322. 1-*Phenyl-2-naphthyl- and* 1 : 2-*Dinaphthyl-ethylenes.*

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The preparation of several diarylethylenes in their stereoisomeric forms is described.

In connection with studies on basically-substituted stilbenes (more strictly, 1 : 2-diarylethylenes) which were found to be carcinogenic and to affect the growth of transplanted tumours in rats (Haddow, Harris, Kon, and Roe, *Phil. Trans.*, 1948, *A*, **241**, 147) certain simple diarylethylenes were required. Since some of these were not known and the data regarding others were not satisfactory, it was decided to prepare them and, if possible, to obtain both stereoisomeric forms.

1-Phenyl-2-(1-naphthyl)ethylene, m. p. 72·5—73·5°, of unknown configuration has been prepared by Balla (*Compt. rend.*, 1934, **198**, 947), whilst Thiele has tentatively ascribed the same structure to a hydrocarbon, m. p. 155° (*Ber.*, 1899, **32**, 1296). Ruggli and Preuss (*Helv. Chim. Acta*, 1941, **24**, 1345) made an unsuccessful attempt to prepare it by decarboxylation of α-phenyl-β-(1-naphthyl)acrylic acid, which should have yielded the *cis*-compound, by analogy with the numerous examples examined by Ruggli and collaborators.

In our hands this reaction gave a good yield of an oil which is evidently the required cis-*stilbene*; it is easily isomerised by boiling it with nitrobenzene and a trace of iodine to the solid *trans*-form, m. p. 70—70·5°, which is also obtained by dehydrating the reaction product of 1-naphthaldehyde and benzylmagnesium chloride. This is evidently identical with the product prepared by Balla, whereas Thiele's hydrocarbon must have a different structure.

The corresponding β-naphthyl *compounds* were obtained by analogous procedures; here again the *cis*-form is an oil which was characterised as the picrate, whereas the trans-*form* obtained from it or by the Grignard reaction is a solid, m. p. 145—146°.

1-(1-Naphthyl)-2-(2-naphthyl)ethylene has been prepared by Badger (*J.*, 1941, 535) by the decarboxylation process and is evidently the *cis*-form because it is easily converted into a new *isomeride*, m. p. 191—192°. αβ-Di-(1-naphthyl)acrylic acid (Badger, *loc. cit.*) is decarboxylated to a new cis-*stilbene*, which is isomerised to the known compound, m. p. 164—165° (Elbs, *J. pr. Chem.*, 1893, **47**, 56) which must therefore be the *trans*-form. Similarly, the di-(2-naphthyl) acid gives a new *stilbene* which is converted into the known compound, m. p. 258° (Friedmann, *Ber.*, 1916, **49**, 277, gives m. p. 255°). The last two *trans*-stilbenes have more recently been prepared by Wood, Bacon, Meibohm, Throckmorton, and Turner (*J. Amer. Chem. Soc.*, 1941, **63**, 1334) by a method somewhat similar to that of Friedmann and of Elbs. We were unable to obtain either of them by the Grignard reaction.

EXPERIMENTAL.

(Melting points are uncorrected.)

1-*Phenyl*-2-(1-*naphthyl*)*ethylene*.—Benzylmagnesium chloride, prepared from 1 g. of magnesium and 4·8 g. of benzyl chloride in ether, was treated dropwise with an ethereal solution of 5·6 g. of 1-naphthaldehyde, the mixture being then warmed for 30 minutes. After decomposition with ammonium chloride the ethereal solution of the product was dried and evaporated, and the residue taken up in 100 c.c. of benzene and boiled for 1 hour with 10 g. of phosphoric oxide. The solution was then diluted with 100 c.c. of petroleum (b. p. 60—80°) and percolated through a column of activated alumina. The percolate on evaporation gave an oil which was converted into the picrate, m. p. 127—128° after crystallisation from benzene–petroleum. The hydrocarbon regenerated from it by passing its benzene solution through a column of alumina formed needles, m. p. 70—70·5°, from light petroleum (yield 1 g.) (Found : C, 93·5; H, 6·0. Calc. : C, 93·9; H, 6·1%).

α-Phenyl-β-(1-naphthyl)acrylic acid (Ruggli and Preuss, *loc. cit.*) (3 g.) was boiled with 30 c.c. of quinoline and 0·3 g. of copper chromate catalyst for 1 hour. The cooled mixture was treated with dilute hydrochloric acid and extracted with ether, and the extract, after being washed with water and then with alkali, was dried and evaporated. The residual oil was chromatographed in light petroleum solution and the recovered oil distilled; the main portion (1·5 g.) boiled at 170°/0·01 mm. and consisted of the cis-*stilbene* (Found : C, 93·7; 6·4. $C_{18}H_{14}$ requires C, 93·9; H, 6·1%). The oil was boiled for 15 minutes with 10 volumes of nitrobenzene and a crystal of iodine. The *trans*-compound recovered had m. p. and mixed m. p. 70° after crystallisation.

1-*Phenyl*-2-(2-*naphthyl*)*ethylene*.—A Grignard reagent prepared from 9·6 g. of benzyl chloride was treated with 11·8 g. of 2-naphthaldehyde exactly as described above and the product worked up in the same way. 4·5 G. of the *trans*-compound were obtained, needles from petroleum or alcohol, m. p. 145—146° (Found : C, 94·1; H, 6·4. $C_{18}H_{14}$ requires C, 93·9; H, 6·1%).

3 G. of 2-naphthaldehyde, 2·8 g. of sodium phenylacetate, 1 g. of anhydrous potassium carbonate, and 15 c.c. of acetic anhydride were boiled under reflux for 3 hours (oil-bath at 170°). α-*Phenyl*-β-(2-*naphthyl*)*acrylic acid* (1·9 g.) was isolated by extraction of the reaction product with sodium carbonate and acidification; it was crystallised from acetic acid, then from alcohol, and formed plates, m. p. 205—206° (Found : C, 83·2; H, 5·1. $C_{19}H_{14}O_2$ requires C, 83·0; H, 5·0%). The acid was decarboxylated and the product purified as described above. The earlier runnings from the chromatogram contained an oil; later fractions gave a solid on evaporation and this proved to be the *trans*-stilbene already described. The oil was converted into the picrate which melted at 68—69° in the crude state, but could not be purified as it dissociated on attempted crystallisation. The hydrocarbon regenerated from it remained oily, and the amount isolated did not permit complete purification; it must have consisted mainly of the *cis*-form because it was completely isomerised to the solid stilbene, m. p. 145—146°, on being heated with iodine in nitrobenzene solution.

1-(1-*Naphthyl*)-2-(2-*naphthyl*)*ethylene*.—The compound, m. p. 103—105° (Badger, *loc. cit.*), is readily isomerised to the trans-*isomeride* which crystallises from benzene–alcohol in plates, m. p. 191—192°; some degree of conversion takes place even on repeated crystallisation of the *cis*-form (Found: C, 94·4; H, 5·6. $C_{22}H_{16}$ requires C, 94·2; H, 5·8%).

1 : 2-*Di*-(1-*naphthyl*)*ethylene*.—αβ-Di-(1-naphthyl)acrylic acid was prepared as described by Badger; it was found to melt somewhat higher than the figure recorded by him, namely at 232—233°. The acid was accompanied by a small amount (about 4%) of a neutral by-product, which proved to be the known *trans*-form of the stilbene. After two purifications by chromatography in petroleum solution and two crystallisations from alcohol it melted at 164—165° (lit. 161°) (Found : C, 94·3; H, 5·8. Calc. : C, 94·2; H, 5·8%).

The acrylic acid (6 g.) was decarboxylated as described above giving 3·3 g. of the cis-*stilbene* which crystallised from alcohol in plates, m. p. 103—104° (Found : C, 93·9; H, 5·8. $C_{22}H_{16}$ requires C, 94·2

H, 5·8%). The isomerisation was carried out as described above and afforded the pure *trans*-form, m. p. and mixed m. p. 164—165°.

1 : 2-*Di*-(2-*naphthyl*)*ethylene*.—In the preparation of 2-naphthaldehyde it was found convenient to prepare the intermediate bromomethylnaphthalene by boiling 2-methylnaphthalene (140 g.) with *N*-bromosuccinimide in carbon tetrachloride solution for 10 hours, using benzoyl peroxide as a catalyst (Schmid and Karrer, *Helv. Chim. Acta*, 1946, **29**, 573) (yield 120 g.). The aldehyde (8·5 g.) was condensed with potassium 2-naphthylacetate as described above; no neutral by-product appeared to be formed and the yield of *αβ-di*-(2-*naphthyl*)*acrylic acid* was 7·7 g. The acid was crystallised twice from acetic acid, then from alcohol and finally from benzene, m. p. 230° (Found: C, 85·2; H, 5·2. $C_{23}H_{16}O_2$ requires C, 85·2; H, 5·0%). Decarboxylation of 6·4 g. of the acid gave 3·5 g. of the cis-*stilbene*, plates from alcohol, m. p. 105·5—106·5° (Found: C, 94·5; H, 5·8. $C_{22}H_{16}$ requires C, 94·2; H, 5·8%). The *cis*-compound was completely isomerised on boiling with iodine in nitrobenzene to the *trans*-form, m. p. 258—259° after two crystallisations from benzene.

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