

494. *Experiments in the cycloButane Series. Part V.\** cis- and trans-1-(4-Dimethylamino- $\alpha$ -phenylbenzylidene)-2-diphenylmethylenecyclobutane.

By F. B. KIPPING and J. J. WREN.

In further attempts to demonstrate optical activity in the 1:2-bis-diphenylmethylenecyclobutane system the isomeric amines (III) and (IV) were prepared. Heat, light, alumina, and acid facilitate their interconversion; acid surprisingly favours the *cis*-configuration. The ultraviolet spectra of these and related compounds, particularly 1-*p*-dimethylamino-phenyl-4-phenylbuta-1:3-diene, are discussed.

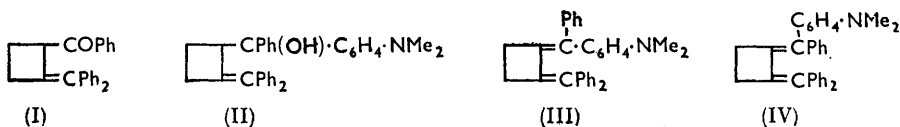
In attempts to demonstrate optical activity in the 1:2-bisdiphenylmethylenecyclobutane system<sup>1</sup> it was decided to synthesise 1-(4-dimethylamino- $\alpha$ -phenylbenzylidene)-2-diphenylmethylenecyclobutane, which might be amenable to resolution by conventional methods. This compound should exist in a *cis*- (III) and a *trans*-modification (IV). ( $\pm$ )-1-Benzoyl-2-diphenylmethylenecyclobutane (I) with *p*-lithio-*NN*-dimethylaniline gave the olefinic alcohol (II) which readily lost water, giving yellow crystals which fluoresced intensely in ultraviolet light. These were evidently a mixture of dienes (III) and (IV) since different specimens had different melting points and infrared and ultraviolet spectra. The spectra (*e.g.*, curve *D*, Fig. 3) appeared to have isosbestic points at  $\sim 280$  and  $\sim 340$  m $\mu$ .

Separation of the isomers was attempted in numerous ways. No enrichment of either

\* Part IV, *J.*, 1957, 3251.

<sup>1</sup> Cf. Kipping and Wren, *J.*, 1957, 3246.

was effected by crystallisation from various solvents or by fractional sublimation *in vacuo*. Column and paper chromatography under various conditions also failed to resolve the mixture. However, the pure isomers were obtained in unexpected ways. When ethanolic mother-liquor from crystallisation of the mixed isomers was left in a stoppered flask long



rods or hard rosettes of the pure *trans*-isomer (IV) were slowly formed. Although no crystalline (+)-3-bromocamphor-8-sulphonate was obtained from the mixed isomers, a crystalline (+)-camphor-10-sulphonate was obtained, and decomposition of it with alkali yielded *optically inactive* material which proved to be the pure *cis*-isomer (III). The pure *trans*-isomer (IV) yielded only the *cis*-(+)-camphor-10-sulphonate, presumably owing to isomerisation catalysed by camphorsulphonic acid.

1-*p*-Dimethylaminophenyl-4-phenylbuta-1:3-diene.—This was studied as a model substance. The ultraviolet spectrum of the *trans-trans*-diene has been described twice<sup>2,3</sup> and the maxima showed roughly the expected bathochromic displacements, compared with those of *trans-trans*-1:4-diphenylbuta-1:3-diene, but showed considerable unexpected hypochromic displacements (hydrocarbon,  $\epsilon_{\max}$  12,700, 55,300; amine,  $\epsilon_{\max}$  10,000, 42,300;<sup>3</sup> solvent, ethanol). In *trans*-stilbene a 4-dimethylamino-substituent gives a hyperchromic shift in addition to a bathochromic shift of over 50  $m\mu$  (*trans*-stilbene,  $\lambda_{\max}$  295  $m\mu$ ,  $\epsilon$  27,000;<sup>4</sup> *trans*-4-dimethylaminostilbene,  $\lambda_{\max}$  346.5  $m\mu$ ,  $\epsilon$  31,500;<sup>5</sup> solvent, ethanol).

Our *trans-trans*-amine, purified by crystallisation and chromatography, had m. p. 183.5–184°, and, as was expected, its spectrum (curve *B*, Fig. 1) does not show considerable hypochromic displacements ( $\epsilon_{\max}$  10,400, 51,800). The *trans-trans*-assignment is confirmed by the following observations, correlated with the work of Pinckard *et al.*<sup>6</sup> on the isomeric 1:4-diphenylbuta-1:3-dienes: (a) The strongly acidic conditions of working-up would convert other isomers largely into the *trans-trans*-form. (b) The relatively high melting point suggests the *trans-trans*-configuration, as does the crystalline form, which is identical with that of the parent hydrocarbon.<sup>7</sup> (c) The ultraviolet spectrum shows an overall bathochromic displacement of roughly 40  $m\mu$ , with loss of fine structure, compared with that of the parent hydrocarbon (see Fig. 1); the general level of absorption is nearly unaltered. (d) The expected hypochromic effect of acid (curve *C*, Fig. 1) is not accompanied by a marked hyperchromic effect, which would result if a *cis*-isomer were treated with acid. The spectrum in acid is consistent with addition of the chromophore  $^+\text{NHMe}_2$  to the *trans-trans*-1:4-diphenylbuta-1:3-diene system. (e) Illumination of solutions in light petroleum caused hypochromic and hypochromic spectral changes (see Fig. 2) analogous to those described for the parent hydrocarbon,<sup>6</sup> which was converted into its *cis-trans*-isomer in this way. (The amine actually has two isomers corresponding to the latter, which may be termed *cis-trans* and *trans-cis* respectively.) Chromatographed on alumina, the product of illumination formed a band below that of the *trans-trans*-amine, and this yielded an oil which crystallised as the *trans-trans*-amine.

Earlier preparations of the *trans-trans*-amine were obviously contaminated with geometrical isomers. In the present work, no appreciable photoisomerisation occurred whilst solutions were actually in the spectrophotometer. (Haddow *et al.*<sup>3</sup> reported a contrary observation.) Solutions were, however, affected by the normal light of the

<sup>2</sup> Hertel and Lührmann, *Z. phys. Chem.*, 1939, **B**, **44**, 261.

<sup>3</sup> Haddow, Harris, Kon, and Roe, *Phil. Trans.*, 1948, **A**, **241**, 147.

<sup>4</sup> Gillam and Stern, "Electronic Absorption Spectroscopy," Arnold, London, 1954, p. 242.

<sup>5</sup> Beale and Moe, *J. Amer. Chem. Soc.*, 1952, **74**, 2302, 6317.

<sup>6</sup> Pinckard, Wille, and Zechmeister, *ibid.*, 1948, **70**, 1938.

<sup>7</sup> Sandoval and Zechmeister, *ibid.*, 1947, **69**, 553.

laboratory; in winter the effect was slight, but in summer  $\epsilon_{\max}$  fell appreciably within five minutes, and during 30 minutes it fell from 51,800 to 40,000 (ethanolic solution).

*Characterisation of the Isomeric Dienes (III and IV).*—The conclusions drawn previously about the configuration of the 1:2-bisdiphenylmethylenecyclobutane molecule<sup>1,8</sup> suggest that the dimethylamino-group in the *trans*-isomer (IV) is almost fully conjugated with the diene system, whereas that in the *cis*-isomer (III) is not. Curve *B* in Fig. 3 should therefore be the spectrum of the *trans*-isomer: its maximum at longest wavelength is 30  $m\mu$  nearer the red than that for the parent hydrocarbon and shows a hyperchromic displacement of

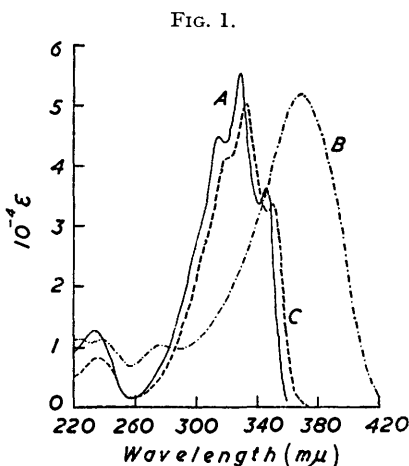


FIG. 1. (A) *trans-trans*-1:4-Diphenylbuta-1:3-diene in ethanol ( $\lambda_{\max}$ . 232, 315, 329, 346  $m\mu$ ;  $\epsilon$  12,700, 44,800, 55,300, 35,900) (the spectrum printed in Fig. 1 of ref. 8 was taken from obsolete data and omitted the maximum at 315  $m\mu$ ). (B) *trans-trans*-1-*p*-Dimethylaminophenyl-4-phenylbuta-1:3-diene in ethanol ( $\lambda_{\max}$ . 276, 369  $m\mu$ ;  $\epsilon$  10,400, 51,800). (C) Same compound as in (B), but in ethanol containing 1% of concentrated hydrochloric acid ( $\lambda_{\max}$ . 235, 333, 350  $m\mu$ ;  $\epsilon$  8400, 50,000, 33,200.  $\lambda_{\text{inf}}$ . 321  $m\mu$ ;  $\epsilon$  41,100).

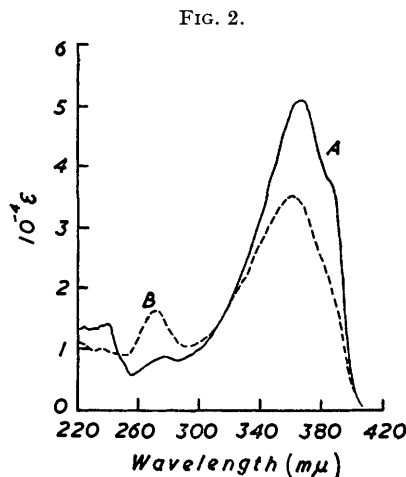
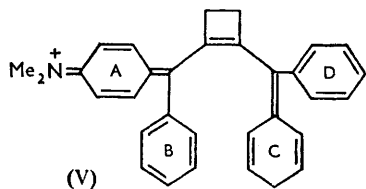


FIG. 2. (A) *trans-trans*-1-*p*-Dimethylaminophenyl-4-phenylbuta-1:3-diene in light petroleum ( $\lambda_{\max}$ . 278, 366  $m\mu$ ;  $\epsilon$  8800, 51,100.  $\lambda_{\text{inf}}$ . 385  $m\mu$ ;  $\epsilon$  38,000). (B) Same solution after illumination during 8 hr. ( $\lambda_{\max}$ . 271, 361  $m\mu$ ;  $\epsilon$  16,300, 35,000.  $\lambda_{\text{inf}}$ . 387  $m\mu$ ;  $\epsilon$  20,400).

about 10,000. The wavelength shift is approximately what would be expected by analogy with *trans*-4-dimethylaminostilbene and the *trans-trans*-amine mentioned above. The intensity change is unexpected and suggests the contribution of resonance forms such as (V), involving ring c of the system. Although twisted considerably out of the plane of the main conjugated system, rings B and c can be expected to participate to a limited extent in conjugation. Turner and his co-workers<sup>9,10</sup> have shown that certain *ortho*-substituted



diphenyls show vestigial conjugation bands despite interplanar angles between the benzene rings as high as 60° in the unexcited state. Moreover, highly conjugative *ortho*- and *para*-substituents can greatly strengthen such bands: for example, 2:2'-dimethyldiphenyl has little "diphenyl" absorption,<sup>10</sup> but (a) the introduction of two *p*-nitro-substituents restores almost fully the "diphenyl" band, and (b) the introduction of two *p*-amino-substituents increases the wavelength of "diphenyl" absorption by *ca.* 20  $m\mu$  and the intensity by *ca.* 11,000.<sup>11</sup>

<sup>8</sup> Alberman, Haszeldine, and Kipping, *J.*, 1952, 3284.

<sup>9</sup> Beaven, Hall, Lesslie, and Turner, *J.*, 1952, 854; see also Braude and Forbes, *J.*, 1955, 3776.

<sup>10</sup> Beaven, Hall, Lesslie, Turner, and Bird, *J.*, 1954, 131.

<sup>11</sup> Pickett, Groth, Duckworth, and Cunliffe, *J. Amer. Chem. Soc.*, 1950, 72, 44.

The spectral curve of the *cis*-isomer (III) (curve C, Fig. 3; a similar curve was obtained for a solution in light petroleum) is strikingly different from those of the other 1 : 2-bisdiphenylmethylenecyclobutanes studied,<sup>1,8</sup> and shows no less than four well-defined maxima above 220  $\mu$ . The maximum at longest wavelength is 4  $\mu$  nearer the red than that of the *trans*-isomer (IV), but its intensity is less than half and is in fact much lower than for the corresponding maximum of the hydrocarbon. Apparently the conjugative dimethylamino-substituent in ring B or C causes that ring to become more coplanar with the diene system (and cyclobutane ring), forcing the other rings to become less coplanar. The *cis*-isomer (III) probably has a molecular configuration more distorted than those of other 1 : 2-bisdiphenylmethylenecyclobutanes. Its spectrum may be explained by the contributions of partial chromophores, owing to the low degree of coplanarity in the molecule.

The spectra of the methiodides of the isomers (III and IV) are shown in Fig. 4. That

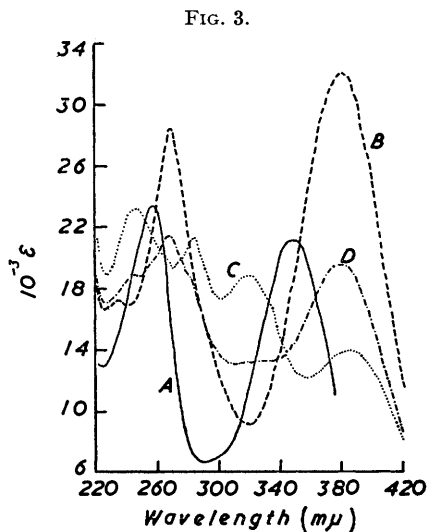


FIG. 3. (Solvent: ethanol.) (A) 1 : 2-Bisdiphenylmethylenecyclobutane ( $\lambda_{\max}$ . 258, 351  $\mu$ ;  $\epsilon$  23,000, 21,400). (B) *trans*-Isomer (IV) ( $\lambda_{\max}$ . 269, 381  $\mu$ ;  $\epsilon$  28,300, 31,900). (C) *cis*-Isomer (III) ( $\lambda_{\max}$ . 246, 284, 319, 385  $\mu$ ;  $\epsilon$  23,100, 21,100, 18,700, 13,800). (D) *cis*- + *trans*-Isomers (III) and (IV).

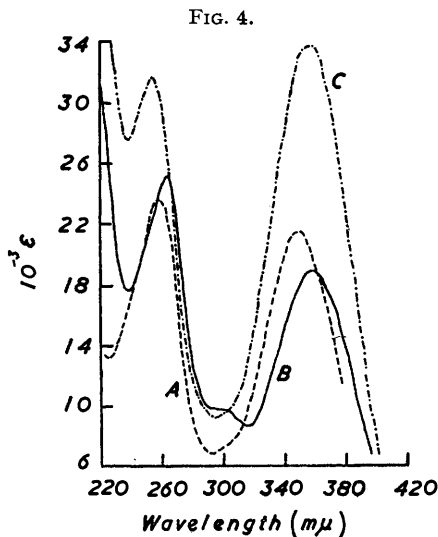


FIG. 4. (Solvent: ethanol.) (A) 1 : 2-Bisdiphenylmethylenecyclobutane ( $\lambda_{\max}$ . 258, 351  $\mu$ ;  $\epsilon$  23,000, 21,400). (B) Methiodide of the *cis*-isomer (III) ( $\lambda_{\max}$ . 264, 358  $\mu$ ;  $\epsilon$  25,000, 18,800.  $\lambda_{\text{inf}}$ . 298  $\mu$ ;  $\epsilon$  9700). (C) Methiodide of the *trans*-isomer (IV) ( $\lambda_{\max}$ . 255, 357  $\mu$ ;  $\epsilon$  31,700, 33,700).

of the *cis*-methiodide (curve B) is unlike that of the parent amine (curve C, Fig. 3), but broadly similar to that of the parent hydrocarbon (curve A), providing confirmatory evidence for the configuration assigned to these compounds. That of the *trans*-methiodide (curve C) is similar in shape but shows a much higher level of absorption than that of the parent hydrocarbon; this hyperchromic effect of the  $^+\text{NMe}_3$  substituent is unexpected, since  $\epsilon_{\max}$  for the *trans-trans*-amine hydrochloride (curve C, Fig. 1) is roughly the same as for its parent hydrocarbon (curve A, Fig. 1).

*Interconversions of the Isomeric Dienes (III and IV).*—(a) *Thermal isomerisation.* The melting points of both isomers (ca. 185°) were dependent upon the rate of heating, and unreliable as criteria of purity: their purity was best assessed by optical-density measurements on ethanolic solutions. Optical-density measurements also showed that both isomers were stable for an hour in boiling cyclohexane (which is therefore a suitable solvent for recrystallisation). But after fusion, during fifteen minutes at 200° under pure, dry nitrogen, both were appreciably isomerised. Fig. 5 shows that the equilibrium under these conditions strongly favours the *trans*-isomer, as would be expected on steric grounds.

(b) *Alumina chromatography.* Benzene solutions of the two isomers, chromatographed

simultaneously on identical alumina columns, formed identical zones, which were eluted at the same rate. Ethanolic solutions of the evaporated eluates had similar spectra, showing that considerable isomerisation had occurred in each case.

(c) *Effect of light.* Crystals of the *cis*-isomer, after two months in the normal light of the laboratory, gave spectra which showed no evidence of isomerisation; under the same conditions, crystals of the *trans*-isomer were slightly affected. The spectra of light petroleum solutions of either isomer which had been illuminated (under conditions employed by Zechmeister and his co-workers<sup>6</sup> for 1 : 4-diphenylbuta-1 : 3-diene) indicated extensive destruction of material. Destruction was much less in ethanolic solution, and Fig. 6 shows that light tends to convert the *trans*- into the *cis*-isomer. Polyenes are generally converted into their thermodynamically least stable *cis*-isomers under the influence of light.<sup>12</sup>

(d) *Effect of acid.* In dilute ethanolic hydrochloric acid the two isomers gave the

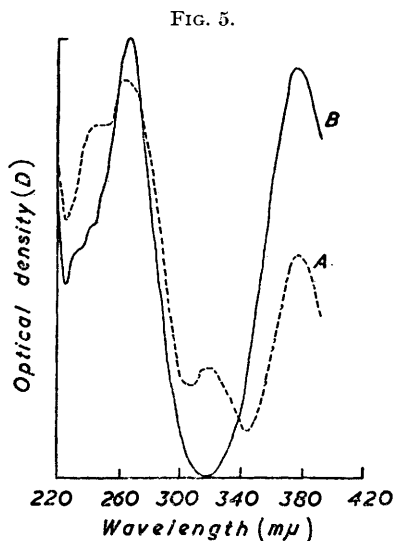


FIG. 5. (Solvent: ethanol.) (A) *cis*-Isomer (III) after fusion during 15 min. at 200° under nitrogen. (B) *trans*-Isomer (IV) after similar treatment.

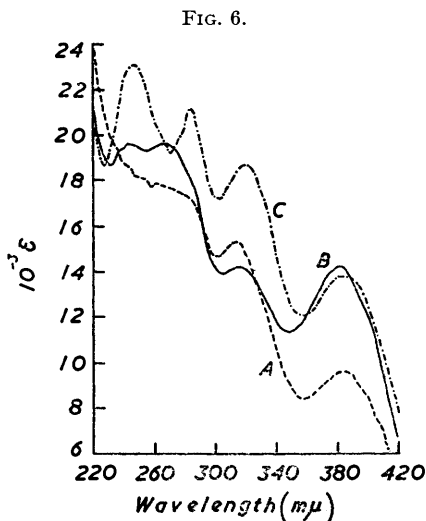


FIG. 6. (Solvent: ethanol.) (A) *cis*-Isomer (III) and (B) *trans*-isomer (IV) after illumination during 8 hr. (C) *cis*-Isomer (III).

same spectrum (curve A, Fig. 7), comparison of which with the spectra of the *cis*- and the *trans*-methiodide (Fig. 4) indicates a mixture of hydrochlorides in which the *cis*-isomer predominates ( $^+\text{NHMe}_2$  and  $^+\text{NMe}_3$  are roughly equivalent chromophores). This was confirmed by treatment of the acid solutions with excess of ammonia; again, both gave the same spectrum (curve B, Fig. 7), which may be compared with that of the *cis*-isomer (curve C, Fig. 3). The spectra of acid solutions were examined within an hour of their preparation and were virtually unchanged one day later. Evidence of the rapidity of acid-catalysed isomerisation was also obtained in an attempt to examine the spectrum of the *cis*-(+)-camphor-10-sulphonate. Since this salt was immediately hydrolysed by water and gave, for example, a strongly yellow solution in 95% ethanol (contrast the hydrochloride, which is not appreciably hydrolysed by water and gives a pale yellow solution in 95% ethanol), anhydrous methanol was used as solvent. The resulting, strongly yellow solution had a spectrum (curve A, Fig. 8) very similar to that of the *cis*-isomer (III) itself (curve C, Fig. 3). Addition of water to the solution caused an immediate shift towards the "*trans*-" type of spectrum (curve B, Fig. 8; cf. curve A, Fig. 7). It

<sup>12</sup> See, e.g., Wyman, *Chem. Rev.*, 1955, **55**, 625.

remains to be explained why in acid solution the equilibrium between the salts of the isomers (III and IV) favours the *cis*-configuration, since polyenes usually tend to give their thermodynamically most stable isomers on acid catalysis. The dimethylamino-group in the *cis*-isomer is largely unconjugated with the diene system, whereas that in the *trans*-isomer is largely conjugated. Thus, the former will be the stronger base, and can be expected to predominate in acidic media. It will also give salts having greater ionic character, which will be less soluble in benzene than salts of the *trans*-isomer: this explains the failure to obtain a *trans*-(+)-camphor-10-sulphonate, mentioned above.

*Attempted Optical Resolution of the Isomeric Dienes (III and IV).*—Their ready acid-catalysed isomerisation prevents resolution of either isomer under acidic conditions. For example, during the unsuccessful attempts to separate the isomers by paper chromatography, mobile phases containing optically active acids were tried,<sup>13</sup> and *cis*-isomer liberated from its (+)-camphor-10-sulphonate was optically inactive. Therefore each isomer was chromatographed on (+)-lactose,<sup>1</sup> but no optical activity could be detected

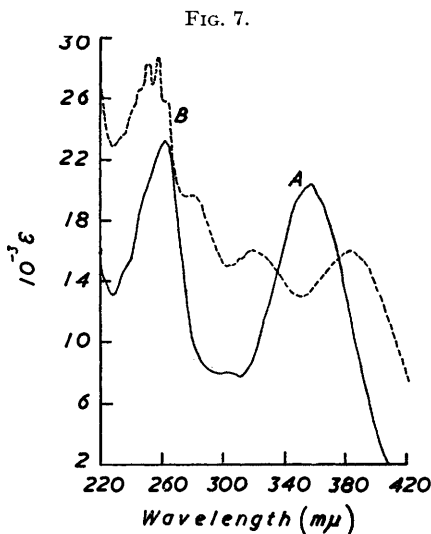


FIG. 7. (A) *cis*- or *trans*-Isomer (III or IV) in ethanol containing 1% of concentrated hydrochloric acid. (B) Same solution after treatment with excess of ammonia ( $\epsilon$  values corrected).

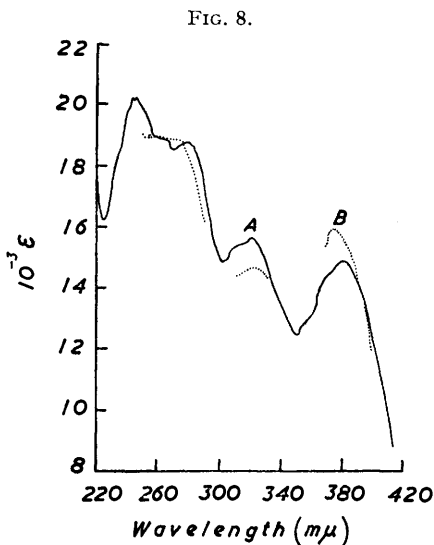


FIG. 8. (A) (+)-Camphor-10-sulphonate of the *cis*-isomer (III) in anhydrous methanol. (B) Same solution with 20% of water added ( $\epsilon$  values corrected).

in any of the eluted fractions; optical-density measurements on the fractions confirmed absence of extensive *cis-trans*-isomerisation during the experiments. Acid-free conditions would be ensured if metho-(+)-camphor-10-sulphonates were prepared by the action of silver (+)-camphor-10-sulphonate on the respective methiodides. Methiodides were therefore prepared from pure specimens of either isomer, and their spectra are discussed above. (Incidentally, the *cis*-methiodide was also obtained, as a crystalline residue, when the oil resulting from the action of methyl iodide on the mixed isomers was extracted with boiling ethyl acetate.) The respective metho-(+)-camphor-10-sulphonates were prepared, but fractional crystallisation failed to suggest the presence of diastereoisomeric salts. Specimens reconverted by ion-exchange into the methiodides were optically inactive.

Thus, all attempts so far to demonstrate optical activity in the 1:2-bisdiphenyl-methylenecyclobutane system have failed.

<sup>13</sup> Bonino and Carassiti, *Nature*, 1951, **167**, 569; Berlingozzi, Serchi, and Ademברי, *Sperimentale, Sez. chim. biol.*, 1951, **2**, 89; *Chem. Abs.*, 1952, **46**, 9070 g; Berlingozzi, Ademברי, and Bucci, *Gazzetta*, 1954, **84**, 383, 393.

## EXPERIMENTAL

M. p.s are corrected. Ultraviolet spectra were measured on Unicam S.P. 500 spectrophotometers; the light petroleum used as solvent was of "AnalaR" grade, aromatic-free, b. p. 60—80°. The curves in Figs. 1—4 (except curve *D*, Fig. 3) represent the mean of at least two determinations in each case. None of the spectra changed perceptibly during determination.

*trans-trans-1:4-Diphenylbuta-1:3-diene*.—A commercial sample was chromatographed<sup>6</sup> and recrystallised from hexane; it had m. p. 153—153.5°.

*trans-trans-1-p-Dimethylaminophenyl-4-phenylbuta-1:3-diene*.—The crude product<sup>14</sup> was a viscous red oil which yielded only a few needles after 3 weeks. Its solution in benzene was extracted twice with concentrated hydrochloric acid (dilute acid was unsatisfactory). The combined extracts were shaken with excess of aqueous sodium hydroxide and benzene, and the benzene layer was evaporated to give brown crystals. Two recrystallisations from acetone gave pale yellow plates, m. p. 181.5—183°. This material (0.90 g.), dissolved in redistilled carbon tetrachloride, was chromatographed on an alumina column (43 × 2.1 cm.), which was developed with chloroform, drained, and cut up. The main yellow band (which fluoresced green-yellow in ultraviolet light) was extracted three times with acetone, the combined extracts were evaporated, and the residue was chromatographed again as before. The product was then recrystallised rapidly from hexane, giving pale yellow, irregular hexagonal plates of the pure *trans-trans-amine*, m. p. 183.5—184° (lit.,<sup>3</sup> 181°) (Found: C, 86.5; H, 8.0; N, 5.8. Calc. for C<sub>18</sub>H<sub>19</sub>N: C, 86.7; H, 7.7; N, 5.6%).

Notes. (a) The alumina had been activated several weeks previously; when it was freshly activated, two small bands of impurity failed to separate from the band of amine. (b) Solutions of the amine in "AnalaR" carbon tetrachloride and hexane, in presence of air, slowly deposited a red-violet precipitate: this gave a red solution in chloroform, which turned yellow-orange with alumina. (c) In ultraviolet light, crystals of the amine fluoresced intensely pale yellow-green, solutions in hexane pale blue (as 1:4-diphenylbuta-1:3-diene<sup>6,7</sup>), and those in ethanol, acetone, or chloroform pale yellow-green. (d) For spectrophotometry solutions of the amine were prepared in the dark.

*cis-trans- and/or trans-cis-1-p-Dimethylaminophenyl-4-phenylbuta-1:3-diene*.—A solution of the *trans-trans-amine* (17.5 mg.) in hexane (75 ml.) was illuminated<sup>7</sup> for 8 hr. Two identical alumina columns, (1) and (2), were then prepared (26.5 × 1.0 cm.) with carbon tetrachloride. The illuminated solution was evaporated and the residual oil chromatographed in carbon tetrachloride on column (1); simultaneously the pure *trans-trans-amine* (17.5 mg.) in an equal quantity of the same solvent was chromatographed on column (2). Both columns were developed with chloroform and allowed to drain. The appearance of column (1), starting from the top, was then as follows: (a) 8 cm., no colour; (b) small, diffuse, pale blue band, visible only in ultraviolet light; (c) small orange band; (d) ca. 4 cm., main yellow zone of *trans-trans-amine*; (e) small band, similar to (b) in appearance; (f) ca. 15 cm., pale yellow zone, yellow in ultraviolet light. The appearance of column (2) was closely similar except that zone (d) occupied ca. 5 cm. and zone (f) was absent. Both columns were cut up and various fractions were eluted with ethanol; after removal of solvent at 40°, portions of the residues were dissolved in 95% ethanol for optical-density measurements. These indicated that zone (f) of column (1) was of *cis-trans-* and/or *trans-cis-*amine: it yielded an oil ( $\lambda_{\max}$ . 364 m $\mu$ ;  $D_{364}/D_{292} = 2.9$ ) which slowly crystallised as the *trans-trans-amine* ( $\lambda_{\max}$ . 368 m $\mu$ ;  $D_{364}/D_{292} = 5.4$ ; see Fig. 2).

*cis- and trans-1-(4-Dimethylamino- $\alpha$ -phenylbenzylidene)-2-diphenylmethylenecyclobutane* (III and IV).—*p*-Lithio-*NN*-dimethylaniline in ether (70 ml.) was prepared from *p*-bromodimethylaniline (13.6 g.) and lithium (0.95 g.).<sup>15</sup> ( $\pm$ )-1-Benzoyl-2-diphenylmethylenecyclobutane (I) (19.6 g.) in pure benzene (40 ml.) was added to the stirred and refluxing solution during  $\frac{1}{2}$  hr. Water was then added, and the product steam-distilled (2 hr.). The residual fawn-yellow crystals were washed with water and recrystallised twice from ethanol, giving colourless, non-fluorescent crystals of the ( $\pm$ )-olefinic alcohol (II), m. p. 158—158.5° (Found: C, 86.0; H, 6.9; N, 3.37. C<sub>32</sub>H<sub>31</sub>ON requires C, 86.3; H, 7.0; N, 3.14%). Treatment of an ethereal solution of the crude alcohol with dry hydrogen chloride or aqueous hydrochloric acid gave off-white crystals, which fluoresced intensely pale green in ultraviolet light and decomposed at ca. 215°, consisting of a mixture of the hydrochlorides of the isomeric dienes (III and IV).

<sup>14</sup> Sachs and Weigert, *Ber.*, 1907, **40**, 4368.

<sup>15</sup> Gilman, Zoellner, and Selby, *J. Amer. Chem. Soc.*, 1933, **55**, 1252.

The whole amount of olefinic alcohol, dissolved in chloroform (brownish solution), was shaken with dilute hydrochloric acid (chloroform layer green), then with excess of dilute aqueous sodium hydroxide (chloroform layer intensely yellow), and finally with water. Evaporation of the chloroform solution gave a viscous, yellow-brown oil, which slowly deposited crystals from a cooled ethanolic solution. After 1 hr. these were separated, yielding 15.7 g. (61%) of the mixed isomers (III and IV), m. p. 141—150° (Found: C, 89.6; H, 6.8; N, 3.25. Calc. for  $C_{32}H_{29}N$ : C, 89.9; H, 6.8; N, 3.3%). Stored in the dark during 1 month, the mother-liquor deposited 3.5 g. (14%) of the almost pure *trans-isomer* (IV), recrystallised as yellow rods from cyclohexane. Its m. p. depended upon the rate of heating: when heated slowly it melted at 178.5—182° after much sintering; after 5 min. at 174—176° it began to melt; placed in a bath at 181° and heated rapidly, it melted at 182—183° (Found: C, 90.1; H, 6.9%). Optical-density measurements on ethanolic solutions provided the best criterion of purity for this compound ( $D_{381}/D_{319} = \sim 3.4$ ;  $D_{269}/D_{319} = \sim 3.1$ ).

(+)-*Camphor-10-sulphonate of the cis-Isomer* (III).—Mixed isomers (10.5 g.) and anhydrous (+)-camphor-10-sulphonic acid (5.7 g.) were dissolved by warming them in pure benzene (10 ml.). The solution was cooled, seeded, and left overnight. (Seeds were first obtained by leaving the residual oil, after evaporation of such a benzene solution, in contact with dry ether.) More benzene (15 ml.) was then added, and the mass of almost colourless rods filtered off rapidly. Drying at room temperature gave 9.9 g. (61%) of the *cis-(+)-camphor-10-sulphonate*, which fluoresced intensely pale green in ultraviolet light. It had m. p. 187.5—190° (decomp.) after recrystallisation, and  $[\alpha]_D^{20} + 17.8^\circ$  ( $c$  2;  $l$  2 in anhydrous benzene) (Found: C, 76.3; H, 6.9; N, 2.1.  $C_{42}H_{45}O_4NS$  requires C, 76.4; H, 6.9; N, 2.1%).

(+)-*Camphor-10-sulphonate from the trans-Isomer* (IV).—When the pure *trans-isomer* was used in place of the mixed isomers in a repetition of the previous experiment the same salt was obtained, m. p. [and mixed with the *cis-(+)-camphor-10-sulphonate*] 187.5—190° (decomp.); amine liberated from it (see next paragraph) had the spectrum of the pure *cis-isomer* (curve C, Fig. 3).

*Preparation of the cis-Isomer* (III).—The (+)-camphor-10-sulphonate was shaken with excess of aqueous sodium hydroxide and ether. When all solid had dissolved the ether layer was separated, washed twice with water, and evaporated. The residue was recrystallised from cyclohexane, giving long yellow rods of the *cis-isomer* (III), which were dried at room temperature (Found: C, 89.9; H, 6.9%). Its m. p. was higher than that of the *trans-isomer* (IV), but also depended upon the rate of heating; placed in a bath at 190° it melted fairly rapidly. Its appearance, both in visible and ultraviolet light (intense deep yellow fluorescence), was identical with that of the *trans-isomer*. Optical density measurements again provided the best criterion of purity ( $D_{319}/D_{385} = \sim 1.3$ ;  $D_{284}/D_{319} = D_{246}/D_{319} = \sim 1.1$ ). Two preparations, before recrystallisation, showed no optical activity when 4% solutions were examined in 4 dm. tubes.

*Methiodide of the cis-Isomer* (III).—The *cis-isomer* was dissolved in boiling methyl iodide, and the solution cooled and left overnight. Very pale, yellow-green rods of the *cis-methiodide* were obtained and washed with acetone. Some of the compound was recrystallised from acetone (Found: C, 69.6; H, 5.7; I, 22.2.  $C_{33}H_{22}NI$  requires C, 69.6; H, 5.7; I, 22.3%). Its m. p. depended upon the rate of heating; when placed in a bath at 193° and heated rapidly it melted at 194—194.5° (decomp.). It fluoresced intensely pale green in ultraviolet light.

*Methiodide of the trans-Isomer* (IV).—Obtained by the same method, this salt formed slightly bluish rods, which fluoresced intensely pale blue in ultraviolet light (Found: C, 69.5; H, 5.7%). Heated slowly, it melted at 191.5—192° (decomp.); placed in a bath at 203.5° and heated rapidly it melted at 205—206° (decomp.); a mixture with the *cis-methiodide* melted at 177.5—180°.

*Metho-(+)-camphor-10-sulphonate of the cis-Isomer* (III).—Hot solutions of silver (+)-camphor-10-sulphonate<sup>16</sup> (580 mg.) and *cis-methiodide* (974 mg.), each in methanol (20 ml.), were mixed and cooled, and filtered. Evaporation of the filtrate under reduced pressure yielded a yellow oil, which was then fractionally crystallised from aqueous acetone: four crops were obtained (1.04 g., 84%), each consisting of very pale, yellow-green hexagonal plates. In ultraviolet light these fluoresced pale green, but less intensely than the methiodide, because they consisted of the *cis-metho-(+)-camphor-10-sulphonate trihydrate*. The first crop was recrystallised and dried at room temperature (Found: C, 70.9; H, 7.6.  $C_{43}H_{47}O_4NS \cdot 3H_2O$  requires C, 71.0; H, 7.4%).

<sup>16</sup> Pope and Gibson, *J.*, 1910, 2211.



This compound evolved water at *ca.* 130° and gave a clear melt at *ca.* 180°. Warmed with benzene it gave an opalescent solution which would not yield crystals after water had been azeotropically distilled from it. The water of crystallisation was removed by drying *in vacuo* at 120°, which yielded an intensely fluorescent material, but rather yellow owing to decomposition. Placed in a bath at 212° and heated rapidly the *anhydrous material* melted at 212—213° (Found: C, 76.0; H, 7.5.  $C_{43}H_{47}O_4NS$  requires C, 76.6; H, 7.0%).

All crops of the trihydrate, including a further one taken from aqueous methanol, had virtually the same rotation,  $[\alpha]_D^{21} +14.8^\circ$  (*c* 0.6, *l* 2 in methanol). When a solution of the recrystallised first crop (0.3 g.) in methanol (30 ml.) and water (10 ml.) was passed through a column of Dowex 1 X2 (10 g., iodide form), the eluate was optically inactive.

*Metho-(+)-camphor-10-sulphonate of the trans-Isomer (IV).*—Prepared by the above method, three crops (79%) of lemon-yellow needles were taken from aqueous methanol. This *compound* fluoresced intensely yellow in ultraviolet light and was not hydrated; placed in a bath at 259° and heated rapidly it melted at 263—265° (decomp.) (Found: C, 76.3; H, 6.9%). The three crops from aqueous methanol, and also one from dioxan, had virtually the same rotation,  $[\alpha]_D^{22} +13.8^\circ$  (*c* 1.6, *l* 2 in methanol). Ion-exchange carried out as above yielded optically inactive eluate.

A Maintenance Grant, provided by the Department of Scientific and Industrial Research, is gratefully acknowledged (by J. J. W.).

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

[Received, December 31st, 1958.]

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