385. *The Dehydration of the α-Forms of* r- *and* (+)-p-*Tolylhydrobenzoins.*

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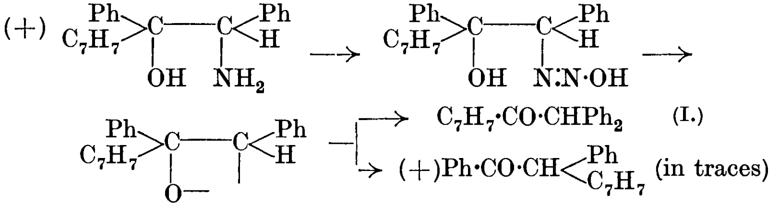
IN the course of a study on the migrational aptitude of the *p*-tolyl group, McKenzie, Mills, and Myles (*Ber.*, 1930, **63**, 904) described the dehydration of *r*-*p*-tolylhydrobenzoin (α-form) by concentrated sulphuric acid, and isolated *p*-tolyl diphenylmethyl ketone (I), m. p. 98·5—99·5°, in small yield. This was unexpected, since both the phenyl and the *p*-tolyl group are characterised by their strong saturation capacities, and on this account the isomeric ketone, *r*-*p*-tolyldeoxybenzoin (II), was the product anticipated. In the same paper it was also shown that (I) was formed by the semipinacolinic deamination of *r*- and of (+)-β-amino-αβ-diphenyl-α-*p*-tolylethyl alcohol, the phenyl group migrating almost exclusively, thus:



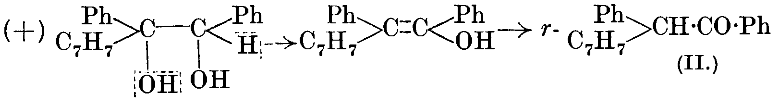
$$(+)\ \mathrm{Ph(C_7H_7)C(OH)\text{—}CH(Ph)NH_2} \longrightarrow \mathrm{Ph(C_7H_7)C(OH)\text{—}CH(Ph)N{:}N{\cdot}OH} \longrightarrow \mathrm{Ph(C_7H_7)C(O\text{—})\text{—}CH(Ph)\text{—}} \begin{cases} \longrightarrow \mathrm{C_7H_7{\cdot}CO{\cdot}CHPh_2} & \text{(I.)} \\ \longrightarrow (+)\mathrm{Ph{\cdot}CO{\cdot}CH}{<}^{\mathrm{Ph}}_{\mathrm{C_7H_7}} & \text{(in traces)} \end{cases}$$

It was mentioned at the time that the dehydration of the glycol needed further investigation, and more particularly so since the ketone (I), which was actually isolated, may not have represented the main trend of the reaction.

The constitution of (I) had been established previously by McKenzie, Mills, and Myles by its synthesis from diphenylacetyl chloride, toluene, and aluminium chloride. This synthesis has been repeated recently by Koelsch (*J. Amer. Chem. Soc.*, 1932, **54**, 2049), who gives experimental details. The m. p. quoted by him is 100—101°. He states that McK., M., and M. give m. p. 97—99·5°, but the m. p. actually given by them for the pure compound is 98·5—99·5°. We now provide further evidence for the constitution of (I) by its synthesis from benzaldehyde.

On dehydrating *r*-*p*-tolylhydrobenzoin (α-form) with oxalic acid, we obtained r-p-*tolyldeoxybenzoin* (II), m. p. 96—97°. When, however, attempts were made to improve the yield of (I) by dehydrating the glycol with concentrated sulphuric acid on the lines described by McK., M., and M., the product obtained had m. p. 92·5—94°, and consisted of almost pure *p*-tolyldeoxybenzoin (II). This is all the more remarkable since Koelsch (*loc. cit.*) states that he isolated (I) only, and thus had confirmed the observation of McK., M., and M. Our failure to reproduce the result of the last authors may have been due to the atmosphere of the laboratory having meanwhile become infected with (II), or possibly the experimental conditions were not exactly reproduced in our various dehydrations.

The dehydration of (+)-*p*-tolylhydrobenzoin (α-form) with oxalic acid and with dilute sulphuric acid respectively gave (II), the formation of which finds its best interpretation on the basis of vinyl dehydration, which does not involve the migration of a phenyl group, and would lead to racemisation :



$$(+)\ {\mathrm{Ph} \atop \mathrm{C_7H_7}}\!>\!\underset{\underset{\mathrm{OH}}{|}}{\mathrm{C}}-\underset{\underset{\mathrm{OH}}{|}}{\mathrm{C}}\!<\!{\mathrm{Ph} \atop \mathrm{H}} \rightarrow {\mathrm{Ph} \atop \mathrm{C_7H_7}}\!>\!\mathrm{C{=}C}\!<\!{\mathrm{Ph} \atop \mathrm{OH}} \rightarrow r\text{-}\ {\mathrm{Ph} \atop \mathrm{C_7H_7}}\!>\!\mathrm{CH{\cdot}CO{\cdot}Ph}$$

(II.)

It is now clear that the dehydration of the *r*-glycol with concentrated sulphuric acid gives (I) and (II) with an excess of (II), and this conclusion has a parallel in the dehydration of the α-form of α-naphthylhydrobenzoin (McKenzie and Richardson, J., 1923, **123**, 79; McKenzie and Roger, J., 1924, **125**, 844; McKenzie and Dennler, *ibid.*, p. 2105; Tiffeneau and Orékhoff, *Compt. rend.*, 1924, **178**, 1619). This similarity is to be expected, since the saturation capacities of the *p*-tolyl and the α-naphthyl group are close (Tiffeneau, McKenzie).

It is noteworthy that the dehydration of the (+)-*p*-tolylhydrobenzoin led to the formation of the *r*-ketone (II), no trace of the optically active ketone being detected, and in this respect there is a striking difference in the elimination of water during the dehydration of (—)-β-1-naphthyl- and of (+)-β-phenyl-αα-dibenzylethylene glycols, where optical activity was preserved in each of these cases, optically pure ketones being obtained by semipinacolinic change (McKenzie and Dennler, *Ber.*, 1927, **60**, 220; Roger and McKenzie, *Ber.*, 1929, **62**, 272).

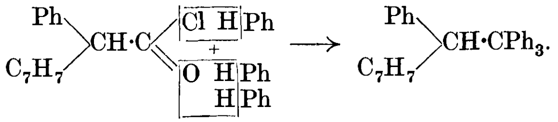
The formation of (I) from the glycol as recorded by McK., M., and M. is not easily accounted for, and this exceptional behaviour has been commented on by Tiffeneau and Lévy (*Bull. Soc. chim.*, 1931, **49**, 1688) : " Ce glycol donne lieu à la formation d'une cétone transposée résultant d'une déshydration suivant le type semipinacolique, avec migration du *radical phényle qui l'emporte ainsi sur le tolyle.* C'est là une exception unique dans la déshydratation des glycols." Semipinacolinic transformation seems, however, to be unlikely, when the strong saturation capacities of the phenyl and the *p*-tolyl group are considered, whilst the intermediate formation either of a substituted ethylenic oxide or of an aldehyde during the dehydration of a *sec.-tert.*-glycol by means of sulphuric acid is a matter for debate (Danilov, Tiffeneau, Lévy, Roger, McKenzie).

The constitution of (II) was determined by various syntheses (see p. 2602).

Now, McKenzie and Widdows (J., 1915, **107**, 702) have described as *r*-phenyl-*p*-tolylacetophenone (*p*-tolyldeoxybenzoin, II) a compound, m. p. 159—160°, which they obtained by application of the

Friedel–Crafts reaction to *r*- and (+)-phenyl-*p*-tolylacetyl chloride. The action seemed to proceed quite normally on the lines $C_7H_7\cdot CHPh\cdot COCl + C_6H_6 + AlCl_3 \longrightarrow C_7H_7\cdot CHPh\cdot COPh$, the compound obtained, with m. p. 159—160°, giving satisfactory analytical figures for (II) (see p. 2603). Since (II), with m. p. 96—97°, has now been prepared by several different methods and there is no dubiety about its constitution, reinvestigation of the preparation of McKenzie and Widdows was obviously required. Our first attempts to repeat the result met with no success, the only crystalline product obtained being triphenylmethane. Koelsch (*loc. cit.*) also failed to obtain the compound of m. p. 159—160°, isolating only diphenylmethane. Now, McKenzie and Widdows distilled under diminished pressure the oil from which their solid of m. p. 159—160° had been withdrawn, and obtained a solid, m. p. 28—29°; the analysis of this was not quoted at the time, but it was : C, 92·9; H, 7·1; *M*, cryoscopic in C_6H_6, 162 (Calc. for $C_{13}H_{12}$: C, 92·8; H, 7·2%; *M*, 168). Zincke (*Annalen*, 1871, **159**, 376) gives m. p. 26—27° for diphenylmethane. The failure of the present authors in their first attempts and also of Koelsch to obtain (II) from phenyl-*p*-tolylacetyl chloride is all the more surprising since diphenylacetyl chloride and toluene under the usual conditions of the Friedel–Crafts reaction give (I) readily.

It happens occasionally that a Friedel–Crafts reaction pursues an abnormal course, and it is possible that with phenyl-*p*-tolylacetyl chloride the action may have occurred on the lines,



Now Schlenk and Herzenstein (*Ber.*, 1910, **43**, 3542) pointed out that pentaphenylethane undergoes scission, and it is thus not improbable that a similar decomposition may have taken place to a certain extent with the tetraphenyl-*p*-tolylethane postulated above, triphenylmethyl being one of the products. Schmidlin and Garcia-Banús (*Ber.*, 1912, **45**, 1344) have further shown that triphenylmethyl undergoes autodecomposition at room temperature under the influence of light (compare Wieland and Müller, *Annalen*, 1913, **401**, 233) to give triphenylmethane, so our production of this compound may perhaps be interpreted in this manner.

Fortunately, the specimen, m. p. 159—160°, originally prepared by Miss Widdows in 1913 was available; re-examination showed it to be triphenylcarbinol. It was crystallised twice, and analysis confirmed the figures obtained previously, which, by a coincidence, are in close agreement with those calculated for triphenylcarbinol (see p. 2603).

We were eventually able to repeat the result of McKenzie and Widdows, obtaining triphenylcarbinol by preparing phenyl-*p*-tolylacetyl chloride by means of thionyl chloride which had been purified by dimethylaniline.

Assuming that triphenylmethyl was formed by the scission of tetraphenyl-*p*-tolylethane, the formation of triphenylcarbinol may be ascribed to the conversion of triphenylmethyl into its peroxide, and the subsequent hydrolysis of the latter, Gomberg (*Ber.*, 1900, **33**, 3150) having shown that triphenylcarbinol is formed in good yield by the action of sulphuric acid on triphenylmethyl peroxide and subsequent dilution with water.

EXPERIMENTAL.

Dehydration of r-p-*Tolylhydrobenzoin* (*α-Form*).—(1) *With oxalic acid.* The glycol (5 g.) from *r*-benzoin and *p*-tolylmagnesium bromide (Acree, *Ber.*, 1904, **37**, 2753) was added to melted $C_2H_2O_4,2H_2O$ (50 g.); after 12 hrs.' gentle boiling, excess of aq. $HKCO_3$ was added, and the product extracted with ether. The oil from the dried extract was dissolved in light petroleum (b. p. 60—80°), and the resulting solid purified by 1 crystn. from the same solvent (yield, 2·5 g.). It remained unchanged after trituration with conc. H_2SO_4, and was therefore neither an aldehyde nor a substituted ethylenic oxide. r-p-*Tolyldeoxybenzoin* (II) separates in colourless needles, m. p. 96—97° (Found: C, 88·3; H, 6·4. $C_{21}H_{18}O$ requires C, 88·1; H, 6·3%) (Koelsch, *loc. cit.*, gives m. p. 97—98° for his product from desyl chloride). It formed neither a semicarbazone nor a *p*-nitrophenylhydrazone. The oil (1·2 g.) obtained by evaporating the solutions from which the ketone had been partially removed, was dissolved in $CHCl_3$–EtOH, and a solid (0·05 g.), m. p. 171—172·5°, separated. (2) *With sulphuric acid.* The glycol (3 g.) was triturated with conc. H_2SO_4 for 4 hrs. The orange-yellow coloration which developed at first changed to brown and finally to a greenish-black. On pouring the mixture over crushed ice and diluting it to 350 c.c. with H_2O, a greenish solid separated; neutralisation was effected by $KHCO_3$, and the product extracted with ether. The resulting dried oil was dissolved in light petroleum (b. p. 60—80°), and the solid (1·1 g.) which separated was crystallised twice from EtOH; needles, m. p. 92·5—94° (Found: C, 88·3; H, 6·4. Calc. for $C_{21}H_{18}O$: C, 88·1; H, 6·3%). The mixture with (II) had m. p. 93—94·5°, but that with (I), prep. by the semipinacolinic deamination of β-amino-αβ-diphenyl-α-*p*-tolylethyl alcohol (McK., M., and M., *loc. cit.*), showed marked depression. The product, m. p. 92·5—94°, was almost pure *p*-tolyldeoxybenzoin.

When a trace of (I) is added to conc. H_2SO_4, a light yellow coloration appears, which changes gradually to a pale green; (II), on the other hand, gives an intense yellow coloration under similar conditions.

This reaction was carried out 4 times, but on no occasion was a pure specimen of (I) isolated. Alcoholic scission of the crude product, and determinations of the relative amounts of benzoic and *p*-toluic acids obtained therefrom (cf. Bailar, *J. Amer. Chem. Soc.*, 1930, **52**, 3596) indicated that (II) preponderated in the mixture of ketones. Bailar's method is not, however, very accurate in this particular case, since the molecular weights of the two acids are close.

(II), m. p. 96—97°, was obtained by boiling the glycol (9 g.) for 5 hrs. with dil. H_2SO_4 (20% by vol.).

Dehydration of (+)-p-*Tolylhydrobenzoin* (*a-Form*).—(1) *With oxalic acid.* 2·5 G. of the (+)glycol from (−)benzoin (Roger and McKay, J., 1931, 2229) were dehydrated as described for the *r*-isomeride. The solid (1·3 g.) which separated from the light petroleum solution was optically inactive in $CHCl_3$ ($\lambda = 5461$, $c = 1{\cdot}965$, $l = 1$), and after 1 crystn. had m. p. 96—97°, alone or mixed with (II). The residual liquors gave a pale yellow oil (0·8 g.) which was also optically inactive in EtOH ($\lambda = 5461$, $c = 3{\cdot}2$, $l = 1$).

(2) *With dilute sulphuric acid.* The (+)glycol (6·1 g.) was boiled for 3 hrs. with conc. H_2SO_4 (30 c.c.) and H_2O (70 c.c.). After dilution to 450 c.c. with H_2O, the mixture was extracted with Et_2O, and the oil from the dried extract dissolved in light petroleum (b. p. 60—80°). 4·2 G. of crystals which were optically inactive in $CHCl_3$ ($\lambda = 5893$, $c = 2$, $l = 2$) separated, and were identified as (II).

From the light-petroleum filtrate, which was also optically inactive, a product (0·2 g.) was obtained by the addition of EtOH; cryst. from C_6H_6–EtOH, it gave hard prisms, m. p. 171—172·5° (Found: C, 88·3; H, 6·1%. $C_{21}H_{18}O$ requires C, 88·1; H, 6·3%), identical with one of the products obtained by dehydration of the *r*-glycol by oxalic acid (p. 2601). This substance was obviously a dehydration product of the glycol; its optical inactivity suggests that it is *diphenyl*-p-*tolylacetaldehyde*, formed by semihydrobenzoin transformation.

Synthesis of p-*Tolyl Diphenylmethyl Ketone* (I) (*p*-Diphenylacetotoluene).—Diphenylacetonitrile, prepared by the stages, $Ph{\cdot}CHO \xrightarrow{PhMgBr} Ph_2CH(OH) \xrightarrow{SOCl_2} Ph_2CHCl \xrightarrow{Hg(CN)_2} Ph_2CH(CN)$, had m. p. 72·5—73° (Wittig and Hopf, *Ber.*, 1932, **65**, 760, using a different method, give m. p. 72·5—73°).

The Grignard reagent, prep. from *p*-bromotoluene (28 g.), was added to an ethereal solution of the nitrile (8 g.) and heated for 4 hrs. The decomp. with ice and dil. H_2SO_4, and the separation of the ethereal layer (A) were conducted as quickly as possible. The ketimine hydrochloride in the acid layer was hydrolysed by heating the solution for ½ hr., and the ketone extracted with Et_2O. The oil from the dried extract was dissolved in light petroleum (b. p. 40—60°), and the separated solid (2 g.) crystallised once from the same solvent; prismatic needles of (I) were deposited, m. p. 99—99·5°, alone, or mixed with the product obtained by McK., M., and M. by semipinacolinic deamination. The Grignard reaction was incomplete under the above conditions, since 3 g. of pure cryst. diphenylacetonitrile were isolated from the ethereal layer (A) which also contained *p*-ditolyl.

Syntheses of r-p-*Tolyldeoxybenzoin* (II).—(1) *r*-Phenyl-*p*-tolylacetonitrile, prep. by the stages, $Ph{\cdot}CHO \xrightarrow{C_7H_7{\cdot}MgBr} C_7H_7{\cdot}CHPh{\cdot}OH \xrightarrow{SOCl_2} C_7H_7{\cdot}CHPhCl \xrightarrow{Hg(CN)_2} C_7H_7{\cdot}CHPh(CN)$, had m. p. 60—62° (Neure, *Annalen*, 1889, **250**, 149, who used a different method, gives m. p. 59°).

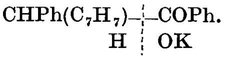
The Grignard reagent prep. from PhBr (20 g.) was added to an ethereal solution of the nitrile (7 g.), heated for 9 hrs., and worked up as in the previous expt. The solid (2 g.) from the light petroleum was crystallised once from the same solvent (b. p. 60—80°); the needles had m. p. 96—97°, alone or mixed with the ketone (II) from the dehydration of *r*-*p*-tolylhydrobenzoin. This Grignard reaction was also incomplete, 3 g. of pure cryst. nitrile being recovered.

(2) From desyl chloride, C_7H_8, and $AlCl_3$ (cf. Koelsch, *loc. cit.*).

(3) Dry HCl was passed into a soln. of *r*-benzoin (20 g.) in hot C_7H_8 (125 c.c.) for 1 hr. $AlCl_3$ (40 g.) was then added gradually, and heating continued for 7 hrs. After the mixture had been poured on ice and conc. HCl, unchanged benzoin was removed, and from the toluene soln. a viscous oil was obtained which became semi-solid on keeping. After several crystns. from EtOH, (II), m. p. 96—97°, was obtained (cf. formation of phenyldeoxybenzoin from *r*-benzoin, McKenzie and Lesslie, *Ber.*, 1928, **61**, 158).

(4) The Grignard reagent prepared from *p*-bromotoluene (15 g.) was added to desyl chloride (10 g.) suspended in Et_2O and heated for 2 hrs. After decomp. with ice, NH_4Cl, and NH_4OH, the oil from the ethereal layer was distilled in steam, and the dried residual oil dissolved in light petroleum to which a small amount of EtOH had been added. The solid (8 g.) which separated gave (II) after several crystns. from EtOH.

$Ph{\cdot}CO_2H$ and phenyl-*p*-tolylmethane were isolated by the scission of the ketone by 20% alc. KOH (cf. Koelsch, *loc. cit.*) :



$$\underset{\mathrm{H}}{\mathrm{CHPh(C_7H_7)}}\!-\!\vdots\!-\!\underset{\mathrm{OK}}{\mathrm{COPh.}}$$

Interaction of r-*Phenyl*-p-*tolylacetyl Chloride*, C_6H_6, *and* $AlCl_3$.—Several unsuccessful attempts were made to repeat the result of McKenzie and Widdows (*loc. cit.*), uncrystallisable oils being obtained. In one expt., however, where phenyl-*p*-tolylacetic acid (15 g.) was converted into its acid chloride by means of $SOCl_2$, and the oil from the Friedel–Crafts reaction was distilled under diminished press., a fraction, b. p. 150—240°/21 mm., was collected. This was dissolved in EtOH–petroleum (b. p. 40—60°), and the solid (2 g.) which separated, after 2 crystns. from methylated spirits, gave needles of $CHPh_3$ (Found : C, 93·5, H, 6·6. Calc. for $C_{19}H_{16}$: C, 93·4; H, 6·6%), m. p. 91—91·5°, alone or mixed with an authentic sample.

The specimen (Found : C, 88·0; H, 6·2%) prep. in 1913 was crystallised twice from EtOH and again analysed [Found : C, 88·0; H, 6·1. $C_{21}H_{18}O$ (*p*-tolyldeoxybenzoin) requires C, 88·1; H, 6·3. $C_{19}H_{16}O$ (triphenylcarbinol) requires C, 87·65; H, 6·2%]. A trace of it gave an orange coloration with conc. H_2SO_4, identical with that given by $CPh_3{\cdot}OH$, and the m. p. was 159—160°, alone or mixed with an authentic sample.

By the use of $SOCl_2$ which had been purified by means of dimethylaniline * (Besthorn, *Ber.*, 1909, **42**, 269), however, we eventually obtained the compound, m. p. 159—160°, found in 1913. Phenyl-*p*-tolylacetyl chloride (dried in vac. over soda–lime but not distilled) is an oil (Found : Cl, 13·7. Calc. : 14·3%). A solution of the undistilled acid chloride (20 g.) in a little CS_2 was added gradually to a mixture of C_6H_6 (88 g.), CS_2 (36 g.), and $AlCl_3$ (18 g.). A brisk reaction followed each addition. The procedure of McK. and W. was followed, and a brown, fluorescent, viscous oil obtained, from which, after 2 days in vac. over $CaCl_2$, solid began to separate. This was drained off (yield, 3 g.), crystallised (m. p. 159·5—160·5°), and identified as triphenylcarbinol.

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* Care should be taken in carrying out this operation, which may proceed explosively.

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