

766. *Vinylanthracenes.*

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9-, 1-, and 2-Vinyl- and -isopropenyl-anthracene have been prepared by dehydration of the corresponding secondary alcohols, and 9-vinylanthracene also by Wittig's method.

THE three isomeric vinylanthracenes have not been described although preparations of 2-isopropenyl-,¹ 9-propyl-10-isopropenyl-,² 1:5-diisopropenyl-,³ and octahydro-9-vinylanthracene⁴ have been reported. Fieser and Hartwell⁵ stated that dehydration of 1-9'-anthrylethanol by potassium hydrogen sulphate, phosphoric oxide in benzene, or sulphuric acid yielded anthracene, 9-ethylanthracene, ethers, and polymeric resins.

It has now been found that distillation of 1-9'-anthrylethanol, usually from potassium hydrogen sulphate, gives 9-vinylanthracene in good yield. Uncatalysed distillation sometimes did, and sometimes did not, cause dehydration, probably depending on the purity of the sample. Distillation from solid alkali, however, gave back the starting compound. The 9-vinylanthracene differed from 9-ethylanthracene in colour, crystalline form, solubility, unsaturation value, and melting point, but the presence of unsaturation in the side-chain could not be distinguished by spectroscopic examination (ultraviolet or infrared, which will be reported later by Mr. W. F. Maddams). Its nature was proved by an independent synthesis by Wittig's method:⁶ reaction of 9-anthraldehyde with triphenylphosphinemethylene yielded identical 9-vinylanthracene.

Dehydration of the 1-1'- and 1-2'-anthrylethanol followed a similar pattern, although the yields of the vinyl compounds were generally lower through thermal polymerisation of the first-formed monomer, and the 2'-compound gave a higher yield of monomer when dehydrated in the absence of a catalyst. The structures of the 1- and 2-vinylanthracene were confirmed by ozonolysis and decomposition under oxidative conditions to the anthraquinonecarboxylic acids.

A Grignard reaction carried out as described by Bergmann and Bergmann¹ for the preparation of 2-isopropenylanthracene gave a product with a similar melting point to theirs but this was found to be the intermediate tertiary alcohol by infrared spectroscopy (to be reported later) and by elementary analysis. Distillation of this alcohol, in the

¹ Bergmann and Bergmann, *J. Amer. Chem. Soc.*, 1940, **62**, 1699.

² Badger, *J.*, 1952, 1175.

³ Coulson, *J.*, 1930, 1931.

⁴ Baddeley and Williamson, *J.*, 1953, 2120.

⁵ Fieser and Hartwell, *J. Amer. Chem. Soc.*, 1938, **60**, 2555.

⁶ Wittig and Schöllkopf, *Chem. Ber.*, 1954, **87**, 1318; Wittig and Haag, *ibid.*, 1955, **88**, 1654.

presence of potassium hydrogen sulphate and a polymerisation inhibitor, gave 2-isopropenylanthracene with a slightly lower melting point than that previously reported.

1-isoPropenylanthracene was prepared by a similar route and was liquid. However, attempts to form the 9-isomer by reaction of 9-acetylanthracene with methylmagnesium iodide or methyl-lithium led to recovery of the ketone. Eventually 9-isopropenylanthracene was synthesised by the reaction of 9-anthrylmagnesium bromide with acetone.

The isomeric acetylanthracenes for this work were obtained according to I.G. patent methods,⁷ although the isomerisation of the 9-isomer to a mixture of 1- and 2-acetylanthracene was found to proceed only with variable and poor yields. The acetylanthracenes were conveniently reduced to the alcohols by lithium aluminium hydride.

Addition of bromine to 9-vinylanthracene, followed by reaction with potassium acetate, provided a solid with analysis consistent with an acetoxyvinylanthracene structure.

EXPERIMENTAL

The anthracene used was of "blue fluorescence" quality.

Acetylanthracenes.—Initial experiments on the acylation of anthracene with acetyl chloride in the presence of aluminium chloride were carried out under a variety of conditions in an attempt to obtain individual isomers in higher yields than those previously reported. The effect of different solvents (chloroform, ethylene dichloride, benzene, and nitrobenzene), various temperatures and times of reaction, and order of addition of the reactants, failed to improve on the conditions described by I.G.⁷ Two diacetylanthracenes were, however, obtained, besides the monoacetylanthracenes, from this preliminary work: the first, from an ethanol-soluble fraction, when recrystallised from light petroleum (b. p. 80—100°) and then chloroform, had m. p. 165—170° [Found: C, 82.2; H, 5.6%; *M* (ebullioscopic in acetone), 250 ± 5. C₁₈H₁₄O₂ requires C, 82.4; H, 5.3%; *M*, 262], and the second, from an ethanol-insoluble portion, when recrystallised from toluene, had m. p. 215—216° [Found: C, 83.0; H, 5.5%; *M* (ebullioscopic in acetone), 265 ± 5].

9-Acetylanthracene.—Anthracene (150 g.) was dissolved in dry benzene (960 c.c.) and acetyl chloride (360 c.c.) added, in a flask fitted with a mercury-sealed stirrer and a reflux condenser. The temperature was maintained at -5° to 0° and aluminium chloride (225 g.) added in portions. Stirring was continued for a further ½ hr. and the temperature then allowed to rise to 10°. The red solid complex was filtered off (sintered glass) and washed with benzene, and added to ice and hydrochloric acid, recovered, combined with the residue obtained by evaporating the liquid organic layer to dryness *in vacuo*, and recrystallised from boiling ethanol and then ethyl acetate (charcoal). It had m. p. 74—76° (Found: C, 86.9; H, 5.4. Calc. for C₁₈H₁₂O: C, 87.3; H, 5.45%).

In several preparations on this scale from anthracene (1680 g.) there were obtained 9-acetylanthracene (1150 g.) and recovered anthracene (170 g.), although yields from individual batches varied from 73 g. to 156 g. from 150 g. of anthracene.

1- and 2-Acetylanthracene.—9-Acetylanthracene (22 g.) was dissolved in nitrobenzene (100 g.), and aluminium chloride (13.4 g.) added gradually with stirring, without control of temperature. After 2½ hr. benzene (100 g.) was added, the red solid complex filtered off and decomposed with water, and the product extracted with chloroform. Evaporation of the solvent from the washed and dried extract left a residue which provided crude 2-acetylanthracene after crystallisation from ethyl acetate. Further recrystallisations from ethyl acetate (charcoal) and light petroleum (b. p. 80—100°) gave the pure compound (8.0 g.), m. p. 190—192° (Found: C, 86.8; H, 5.4%).

The filtrate from the initial crystallisation from ethyl acetate provided 1-acetylanthracene (2.5 g.), m. p. 107.5—109° (Found: C, 87.1; H, 4.9%).

Isomerisation of larger quantities of 9-acetylanthracene (110 g. or 220 g.) gave 40—50% yields of crude product, but after separation of the isomers and purification the yield had been reduced to 15—20% with the two separated isomers obtained in approximately equal amount.

1-9'-Anthrylethanol.—(i) 9-Acetylanthracene (98 g.) was extracted from a Soxhlet thimble by refluxing ether (1.5 l.) under nitrogen on to lithium aluminium hydride (10 g.). Excess of

⁷ I.G. Farbenind. A.-G., G.P. 492,247, 493,688, 499,051; cf. *Org. Synth.*, 1950, 30, 1.

hydride was removed with wet ether and the mixture treated with ice and dilute sulphuric acid. Normal working up followed by crystallisation of the residue from ethanol afforded 1-9'-anthrylethanol (82.5 g.), m. p. 120—122.5° (Found: C, 86.7; H, 6.6. Calc. for $C_{16}H_{14}O$: C, 86.5; H, 6.3%).

(ii) From another reduction there was obtained, after evaporation of the ether, a residue from which the desired alcohol was extracted by ethanol. There remained an ethanol-insoluble portion which, after recrystallisation from benzene-acetone, had m. p. *ca.* 220°, raised to 240—245° by distillation under reduced pressure, was an ether (infrared spectrum), and corresponded in m. p. with the ether, presumably bis-(1-9'-anthrylethyl) ether, obtained by Fieser and Hartwell⁵ [Found: C, 90.0; H, 5.8%; *M* (ebullioscopic), *ca.* 450. Calc. for $C_{32}H_{26}O$: C, 90.1; H, 6.1%; *M*, 426].

Attempts to purify the mother-liquors from these crystallisations by distillation led to decomposition.

1-1'-*Anthrylethanol*.—Reduction was carried out in a similar way to that for 9-acetyl-anthracene. The 1-acetylanthracene (84 g.) yielded the required *alcohol*, m. p. 116—118° (from ethanol) (Found: C, 86.1; H, 6.4%).

1-2'-*Anthrylethanol*.—The much lower solubility of 2-acetylanthracene in ether caused the reduction, carried out as for the other isomers, to take longer. The ketone (81 g.) gave the *ethanol* (72 g.), m. p. 162—163.5° (from methylene chloride or methylene chloride-ether) (Found: C, 86.5; H, 6.3. $C_{16}H_{14}O$ requires C, 86.5; H, 6.3%).

9-*Vinylnanthracene*.—(i) Pure 1-9'-anthrylethanol (20 g.) was heated at 200—250°/1 mm. in the presence of powdered potassium hydrogen sulphate (0.5 g.): an orange-yellow oil distilled and left a brown residue (1.6 g.). The oil crystallised in the condenser and recrystallisation from light petroleum (b. p. 40—60°) and then from methanol (400 c.c.)-ethanol (50 c.c.)-light petroleum (25 c.c.) gave yellow crystals (12 g.), m. p. 64—67°, of 9-*vinylnanthracene* (Found: C, 93.8, 93.9; H, 6.0, 6.1%; unsaturation equiv., 102.5%. $C_{16}H_{12}$ requires C, 94.1; H, 5.9%). This product depressed the m. p. of 9-ethylanthracene, which gave an apparent unsaturation value of 4.3% of a double bond/mole.

(ii) Distillation of pure alcohol in the absence of potassium hydrogen sulphate gave little residue, but the distillate was unchanged alcohol. However, distillation of a different sample (5.0 g.), apparently equally pure, gave a residue (0.5 g.) and a distillate (4.5 g.), which on crystallisation provided 9-*vinylnanthracene*, m. p. 63—66°, and a trace of white solid (more soluble in ethanol), m. p. 89—91°.

(iii) Distillation of mother-liquors from crystallisation of the alcohol provided an oil which deposited both white and yellow crystals from a light petroleum solution. These were separated mechanically as far as possible: recrystallisation of the yellow solid yielded 9-*vinylnanthracene*, m. p. 59—61°, whilst the white solid after purification had m. p. 89—91° (from light petroleum). Spectroscopic examination of the latter compound showed the presence of a hydroxyl group and a dihydroanthracene system, and its m. p. agreed with that reported⁸ for 1-(9:10-dihydro-9-anthryl)ethanol (m. p. 89.5—90.5°) (Found: C, 85.5; H, 7.3. Calc. for $C_{16}H_{16}O$: C, 85.7; H, 7.1%).

(iv) The alcohol (5.0 g.) and potassium hydroxide (0.5 g.) were heated at 0.5 mm. At a bath temperature of *ca.* 200° a nearly colourless oil distilled and left a residue (2.8 g.). The distillate was found to be unchanged alcohol containing a small amount of anthracene.

(v) Methyltriphenylphosphonium bromide (3.6 g.) was suspended in dry ether (10 c.c.) and there was added, with stirring under nitrogen, sufficient of an ethereal solution of phenyllithium (prepared from ethyl-lithium and diphenylmercury) to bring about reaction of the phosphonium bromide as indicated by the disappearance of solid and the colour of the solution becoming orange-red (cf. ref. 6). This ethereal solution, containing triphenylphosphine-methylene, was sealed in glass with 9-anthraldehyde (2.5 g.), partly dissolved in ether (30 c.c.); the mixture was heated at 65° overnight. The tube was cooled, and the contents washed out with ether and treated with dilute hydrochloric acid: some light brown solid (polymer?) was insoluble in both phases. The ethereal solution was evaporated to dryness and the residue extracted with light petroleum containing ethanol: this extract, on cooling, provided crystalline 9-*vinylnanthracene* (0.8 g.), which on further recrystallisation from light petroleum had m. p. 63—64.5°, undepressed on admixture with the compound formed by dehydration of 1-9'-anthrylethanol.

⁸ May and Mosettig, *J. Amer. Chem. Soc.*, 1948, **70**, 688.

1-*Vinylanthracene*.—(i) 1-1'-Anthrylethanol (4.0 g.) was heated with a trace of powdered potassium hydrogen sulphate at 0.5 mm.: at 200° an oil distilled and crystallised in the condenser, and left a polymeric residue (1.2 g.). The distillate of 1-*vinylanthracene*, after twice recrystallising from ethanol, had m. p. 58—61° (Found: C, 94.2; H, 6.0. $C_{16}H_{12}$ requires C, 94.1; H, 5.9%). The infra-red spectrum confirmed the presence of a vinyl group.

(ii) In two experiments where the alcohol was distilled at 0.8 mm. in the absence of a dehydration catalyst the results differed. In one case dehydration took place and 1-*vinylanthracene* was formed, and in the other case the alcohol distilled unchanged.

Distillation from activated alumina or calcium chloride caused no dehydration, whilst oxalic acid brought about incomplete reaction. Larger-scale dehydrations, in the presence of potassium hydrogen sulphate, often led to greater quantities of polymeric residues, which distilled at ca. 340° (bath)/0.8 mm. and were probably dimers.

1-*Vinylanthracene* (0.5 g.) in chloroform (50 c.c.) was treated with ozone at room temperature and then the solvent removed under reduced pressure. The residue was heated for 1½ hr. with acetic acid (15 c.c.) and 90% hydrogen peroxide (5 c.c.). The solid product (0.2 g.) had m. p. 281—286° (from ethanol), undepressed on admixture with authentic anthraquinone-1-carboxylic acid (prepared by chromic acid oxidation of 1-anthroic acid; m. p. 285—287°) (Found: C, 70.8; H, 3.1. Calc. for $C_{15}H_8O_4$: C, 71.4; H, 3.2%). The spectra of the two acids were also identical.

2-*Vinylanthracene*.—(i) 1-2'-Anthrylethanol (5.0 g.) mixed with a trace of phenyl- β -naphthylamine, was heated in a small Claisen flask at 1.0 mm. with the initial bath-temperature at 250°. The residue (1.7 g.) was polymeric, and the distillate, after recrystallisation from benzene, had m. p. 180—188°; further recrystallisation from ethanol provided 2-*vinylanthracene*, m. p. 186.5—188° (Found: C, 92.9; H, 5.9%). 2-Ethylanthracene has m. p. 150—151°.

The quantity of polymeric residue was unaffected by the presence of an inhibitor. Use of potassium hydrogen sulphate was unnecessary, and with this alcohol gave more polymer and less distillate.

(ii) The alcohol (1.5 g.) and potassium hydroxide (trace) were heated together as above, and the bath-temperature gradually raised to 300°. The material in the flask frothed and became dark brown and the distillate was found to consist mainly of unchanged alcohol containing a trace of 1-*vinylanthracene*. Residue, 0.7 g.

2-*Vinylanthracene* was ozonised and the product worked up as for the 1-vinyl isomer, to give anthraquinone-2-carboxylic acid, m. p. 287—288° (from acetic acid) undepressed on admixture with an authentic specimen, m. p. 287—289°, prepared by oxidation of 2-anthroic acid with chromic acid.

1-*isopropenylanthracene*.—A Grignard solution was prepared from methyl iodide (7 g.) and magnesium (1 g.) in ether, and 1-acetylanthracene (5 g.) in dry benzene (100 c.c.) added. The mixture was boiled for 4 hr., cooled, and poured into ice and hydrochloric acid. The organic phase was evaporated and the residue distilled under reduced pressure. The *hydrocarbon* (4.5 g.) did not crystallise, but infrared spectroscopy showed it to contain an unsaturated side-chain (Found: C, 93.2, 93.3; H, 6.3, 6.5. $C_{17}H_{14}$ requires C, 93.6; H, 6.4%).

2-*isopropenylanthracene*.—A Grignard reaction was carried out as above, but with 2-acetylanthracene (5 g.). The ether and benzene were removed under reduced pressure and the residue crystallised successively from benzene and ethanol. The product (5.0 g.) had m. p. 152—154° (reported ¹ m. p. for 2-*isopropenylanthracene*, 154°) but its infrared spectrum showed the presence of a hydroxy-group and elementary analysis gave results in agreement with those expected for 2-2'-*anthrylpropan-2-ol* (Found: C, 86.5, 86.7; H, 6.5, 6.7. $C_{17}H_{16}O$ requires C, 86.4; H, 6.8%).

Distillation of this alcohol under reduced pressure in the presence of potassium hydrogen sulphate and phenyl- β -naphthylamine gave a solid product, m. p. 150—152°, after crystallisation from light petroleum and methanol-ethanol, the m. p. being depressed on admixture with the above alcohol (Found: C, 93.3; H, 6.0. $C_{17}H_{14}$ requires C, 93.6; H, 6.4%).

9-*isopropenylanthracene*.—(i) The same method was used as for the two above isomers, but the 9-acetylanthracene was recovered unchanged, at the end of the reaction. Similarly, the reaction of a benzene solution of 9-acetylanthracene (5 g.) with ethereal methyl-lithium (from lithium, 1.3 g.), followed by heating for 7 hr. under reflux, yielded unchanged acetylanthracene (3.8 g.) and a little polymeric resin.

(ii) 9-Bromoanthracene was prepared by Barnett and Cook's method,⁹ and after successive recrystallisations from light petroleum (b. p. 80—100°) had m. p. 100—101°. Magnesium (1.0 g.) was powdered in a mortar, boiled with dry carbon tetrachloride, washed with dry ether, and allowed to react, in dry ether, with a small quantity of ethyl bromide: when the reaction had been initiated a warm solution of 9-bromoanthracene (5.0 g.) in dry ether was added gradually, and finally the mixture heated under reflux for 24 hr. Acetone (5 c.c.) in dry ether was then added, and the solution heated for 1 hr., kept at room temperature overnight, and worked up normally. The final residue was dissolved in hot benzene and from this anthracene (1.7 g.) crystallised: the mother-liquors were evaporated to dryness and the residue distilled at 0.5 mm. to give a gum (1.9 g.). This gum, by suitable fractional crystallisation from light petroleum, ethanol, and methanol as solvents, was separated into yellow 9-bromoanthracene, m. p. 100—101° (from ethanol), and scales of 9-isopropenylantracene, m. p. 84.5—86° (from ethanol) (Found: C, 93.5; H, 6.3. $C_{17}H_{14}$ requires C, 93.6; H, 6.4%). The infrared spectrum confirmed the presence of an unsaturated sidechain.

Addition of Bromine to 9-Vinylantracene.—Bromine (0.8 g.) in carbon disulphide (5 c.c.) was added during 10 min. to an ice-cooled solution of 9-vinylantracene (1.0 g.) in carbon disulphide (7 c.c.). Very little hydrogen bromide appeared to be liberated during this addition. After evaporation of the solvent the residual oil (1.7 g.) did not crystallise: distillation of a portion at 0.5 mm. gave a crystalline distillate, which after recrystallisation from ethanol yielded a wide-melting solid, obviously a mixture [Found: C, 64.6; H, 3.7; Br, 31.6. Calc. for $C_{16}H_{11}Br$ (bromovinylantracene): C, 67.8; H, 3.9; Br, 28.2. Calc. for $C_{16}H_{12}Br_2$ (dibromomethylantracene): C, 52.8; H, 3.3; Br, 44.0%].

A portion of the undistilled product was heated with potassium acetate in acetic acid. After normal working up the product was distilled at 1.0 mm., to give a residue (0.7 g.) and a distillate (0.5 g.) which, when recrystallised from ethanol and then light petroleum, gave anthraquinone and yellow crystals, m. p. 97—101°, probably an *acetoxylvinylantracene* (Found: C, 82.7; H, 5.7. $C_{18}H_{14}O_2$ requires C, 82.4; H, 5.3%); the infrared spectrum confirmed the presence of an ester group.

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⁹ Barnett and Cook, *J.*, 1924, 125, 1084.