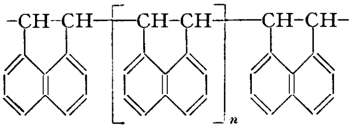
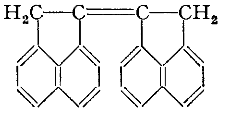
654. *The Preparation of the Two Stereoisomeric Forms of 7 : 7′-Diacenaphthenyl.**

By J. Idris Jones.

Diacenaphthenylidene has been reduced with sodium in boiling methyl*cyclo*hexanol to 7 : 7′-*diacenaphthenyl*, m. p. 168·5°. Catalytic hydrogenation with a copper chromite catalyst yields the same hydrocarbon together with the known stereoisomeric modification, m. p. 124° (lit., 120°). Raney nickel, on the other hand, favours further hydrogenation in the nuclei. The following additional reduction products have also been isolated : *octahydro-*, *decahydro-*, and *tetradecahydro-*7 : 7′-*diacenaphthenyl.* By an unexplained reaction 7 : 7′-diacenaphthenyl, m. p. 168·5°, is formed by treating acenaphthylene with benzylmagnesium bromide.

Acenaphthylene, obtained by the catalytic dehydrogenation of acenaphthene (Kynaston and Jones, *J. Soc. Chem. Ind.*, 1949, **68**, 225, 228), polymerises to give a linear polymer (I) (Dziewoński and Leyko, *Ber.*, 1914, **47**, 1679; Jones, *Brit. Plastics*, 1946, **18**, 286; Flowers and Miller, *J. Amer. Chem. Soc.*, 1947, **69**, 1388) but with acid catalysts the predominant tendency is to form the dimer diacenaphthenylidene (II) (Dziewoński, *Ber.*, 1915, **48**, 1917).


(I.)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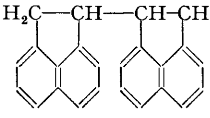
(III.)

In connection with a study of the ultra-violet absorption spectra of polymers and copolymers of acenaphthylene (Herington and Jones, *J. Polymer Sci.*, in the press) it became necessary to prepare 7 : 7′-diacenaphthenyl (III). This hydrocarbon, having two asymmetric carbon atoms, should exist in two stereosiomeric modifications—a *meso-* and a racemic form—but only one form, m. p. 120°, has hitherto been described. This was first prepared by Dziewoński and Paschalski (*Ber.*, 1914, **47**, 2685) by reduction of the lower-melting isomer of 1 : 2 : 3 : 4-di-1′ : 8′-naphthylene*cyclo*butane ("β-heptacyclene," one of the dimeric forms of acenaphthylene obtained by photochemical polymerisation) with hydriodic acid and red phosphorus, and later (Dziewoński and Dolinski, *Ber.*, 1915, **48**, 1925) by a similar reduction of diacenaphthenylidene. Repetition of the latter experiment by the present author failed to give the desired hydrocarbon; instead a mixture of more highly hydrogenated hydrocarbons resulted. Other methods of reduction were therefore investigated.

Diacenaphthenylidene is conveniently prepared by Dziewoński and Dolinski's method (*loc. cit.*, 1922) which consists in heating acenaphthylene picrate in acetic acid solution with concentrated hydrochloric acid and regenerating the product from the picrate. In the preparation of diacenaphthenyl from diacenaphthenylidene the difficulty is to restrict the reduction to the ethylenic double bond. If the reduction goes beyond this stage a multiplicity of products becomes possible with various degrees of nuclear hydrogenation and different stereochemical configurations caused by the presence of two asymmetric carbon atoms and the possibility of *cis-trans*-isomerism in the higher hydrogenated states. Another difficulty arises from the very low solubility of diacenaphthenylidene in the usual solvents. Thus, no reduction could be effected with zinc dust in boiling acetic acid, with or without pyridine. With Raney nickel or Adams's catalyst in alcohol, acetic acid, dioxan, or piperidine, even at the boiling point, no reduction was observed. Hydrogenation with palladised asbestos in boiling decalin or acetic acid also failed. However, diacenaphthenylidene is appreciably soluble in boiling methyl-

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* In the author's American publications, this compound was termed 1 : 1′-biacenaphthyl. In this paper British nomenclature is used. *Editor.*

*cyclo*hexanol and in this medium it was possible to effect reduction with sodium. When a small proportion of sodium was used the product was contaminated with unchanged diacenaphthenylidene which made purification difficult. On the other hand, higher proportions of sodium led to nuclear hydrogenation and the separation of the products was again difficult. However, by this means, two reduction products were isolated, one of which proved to be 7 : *7′-diacenaphthenyl,* $C_{24}H_{18}$, m. p. 168·5°, a stereoisomer of the hydrocarbon, m. p. 120°, reported by Dziewoński and co-workers. The other product was an octahydro-derivative of diacenaphthenyl, one of the isomeric forms of *bistetrahydro-*7*-acenaphthenyl,* $C_{24}H_{26}$, m. p. 253°, in which the location of the reduced rings is not known.

Hydrogenation of diacenaphthenylidene with Raney nickel at 150° and 140 atmospheres' pressure yielded a complex mixture of solid and liquid products, only two of which were characterised—a *decahydro-*7 : *7′-diacenaphthenyl,* $C_{24}H_{28}$, m. p. 176°, and a *tetradecahydro-*7 : *7′-diacenaphthenyl,* $C_{24}H_{32}$, m. p. 146°; the structures are unknown, since here again nothing is known of the disposition of the tetrahydro- and decahydro-nuclei. Under similar conditions, but at only 70 atmospheres of hydrogen, the main product was the decahydro-derivative, 30% of the diacenaphthenylidene being recovered unchanged.

Copper chromite has proved a valuable catalyst for certain selective hydrogenations of carbon–carbon double bonds, as in the hydrogenation of phenanthrene to 9 : 10-dihydrophenanthrene (Burger and Mosettig, *J. Amer. Chem. Soc.*, 1935, **57**, 2731). This selective activity has been found also in the case of diacenaphthenylidene, hydrogenation being confined almost exclusively to the olefinic double bond; the product consists of the two forms of diacenaphthenyl, one of m. p. 168·5° identical with that derived from the foregoing sodium-methyl*cyclo*hexanol reduction, the other of m. p. 124° (picrate, m. p. 222—223°) corresponding to Dziewoński's substance (m. p. 120°; picrate, m. p. 222—223°). The ultra-violet absorption spectra of the isomeric forms of 7 : 7′-diacenaphthenyl have been plotted (Herington and Jones, *loc. cit.*). The curves were of the same form and, as was to be expected, they showed a close parallelism with the spectrum of acenaphthene. However, there were significant differences between the relative intensities of certain absorption bands for the two diacenaphthenyls. Within the limits of experimental error it has been shown that the absorption spectra of the two isomeric forms of optical antipodes and the racemic form are identical (Brode, "Chemical Spectroscopy," John Wiley & Sons, 1945, p. 219), but little information appears to be available on the spectra of *meso-* and racemic compounds. However, for the tartaric acids Stewart (*J.*, 1907, **91**, 1537) did observe differences in absorption. Dissimilarities are common in the spectra of *cis-* and *trans*-isomers (Jones, *Chem. Reviews*, 1943, **32**, 41), but, in general, too little is known of the effects of stereochemical factors on absorption to permit a deduction of the configuration by a study of the spectra alone.

The higher-melting isomer of 7 : 7′-diacenaphthenyl has also been prepared from acenaphthylene by a somewhat novel reaction involving a Grignard reagent. Fuson and Porter (*J. Amer. Chem. Soc.*, 1948, **70**, 895) have shown that Grignard reagents (*tert.*-butyl-, benzyl-, and *p*-chlorobenzyl-magnesium chloride) react additively with the highly conjugated olefin bisdiphenylene-ethylene. It appeared of interest to see whether acenaphthylene similarly would add on Grignard reagents. When an ethereal solution of acenaphthylene (1 mole) was added to benzylmagnesium bromide (1 mole) and the mixture was heated under reflux for 4 hours the products obtained were 7 : 7′-diacenaphthenyl, m. p. 168·5°, together with dibenzyl and some unchanged acenaphthylene. An extra mole of benzyl bromide added to the Grignard reagent after the addition of the acenaphthylene gave only some polyacenaphthylene. Although this reaction presented interesting features it was not possible to examine it beyond this stage and further work is not contemplated. It is not clear whether this is a reaction of acenaphthylene *per se* or of its dimer diacenaphthenylidene which might have been formed by polymerisation under the influence of the Grignard reagent. Ethylmagnesium bromide is known to polymerise allyl cyanide (Bruylants *et al.*, *Bull. Soc. chim. Belg.*, 1923, **32**, 317; 1926, **35**, 239) and butyl- and phenyl-magnesium bromide induce rapid polymerisation of methylacrylonitrile (Beaman, *J. Amer. Chem. Soc.*, 1948, **70**, 3115).

EXPERIMENTAL.

(Analyses are by Drs. Weiler and Strauss, Oxford.)

Diacenaphthenylidene (Dziewoński and Dolinski, *loc. cit.*) was obtained as yellow needles, m. p. 277° (picrate, m. p. 216—217°). This presumably is the stable *trans*-modification, for it sublimes unchanged at 300° in a vacuum. Choknacki (*Bull. Acad. Polonaise,* 1939, A, No. 1—3A, 101) described two crystalline modifications of diacenaphthenylidene, the α-form stable at < 100° and the β-form from 100° to the m. p. 277°, but there is no mention of a *cis*-isomer in the literature.

Reduction of Diacenaphthenylidene. Preparation of 7 : 7′-*Diacenaphthenyl.*—(a) *With hydriodic acid and red phosphorus.* Repetition of Dziewoński and Dolinski's experiment (*loc. cit.*) failed to yield any picrate-forming material. The product was an oil and was clearly a mixture of more highly hydrogenated material from which no pure individual product could be isolated.

(b) *With zinc dust in boiling acetic acid.* Diacenaphthenylidene (5 g.) in glacial acetic acid (250 ml.) was treated under reflux with zinc dust (15 g.), and boiling was continued for 7 hours. The diacenaphthenylidene was recovered unchanged. Addition of pyridine (25 g.) and a trace of water (0·5 ml.) failed to induce reduction.

(c) *With sodium in methyl*cyclo*hexanol.* Diacenaphthenylidene is not appreciably soluble in boiling ethyl or amyl alcohol, and was not reduced with sodium in either of these media. In methyl*cyclo*hexanol (Howard's " Sextol ") it dissolves readily at the b. p. Sodium (5 g.) was added in small pieces during 1 hour to a boiling solution of diacenaphthenylidene (3 g.) in "Sextol" (250 ml.). At the end of the reaction the solution still exhibited the characteristic blue fluorescence of diacenaphthenylidene. The solvent was removed by distillation in steam, the semi-solid residue separated, and the accompanying liquid extracted with ether. On removal of the ether the product was obtained as a thick oil (3 g.) which partly solidified at 0°. Attempts at crystallisation afforded only a little impure diacenaphthenylidene, so the product was treated with picric acid (2·5 g.) in boiling alcohol. In this way pure diacenaphthenylidene picrate (1 g.), m. p. 216—217°, was recovered. Further crystallisation from alcohol yielded a crop of glistening plates (1·1 g.), not a picrate, which after purification by washing with dilute ammonia and recrystallisation from alcohol plus a little benzene left 0·9 g. of plate-like crystals with a pale yellowish tint, melting at 168·5°, and exhibiting a slight bluish fluorescence in solution. This compound in benzene solution was chromatographed on an alumina column. A broad band showing an intense bluish fluorescence in ultra-violet light travelled down the column and was eluted with more of the same solvent. A very narrow band of fluorescent material was retained on the column. From the eluted fraction on crystallisation 7 : 7′-*diacenaphthenyl*, m. p. 168·5°, was obtained (Found : C, 94·0; H, 6·0. $C_{24}H_{18}$ requires C, 94·1 ; H, 5·9%). The purified material in benzene solution no longer exhibited any fluorescence in ordinary daylight. The product regenerated from the mother-liquor containing the picric acid was an oil from which no pure compound could be separated. Analysis showed that hydrogenation had proceeded well beyond the diacenaphthenyl stage.

When diacenaphthenylidene (5 g.) in 500 ml. of boiling " Sextol " was treated during 1 hour with 12 g. of sodium and the solvent removed with steam, 5·5 g. of an oil were recovered from which only diacenaphthenylidene picrate (0·7 g.) separated on treatment with picric acid. Considerable difficulty was experienced in working up the oil recovered from the picric acid. It contained a little solid material, at least part of which eventually separated from alcohol–toluene on prolonged cooling. By repeated crystallisation from alcohol containing a little benzene this afforded colourless fine needles (0·1 g.) of *octahydro*-7 : 7′-*diacenaphthenyl*, m. p. 253° (Found : C, 91·7; H, 8·05. $C_{24}H_{26}$ requires C, 91·7; H, 8·3%), presumably one of the isomeric forms of bistetrahydro-7-acenaphthenyl. The remainder of the product consisted of a mixture of hydrocarbons of different degrees of hydrogenation from which no single pure individual could be isolated, either by distillation or by chromatography taking advantage of the intense blue fluorescence of the material in ultra-violet light.

(d) *Hydrogenation with noble-metal catalysts.* Diacenaphthenylidene does not dissolve appreciably in acetic acid, ethyl alcohol, dioxan, benzene, toluene, chloroform, or piperidine at room temperature, and no hydrogenation could be effected with Adams's catalyst in any of the these media even at the b. p. Attempts at hydrogenation with palladium–asbestos in boiling decalin or glacial acetic acid were also unsuccessful.

(e) *Hydrogenation with a Raney nickel catalyst.* As was the case with Adams's catalyst and the solvents listed above, diacenaphthenylidene resisted hydrogenation under the same conditions with Raney nickel. However, under pressure, reduction products were obtained but in these the naphthalene nuclei had also been hydrogenated. An autoclave containing diacenaphthenylidene (5 g.), ethyl alcohol (250 ml.), and about 1 g. of Raney nickel was charged with hydrogen to a pressure of 100 atmospheres. The temperature was raised to 150°, with stirring, and was maintained thereat for 3 hours, the maximum pressure recorded being 140 atmospheres. The contents of the autoclave were filtered to remove the Raney nickel, and the catalyst was washed with hot alcohol and benzene. Addition of picric acid (3·5 g.) to the bluish fluorescent solution yielded some diacenaphthenylidene picrate (1 g.) but no other picrate. After removal of the excess picric acid, the remainder of the product (semi-solid) was crystallised from benzene–alcohol (1 : 1), giving, first, white glistening plates (1·8 g.), m. p. 176° after further recrystallisations from the same solvent mixture. This compound was a form of *decahydro*-7 : 7′-*diacenaphthenyl* (Found : C, 91·2; H, 8·9. $C_{24}H_{28}$ requires C, 91·1; H, 8·9%). After further crystallisation and recrystallisation another hydrocarbon was isolated as rosettes of colourless crystals (0·8 g.), m. p. 146°. Analysis showed this to be a *tetradecahydro*-7 : 7′-*diacenaphthenyl* (Found : C, 89·95; H, 10·2. $C_{24}H_{32}$ requires C, 89·9; H, 10·1%). What was left of the product was liquid and, although some segregation of the constituents was achieved by chromatographic analysis on alumina in ultra-violet light using light petroleum (b. p. 40—60°), not enough material was available for characterisation. Both the deca- and tetradeca-hydro-derivatives fluoresced (blue) strongly in the ultra-violet. During the chromatographic separation more than one intensely fluorescent band was obtained on the column, while part of the product was not so strongly adsorbed and was eluted. This did not fluoresce and on examination was found to be a mixture of highly hydrogenated material, partly crystalline.

When the hydrogenation was repeated with the same proportions of the reagents but with an initial pressure of only 50 atmospheres of hydrogen (maximum pressure, 70 atmospheres), 1·2 g. of diacenaphthenylidene were recovered unchanged and a further 0·3 g. was isolated through the picrate. The only crystalline product isolated in this case was decahydrodiacenaphthenyl, m. p. 176° (1 g.).

(f) *Hydrogenation with copper chromite catalyst.* Diacenaphthenylidene (5 g.), ethyl alcohol (250 ml.), and a copper–chromium oxide catalyst (1 g.) (Adkins, Folkers, and Connor, *J. Amer. Chem. Soc.*, 1932, **54**, 1138) were heated with stirring for 6 hours at 170°, the maximum pressure of hydrogen being 158 atmospheres. The charge, after opening of the autoclave, was brought to the boil and was filtered while hot, fresh quantities of boiling alcohol being added to wash the catalyst. The filtrate was reduced to a small volume and was allowed to crystallise. Altogether, 2·5 g. of almost colourless plates, m. p. 158—164°, separated which, after repeated crystallisation from light petroleum (b. p. 80—100°) plus a little benzene yielded 7 : 7′-diacenaphthenyl, m. p. 168·5 (1·5 g.). The combined mother-liquors did not crystallise, separating as an oil from alcohol and other solvents. Addition of picric acid (4·6 g.) to a benzene–alcohol solution of the residual product yielded golden-yellow needles of 7 : 7′-diacenaphthenyl picrate, m. p. 222—223° (1·5 g.), identical with the product described by Dziewoński (*loc. cit.*) (Found : C, 56·9; H, 3·2; N, 10·8. Calc. for $C_{36}H_{24}O_{14}N_6$: C, 56·5; H, 3·16; N, 11·0%). On regeneration with dilute ammonia, 7 : 7′-diacenaphthenyl, m. p. 124° (lit., 120°) (Found : C, 93·9; H, 5·9. Calc. for $C_{24}H_{18}$: C, 94·1 ; H, 5·9%), was obtained in the form of colourless plates (from alcohol).

Reaction of Acenaphthene with Benzylmagnesium Bromide.—To benzylmagnesium bromide prepared from benzyl bromide (17·1 g.) and magnesium (2·43 g.) in dry ether (100 ml.) was added a solution of acenaphthylene (15·2 g.) in ether (100 ml.). After being heated under reflux for 4 hours the solution, from which some crystalline material had separated, was poured on a mixture of broken ice and ammonium chloride. A white insoluble material separated, and from the ethereal solution after concentration and addition of alcohol a further quantity was obtained. After crystallisation from benzene–alcohol (1 : 1) this solid material yielded crystalline plates of 7 : 7′-diacenaphthenyl, m. p. 169° (8 g.) (Found: C, 93·9; H, 5·85% ; *M*, 328. $C_{24}H_{18}$ requires C, 94·1 ; H, 5·9% ; *M*, 306). Its identity was confirmed by the exact correspondence of its ultra-violet absorption spectrum in benzene solution with that of the corresponding diacenaphthenyl obtained by reduction of diacenaphthenylidene and by the absence of any depression in a mixed m. p. determination. No picrate could be prepared from it. Distillation of the product left after recovery of the diacenaphthenyl furnished a yellow oil (12·1 g.), the bulk of which distilled at 118—122°/6 mm. Addition of picric acid to an alcoholic solution of this distillate afforded acenaphthylene picrate (14·4 g.), m. p. 203° (decomp.), and from the residue, after removal of excess of picric acid, dibenzyl (5·9 g.), m. p. 52°.

In a second experiment, to benzylmagnesium bromide, prepared as above, a solution of acenaphthylene (15·2 g.) in ether (100 ml.) was run in and the mixture was heated under reflux for 5½ hours. Next morning more benzyl bromide (17·1 g.) was added and refluxing was continued for 2½ hours. The product was isolated by pouring on ice–ammonium chloride and was extracted with ether. The dried ethereal solution was poured into excess of ethyl alcohol whence there separated an amorphous biscuit-coloured solid (5·8 g.) which proved to be exclusively polyacenaphthylene, soluble in benzene and chloroform, moderately soluble in acetone, and insoluble in light petroleum and alcohol. It showed signs of softening at *ca.* 220° but had no definite m. p. No diacenaphthenyl was found. From the alcohol-soluble portion of the product, by distillation at 7 mm., benzyl bromide, dibenzyl, and acenaphthylene were recovered, but it was difficult to determine the exact amounts present in the total distillate (21 g.). The distillation was made difficult by the presence of polymeric material which either had not been completely precipitated in the alcohol or had formed during the early stages of the distillation. The temperature was raised to 265° but still much material remained undistilled. Some pyrolysis occurred as the last fraction to distil contained acenaphthylene and some diacenaphthenylidene.

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