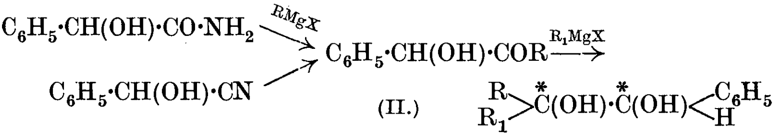
CCCIV.—*Studies in Stereochemical Structure. Part III.* Glycols derived from* d (−)-*Mandelic Acid.*

By ROBERT ROGER and WILLIAM BYRES MCKAY.

THE suitability of mandelic acid as a starting point for the synthesis of glycols has long been recognised, and many such compounds derived therefrom have been described by, *e.g.*, McKenzie and Tiffeneau and their respective co-workers. As a consequence, considerable light has been thrown on the mechanism of glycol dehydration. The comparative ease with which the optically active forms of mandelic acid can be obtained has also ensured this acid an important place in stereochemical studies. It offers two starting points for the synthesis of glycols; for instance, by the action of Grignard reagents on esters of mandelic acid, a change such as the following can be effected,

$$C_6H_5\cdot CH(OH)\cdot CO_2C_2H_5 + RMgX \longrightarrow CR_2(OH)\cdot\overset{*}{C}HPh(OH) \qquad (I.)$$

and glycols containing only one asymmetric carbon atom in the molecule are obtained. By the use of mandelamide or mandelonitrile, however, another type of synthesis is possible (McKenzie and Wren, J., 1908, **93**, 309; Wren, J., 1909, **95**, 1583; McKenzie, Martin, and Rule, J., 1914, **105**, 1583; Tiffeneau and Lévy, *Bull. Soc. chim.*, 1925, **37**, 1247; Asahina and Teresaka, *J. Pharm. Soc. Japan*, 1923, **494**, 219) according to the scheme :



$$\left.\begin{array}{l} C_6H_5\cdot CH(OH)\cdot CO\cdot NH_2 \xrightarrow{RMgX} \\ C_6H_5\cdot CH(OH)\cdot CN \nearrow \end{array}\right\} C_6H_5\cdot CH(OH)\cdot COR \xrightarrow{R_1MgX} \begin{matrix}R\\R_1\end{matrix}{>}\overset{*}{C}(OH)\cdot\overset{*}{C}(OH){<}\begin{matrix}C_6H_5\\H\end{matrix} \qquad (II.)$$

and glycols containing two asymmetric carbon atoms can be isolated. Glycols of this type have been shown to afford two optically inactive forms and two pairs of optically active diastereoisomerides (Tiffeneau and Lévy, *Bull. Soc. chim.*, 1927, **41**, 1351; Roger, Parts I and II, *locc. cit.*).

The (+), (−), and racemic forms of triphenylethylene glycol (McKenzie and Wren, J., 1910, **97**, 473; McKenzie, Drew, and Martin, J., 1915, **107**, 26; McKenzie and Boyle, J., 1921, **119**, 1131) constitute one of the most interesting examples of the glycols classified under (I). This glycol, however, may also be classified under (II), since it can be prepared from benzoin by the action of

---

* Parts I and II, *Helv. Chim. Acta,* 1929, **12**, 1060; *Biochem. Z.*, 1931, **230**, 320.

phenylmagnesium bromide and has been designated as phenylhydrobenzoin.

The tolylhydrobenzoins, $\overset{2}{\overset{*}{C}}Ph(C_7H_7)(OH)\cdot\overset{1}{\overset{*}{C}}HPh(OH)$, are members of class (II). They are structurally related to triphenylethylene glycol (I; R = Ph), but there is an additional asymmetric carbon atom, inasmuch as one of the phenyl groups attached to the tertiary carbon atom in triphenylethylene glycol is replaced by a tolyl group.

In spite of the fact that a number of optically active substituted hydrobenzoins of type (II) have been synthesised from optically active mandelic acid (McKenzie and Wren, J., 1910, **97**, 473; McKenzie, Drew, and Martin, *loc. cit.*; McKenzie and Roger, J., 1924, **125**, 2148; Roger and McKenzie, *Ber.*, 1929, **62**, 272; Roger, *loc. cit.*), the stereochemical environment of the groups attached to the tertiary carbon atom in such compounds is still a matter for conjecture. Does the new system have a *lævo-* or a *dextro*-rotatory effect, or does it exert no rotatory influence at all ? A study of the rotatory powers of optically active triphenylethylene glycol and the optically active tolylhydrobenzoins might, therefore, present a suitable starting point for the examination of this problem.

It is now shown that the action of *m*- and *p*-tolylmagnesium bromides on *d*(—)-benzoin furnishes optically pure specimens of the α-forms of the corresponding tolylhydrobenzoins. These compounds are strongly dextrorotatory, and there is thus a change of sign of rotation in the passage from the *d*(—)-benzoin. By the action of *o*-tolylmagnesium bromide, (+)o-*tolylhydrobenzoin* (α-form) was similarly obtained, but, although it was also dextrorotatory, it was invariably accompanied by considerable amounts of racemic benzoin, which was not detected in the preparation of the *m*- and *p*-isomerides. This result was obtained in spite of the fact that every precaution was taken to exclude traces of alkali or any known racemising agent (Wren, J., 1909, **95**, 1583; McKenzie and Wren, *loc. cit.*; McKenzie and Smith, *Ber.*, 1925, **58**, 894; McKenzie, Roger, and Wills, J., 1926,. 779). It would, therefore, appear that *o*-tolylmagnesium bromide acted in this case as a racemising agent. This is curious, because no such racemisation has been observed in the application of Grignard reagents to optically active benzoins.

The rotatory powers of these three glycols and of (+)-triphenylethylene glycol were determined in acetone, chloroform, benzene, and ethyl alcohol, and the specific rotations in the first two solvents were :

Glycol.	In $COMe_2$. $[\alpha]_{5893}$.	In $CHCl_3$. $[\alpha]_{5893}$.
(+)*o*-Tolylhydrobenzoin (α-form)	+ 250°	+ 255°
(+)*m*-Tolylhydrobenzoin (α-form)	+ 223	+ 224
(+)*p*-Tolylhydrobenzoin (α-form)	+ 211	+ 218
(+)-Triphenylethylene glycol	+ 219	+ 232

It will be seen that there is little significant difference in the specific rotations of (+)-triphenylethylene glycol and the (+)-tolylhydrobenzoins (α-forms). The differences between the specific rotations of the four glycols in the solvents examined may be explained by the slight variance of the group G in the optically active complex, $C_6H_5{\cdot}\overset{*}{C}H(OH){\cdot}G$, irrespective of the presence of a second asymmetric centre in the group G. It is only in the case of the (+)*o*-tolylhydrobenzoin that any outstanding difference in the rotatory power is noted, and that may also be explained by the preceding statement. The order of increasing positive rotation for the four glycols is, therefore,

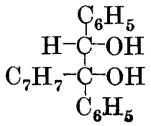
$$\text{para-} \longrightarrow \left\{\begin{matrix}\text{meta-}\\ \text{unsubstituted}\end{matrix}\right\} \longrightarrow \text{ortho-}.$$

A similar sequence was observed by Tschugaev (*Ber.*, 1898, **31**, 1775) in the rotatory powers of the *l*-menthyl esters of *o*-, *m*-, and *p*-toluic acids and also of benzoic acid :

l-Menthyl ester.	$[\alpha]_{5893}$.	*l*-Menthyl ester.	$[\alpha]_{5893}$.
o-Toluate	− 84·42°	*p*-Toluate	− 92·15°
m-Toluate	− 87·94	Benzoate	− 90·9

This increase in positive rotation with substitution in the ortho-position has been confirmed by Cohen and Dudley (J., 1910, **97**, 1732; see also Cohen, J., 1914, **105**, 1892) and summarised by Rule (J., 1924, **125**, 1126) : " It will be observed that the only marked differences are those occurring in the ortho-series, where the replacement of hydrogen by a negative group lowers the rotation and substitution by a positive group raises the value. . . . The rotations of the *m*- and *p*-derivatives do not differ greatly from that of the unsubstituted compound " (see also Rule and Numbers, J., 1926, 2119; Pickard and Kenyon, J., 1915, **107**, 122; Goldschmidt and Freund, *Z. physikal. Chem.*, 1894, **14**, 398). The above menthyl esters contain only one centre of asymmetry in the molecule.

If the principle of optical superposition is accepted, the above-mentioned facts would appear to support the view that the variation of the groupings round the asymmetric centre $\overset{\overset{2}{*}}{C}$ (p. 2230) in these substituted tolylhydrobenzoins has little influence on the rotatory power, since their rotations are very close to those of the related (+)-triphenylethylene glycol. We do not think, however, that the (+)-tolylhydrobenzoins (α-forms) can be depicted in the formulation



$$\begin{array}{r}C_6H_5\\ H-C-OH\\ C_7H_7-C-OH\\ C_6H_5\end{array}$$

(lævo-)

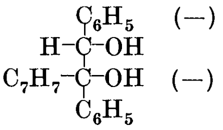
(optically inactive)

The so-called " partially racemic " compounds could be identified with such a representation, but these compounds may sometimes be resolved into two diastereoisomeric substances by crystallisation under suitable conditions of temperature. It has not yet been found possible to separate any of the (+)-tolylhydrobenzoins (α-forms) into diastereoisomerides by any such means.

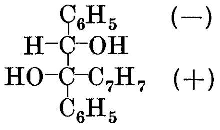
A more probable explanation lies in the supposition that the introduction of a methyl group into one of the phenyl groups of the benzilic [$CPh_2(OH)\cdot C\cdot$] part of the triphenylethylene glycol molecule results in the synthesis of an asymmetric system [$CPh(C_7H_7)(OH)\cdot C\cdot$] of very low rotatory influence.

These (+)-tolylhydrobenzoins may, therefore, possess one of the configurations (III) and (IV). In the first of these, both asymmetric

(III.)



$$\begin{array}{cc} C_6H_5 & \\ H-C-OH & (-) \\ C_7H_7-C-OH & (-) \\ C_6H_5 & \end{array}$$



$$\begin{array}{cc} C_6H_5 & \\ H-C-OH & (-) \\ HO-C-C_7H_7 & (+) \\ C_6H_5 & \end{array}$$

(IV.)

centres are depicted as exercising optical influences in the same direction, whilst in the second, the rotatory influences are antagonistic. Now, in the study of rotation dispersion, cases of anomalous dispersion have been described in which the anomaly is ascribed to the presence within the molecule of two unequal and opposing rotatory influences (Tschugaev, *Ber.*, 1911, **44**, 2029). As configuration (IV) might fall into this category, the dispersions in various solvents of (+)-triphenylethylene glycol and the three (+)-tolylhydrobenzoins (α-forms) were determined. It was found that all four glycols had rotation dispersions which, within the limited range of the visible spectrum examined, would be classified as normal. That this classification of Tschugaev requires further definition has been shown by Rupe (*Annalen*, 1924, **440**, 215).

No definite configuration can, therefore, be assigned to the α-forms of *o*-, *m*-, and *p*-(+)-tolylhydrobenzoins, but it is hoped that a study of the β-forms of these glycols may throw some light on this problem.

It was not possible to isolate a crystalline glycol from the action of *o*-tolylmagnesium bromide on ethyl *r*-mandelate. Such a glycol was, however, obtained by the action of the corresponding *m*-tolyl Grignard reagent on this ester, and also by the action of *p*-tolylmagnesium bromide on ethyl *d*(—)-mandelate.

From the figures quoted (see Experimental) for the rotation dis persions of the four substituted hydrobenzoins, it will be observed that the calculated and experimental values for the specific rotations are satisfied, within the limits of experimental error, by one-term

Drude equations. The graph of the reciprocals of the specific rotations against λ^2 (Lowry and Dickson, J., 1913, **103**, 1067) gave straight lines, indicating that the dispersions of the compounds were simple. It must be recognised, however, that objections have been raised to this criterion in the work of Rupe (Rupe and Krethlow, *Annalen*, 1921, **423**, 324; Rupe, Héritier, and Schaefer, *ibid.*, 1927, **459**, 171) and also of Hunter (J., 1924, **125**, 1198, 1389).

Evidence for the close relationship in stereochemical structure between (+)-triphenylethylene glycol and the (+)-tolylhydrobenzoins (α-forms) was obtained by employing the useful criterion which has been developed by Rupe and his co-workers (*Z. physikal. Chem.*, 1915, **89**, 570; Rupe and Akermann, *Annalen*, 1920, **420**, 1). The " characteristic wave-lengths " of these compounds were calculated according to the formula

$$\lambda_a^2 = \lambda_0^2 + K/([\alpha]_{4861} - [\alpha]_{6563}),$$

and were found to be similar, within the limits of experimental error, for each of the four substances in the solvents examined. The comparison is shown thus :

Characteristic wave-lengths, λ_a.

Substance.	Acetone.	Benzene.	Chloroform.	Ethyl alcohol.
(+)-Triphenylethylene glycol ...	651	638	650	639
(+)*o*-Tolylhydrobenzoin (α-form) ...	644	640	642	633
(+)*m*-Tolylhydrobenzoin (α-form) ...	640	634	637	636
(+)*p*-Tolylhydrobenzoin (α-form) ...	637	638	638	648

These values for the " characteristic wave-lengths " do not indicate any marked difference in stereochemical character between (+)-triphenylethylene glycol and the three (+)-tolylhydrobenzoins (α-forms). Calculations on the basis of Rupe's P.R.D. ($\lambda_0 \times \lambda_a$; *Annalen*, 1922, **428**, 188; λ_0 is obtained by means of the Drude–Akermann equation, see footnote, p. 2234) led to the same conclusion.

Values for P.R.D.

Substance.	Acetone.	Benzene.	Chloroform.	Ethyl alcohol.
(+)-Triphenylethylene glycol.........	138	149	139	147
(+)*o*-Tolylhydrobenzoin (α-form) ...	144	146	145	141
(+)*m*-Tolylhydrobenzoin (α-form)...	148	154	149	148
(+)*p*-Tolylhydrobenzoin (α-form) ...	143	148	147	145

Further evidence as to the normality of dispersion in the region of the spectrum examined was found in the close agreement between the values of the dispersion parameter λ_0^2*, whether calculated by the Drude–Akermann formula (*a*) or by the " Endglieder " formula (*b*). Whilst the differences ($\Delta \times 10^3$) between the values of λ_0^2 do not always fall under the limit of 1 laid down by Rupe, Héritier, and Schaefer (*loc. cit.*), it seems to us that this margin of difference is too small, and that our results are sufficient to indicate that there is no complexity of rotation dispersion (within the region of spectrum examined) in the compounds studied.

EXPERIMENTAL.

Action of o-*Tolylmagnesium Bromide on* r-*Benzoin.*—*r*-Benzoin (10 g., 1 mol.) was added gradually to the Grignard reagent prepared from *o*-bromotoluene (25 g., 3 mols.), and the mixture was heated for 5 hours and treated as usual. The oil resulting from the ethereal layer was dissolved in hot light petroleum, and the solid (9·8 g.) which separated was purified by recrystallisation from the same solvent. r-o-*Tolylhydrobenzoin* (α-form) crystallises in rhombic plates, m. p. 154—155° (Found : C, 82·7 ; H, 6·5. $C_{21}H_{20}O_2$ requires C, 82·9 ; H, 6·6%). A trace of this glycol gave a yellow coloration with concentrated sulphuric acid. This colour reaction was given by all the tolylhydrobenzoins subsequently described.

Action of m-*Tolylmagnesium Bromide on* r-*Benzoin.*—*r*-Benzoin (10 g. 1 mol.) was added to the Grignard reagent prepared from *m*-bromotoluene (40 g., 5 mols.). After the usual treatment an oil was obtained from the ethereal layer. The solid (10·1 g.) which crystallised on dissolving this oil in hot light petroleum and cooling was recrystallised from light petroleum to which a small amount of ethyl alcohol had been added. r-m-*Tolylhydrobenzoin* (α-form) separated in rectangular needles, m. p. 135—137° (Found : C, 82·9 ; H, 6·65%).

d(+)o-*Tolylhydrobenzoin* (α-Form).—d(−)-Benzoin (McKenzie and Wren, J., 1908, **93**, 309) (9 g., 1 mol.) was added gradually to the Grignard reagent prepared from *o*-bromotoluene (32 g., 4 mols.), and the product worked up as for the *r*-glycol. Rosettes of rectangular plates (crop A, 4·2 g.) separated when the solution of

---

* λ_0^2 may be calculated for use in the Drude equation by means of the following expressions :

$$(a)\ \lambda_0^2 = \frac{\lambda_C^2[\alpha]_C + \lambda_{Na}^2[\alpha]_{Na} - (\lambda_{Hg}^2[\alpha]_{Hg} + \lambda_F^2[\alpha]_F)}{[\alpha]_C + [\alpha]_{Na} - ([\alpha]_{Hg} + [\alpha]_F)}.$$

$$(b)\ \lambda_0^{2\prime} = \frac{q(\lambda_F^2) - \lambda_C^2}{q - 1},\ \text{where } q = \frac{[\alpha]}{[\alpha]_C}.$$

In the cases of compounds whose dispersion is normal and simple, the two values of λ_0^2 thus calculated should be identical.

the resulting oil in light petroleum was cooled. These were filtered off, and then a crop (B) of fine needles (1·4 g.) gradually separated from the mother-liquor.

Crop A was recrystallised from light petroleum to which a small amount of ethyl alcohol was added. The resulting prisms were dried in a vacuum over paraffin wax at the ordinary temperature—drying in a vacuum at 70° produced softening and lowered the m. p. of the crude product. This solid was recrystallised from ethyl alcohol–light petroleum until the rotatory power was constant. d(+)o-*Tolylhydrobenzoin* (α-form) crystallises in rectangular prisms, m. p. 113—115° (Found : C, 82·9; H, 6·7%).

Crop B was recrystallised from ethyl alcohol, in which it was much less soluble than was the preceding compound. Fine needles (1·1 g.) separated, m. p. 132—133°. The compound displayed no rotatory power for λ_{5893} in benzene ($c = 1·9880$, $l = 2$) and was identified as *r*-benzoin (Found : C, 78·9; H, 5·6. Calc. : C, 79·2; H, 5·7%).

This reaction was carried out three times, and the same result was recorded in each case.

Rotation dispersions of d(+)o-*tolylhydrobenzoin* (α-form).

(All rotations are positive.)

	λ.							λ^2_0.			
	6563.	6162.	5893.	5461.	5106.	4861.	*K*.	Eq. (*a*).*	Eq. (*b*).*	$\Delta \times 10^3$.	$\frac{[\alpha]_{4861}}{[\alpha]_{6563}}$.
(1) In acetone ($c = 1·9475$, $l = 2$, $t = 20·1°$).											
α	7·61°	8·75°	9·72°	11·64°	13·75°	15·56°					
$[\alpha]$ Obs.	195·4	221·7	249·6	298·8	353·0	399·5					
$[\alpha]$ Calc.	195·2	225·4	250·0	299·7	353·3	399·7	74·11	0·05087	0·05015	0·72	2·045
(2) In benzene ($c = 1·8530$, $l = 2$, $t = 19·9°$).											
α	8·62	9·47	10·57	12·65	14·98	16·99					
$[\alpha]$ Obs.	222·9	255·5	285·2	341·4	404·2	458·5					
$[\alpha]$ Calc.	222·9	255·8	285·2	342·2	404·0	458·0	83·86	0·05316	0·05241	0·75	2·057
(3) In chloroform ($c = 1·9505$, $l = 2$, $t = 20·1°$).											
α	7·80	8·94	9·96	11·94	14·07	15·93					
$[\alpha]$ Obs.	199·9	229·2	255·4	306·1	360·6	408·3					
$[\alpha]$ Calc.	199·2	230·1	255·3	306·1	360·8	408·3	75·26	0·05109	0·04981	1·28	2·042
(4) In ethyl alcohol ($c = 1·8865$, $l = 2$, $t = 20°$).											
α	7·20	8·25	9·17	10·99	12·93	14·63					
$[\alpha]$ Obs.	190·8	218·7	243·1	291·4	342·8	387·8					
$[\alpha]$ Calc.	190·1	219·5	243·3	291·4	343·0	387·8	72·49	0·04936	0·04807	1·29	2·032

* See p. 2234 (footnote).

The effect of temperature on the rotatory power of this glycol was observed in the above ethyl-alcoholic solution; the specific rotation decreased with increasing temperature :

t	0°	20°	39°
$[\alpha]_{5893}$	—	+ 243·1°	+ 232·4°

d(+)m-*Tolylhydrobenzoin* (α-Form).—*d*(—)-Benzoin (4·6 g., 1 mol.) was added to the Grignard reagent prepared from *m*-bromotoluene

(17 g., 4 mols.). The conditions of heating and decomposition of the addition complex were similar to those adopted for the *r*-glycol. No solid was, however, obtained directly from the resulting oil by the use of solvents. The oil, therefore, was distilled in a current of steam to remove toluene and di-*m*-tolyl. After being dried, the oil was dissolved in light petroleum. The impure glycol which separated was recrystallised until of constant specific rotation (yield 4 g.). d(+)m-*Tolylhydrobenzoin* (α-form) crystallises in rosettes of rectangular needles, m. p. 106—108° (Found : C, 83·1; H, 6·7%).

Rotation dispersions of d(+)m-*tolylhydrobenzoin* (α-form).

	λ.							λ^2_0.			
	6563.	6162.	5893.	5461.	5106.	4861.	*K*.	Eq. (*a*).	Eq. (*b*).	$\Delta \times 10^3$.	$\frac{[\alpha]_{4861}}{[\alpha]_{6563}}$.
(1) In acetone ($c = 2{\cdot}0145$, $l = 2$, $t = 20°$).											
α	6·99°	—	9·03°	10·82°	—	14·43°					
[α] Obs.	173·5	—	224·1	268·6	—	358·2					
[α] Calc.	174·0	—	223·4	268·1	—	358·6	65·69	0·05316	0·0538	0·64	2·065
(2) In benzene ($c = 1{\cdot}9980$, $l = 2$, $t = 21°$).											
α	8·14	9·42	10·44	12·64	14·98	16·95					
[α] Obs.	203·6	235·5	261·2	316·3	374·9	424·1					
[α] Calc.	203·2	235·5	261·9	315·6	374·3	425·7	75·54	0·05887	0·05762	1·25	2·083
(3) In chloroform ($c = 2{\cdot}0080$, $l = 2$, $t = 20{\cdot}2°$).											
α	7·00	—	8·99	10·80	—	14·51					
[α] Obs.	174·4	—	224·0	269·0	—	361·4					
[α] Calc.	174·4	—	224·1	269·2	—	361·1	65·61	0·05486	0·05516	0·3	2·073
(4) In ethyl alcohol ($c = 2{\cdot}0052$, $l = 2$, $t = 20{\cdot}3°$).											
α	7·07	8·22	9·14	10·96	12·92	14·70					
[α] Obs.	176·3	205·0	227·8	273·4	322·2	366·6					
[α] Calc.	177·0	204·8	227·4	273·2	322·8	366·3	66·58	0·05453	0·05614	1·61	2·079

The specific rotation of the glycol in benzene solution (see above) decreased with increasing temperature :

t	5·5°	21°	41°
$[\alpha]_{5893}$	+ 279·4°	+ 261·2°	+ 240·2°

d(+)p-*Tolylhydrobenzoin* (α-Form).—*d*(—)-Benzoin (4·2 g., 1 mol.) was added to the Grignard reagent prepared from *p*-bromotoluene (15 g., 4 mols.). After treatment as before, the oil from the ethereal extract was dissolved in light petroleum–ethyl alcohol. Rectangular needles separated, m. p. 112—114°, $[\alpha]_{5893}$ + 191·5° ($c = 2{\cdot}065$ in benzene, $l = 2$). After four recrystallisations from light petroleum–benzene, the rotatory power was unchanged. Analysis, however, showed that this substance was not the pure glycol (Found : C, 81·2; H, 6·9%). After several weeks in a vacuum, the m. p. had risen to 120—121°. The specific rotation had also changed. After further recrystallisation the glycol was obtained in an optically pure state. d(+)p-*Tolylhydrobenzoin* (α-form) separates as rectangular needles, m. p. 120—121°, $[\alpha]^{21°}_{5893}$ + 256·7° ($c = 1{\cdot}965$ in benzene, $l = 2$) (Found : C, 83·0; H, 6·7%).

Rotation dispersions of d(+)p-*tolylhydrobenzoin* (α-form).

	λ.							λ^2_0.			
	6563.	6162.	5893.	5461.	5106.	4861.	*K*.	Eq. (*a*).	Eq. (*b*).	$\Delta \times 10^3$.	$\frac{[\alpha]_{4861}}{[\alpha]_{6563}}$.
(1) In acetone ($c = 1{\cdot}9735$, $l = 2$, $t = 21{\cdot}2°$).											
α	6·50°	7·50°	8·33°	9·97°	11·77°	13·29°					
[α] Obs.	164·7	190·0	211·1	252·6	298·2	336·7					
[α] Calc.	164·7	190·2	211·0	252·8	297·8	336·9	62·63	0·05042	0·05026	0·16	2·044
(2) In benzene ($c = 1{\cdot}9650$, $l = 2$, $t = 21°$).											
α	7·90	—	10·09	12·12	—	16·32					
[α] Obs.	201·0	—	256·7	308·4	—	415·3					
[α] Calc.	200·4	—	257·4	309·1	—	414·1	75·5	0·05405	0·05398	0·07	2·065
(3) In chloroform ($c = 2{\cdot}0065$, $l = 2$, $t = 20{\cdot}3°$).											
....	6·67	—	8·74	10·45	—	14·01					
[α] Obs.	168·5	—	217·8	260·4	—	349·2					
[α] Calc.	169·1	—	217·1	260·6	—	348·8	63·80	0·05342	0·05508	1·66	2·073
(4) In ethyl alcohol ($c = 1{\cdot}945$, $l = 2$, $t = 21{\cdot}3°$).											
α	6·71	7·73	8·61	10·29	12·20	13·60					
[α] Obs.	172·5	198·7	221·4	264·5	313·7	349·6					
[α] Calc.	172·6	199·2	220·9	264·4	311·5	352·2	65·74	0·04964	0·04693	2·51	2·027

The specific rotation of this glycol in acetone solution (see above) was also found to decrease with increasing temperature :

t	0°	19·5°	30°
$[\alpha]_{5893}$	+ 232·0°	+ 210·6°	+ 205·1°

d(+)-*Triphenylethylene Glycol.*—This glycol was prepared by the method of McKenzie and Wren (*loc. cit.*) through the action of phenylmagnesium bromide on ethyl *d*(—)-mandelate. The values for the rotation of our specimen were :

In acetone, $[\alpha]_{5893} + 219°$ ($c = 1{\cdot}9985$, $l = 2$); in chloroform, $[\alpha]^{20°}_{5893} + 232°$ ($c = 2{\cdot}0120$, $l = 2$). McKenzie and Wren give $[\alpha]^{12{\cdot}5°}_{5893}$ 221·3° ($c = 1{\cdot}0156$, $l = 4$) in acetone, and $[\alpha]^{15°}_{5893} +$ 233·6° ($c = 1{\cdot}3196$, $l = 4$) in chloroform.

Rotation dispersions of d(+)-*triphenylethylene glycol.*

	λ.							λ^2_0.			
	6563.	6162.	5893.	5461.	5106.	4861.	*K*.	Eq. (*a*).	Eq. (*b*).	$\Delta \times 10^3$.	$\frac{[\alpha]_{4861}}{[\alpha]_{6563}}$.
(1) In acetone ($c = 1{\cdot}9985$, $l = 2$, $t = 20{\cdot}4°$).											
α	6·90°	7·89°	8·75°	10·44°	12·27°	13·87°					
[α] Obs.	172·6	197·3	218·9	261·1	306·9	347·0					
[α] Calc.	171·8	198·0	219·2	261·7	307·1	346·3	66·30	0·04482	0·04402	0·80	2·011
(2) In benzene ($c = 2{\cdot}000$, $l = 2$, $t = 20{\cdot}5°$).											
α	8·23	—	10·50	12·65	—	17·00					
[α] Obs.	205·8	—	262·5	316·3	—	425·0					
[α] Calc.	205·1	—	263·5	316·7	—	424·8	77·06	0·05491	0·05380	1·11	2·065
(3) In chloroform ($c = 2{\cdot}0120$, $l = 2$, $t = 20{\cdot}1°$).											
α	7·31	—	9·30	11·12	—	14·76					
[α] Obs.	181·4	—	231·6	276·7	—	366·5					
[α] Calc.	181·7	—	231·2	276·4	—	366·8	69·79	0·04594	0·04565	0·29	2·019
(4) In ethyl alcohol ($c = 2{\cdot}0056$, $l = 2$, $t = 20{\cdot}5°$).											
α	6·91	—	8·90	10·66	—	14·25					
[α] Obs.	172·4	—	222·0	265·9	—	355·4					
[α] Calc.	172·6	—	221·5	265·7	—	355·3	65·29	0·05263	0·05330	0·67	2·062

The specific rotation of this glycol also decreased with increasing emperature. In acetone solution (see above) :

t	0°	20·4°	30·4°
$[\alpha]_{5893}$	+ 238·9°	+ 218·9°	+ 210·4°

Action of o-*Tolylmagnesium Bromide on Ethyl* r-*Mandelate.*—Ethyl *r*-mandelate (5 g., 1 mol.) was added in ethereal solution to the Grignard reagent prepared from *o*-bromotoluene (22 g., 4·5 mols.). A vigorous action ensued and the mixture was boiled for 5 hours to complete it. After decomposition with ice and ammonium chloride, a yellow oil was obtained from the ethereal layer, and this was distilled in a current of steam to remove di-*o*-tolyl. The residual oil was extracted with ether and dried, but could not be induced to crystallise. An oil was also obtained when the decomposition of the Grignard complex was carried out with ice and dilute sulphuric acid, but it decomposed explosively when distilled under 15 mm. pressure. Stoermer (*Ber.*, 1906, **39**, 2288) was similarly unsuccessful in his attempt to isolate a glycol by the action of *o*-tolylmagnesium bromide on ethyl lactate.

Action of m-*Tolylmagnesium Bromide on Ethyl* r-*Mandelate.*—Ethyl *r*-mandelate (10 g., 1 mol.) was added to the Grignard reagent prepared from bromotoluene (39 g., 4 mols.), and the product was worked up as in the previous experiment. The oil obtained after removal of the di-*m*-tolyl was dissolved in light petroleum, and the solid which separated was repeatedly recrystallised from the same solvent. α-*Phenyl*-ββ-*di*-m-*tolylethylene glycol* crystallises in needles, m. p. 132—134° (Found: C, 83·2; H, 7·2. $C_{22}H_{22}O_2$ requires C, 83·0; H, 6·9%).

Action of p-*Tolylmagnesium Bromide on Ethyl* d(—)-*Mandelate.*—Ethyl *d*(—)-mandelate (4 g., 1 mol.) was added to the Grignard reagent prepared from *p*-bromotoluene (19 g., 5 mols.). The mixture was boiled for 4 hours, and after decomposition with ice and dilute sulphuric acid an oil was obtained from the ethereal layer. This oil was dissolved in hot light petroleum, and on cooling, long needles separated, which were recrystallised several times from light petroleum. d(+)-α-*Phenyl*-ββ-*di*-p-*tolylethylene glycol* separates in long fine needles, m. p. 149—150° (Found: C, 83·1; H, 7·1%); $[\alpha]^{20^\circ}_{5893}$ 209·1° ($c = 1·9685$ in benzene, $l = 2$).

We should like to acknowledge our indebtedness to the Carnegie Trust for the Universities of Scotland, one of us (W. B. M.) for the award of a Carnegie Research Scholarship, and the other (R. R.) for the tenure of a Carnegie Teaching Fellowship. We also thank Imperial Chemical Industries Ltd. for a grant for the purchase of research material.

UNIVERSITY COLLEGE, DUNDEE,
UNIVERSITY OF ST. ANDREWS.

[*Received, May* 11*th*, 1931.]