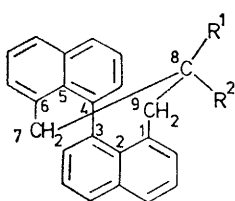


## Optically Active Nine-membered Rings incorporating the 8- and 8'-Positions of 1,1'-Binaphthyl

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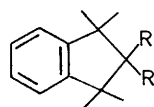
Diethyl sodiomalonate reacts readily with 8,8'-bisbromomethyl-1,1'-binaphthyl to form a nine-membered carbocyclic ring: this behaviour is similar to the reactions of diethyl sodiomalonate with 2,2'-bisbromomethylbiphenyl to form a seven-membered ring, and with *o*-xylylene dibromide to form a five-membered ring. The preparation of diethyl 8,9-dihydro-7*H*-cyclonona[1,2,3-*de*:4,5,6-*d'e'*]dinaphthalene-8,8-dicarboxylate, in the racemic and in the optically active state, and of derived substances, is described.

BEFORE the discovery of the acyloin reaction, nine-membered carbocyclic rings were far from easy to prepare.<sup>1</sup> It has come as a welcome surprise to us to find that 8,8'-bisbromomethyl-1,1'-binaphthyl<sup>2</sup> reacts readily with diethyl sodiomalonate to form diethyl 8,9-dihydro-7*H*-cyclonona[1,2,3-*de*:4,5,6-*d'e'*]dinaphthalene-8,8-dicarboxylate (I). This type of ring forming reaction

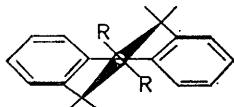


- (I)  $R^1 = R^2 = \text{CO}_2\text{Et}$   
 (II)  $R^1 = R^2 = \text{CO}_2\text{H}$   
 (III)  $R^1 = \text{CO}_2\text{H}, R^2 = \text{H}$   
 (IV)  $R^1 = R^2 = \text{CO}_2\text{Me}$   
 (V)  $R^1 = \text{CO}_2\text{Me}, R^2 = \text{H}$   
 (VI)  $R^1 = R^2 = \text{CH}_2\text{OH}$   
 (VII)  $R^1 = \text{CH}_2\text{OH}, R^2 = \text{H}$

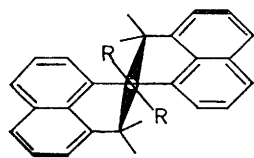
is not amenable to kinetic study, but qualitative comparisons can be drawn with similarly successful uses of it. Baeyer and Perkin<sup>3</sup> made the five-membered ring (VIII) from *o*-xylylene dibromide, and later Kenner,<sup>4</sup> employing Baeyer and Perkin's procedure, prepared the seven-membered ring (IX) from 2,2'-bisbromomethyl-



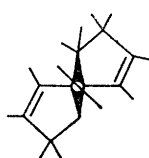
(VIII)  $R = \text{CO}_2\text{Et}$



(IX)  $R = \text{CO}_2\text{Et}$



(X)



(XI)

biphenyl. Kenner commented that there appeared to be a close relationship between these derivatives of *o*-xylene and of 2,2'-bitolyl; the tendency to form the

<sup>1</sup> L. Ruzicka, *Chem. and Ind.*, 1935, 2; J. Sicher, *Progr. Stereochem.* 1958, **3**, 202.

<sup>2</sup> Y. Badar, A. S. Cooke, and M. M. Harris, *J. Chem. Soc.*, 1965, 1412.

<sup>3</sup> A. Baeyer and W. H. Perkin, jun., *Ber.*, 1834, **17**, 122; W. H. Perkin, jun., *J. Chem. Soc.*, 1888, 1.

<sup>4</sup> J. Kenner, *J. Chem. Soc.*, 1913, 613.

<sup>5</sup> G. H. Beaven, G. R. Bird, D. M. Hall, E. A. Johnson, J. E. Ladbury, M. S. Lesslie, and E. E. Turner, *J. Chem. Soc.*, 1955, 2708.

<sup>6</sup> D. M. Hall and F. Minhaj, *J. Chem. Soc.*, 1957, 4584.

cycloheptadiene derivative is so great that it was formed even in the presence of two proportions of diethyl malonate. Moreover, Turner and his co-workers<sup>5</sup> found that 2,2'-bisbromomethylbiphenyl reacted with tetraethyl propane-1,1,3,3-tetracarboxylate by an extraordinary reaction, involving fission of the reagent, to give the same seven-membered ring. The generality of the facile closure to rings of this size in the 2,2'-biphenyl series has been amply demonstrated.<sup>6,7</sup> In contrast, preparation of the parent fully saturated ring from 1,6-di-iodohexane,<sup>8</sup> was unsatisfactory. When an attempt was made to prepare a nine-membered ring in the bridged biphenyl series from diethyl sodiomalonate and 2,2'-bis-(2-bromoethyl)biphenyl, only 2,2'-divinylbiphenyl was formed,<sup>9</sup> a result which had not been expected as  $\beta$ -phenylethyl bromide under the same conditions gives  $\beta$ -phenylethylmalonic ester: the authors concluded that steric inhibition of nucleophilic replacement of bromide by sodiomalonic ester must slow down that process in comparison with elimination.

In the reaction now described, elimination is not an alternative, and the nine-membered ring (I) is formed, even in the presence of an excess of diethyl malonate, in the conditions previously used to make (VIII) and (IX). Internal nucleophilic attack by the substituted diethyl malonate anion on the second  $\text{CH}_2\text{Br}$  group must be highly favoured by the stereochemistry of the molecule.

We have not found the same correspondence in reactivity between the *o*-xylyl, 2,2'-biphenyl, and 8,8'-(1,1'-binaphthyl) systems in Dieckmann or in Thorpe-Ziegler reactions. Kenner,<sup>4</sup> by the method Dieckmann<sup>10</sup> had used originally on diethyl adipate, prepared the seven-membered ring from 2,2'-bis(ethoxycarbonylmethyl)biphenyl; Perkin and Titley<sup>11</sup> obtained the five-membered ring from 1,2-bis(ethoxycarbonylmethyl)benzene in 90% yield. Use of a similar procedure in our hands on 8,8'-bis(ethoxycarbonylmethyl)-1,1'-binaphthyl<sup>12</sup> has failed to give any detectable ring closure.

<sup>7</sup> K. Mislow, M. A. W. Glass, R. E. O'Brien, P. Rutkin, D. H. Steinberg, J. Weiss, and C. Djerassi, *J. Amer. Chem. Soc.*, 1962, **84**, 1455; R. E. Buntrick and E. C. Taylor, *Chem. Rev.*, 1968, **68**, 209.

<sup>8</sup> V. P. Gol'mov, *Zhur. obshchei Khim.*, 1952, **22**, 809; (*Chem. Abs.*, 1953, **47**, 3251).

<sup>9</sup> K. Mislow, S. Hyden, and H. Schaefer, *J. Amer. Chem. Soc.*, 1962, **84**, 1449.

<sup>10</sup> W. Dieckmann, *Annalen*, 1901, **317**, 32.

<sup>11</sup> W. H. Perkin, jun. and A. F. Titley, *J. Chem. Soc.*, 1922, 1562.

<sup>12</sup> H. E. Harris, M. M. Harris, R. Z. Mazengo, and S. Singh, *J.C.S. Perkin II*, 1974, 1059.

Moore and Thorpe<sup>13</sup> found that 1,2-bis(cyanomethyl)-benzene cyclised quantitatively in the presence of sodium ethoxide to form the five-membered ring cyano-imine (some evidence suggests that this may have the tautomeric cyano-enamine structure<sup>14</sup>); Kenner and Turner<sup>15</sup> carried out a similar reaction successfully on 2,2'-bis(cyanomethyl)biphenyl to form the seven-membered ring, and Mislow<sup>16,17</sup> has used the process to incorporate the 2,2'-positions of various substituted biphenyls, including 1,1'-binaphthyl, into seven-membered rings. However, as with the Dieckmann reaction, we have been unable to extend the use of the method into formation of the nine-membered ring from 8,8'-bis(cyanomethyl)-1,1'-binaphthyl.\* The proposition that the Thorpe<sup>4</sup> and Dieckmann reactions are more sensitive tests for ease of ring formation is worth examination in this context.

The success of all these reactions depends upon the frequency of meeting of the reaction sites and also upon the stability of the ring when it is formed, so strain in the ring, and reversibility of the reaction, must affect the outcome. Kenner<sup>4</sup> pointed out that the stiffening effect of two aromatic double bonds in his biphenyl compounds could increase the ease of approach of the reacting sites for forming the seven-membered rings; it now seems probable that the two naphthalene systems can assist formation of the nine-membered ring in a similar way, that is, can significantly decrease unfavourable entropy by limiting the conformational range. The reaction between the bromo-compounds and diethyl malonate is not reversible, but the Dieckmann and Thorpe reactions have an element of reversibility, and hence product formation in these reactions can be expected to be more sensitive to strain. There is a stricture on the Dieckmann reaction,<sup>18</sup> namely that condensation fails when a stable enolate of the product cannot be formed: for the Thorpe reaction, Baldwin<sup>14</sup> has collected evidence in favour of a cyano-enamine structure of the product being more usual than a cyano-imine structure. These observations may be of real significance in the present series, as can be seen from a model.

If a model is made in which the 8,8'-positions of 1,1'-binaphthyl are linked by  $\text{CH}_2\text{CR}_2\text{CH}_2$  (X) [Fieser models (Rinco Instruments Co.) are satisfactory for this purpose as they will accommodate the necessary degree of strain] it is clear that (a) the ring could not be formed at all without a large deviation from parallel of the 1,1'-bond and the 8- or 8'- to  $\text{CH}_2$  bond (the out-of-plane or twisting component of the recognised *peri*-naphthalene deformation) and (b) the nine-membered ring so formed could not contain a further double bond, as required by enolate or cyano-enamine systems, without enormously

increasing the strain. It appears that one conformation of the cyclononadinaphthalene is greatly preferred, (X), probably to the exclusion of others; it has a  $C_2$  axis, a conclusion borne out by the  $^1\text{H}$  n.m.r. spectrum (see Table) which shows an identical pair of well separated

$^1\text{H}$  N.m.r. spectra in  $\text{CDCl}_3$  [60 or 100 Mz;  $\delta$  (p.p.m.); J/Hz;  $\text{Me}_4\text{Si}$  as internal standard]

Compound	Chemical shift	Assignment
(I)	7.79 (2 H, d), 7.66 (2 H, d)	Ar 4', 4'' and 5', 5''
	7.45—6.95 (6 H, m)	Ar
	6.75 (H, d), 6.63 (H, d)	Ar 7', 7''
	3.93, 3.11 (4 H, q, J —14)	$\text{CH}_2$ -naphthyl
	3.86 (4 H, q, J 7)	$\text{CH}_2\text{CH}_3$
	1.07 (6 H, t, J 7)	$\text{CH}_2\text{CH}_3$
(IV)	7.79 (2 H, d), 7.66 (2 H, d)	Ar 4', 4'' and 5', 5''
	7.4—6.9 (6 H, m)	Ar
	6.75 (H, d), 6.63 (H, d)	Ar 7', 7''
	3.98, 3.09 (4 H, q, J —14)	$\text{CH}_2$ -naphthyl
	3.37 (6 H, s)	$\text{COOCH}_3$
(V)	7.82 (2 H, t), 7.76 (2 H, t)	Ar 4', 4'' and 5', 5''
	7.5—7.0 (6 H, m)	Ar
	6.82 (H, t), 6.75 (H, t)	Ar 7', 7''
	3.84—3.56 (2 H, m)	Deshielded H of $\text{CH}_2$ -naphthyl
	3.40 (3 H, s)	$\text{COOCH}_3$
(VI)	7.83 (2 H, d), 7.75 (2 H, d)	Ar 4', 4'' and 5', 5''
	7.20—7.45 (6 H, m)	Ar
	6.75 (H, d), 6.68 (H, d)	Ar 7', 7''
	3.32, 2.46 (4 H, q, J —14.5)	$\text{CH}_2$ -naphthyl
	2.84 (4 H, s)	$\text{CH}_2\text{OH}$
(VII)	7.79 (2 H, q), 7.71 (2 H, q)	Ar 4', 4'' and 5', 5''
	7.48—7.10 (6 H, m)	Ar
	6.76 (H, q), 6.69 (H, q)	Ar 7', 7''
	3.63—3.11 (2 H, m)	Deshielded H of $\text{CH}_2$ -naphthyl
	2.86 (2 H, m)	$\text{CH}_2\text{OH}$
	2.64—2.36 (2 H, m)	Shielded H of $\text{CH}_2$ -naphthyl
	1.7br (H, s)	OH
1.40 (H, s)	CH	

methylene protons ( $\text{CH}_2$ -naphthyl) with a large coupling constant, as would be expected for diastereotopic protons in very different environments.<sup>19,20</sup> It seems, for the following reasons, that the best stereochemical analogy with our dinaphtho-nine-membered ring is *Z,Z*-cyclonona-1,3-diene.<sup>21</sup> If the model of this molecule is made up, and put into the conformation with all the methylene hydrogen atoms fully staggered, (XI), it has a  $C_2$  axis and the two double bonds are at a dihedral angle of *ca.*  $90^\circ$ . Although it has been suggested<sup>22</sup> that a conformation with the dihedral angle of  $65^\circ$  is preferred, inspection of models shows that the symmetrical model, with dihedral angle *ca.*  $90^\circ$  cannot have much higher energy: this model has a  $C_2$  symmetry axis. We find

<sup>17</sup> K. Mislow and F. A. McGinn, *J. Amer. Chem. Soc.*, 1958, **80**, 6036.

<sup>18</sup> J. P. Schaefer and J. J. Bloomfield, *Org. Reactions*, 1967, **15**, 1.

<sup>19</sup> C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, 1958, **29**, 1012; K. Mislow, M. A. W. Glass, H. B. Hopps, E. Simon, and G. H. Wahl, jun., *J. Amer. Chem. Soc.*, 1964, **86**, 1710.

<sup>20</sup> D. M. Hall, *Progr. Stereochem.*, 1969, **4**, 1.

<sup>21</sup> R. W. Fawcett and J. O. Harris, *J. Chem. Soc.*, 1964, 2673.

<sup>22</sup> N. L. Allinger and M. A. Miller, *J. Amer. Chem. Soc.*, 1964, **86**, 2811.

\* We regret an error in the published  $^1\text{H}$  n.m.r. spectrum of this compound: in ref. 12, p. 1062, line 23, 5.83—6.08 should read 6.67—7.13 and J 10 should read J 19.

<sup>13</sup> C. W. Moore and J. F. Thorpe, *J. Chem. Soc.*, 1908, 165.

<sup>14</sup> S. Baldwin, *J. Org. Chem.*, 1961, **26**, 3288.

<sup>15</sup> J. Kenner and E. G. Turner, *J. Chem. Soc.*, 1911, 2101.

<sup>16</sup> P. Newman, P. Rutkin, and K. Mislow, *J. Amer. Chem. Soc.*, 1958, 465.

that the model of (*Z,Z*)-cyclonona-1,3-diene with the  $C_2$  axis is almost exactly superposable upon the nine-membered ring of our model which we believe represents a unique conformation for these dinaphtho-nine-membered ring compounds: the magnitude of the two *peri*-naphthalene distortions is sufficient to permit the same steric consequence as the group (*Z,Z*)- $CH_2-CH=CH-CH=CH-CH_2$ .

The diethyl ester (I) on hydrolysis gave the dicarboxylic acid (II) which melted at 235° with loss of carbon dioxide to form the monocarboxylic acid (III); (II) and (III) were converted into methyl esters (IV) and (V) by diazomethane; the ethyl and methyl esters (I), (IV), and (V) were reduced by lithium aluminium hydride to form the alcohols (VI) and (VII).

These molecules are all chiral. Optically active (II) was obtained in two ways: either the racemate was resolved using the quinidine salt and crystallising from ethanol, or optically active (I), prepared from (+)-8,8'-bisbromomethyl-1,1'-binaphthyl, was hydrolysed. The highest specific rotation observed using the first method was +349° ( $\lambda$  546 nm), while from the second it was +356° ( $\lambda$  561 nm). When this specimen was heated it formed monocarboxylic acid (III),  $[\alpha]_{561}^{25} + 787^\circ$ ; this marked change in rotation accompanies the loss of the  $C_2$  axis, a change from dissymmetry to asymmetry: the rotations of the methyl esters (IV) and (V) and those of their reduction products (VI) and (VII) followed the same trend.

#### EXPERIMENTAL

*Diethyl 8,9-Dihydro-7H-cyclonona*[1,2,3-de:4,5,6-d'e']*dinaphthalene-8,8-dicarboxylate* (I).—To 8,8'-bisbromomethyl-1,1'-binaphthyl<sup>2</sup> (10.0 g) suspended in dioxan (10 ml) was added, with stirring, diethyl disodium malonate [sodium (1.6 g), ethanol (40 ml), diethyl malonate (5.1 g, >1 equiv.)] and the mixture was boiled for 3 h. Water was added to complete the precipitation of the solid which separated on cooling. Crystallisation from benzene gave the *diester* (I) (9.6 g, 96%), m.p. 269–271° [Found: C, 79.3; H, 5.9; O, 14.7%; *M*, 438.1826 (mass spectrum).  $C_{25}H_{18}O_4$  requires C, 79.4; H, 6.0; O, 14.6%; *M*, 438.1831, *m/e* 291.1172 (*M* – H – 2CO<sub>2</sub>Et) and 364.1470 (*M* – H – CO<sub>2</sub>Et), *m*\* 302.5 (= 364<sup>2</sup>/438).

*Optically Active* (I).—Use of (+)-8,8'-bisbromomethyl-1,1'-binaphthyl,  $[\alpha]_{546}^{25} + 348^\circ$ ; 1.0 g in the above preparation gave, on crystallisation, 0.3 g of optically inactive ester, m.p. 263–264°, followed by 0.5 g of ester,  $[\alpha]_{546}^{25} + 317^\circ$  (*c* 0.214, 95% ethanol), m.p. 145–149° with cloudiness clearing at 190–200° (probably contamination by racemate).

*8,9-Dihydro-7H-cyclonona*[1,2,3-de:4,5,6-d'e']*dinaphthalene-8,8-dicarboxylic Acid* (II).—Hydrolysis of (I) (6 g) by boiling with ethanolic potassium hydroxide for 3 h gave the potassium salt which when dissolved in cold water and acidified with dilute aqueous hydrochloric acid gave the *diacid monohydrate* (4.8 g) which melted at 235–236° with brisk effervescence, solidified, and re-melted at 252–254° (Found: C, 74.9; H, 5.0; O, 19.8.  $C_{25}H_{18}O_4 \cdot H_2O$  requires C, 75.0; H, 5.0; O, 20.0%), *m/e* (220°, 70 eV) 338.1301 (*M*, 100%). Sparging solubility in suitable solvents precluded satisfactory observation of the n.m.r. spectrum.

*Optically Active* (II).—(a) The racemic acid (5.0 g) and quinidine (4.25 g, 1 equiv.) were dissolved in ethanol and three crops of crystals obtained: (i) 4.0 g, m.p. 198–200°,  $[\alpha]_{546}^{21} - 42^\circ$  (*c* 0.38; *l*, 0.5; *NN*-dimethylformamide) (Found: C, 76.3; H, 6.1; N, 4.0; O, 13.7.  $C_{45}H_{42}N_2O_6$  requires C, 76.5; H, 5.9; N, 4.0; O, 13.6%); (ii) 1.5 g, m.p. 185–192°,  $[\alpha]_{546}^{21} + 44.1^\circ$ ; (iii) 3.0 g, m.p. 198–201°,  $[\alpha]_{546}^{21} + 187.5^\circ$  (*c* 0.208; *l* 0.5; *NN*-dimethylformamide) (Found: C, 74.4; H, 6.0; N, 4.0; O, 15.3.  $C_{45}H_{42}N_2O_6 \cdot H_2O$  requires C, 74.6; H, 6.1; N, 3.9; O, 15.5%). These crops were then decomposed, severally, by extraction of a chloroform solution with dilute aqueous sodium hydroxide, followed by acidification with hydrochloric acid. The acid from crop (i) had m.p. 198° (effervescence),  $[\alpha]_{546}^{19} - 318^\circ$  (*c* 0.085; *l* 2; 95% ethanol), not raised by crystallisation from ethanol (Found: C, 74.9; H, 5.2; O, 19.9.  $C_{25}H_{18}O_4 \cdot H_2O$  requires C, 75.0; H, 5.0; O, 20.0%). Crop (ii) gave acid  $[\alpha]_{546}^{19} - 51^\circ$ . Crop (iii) gave acid, m.p. 195–200° (effervescence),  $[\alpha]_{546}^{21} + 349^\circ$  (*c* 0.412; *l* 0.5; 95% ethanol) (Found: C, 74.8; H, 5.2; O, 19.9%). Repetition of this procedure gave a less effective resolution,  $[\alpha]_{546} - 235$  and  $+257^\circ$ .

(b) Hydrolysis of (+)-(I) gave (+)-(II), m.p. 198–200°, mixed m.p. with a specimen prepared from crop (iii), 197–200°,  $[\alpha]_{546}^{19} + 356^\circ$  (*c* 0.08; *l* 2; 95% ethanol).

*8,9-Dihydro-7H-cyclonona*[1,2,3-de:4,5,6-d'e']*dinaphthalene-8-carboxylic Acid* (III).—Compound (II) (4 g), heated in a metal bath at 240° for 15 min, melted, effervesced briskly, and solidified, giving the *acid* (III) which was crystallised from ethanol, m.p. 252–254° (Found: C, 85.1; H, 5.4; O, 9.3.  $C_{24}H_{18}O_2$  requires C, 85.2; H, 5.3; O, 9.5%).

*Optically Active* (III).—A specimen of (–)-(II) (5 g;  $[\alpha]_{546}^{20} - 235^\circ$ ) treated as above gave (–)-(III) (3.9 g), m.p. 220–222°,  $[\alpha]_{546}^{22} - 515^\circ$  (*c* 0.132; *l* 0.5; 95% ethanol) (Found: C, 85.1; H, 5.3; O, 9.5%). Further specimens of (–)-(II), similarly treated, gave (–)-(III) with the following changes in specific rotation:  $[\alpha]_{546} - 309 \rightarrow -593^\circ$ ;  $-240 \rightarrow -565^\circ$ . Similarly (+)-(II)  $\rightarrow$  (+)-(III) gave  $[\alpha]_{561}^{25} + 357 \rightarrow +787^\circ$ ;  $[\alpha]_{546}^{25} + 258 \rightarrow +522^\circ$ , m.p. 220–222° (Found: C, 85.0; H, 5.5; O, 9.3%).

*Dimethyl 8,9-Dihydro-7H-cyclonona*[1,2,3-de:4,5,6-d'e']*dinaphthalene 8,8-dicarboxylate* (IV).—Compound (II) (1.0 g) was added to a cold ethereal solution of diazomethane (0.3 g); after effervescence subsided the solution was washed with aqueous sodium carbonate, worked-up normally, and the product crystallised from benzene, giving (IV), m.p. 258–260° (Found: C, 78.9; H, 5.2; O, 15.7.  $C_{27}H_{22}O_4$  requires C, 79.0; H, 5.4; O, 15.6%).

*Optically Active* (IV).—Compound (–)-(II) (1.0 g;  $[\alpha]_{546}^{20} - 235^\circ$ ), treated as above except for crystallisation from methanol, gave (–)-(IV), m.p. 165–167°,  $[\alpha]_{546}^{20} - 263^\circ$  (*c* 0.072; *l* 0.5; 95% ethanol) (Found: C, 78.9; H, 5.4; O, 15.7%). Compound (+)-(II) (1.0 g;  $[\alpha]_{546}^{20} + 257^\circ$ ) treated similarly gave (+)-(IV), m.p. 164–165°,  $[\alpha]_{546}^{20} + 234^\circ$  (*c* 0.064; *l* 0.5; 95% ethanol) (Found: C, 79.0; H, 5.3; O, 15.7%). Both of these optically active specimens melted to give a cloudy liquid which cleared at ca. 235°; presumably they contain some racemic ester.

*Methyl 8,9-Dihydro-7H-cyclonona*[1,2,3-de:4,5,6-d'e']*dinaphthalene-8-carboxylate* (V).—To the acid (III) (3 g), suspended in boiling benzene, was added thionyl chloride (1 ml) and boiling continued to complete dissolution (3 h); methanol (5 ml) was added and the solution boiled for a further 30 min. Normal working up gave recovered (III)

(1.5 g) and the ester (V) (1.4 g) which crystallised from benzene, m.p. 186—188° [Found: C, 85.1; H, 5.7; O, 9.2%; *M* (Mechrolab osmometer), 351. C<sub>25</sub>H<sub>20</sub>O<sub>2</sub> requires C, 85.2; H, 5.7; O, 9.1%; *M*, 352].

*Optically Active* (V).—Compound (–)-(III) ( $[\alpha]_{546} -515^\circ$ ) with ethereal diazomethane gave (–)-(V), crystallised from methanol, m.p. 112°,  $[\alpha]_{546} -478^\circ$  (*c* 0.14; *l* 0.5; 95% ethanol) (Found: C, 85.1; H, 5.6; O, 9.0%). Compound (+)-(III),  $[\alpha]_{546} +522^\circ$ , similarly gave (+)-(V), m.p. 112°,  $[\alpha]_{546} +444^\circ$  (*c* 0.036; *l* 0.5; 95% ethanol) (Found: C, 85.1; H, 5.5; O, 9.1%).

8,8-Bishydroxymethyl-8,9-dihydro-7H-cyclonona[1,2,3-de:4,5,6-d'e']dinaphthalene (VI).—Powdered (I) (1 g) was boiled with lithium aluminium hydride (0.5 g) in anhydrous ether for 5 h. Normal working up and crystallisation from benzene gave the diol (VI) (0.6 g), m.p. 196° (Found: C, 84.6; H, 6.3; O, 9.0%; *M*, 354.161 5. C<sub>25</sub>H<sub>22</sub>O<sub>2</sub> requires C, 84.7; H, 6.3; O, 9.0%; *M*, 354.162 0).

*Optically Active* (VI).—Reduction of (+)-(IV) ( $[\alpha]_{546} +234^\circ$ ; 0.5 g) gave (+)-(VI), m.p. 155—157°,  $[\alpha]_{546} +320^\circ$  (*c* 0.106, *l* 0.5; 95% ethanol) (Found: C, 84.6; H, 6.4%). Similarly (–)-(IV) ( $[\alpha]_{546} -263^\circ$ ) gave (–)-(VI), m.p. 155—156°,  $[\alpha]_{546} -378^\circ$  (*c* 0.164; *l* 0.5; 95% ethanol) (Found: C, 84.6; H, 6.2%).

8-Hydroxymethyl-8,9-dihydro-7H-cyclonona[1,2,3-de:4,5,6-

d'e']dinaphthalene (VII).—The methyl ester (V) (3 g) was boiled with lithium aluminium hydride (0.75 g) in anhydrous ether using a Soxhlet apparatus with the sparingly soluble (V) in the thimble. After 3 h boiling, the product was worked-up normally. The product (VII) crystallised from either cyclohexane or chloroform with occluded solvent which was lost partially on standing, or more rapidly on heating; the remaining glass had no definite m.p., and traces of solvent were apparent in the mass spectra and n.m.r. spectra (Found: C, 88.6; H, 6.3; O, 5.0%; *M*, 324.151 8. C<sub>24</sub>H<sub>20</sub>O requires C, 88.8; H, 6.2; O, 4.9%; *M*, 324.151 4).

*Optically Active* (VII).—Use of (+)-(V) (0.5 g,  $[\alpha]_{546} +444^\circ$ ) in the above preparation gave (+)-(VII) (0.3 g), m.p. indeterminate from 81° (effervescence),  $[\alpha]_{546} ca. +500^\circ$  (*c* 0.052; *l* 0.5; 95% ethanol) (Found: C, 88.6; H, 6.2%). Compound (–)-(V) (0.5 g,  $[\alpha]_{546} -478^\circ$ ) treated as above gave (–)-(VII) (0.20 g),  $[\alpha]_{546} -550^\circ$  (*c* 0.184, *l* 0.5, 95% ethanol).

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