130°/13 mm., identified by hydrolysis with caustic alkali to cinnamic acid.

Cinnamaldehyde cyanohydrin (15 g.) was added slowly to thionyl chloride (12·3 g.) cooled in ice, and the reaction completed by gentle warming. The product was twice fractionated in a vacuum, the fraction, b. p. 130—140°/15 mm., being collected. This was evidently mainly α-chloro-γ-phenylvinylacetonitrile, but it could not be obtained pure, as it continually deposited colourless halogen-free crystals, probably 2 : *5-diphenyldihydroterephthalonitrile*. The latter separated from methanol in needles, m. p. 114° (Found : N, 9·9. $C_{20}H_{14}N_2$ requires N, 10·0%).

Anisaldehyde cyanohydrin (12 g.) was slowly treated with thionyl chloride (10% excess over the theoretical quantity) with cooling. Reaction was completed by warming, and the product twice fractionated, giving p-*methoxyphenylchloroacetonitrile* (7 g.), b. p. 153—155°/13 mm. (Found : N, 7·8. C_9H_8ONCl requires N, 7·7%). The residue in the distillation flask was sublimed in a vacuum. The crystalline sublimate separated in almost colourless leaflets, m. p. 186—187°, from methanol. A pyridine extract of the melt obtained on heating with iron at 300° was intensely green and showed characteristic porphyrazine spectral absorption bands (6320, 5800 A.). This product, pp′-*dimethoxydiphenylmaleonitrile* (Found : N, 9·6. $C_{18}H_{14}O_2N_2$ requires N, 9·6%), was also obtained by the direct action of pyridine on methoxyphenylchloroacetonitrile.

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