88. *The Dehydration of the α-Forms of* r- *and* (+)-o- *and* -m-
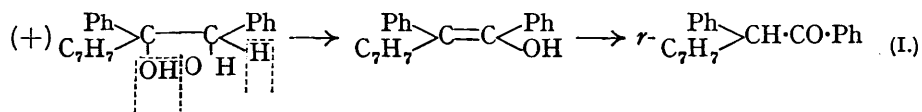*Tolylhydrobenzoins.*

By ROBERT ROGER and WILLIAM B. McKAY.

THE dehydration of *r-p*-tolylhydrobenzoin (α-form) was first investigated by McKenzie, Mills, and Myles (*Ber.*, 1930, **63**, 904), who found that concentrated sulphuric acid led to the formation of *p*-tolyl diphenylmethyl ketone; Koelsch (*J. Amer. Chem. Soc.*, 1932, **54**, 2049) confirmed this result. Later, McKenzie, Roger, and McKay (J., 1932, 2597) showed that the main product of the reaction was not this ketone but *p*-tolyldeoxybenzoin; they also showed that the action of dilute sulphuric acid or oxalic acid on either the *r*- or the (+)form of the glycol gave almost exclusively *r-p*-tolyldeoxybenzoin.

The dehydration of the α-forms of the *r*- and (+)-*o*- and -*m*-tolylhydrobenzoins (Roger and McKay, J., 1931, 2229) is now described. With dilute sulphuric acid *r-m*-tolylhydrobenzoin gave mainly *r-m*-tolyldeoxybenzoin, whilst concentrated acid gave the two isomeric ketones, *r-m*-tolyldeoxybenzoin and *m*-tolyl diphenylmethyl ketone, but only the former could be isolated. Dehydration of (+)-*m*-tolylhydrobenzoin (α-form) gave mainly *r-m*-tolyldeoxybenzoin, but a small amount of dextrorotatory oil was also obtained. The addition of a trace of alcoholic potash to an ethyl-alcoholic solution of this oil indicated the presence of a trace of (+)-*m*-tolyldeoxybenzoin. Dehydration of the (+)form of the glycol with oxalic acid gave *r-m*-tolyldeoxybenzoin. The syntheses of the isomeric ketones by Grignard reactions are described.

The action of concentrated sulphuric acid on *r-o*-tolylhydrobenzoin gave a small amount of a compound, m. p. 47—48°, apparently *o*-tolyl diphenylmethyl ketone. The residual oil was a mixture of the isomeric ketones, *r-o*-tolyldeoxybenzoin and *o*-tolyl diphenylmethyl ketone, the latter preponderating. Dilute sulphuric acid gave diphenyl-*o*-tolylacetaldehyde. Another compound, m. p. 55—56°, provisionally regarded as *o*-tolyldeoxybenzoin, was also isolated. The first transformation of the aldehyde with concentrated sulphuric acid gave the compound, m. p. 48—49°, but later experiments always yielded an oil which was a mixture of the two isomeric ketones. When (+)-*o*-tolylhydrobenzoin (α-form) was dehydrated with dilute sulphuric acid, the aldehyde and a highly dextrorotatory compound, m. p. 79·5—80·5°, were obtained. An ethyl-alcoholic solution of the latter was gradually racemised completely by a trace of alcoholic potash. From the racemised solution a compound, m. p. 55—56°, was isolated, identical with that of similar m. p. obtained in the dehydration of the *r*-glycol with dilute sulphuric acid.

McKenzie, Roger, and McKay (*loc. cit.*) regarded the formation of *r-p*-tolyldeoxy-benzoin from the dehydration of (+)-*p*-tolylhydrobenzoin (α-form) with dilute sulphuric acid or oxalic acid as an example of vinyl dehydration :

$$(+)\ \mathrm{{}^{Ph}_{C_7H_7}{>}C{-\!-}C{<}{}^{Ph}_{H}} \longrightarrow \mathrm{{}^{Ph}_{C_7H_7}{>}C{=}C{<}{}^{Ph}_{OH}} \longrightarrow r\text{-}\ \mathrm{{}^{Ph}_{C_7H_7}{>}CH{\cdot}CO{\cdot}Ph} \quad \text{(I.)}$$
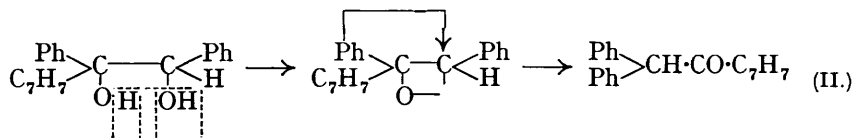
a mechanism which is not necessarily confined to the use of concentrated sulphuric acid [cf. the dehydration of *r*-anisylhydrobenzoin (α-form), Tiffeneau and Orékhoff, *Bull. Soc. chim.*, 1921, **29**, 445]. It is extremely improbable that the formation of *r-p*-tolyldeoxy-benzoin can be attributed to a semipinacolinic change, since the work of Roger and McKenzie
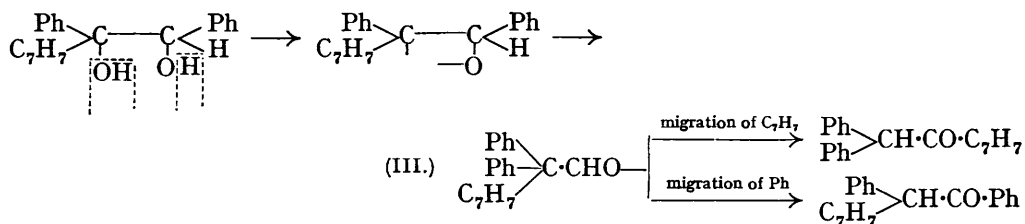
(*Ber.*, 1929, **62**, 272; cf. McKenzie and Dennler, *Ber.*, 1927, **60**, 220) suggests that an optically active ketone should be produced as the result of such a mechanism.

McKenzie, Roger, and McKay (*loc. cit.*) made no attempt to explain the formation of the *p*-tolyl diphenylmethyl ketone from *p*-tolylhydrobenzoin (α-form) but stated that semipinacolinic transformation appeared unlikely. Such a change would give the most straightforward mechanism (II). This, however, is not in accordance with our knowledge

$$\underset{C_7H_7}{\overset{Ph}{>}}\!\!C\!\!-\!\!C\!\!\underset{H}{\overset{Ph}{<}} \longrightarrow \underset{C_7H_7}{\overset{Ph}{>}}\!\!C\!\!-\!\!C\!\!\underset{H}{\overset{Ph}{<}} \longrightarrow \underset{Ph}{\overset{Ph}{>}}CH{\cdot}CO{\cdot}C_7H_7 \quad \text{(II.)}$$

of the saturation capacities of the phenyl and the *p*-tolyl group. In the dehydration of the glycol with dilute sulphuric acid a small amount of a compound, m. p. 171—172°, probably diphenyl-*p*-tolylacetaldehyde, was isolated by those authors. This is suggestive, for Danilov has claimed that such aldehydes can play the part of intermediates in glycol dehydration; but such a mechanism is in certain cases definitely excluded (Roger and McKenzie, *loc. cit.*). The dehydration of *p*-tolylhydrobenzoin (α-form) with concentrated sulphuric acid can, however, be depicted along the lines suggested by Danilov :

$$\underset{C_7H_7}{\overset{Ph}{>}}\!\!C\!\!-\!\!C\!\!\underset{H}{\overset{Ph}{<}} \longrightarrow \underset{C_7H_7}{\overset{Ph}{>}}\!\!C\!\!-\!\!C\!\!\underset{H}{\overset{Ph}{<}} \longrightarrow$$

(III.) $\underset{C_7H_7}{\overset{Ph}{\underset{}{>}}}\!\!C{\cdot}CHO\!\!-\!\!\left[\begin{array}{l} \xrightarrow{\text{migration of } C_7H_7} \underset{Ph}{\overset{Ph}{>}}CH{\cdot}CO{\cdot}C_7H_7 \\ \xrightarrow{\text{migration of } Ph} \underset{C_7H_7}{\overset{Ph}{>}}CH{\cdot}CO{\cdot}Ph \end{array} \right.$
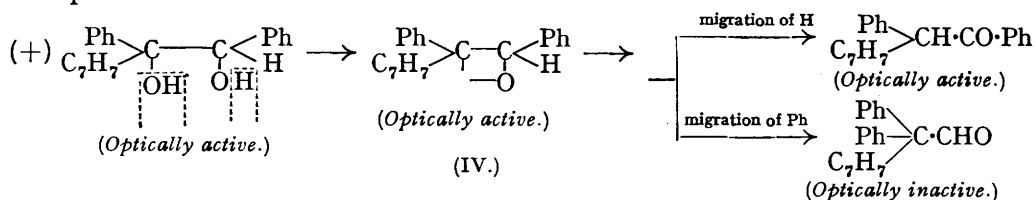
The production of *p*-tolyldeoxybenzoin during the dilute sulphuric acid or oxalic acid dehydration of *p*-tolylhydrobenzoin (α-form) can still be regarded as the result of vinyl dehydration, otherwise one would expect that the aldehyde would have been isolated in much more than a mere trace.

Similar considerations can also be applied to the dehydration of *r*-*m*-tolylhydrobenzoin (α-form). Dehydration of the (+) stereoisomeride (α-form) with dilute sulphuric acid was interesting as it showed the presence of a small amount of optically active *m*-tolyldeoxybenzoin. Now this ketone could not have been formed according to either of the schemes (I) or (III), and the obvious alternative is scheme (II), *i.e.*, semipinacolinic transformation. Little is known definitely about the saturation capacity of the *m*-tolyl group, but, if it were much smaller than that of phenyl, then the possibility of semipinacolinic transformation taking place would be greatly enhanced.

In some respects the dehydration of *r*- and (+)-*o*-tolylhydrobenzoins differed materially from those of the other tolylhydrobenzoins. Dehydration with *concentrated* sulphuric acid again gave a mixture of isomeric ketones. On the other hand, dehydration with *dilute* acid gave a product consisting largely of diphenyl-*o*-tolylacetaldehyde, the residue probably containing a large proportion of *o*-tolyldeoxybenzoin. The dehydration thus resembles that of triphenylethylene glycol and of α-naphthylhydrobenzoin (McKenzie and Roger, *J.*, 1924, **125**, 844; McKenzie and Dennler, *ibid.*, p. 2105). Dehydration of the optically active glycol yielded a compound, provisionally regarded as the *o*-tolyldeoxy-benzoin, in an almost optically pure state. Of the schemes outlined so far, (II) is the only one which explains this result. On the basis of this scheme, however, the assumption is made that the *o*-tolyl group has a saturation capacity smaller than that of hydrogen (cf., however, Bailar, *J. Amer. Chem. Soc.*, 1930, **52**, 3596). The formation of the aldehyde presupposes the transient existence of the intermediate complex, –CPh(C₇H₇)·CHPh·O–, and consequently the tertiary hydroxyl group in the glycol is the least firmly held. If the hydrogen atom migrates in preference to phenyl, then this complex can be utilised to explain

the formation of *o*-tolyldeoxybenzoin. The dehydration with dilute acid could therefore be depicted as follows :

$$(+)\ \underset{C_7H_7}{\overset{Ph}{>}}\!\!C\underset{\overline{|OH|}}{\overset{|}{-}}\!\!C\underset{\overline{O|H|}}{\overset{Ph}{<}}H \longrightarrow \underset{C_7H_7}{\overset{Ph}{>}}\!\!C\underset{\overline{-O}}{\overset{|}{-}}\!\!C\underset{}{\overset{Ph}{<}}H \longrightarrow \ \left|\ \begin{array}{l} \xrightarrow{\text{migration of H}}\ \underset{C_7H_7}{\overset{Ph}{>}}CH\cdot CO\cdot Ph \\ \\ \xrightarrow{\text{migration of Ph}}\ \underset{C_7H_7}{\overset{Ph}{\underset{Ph}{>}}}C\cdot CHO \end{array} \right.$$

(*Optically active.*) (*Optically active.*) (*Optically active.*)

(IV.) (*Optically inactive.*)

This example would, therefore, constitute the first application of polarimetric methods to the study of the " semihydrobenzoin migration of hydrogen." We do not, however, wish to commit ourselves definitely to this principle until we have gained further knowledge of the saturation capacity of the *o*-tolyl group and also until we are certain of the constitution of the compound which we provisionally regard as *o*-tolyldeoxybenzoin. Tiffeneau and Lévy (*Bull. Soc. chim.*, 1931, **49**, 1688) do not favour this mechanism in many cases; but Lagrave (*Ann. Chim.*, 1927, **8**, 363) favours this semihydrobenzoin migration of hydrogen in preference to vinyl dehydration as an explanation of the formation of anisyldeoxybenzoin from anisylhydrobenzoin.

None of these theories takes into account the possibility of the interconversion of the isomeric ketones arising in the dehydrations, *e.g.*, *o*-tolyldeoxybenzoin ⇌ *o*-tolyl diphenylmethyl ketone. This possibility was tested by triturating *r*-*o*-tolyldeoxybenzoin with concentrated sulphuric acid for some hours, but the original ketone only was recovered. The reverse action could not have taken place in the presence of dilute sulphuric acid, since the compound presumed to be *o*-tolyldeoxybenzoin is obtained in an optically active condition on dehydration of the (+)glycol.

The amount of *r*-ketone formed in the dehydration of (+)-*o*-tolylhydrobenzoin with dilute acid was apparently much smaller than was the case during the dehydration of (+)-β-phenyl-αα-dibenzylethylene glycol (Roger and McKenzie, *loc. cit.*). This may be due to a smaller susceptibility to racemisation on the part of (+)-*o*-tolyldeoxybenzoin. If the formation of optically active ketones takes place along the lines indicated in schemes (II) or (IV), then the reaction is one of displacement, a hydrogen atom or a group replacing an electric charge (McKenzie, Roger, and Wills, J., 1926, 779). In displacement reactions with optically active compounds some racemisation often takes place (cf. the work of McKenzie and collaborators). The sulphuric acid used in the dehydrations also exercises a racemising effect. The partial loss of activity in the formation of these ketones would thus be the combined result of both displacement and sulphuric acid racemisation.

By comparison of the rotatory powers of the (+)tolylhydrobenzoins and triphenylethylene glycol, Roger and McKay (*loc. cit.*) showed that the new asymmetric centres arising in the formation of the former glycols had little, if any, influence on their rotatory powers. The rotatory powers of (+)triphenylethylene glycol and of (+)-*m*- and (+)-*p*-tolylhydrobenzoins were very similar in various solvents. (+)-*o*-Tolylhydrobenzoin was more definitely dextrorotatory than these three glycols, but it was not possible to assign any definite configurations to the three tolylhydrobenzoins. It is of interest, then, that (+)-*o*-tolylhydrobenzoin should give rise to a highly dextrorotatory dehydration product. If this product is (+)-*o*-tolyldeoxybenzoin and it is formed by migration of hydrogen (scheme IV), then we have some evidence that the new asymmetric centre arising in the synthesis of the glycol is really a centre of optical activity.

<div align="center">EXPERIMENTAL.</div>

<div align="center">*Dehydration of* r- *and* (+)-m-*Tolylhydrobenzoins* (α-*Forms*).</div>

A. r-m-*Tolylhydrobenzoin.*—(1) *With concentrated sulphuric acid.* 8 G. of *r*-*m*-tolylhydrobenzoin (α-form) were triturated with conc. H_2SO_4 (25 c.c.) at $-2°$. A yellow colour appeared which gradually deepened to a greenish-black, and after 4 hr. the mixture was poured into ice–H_2O and extracted with Et_2O. The resulting oil was obtained as a solid (m. p. 60—80°, 2·6 g.) by crystn. from light petroleum; after 5 recrystns. from petroleum–EtOH, *r*-m-*tolyldeoxy*-

benzoin formed needles, m. p. 83—84° (Found : C, 87·9; H, 6·4. $C_{21}H_{18}O$ requires C, 88·1; H, 6·3%). All the mother-liquors were evaporated and the united solid had m. p. 60—65°. Repeated recrystn. of this solid did not give a pure compound and ultimately the whole of it (2·4 g.) was shown by the action of alc. KOH to consist of a mixture of *m*-tolyldeoxybenzoin and *m*-tolyl diphenylmethyl ketone, the latter preponderating.

(2) *With dilute sulphuric acid.* 8 G. of glycol were boiled for 3 hr. with dil. H_2SO_4 (30% by vol.) and the product worked up as in (1) ; solid (m. p. 80—84°, 5 g.) separated. After several recrystns. from petroleum, pure *r*-*m*-tolyldeoxybenzoin, m. p. 83—84°, was obtained. From the original liquor, 2·2 g. of oil were obtained which did not yield any solid on keeping or after distillation in vac.

Synthesis of r-m-*Tolyldeoxybenzoin.*—This was carried out by the following reactions : $Ph \cdot CHO \longrightarrow C_7H_7 \cdot CHPh \cdot OH \longrightarrow C_7H_7 \cdot CHPhCl \longrightarrow C_7H_7 \cdot CHPh \cdot CN$. r-*Phenyl*-m-*tolylaceto-nitrile* separated from petroleum as large prisms, m. p. 38·5—39° (Found : C, 87·1; H, 6·1. $C_{15}H_{13}N$ requires C, 86·9; H, 6·3%).

The Grignard reagent prepared from PhBr (15 g.) was added to an ethereal solution of the nitrile (4·3 g.) and heated for 10 hr. After decomp. in the manner described by McK., R., and McK. (*loc. cit.*), a solid was obtained from the acid layer. This, recryst. from petroleum, separated in small plates, m. p. 84—85°, identical with the *r*-*m*-tolyldeoxybenzoin obtained as above.

Synthesis of m-*Tolyl Diphenylmethyl Ketone.*—The Grignard reagent prepared from *m*-bromo-toluene (13 g.) was added to diphenylacetonitrile (5 g.) in Et_2O, heated for 4 hr., and worked up as in the previous synthesis. The solid obtained was recryst. from light petroleum. m-*Tolyl diphenylmethyl ketone* (m-*diphenylacetotoluene*) separates from petroleum in small plates, m. p. 97° (Found : C, 88·3; H, 6·5. $C_{21}H_{18}O$ requires C, 88·1; H, 6·3%) ; mixed m. p. with *m*-tolyl-deoxybenzoin, 63—72°.

Action of Concentrated Sulphuric Acid on r-m-*Tolyldeoxybenzoin.*—The ketone (1 g.) was triturated with conc. H_2SO_4. A bright yellow colour developed, and after 4 hr. the mixture was treated successively as before with ice, ether, and petroleum. A solid, containing S, separated, and on recrystn. from C_6H_6–EtOH formed large, hard, rectangular prisms, m. p. 173—174° (Found : C, 72·2; H, 4·7%). From the original petroleum liquors, solid (0·6 g.) was recovered; after recrystn. from light petroleum this melted at 83—84° and was unchanged *m*-tolyldeoxy-benzoin.

B. (+)-m-*Tolylhydrobenzoin* (α-*Form*).—(1) *With dilute sulphuric acid.* The (+)glycol (4·5 g.) was boiled for 3 hr. with dil. H_2SO_4 (30% by vol.). After dilution to 400 c.c. with H_2O, the mixture was worked up as before. The solid (1·7 g., m. p. 83—84°) which separated from petroleum was optically inactive in $CHCl_3$ ($\lambda = 5893$, $c = 2 \cdot 0765$, $l = 2$) ; this was *r*-*m*-tolyldeoxybenzoin. The residual oil left after the separation of this solid, however, was optically active ($[\alpha]_{5893} = + 24 \cdot 6°$, $c = 1 \cdot 914$, $l = 2$) in $CHCl_3$. When this oil was dissolved in EtOH a small amount of solid remained (m. p. 163—165°), which was optically inactive in $CHCl_3$ ($l = 2$, $c = 0 \cdot 625$). The oil from which this solid was removed was dissolved in EtOH ($c = 1 \cdot 894$, $l = 1$) and had $[\alpha]_{5893} + 41 \cdot 5°$ ($\alpha = + 0 \cdot 79°$). The addition of 3 drops of $N/2$-alc. KOH reduced α to $+ 0 \cdot 48°$ after 20 min.; further addition of alkali then caused no further diminution in α. The residual activity was probably due to some unchanged glycol.

(2) *With oxalic acid.* 2·5 G. of (+)glycol were boiled with molten $C_2H_2O_4, 2H_2O$ (40 g.) for 8 hr. The product of dehydration was recovered as described by McK., R., and McK. (*loc. cit.*) for *p*-tolylhydrobenzoin (α-form). The solid which separated from the petroleum solution was optically inactive in acetone ($c = 1 \cdot 996$, $l = 2$, $\lambda = 5893$), and after one crystn. from petroleum–EtOH had m. p. 84—85°, alone or mixed with *r*-*m*-tolyldeoxybenzoin. The oil recovered from the mother-liquors was dextrorotatory ($[\alpha]_{5893} = + 0 \cdot 87°$, $\alpha = + 0 \cdot 15°$, $c = 8 \cdot 645$, $l = 1$) in EtOH. This alc. solution was not racemised by a trace of alc. KOH and the small dextro-rotation was, therefore, probably due to unchanged glycol.

Dehydration of r- *and* (+)-o-*Tolylhydrobenzoins* (α-*Forms*).

A. r-o-*Tolylhydrobenzoin.*—(1) *With concentrated sulphuric acid.* The glycol [8 g., from *r*-benzoin and *o*-tolylmagnesium bromide (Roger and McKay, *loc. cit.*)] was triturated with conc. H_2SO_4 (25 c.c.). The initial yellow coloration deepened to a brownish-yellow after 4 hr.; the semi-solid which separated when the mixture was poured into H_2O was extracted with Et_2O. The oil from the extract was dissolved in aq. EtOH, and solid, m. p. 44—45°, separated after 4 days in the ice-chest ; recrystn. from light petroleum gave large colourless prisms (0·6 g.), m. p. 47—48°

(Found : C, 87·8; H, 6·3. $C_{21}H_{18}O$ requires C, 88·1; H, 6·3%). This was probably o-*tolyl diphenylmethyl ketone*. The residual oil (2·2 g.) could not be induced to crystallise. This expt. was repeated 3 times, but only oils were obtained. Alc. KOH scission of one of these oils showed that it consisted of a mixture of o-tolyldeoxybenzoin and o-tolyl diphenylmethyl ketone, the latter preponderating.

(2) *With dilute sulphuric acid.* 10 G. of r-glycol were boiled with conc. H_2SO_4 (30 c.c.) and H_2O (70 c.c.) for 3 hr. After dilution to 450 c.c. with H_2O and the usual treatment with Et_2O followed by petroleum–EtOH, large, hard clumps of solid (m. p. 161—163°, 2·5 g.) separated and were recryst. from C_6H_6–EtOH. *Diphenyl-o-tolylacetaldehyde* forms large prisms, m. p. 163—164° [Found: C, 88·0; H, 6·4; *M* (Rast), 300, 270. $C_{21}H_{18}O$ requires C, 88·1; H, 6·3%; *M*, 286]. This compound gave a yellow coloration with conc. H_2SO_4, and its constitution was proved by scission with alc. KOH, diphenyl-o-tolylmethane, m. p. 82—83° (Found : C, 93·3; H, 7·2. $C_{20}H_{18}$ requires C, 93·0; H, 7·0%), being obtained. After removal of the aldehyde, the mother-liquors deposited further solid, m. p. 40—60° (1·5 g.). This was recrystallised several times from light petroleum–EtOH; r-o-*tolyldeoxybenzoin* forms small glistening plates, m. p. 56—57° (Found : C, 88·2; H, 6·5. $C_{21}H_{18}O$ requires C, 88·1; H, 6·3%); it formed no semi-carbazone.

Transformation of Diphenyl-o-tolylacetaldehyde with Concentrated Sulphuric Acid.—0·5 G. of the aldehyde was triturated with conc. H_2SO_4 (17 c.c.) for $2\frac{1}{2}$ hr. A yellow coloration developed, and then the mixture was poured into ice–H_2O (300 g.). From the dried Et_2O extract an oil was obtained which was dissolved in EtOH. After some days large prisms (0·25 g.), m. p. 45—47°, separated. After further recryst. the m. p. was 46—47° alone or mixed with o-tolyl diphenylmethyl ketone (?) obtained from the dehydration of the glycol with conc. H_2SO_4. The oil remaining after removal of this ketone would not solidify and was a mixture of r-o-tolyldeoxybenzoin and o-tolyl diphenylmethyl ketone.

Transformation of o-*Tolyldeoxybenzoin.*—r-o-Tolyldeoxybenzoin(?) (0·4 g.) was triturated with conc. H_2SO_4 for 4 hr. A bright yellow coloration developed which did not change on standing. After treatment of the mixture as described for the m-isomeride, 0·1 g. of unchanged ketone was obtained. A very small amount of oil was also present but would not crystallise. In view of the large loss of material in this expt., it is not possible to state definitely whether some transformation had not taken place.

The synthesis of r-o-tolyldeoxybenzoin was attempted by the reaction of r-phenyl-o-tolyl-acetonitrile and MgPhBr, but only unchanged nitrile was obtained. The action of phenyl-o-tolylmethylmagnesium chloride on benzonitrile yielded only a complex hydrocarbon, and o-tolylmagnesium bromide failed to react with diphenylacetonitrile.

B. (+)-o-*Tolylhydrobenzoin (α-Form).*—*With dilute sulphuric acid.* 6·4 G. of the (+)glycol (Roger and McKay, *loc. cit.*) were boiled with dil. H_2SO_4 (30% by vol.) for 3 hr.; treatment with ice–H_2O, Et_2O, and petroleum yielded diphenyl-o-tolylacetaldehyde; after recrystn. from C_6H_6–EtOH, it had m. p. 163—164° and showed no optical activity in $CHCl_3$ ($c = 2·0185, l = 2$). The mother-liquors from which the crude aldehyde had been separated deposited 1·6 g. of fine needles, m. p. 71—78°, which, after several recrystns. from light petroleum, afforded (+)-o-*tolyl-deoxybenzoin* (?), m. p. 79·5—80·5° (Found : C, 88·2; H, 6·4. $C_{21}H_{18}O$ requires C, 88·1; H, 6·3%); in $CHCl_3$, $[\alpha]_{5893}^{20°} +202·5°$ ($c = 2·01, l = 2, \alpha_{5893}^{20°} = +8·14°$), in EtOH, $[\alpha]_{5893}^{20°} +174°$ ($c = 2·02, l = 2, \alpha_{5893}^{20°} = +3·50°$). No mutarotation could be observed in this solution. When, however, 3 drops of $N/2$-alc. KOH were added to the foregoing solution, racemisation was rapid :

t (min.)	2	4	6	9	13	17	21	30	58	88
$\alpha_{5893}^{20°}$	+3·21°	2·76°	2·39°	1·86°	1·29°	0·93°	0·73°	0·37°	0·07°	0·0°

From this racemised solution an oil was recovered which was cryst. from aq. EtOH. Needles, m. p. 55—56°, separated, identical with the r-o-tolyldeoxybenzoin(?) obtained in the dil. acid dehydration of r-o-tolylhydrobenzoin.