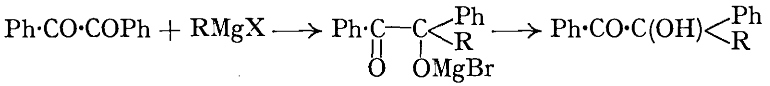
102. *The Synthesis of Substituted Benzoins and of Deoxybenzoins.*

By Robert Roger and Alexander McGregor.

Benzil has been used in the synthesis of substituted benzoins according to the scheme,



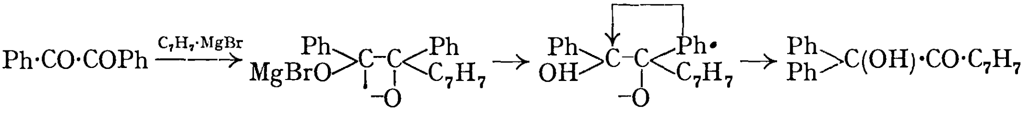
$$\mathrm{Ph{\cdot}CO{\cdot}COPh + RMgX \longrightarrow Ph{\cdot}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{OMgBr}{|}}{C}{<}^{Ph}_{R} \longrightarrow Ph{\cdot}CO{\cdot}C(OH){<}^{Ph}_{R}}$$

(Acree, *Ber.*, 1904, **37**, 2753; Roger, J., 1925, **127**, 518; Ramart-Lucas and Salmon-Legagneur, *Bull. Soc. chim.*, 1929, **45**, 718; Cameron, *Trans. Roy. Soc. Canada*, 1929, **23**, 53), the reaction being restricted mainly to one ketonic group by proper selection of practical conditions.

The reaction has now been extended to the preparation of ketols by the action of *o*-, *m*-, and *p*-tolylmagnesium bromides on benzil. *m*-Tolylmagnesium bromide gave the expected ketol. *p*-Tolylmagnesium bromide gave an oil which would not crystallise but on reduction gave an excellent yield of *p*-tolyldeoxybenzoin, showing that it consisted mainly of the ketol. *o*-Tolylmagnesium bromide gave a compound, m. p. 116—117°, corresponding in formula to the ketol. Scission with alcoholic potash gave, however, benzhydrol and *o*-toluic acid, but the conclusion must not be definitely drawn from this observation that the compound is necessarily *o*-toluoyldiphenylcarbinol, $\mathrm{OH{\cdot}CPh_2{\cdot}CO{\cdot}C_7H_7}$, and not *o*-tolylbenzoin, $\mathrm{C_7H_7{\cdot}CPh(OH){\cdot}COPh}$.

It is possible that *o*-tolylbenzoin had really been formed in the Grignard reaction but that it had been transformed into *o*-toluoyldiphenylcarbinol in the course of the scission. In view of this anomalous result other similar ketols were submitted to scission with potash and only in one case was any exceptional behaviour noted. In several scissions of methylbenzoin benzhydrol invariably appeared, but the quantity was so minute that it did not affect the conclusion that methylbenzoin has the formula $\mathrm{Ph{\cdot}CMe(OH){\cdot}COPh}$.

Previous work has shown that *o*-tolylmagnesium bromide is exceptional in some of its reactions (Roger and McKay, J., 1931, 2229; 1933, 332; Stoermer, *Ber.*, 1906, **39**, 2288). The only explanation that we can offer for this apparent rearrangement is that *o*-tolylmagnesium bromide adds on to the benzil in a different manner from the other Grignard reagents, thus :



$$\mathrm{Ph{\cdot}CO{\cdot}COPh \xrightarrow{C_7H_7{\cdot}MgBr} {}^{Ph}_{MgBrO}{>}\underset{|}{C}{-}\underset{\underset{-O}{|}}{C}{<}^{Ph}_{C_7H_7} \rightarrow {}^{Ph}_{OH}{>}C{-}\underset{\underset{-O}{|}}{C}{<}^{Ph\bullet}_{C_7H_7} \rightarrow {}^{Ph}_{Ph}{>}C(OH){\cdot}CO{\cdot}C_7H_7}$$

This involves the formation of an unstable intermediate complex not unlike those used to depict the mechanism of glycol dehydrations, and would assume the migration of the phenyl radical in preference to *o*-tolyl (cf. Roger and McKay, *loc. cit.*).

We found that the ketols described were easily reduced to the corresponding ketones by hydriodic acid and red phosphorus. *m*-Tolylbenzoin gave *m*-tolyldeoxybenzoin, whose constitution had already been determined by Roger and McKay (*loc. cit.*), whilst methylbenzoin gave methyldeoxybenzoin. The *o*-toluoyldiphenylcarbinol (m. p. 116—117°) from the action of *o*-tolylmagnesium bromide on benzil gave a compound, m. p. 48—49°, identical with that described provisionally by Roger and McKay (*loc. cit.*) as *o*-tolyl diphenylmethyl ketone. The latter authors had at the time been able neither to obtain enough of this compound to prove its constitution by scission with potash nor to effect its synthesis by any means. The reduction product was submitted to scission with potash, and *o*-toluic acid was obtained from the acid portion. The neutral part of the scission gave only a smell of diphenylmethane and the solid which emerged was benzhydrol, *i.e.*, oxidation must also have taken place during the scission (cf. Luis, J., 1932, 2547). Once again, however, the objection may be lodged that rearrangement of the ketone had taken place in this instance before scission, and we therefore cannot regard the constitution of the dehydration products of *o*-tolylhydrobenzoin (α-form) as being finally settled.

EXPERIMENTAL.

Action of m-*Tolylmagnesium Bromide on Benzil.*—The Grignard reagent (from 25 g. of *m*-bromotoluene, 1½ mols.) was added gradually to benzil (21 g., 1 mol.) in dry ether. The mixture became dark brown and after boiling for 5 hours was decomposed in the usual manner. The oil from the ethereal layer was distilled in a high vacuum and unchanged benzil and benzoin were isolated from the first fraction. A second fraction, b. p. 210—240°, gave a solid (9·5 g.) after several weeks. This was crystallised from light petroleum, *m*-tolylbenzoin separating as colourless rosettes of needles (4 g.), m. p. 82—83° (Found : C, 83·2; H, 6·35. Calc. for $C_{21}H_{18}O_2$: C, 83·4; H, 6·0%).

The ketol (2 g.) was disrupted with alcoholic potash. The acid part of the scission gave 0·4 g. of benzoic acid, m. p. (after one recrystallisation from water) and mixed m. p. 120—121°. The neutral part of the scission gave phenyl-*m*-tolylcarbinol, m. p. 52° after several recrystallisations from light petroleum (Cohen, *Rec. trav. chim.*, 1919, **38**, 72, gives 61°) and unaltered in admixture with an authentic sample prepared from *m*-tolylmagnesium bromide and benzaldehyde.

m-Tolylbenzoin (1·5 g.) was reduced with hydriodic acid (5 c.c.) and red phosphorus (1 g.) in acetic acid. Crude *m*-tolyldeoxybenzoin (0·9 g.) was obtained, m. p. (after several recrystallisations from light petroleum) 85—86°, alone or mixed with an authentic sample (Roger and McKay, *loc. cit.*).

Action of p-*Tolylmagnesium Bromide on Benzil.*—(A) *Addition of the Grignard reagent to benzil.* The Grignard reagent (from *p*-bromotoluene, 25 g.; 1½ mols.) was added to an ethereal solution of benzil (22 g.; 1 mol.). A white precipitate formed but later became chocolate-brown. After heating for 1 hour, the mixture was decomposed with ice and dilute sulphuric acid, and from the ethereal layer a dark red oil was obtained. After distillation in steam the residue was dissolved in various solvents but no solid separated, even after several months. The oil was distilled in a high vacuum and a fraction (9 g.), b. p. 220—230°, was reduced by heating with hydriodic acid (15 c.c.) and red phosphorus (3 g.) in acetic acid solution. *p*-Tolyldeoxybenzoin (6·5 g.) was isolated, m. p. (after several recrystallisations from alcohol) and mixed m. p. 97·5—98·5°.

(B) *Addition of benzil to the Grignard reagent.* Benzil (10 g.; 1 mol.) in dry ether was added to the Grignard reagent (from *p*-bromotoluene, 18 g.; 2 mols.). There was a fairly vigorous reaction and the liquid became dark yellow. After heating for 1 hour, the mixture was decomposed in the usual fashion. The oil from the ethereal layer was distilled in a high vacuum, yielding benzoin (m. p. 132—133°) and two other solids, m. p. 212—213° and 159—160°, respectively, after recrystallisation from alcohol. Both of these compounds (Found : C, 89·1; H, 6·6. Calc. for $C_{28}H_{24}O$: C, 89·3; H, 6·4%) had the formula of the pinacolins which were obtained by dehydration of *s.*-diphenyldi-*p*-tolylpinacol by Thörner (*Annalen*, 1877, **189**, 109), who gives m. p. 214—215° and 136—137° for the two pinacolins he obtained. There are at least three pinacolins possible.

In a second experiment the oil from the Grignard reaction was dissolved in light petroleum and a solid (8 g.) was obtained which, after several recrystallisations from alcohol, had m. p. 162—163°, markedly depressed the m. p. of the compound, m. p. 159—160°, described above, and would seem to be *s.*-diphenyldi-*p*-tolylpinacol, described by Acree (*loc. cit.*) with m. p. 164° (Found : C, 85·4; H, 6·8. Calc. for $C_{28}H_{26}O_2$: C, 85·2; H, 6·6%).

Action of o-*Tolylmagnesium Bromide on Benzil.*—The Grignard reagent (from *o*-bromotoluene, 20 g.; 1¼ mols.) was added to benzil (21 g.) in dry ether. A chocolate-brown precipitate was formed and after boiling for 2 hours the mixture was decomposed in the usual manner. The dark red oil from the ethereal layer was distilled in a high vacuum and a fraction was isolated which on solution in light petroleum gave a solid (8 g.). This after several recrystallisations from light petroleum separated in rhombic prisms, m. p. 116—117° (Found : C, 83·35; H, 6·2.

$C_{21}H_{18}O_2$ requires C, 83·4; H, 6·0%). This solid is either *o*-tolyldeoxybenzoin or, more probably, *o*-toluoyldiphenylcarbinol, as the following experiments would indicate.

On scission with alcoholic potash the above compound (1 g.) gave 0·35 g. of *o*-toluic acid, m. p. (after recrystallisation from water) and mixed m. p. 104—105°. The neutral part of the scission gave 0·65 g. of benzhydrol, m. p. (after recrystallisation from light petroleum) and mixed m. p. 64—65°.

The ketol (2 g.), reduced with hydriodic acid (15 c.c.) and red phosphorus in acetic acid solution, gave a solid (1·5 g.) which, after several recrystallisations from light petroleum, had m. p. 47·5—49°, alone or mixed with the ketone provisionally designated *o*-tolyl diphenylmethyl ketone (m. p. 48—49°) by Roger and McKay (*loc. cit.*) (Found : C, 88·0; H, 6·6. Calc. for $C_{21}H_{18}O$: C, 88·06; H, 6·34%).

Scission of the above ketone (1 g.) gave 0·3 g. of *o*-toluic acid, m. p. (after recrystallisation from water) and mixed m. p. 105—106°. The other part of the scission yielded 0·45 g. of benzhydrol, m. p. (after recrystallisation from light petroleum) and mixed m. p. 64—65°.

The Constitution of Methylbenzoin.—Roger (*loc. cit.*) described the synthesis of methylbenzoin from benzil, but at the time made no attempt to confirm the constitution of the compound.

Methylbenzoin (4 g.) was submitted to scission with alcoholic potash, benzoic acid (1 g.) being obtained from the acid portion. From the neutral part an oil was obtained which was distilled in a vacuum. One fraction (0·8 g.), b. p. 110—115°/37 mm., was collected. Klages and Allendorf (*Ber.*, 1898, **31**, 1003) give b. p. 118°/40 mm. for *dl*-phenylmethylcarbinol. A higher-boiling fraction (115—170°/37 mm.) was also collected and from this, benzhydrol (m. p. 63·5—65·5°, 0·1 g.) was isolated.

Methylbenzoin (8·5 g.) was reduced with hydriodic acid and red phosphorus in acetic acid solution. The solid (5·9 g.) isolated had, after several recrystallisations from light petroleum, m. p. 49·5—51°, alone or mixed with authentic methyldeoxybenzoin (McKenzie and Roger, J., 1924, **125**, 844).

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