

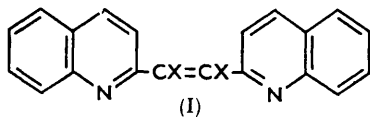
**293.** *ω*-Halogenomethyl-pyridines, -quinolines, and -isoquinolines.  
Part VI.<sup>1</sup> Compounds related to 1 : 2-Di-2'-quinolylethylene.

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The reactions of some non-planar halogenated diquinolylethylenes are described, and, for the principal members of the series, configurations are assigned and dipole moments recorded.

IN Part V<sup>1</sup> we described the preparation of two stereoisomers of 1 : 2-di-2'-quinolylethylene (I; X = H) and of its dichloro- and dibromo-analogues (I; X = Cl, Br). On the evidence of the ultraviolet spectra we assigned the *trans*-configuration to the more stable β-1 : 2-di-2'-quinolylethylene. The present paper is concerned with the elucidation of the stereochemistry of the halogenoethylenes and with the preparation of some additional compounds of this series.

ωωω-Tribromoquinaldine reacts with copper in boiling pyridine to give a mixture of β-1 : 2-dibromo-1 : 2-di-2'-quinolylethylene (I; X = Br) and 1 : 2-di-2'-quinolylacetylene. The same reaction with ωωω-trichloroquinaldine has afforded only β-1 : 2-dichloro-1 : 2-di-2'-quinolylethylene (I; X = Cl). A comparative study of the dehalogenation with copper in boiling pyridine of the isomeric dihalogenoethylenes has shown that the α-isomers give the acetylene very much more readily than do the β-isomers. We take this to mean that the α-isomers have the *trans*-configuration and react by a *trans*-elimination of the halogen atoms.<sup>2</sup> This conclusion is supported by the fact that α-1 : 2-dibromo-1 : 2-di-2'-quinolylethylene is the only product obtained by the action of bromine on 1 : 2-di-2'-quinolylacetylene.



<sup>1</sup> Part V, Hammick, Lammiman, Morgan, and Roe, *J.*, 1955, 2436.

<sup>2</sup> Crombie, *Quart. Rev.*, 1952, 6, 130; Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell and Sons, London, 1953, p. 465.

The debromination of 1 : 2-dibromo-compounds by the action of copper in pyridine is probably a stereospecific *trans*-elimination. When 1 : 2-dibromo-1 : 2-di-2'-quinolyethane, made by the presumably *trans*-addition of bromine to the *trans*-ethylene, is treated with copper in pyridine, *trans*(or  $\beta$ )-1 : 2-di-2'-quinolyethylene is isolated in 69% yield. The methods of preparation and all the physical and chemical properties of each pair of isomeric dihalogenoethylenes are comparable : thus, the higher-melting, less soluble  $\alpha$ -isomers are obtained by irradiation of the  $\beta$ -isomers, and absorb less strongly in the ultraviolet region. For this reason we conclude, by analogy with the corresponding debromination reactions, that the relatively rapid dechlorination of  $\alpha$ -1 : 2-dichloro-1 : 2-di-2'-quinolyethylene is also a *trans*-elimination.

The relative stability of the isomeric dibromoethylenes under various conditions has been studied. Treatment of each isomer with a catalytic quantity of iodine in boiling pyridine did not cause isomerisation ; in nitrobenzene, however, equilibration appeared to occur along with much decomposition. Treatment of the  $\alpha$ -isomer with potassium hydroxide in boiling methanol gave the  $\beta$ -isomer. This lower stability of the  $\alpha$ -isomer may be due to the fact that in the *trans*-configuration neither quinoline ring can, owing to the size of the bromine atoms, lie in the same plane as the ethylenic bond. However, in the *cis*-configuration one of the quinoline rings can conjugate with the ethylenic bond : this may be related to the similar, but more intense, ultraviolet absorption of the  $\beta$ (or *cis*)-isomer.

This argument may be further pursued in the case of the new compounds obtained by the action of the halogen acids on 1 : 2-di-2'-quinolylacetylene. Whereas the  $\beta$ -ethylene is stable to prolonged treatment with 2*N*-hydrochloric acid, the acetylene readily furnishes 1-chloro-1 : 2-di-2'-quinolyethylene. Hydrobromic acid gives, less readily, 1-bromo-1 : 2-di-2'-quinolyethylene. The action of hydriodic acid on the acetylene produced  $\beta$ -1 : 2-di-2'-quinolyethylene and a compound melting at 102—103°, which readily lost iodine.

In passing from the unsubstituted ethylene to the dihalogenated ethylenes we have found that the order of stability shifts from the *trans*- to the *cis*-isomer, apparently because of the steric effect of the halogen atoms. In the monohalogenated ethylenes an intermediate state is found, where the *trans*- are only slightly more stable than the *cis*-forms. Addition of hydrogen chloride to diquinolylacetylene gave *trans*-1-chloro-1 : 2-di-2'-quinolyethylene together with a trace of the *cis*-isomer (identified by its ultraviolet spectrum). Addition of hydrogen bromide gives *trans*-1-bromo-1 : 2-di-2'-quinolyethylene, contaminated with larger amounts of the *cis*-isomer. The *trans*-isomer crystallises more readily from light petroleum or benzene, and is eluted more readily when the mixture is chromatographed on a column of alumina prepared in carbon tetrachloride ; pure isomers, however, have not been isolated.

Thus there is a gradual diminution in the relative stabilities of the *trans*-isomers in the series 1 : 2-diquinolyl-, 1-chloro-1 : 2-diquinolyl-, 1-bromo-1 : 2-diquinolyl-, to the 1 : 2-dichloro- and 1 : 2-dibromo-1 : 2-diquinolyl-ethylenes, which are of comparable stability.

1-Chloro- and 1-bromo-1 : 2-di-2'-quinolyethylene have been treated with chlorine and bromine respectively to give the corresponding 1 : 1 : 2-trihalogeno-1 : 2-di-2'-quinolyethanes.

An attempt has been made to prepare the  $\alpha$ (or *cis*)-1 : 2-di-2'-quinolyethylene by catalytic reduction of a dibromoethylene or from diquinolylacetylene.<sup>3</sup> With a palladium on strontium carbonate catalyst in the presence of potassium hydroxide<sup>4</sup> both isomeric dibromoethylenes gave the same  $\beta$ (or *trans*)-1 : 2-di-2'-quinolyethylene. In the case of the  $\beta$ (or *cis*)-dibromoethylene isomerisation occurs ; the same thing apparently happens during the reduction of 1 : 2-di-2'-quinolylacetylene which also affords the *trans*-olefin.<sup>5</sup>

Dipole moments were made available by the kindness of Dr. L. E. Sutton, F.R.S., in

<sup>3</sup> Cf. Ahmad, Bumpus, and Strong, *J. Amer. Chem. Soc.*, 1948, **70**, 3391.

<sup>4</sup> Cf. Busch and Stove, *Ber.*, 1916, **49**, 1063.

<sup>5</sup> Cf. Bourguel, *Bull. Soc. chim. France*, 1929, **45**, 1067.

whose laboratory they were measured by Mr. C. J. M. Cutcliffe. The figures in the Table are in accordance with the above assignments.

*Dipole moments (D) (Q = 2-quinolyl).*

<i>trans</i> -Q·CH:CH·Q .....	1.60	<i>trans</i> -Q·CBr:CBBr·Q .....	1.36
<i>trans</i> -Q·CCl:CCl·Q .....	1.54	<i>cis</i> -Q·CBr:CBBr·Q .....	4.68
<i>cis</i> -Q·CCl:CCl·Q .....	4.87		

EXPERIMENTAL

*Debromination of ωωω-Tribromoquinaldine.*—ωωω-Tribromoquinaldine (20 g.) in pyridine (40 ml.) was added during 1 hr. to a stirred refluxing mixture of pyridine (60 ml.) and copper bronze powder (10 g.). The stirred mixture was refluxed for a further 0.5 hr., then water (1 l.) was added after cooling. The solid was collected next day, washed with aqueous ammonia (*d* 0.880) and water, and dried. The organic material was dissolved in the minimum quantity of benzene-carbon tetrachloride (1 : 1) and chromatographed on alumina; elution with the same solvent gave β-1 : 2-dibromo-1 : 2-di-2'-quinolyethylene (2.9 g., 28%) as pale yellow needles [from light petroleum (b. p. 80—100°)], m. p. 142—143°. Elution with benzene-ether (1 : 1) gave 1 : 2-di-2'-quinolylacetylene (3 g., 40%), m. p. 179—180°.

*Dehalogenation of 1 : 2-Dihalogeno-1 : 2-di-2'-quinolyethylenes.*—The dehalogenations described<sup>1</sup> were carried out under standard conditions with various periods of reflux. A summary of results obtained is given.

	Q·CX: CX·Q (Q = 2-quinolyl)					
	X = Br			X = Cl		
	α-	β-		α-	β-	
Time (min.) .....	25	60	1080	60	60	1080
Recovered ethylene (%) .....	—	68	—	—	50	—
Yield of acetylene (%) .....	52	—	34	38	—	—

*Debromination of 1 : 2-Dibromo-1 : 2-di-2'-quinolyethane.*—1 : 2-Dibromo-1 : 2-di-2'-quinolyethane, prepared from β-1 : 2-di-2'-quinolyethylene by the method of Walker *et al.*,<sup>6</sup> had m. p. 172—173°.

Copper bronze powder (0.2 g.) was slowly added to 1 : 2-dibromo-1 : 2-di-2'-quinolyethane (0.34 g.) in pyridine (20 ml.). The mixture was boiled under reflux for 3 hr., cooled, and poured into ice and water. Next day the solid was collected and washed with ammonia (*d* 0.880) and water. The dried residue crystallised from light petroleum (b. p. 80—100°) to give colourless needles of β-1 : 2-di-2'-quinolyethylene (0.15 g., 69%), m. p. and mixed m. p. 192—193°.

*1-Chloro-1 : 2-di-2'-quinolyethylene.*—1 : 2-Di-2'-quinolylacetylene (2 g.) was boiled in 2*N*-hydrochloric acid (100 ml.) for 6 min. and while still hot was poured into 2*N*-ammonia. The precipitated solid was purified on alumina in benzene-carbon tetrachloride (1 : 1) and crystallised from light petroleum (b. p. 80—100°) to give *1-chloro-1 : 2-di-2'-quinolyethylene* as white needles, m. p. 110° (Found : C, 75.6; H, 4.1; N, 9.0; Cl, 11.2. C<sub>20</sub>H<sub>13</sub>N<sub>2</sub>Cl requires C, 75.6; H, 4.1; N, 8.8; Cl, 11.2%), λ<sub>max</sub> 2725 3450 (ε 49,500 36,000). The *dipicrate* separated as yellow plates, m. p. 235—236°, from boiling methanol (Found : C, 49.4; H, 2.7; N, 14.1; Cl, 5.0. C<sub>32</sub>H<sub>19</sub>O<sub>14</sub>N<sub>3</sub>Cl requires C, 49.6; H, 2.5; N, 14.4; Cl, 4.6%).

When β-1 : 2-di-2'-quinolyethylene was treated with 2*N*-hydrochloric acid the only product isolated was β-1 : 2-di-2'-quinolyethylene *dihydrochloride*, which separated from hot water as colourless needles, m. p. 249—250° (decomp.) (Found : C, 66.4; H, 4.8; N, 7.9; Cl, 20.4. C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>Cl<sub>2</sub> requires C, 67.6; H, 4.5; N, 7.9; Cl, 20.0%).

*1-Bromo-1 : 2-di-2'-quinolyethylene.*—1 : 2-Di-2'-quinolylacetylene (1.5 g.) was boiled for 15 min. in hydrobromic acid (40 ml.; 25% w/w) and while hot was poured into 2*N*-ammonia. Three crystallisations of the precipitated solid from light petroleum (b. p. 80—100°) gave *1-bromo-1 : 2-di-2'-quinolyethylene* (1.3 g.) as lemon-yellow prisms, m. p. 115—116° (Found : C, 66.0; H, 3.6; N, 7.9; Br, 22.4. C<sub>20</sub>H<sub>13</sub>N<sub>2</sub>Br requires C, 66.4; H, 3.6; N, 7.8; Br, 22.2%), λ<sub>max</sub> 2725 3400 (ε 40,000 26,800). The *dipicrate* (from boiling methanol) had m. p. 211—212° (Found : C, 47.2; H, 2.7; N, 13.9; Br, 10.2. C<sub>32</sub>H<sub>19</sub>O<sub>14</sub>N<sub>3</sub>Br requires C, 46.9; H, 2.3; N, 13.9; Br, 9.8%).

*1 : 1 : 2-Trichloro-1 : 2-di-2'-quinolyethane.*—1-Chloro-1 : 2-di-2'-quinolyethylene (0.5 g.) in dry boiling carbon tetrachloride (100 ml.) was treated with chlorine for 30 min. After excess of

<sup>6</sup> Walker, Baldwin, Thayer, and Corson, *J. Org. Chem.*, 1951, **16**, 1805.

chlorine had been boiled off, the cold solution was washed with aqueous ammonia and evaporated. The residue crystallised from light petroleum and was twice recrystallised from acetone-water to give 1 : 1 : 2-*trichloro-1 : 2-di-2'-quinolyethane* (0.2 g.) as fine white prisms, m. p. 138—139°, resolidifying to melt again at 187—190° (Found : C, 61.9; H, 3.4; N, 7.1; Cl, 27.5.  $C_{20}H_{13}N_2Cl_3$  requires C, 61.8; H, 3.4; N, 7.1; Cl, 27.9%).

1 : 1 : 2-*Tribromo-1 : 2-di-2'-quinolyethane*.—1-Bromo-1 : 2-di-2'-quinolyethylene (0.4 g.) in dry carbon tetrachloride (50 ml.) was refluxed with bromine (0.4 ml.) for 10 min. The carbon tetrachloride was removed and the residue treated with dilute aqueous ammonia. Recrystallisation of the product from light petroleum (b. p. 60—80°) containing a little benzene, followed by recrystallisation from acetone-water, gave white prisms of 1 : 1 : 2-*tribromo-1 : 2-di-2'-quinolyethane*, m. p. 150—151° (decomp.) (Found : C, 46.1; H, 2.7; N, 5.3; Br, 45.6.  $C_{20}H_{13}N_2Br_3$  requires C, 46.1; H, 2.5; N, 5.4; Br, 46.0%).

*Reduction of  $\alpha$ -1 : 2-Dibromo-1 : 2-di-2'-quinolyethylene*.— $\alpha$ -1 : 2-Dibromo-1 : 2-di-2'-quinolyethylene (0.4 g.) in dry methanol (25 ml.) and dioxan (25 ml.) containing potassium hydroxide (0.1 g.) and pre-reduced palladium on strontium carbonate (0.1 g.) was shaken under hydrogen. Absorption of hydrogen (11 c.c. at 18°/700 mm. Calc. for 2H : 10 c.c.) ceased after 10 min. The solution was filtered and evaporated under reduced pressure; crystallisation of the residue from benzene gave  $\beta$ -1 : 2-di-2'-quinolyethylene (0.12 g., 94%), m. p. and mixed m. p. 185—186°.

*Reduction of  $\beta$ -1 : 2-Dibromo-1 : 2-di-2'-quinolyethylene*.— $\beta$ -1 : 2-Dibromo-1 : 2-di-2'-quinolyethylene (1 g.) in dry methanol (100 ml.) containing potassium hydroxide (0.2 g.) and pre-reduced palladium on strontium carbonate (0.2 g.) was shaken under hydrogen. Absorption of hydrogen (62 c.c. at 23°/744 mm. Calc. for 2H : 59 c.c.) ceased after 15 min.  $\beta$ -1 : 2-Di-2'-quinolyethylene was isolated as above.

*Reduction of 1 : 2-Di-2'-quinolyacetylene*.—The diquinolyacetylene (0.5 g.) in dry ethyl acetate (20 ml.) containing pre-reduced palladium on strontium carbonate (0.2 g.) was shaken under hydrogen. Absorption of hydrogen (49 c.c. at 23°/740 mm. Calc. for 2H : 47 c.c.) ceased after 15 min.  $\beta$ -1 : 2-Di-2'-quinolyethylene was isolated as before.