225. *Action of Acidic Reagents on Methyl 2-Arylvinylcarbamates.*

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N-2-Arylvinylcarbamates with activating substituents in the ring are converted into 2-arylnaphthalenes by acidic reagents. With phosphorus oxychloride, methyl styrylcarbamate yields predominantly 3 : 5-diphenylpyridine.

Dey and Parikshit [1] obtained in high yield a neutral nitrogen-free compound, m. p. 200°, by the action of alcoholic hydrogen chloride or phosphorus oxychloride in toluene or hot dilute sulphuric acid on methyl *N*-3 : 4-methylenedioxystyrylcarbamate. In a re-investigation we found that the melting point and analysis agreed with those for 2 : 3-methylenedioxy-6-(3 : 4-methylenedioxyphenyl)naphthalene,[2] and that its ultraviolet absorption was that of a 2-arylnaphthalene. The compound should have resulted by the condensation of two molecules of homopiperonaldehyde produced by hydrolysis of the carbamate.

2 : 3-Dimethoxy-6-(3 : 4-dimethoxyphenyl)naphthalene was similarly prepared from methyl *N*-(3 : 4-dimethoxystyryl)carbamate and its melting point and absorption spectrum agreed with those reported by Bailey, Robinson, and Staunton [3] who had obtained it by dehydrogenation of a by-product in the Leuckart reaction on 2-(3 : 4-dimethoxyphenyl)-1 : 2 : 3 : 4-tetrahydro-6 : 7-dimethoxy-1-oxonaphthalene. The structure was confirmed by comparison with a specimen synthesised as follows: Veratrole was subjected to a Friedel–Crafts reaction with 3 : 4-dimethoxyphenylsuccinic anhydride, to give α-(3 : 4-dimethoxyphenyl)-β-veratroylpropionic acid. Clemmensen reduction followed by cyclisation then gave the tetralone, which by a second Clemmensen reduction followed by dehydrogenation yielded 6-(3 : 4-dimethoxyphenyl)-2 : 3-dimethoxynaphthalene.

2-Methoxy-6-*m*-methoxyphenyl-, 6-(2 : 3-dimethoxyphenyl)-1 : 2-dimethoxy-, and 6-(2 : 5-dimethoxyphenyl)-1 : 4-dimethoxy-naphthalene have also been prepared in fair yield from the corresponding carbamates. The action of phosphoric oxide on methyl 2-β-naphthyl- and 2-9′-phenanthryl-vinylcarbamate gave products in *ca.* 1·5 and 25% yield respectively to which, in analogy with the previous examples, the structures 2-β-naphthylphenanthrene and 6-9′-phenanthryltriphenylene may be assigned. Under the same conditions methyl 2-α-naphthylvinylcarbamate yielded a nitrogen-containing compound which was not further investigated.

Treatment of methyl styrylcarbamate with cold alcoholic hydrogen chloride or with

[1] Dey and Parikshit, *Proc. Nat. Inst. Sci. India*, 1945, **11**, 37.
[2] Erdtman and Robinson, *J.*, 1933, 1530.
[3] Bailey, Robinson, and Staunton, *J.*, 1950, 2277.

phosphorus oxychloride in boiling toluene led to uncrystallisable resins. The last reagent in cold benzene, however, gave a neutral, unidentified compound, $C_{14}H_{15}O_2N$, and a base, $C_{17}H_{13}N$, m. p. 138—139°, in *ca.* 30—40% yield. The base yielded, readily in the cold, a methiodide which was oxidised by aqueous potassium permanganate to benzoic acid. The base could not be reduced in neutral or acid solution, but its methiodide was reduced in methanol in presence of Adams catalyst, with absorption of 3 mols. of hydrogen, to a mixture of two isomeric bases separated by crystallisation of the hydrochlorides. The major product was converted by a two-stage Hofmann degradation into a nitrogen-free oil which yielded only benzoic acid on oxidation. This observation taken in conjunction with the molecular formula suggested that the base could be a diphenylpyridine, and its properties corresponded with those of 3 : 5-diphenylpyridine prepared recently by Eliel, McBride, and Kaufmann;[4] comparison with a sample kindly provided by Dr. E. L. Eliel confirmed the identity. Incidentally, it may be noted that two products are formed by reduction of 3 : 5-diphenylpyridine methiodide, the major product being presumably the more stable *cis*-1-methyl-3 : 5-diphenylpiperidine.

Experimental

Ultraviolet measurements are for 95% ethanol solutions.

2 : 3-*Methylenedioxy*-6-(3 : 4-*methylenedioxyphenyl*)*naphthalene*.—A solution of methyl *N*-(3 : 4-methylenedioxystyryl)carbamate [1] (2 g.) in alcohol (50 ml.) was saturated at 0° with hydrogen chloride. The precipitate, recrystallised from acetic acid, gave the naphthalene (1·1 g.), m. p. 200—201°, $\lambda_{max.}$ 233, 260, 305 mμ (log ε 4·60, 4·52, 4·24) (Found: C, 74·0; H, 3·8. Calc. for $C_{18}H_{12}O_4$: C, 74·0; H, 4·1%) (Erdtman and Robinson [2] reported m. p. 201°). The naphthalene could also be got from the carbamate by the action of phosphorus oxychloride or phosphoric oxide in boiling toluene.

6-(3 : 4-*Dimethoxyphenyl*)-2 : 3-*dimethoxynaphthalene*.—3 : 4-*Dimethoxycinnamamide*. 3 : 4-Dimethoxycinnamic acid [5] (10 g.) in benzene (50 ml.) was refluxed with thionyl chloride (10 ml.) at 100° for 1 hr. The resulting solution was added gradually to an excess of aqueous ammonia (*d* 0·9) at 0° with stirring during 2 hr. The precipitate was filtered off and washed with water. Crystallisation from alcohol gave the amide (8 g.), m. p. 166° (Found: C, 64·0; H, 6·6; N, 6·8. Calc. for $C_{11}H_{13}O_3N$: C, 63·8; H, 6·3; N, 6·8%) (Lorz *et al.*[6] reported m. p. 166·5°).

Methyl N-3 : 4-*dimethoxystyrylcarbamate*. The foregoing amide (8 g.) dissolved in the minimum quantity of cold methanol was treated slowly with 5% aqueous sodium hypochlorite [7](48·8 ml.) with good shaking. The mixture was heated at 100° for a few minutes and cooled. The precipitate was crystallised from alcohol, to give the *carbamate* (5·4 g.), m. p. 104° (Found: C, 60·7; H, 6·3; N, 6·0. $C_{12}H_{15}O_4N$ requires C, 60·8; H, 6·3; N, 5·9%).

6-(3 : 4-*Dimethoxyphenyl*)-2 : 3-*dimethoxynaphthalene*. The above carbamate (2 g.) in alcohol (30 ml.) was saturated with hydrogen chloride at 0°, evaporated to the point of crystallisation, and left at 0°. The precipitate, on recrystallisation from alcohol, gave the *naphthalene* (1 g.), m. p. 178°, undepressed on admixture with another specimen (see below), $\lambda_{max.}$ 230, 260, 295 mμ (log ε 4·47, 4·53, 4·36) (Found: C, 74·2; H, 6·3. $C_{20}H_{20}O_4$ requires C, 74·1; H, 6·2%).

6-(2 : 3-*Dimethoxyphenyl*)-1 : 2-*dimethoxynaphthalene*.—2 : 3-Dimethoxycinnamic acid [8] (8 g.) was converted through the *amide* (6 g.), m. p. 131° (Found: C, 64·2; H 6·2; N, 6·7%), into *methyl* N-2 : 3-*dimethoxystyrylcarbamate* (3·8 g.), m. p. 138° (from dilute alcohol) (Found: C, 61·0; H, 6·0; N, 5·7%). Treatment of this with alcoholic hydrogen chloride did not give the naphthalene. The carbamate (2 g.), dry toluene (16 ml.), and phosphorus oxychloride (6 ml.) were refluxed for 3 hr. The mixture was decomposed with ice, and the neutral material from the product chromatographed in benzene over alumina. The residue from the eluate crystallised from dilute alcohol or light petroleum, to yield needles of 6-(2 : 3-*dimethoxyphenyl*)-1 : 2-*dimethoxynaphthalene* (0·25 g.), m. p. 68—69°, $\lambda_{max.}$ 230, 253, 290 mμ (log ε 4·67, 4·70, 4·05) (Found: C, 74·2; H, 6·3%).

[4] Eliel, McBride, and Kaufmann, *J. Amer. Chem. Soc.*, 1953, **75**, 4291.
[5] Robinson and Shinoda, *J.*, 1925, **127**, 1977.
[6] Lorz, Albro, and Baltzly, *J. Amer. Chem. Soc.*, 1951, **73**, 483.
[7] Weerman, *Annalen*, 1913, **401**, 6.
[8] Haworth, *J.*, 1927, 2282.

6-(2 : 5-*Dimethoxyphenyl*)-1 : 4-*dimethoxynaphthalene*.—2 : 5-Dimethoxycinnamic acid[9] (8 g.) gave the *amide* (7·2 g.), m. p. 168° (from alcohol) (Found : C, 64·2; H, 6·2; N, 6·7%), and then *methyl* N-(2 : 5-*dimethoxystyryl*)*carbamate* (5 g.), m. p. 97° (from dilute alcohol) (Found : C, 61·0; H, 6·3; N, 6·1%). An alcoholic solution of the carbamate (1 g.) was saturated with hydrogen chloride and then evaporated. The residue was washed with water and dried. Purification by chromatography gave 6-(2 : 5-*dimethoxyphenyl*)-1 : 4-*dimethoxynaphthalene* (0·3 g.) as light greenish-yellow cubes (from alcohol), m. p. 99°, $\lambda_{max.}$ 220, 255, 310 mμ (log ε 4·65, 4·45, 4·10) (Found : C, 74·2; H, 6·1%).

2-*Methoxy*-6-m-*methoxyphenylnaphthalene*.—3-Methoxycinnamic acid[10] (6 g.) gave the *amide* (4·7 g.), m. p. 133° (from alcohol) (Found : C, 67·6; H, 6·6; N, 8·0. $C_{16}H_{11}O_2N$ requires C, 67·8; H, 6·2; N, 7·9%), which in turn yielded *methyl* N-3-*methoxystyrylcarbamate* (2·7 g.), m. p. 111° (from alcohol) (Found : C, 64·2; H, 5·9; N, 7·0. $C_{11}H_{13}O_3N$ requires C, 63·8; H, 6·3; N, 6·8%). Treatment of this with alcoholic hydrogen chloride and purification of the product by chromatography gave 2-*methoxy*-6-m-*methoxyphenylnaphthalene* (0·4 g.), m. p. 92° (from alcohol), $\lambda_{max.}$ 225, 255, 297 mμ (log ε 4·55, 4·60, 4·20) (Found : C, 81·4; H, 6·5. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1%).

Action of Phosphorus Oxychloride on Methyl 2-α-*Naphthylvinylcarbamate*.—β-1-Naphthylacrylic acid[11] (10 g.) gave the amide (9 g.), m. p. 173° (Found : C, 79·3; H, 5·6; N, 7·0. Calc. for $C_{13}H_{11}ON$: C, 79·2; H, 5·6; N, 7·1%) (Jensen and Christenson[11] recorded m. p. 172—173°), which yielded methyl 2-α-naphthylvinylcarbamate (4·2 g.), m. p. 121° (from alcohol) (Found : C, 74·2; H, 5·6; N, 6·4. Calc. for $C_{14}H_{13}O_2N$: C, 74·0; H, 5·7; N, 6·2%) (Jensen and Christenson[11] recorded m. p. 121°). Treatment of the carbamate with alcoholic hydrogen chloride failed to yield crystallisable material. The carbamate (1 g.) was refluxed with phosphorus oxychloride (3 ml.) in toluene (10 ml.) for 3 hr. Purification of the neutral matter from the reaction by chromatography and crystallisation from alcohol gave an unidentified *compound* as greenish-yellow needles (0·2 g.), m. p. 168° (Found : C, 84·5; H, 5·8; N, 4·2. $C_{21}H_{17}ON$ requires C, 84·3; H, 5·7; N, 4·7%). This was obtained also by the use of phosphoric oxide instead of oxychloride.

2-2′-*Naphthylphenanthrene*.—β-2-Naphthylacrylic acid[12] (10 g.) was converted through the *amide* (8·5 g.), m. p. 193° (from alcohol) (Found : C, 79·6; H, 5·6; N, 7·2%), into *methyl* 2-2′-*naphthylvinylcarbamate* (3·7 g.), m. p. 122° (from benzene) (Found : C, 73·3; H, 6·1; N, 6·2%). This (1 g.) was refluxed with phosphoric oxide (5 g.) in xylene (10 ml.) for 2 hr. The neutral matter from the product was passed in benzene through alumina. The residue from evaporation of the eluate, after two crystallisations from alcohol, gave the *phenanthrene* (10 mg.), m. p. 234—235° (Found : C, 95·4; H, 4·9. $C_{24}H_{16}$ requires C, 94·7; H, 5·3%).

6-9′-*Phenanthryltriphenylene*.—2-9′-Phenanthrylacrylic acid[13] (5 g.) gave the *amide* (3·4 g.), m. p. 227° (from alcohol) (Found : C, 82·6; H, 5·0; N, 5·6. $C_{17}H_{13}ON$ requires C, 82·6; H, 5·3; N, 5·7%), and then *methyl* 2-9′-*phenanthrylvinylcarbamate* (1·5 g.), m. p. 155—157° (from benzene) (Found : C, 78·6; H, 5·0; N, 5·3. $C_{18}H_{15}O_2N$ requires C, 78·0; H, 5·4; N, 5·1%). The carbamate (0·5 g.) on being refluxed with phosphoric oxide (5 g.) in toluene (10 ml.) for 2 hr. and chromatographed (neutral product), gave the *hydrocarbon*, pale yellow cubes (from light petroleum, b. p. 60—80°), m. p. 214—216°, $\lambda_{max.}$ 260 mμ (log ε 5·10), $\lambda_{infl.}$ 303 mμ (log ε 4·45) (Found : C, 94·6; H, 5·3. $C_{32}H_{30}$ requires C, 95·0; H, 5·0%).

6-(3 : 4-*Dimethoxyphenyl*)-2 : 3-*dimethoxynaphthalene*.—α-(3 : 4-*Dimethoxyphenyl*)-β-*veratroylpropionic acid*. Veratrole (11 g.) and aluminium chloride (12 g.) were added to 3 : 4-dimethoxyphenylsuccinic anhydride (9·4 g.) in nitrobenzene (30 ml.) with stirring. After 48 hr. the mixture was decomposed with ice and hydrochloric acid and diluted with water (600 ml.). After removal of nitrobenzene by steam-distillation, the acid separated and was filtered off. More was obtained after precipitation of aluminium from the mother-liquor by sodium carbonate and acidification of the filtrate. The total acid (7·4 g.), after three crystallisations from alcohol, melted at 186—188° (Found : C, 64·5; H, 5·6. Calc. for $C_{20}H_{22}O_7$: C, 64·1; H, 6·0%) (Richardson, Robinson, and Seijo[14] reported m. p. 193—194°).

[9] Posternak and Castro, *Helv. Chim. Acta*, 1948, **31**, 536.
[10] Chakravarti, Haworth, and Perkin, *J.*, 1927, 2269.
[11] Jensen and Christenson, *Acta Chem. Scand.*, 1950, **4**, 703.
[12] Monier-Williams, *J.*, 1906, **89**, 277.
[13] Bachmann and Kloetzel, *J. Amer. Chem. Soc.*, 1937, **59**, 2207.
[14] Richardson, Robinson, and Seijo, *J.*, 1937, 835.

(3 : 4-*Dimethoxyphenyl*)-1 : 2 : 3 : 4-*tetrahydro*-6 : 7-*dimethoxy*-1-*oxonaphthalene*.—The preceding acid (5 g.) reduced by the Clemmensen procedure gave αγ-di-(3 : 4-dimethoxyphenyl)-butyric acid (3 g.) as a viscous oil. This was shaken with 50% sulphuric acid (35 ml.) at 100° for 15 min. and the mixture extracted with ether. The ethereal layer was washed with alkali and evaporated. Crystallisation of the residue from alcohol gave the tetralone (1 g.), m. p. 150° (Found: C, 70·1; H, 6·0. Calc. for $C_{20}H_{22}O_5$: C, 70·2; H, 6·4%) (Richardson *et al.*[14] give m. p. 147—149°).

6-(3 : 4-*Dimethoxyphenyl*)-5 : 6 : 7 : 8-*tetrahydro*-2 : 3-*dimethoxynaphthalene*.—The above tetralone (1 g.), reduced by the Clemmensen procedure, gave the *tetrahydronaphthalene*, m. p. 117° (from dilute alcohol) (Found: C, 73·5; H, 7·5. $C_{20}H_{24}O_4$ requires C, 73·2; H, 7·3%).

6-(3 : 4-*Dimethoxyphenyl*)-2 : 3-*dimethoxynaphthalene*.—The foregoing tetrahydronaphthalene (0·3 g.), dehydrogenated with 5% palladium–charcoal (0·2 g.) in *p*-cymene (40 ml.), gave the naphthalene, crystallising from alcohol as plates, m. p. 178° (Found: C, 74·3; H, 6·3%) (Bailey, Robinson, and Staunton [3] recorded m. p. 179—180°).

3 : 5-*Diphenylpyridine*.—A solution of methyl styrylcarbamate [7] (20 g.) in benzene (200 ml.) containing phosphorus oxychloride (60 ml.) was left at 30° for 5 days. After decomposition with ice, the aqueous acidic layer was separated, and the benzene layer extracted with N-hydrochloric acid (3 × 50 ml.). The combined acid extracts were shaken twice with ether, basified by addition of solid potassium carbonate, and extracted repeatedly with ether. Evaporation of the dried (KOH) extracts and crystallisation of the residue from alcohol gave 3 : 5-diphenylpyridine (3—4 g.) as plates, m. p. and mixed m. p. 137—138°, $\lambda_{max.}$ 245 (log ε 4·40), $\lambda_{infl.}$ 295 mμ (log ε 3·65) (Found: C, 88·3, 88·2; H, 5·5, 5·5; N, 6·1, 6·1. Calc. for $C_{17}H_{13}N$: C, 88·3; H, 5·6; N, 6·1%), yielding a picrate, yellow needles (from acetic acid), m. p. 201—202°, and a hydrochloride, needles (from alcohol–ether), m. p. 187—189°. The methiodide, prepared by methyl iodide in chloroform at 30°, formed pale yellow needles (from alcohol), m. p. 203—205°, $\lambda_{max.}$ 260, 315 mμ (log ε 4·40, 3·75) (Found: C, 57·6; H, 4·2; N, 4·0. Calc. for $C_{18}H_{16}NI$: C, 57·9; H, 4·3; N, 3·7%) (Eliel, McBride, and Kaufmann [4] reported m. p.s: picrate, 204—205·5°; hydrochloride, 194—195°; methiodide, 202—203°).

The acid-washed benzene solution from the reaction left on evaporation a gum which solidified on long contact with alcohol. Crystallisation from alcohol gave colourless needles of a neutral *substance* (Found: C, 73·3; H, 6·2; N, 6·4. $C_{14}H_{15}O_2N$ requires C, 73·4; H, 6·6; N, 6·1%).

Oxidation of 3 : 5-*Diphenylpyridine Methiodide*.—A suspension of the above methiodide (1 g.) in water (75 ml.) containing potassium permanganate (1 g.) was refluxed with addition of more of a 2·5% solution of the oxidant, till a pink colour persisted. The mixture was filtered and the manganese dioxide residue washed with hot water. The filtrate was concentrated to a small volume and saturated with sulphur dioxide. The precipitated benzoic acid, after crystallisation from water, had m. p. and mixed m. p. 120—121°.

cis- *and* trans-1-*Methyl*-3 : 5-*diphenylpiperidine*.—3 : 5-Diphenylpyridine methiodide (3·5 g.) in methanol (100 ml.) was shaken with hydrogen (60 lb./sq. in.) in the presence of Adams catalyst (0·35 g.) till absorption of hydrogen ceased (5 hr.; 3 mols.). The solution was filtered from the catalyst which was washed with more methanol. The filtrate was evaporated and the residual gum triturated with alkali. Extraction with ether and evaporation gave an oil (2·1 g.) which was treated in ether with hydrogen chloride. Addition of dry ether to an alcoholic solution of the precipitate gave needles of cis-1-*methyl*-3 : 5-*diphenylpiperidine hydrochloride* (0·7 g.), m. p. 209—212°, raised by a second crystallisation from the same solvent mixture to 215—217° (Found: C, 74·6, 74·6; H, 7·5, 7·6. $C_{18}H_{22}NCl$ requires C, 75·1; H, 7·7%) and yielding, by basification and ether-extraction, the base, needles (from light petroleum), m. p. 58—61°. The *methiodide*, obtained by methyl iodide in chloroform at 100°, formed plates (from alcohol), m. p. 233—234°, $\lambda_{infl.}$ 257 mμ (log ε 2·35) (Found: C, 57·8; H, 5·9. $C_{19}H_{24}NI$ requires C, 58·0; H, 6·1%).

The alcohol–ether mother-liquor from the crystallisation of the above hydrochloride was evaporated and the residue converted into the free base (0·65 g.) and then into the methiodide by methyl iodide in chloroform at 100°. The gum thus obtained was dissolved in alcohol and treated with small volumes of ether, step-wise. After the separation of more (0·3 g.) of the *cis*-methiodide, m. p. and mixed m. p. 232—234°, trans-1 : 1-*dimethyl*-3 : 5-*diphenylpiperidinium iodide* (0·15 g.) was obtained. Recrystallised from alcohol–ether, it had m. p. 231—234°, and mixed m. p. with the *cis*-isomer, 195—200°, $\lambda_{infl.}$ 257 mμ (log ε 2·66) (Found: C, 58·3, 58·4; H, 6·0, 6·3%).

Degradation. The *cis*-methiodide (1 g.), 50% potassium hydroxide solution (20 ml.), and alcohol (20 ml.) were refluxed for 3 hr. The solution was cooled, diluted with water, and extracted with ether. The ether layer was dried (K_2CO_3) and treated with hydrogen chloride. Recrystallisation of the precipitate from alcohol–ether mixture gave the *methine hydrochloride* (0·6 g.), m. p. 205—206° (Found: C, 75·0; H, 8·0. $C_{19}H_{24}NCl$ requires C, 75·6; H, 7·6%). The *base*, got from the hydrochloride by basification and ether extraction, was an oil, b. p. 141—142°/0·05 mm. (Found: C, 85·9; H, 8·4. $C_{19}H_{23}N$ requires C, 86·0; H, 8·7%).

This base (1·2 g.), after being heated with methyl iodide (3 g.) in chloroform (20 ml.) for 2 hr., gave on evaporation a gummy methiodide. This was converted into the methohydroxide by shaking its aqueous solution for 3 hr. with silver oxide (from 5 g. of silver nitrate), filtering, and evaporating the filtrate to dryness at 50° *in vacuo*. The methohydroxide was boiled with 50% potassium hydroxide solution (20 ml.), and the product distilled with steam. The distillate was made acidic and extracted with ether. The ether layer was separated, washed with alkali and then with water and dried (Na_2SO_4). Evaporation left a pale yellow oil (0·4 g.), b. p. 88°/0·05 mm. (Found: C, 89·4; H, 7·3%).

This oil (0·4 g.) was treated with potassium permanganate (2·5 g.) in acetone (85 ml.). The solution was filtered. The manganese dioxide residue was boiled with water and filtered. The filtrate was concentrated and acidified. The precipitated benzoic acid, after crystallisation from water, had m. p. and mixed m. p. 120—121°.

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