*ω-Halogenomethyl-pyridines, -quinolines, and -*iso*quinolines. Part V.* Preparation of Compounds related to 1 : 2-Di-2′-quinolylethane.*

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Dehalogenation of ω-halogenoquinaldines with copper in pyridine has given symmetrical diquinolyl-acetylene, -ethylene, -dibromoethylene, and -dichloroethylene. The ethylenes have been isomerized by irradiation, and in the case of diquinolylethylene, configurations have been assigned.

In continuation of our studies of ω-halogenomethyl quinolines, we have sought a convenient route to 1 : 2-di-2′-quinolylethane and related coumponds from the readily prepared ω-halogenoquinaldines. 1 : 2-Di-2′-quinolylethane was prepared by Brown, Hammick, and Thewlis (*J.*, 1951, 1145) by Würtz synthesis from ω-monobromoquinaldine. It was earlier obtained from the products of the action of sulphur on quinaldine by von Miller (*Ber.*, 1888, **21**, 1827), who called it "diquinaldyl" but did not establish its structure. Walker, Baldwin, Thayer, and Corson (*J. Org. Chem.*, 1951, **16**, 1805) repeated von Miller's work and identified the product as 1 : 2-di-2′-quinolylethane. This method is simple but wasteful; it has now been modified to give fair yields and is superior to the four-stage synthesis *via* ω-monobromoquinaldine with its very inefficient Würtz reaction.

Johnson, Smith, Stacey, and Tatlow (*J.*, 1952, 4710) report a reaction with copper in pyridine, of aromatic compounds having a trichloromethyl or dichloromethylene group, in which chlorine is eliminated to give substituted ethylenes and ethanes. We have successfully adapted this reaction to the preparation of 1 : 2-di-2′-quinolyl-acetylene and -ethylene, and of the 1 : 2-dihalogenated derivatives of the latter from ω-halogenoquinaldines.

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* Part IV, *J.*, 1953, 1369.

ωωω-Tribromoquinaldine reacts exothermally with copper in pyridine to give 1 : 2-di-2′-quinolylacetylene. By controlling the conditions we have been able to isolate either the acetylene or β-1 : 2-dibromo-1 : 2-di-2′-quinolylethylene.* ωωω-Trichloroquinaldine will only yield β-1 : 2-dichloro-1 : 2-di-2′-quinolylethylene. Attempts to make 1 : 1 : 2 : 2-tetrabromo- and 1 : 1 : 2 : 2-tetrachloro-1 : 2-di-2′-quinolylethane have been unsuccessful.

ωω-Dibromoquinaldine under similar treatment gives β-1 : 2-di-2′-quinolylethylene. Slow reaction at room temperature in an attempt to make 1 : 2-dibromo-1 : 2-di-2′-quinolylethane also gave β-1 : 2-di-2′-quinolylethylene. This compound (m. p. 189—190°) has been shown by mixed melting point and infrared spectrum to be identical with the compound made by the method of Walker *et al.* (*loc. cit.*). Attempts to obtain the compound reported by Kaplan and Lindwall (*J. Amer. Chem. Soc.*, **1943**, **65**, 927) as 1 : 2-di-2′-quinolylethylene (m. p. 325°) were unsuccessful and gave either the ethylene melting at 190° or deoxyquinaldoin, m. p. 221°. Walker *et al.* (*loc. cit.*) reported the compound as yellow needles, but after careful purification the compound is colourless.

The reaction could not be extended to the preparation of 1 : 2-di-2′-quinolylethane because ω-monobromoquinaldine reacts with pyridine (or quinoline) with the rapid formation of quaternary salts (cf. Brown, Hammick, and Thewlis, *loc. cit.*). During this work a single-stage reduction of ωωω-tribromoquinaldine to ω-monobromoquinaldine (74%) in tetralin has been developed which is superior to previous preparations from the tribromo- or dibromo-quinaldine (cf. Brown and Hammick, *J.*, 1950, 628; Brown, Grice, Hammick, and Thewlis, *J.*, 1951, 1149). The Würtz synthesis of the ethane is not of preparative value; the compound may be obtained in fair yield by a modification of the procedure of Walker *et al.* (*loc. cit.*). When pure, the ethane is colourless.†

The β-unsaturated compounds are unusually resistant to bromine or chlorine under normal conditions. The dibromoethylene is very inert: it resists prolonged treatment with alcoholic silver nitrate, silver acetate in acetic acid, potassium permanganate in acetone, dilute or concentrated sulphuric acid, aqueous sodium hydroxide, and even fusion with potassium hydroxide. The infrared spectrum showed that the bromine was not attached to the quinolyl nuclei, and this was confirmed by treatment for eight hours with copper in pyridine, which gave the acetylene. Even 1 : 2-dibromo-1 : 2-di-2′-quinolylethane (made by the method of Walker *et al.*, *loc. cit.*) resists debromination with silver nitrate and acid and alkaline hydrolysis.

From the reaction of the acetylene with bromine, the only compound obtained analysed as dibromodiquinolylethylene, but it melted 80° higher, and its monopicrate decomposed 60° higher than that of β-dibromodiquinolylethylene. We have shown that this compound is an isomer of β-1 : 2-dibromo-1 : 2-di-2′-quinolylethylene. Irradiation of β-dibromodiquinolylethylene with ultraviolet light converted it into the higher-melting isomer. Similarly, ultraviolet irradiation of β-dichlorodiquinolylethylene and β-diquinolylethylene produced higher-melting, less soluble isomers. We distinguish these new forms of the ethylenic compounds by the prefix α, and the lower-melting, more soluble forms by the prefix β.

In order to confirm the structure of α-1 : 2-dichloro-1 : 2-di-2′-quinolylethylene, it was converted into 1 : 2-di-2′-quinolylacetylene, which was isolated after one hour's treatment with copper in boiling pyridine. The β-dichlorodiquinolylethylene, after five hours under similar conditions, was recovered unchanged.

$$\begin{tikzcd}
\alpha\text{-}\mathrm{Q{\cdot}CBr{:}CBr{\cdot}Q} & \mathrm{Q{\cdot}C{\vdots}C{\cdot}Q} \arrow[l, "\mathrm{Br_2}"'] & \alpha\text{-}\mathrm{Q{\cdot}CCl{:}CCl{\cdot}Q} \arrow[l, "\mathrm{Cu-}"', "\mathrm{Py}"] \\
\beta\text{-}\mathrm{Q{\cdot}CBr{:}CBr{\cdot}Q} \arrow[u, "h\nu"'] \arrow[ur, "\mathrm{Cu-}", "\mathrm{Py}"'] & \mathrm{Q{\cdot}CBr_3} \arrow[l, "\mathrm{Cu-}"', "\mathrm{Py}"] \arrow[u, "\mathrm{Cu-}", "\mathrm{Py}"'] & \beta\text{-}\mathrm{Q{\cdot}CCl{:}CCl{\cdot}Q} \arrow[u, "h\nu"']
\end{tikzcd}$$

Q = 2-quinolyl. Py = pyridine.

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* For significance of *β*-, see below.

† *Added, June 3rd*, 1955.—Mr. J. A. Veitch, in this laboratory, has succeeded in preparing this compound from quinaldinyl-lithium in better yield.

When *cis-trans*-isomers of a substance exist, generally one of the isomers will approach more closely to coplanarity (the position of maximum elongation) than the other, and will therefore exhibit greater resonance; the optical absorption of the two isomers will therefore differ, that of the elongated isomer being the more intense (Mulliken, *J. Chem. Phys.*, 1939, **7**, 364).

Molecular models of 1 : 2-di-2′-quinolylethylene show that the *trans*-isomer can assume a planar configuration, whereas in the *cis*-form the molecule can never be planar because the quinolyl rings overlap. Thus we would predict that the *trans*-form, having the longer conjugated path, would absorb more intensely in the ultraviolet region. The spectrum of the β-ethylene bears a strong resemblance to that of 2 : 2′-dinaphthyl which can assume a completely conjugated planar structure. The α-ethylene has an absorption spectrum similar to that of quinoline itself but with twice the intensity, indicating loss of conjugation between the quinolyl rings. This is parallel to the case of the considerably sterically hindered 1 : 1′-dinaphthyl which has an absorption similar to that of naphthalene (Friedel, Orchin, and Reggel, *J. Amer. Chem. Soc.*, 1948, **70**, 199) (see Table).

Compound *	$\lambda_{max.}$	ϵ	$\lambda_{max.}$	ϵ	$\lambda_{max.}$	ϵ
β-Di-Q-ethylene	2725	49,500	—	—	3500	36,000
2 : 2′-Dinaphthyl †	2550	89,000	—	—	3100	18,000
α-Di-Q-ethylene	2350	30,000	2700	10,000	3130 ¶	12,500
1 : 1′-Dinaphthyl †	2300	39,000	—	—	2900 ¶	12,600
Quinoline ‡	—	—	2750	4,500	3110 ¶	6,300
α-Di-Cl-di-Q-ethylene	2350	31,500	—	—	3150 ¶	8,000
β-Di-Cl-di-Q-ethylene	2300	49,000	—	—	3200 ¶	12,800
α-Di-Br-di-Q-ethylene	2400	35,000	—	—	3150 ¶	8,000
β-Di-Br-di-Q-ethylene	2400	46,500	—	—	3200 ¶	13,300

* Q = 2-quinolyl. † Friedel, Orchin, and Reggel, *loc. cit.* ‡ Morton and de Gouveia, *J.*, 1934, 916; Sutherland and Compton, *J. Org. Chem.*, 1952, **17**, 1257. ¶ Approximate centre of fine-structure bands.

The infrared spectra support the evidence that α-1 : 2-di-2′-quinolylethylene is the *cis*-isomer, and the β-compound is *trans*.

The steric effect of the halogen atoms in the halogenoethylenes prevents *both cis*- and *trans*-isomers being completely planar, and hence all their ultraviolet spectra are different from that of β-1 : 2-di-2′-quinolylethylene; hence the spectral evidence cannot be used to determine the configuration of the halogenated ethylenes.

We note that 1 : 2-di-(6-methyl-2-quinolyl)ethylene-1 : 2-diol has been formulated as a hydrogen-bonded, completely conjugated, *trans*-structure (Buehler and Edwards, *J. Amer. Chem. Soc.*, 1952, **74**, 977); but it now appears that this is not supported by the ultraviolet spectrum which resembles that of quinoline and of our non-conjugated diquinolylethylenes.

EXPERIMENTAL

1 : 2-*Di-2′-quinolylacetylene*.—ωωω-Tribromoquinaldine (Hammick, *J.*, 1923, **123**, 2882) (20 g.) was dissolved in purified pyridine (125 ml.), and copper bronze powder (15 g.) added. Commercial copper bronze powder was used, freshly prepared copper powder as used by Johnson *et al.* (*loc. cit.*) showing no advantages. The mixture was refluxed for 3 hr., then cooled slightly and filtered, and the residual copper washed with pyridine. The filtrate, combined with the washings, was poured with stirring on crushed ice (1 kg.), diluted with water, and set aside for several hours. The mixture was then filtered and the solid washed free from copper salts with aqueous ammonia (*d* 0·880), then with water, dried at 100°, and crystallized from light petroleum (b. p. 100—120°) giving colourless needles of 1 : 2-di-2′-quinolylacetylene (1·9 g., 25%), m. p. 176—178° (Walker *et al.*, *loc. cit.*, record m. p. 179—180°) (Found : C, 85·0; H, 4·8; N, 9·5. Calc. for $C_{20}H_{12}N_2$: C, 85·7; H, 4·3; N, 10·0%). From ethanol it forms an insoluble dipicrate, m. p. 286—288° (decomp.).

β-1 : 2-*Dibromo*-1 : 2-*di-2′-quinolylethylene*.—A mixture of copper bronze powder (10 g.) and purified pyridine (30 ml.) was placed in a 1-l. 3-necked flask fitted with a mechanical stirrer, a dropping funnel, and a calcium chloride tube. A solution of ωωω-tribromoquinaldine (20 g.) in pyridine (100 ml.) was added dropwise during 1 hr. at room temperature. The solution was stirred for a further 2 hr., then filtered and washed as in the previous experiment and poured on ice. The insoluble material was filtered off and washed as before. Crystallization from light petroleum gave β-1 : *2-dibromo-*1 : *2-di-2′-quinolylethylene* (4 g., 36%) as pale yellow needles, m. p. 141—142° (Found : C, 54·4; H, 3·0; N, 6·4; Br, 36·2. $C_{20}H_{12}N_2Br_2$ requires C, 54·5; H, 2·7; N, 6·4; Br, 36·4%). The *monopicrate* crystallized from methanol as yellow plates, m. p. 188—189° (Found : C, 46·8; H, 2·5; N, 9·8; Br, 23·4. $C_{26}H_{15}O_7N_5Br_2$ requires C, 46·7; H, 2·2; N, 10·5; Br, 23·9%). The *dihydrobromide,* m. p. 260—263° (decomp.), crystallizes from acetone (Found : C, 40·1; H, 2·3; N, 4·9; Br, 53·0. $C_{20}H_{14}N_2Br_4$ requires C, 39·9; H, 2·3; N, 4·7; Br, 53·2%).

The dibromoethylene is recovered substantially unchanged after 25 hr. in concentrated sulphuric acid at 145°, or after fusion with potassium hydroxide for 2½ min.

FIG. 1.

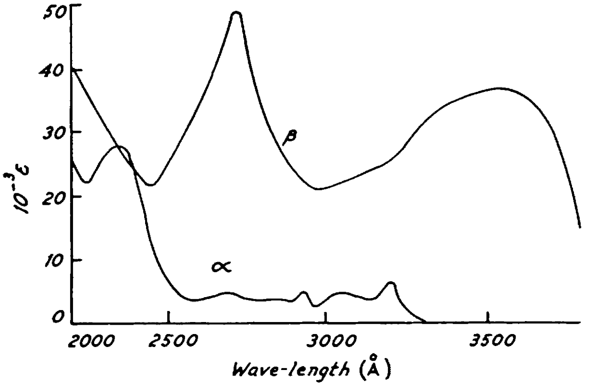
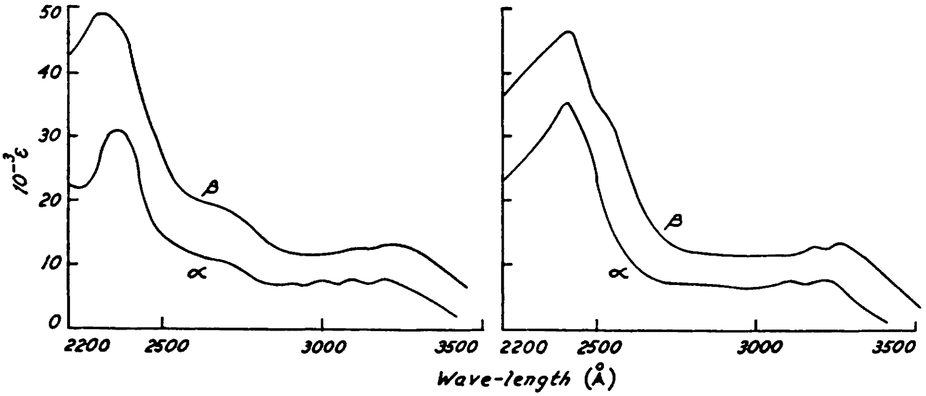


FIG. 2. FIG. 3.



Absorption spectra of (FIG. 1) 1 : *2-di-2′-quinolylethylene,* (FIG. 2) 1 : *2-dichloro-*1 : *2-di-2′-quinolylethylene, and* (FIG. 3) 1 : *2-dibromo-*1 : *2-di-2′-quinolylethylene.*

β-1 : *2-Dichloro-*1 : *2-di-2′-quinolylethylene.*—Copper bronze powder (2 g.) was added to a solution of ωωω-trichloroquinaldine (Hammick, *loc. cit.*) (2 g.) in pyridine (30 ml.), and the mixture refluxed for 15 min., then filtered and the filtrate poured on crushed ice. The material which separated was collected and washed with water and aqueous ammonia (*d* 0·880). β-1 : *2-Dichloro-*1 : *2-di-2′-quinolylethylene* (0·3 g., 22%) crystallized from light petroleum as colourless prisms, m. p. 94—95° (Found : C, 68·1; H, 3·5; N, 8·1; Cl, 20·5. $C_{20}H_{12}N_2Cl_2$ requires C, 68·4; H, 3·4; N, 8·0; Cl, 20·2%). The *monopicrate* crystallized from ethanol as yellow needles, m. p. 184—185° (Found : C, 54·1; H, 2·9; N, 12·6; Cl, 12·5. $C_{26}H_{15}O_7N_5Cl_2$ requires C, 53·8; H, 2·6; N, 12·1; Cl, 12·5%).

Debromination of β-1 : *2-Dibromo-*1 : *2-di-2′-quinolylethylene.*—β-Dibromodiquinolylethylene (0·7 g.) was dissolved in purified pyridine (25 ml.), and copper bronze powder (1 g.) added. This mixture was refluxed for 8 hr., filtered and poured on crushed ice. After the usual washing, the dark brown solid was recrystallized several times from methanol. It was identified as 1 : 2-di-2′-quinolylacetylene (0·07 g., 15%), m. p. 175—177° (mixed m. p. 175—176°) (Found: C, 84·9; H, 4·7; N, 10·7. Calc. for $C_{20}H_{12}N_2$: C, 85·7; H, 4·3; N, 10·0%).

β-1 : 2-*Di-2′-quinolylethylene.*—Copper bronze powder (6 g.) was heated with ωω-dibromoquinaldine (Sharp, *J. Pharm. Pharmacol.*, 1949, **1**, 395) (10 g.) in purified pyridine (100 ml.) for 30 min. The product was isolated as in the previous experiments, and after drying at 100° crystallized from light petroleum as colourless crystals of β-1 : 2-di-2′-quinolylethylene (0·85 g., 18%), m. p. 189—190° (no depression on admixture with a sample made by the method of Walker *et al.*, *loc. cit.*) (Found: C, 84·9; H, 5·0; N, 9·1. Calc. for $C_{20}H_{14}N_2$: C, 85·1; H, 5·0; N, 9·9%). It forms an insoluble dipicrate from ethanol, m. p. 286—288° (decomp.).

Kaplan and Lindwall's method (*loc. cit.*) gave only deoxyquinaldoin, m. p. 221° (Found: N, 9·4. Calc. for $C_{20}H_{14}ON_2$: N, 9·5%), which gave a phenylhydrazone from ethanol, m. p. 148—149° (Walker *et al.*, *loc. cit.*, give m. p. 149—150·5°).

ω-Monobromoquinaldine.—ωωω-Tribromoquinaldine (30 g.) was stirred in purified tetralin (480 ml.; Vogel, " Practical Organic Chemistry," Longmans, Green and Co., London, 1948, p. 825) at 100° for 6 hr., then at 150° for 2 hr. The cooled solution was extracted with dilute sulphuric acid (25% by vol.), and the aqueous portion washed with a little chloroform to remove tetralin. The acid solution was then neutralized with aqueous ammonia, in an ice-bath. Crystallization of the precipitated material from light petroleum (b. p. 60—80°) gave ω-monobromoquinaldine (12·9 g., 74%) as long colourless needles, m. p. 57°. Brown, Hammick, and Thewlis (*loc. cit.*) record m. p. 57°.

N-2-*Quinolylmethylquinolinium Bromide.*—ω-Monobromoquinaldine (0·5 g.) was dissolved in purified quinoline (7 ml.) and within 48 hr., at room temperature, solid was deposited. N-2-*Quinolylmethylquinolinium bromide* recrystallized from ethanol as yellow plates, m. p. 222—223° (Found: C, 64·3; H, 4·3; Br, 22·7. $C_{19}H_{15}N_2Br$ requires C, 6·49; H, 4·3; Br, 22·8%).

1 : 2-*Di-2′-quinolylethane.*—Purified quinaldine (71·5 g.) was stirred under nitrogen with sulphur (16 g.) and copper bronze powder (0·5 g.) for 9 hr. at 165—170°. The temperature is critical for optimum yield. The cold solution was poured into 6N-sulphuric acid (200 ml.) and aqueous sodium hydroxide (10%) added to the filtered solution. The tar deposited below pH 4·0 was removed, and the 1 : 2-di-2′-quinolylethane collected at pH 4·5. From the residue, made strongly alkaline, quinaldine (42·3 g.) was recovered. 1 : 2-Di-2′-quinolylethane (5·8 g., 20% based on unrecovered quinaldine), crystallized from benzene, had m. p. 162·5—163° (Found: C, 84·6; H, 5·7; N, 9·9. Calc. for $C_{20}H_{16}N_2$: C, 84·3; H, 5·7; N, 9·9%). Walker *et al.* (*loc. cit.*) record m. p. 164—165°. The extremely insoluble dipicrate had m. p. 273—275° (decomp.) (Found: C, 52·2; H, 3·0; N, 15·1. Calc. for $C_{32}H_{22}O_{14}N_8$: C, 51·8; H, 3·0; N, 15·1%). Walker *et al.* (*loc. cit.*) record m. p. 275—280° (decomp.); Brown, Hammick, and Thewlis's value of 177° (*loc. cit.*) was an error.

α-1 : 2-*Dibromo*-1 : 2-*di-2′-quinolylethylene.*—A solution of bromine (0·5 ml.) in carbon tetrachloride (5 ml.) was added to one of 1 : 2-di-2′-quinolylacetylene (0·5 g.) in dry carbon tetrachloride (50 ml.). The mixture was refluxed for 10 min., by which time all the solid first precipitated had redissolved. The hot solution was filtered, and the solid which crystallized from the filtrate on cooling was dissolved in methanol and reprecipitated with 2N-aqueous ammonia. The white solid crystallized from methanol, giving colourless prisms of α-1 : 2-*dibromo*-1 : 2-*di-2′-quinolylethylene*, m. p. 222—223° (Found: C, 54·6; H, 3·0; N, 6·4; Br, 36·3. $C_{20}H_{12}N_2Br_2$ requires C, 54·5; H, 2·7; N, 6·4; Br, 36·4%). It formed a *monopicrate* which crystallized from ethanol as yellow needles, m. p. 238—239° (decomp.) (Found: C, 46·9; H, 2·3; N, 10·7; Br, 23·9. $C_{26}H_{15}O_7N_5Br_2$ requires C, 46·7; H, 2·2; N, 10·5; Br, 23·9%).

Irradiation of β-1 : 2-*Dibromo*-1 : 2-*di-2′-quinolylethylene.*—A solution of β-1 : 2-dibromo-1 : 2-di-2′-quinolylethylene (1 g.) in dry methanol (50 ml.) was irradiated with ultraviolet light from an 80-w mercury-vapour lamp for 5 days, by which time a deposit of crystals had formed in the container (a thin-walled soda-glass test-tube). The crystals were collected and recrystallized from methanol as colourless needles, m. p. 220—221°. There was no depression of the melting point when this substance was mixed with α-1 : 2-dibromo-1 : 2-di-2′-quinolylethylene prepared as above. The product formed a monopicrate, yellow needles (from ethanol), m. p. and mixed m. p. 240—241° (decomp.).

Irradiation of β-1 : 2-*Dichloro*-1 : 2-*di-2′-quinolylethylene.*—β-1 : 2-Dichloro-1 : 2-di-2′-quinolylethylene (1 g.) in dry methanol (200 ml.) was irradiated as for β-1 : 2-dibromo-1 : 2-di-2′-quinolylethylene. α-1 : 2-*Dichloro*-1 : 2-*di-2′-quinolylethylene* recrystallized from methanol as colourless needles, m. p. 172—173°, depressed to 90° on admixture with the β-form. A *monopicrate* crystallized from methanol as yellow needles, m. p. 222—224° (decomp.) (Found:

C, 53·4; H, 2·9; N, 12·3; Cl, 12·2. $C_{28}H_{15}O_7N_5Cl_2$ requires C, 53·8; H, 2·6; N, 12·1; Cl, 12·5%).

Dechlorination of α-1 : 2-*Dichloro*-1 : 2-*di*-2′-*quinolylethylene*.—α-1 : 2-Dichloro-1 : 2-di-2′-quinolylethylene (0·45 g.) was refluxed in purified pyridine (2·5 ml.) with copper bronze powder for 1 hr. and, after cooling, poured on crushed ice. After isolation in the usual way, 1 : 2-di-2′-quinolylacetylene recrystallized from light petroleum as pale brown needles, m. p. and mixed m. p. 177—178°.

Irradiation of β-1 : 2-*Di*-2′-*quinolylethylene*.—The α-isomer is comparatively soluble in methanol, so the irradiation was carried out on a saturated solution of β-1 : 2-di-2′-quinolylethylene in methanol over an excess of the same compound. After several days' irradiation with ultraviolet light, crystals had been formed on the walls of the tube, and the original solid had dissolved. The product was recrystallized from benzene–methanol to give α-1 : 2-*di*-2′-*quinolylethylene* as colourless needles, m. p. 245° (Found : C, 85·0; H, 5·1; N, 9·95. $C_{20}H_{14}N_2$ requires C, 85·1; H, 5·0; N, 9·9%). It formed a comparatively unstable *dipicrate*, m. p. 147—151° (decomp.) (Found : N, 15·0. $C_{32}H_{20}O_{14}N_8$ requires N, 15·1%).

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