## Restricted Rotation about the Aliphatic Carbon–Carbon Bond in 1,2-Disubstituted Tetra-arylethanes

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The existence of stable rotational isomers of 1,2-dichlorotetraphenylethane previously reported, is shown to be incorrect, since dipole moment measurements indicate the presence of the trans-form only. Infrared studies of a number of 1,2-disubstituted tetra-arylethanes fail to account for the existence of possible gauche-forms, except in the case of the ethane-1,2-diols which occur exclusively in this conformation.

Chlorine addition reactions with sulphuryl chloride as reagent follow a heterolytic path.

RESTRICTED rotation about the aliphatic carboncarbon bond has been demonstrated by evidence from thermodynamic data,<sup>1</sup> dipole moments,<sup>2</sup> and X-ray diffraction,<sup>3</sup> electron diffraction,<sup>4</sup> Raman,<sup>5</sup> infrared,<sup>6</sup> nuclear magnetic resonance,7 and microwave spectra.8 Theoretically, it should be possible to isolate rotational isomers of highly substituted ethanes the potential energy barriers to internal rotation of which are sufficiently large for interconversion of the isomers to be a slow process. This would require a barrier height of 16—20 kcal./mole for a separation at room temperature. Although a separation has been reported for tetrabromoethane at low temperatures,<sup>9</sup> the only report of an isolation at room temperature has been made by Bassett, Thorne, and Young,<sup>10</sup> who claim to have separated trans- and gauche-forms of 1,2-dichlorotetraphenylethane. More recent work by Williams,<sup>11</sup> has shown that the high-melting form used in various measurements by these authors, was, owing to the method of preparation, a stable complex of the high-melting dichloride and carbon tetrachloride. However, Williams again concludes that the two forms of 1,2-dichlorotetraphenylethane are rotational isomers from evidence such as a positive result from Sidgwick's method,<sup>12</sup> small differences in the refractive indices of equivalent solutions of the two forms, and a mixed melting point depression.

In the work reported here we prepared a number of 1.2-disubstituted tetra-arylethanes in high- and lowmelting forms, and examined the compounds using modern physical methods.

Tetra-p-tolylethylene,<sup>13</sup> and tetra-p-ethylphenylethylene were prepared by the route involving the pinacolpinacolone and the retropinacol rearrangements from the respective ketones. The former ethylene was also

RCOR 
$$\xrightarrow{\text{Mg-MgI}}$$
 R<sub>2</sub>C(OH)·C(OH)R<sub>2</sub>  $\xrightarrow{I_2}$  R<sub>3</sub>C·COR  $\xrightarrow{\text{EtMgBr}}$   
R<sub>3</sub>C·C(OH)HR  $\xrightarrow{I_3}$  R<sub>2</sub>C:CR<sub>2</sub>

prepared by the dehydration of 1,1,2,2-tetra-p-tolylethanol, formed by the action of lithium di-p-tolylketyl

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on chloro-di-p-tolymethane. Tetraphenylethylene,<sup>14</sup> and tetra-p-fluorophenylethylene were prepared by the action of copper bronze on the corresponding dichloromethane. According to Johnson et al.,15 tetra-p-fl 10rophenylethylene melts at 189°, but by careful purification of the starting materials we obtained the ethylene melting at 203°. Its identity was confirmed by elemental analysis, oxidation with chromium trioxide to 4,4'-difluorobenzophenone in 78% yield, and by reduction to 1,1,2,2-tetra-p-fluorophenylethane.

High- and low-melting forms of the 1,2-dichlorotetraarylethanes were prepared by the action of either chlorine or sulphuryl chloride on solutions of the ethylenes. With tetra-p-tolylethylene and tetra-p-ethylphenylethylene, chlorine gave the low-melting form of the dichloride, while sulphuryl chloride gave the highmelting form. The reverse was found for tetraphenylethylene, while tetra-p-fluorophenylethylene yielded one form of the dichloride only. The high-melting form of 1,2-dichlorotetraphenylethane was also prepared by the action of sodium iodide on benzophenone dichloride.<sup>16</sup> The identity of the dichlorides was confirmed by elemental analysis, <sup>1</sup>H n.m.r. and i.r. spectroscopy, and oxidation by chromium trioxide to give the related ketones in good yield. Mild hydrolysis of the dichlorides gave the corresponding ethylene oxide.

It has been suggested that addition reactions involving sulphuryl chloride proceed by a homolytic path, and are catalysed by the presence of peroxides.<sup>17</sup> We have investigated the reaction between sulphuryl chloride and tetraphenylethylene at  $20^{\circ}$ , and find that the rate is affected by the polarity of the solvent, but not by the presence of peroxides (Table 1). Electron spin resonance investigations also fail to indicate the presence of free radicals. Since it has been shown that certain substitution reactions with sulphuryl chloride are due to electrophilic attack by the reagent,<sup>18</sup> we consider that the reaction proceeds through the intermediates (I)

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- 61, 3432. <sup>18</sup> R. Bolton, P. B. D. de La Mare, and H. Suzuki, *Rec. Trav.*

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and (II) involving the formation of a donor-acceptor charge-transfer complex with the ethylenic double bond. In such a scheme an increase in the polarity of

### TABLE 1

Effect of solvent on the reaction between sulphuryl chloride and tetraphenylethylene

| Solvent              | CHCl <sub>3</sub> | C <sub>6</sub> H <sub>5</sub> Cl | CCl4   | C <sub>6</sub> H <sub>6</sub> |
|----------------------|-------------------|----------------------------------|--------|-------------------------------|
| Dichloride yield (%) | 98                | 67                               | 60     | Nil                           |
| Time                 | 1 hr.             | 24 hr.                           | 7 days | 7 days                        |

the solvent will stabilise any ion-forming reaction, and push the reaction to completion, while such a reaction will be unaffected by peroxides.

A dipole-moment determination on the two forms of 1,2-dichlorotetraphenylethane has been made using the method suggested by Guggenheim.<sup>19</sup> The dielectric constants of the solutions were measured with apparatus

small dipole moment, 0.77 D units. This dichloride must therefore exist in the trans-form, since calculation requires a dipole of around 3 D units for the gaucheconformation.

Proton magnetic resonance spectroscopy is of little help in studying rotational isomerism in compounds of this type, since only long-range effects could be expected, and in fact it is found that the high- and low-melting forms of each dichloride give identical spectra.

It is also seen that the high- and low-melting forms of each dichloride have identical i.r. spectra, and only one reasonably strong absorption occurring at  $633 \text{ cm}^{-1}$  +  $2 \text{ cm.}^{-1}$  is observed which is not also present in the spectra of the corresponding ethanes. From a study of the model compound 2,3-dichloro-2,3-dimethylbutane, the carbon-chlorine stretching vibrations of the transform is seen as a peak at 618 cm.<sup>-1</sup>, while peaks at 650



described by Davidson,<sup>20</sup> and the refractive indices with an Abbé refractometer (Table 2).

#### TABLE 2

#### Dielectric constants and refractive indices of solutions of 1,2-dichlorotetraphenylethane in benzene

| w         | $\varepsilon_0^{20}$ | $\varepsilon_1^{20\circ}$ | $(n_1^2 - n_0^2)$ | $(\varepsilon_1 - \varepsilon_0)/w$ | $(n_1^2 - n_0^2)/w$ |
|-----------|----------------------|---------------------------|-------------------|-------------------------------------|---------------------|
| 0.00638 † | $2 \cdot 28440$      | $2 \cdot 28819$           | 0.00240           | 0.5943                              | 0.3764              |
| 0.02562 * | $2 \cdot 28482$      | 2.29621                   | 0.01021           | 0.4445                              | 0.3985              |
| 0.02366 + | $2 \cdot 28345$      | $2 \cdot 29381$           | 0.00870           | 0.4379                              | 0.3678              |
| 0.00524 * | $2 \cdot 28419$      | 2.28676                   | 0.00180           | 0.4909                              | 0.3438              |
| 0.03717 * | 2.28398              | 2.29932                   | 0.01382           | 0.4128                              | 0.3719              |

\* Measurements using dichloride, m. p. 186°. † Measurements using dichloride, m. p. 172°.

The symbols used denote the following quantities: w weight fraction,  $\varepsilon$  dielectric constant, n refractive index. The subscripts 0 and 1 refer to the solvent and solution respectively.

Plotting the functions  $(\varepsilon_1 - \varepsilon_0)/w$ , and  $(n_1^2 - n_0^2)/w$ , against weight fraction, and extrapolating to infinite dilution, gives the value for

 $(\Delta/w)_{w\to 0} \equiv [(\epsilon_1 - \epsilon_0) - (n_1^2 - n_0^2)]/w \text{ as } 0.165.$  The dipole moment is then calculated from the expression:

$$\mu^2 = \frac{10^{36}}{N} \cdot \frac{9kT}{4\pi} \cdot \frac{3}{(\varepsilon_0 + 2)^2} \cdot \frac{M}{d_0} \cdot \left(\frac{\Delta}{w}\right)_{w \to 0}$$

where M is the molecular weight of the solute, and  $d_0$  is the density of the solvent.

The results show that the two forms of 1,2-dichlorotetraphenylethane are indistinguishable and have only a

ΖZ

and 568 cm.<sup>-1</sup> denote the carbon-chlorine stretching vibrations of the gauche-forms. Since these latter peaks are not present in the spectra of the dichlorides, it must be concluded that the molecules exist only in the symmetrical form, and the absorption occurring at 633 cm.<sup>-1</sup> must be assigned to the carbon-chlorine stretching mode of the trans-conformation. In addition, the complete identity of solution- and solid-phase spectra of these compounds indicates that the trans-form must be appreciably more stable than the possible gaucheforms.<sup>21,22</sup>

The application of Sidgwicks method for distinguishing between dimorphs and isomers to the high- and lowmelting forms of each dichloride shows that the least soluble form of each pair is slightly soluble in a saturated solution of the more soluble form. However this solubility is found to be within the range of experimental error so that the results become inconclusive.

It can also be shown that the high- and low-melting forms of the dichlorides are not dimorphs, since in the case of 1,2-dichlorotetraphenylethane, and 1,2-dichlorotetra-p-tolylethane, the X-ray powder patterns of each pair are identical. The absence of additional lines in the powder patterns of the low-melting forms suggests that impurities are not present. Analysis by t.l.c. also fails to show the presence of impurities, but repeated recrystallisation of the low-melting forms eventually raises their melting points. At first, it was considered that this change was due to isomerisation. However, in order to

<sup>21</sup> San-Ichiro Mizushima, 'Structure of Molecules and Internal Rotation,' Academic Press, New York, 1954.

22 N. Sheppard, Adv. Spectroscopy, 1959, 1, 288.

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account for the existence of two forms of the dichlorides, it must be concluded that the low-melting forms contain minute traces of impurity, which catalyses their thermal decomposition, causing them to melt with decomposition at lower temperatures.

The action of peracetic acid, perbenzoic acid, and a mixture of formic acid and hydrogen peroxide, on a number of tetra-arylethylenes has been investigated, since it is well known that hydroxylation of olefins by peracids is by addition in the *trans* sense. However, it was found that all these reagents give the corresponding ethylene oxide, which tends to be very unreactive, and resists the action of reagents (water under high temperature and pressure, methyl magnesium iodide, and alcoholic potassium hydroxide) employed in attempts to open the ring to give the desired diol. Eliel and Rerick,<sup>23</sup> record that tetraphenylethylene oxide does not react with lithium aluminium hydride.

The formation of 4,4',4",4"'-tetra(dimethylamino)benzopinacol from 4,4'-dimethylaminobenzophenone has been investigated, since it has been shown that cis- and trans-forms of diols can be produced by methods employing different reducing agents,<sup>24</sup> and this diol melting at 210° has been prepared by Cohen,25 using aluminium amalgam as reducing agent, while Gomberg and Bachmann,<sup>26</sup> using magnesium-magnesium iodide, have isolated the same diol melting at 196°. We have found that reduction with aluminium amalgam gives a white crystalline compound melting at 205°, while reduction with magnesium-magnesium iodide gives a pale green product melting at 196°, which after careful purification becomes colourless and melts at 205°. Further proof of the identity of the two products is given by the i.r. spectra, both of which have absorption peaks at 3564 (strong), and 3610 cm.<sup>-1</sup> (weak), corresponding to the intramolecular hydrogen bonded hydroxy, and the free hydroxy respectively. The i.r. spectra of 4,4',4",4"'tetramethylbenzopinacol, and 4,4',4"',4"'-tetraethylbenzopinacol have also been examined, and the presence of free, and intramolecular hydrogen-bonded hydroxygroups is again seen, with absorption peaks similar to the above values. For benzopinacol, Kuhn<sup>27</sup> found values of 3608 and 3567 cm.<sup>-1</sup>, for the free and bonded hydroxyl respectively. The presence of intramolecular hydrogen-bonding in these diols shows that they must exist in the gauche conformation since, in such compounds, hydrogen bonding can occur only in this form. The gauche-form is thus stabilised so that it is of lower energy than the trans-form.

#### EXPERIMENTAL

The <sup>1</sup>H n.m.r. spectra were recorded on a Perkin-Elmer R10, 60 Mc./sec. spectrometer in deuteriochloroform, with tetramethylsilane as internal reference. The i.r. spectra were recorded on a Perkin-Elmer **337** spectrometer, the dichloride spectra as Nujol mulls and solutions in benzene

<sup>23</sup> E. L. Eliel and M. N. Rerick, J. Amer. Chem. Soc., 1960, **82**, 1362.

<sup>24</sup> G. Wittig and W. Weimer, Ber., 1931, 64, 2405; P. D. Bartlett and R. F. Brown, J. Amer. Chem. Soc., 1940, 62, 2927.

and chloroform. Light petroleum refers to the fraction of b. p.  $40-60^{\circ}$ .

1,2-Dichlorotetraphenylethane.—(a) The ethylene (10 g.), in chloroform (100 ml.), was treated with chlorine for 1 hr. Crystallisation of the product twice from light petroleum– dichloromethane (1:1) gave the dichloride (12 g.), m. p. 172° (decomp.) [Found: C, 77·4; H, 4·85; Cl, 17·6%; M (cryoscopic in benzene), 395. Calc. for C<sub>26</sub>H<sub>20</sub>Cl<sub>2</sub>: C, 77·4; H, 4·95; Cl, 17·6%; M, 403],  $\nu_{max}$  632 cm.<sup>-1</sup> (C-Cl);  $\tau$  3·05—2·50 (C<sub>6</sub>H<sub>5</sub>).

(b) Dichlorodiphenylmethane (20 g.) in acetone (50 ml.) was added to a solution of sodium iodide (14 g.) in acetone (250 ml.) at room temperature. After 48 hr. the precipitate was collected, washed with aqueous sodium thiosulphate and then dissolved in chloroform; the solution was dried (CaCl<sub>2</sub>) and evaporated. The product was crystallised twice from light petroleum-dichloromethane (1:1) to give the dichloride (9.6 g.), m. p. 186° (decomp.) (Found: C, 77.6; H, 4.9; Cl, 17.65%; M, 397); i.r. and <sup>1</sup>H n.m.r. spectra identical with previous dichloride.

Tetra-p-fluorophenylethylene.—Dichlorodi-p-fluorophenylmethane from 4,4'-difluorobenzophenone (10 g.) and phosphorus pentachloride (20 g.) was dissolved in dry benzene (100 ml.) and copper bronze (20 g.) was added. After being heated under reflux for 2 hr, the solution was filtered whilst hot, and then evaporated to give the *ethylene* (10 g.), m. p. 203° (from ethanol) (Found: C, 77.0; H, 4.05; F, 19.2.  $C_{26}H_{16}F_4$  requires C, 77.2; H, 3.95; F, 18.8%).

1,2-Dichlorotetra-p-fluorophenylethane.— Tetra-p-fluorophenylethylene (1 g.) in chloroform (50 ml.) was set aside at room temperature for 72 hr. after being treated either with a slow stream of chlorine for 2 hr. or with sulphuryl chloride (0.4 ml.). The solvent was removed and the residue was crystallised from light petroleum-dichloromethane (1:1) to give the *dichloride* (0.9 g.) as prisms, m. p. 168° (Found: C, 65.75; H, 3.8; Cl, 15.3; F, 15.8.  $C_{26}H_{16}Cl_2F_4$  requires C, 65.7; H, 3.4; Cl, 14.95; F, 16.0%).  $v_{max}$ . 630 cm.<sup>-1</sup> (C-Cl).

1,1,2,2-Tetra-p-fluorophenylethane.— Tetra-p-fluorophenylethylene (1 g.) in ether (50 ml.) and ethanol (50 ml.) was treated with sodium (1 g.) during 2 hr. The solution was washed with water, dried ( $K_2CO_3$ ), and evaporated. Crystallisation of the residue from benzene-ethanol (1:1) gave the ethane (1 g.), m. p. 281° (Found: C, 76.75; H, 4.4; F, 18.55.  $C_{26}H_{18}F_4$  requires C, 76.85; H, 4.4; F, 18.7%).

Tetra-p-fluorophenylethylene Oxide.—(a) Tetra-p-fluorophenylethylene (1 g.) in chloroform (50 ml.) and 40% peracetic acid (5 ml.) was heated to 60° for 48 hr. The solution was washed with dilute alkali and water, and was then dried (CaCl<sub>2</sub>) and evaporated. Crystallisation of the residue from ethanol gave the *ethylene oxide* (0.8 g.) as needles, m. p. 208° (Found: C, 74.35; H, 3.9; F, 18.0. C<sub>26</sub>H<sub>16</sub>F<sub>4</sub>O requires C, 74.3; H, 3.8; F, 18.1%).

(b) A solution of 1,2-dichlorotetra-p-fluorophenylethane (0.5 g.) in dioxan (10 ml.) and water (40 ml.) was heated to 60° for 24 hr. and then poured into water, and the product was extracted with ether. The ether was removed to give the *ethylene oxide* (0.4 g.), m. p. 208° (from ethanol); identical (mixed m. p. and i.r. spectra) with the previous compound.

<sup>25</sup> N. D. Cohen, Rec. Trav. chim., 1919, 38, 121.

<sup>26</sup> M. Gomberg and W. E. Bachmann, J. Amer. Chem. Soc., 1927, **49**, 236.

<sup>27</sup> L. P. Kuhn, J. Amer. Chem. Soc., 1952, 74, 2492.

1,1,2,2-Tetra-p-tolylethanol.—To a cooled solution of lithium di-p-tolylketyl, from di-p-tolyl ketone (6 g.), lithium (0.4 g.), and dry ether (100 ml.), chlorodi-p-tolylmethane (5 g.) in ether (50 ml.) was added during 1 hr. The mixture was heated under reflux for 2 hr. and then decomposed with ethanol and poured into water (1 l.). The ethereal layer was washed with water, dried  $(Na_2SO_4)$ , and evaporated, and the residue was fractionally crystallised from benzene-ethanol (1:1). The first fraction was recrystallised from chloroform-ethanol (1:1) to give 1,1,2,2-tetra-p-tolylethane (2 g.), m. p. 282°, identical (mixed m. p. and i.r. spectra) with an authentic sample. The second fraction on crystallisation from chloroformethanol (1:1) gave prisms of 1,1,2,2-tetra-p-tolylethanol (4.5 g.), m. p. 222° (Found: C, 88.9; H, 7.7. C<sub>30</sub>H<sub>30</sub>O requires C, 88·7; H, 7·4%), τ 7·68 (CH<sub>3</sub>), 7·25 (OH), 4·80 (CH), and 3.14-2.60 (complex tolyl resonances).

Tetra-p-tolylethylene.—1,1,2,2-Tetra-p-tolylethanol (4.5 g.) was heated under reflux with acetyl chloride (20 ml.) for 30 min., and the solution was then evaporated to dryness to give the ethylene (4.2 g.), m. p. 150° (from ethanol) (Found: C, 92.5; H, 7.55%. Calc. for  $C_{30}H_{28}$ : C, 92.8; H, 7.2%).

1,2-Dichlorotetra-p-tolylethane.—(a) Chlorine was passed into a solution of tetra-p-tolylethylene (1 g.) in chloroform or carbon tetrachloride (50 ml.) for 15 min. The solvent was removed to leave the dichloride (0.9 g.) [from benzene-acetone (1:1)], m. p. 183° (decomp.) [Found: C, 78·1; H, 6·1; Cl, 15·7%; M (cryoscopic in benzene), 456.  $C_{30}H_{28}Cl_2$  requires C, 78·4; H, 6·1; Cl, 15·5%; M, 459].  $v_{max}$ . 634 cm. (C-Cl);  $\tau$  7·67 (CH<sub>3</sub>), and 3·17—2·70 (complex tolyl resonances).

(b) Tetra-p-tolylethylene (1 g.) in 1,1,2,2-tetrachloroethane (20 ml.) was treated with sulphuryl chloride (0.35 ml.) at 0°, and was then set aside, with occasional shaking, for 3 hr. The precipitate was washed with light petroleum to give the *dichloride* (0.7 g.), m. p. 145° (decomp.) [Found: C, 78.7; H, 5.95; Cl, 15.3%; M (cryoscopic in benzene), 469]; i.r. and <sup>1</sup>H n.m.r. spectra were identical with the previous compound.

Tetra-p-tolylethylene Oxide.—This was prepared from the corresponding ethylene or dichloroethane as previously described. The product was crystallised from benzene-ethanol (1:1) to give the ethylene oxide as needles, m. p. 210° (Found: C, 89.1; H, 6.95.  $C_{30}H_{28}O$  requires C, 89.1; H, 7.15%).

4,4',4'',4'''-Tetraethylbenzopinacol.— 4,4'-Diethylbenzophenone (20 g.) in ether (50 ml.) and benzene (50 ml.) was added to a magnesium-magnesium iodide reducing agent prepared by Gomberg and Bachmann's method <sup>26</sup> from magnesium (8 g.) and iodine (21 g.) in ether (50 ml.) and benzene (50 ml.). The mixture was shaken for 20 min. at room temperature, and was then poured into aqueous ammonium chloride at 0°. The organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated to give an oil which solidified on cooling. Crystallisation from chloroform-methanol (1:1) gave the *diol* (16 g.), m. p. 143° (Found: C, 84·85; H, 7·95%. C<sub>34</sub>H<sub>38</sub>O<sub>2</sub> requires C, 85·35; H, 7·65%), v<sub>max.</sub> (CCl<sub>4</sub>) 3620 (free OH) and 3578 cm.<sup>-1</sup> (intramolecular bonded O-H).

4,4',4'',*Tetramethylbenzopinacol.*—This was prepared from 4,4'-dimethylbenzophenone as above. Crystals from chloroform–methanol (1:1), m. p. 175°,  $\nu_{max}$ , (CCl<sub>4</sub>) 3615 (free OH) and 3572 cm.<sup>-1</sup> (intramolecular bonded O–H).

1,1,1,2-*Tetra*-p-ethylphenylethan-2-one.— 4,4',4'',4''-Tetraethylbenzopinacol (20 g.) in acetic acid (100 ml.) was heated under reflux for 1 hr. with a crystal of iodine. The precipitate which separated on cooling was recrystallised from ethanol to give the *ketone* (18 g.), m. p. 83° (Found: C, 87.95; H, 7.8.  $C_{34}H_{36}O$  requires C, 88.7; H, 7.8%),  $v_{max}$ . 1667 cm.<sup>-1</sup> (C=O).

1,1,1,2-*Tetra*-p-*ethylphenylethanol.*—The above ketone (2 g.) was reduced with ethyl magnesium bromide from ethyl bromide (10 ml.), magnesium (2.5 g.), and ether (50 ml.). The solution was set aside at room temperature for 30 min. and then heated under reflux for 1 min.; it was then cooled and decomposed with ice-hydrochloric acid. The ethereal layer was separated, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated to give the alcohol (1.8 g.) as an oil which could not be purified further, but was identified by its i.r. spectrum.  $\nu_{max}$ . 3630 cm.<sup>-1</sup> (OH).

Tetra-p-ethylphenylethylene.—The above alcohol (2 g.), in acetic acid (20 ml.), was heated under reflux with a small crystal of iodine for 1 hr. The hot solution was decolourised with sulphur dioxide and cooled to yield a precipitate, which was washed with methanol. Crystallisation from ethanol gave the ethylene (1.4 g.) as needles, m. p. 137° (Found: C, 92.1; H, 8.2.  $C_{34}H_{36}$  requires C, 91.9; H, 8.1%).

1,2-Dichlorotetra-p-ethylphenylethane.—(a) Chlorine was passed into a solution of tetra-p-ethylphenylethylene (1 g.) in chloroform or carbon tetrachloride (50 ml.) for 15 min. Removal of the solvent and crystallisation of the residue from light petroleum-dichloromethane (1:1) gave the dichloride (0.8 g.), m. p. 159° (decomp.) [Found: C, 79.4; H, 7.2; Cl, 14.2%; M (cryoscopic in benzene), 508. C<sub>34</sub>H<sub>36</sub>Cl<sub>2</sub> requires C, 79.2; H, 7.0; Cl, 13.8%; M, 515],  $\nu_{max}$ . 635 cm.<sup>-1</sup> (C-Cl),  $\tau$  8.75 (CH<sub>3</sub> triplet J = 7.5 c./sec.), 7.36 (CH<sub>2</sub> quartet J = 7.5 c./sec.) and 3.16—2.60 (C<sub>6</sub>H<sub>4</sub>).

(b) The ethylene (1 g.) in 1,2-dichloroethane (20 ml.) was treated with sulphuryl chloride (0.35 ml.) at 0°, and was then set aside for 3 hr. The precipitate which formed was recrystallised quickly from light petroleum-dichloromethane (1:1) to give the *dichloride* (0.7 g.), m. p. 122° (decomp.) [Found: C, 78.8; H, 7.2; Cl, 14.2%; *M* (cryoscopic in benzene), 499]; i.r. and <sup>1</sup>H n.m.r. spectra were identical with preceding dichloride.

Tetra-p-ethylphenylethylene Oxide.—This was prepared from the corresponding ethylene or dichloroethane as previously described. The product was crystallised from benzene-ethanol (1:1) to give the ethylene oxide as needles, m. p. 152° (Found: C, 89.1; H, 8.0.  $C_{34}H_{36}O$  requires C, 88.7; H, 7.85%).

Di-p-ethylphenylmethyl Chloride.—Di-p-ethylphenylmethanol (6 g.) in benzene (20 ml.) was heated under reflux with thionyl chloride (10 ml.), for 30 min. Removal of the solvent left an oil which was distilled under reduced pressure to give the methyl chloride (5 g.), b. p. 143°/0·1 mm. (Found: C, 78·85; H, 7·5; Cl, 13·7.  $C_{17}H_{19}Cl$  requires C, 78·9; H, 7·35; Cl, 13·75%).

1,1,2,2-Tetra-p-ethylphenylethane.— Di-p-ethylphenylmethyl chloride (5 g.) in ether (50 ml.) was treated with magnesium according to the method described by Gilman and Kirby.<sup>28</sup> The product was crystallised from ethanol to give the ethane (3 g.), m. p. 156° (Found: C, 91.2; H, 8.45. C<sub>34</sub>H<sub>38</sub> requires C, 91.4; H, 8.6%).

4,4',4'',4'''-Teira(dimethylamino)benzopinacol.---(a) 4,4'-Dimethylaminobenzophenone (5 g.) in ethanol (100 ml.) was treated with aluminium amalgam (10 g.).<sup>25</sup> The product

<sup>28</sup> H. Gilman and J. E. Kirby, J. Amer. Chem. Soc., 1926, 48, 1733.

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(2.5 g.) was crystallised from acetone to give the diol, m. p. 205° (Found: C, 75.95; H, 7.5; N, 10.45. Calc. for  $C_{34}H_{30}N_4O_2$ : C, 75.85; H, 7.8; N, 10.4%),  $\nu_{max}$  (CCl<sub>4</sub>) 3610 (free OH), 3564 cm<sup>-1</sup> (intramolecular bonded O-H).

(b) 4,4'-Dimethylaminobenzophenone (45 g.) in ether (50 ml.), and benzene (50 ml.) was treated with a magnesium-magnesium iodide reducing agent prepared from magnesium (15 g.) and iodine (39 g.) in benzene (100 ml.).<sup>26</sup> The product from ethanol gave pale green crystals of the diol (11 g.), m. p. 195–197°. Further recrystallisation

from benzene-ligroin (1:1), dichloromethane-ethanol (1:1)and finally acetone gave the diol as white crystals, m. p. 205° (Found: C, 75.6; H, 7.7; N, 10.5%); the i.r. spectrum was identical with that for the preceding compound.

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