

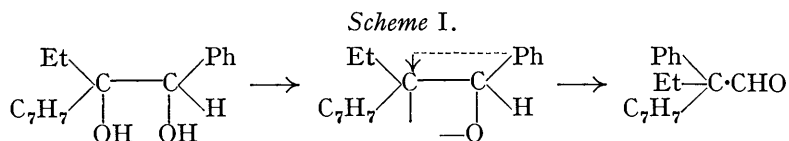
367. The Dehydration of *r*-2-Phenyl-1-*o*-, -*m*-, and -*p*-tolyl-1-ethylene Glycols (α -Forms).

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The dehydration of the *r*-2-phenyl-1-*o*-, -*m*-, and -*p*-tolyl-1-ethylene glycols (α -forms) is described. All three glycols give aldehydes with dilute sulphuric acid or oxalic acid by semihydrobenzoin transformation. With concentrated sulphuric acid, the *o*- and the *m*-glycol give the corresponding tolyl α -phenylpropyl ketones by semipinacolinic transformation. The migration of the ethyl group is unexpected, and shows that transformations previously termed vinyl may really have been semipinacolinic in character. The results of the transformation of the aldehydes and the direct dehydration of the glycols with concentrated sulphuric acid are compared.

THE dehydration of *r*-*p*-tolylhydrobenzoin (α -form) was first investigated by McKenzie, Mills, and Myles (*Ber.*, 1930, **63**, 904). The study was extended by McKenzie, Roger, and McKay (*J.*, 1932, 2597) (see also Koelsch, *J. Amer. Chem. Soc.*, 1932, **54**, 2049) to the optically active form of the glycol. Roger and McKay (*J.*, 1933, 332) made a comparative study of the *o*-, *m*-, and *p*-tolylhydrobenzoin and found that, with dilute sulphuric acid, *r*-*o*-tolylhydrobenzoin gave a mixture of *r*-*o*-tolyldeoxybenzoin and diphenyl-*o*-tolylacet-aldehyde, whilst the *m*- and *p*-isomers gave the corresponding deoxybenzoin and only traces of the aldehydes. This difference became more striking when the optically active forms of these glycols were dehydrated with dilute sulphuric acid, since the *o*-glycol gave almost pure optically active *o*-tolyldeoxybenzoin, but the *m*- and *p*-glycols gave deoxybenzoin which were almost optically inactive. At that time, the authors were inclined to the view that the *o*-ketone had been formed by semihydrobenzoin migration of hydrogen (*e.g.*, Scheme II), but that the *m*- and *p*-ketones had been formed by vinyl dehydration (*e.g.*, Scheme III). The only other explanation that can be offered is that the *m*- and *p*-tolyldeoxybenzoin are formed through the aldehydes as intermediates. These aldehydes contain no centre of asymmetry and, therefore, in transformation could not give optically active ketones. There was thus ambiguity as to the mechanism of formation of the *m*- and *p*-tolyldeoxybenzoin.

Phenylpropionylcarbinol can give rise to glycols which contain two centres of asymmetry and in which all the hydrocarbon radicals may be different. For instance, with the tolylmagnesium bromides, the glycols $C_6H_4Me \cdot CEt(OH) \cdot CHPh(OH)$ were obtained, and their dehydration was interesting from three points of view. With dilute acid, they gave aldehydes



in each case. These would arise by the semihydrobenzoin migration of phenyl (Scheme I). The mechanism of dehydration being the same for each glycol, the ambiguity of mechanism which arose in the formation of the tolyldeoxybenzoin from the respective tolylhydrobenzoin is removed. Secondly, the transformation of the aldehydes into ketones was studied, and compared with the results of the direct dehydrations of the glycols.

Thirdly, the results contrast with the dehydration of ethylhydrobenzoin and throw light on the problem of "vinyl dehydration."

With dilute sulphuric acid no appreciable amounts of ketones or oxides could be detected, whereas ethylhydrobenzoin can give rise to either diphenylethylacetaldehyde, diphenylbutanone, or a diethylenic oxide on dehydration with dilute sulphuric acid under different experimental conditions (Tiffeneau and Dorlencourt, *Ann. Chim. Phys.*, 1909, **16**, 237; Lévy, *Bull. Soc. chim.*, 1921, **29**, 865; McKenzie and Roger, *J.*, 1924, **125**, 2148). It would seem that the presence of the *o*-, *m*-, and *p*-tolyl groups, therefore, causes a certain bias in favour of aldehyde formation (semihydrobenzoin transformation), and the saturation capacities of Et + C₇H₇ (*o*-, *m*-, or *p*-) must be definitely greater than those of Ph + H. *o*-Tolylhydrobenzoin was the only one of the three isomers from which the formation of aldehyde was definitely detected. The alteration in trend of the dehydrations of different trisubstituted ethylene glycols of the type CR₁R₂(OH)·CHAr(OH) with dilute sulphuric acid or oxalic acid is shown in Table I.

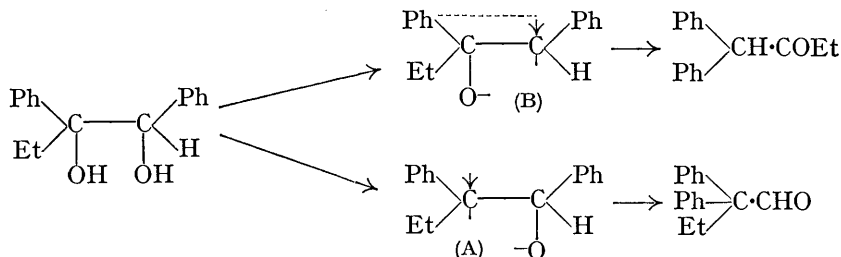
TABLE I.

Dehydration of glycols by dilute sulphuric acid or oxalic acid.

No.	Glycol,			Product.	Mechanism of formation.	
	R ₁ .	R ₂ .	R ₃ .		Type.*	Migrtn. of
1	Ph	Et	Ph	Diphenylethylacetaldehyde Diethylene oxide Diphenylbutanone	A — B	Ph — Ph
2	Ph	Me	Ph	Diphenylmethylacetaldehyde Diethylene oxide	A —	Ph —
3	<i>o</i> -C ₇ H ₇	Et	Ph	Phenyl- <i>o</i> -tolylethylacetaldehyde	A	Ph
4	<i>m</i> -C ₇ H ₇	Et	Ph	Phenyl- <i>m</i> -tolylethylacetaldehyde	A	Ph
5	<i>p</i> -C ₇ H ₇	Et	Ph	Phenyl- <i>p</i> -tolylethylacetaldehyde	A	Ph
6	Ph	Ph	<i>o</i> -C ₇ H ₇	Diphenyl- <i>o</i> -tolylacetaldehyde Diphenylmethyl <i>o</i> -tolyl ketone	A A	<i>o</i> -C ₇ H ₇ H
7	Ph	Ph	Ph	Triphenylacetaldehyde Phenyldeoxybenzoin	A A or C?	Ph H
8	Ph	<i>o</i> -C ₇ H ₇	Ph	Diphenyl- <i>o</i> -tolylacetaldehyde <i>o</i> -Tolyldeoxybenzoin	A A or C?	Ph H
9	Ph	<i>m</i> -C ₇ H ₇	Ph	Diphenyl- <i>m</i> -tolylacetaldehyde (trace) <i>m</i> -Tolyldeoxybenzoin	A A or C?	Ph H
10	Ph	<i>p</i> -C ₇ H ₇	Ph	Diphenyl- <i>p</i> -tolylacetaldehyde (trace) <i>p</i> -Tolyldeoxybenzoin	A A or C?	Ph H

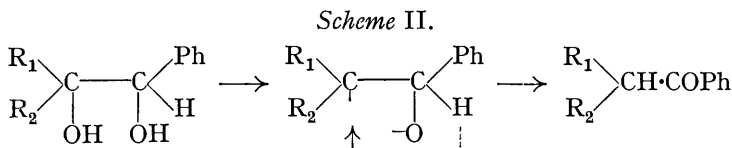
* A = Semihydrobenzoin. B = Semipinacolinic. C = Vinyl.

This table shows the gradation in the dehydration mechanism of such a series of glycols according to the saturation capacities of the groups involved. In example (1) the relationship Ph + Et = Ph + H holds and the result is that the two possible intermediate



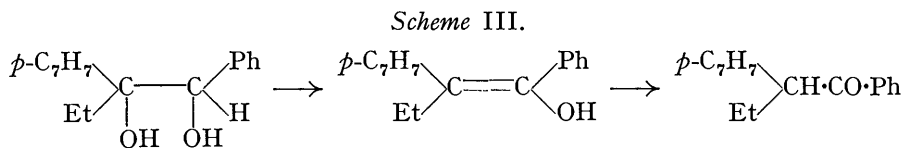
complexes may be formed simultaneously. The phase (B) rearranges to give diphenylbutanone, whilst (A) gives diphenylethylacetaldehyde: the combination of (A) and (B)

would give the diethylene oxide. In examples 2, 3, 4, and 5, Ph + Me or C₇H₇(*o*-, *m*-, or *p*-) + Et > Ph + H, but not to a large extent, and the result seems to be the exclusive formation of the aldehyde by semihydrobenzoin migration of Ph. Examples 6, 7, and 8 are particularly interesting since they form a "transition period" in the table. Here the relationship Ph + Ph or C₇H₇(*o*-, *m*-, or *p*-) > Ph + H or *o*-C₇H₇ + H is quite definite but not so marked as in cases 9 and 10. As a result of this, in cases 6, 7, and 8, aldehydes are formed by semihydrobenzoin migration of an aryl group, but simultaneously ketones are formed by competitive semihydrobenzoin migration of hydrogen. In cases 9 and 10, the disparity in the relationship Ph + C₇H₇(*m*- or *p*-) > Ph + H is so large, and the residual affinity of the receptor carbon atom so small, as to ensure exclusive formation of ketones, probably by semihydrobenzoin migration of hydrogen as in Scheme II (Roger and McKay, *loc. cit.*; Lagrave, *Ann. Chim.*, 1927, 8, 363).

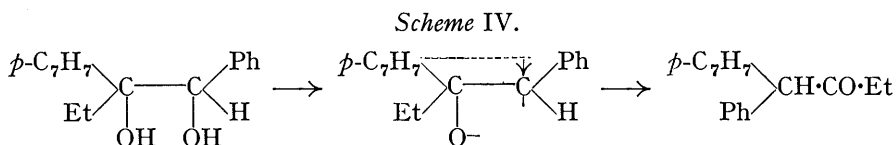


These considerations have an important bearing on the saturation capacity of the *o*-tolyl group. At the time, Roger and McKay (*loc. cit.*), in considering the results of dehydration of *o*-tolylhydrobenzoin, could not exclude the possibility that the *o*-tolyl group had a very small saturation capacity and, therefore, that *o*-tolyldeoxybenzoin had been formed by semipinacolinic migration of the *o*-tolyl group. The fact that optically active *o*-tolyldeoxybenzoin was obtained from the (+)-*o*-tolylhydrobenzoin lent a certain support to this hypothesis, since it had been previously shown that optical activity could be maintained during semipinacolinic transformation (McKenzie and Dennler, *Ber.*, 1927, 60, 220; Roger and McKenzie, *Ber.*, 1929, 62, 272). Roger and Harper (*Rec. trav. chim.*, 1937, 56, 202), as a result of a study of the dehydration of 2 : 2-diphenyl-1-*o*-tolylethylene glycol, concluded that the saturation capacity of the *o*-tolyl group could not differ much from that of the phenyl group. The results of the dehydration of the three glycols now described show that the saturation capacity of the *o*-tolyl group is probably greater than that of phenyl; otherwise, there would not be exclusive formation of the aldehyde by the action of dilute sulphuric acid or molten oxalic acid.

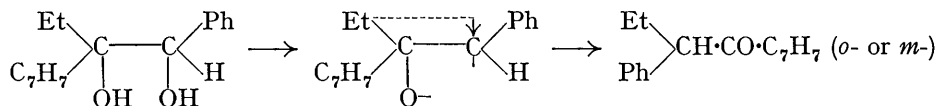
It will be noted from the table that the formation of ketones in certain cases is ascribed to either semihydrobenzoin migration of hydrogen or vinyl dehydration. It seems to us that with dilute acid the vinyl dehydration mechanism is not generally suitable. Indeed, in certain cases, such as the formation of pure optically active *o*-tolyldeoxybenzoin from *o*-tolylhydrobenzoin, the mechanism is inadmissible. This point will be dealt with more fully in a later communication.



Dehydration with concentrated sulphuric acid of the three glycols described showed that here there was no common trend in mechanism. The *p*-glycol yielded α -*p*-tolylbutyrophenone [through the semihydrobenzoin migration of H (*e.g.*, Scheme II) or by vinyl dehydration (Scheme III)] and phenyl-*p*-tolylmethyl ethyl ketone [by semipinacolinic migration



of the *p*-tolyl group (Scheme IV)]. On the other hand, the *o*- and the *m*-glycol gave the unusual result that in each case the ethyl group had migrated (by semipinacolinic transformation) in preference to the tolyl group with the formation of *o*- or *m*-tolyl α -phenylpropyl ketone, although it is generally accepted that the aryl migrates in preference to the alkyl group (Tiffeneau and Lévy, *Bull. Soc. chim.*, 1931, **49**, 1661) :



Now the formation of ethyldeoxybenzoin from ethylhydrobenzoin (with concentrated sulphuric acid) has always previously been considered to be the result of vinyl dehydration (*e.g.*, Scheme III). The detection of the migration of the ethyl group in the cases recorded here has only been rendered possible by the fact that the two aryl groups attached to the skeleton carbon atoms of the glycol are not identical as in the case of ethylhydrobenzoin. The formation of alkyldeoxybenzoin, therefore, from the corresponding alkylhydrobenzoin under these conditions (Orékhoff, *Bull. Soc. chim.*, 1919, **25**, 182; Billard, *ibid.*, 1921, **29**, 429; Tiffeneau and Orékhoff, *ibid.*, 1923, **33**, 195) can now be considered to be the result of semipinacolinic migration of an alkyl group and not of vinyl dehydration. Table II shows the results recorded for the dehydration with concentrated sulphuric acid of the same glycols as in Table I, and also, where the data are available, the transformations of the corresponding aldehydes.

TABLE II.

Dehydration of glycols with concentrated sulphuric acid.

Glycol (see Table I).	Product of dehydration.	Mechanism.		Transformation of aldehyde : product.
		Type.*	Migrtn. of	
1	Ethyldeoxybenzoin	A or C ? or B	H Et Ph	Ethyldeoxybenzoin and di- phenylbutanone
	Diphenylbutanone			
2	Methyldeoxybenzoin	A or C ? or B	H Me Ph	Methyldeoxybenzoin
	Diphenylacetone (trace)			
3	<i>o</i> -Tolyl α -phenylpropyl ketone	B	Et	<i>o</i> -Tolyl α -phenylpropyl ketone
4	<i>m</i> -Tolyl α -phenylpropyl ketone	B	Et	<i>m</i> -Tolylbutyrophenone
5	α - <i>p</i> -Tolylbutyrophenone	A or C ?	H	α - <i>p</i> -Tolylbutyrophenone
	Phenyl- <i>p</i> -tolylmethyl ethyl ketone	B	<i>p</i> -C ₇ H ₇	Phenyl- <i>p</i> -tolylmethyl ethyl ketone
6	Diphenylmethyl <i>o</i> -tolyl ketone	A or C ?	H	See 8
7	Phenyldeoxybenzoin	A or C ?	H	Phenyldeoxybenzoin
8	<i>o</i> -Tolyldeoxybenzoin	A	H	<i>o</i> -Tolyldeoxybenzoin and diphenylmethyl <i>o</i> -tolyl ketone
	Diphenylmethyl <i>o</i> -tolyl ketone	Trans. of aldehyde ?		
9	<i>m</i> -Tolyldeoxybenzoin	A or C ?	H	—
	Diphenylmethyl <i>m</i> -tolyl ketone (trace)	Trans. of aldehyde ?		
10	<i>p</i> -Tolyldeoxybenzoin	A or C ?	H	—
	Diphenylmethyl <i>p</i> -tolyl ketone (trace)	Trans. of aldehyde ?		

* See Table I.

It will be seen that certain glycols recorded in the table underwent semipinacolinic transformation. In most cases also, ketones arise by vinyl dehydration or the alternative semihydrobenzoin migration of hydrogen. The transformations of the aldehydes, where they have been isolated, would support the theory of Danilov that the aldehydes form the intermediate phase in glycol dehydration; but 2-phenyl-1-*m*-tolyl-1-ethylethylene glycol (α -form) is an exception, for apparently a different ketone from that obtained by the direct dehydration of the glycol was isolated. In this case, however, both the glycol and the aldehyde gave small amounts of the same sulphur-containing compound accompanying

the ketonic products, and the total yield was very poor, much of the glycol and aldehyde being unaccounted for in the transformations.

From this result and previously known cases (Tiffeneau, Lévy, and Weill, *Bull. Soc. chim.*, 1931, 49, 1606; Lévy and Pernot, *ibid.*, p. 1721), it will be seen, however, that the conception of the aldehyde as the intermediate phase is only applicable to certain cases of glycol dehydration with concentrated sulphuric acid and cannot be accepted as general. It must be noted, however, that in dehydration or transformation with concentrated sulphuric acid, the results tend to be irregular (*e.g.*, the dehydration of *p*-tolylhydrobenzoin with concentrated sulphuric acid: Koelsch, *loc. cit.*; McKenzie, Mills, and Myles, *loc. cit.*; McKenzie, Roger, and McKay, *loc. cit.*), and the yields are often meagre. The actual isolation, in some cases, of compounds containing sulphur may explain this loss to a certain extent. These factors render it difficult to make rigid conclusions from such experiments.

EXPERIMENTAL.

r-2-Phenyl-1-p-tolyl-1-ethylethylene Glycol (α -form).

Preparation.—Phenylpropionylcarbinol (15 g., 1 mol.) was added to the Grignard reagent prepared from *p*-bromotoluene (48 g., 3 mols.). After 5 hours' boiling, the mixture was decomposed with ice and dilute sulphuric acid. From the ethereal layer a white solid (13.6 g., m. p. 97—100°) was obtained. The glycol (α -form) separated from light petroleum in hexagonal plates, m. p. 100—101° (Found: C, 79.9; H, 8.0. $C_{17}H_{20}O_2$ requires C, 79.6; H, 7.9%).

Dehydration with Concentrated Sulphuric Acid.—Finely pulverised glycol (10 g.) was added in small amounts to concentrated sulphuric acid (25 c.c.) and triturated intermittently for 19 hours. The mixture was poured into ice and water, and extracted with ether. From the ethereal extract, an oil (b. p. 177°/16 mm., 5.2 g.) was obtained. This partly solidified on keeping, and after addition of some light petroleum, the solid was filtered off (1.5 g.) and crystallised from light petroleum, α -p-tolylbutyrophenone separating as octahedra, m. p. 54—55° (Found: C, 85.5; H, 7.9. $C_{17}H_{18}O$ requires C, 85.7; H, 7.6%). The residue from the separation of this ketone gave α -p-tolylbutyrophenone semicarbazone, m. p. 160—161° (Found: C, 73.4; H, 7.2. $C_{18}H_{21}ON_3$ requires C, 73.2; H, 7.2%). On hydrolysis with hydrochloric acid (20%), it gave back the solid ketone, m. p. 54—55°. From the mother-liquor of crystallisation of this semicarbazone, the semicarbazone of phenyl-*p*-tolylmethyl ethyl ketone (see later) was obtained; it separated from benzene in needles, m. p. 202.5—203.5° (Found: C, 73.5; H, 7.2; N, 14.6. $C_{18}H_{21}ON_3$ requires C, 73.2; H, 7.2; N, 14.2%).

Some of the distilled dehydration product, b. p. 177°/16 mm., was treated with 2:4-dinitrophenylhydrazine and only the 2:4-dinitrophenylhydrazone of α -p-tolylbutyrophenone was isolated; this separated from ethyl alcohol as yellow prisms, m. p. 145.5—146.5° (Found: C, 65.8; H, 5.1. $C_{23}H_{22}O_4N_4$ requires C, 66.0; H, 5.3%). With alcoholic potash (15%), the attempted scission of the ketone mixture from a similar dehydration gave mainly unchanged material.

Dehydration with Dilute Sulphuric Acid.—The glycol (6 g.) was boiled for 5 hours with 25% (by vol.) sulphuric acid. After dilution and extraction with ether, an oil (5.2 g., b. p. 175—181°/22 mm.) was obtained from the extract.

Phenyl-p-tolylethylacetaldehydesemicarbazone, m. p. 154—155° (Found: C, 72.9; H, 7.1. $C_{18}H_{21}ON_3$ requires C, 73.2; H, 7.2%), separated from benzene in spear-shaped plates.

This semicarbazone was boiled with 20% hydrochloric acid and afforded *phenyl-p-tolylethylacetaldehyde*, b. p. 182—183°/20 mm., n_{D}^{19} 1.5742 (Found: C, 85.5; H, 7.6. $C_{17}H_{18}O$ requires C, 85.7; H, 7.6%).

The semicarbazone prepared from this oil had m. p. 154—155°, so no transformation could have occurred in the presence of the acid used for the hydrolysis. *Phenyl-p-tolylethylacetaldehyde-2:4-dinitrophenylhydrazone*, m. p. 162—163°, crystallised from ethyl alcohol-acetone in yellow, rectangular prisms (Found: C, 66.0; H, 5.5. $C_{23}H_{22}O_4N_4$ requires C, 66.0; H, 5.3%), and was also prepared directly from the dehydration product.

Dehydration of the glycol with 20% acid (by vol.) afforded considerable amounts of unchanged glycol together with the aldehyde.

Dehydration with Oxalic Acid.—The glycol (12 g.) was boiled gently with fused hydrated oxalic acid (80 g.) for 7 hours. The product had b. p. 170—173°/17 mm., n_{D}^{15} 1.5780 (7.6 g.). The semicarbazone of phenyl-*p*-tolylethylacetaldehyde, m. p. 154—155° (spear-shaped plates from

alcohol or benzene), was obtained, identical with that from the dehydration with dilute sulphuric acid; it also gave the same 2 : 4-dinitrophenylhydrazone, m. p. 162—163°.

Dehydration with Ethereal Hydrogen Chloride.—The glycol (3 g.) in 50 c.c. of dry ether was saturated with dry hydrogen chloride and kept for 2 days at the ordinary temperature. From the ether, an oil (2.75 g.) was obtained, which gave the 2 : 4-dinitrophenylhydrazone of phenyl-*p*-tolylethylacetaldehyde, m. p. 162—163°, identical with that described.

Dehydration with Fuming Hydrochloric Acid.—The glycol (3 g.) was shaken with fuming hydrochloric acid for one week. The oil (2.9 g.) obtained from the ethereal extract gave the same 2 : 4-dinitrophenylhydrazone, m. p. 162—163°.

Dehydration with Sulphuric Acid (d 1.51).—Finely powdered glycol (3.7 g.) was added in small amounts to dilute sulphuric acid (d 1.51, 45 c.c.) with intermittent shaking, and kept for 6 days. By extraction with ether, an oil (3.25 g.) was obtained. This deposited unchanged glycol (0.75 g.), which was removed, and from the residue was prepared the semicarbazone of phenyl-*p*-tolylethylacetaldehyde (1 g.), m. p. 154—155°.

The Isomerisation of Phenyl-p-tolylethylacetaldehyde.—The aldehyde (4 g.) was added slowly to concentrated sulphuric acid (10 c.c.) with stirring. After 19 hours, the claret-coloured mixture was poured into ice and water, and extracted with ether. The extract afforded an oil (1.7 g.), which gave a white solid when treated with semicarbazide. Two semicarbazones were separated from the crude product by fractional crystallisation : (a) prisms, m. p. 159.5—160.5°, alone or mixed with the semicarbazone of α -*p*-tolylbutyrophenone; (b) needles, m. p. 202—203°, alone or mixed with the semicarbazone of phenyl-*p*-tolylmethyl ethyl ketone.

Constitution and Syntheses of the Dehydration Products.

Scission of Phenyl-p-tolylethylacetaldehyde.—The aldehyde (5 g.) was boiled with alcoholic potassium hydroxide (30%, 80 c.c.) for 24 hours. Extraction of the diluted alkaline liquors with ether yielded an oil (1.9 g.), b. p. 150—160°/23 mm. This was redistilled and a fraction, b. p. 154—156°/23 mm. (n_{D}^{20} 1.5683), obtained (Found : C, 91.2; H, 8.4. $C_{17}H_{18}$ requires C, 91.4; H, 8.6%). This was α -phenyl- α -*p*-tolylpropane. On acidifying the alkaline liquor and extracting it with ether, a small amount of liquid was obtained. This had strong reducing properties, but there was insufficient for definite identification as formic acid. No traces of benzoic or *p*-toluic acids were found.

Oxidation of Phenyl-p-tolylethylacetaldehyde.—Silver oxide and sodium hypobromite did not oxidise the aldehyde; but chromic acid in glacial acetic acid afforded phenyl *p*-tolyl ketone, m. p. 54—55°, and 4-benzoylbenzoic acid, m. p. 193—194° (Found : C, 74.2; H, 4.6. Calc. for $C_{14}H_{10}O_3$: C, 74.3; H, 4.5%) (Zincke, *Annalen*, 1872, 161, 109, gives m. p. 194°).

Oxidation of the Mixture obtained by Dehydration with Concentrated Sulphuric Acid.—The mixture (4 g.) was added to chromic anhydride (12 g.) in glacial acetic acid (70 c.c.) and boiled gently for 45 minutes. On making the solution alkaline with sodium hydroxide and extracting it with ether, an oil (0.9 g.) was got, but it did not give a semicarbazone. On acidification of the oxidation liquors and re-extraction with ether, a dark oil was obtained after removal of the acetic acid. This gave clusters of colourless needles from aqueous alcohol, m. p. 138—139° (0.2 g.) (Found : C, 75.7; H, 5.9. $C_{17}H_{16}O_3$ requires C, 76.1; H, 6.0%). This solid dissolved in cold sodium hydroxide, and analysis indicates that it is derived from either of the ketones in the dehydration mixture by the oxidation of the *p*-methyl substituent to a carboxyl group : it may thus be either $CO_2H \cdot C_6H_4 \cdot CHEt \cdot CPh$ or $CO_2H \cdot C_6H_4 \cdot CHPh \cdot COEt$.

Synthesis of r- α -p-Tolylbutyrophenone.—(a) *p*-Tolylethylcarbinol. *p*-Tolyl ethyl ketone (40 g.) was reduced with sodium (35 g.) in alcohol (500 c.c.). The carbinol (32 g.) had b. p. 110°/21 mm. (cf. v. Auwers and Kolligs, *Ber.*, 1922, 55, 43, who give b. p. 114°/12 mm. for a preparation from propaldehyde and *p*-tolylmagnesium bromide). Reduction with sodium amalgam gave *s*-*p*-tolylethylpinacol, m. p. 101—102° (aggregates of prisms from light petroleum) (Found : C, 80.2; H, 8.7. $C_{20}H_{26}O_2$ requires C, 80.5; H, 8.8%).

(b) *p*-Tolylethylchloromethane. The carbinol (20 g.) was treated with thionyl chloride (50 g.), and after removal of excess of the latter, a colourless oil, b. p. 94—95°/15 mm., was obtained; n_{D}^{20} 1.5230 (Found : C, 71.5; H, 7.7; Cl, 21.0. $C_{10}H_{13}Cl$ requires C, 71.2; H, 7.8; Cl, 21.1%).

(c) *p*-Tolylethylacetoneitrile. The above chloride (10 g.) was heated with mercuric cyanide (30 g.) at 160°. An impure oil was obtained from the benzene extract, which did not yield a sharp-boiling fraction. Similar results were got with mercuric cyanide at 100° and with alcoholic potassium cyanide at 100°. The products contained nitrogen, however.

(d) *r- α -p-Tolylbutyrophenone.* The combined crude product from the above preparation of the nitrile (6.2 g.) was added to the Grignard reagent prepared from bromobenzene (24 g.),

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and the mixture boiled for 16 hours. After decomposition with ice and concentrated hydrochloric acid, a solid was obtained from the acid layer. This crystallised from light petroleum in octahedra, m. p. 54—55°, alone or mixed with *r*- α -*p*-tolylbutyrophenone obtained from the dehydration; and it formed a 2 : 4-dinitrophenylhydrazone, m. p. 145.5—146.5°, alone or mixed with the similar compound obtained from the concentrated sulphuric acid dehydration product of the glycol.

Synthesis of Phenyl-p-tolylmethyl ethyl ketone. Phenyl-*p*-tolylacetonitrile (McKenzie, Roger, and McKay, J., 1932, 2597) (10 g.) was added to the Grignard reagent prepared from ethyl bromide (21 g.). After 4 hours' boiling and decomposition with ice and dilute sulphuric acid, an oil was obtained from the ethereal layer. This deposited unchanged nitrile (3 g., m. p. 62—63°). The residue was treated with semicarbazide, and fine colourless needles (from benzene), m. p. 203.5°, alone or mixed with the semicarbazone of phenyl-*p*-tolylmethyl ethyl ketone were obtained. No 2 : 4-dinitrophenylhydrazone could be isolated.

r-2-Phenyl-1-*m*-tolyl-1-ethylethylene Glycol (α -Form).

Preparation.—By the action of *m*-tolylmagnesium bromide (from *m*-bromotoluene, 44 g.) on phenylpropionylcarbinol (14 g.), *r*-2-phenyl-1-*m*-tolyl-1-ethylethylene glycol (α -form) was obtained (14 g.) as described for the *p*-isomeride. It separated from light petroleum in rosettes of colourless needles, m. p. 101—102° (Found : C, 79.9; H, 7.8. $C_{17}H_{20}O_2$ requires C, 79.6; H, 7.9%).

Dehydration with Concentrated Sulphuric Acid.—The glycol (17 g.) was triturated with concentrated sulphuric acid for 19 hours; a claret coloration developed, and the product was isolated as described for the *p*-glycol. An oil was obtained which, on solution in alcohol, yielded a compound, m. p. 80—83°; recrystallisation from alcohol afforded *r*-*m*-tolyl α -phenylpropyl ketone as octagons, m. p. 82—83° (Found : C, 85.4; H, 7.5. $C_{17}H_{18}O$ requires C, 85.7; H, 7.6%). This ketone did not form a semicarbazone but gave a 2 : 4-dinitrophenylhydrazone, m. p. 130—131° (yellow needles from alcohol) (Found : C, 65.8; H, 5.1. $C_{23}H_{22}O_4N_4$ requires C, 66.0; H, 5.3%). From the mother-liquors another compound separated in the form of prisms, m. p. 97—98°, 1.3 g. (after several crystallisations from light petroleum). This solid was saturated, contained sulphur, was insoluble in cold, but slightly soluble in hot sodium hydroxide, and gave no semicarbazone (Found : C, 68.8; H, 5.4%). Its constitution was not determined.

Dehydration with Dilute Sulphuric Acid.—This was carried out as described for the *p*-glycol. The glycol (8 g.) gave a crude oil (7.5 g.), which had b. p. 175—177°/18 mm. and yielded the semicarbazone of phenyl-*m*-tolylethylacetaldehyde, m. p. 164—165° (fine needles from benzene) (Found : C, 73.4; H, 7.2. $C_{18}H_{21}ON_3$ requires C, 73.2; H, 7.2%); the 2 : 4-dinitrophenylhydrazone, yellow hexagonal prisms from alcohol-acetone, had m. p. 169.5—170.5° (Found : C, 66.1; H, 4.9. $C_{23}H_{22}O_4N_4$ requires C, 66.0; H, 5.3%).

Dehydration with Oxalic Acid.—The glycol (16 g.) was dehydrated as described for the *p*-glycol. An oil was obtained, b. p. 175—177°/18 mm., n_D^{14} 1.5789, 15 g. (crude yield). This gave the semicarbazone, m. p. 164—165°, and the 2 : 4-dinitrophenylhydrazone, m. p. 169.5—170.5°, of phenyl-*m*-tolylethylacetaldehyde identical with those described above.

Isomerisation of Phenyl-m-tolylethylacetaldehyde.—The aldehyde (4 g.) was triturated with concentrated sulphuric acid (10 c.c.). A purple coloration developed, and after 19 hours' standing, the product was worked up as described for the *p*-isomer. An oil (1.5 g.) was obtained which did not solidify and was treated with semicarbazide. A small amount of a semicarbazone, m. p. 134—135°, probably that of *r*- α -*m*-tolylbutyrophenone (since all the other possible dehydration products containing ketonic groups are known), was obtained (Found : C, 73.6; H, 6.6. $C_{18}H_{21}ON_3$ requires C, 73.2; H, 7.2%). Accompanying this derivative was another compound, m. p. 97—98°, identical with that obtained by dehydration of the glycol with concentrated sulphuric acid.

An attempt to isomerise *r*-*m*-tolyl α -phenylpropyl ketone similarly by the action of concentrated sulphuric acid failed, the ketone being recovered unchanged.

Constitution and Syntheses of the Dehydration Products.

(1) *Scission of Phenyl-m-tolylethylacetaldehyde.*—The aldehyde (5 g.) was boiled with potassium hydroxide (24 g. in 80 c.c. of ethyl alcohol) for 20 hours. The ethereal extract of the alkaline liquor yielded α -phenyl- α -*m*-tolylpropane as an oil, b. p. 143—144°/17 mm. (1.8 g., n_D^{16} 1.5650) (Found : C, 91.9; H, 8.3. $C_{16}H_{18}$ requires C, 91.4; H, 8.6%). On acidification of the liquors and extraction with ether, the presence of formic acid was noted in the residue from the ethereal solution.

(2) *Attempted Scission of *r*-m-Tolyl- α -Phenylpropyl Ketone.*—The ketone (1 g.) was boiled for 10 hours with alcoholic potash (10 g. of potassium hydroxide in 35 c.c. of ethyl alcohol). Extraction of the alkaline liquor yielded 0.85 g. of unchanged ketone, and no acid was detected in the acid portion.

(3) *Synthesis of *r*-m-Tolyl α -Phenylpropyl Ketone.*—Phenylethylacetonitrile (Bodroux and Taboury, *Compt. rend.*, 1910, **150**, 531) (19 g., 1 mol.) was added in ethereal solution to the Grignard reagent prepared from *m*-bromotoluene (47 g., 4 mols.) and boiled for 4 hours. After decomposition with ice and concentrated hydrochloric acid and immediate separation of the acid and the ethereal layer, a solid (1 g.) separated from the former. After crystallisation from light petroleum, prisms, m. p. 82—83°, alone or mixed with the ketone of similar m. p. obtained by dehydrating the glycol with concentrated sulphuric acid, were obtained.

(4) *Synthesis of *r*-Phenyl-*m*-tolylmethyl Ethyl Ketone.*—Phenyl-*m*-tolylacetonitrile (10 g., 1 mol.) (Roger and McKay, J., 1933, **332**) was added to the Grignard reagent prepared from ethyl bromide (27 g., 5 mols.) and boiled for 11 hours. The mixture was worked up as in (3), and from the acid layer, after 24 hours' standing, an oil (3.1 g.) was obtained. This did not solidify, but gave a *semicarbazone*, m. p. 161°, as hard incrustated masses from alcohol (Found: C, 73.4; H, 7.5. $C_{18}H_{21}ON_3$ requires C, 73.2; H, 7.2%), probably that of *r*-phenyl-*m*-tolylmethyl ethyl ketone.

(5) *Attempted Synthesis of *r*- α -m-Tolylbutyrophenone.*—*m*-Tolylethylcarbinol (25 g.) (Auwers and Kolligs, *Ber.*, 1922, **55**, 43) was converted by means of thionyl chloride into α -chloro- α -*m*-tolylpropane (13 g.), b. p. 104—106°/21 mm. (Found: Cl, 21.3. Calc. for $C_{10}H_{13}Cl$: Cl, 21.1%). Heating with mercuric cyanide in benzene solution did not give the required cyanide, but resulted in the scission of a molecule of hydrogen chloride and the formation of an unsaturated hydrocarbon, a colourless oil, b. p. 87—88°/25 mm., 194—197°/761 mm. (Found: C, 91.0; H, 9.2. $C_{10}H_{12}$ requires C, 90.9; H, 9.1), probably *m*-propenyitoluene. The synthesis of the ketone was thus unsuccessful.

r-2-Phenyl-1-*o*-tolyl-1-ethylethylene Glycol (α -Form).

Preparation.—Phenylpropionylcarbinol (17 g., 1 mol.) was added to the Grignard reagent prepared from *o*-bromotoluene (58 g., 3 mols.), and the mixture treated in the same manner as described for the *p*-isomer. The crude *solid* had m. p. 76—79°, and crystallised from light petroleum in hard nodules of needles, m. p. 80—81° (Found: C, 79.4; H, 8.1. $C_{17}H_{20}O_2$ requires C, 79.6; H, 7.9%).

Dehydration with Concentrated Sulphuric Acid.—The glycol (6 g.) was added in small amounts to concentrated sulphuric acid (20 c.c.) with stirring, and a claret coloration developed. After 19 hours, the mixture was poured into ice and water, and a solid separated (m. p. 36—40°, 2.8 g.). The filtrate was extracted with ether, and the extract yielded a small amount of the above solid. The combined solids were recrystallised twice from aqueous alcohol. *r*-*o*-Tolyl α -phenylpropyl ketone separated from aqueous alcohol in colourless rectangular plates, m. p. 39.5° (Found: C, 85.3; H, 7.3. $C_{17}H_{18}O$ requires C, 85.7; H, 7.6%). This ketone did not form either a *semicarbazone* or a 2 : 4-dinitrophenylhydrazone.

Dehydration with Dilute Sulphuric Acid.—The glycol (4 g.) was boiled with dilute sulphuric acid (25% by vol.) for 6.5 hours. The oil obtained had b. p. 165—175°/16 mm., n_{D}^{14} 1.5936, and was converted into the *semicarbazone* of phenyl-*o*-tolylethylacetaldehyde, which separated from benzene as fine needles, m. p. 168—169° (Found: C, 73.1; H, 7.5. $C_{18}H_{21}ON_3$ requires C, 73.2; H, 7.2%).

Dehydration with Oxalic Acid.—The glycol (13 g.) was boiled with fused hydrated oxalic acid for 7 hours. The product was an oil, b. p. 176—178°/20 mm. (10 g., n_{D}^{12} 1.5878), which yielded the *semicarbazone* of phenyl-*o*-tolylethylacetaldehyde, m. p. 168—169° (fine needles from benzene), alone or mixed with the foregoing *semicarbazone*.

*Isomerisation of Phenyl-*o*-tolylethylacetaldehyde.*—The aldehyde (4.6 g.) was triturated with concentrated sulphuric acid (15 c.c.) for 19 hours. A brown-red coloration developed, and the product was finally extracted in the usual manner. The solid was recrystallised from aqueous alcohol and separated as colourless, rectangular plates, m. p. 39—40°, alone or mixed with *r*-*o*-tolyl α -phenylpropyl ketone obtained by the dehydration of the glycol with concentrated sulphuric acid.

Constitution and Synthesis of the Dehydration Product.

*Synthesis of *r*-*o*-Tolyl α -Phenylpropyl Ketone.*—Phenylethylacetonitrile (11 g.) was added to the Grignard reagent prepared from *o*-bromotoluene (52 g., 4 mols.). After 4 hours' boiling, the product was worked up as in the analogous preparations, and the ethereal extract of the acid

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layer yielded an oil (1.5 g.); when this was dissolved in aqueous alcohol, colourless, rectangular plates separated, m. p. 39—40°, alone or mixed with the ketone described in the preceding paragraph.

We wish to thank the Carnegie Trust for the Universities of Scotland for the award of a scholarship to one of us (A. M. R.), and for a grant in aid of material (R. R.).

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[Received, June 21st, 1937.]
