1013. *ω-Halogenomethyl-pyridines, -quinolines, and -isoquinolines. Part VII.* αβ-Di-2′-quinolylacrylic Acid.*

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The new compound, αβ-di-2′-quinolylacrylic acid, has been prepared in good yield by a Perkin synthesis and found to have the quinolyl groups in the unexpected *trans*-relation. Decarboxylation of the acid gives *trans*-1 : 2-di-2′-quinolylethylene.

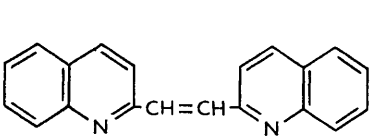
In studies of 1 : 2-di-2′-quinolylethylene (I) in this laboratory, the *cis*-isomer has been prepared by irradiation of the stable *trans*-form with ultraviolet light.[1] However, the method is not suitable for large-scale working. Since decarboxylation of α-phenylcinnamic acid with copper chromite is known to give *cis*-stilbene,[2] it was hoped that decarboxylation of the hitherto unknown, analogous quinolyl compound, αβ-di-2′-quinolylacrylic acid (II) might produce *cis*-1 : 2-di-2′-quinolylethylene. Ruggli and Staub [3] have shown that condensation of substituted benzaldehydes with phenylacetic acid gives α-phenylcinnamic acids with the phenyl groups *cis* to each other, and Stephenson [4] has obtained similar results with fluorenylacetic acids. Further, Curtin and Harris [5] have shown that configuration is retained during decarboxylation with copper chromite. However, in the present case the condensation did not take the same course: the acid (II) was found to have the *trans*-configuration and gave the *trans*-ethylene on decarboxylation.

Ethyl 2-quinolylacetate and quinoline-2-aldehyde were required as intermediates. The recorded methods of preparing the ester [6] were found to give yields of less than 10%;

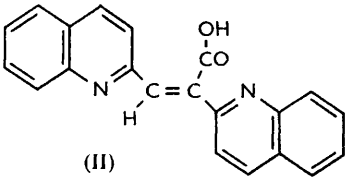
* Part VI, *J.*, 1957, 1533.

[1] Hammick, Lammiman, Morgan, and Roe, *J.*, 1955, 2436.
[2] Taylor and Crawford, *J.*, 1934, 1130.
[3] Ruggli and Staub, *Helv. Chim. Acta*, 1936, **19**, 1288.
[4] Stephenson, *J.*, 1949, 655.
[5] Curtin and Harris, *J. Amer. Chem. Soc.*, 1951, **73**, 2716, 4519.
[6] Cf. Clemo and Nath, *J.*, 1952, 2197.

we have now prepared it in a new way from quinaldinyl-lithium and ethyl carbonate in 60% yield, based on unrecovered quinaldine. The usual preparation of quinoline-2-aldehyde, by oxidation of quinaldine with selenium dioxide, is unpleasant and gives several by-products; hydrolysis of dibromoquinaldine [7] is intrinsically better but sometimes



(I)



(II)

the aldehyde polymerizes in the alkaline conditions of its isolation. We have improved the latter method to give reliably good yields. Ethyl 2-quinolylacetate and quinoline-2-aldehyde, thus prepared, were condensed in the presence of piperidine; hydrolysis of the resulting acrylic ester gave αβ-di-2′-quinolylacrylic acid (II).

As in the case of the diquinolylethylenes,[1] it can be shown that if the quinolyl groups of the acrylic acid and its ester are *cis* to each other then their electron systems will not be conjugated and the ultraviolet spectrum of the molecule will resemble that of quinoline or *cis*-diquinolylethylene. When the groups are *trans*, then conjugation is possible and there will be an entirely different ultraviolet spectrum, resembling that of *trans*-diquinolylethylene. The intense ultraviolet absorption of both the diquinolylacrylic acid [$\lambda_{max.}$ 2700 and 3450 Å (ε 34,740 and 34,120)] and its ethyl ester [$\lambda_{max.}$ 2720 and 3475 Å (ε 49,420 and 24,500)], as prepared here, showed that the quinolyl groups in both compounds were in the planar, conjugated, *trans*-position. Attempts to isomerize both the acid and the ester by ultraviolet irradiation or by refluxing them in nitrobenzene with a trace of iodine were unsuccessful. Decarboxylation of the acid (II) at 125—130° gave only the stable *trans*-ethylene, *i.e.*, configuration was retained during decarboxylation.

Experimental

Ethyl 2-Quinolylacetate.—Dry bromobenzene (53 ml., 0·5 mole) was added, with stirring, to lithium (7 g., 1 g.-atom), cut into small pieces, under dry ether (400 ml.) in a 1-l. flask, at a rate sufficient to keep the mixture refluxing. When practically all the lithium had dissolved, freshly distilled quinaldine (68 ml., 0·5 mole; dried over potassium hydroxide) was added every 15 min., the mixture was then refluxed for 15 min., to give a deep red solution of quinaldinyl-lithium.

Freshly distilled diethyl carbonate (29·5 g., 0·25 mole) was added during 30 min., and the mixture stirred at room temperature for 3 hr. Then the product was cooled in an ice-bath and carefully acidified with 3N-hydrochloric acid. The aqueous layer was removed, and the ether layer shaken with more 3N-hydrochloric acid. The combined aqueous portions were neutralized with solid sodium carbonate, and the liberated oil was extracted with ether. The ether extract was dried, and the ether removed; the residue was distilled through a short fractionating column. Fraction (*a*), b. p. 65—100°/0·7 mm., was identified as quinaldine (35·6 g., 49% recovery); fraction (*b*), b. p. 128—135°/0·8 mm., gave analyses correct for ethyl 2-quinolylacetate (32·5 g., 60% on unrecovered quinaldine) (Found: C, 72·3; H, 5·9; N, 6·6. Calc. for $C_{13}H_{13}O_2N$: C, 72·55; H, 6·0; N, 6·5%) and formed a yellow picrate (from ethanol), m. p. 148—150° (decomp.). Borsche and Manteufel [8] report a picrate, m. p. 150—152°. Higher-boiling material (2·5 g.), b. p. 135—175°/0·8 mm., appeared to be chiefly 1 : 2-dihydro-2-methyl-2-phenylquinoline, m. p. 90—91°, formed by the addition of phenyl-lithium to quinaldine.

Quinoline-2-aldehyde.—Dibromoquinaldine [9] (12 g.) was dissolved in boiling ethanol (100 ml.) and treated with silver nitrate (17·2 g.) in boiling water (20 ml.) and refluxed for 10 min. Concentrated hydrochloric acid was added to precipitate excess of silver, and the mixture of silver

[7] Hammick, *J.*, 1926, 1302.
[8] Borsche and Manteufel, *Annalen*, 1936, **526**, 25.
[9] Sharp, *J. Pharm. Pharmacol.*, 1949, **1**, 395.

halides was filtered from the hot solution. The ethanol was removed from the acid solution by steam-distillation. The residue from the steam-distillation was cooled in ice and neutralized with calcium carbonate. The yellow solid which separated was filtered off, dried in a desiccator, and crystallized from light petroleum (b. p. 60—80°), to give quinoline-2-aldehyde (5·3 g., 85%), m. p. 70—71°. Hammick [7] gives m. p. 71°.

Ethyl αβ-*Di*-2′-*quinolylacrylate*.—Quinoline-2-aldehyde (3·14 g., 0·02 mole) and ethyl 2-quinolylacetate (4·3 g., 0·02 mole) in ethanol (50 ml.) and piperidine (2 ml.) were refluxed for 12 hr., then cooled in ice. The solid which formed was recrystallized from ethanol, to give white needles of *ethyl* αβ-*di*-2′-*quinolylacrylate* (3·8 g., 54%), m. p. 143° (Found: C, 77·8; H, 5·1; N, 7·75. $C_{23}H_{18}O_2N_2$ requires C, 77·9; H, 5·1; N, 7·9%).

αβ-*Di*-2′-*quinolylacrylic Acid*.—Ethyl αβ-di-2′-quinolylacrylate (3·54 g.) was dissolved in warm ethanol (60 ml.) and added to potassium hydroxide (6 g.) in water (60 ml.). The mixture was gently refluxed for 20 min., then poured into water (500 ml.) and adjusted to pH 7 with dilute hydrochloric acid. After filtration and drying, the precipitate which was formed recrystallized from chloroform, to give colourless needles of αβ-*di*-2′-*quinolylacrylic acid* (2·5 g., 75%), m. p. 169° (decomp.) (Found: C, 77·1; H, 4·4. $C_{21}H_{14}O_2N_2$ requires C, 77·3; H, 4·3%).

Decarboxylation of αβ-*Di*-2′-*quinolylacrylic Acid*.—αβ-Di-2′-quinolylacrylic acid (0·5 g.) was heated in freshly distilled quinoline (5 ml.) with copper chromite (0·1 g.) at 130° until no more carbon dioxide was evolved (20 min.). The hot mixture was filtered and the filtrate diluted with ethanol (20 ml.). Dropwise addition of water precipitated a solid product which crystallized from benzene–methanol (1 : 1), to give *trans*-(β)-1 : 2-di-2′-quinolylethylene (0·37 g., 80%), m. p. 188—190°, undepressed on admixture with an authentic specimen.

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