

64. *Researches on Acetylenic Compounds. Part LXII.* The Preparation and Some Synthetical Applications of Penta-1,2,4-triene and Penta-1,2-dien-4-yne.*

By E. R. H. JONES, H. H. LEE, and M. C. WHITING.

Penta-1,2,4-triene and penta-1,2-dien-4-yne, the first simple ethylenic and acetylenic derivatives of allene, have been prepared by convenient and apparently general methods. Some of their reactions, especially Diels-Alder reactions of the triene, have been investigated.

ALTHOUGH several fungal metabolites¹ contain the systems $R^1C\equiv C-CH=C-CHR^2$ and $R^3CH=C=CH-CH=CHR^4$, the parent hydrocarbons, penta-1,2-dien-4-yne (II) and penta-1,2,4-triene (IV), are unknown. This paper describes their syntheses and some of their reactions.

Penta-1,4-diyn-3-ol, now readily available from the reaction of ethynylmagnesium bromide and ethyl formate,² was converted in 35–45% yield into 3-chloropenta-1,4-diyne (I) with thionyl chloride and pyridine. Treatment of the chloro-compound (I) with a zinc-copper couple³ in butanol at 5–10° gave 60% of a mixture of three hydrocarbons, with the major component constituting about 95%. This, isolated by gas-liquid chromatography, had b. p. 57° (slight decomp.) and had ultraviolet and infrared spectra in accord with the structure (II). The minor components were the triene (IV) and an acetylenic hydrocarbon, possibly a pentenyne. When the reaction with the zinc-copper couple was carried out at a higher temperature (ca. 35°), a lower yield (40%) of a mixture of hydrocarbons was obtained. Gas-liquid chromatography indicated that this mixture consisted of about 71% of (II), 27% of (IV), and 2% of an unknown hydrocarbon. Attempts to convert the mixture into pentatriene (IV) by further reduction at 60–65° with an excess of the zinc-copper couple were unsuccessful, no appreciable change in composition being detected.

The pentadienyne (II) readily underwent oxidative coupling to give an unstable solid, m. p. 35–36°, which showed the expected ultraviolet and infrared spectra for deca-1,2,8,9-tetraene-4,6-diyne (III), and this was further supported by its ready isomerization with base to the known deca-2,4,6,8-tetrayne.

A more convenient preparation of penta-1,2,4-triene (IV) was found in the reaction of a mixture of chloropentenynes, obtained⁴ from pent-1-en-4-yn-3-ol, with the zinc-copper couple, which gave in 75% yield a mixture of hydrocarbons from which the triene (IV) (~94%) could be readily separated by fractional distillation. Alternatively, and preferably, pure *trans*-5-chloropent-3-en-1-yne, from *trans*-pent-2-en-4-yn-1-ol,⁴ gave under similar conditions a 70% yield of pentatriene of ~97% purity. The triene (IV), b. p. 47.5–48°, had the expected spectral properties and was fairly stable at 20° under nitrogen or in the presence of quinol. When heated to 110° in a sealed tube with quinol it exploded violently.

It seemed probable that penta-1,2,4-triene would undergo Diels-Alder reactions under milder conditions than are needed for the isomeric vinylacetylenes. This proved to be the case and, as was expected, the products were much more easily aromatized than those derived from simple dienes. It is thus clear that pentatriene (and related alkenylallenes—the method of preparation now described is in principle very flexible) may have synthetical value for the preparation of aromatic derivatives (e.g., 1,5-dimethylantraquinone), apart,

* Part LXI, *J.*, 1958, 131.

¹ Celmer and Solomons, *J. Amer. Chem. Soc.*, 1953, **75**, 1372; Bu'Lock, Jones, and Leeming, *J.*, 1955, 4270; 1957, 1097.

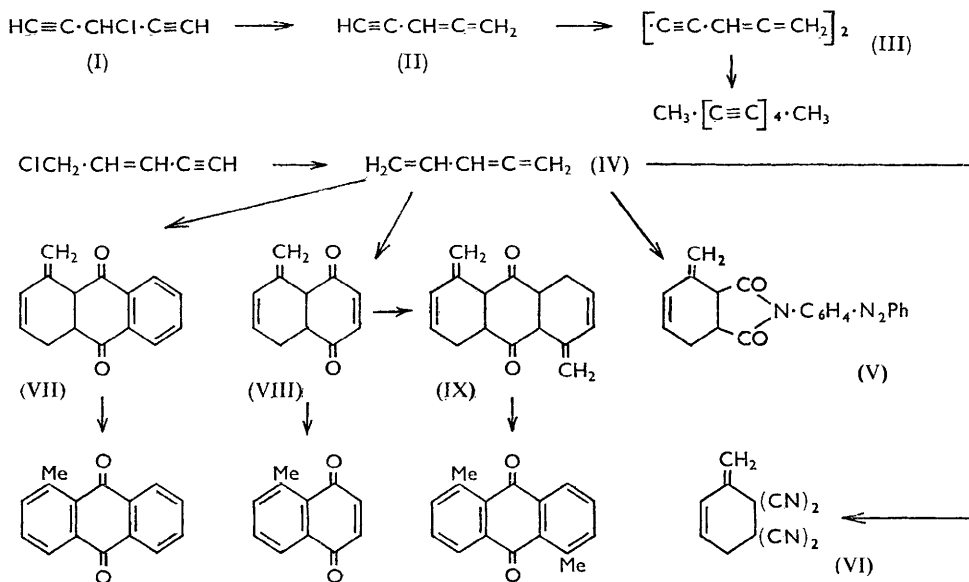
² Jones, Skatteböl, and Whiting, *J.*, 1956, 4765.

³ Hennion and Sheehan, *J. Amer. Chem. Soc.*, 1949, **71**, 1964.

⁴ Bell, Jones, and Whiting, *J.*, 1957, 2597.

of course, from giving directly some otherwise inaccessible derivatives of methylenecyclohexene. With the acetylenic dienophiles examined the interesting methylenecyclohexadiene derivatives sought were not obtained, either aromatic or polymeric products being formed.

Pentatriene (IV) reacted with *p*-phenylazomaleinanil⁵ and tetracyanoethylene⁶ under mild conditions to give crystalline adducts, which on ultraviolet and infrared evidence were assigned the structures (V) and (VI), respectively. From the reaction of the triene (IV) with dimethyl acetylenedicarboxylate only dimethyl 3-methylphthalate was isolated, identified as 3-methylphthalic acid and its anhydride. When pentatriene was heated with 1,4-naphthaquinone in ethanol a crystalline adduct (VII) was formed, which was stable to 0.01N-hydrochloric acid (ultraviolet spectrum unchanged after 16 hr.) but was converted immediately in the presence of charcoal (pH ~8) into 1-methylantraquinone. Equimolar quantities of pentatriene and *p*-benzoquinone after 3 days at room temperature gave a rather unstable adduct, m. p. 33–34°. The ultraviolet and infrared absorption spectra agreed with structure (VIII), which was confirmed by conversion under alkaline



conditions, by aerial oxidation, to 5-methyl-1:4-naphthaquinone. The monoadduct (VIII) underwent further addition of pentatriene to give a stable compound which is assigned structure (IX) since it was converted quantitatively into the known, but not readily accessible, 1,5-dimethylantraquinone, further identified as dimethyl anthraquinone-1,5-dicarboxylate.

The infrared spectra of the products discussed require little comment; the two allenes showed strong bands at 840 (pentadienyne) and 845 cm^{-1} (pentatriene), while the decatetraenediyne (III) absorbed at 840 and 848 cm^{-1} . All are in the usual range for the $\text{>C}=\text{C}=\text{CH}_2$ out-of-plane deformation.⁷ In the Diels–Alder adducts this band appeared near to the usual position of 890 cm^{-1} . The ultraviolet spectra showed, in addition to absorption

⁵ Naylor and Whiting, *J.*, 1955, 2970.

⁶ Cairns, Carboni, Coffman, Engelhardt, Heckert, Little, McGeer, McKusick, Middleton, Scribner, Theobald, and Winberg, *J. Amer. Chem. Soc.*, 1958, **80**, 2775.

⁷ Jones, Whitham, and Whiting, *J.*, 1957, 4628.

attributed to other chromophores, a conjugated diene band at *ca.* 2250 Å (ϵ *ca.* 10,000), reduced in intensity (to ϵ 2900) but not changed in position, in the tetracyano-derivative, presumably through the strong electrostatic effect of these substituents. The *p*-benzoquinone adduct showed a long-wavelength band at 3100 Å (ϵ 215) (with signs of a shoulder, ϵ *ca.* 50, at *ca.* 3600 Å), as compared with λ_{max} 3600 Å (ϵ 71) for the corresponding butadiene adduct,⁸ and similar values for typical *cisoid* O=C-C=C-C=O compounds without other unsaturated linkages.⁸ These differences clearly concern intra-annular effects of the type first described by Bowden and Jones,⁹ and clarified in Part LII.¹⁰

EXPERIMENTAL

M. p.s were determined on a Kofler block and are corrected; b. p.s are uncorrected. "Light petroleum" refers to the fraction of b. p. 40–60°. "Deactivated alumina" was Peter Spence "Grade H" alumina neutralized and deactivated with 5% of 10% acetic acid.

3-Chloropenta-1,4-diyne (I).—Purified thionyl chloride (57 g.) was added, dropwise with stirring, during 1.5 hr. to a solution of penta-1,4-diyn-3-ol² (36 g.) in dry pyridine (38 g.) at 25–30°. When addition was complete, the dark viscous mixture was warmed cautiously to 45–50°, whereupon vigorous effervescence occurred. The mixture was kept at 45–50° for 1 hr., then cooled and treated with ice-water (200 c.c.). The chloride was separated from the polymeric material by distillation at 40–50° (bath temp.)/10 mm. into two receivers connected in series and cooled to –75°. The distillate was poured into a mixture of ether (100 c.c.) and water, and the ethereal layer was separated, washed successively with saturated hydrogen carbonate solution and water, and dried (CaCl₂). Ether was removed under partial reflux (–10°) at 200 mm. in nitrogen. Distillation of the residue afforded the acetylenic *chloride* (18.2 g.; 41%), b. p. 43–44°/90 mm., n_D^{19} 1.4640 (Found: C, 61.2; H, 3.3. C₅H₃Cl requires C, 60.95; H, 3.05%). The chloride coloured rapidly at room temperature, but solidified at –40°, and could be stored at that temperature for several months; it showed ν_{max} (CS₂) 3300 (\equiv CH) and 710 cm.^{–1} (C–Cl), negligible absorption at 1950 cm.^{–1}. Its ultraviolet spectrum showed only weak end absorption.

Penta-1,2-dien-4-yne (II).—A solution of 3-chloropenta-1,4-diyne (6 g.) in butanol (10 c.c.) was added, dropwise, under nitrogen to a rapidly stirred mixture of zinc–copper couple³ (5 g.) in butanol (30 c.c.), the temperature of the mixture being kept at 5–10°. After 5 hours' stirring the hydrocarbon was distilled directly from the mixture at 25–40° (bath temp.)/10 mm. into two receivers connected in series and cooled to –75°. Redistillation of the product after drying (CaCl₂) gave an almost colourless liquid (2.4 g.; 61%) which turned yellow rapidly at room temperature, b. p. 35–37°/250 mm., n_D^{20} 1.4790. Gas-liquid chromatography (dibutyl phthalate on firebrick, 65°, nitrogen) showed a major peak (~95%) well separated from two other lower-boiling components (4% and 1%, respectively, judged by peak heights). The major component, collected in a receiver cooled with liquid air, was pure *penta-1,2-dien-4-yne*, b. p. 57° (slight decomp.), n_D^{18} 1.4850 (Found: C, 93.3; H, 6.3. C₅H₄ requires C, 93.75; H, 6.25%); λ_{max} (in ethanol) 2115 Å (ϵ 11,000), inflexion 2220 Å (ϵ 8,900); ν_{max} (carbon disulphide and tetrachloride) included bands at 3300, 2120 ($\text{--C}\equiv\text{CH}$), 1975, 1950 (>C=C<), 938, and 840 (=CH_2) cm.^{–1}. The two minor components, collected together, similarly were found to be a mixture containing mainly penta-1,2,4-triene (see below) and a small amount of another acetylene responsible for a band at 3300 cm.^{–1}.

In another experiment, the reaction mixture was kept at 25–35° during addition of the chloride and then at 35–50° for a further 3 hr. The product, isolated in 41% yield, was shown by gas-liquid chromatography to consist of 71% of penta-1,4-dien-4-yne, 27% of penta-1,2,4-triene, and 2% of an unknown hydrocarbon. Stirring and heating the mixture in butanol with excess of zinc–copper couple at 60–65° for 6 hr. did not change the composition appreciably.

Penta-1,2,4-triene (IV).—(a) A solution of pure *trans*-5-chloropent-3-en-1-yne⁴ (freshly redistilled; 3.1 g.) in butanol (5 c.c.) was added dropwise to a rapidly stirred mixture of zinc–copper couple³ (3 g.), the temperature being kept at 35–40°. The mixture was stirred for a further 2.5 hr. and the product was distilled from the mixture into two receivers, connected in

⁸ Bartrop and Topliss, unpublished work.

⁹ Bowden and Jones, *J.*, 1946, 52.

¹⁰ Jones, Mansfield, and Whiting, *J.*, 1956, 4073.

series and cooled to -75° , at $20-40^{\circ}$ (bath temp.)/100—10 mm. On redistillation the *penta-1,2,4-triene* (1.42 g.; 72%) had b. p. $46.5-47.5^{\circ}$, n_D^{19} 1.4710—1.4715. Gas-liquid chromatography showed two peaks, the major one being of $\sim 97\%$ quantity, although agreement in refractive index with the analysed sample (below) is only moderately good.

(b) A solution of mixed chloropentenyne (56 g.) in butanol (60 c.c.) was added dropwise during 1.5 hr. to a rapidly stirred mixture of zinc-copper couple⁸ (65 g.), the temperature being kept at $35-40^{\circ}$ by occasional cooling with ice. After a further 2 hours' stirring the product was distilled at $20-40^{\circ}$ (bath temp.)/100—10 mm. into two receivers cooled to -75° . Drying (CaCl_2) and distillation gave the hydrocarbon, b. p. $45-47^{\circ}$, n_D^{17} 1.4620—1.4740 (27 g.; 73%). Gas-chromatographic analysis of a sample showed the presence of three peaks with the major component constituting 94%. Redistillation of the appropriate fractions furnished a sample of $\sim 98\%$ purity, b. p. $47.5-48^{\circ}$, n_D^{18} 1.4750 (Found: C, 90.85; H, 9.35. C_5H_6 requires C, 90.85; H, 9.15%); λ_{max} (in ethanol) 2165 Å (ϵ 15,600); ν_{max} (in carbon disulphide and tetrachloride) 1940, 990, 900, and 845 cm^{-1} .

Penta-1,2,4-triene decomposed comparatively slowly at room temperature ($15-17^{\circ}$) as shown by the change in refractive index (from 1.4750 to 1.4780) of a sample after 6 hr. in the presence of air. A sample was stored at -40° for several months without evident decomposition. The hydrocarbon exploded violently when heated to 110° in a sealed tube in the presence of quinol.

Deca-1,2,8,9-tetraene-4,6-diyne (III).—Penta-1,2-dien-4-yne (1.0 g.), cuprous chloride (4 g.), and ammonium chloride (6 g.) in water (50 c.c.) were shaken in the dark with oxygen for 4.5 hr. Isolation with ether and removal of the solvent under reduced pressure afforded a mixture of oil and amorphous solid, which was dissolved in light petroleum (50 c.c.) and filtered to remove insoluble polymer. The filtrate was concentrated (~ 20 c.c.) and cooled to -75° in the dark, whereupon cream-coloured needles separated. Three recrystallizations at -70° in the dark afforded the pure *hydrocarbon* (210 mg., 21%), m. p. $35-36^{\circ}$ (Found: C, 93.6; H, 4.9. C_{10}H_8 requires C, 95.2; H, 4.8%); λ_{max} 2165 (ϵ 47,000), 2560 (ϵ 84,000), 2710 (ϵ 14,700), 2875 (ϵ 21,000), and 3055 (ϵ 17,000), infl. 2420 Å (ϵ 21,300); ν_{max} (in carbon disulphide and tetrachloride) 2250, 2100, 1960, 1930, 848, and 840 cm^{-1} . The hydrocarbon darkened slightly after exposure to light and air for 1 hr.; overnight at room temperature it became dark brown and completely insoluble in light petroleum.

Deca-2,4,6,8-tetrayne.—A solution of the hydrocarbon (IV) (270 mg.) in methanol (10 c.c.) was treated with 5% methanolic potassium hydroxide (10 c.c.) at 0° and then set aside in the dark at -8° for 10 hr. Dilution with water and isolation with ether yielded a brown solid (131 mg.) which crystallized from light petroleum to give pale yellow needles of the tetrayne, turning pink after 5 min. in light, and decomposing above 85° without melting. Its light-absorption properties (in ethanol) were in agreement with earlier values; λ_{max} 2140 (ϵ 72,000), 2240 (ϵ 190,000) and 2340 Å (ϵ 266,000).

3-Methylenecyclohex-4-ene-1,2-dicarboxylic p-Phenylazoanil (V).—A mixture of *p*-phenylazomaleinanil⁵ (330 mg.), penta-1,2,4-triene (160 mg.), and dimethylformamide (2 c.c.) was set aside at 20° in the dark for 26 hr. The resulting solution was poured into water, and the adduct was isolated by extraction with ether and chromatography on neutral deactivated alumina (120 g.). From the benzene-light petroleum (1:1) eluate the *adduct* (224 mg.; 58%) was obtained; it formed orange-red needles, m. p. $155-157^{\circ}$, from light petroleum (Found: C, 73.45; H, 5.3; N, 12.1. $\text{C}_{21}\text{H}_{17}\text{O}_2\text{N}_3$ requires C, 73.45; H, 5.0; N, 12.25%); λ_{max} (in ethanol) 2260 (ϵ 24,600), and 3240 Å (ϵ 22,000) [*p*-phenylazosuccinanil has λ_{max} (in ethanol) 2260 (ϵ 15,000) and 3240 Å (ϵ 22,900)]; ν_{max} (Nujol) 895 cm^{-1} ($\text{C}=\text{CH}_2$), not shown by the succinanil.⁵

4,4,5,5-Tetracyano-3-methylenecyclohexene (VI).—Tetracyanoethylene⁶ (470 mg.) was added to penta-1,2,4-triene (400 mg.) in acetonitrile (10 c.c.) at 0° , and the solution was kept at 0° for a further 3 hr. Removal of the solvent under reduced pressure and crystallization from benzene-light petroleum afforded the *adduct* (650 mg.; 88%), m. p. $131-132^{\circ}$ (Found: C, 68.25; H, 3.2; N, 28.65. $\text{C}_{11}\text{H}_6\text{N}_4$ requires C, 68.05; H, 3.1; N, 28.85%); λ_{max} (in ethanol) 2290 Å (ϵ 2880); ν_{max} (in chloroform) 2240 and 850 cm^{-1} .

Dimethyl 3-Methylphthalate.—A mixture of penta-1,2,4-triene (1.2 g.) and dimethyl acetylenedicarboxylate (1.5 g.) was heated at $90-100^{\circ}$ for 3 hr. Distillation of the resulting mixture gave a viscous oil (750 mg.), b. p. $105-115^{\circ}/0.03$ mm., and a polymeric residue (1.09 g.).

¹¹ Armitage, Jones, and Whiting, *J.*, 1952, 2014.

Hydrolysis (10% methanolic potassium hydroxide) of the distillate (250 mg.) gave a pale yellow amorphous powder (164 mg.) which was difficult to crystallize. Sublimation at 120—150° (bath temp.)/12 mm. gave needles (86 mg.), which were recrystallized from light petroleum and had m. p. 117—118° (for 3-methylphthalic anhydride Parker and Goldblatt¹² give m. p. 118—119°); ν_{max} (Nujol) 1835, 1770, and 730 cm^{-1} . The anhydride was hydrolysed to the dicarboxylic acid, which crystallized readily from ethyl acetate–light petroleum as needles, m. p. 154—156° (decomp.) [lit.,¹² m. p. 158° (decomp.)]. Treatment of the acid with diazomethane furnished pure dimethyl 3-methylphthalate, m. p. 40—41°, as rods from aqueous methanol (lit.,¹² m. p. 42·5—44°); ν_{max} (in carbon disulphide) 1730 and 755 cm^{-1} . Comparison of infrared spectra showed that the distillate from the Diels–Alder reaction was a mixture of dimethyl 3-methylphthalate and some unidentified aromatic material.

1,4,11,12-Tetrahydro-1-methylene-9,10-dioxoanthracene (VII).—A solution of penta-1,2,4-triene (1·0 g.) and 1,4-naphthaquinone (1·5 g.) in ethanol (15 c.c.) was heated under reflux for 5 hr. and then cooled in an ice-bath. The adduct (1·60 g.) after crystallization from methanol had m. p. 77—78° (Found: C, 80·05; H, 5·35. $\text{C}_{15}\text{H}_{12}\text{O}_2$ requires C, 80·35; H, 5·4%); λ_{max} (in ethanol) 2230 (ϵ 51,000), 2500 (ϵ 10,000), 2960 (ϵ 2000), and 3050 (ϵ 2000); ν_{max} (in carbon disulphide) 1700 and 890 cm^{-1} .

1-Methylanthraquinone.—The adduct (VII) (500 mg.) in ethanol (30 c.c.) was treated with “Norite” and boiled for 10 min. More ethanol (100 c.c.) had to be added to the mixture to dissolve the yellow solid which precipitated suddenly. The filtrate, on cooling, deposited 1-methylanthraquinone (320 mg.; 64%) as yellow needles, m. p. 172—173° (Ullmann and Minajeff¹³ give m. p. 171—172°).

1,4,5,8,9,10-Hexahydro-5-methylene-1,4-dioxonaphthalene (VIII).—A mixture of *p*-benzoquinone (2·0 g.) and penta-1,2,4-triene (1·4 g.) in ethanol (25 c.c.) was set aside in the dark for 3 days at 20°. Removal of solvent under reduced pressure yielded an oil, which was redissolved in ether–light petroleum, cooled to –75°, and seeded with some crystals obtained from sublimation of a small amount of the oil at 80—100° (bath temp.)/0·03 mm. Three recrystallizations at low temperature afforded the pure adduct (2·25 g.; 68%) as pale yellow needles, m. p. 33—34° (Found: C, 75·8; H, 5·95. $\text{C}_{11}\text{H}_{10}\text{O}_2$ requires C, 75·85; H, 5·8%); λ_{max} (in ethanol), 2200 (ϵ 26,600) and 3100 (ϵ 215); ν_{max} (in carbon disulphide) 1690 and 892 cm^{-1} . The crystalline adduct partially resinsified at room temperature overnight.

5-Methyl-1,4-naphthaquinone.—A solution of the above adduct (250 mg.) in methanol (20 c.c.) was treated with 0·1N-sodium hydroxide (5 c.c.) under nitrogen at 20° for 5 min. The resulting dark green solution was poured into acetic acid (20 c.c.), and the acidic solution concentrated under reduced pressure. A saturated solution (5 c.c.) of potassium dichromate was then added, followed by a drop of concentrated sulphuric acid, and the yellow-green solution was set aside at room temperature for 15 min. Dilution with water and extraction with ether gave material which was chromatographed on deactivated alumina. From the benzene–light petroleum (1 : 5) eluate 5-methylnaphthaquinone (145 mg.; 58%) was obtained as yellow needles, m. p. 121—123° (from light petroleum) (Cooke, Dowd, and Segal¹⁴ give m. p. 122—123°) (Found: C, 76·75; H, 4·75. Calc. for $\text{C}_{11}\text{H}_8\text{O}_2$: C, 76·75; H, 4·65%).

1,4,5,8,9,10,11,12,13,14-Decahydro-1,5-dimethylene-9,10-dioxoanthracene (IX).—A solution of the monoadduct (VIII) (500 mg.) and penta-1,2,4-triene (600 mg.) in ethanol (5 c.c.) was heated under reflux for 10 hr. The solid residue, after removal of solvent under reduced pressure, was washed with ice-cold methanol (2 c.c.) and filtered, giving the adduct (400 mg.; 60%). An analytical sample, rods from methanol, had m. p. 153—157° (decomp.) (Found: C, 79·8; H, 6·75. $\text{C}_{16}\text{H}_{16}\text{O}_2$ requires C, 79·95; H, 6·7%); λ_{max} (in ethanol) 2250 (ϵ 29,000), inf. 2960 (ϵ 165); ν_{max} (Nujol) 1705, 1630, 1590, 912, and 775 cm^{-1} .

1,5-Dimethylanthraquinone.—A solution of the diadduct (IX) (50 mg.) in methanol (40 c.c.) was treated with 0·1N-sodium hydroxide (5 c.c.). A dark red colour appeared, which gradually turned brown and finally pale yellow, with the deposition of fine yellow needles (40 mg.; 80%), m. p. 191—193° (Haworth and Sheldrick¹⁵ give m. p. 190°).

Dimethyl Anthraquinone-1,5-dicarboxylate.—A mixture of 1,5-dimethylanthraquinone (140 mg.; prepared as above) and nitric acid (*d* 1·1; 3 c.c.) was heated in a sealed tube at 160—180°

¹² Parker and Goldblatt, *J. Amer. Chem. Soc.*, 1950, **72**, 2151.

¹³ Ullmann and Minajeff, *Ber.*, 1912, **45**, 687.

¹⁴ Cooke, Dowd, and Segal, *Austral. J. Chem.*, 1953, **6**, 38.

¹⁵ Haworth and Sheldrick, *J.*, 1934, 1950.

346 *Smith and Thomson: The Structure of Sorbicillin:*

for 6 hr. The dicarboxylic acid was collected by filtration, washed with ice-cold water and dried (157 mg.; 93%), m. p. $>340^{\circ}$. It was converted into the diacyl chloride, and then into the dimethyl ester which from methanol formed pale yellow leaflets, m. p. and mixed m. p. $238\text{--}239^{\circ}$ (cf. Sholl, Hass, and Meyer¹⁶ who give m. p. 236°). The infrared spectra were identical.

This work was carried out during the tenure by H. H. Lee of an I.C.I. Fellowship. We thank Dr. T. L. Cairns for a sample of tetracyanoethylene.

THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY.

[Received, July 14th, 1959.]

¹⁶ Sholl, Hass, and Meyer, *Ber.*, 1929, **62**, 109.
