# 408. *The Action of Grignard Reagents on Desyl Chloride.* Part I. Aryl Grignard Reagents.*

By ROBERT ROGER and ALEXANDER MCGREGOR.

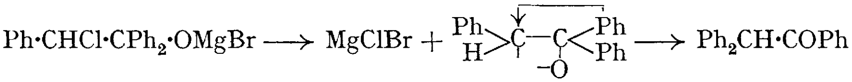
MCKENZIE, ROGER, and MCKAY (J., 1932, 2603) described the synthesis of *p*-tolyldeoxybenzoin by the action of *p*-tolylmagnesium bromide on desyl chloride. The action of other Grignard reagents on desyl chloride has now been performed to see if this offered a general method for the preparation of aryl-substituted deoxybenzoins which are not easily synthesised by the method of Meyer and Oelkers (*Ber.*, 1888, **21**, 1291) available for the alkyldeoxybenzoins.

The action of *m*-tolylmagnesium bromide gave the corresponding tolyldeoxybenzoin. Phenylmagnesium bromide also gave phenyldeoxybenzoin, but this was accompanied by a large amount of 1 : 1 : 2 : 2-tetraphenylethanol. *o*-Tolylmagnesium bromide gave a solid, m. p. 185°, which seemed to be a diethylene oxide derivative, and also a large amount of oil, from which a solid ketone could not be separated.

Desyl chloride offers two points of attack to a Grignard reagent, namely, the chlorine atom and the ketonic group. The simplest explanation that can be given is that the chlorine atom is first replaced by the radical from the Grignard reagent, giving the ketone (cf. Godchot and Bedos, *Bull. Soc. chim.*, 1926, **39**, 96; Perlin-Borrel, *ibid.*, 1932, **51**, 994), which may sometimes react further with more reagent to give a carbinol, thus :

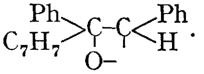
$$\mathrm{Ph\cdot CHCl\cdot COPh} \xrightarrow{\mathrm{PhMgBr}} \mathrm{Ph_2CH\cdot COPh} \xrightarrow{\mathrm{PhMgBr}} \mathrm{Ph_2CH\cdot CPh_2\cdot OH}$$

On the other hand the ketonic group might be first attacked and the halogenohydrin, $\mathrm{Ph\cdot CHCl\cdot CPh_2\cdot OH}$ produced (cf. Tiffeneau, *Compt. rend.*, 1902, **134**, 774). Tiffeneau and Tchoubar (*ibid.*, 1934, **198**, 941) have shown that such compounds can be isolated by the regulation of the Grignard reaction and that the magnesium derivatives of these halogenohydrins on heating decompose with loss of a molecule of magnesium halide and ketones are formed. The ketone formation may be the result of a radical migration. In the action of phenylmagnesium bromide on desyl chloride the intermediate compound $\mathrm{Ph\cdot CHCl\cdot CPh_2\cdot OMgBr}$ would be formed and on loss of a molecule of magnesium chlorobromide give phenyldeoxybenzoin as a result of the migration of a phenyl radical :



$$\mathrm{Ph\cdot CHCl\cdot CPh_2\cdot OMgBr} \longrightarrow \mathrm{MgClBr} + {}^{\mathrm{Ph}}_{\mathrm{H}}{>}\underset{|}{\mathrm{C}}-\underset{\underset{-\mathrm{O}}{|}}{\mathrm{C}}{<}^{\mathrm{Ph}}_{\mathrm{Ph}} \longrightarrow \mathrm{Ph_2CH\cdot COPh}$$

In this case, however, the three radicals are identical. In the action of *p*- or *m*-tolylmagnesium bromide on desyl chloride, the intermediate phase would be of the type



${}^{\mathrm{Ph}}_{\mathrm{C_7H_7}}{>}\underset{\underset{\mathrm{O-}}{|}}{\mathrm{C}}-\underset{|}{\mathrm{C}}{<}^{\mathrm{Ph}}_{\mathrm{H}}$. Now, McKenzie, Mills, and Myles (*Ber.*, 1930, **63**, 904) used this identical phase to depict the deamination of β-amino-αβ-diphenyl-α-*p*-tolylethyl alcohol and showed that the phenyl group migrates in preference to the tolyl group, *p*-tolyl diphenylmethyl ketone being formed and not *p*-tolyldeoxybenzoin as we have described in the desyl chloride action (cf. also McKenzie, Roger, and McKay, *loc. cit.*; Roger and McKay, J., 1933, 332; Lévy, Gallais, and Abragam, *Bull. Soc. chim.*, 1928, **43**, 868).

Other mechanisms must, however, be considered. McKenzie and Boyle (J., 1921, **119**, 1132) isolated phenyldeoxybenzoin by the action of phenylmagnesium bromide on diphenylchloroacetyl chloride, picturing diphenylketen as the intermediate phase, and on this basis the action of *p*-tolylmagnesium bromide on desyl chloride should take place thus : desyl chloride $\longrightarrow \mathrm{Ph_2C{:}CO} \longrightarrow \mathrm{Ph_2C{:}C(OH)\cdot C_7H_7} \longrightarrow \mathrm{Ph_2CH\cdot CO\cdot C_7H_7}$.

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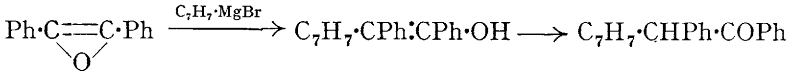
* Richard (*Compt. rend.*, 1934, **198**, 1242) has described the action of phenylmagnesium bromide on desyl chloride. He only isolated 1 : 1 : 2 : 2-tetraphenylethanol and apparently is not aware that the action of *p*-tolylmagnesium bromide on desyl chloride has been recorded by McKenzie, Roger, and McKay (*loc. cit.*).

*p*-Tolyl diphenylmethyl ketone ought to be formed, whereas *p*-tolyldeoxybenzoin was actually found.

Whilst the intermediate formation of diphenylketen seems, therefore, to be not feasible, Madelung and Oberwegner (*Annalen*, 1931, **490**, 224) have described the preparation of the isomeric diphenyloxen, $\underset{\diagdown\mathrm{O}\diagup}{\mathrm{Ph{\cdot}C{=\!=}C{\cdot}Ph}}$ from desyl chloride. Now, this compound offers itself at once as an intermediate phase in the reactions we are considering: desyl chloride ⟶



$$\underset{\diagdown\mathrm{O}\diagup}{\mathrm{Ph{\cdot}C{=\!=}C{\cdot}Ph}} \xrightarrow{\mathrm{C_7H_7{\cdot}MgBr}} \mathrm{C_7H_7{\cdot}CPh{:}CPh{\cdot}OH} \longrightarrow \mathrm{C_7H_7{\cdot}CHPh{\cdot}COPh}$$

Unfortunately, we have not managed to isolate diphenyloxen in order to test this thesis experimentally. We have carried out repeatedly the two principal methods advocated by Madelung and Oberwegner, and modifications thereof, for the preparation of diphenyloxen, and in no instance have we obtained any of this compound. By one method we isolated small amounts of a compound, m. p. 48—49°, agreeing fairly closely with their description of diphenyloxen. Analysis of this compound, however, invariably gave values for carbon which were about 10% low. This compound, m. p. 48—49°, gave with *p*-tolylmagnesium bromide a solid, m. p. 142—143°, which was neither *p*-tolyldeoxybenzoin nor the isomeric ketone. Richard (*Compt. rend.*, 1933, **196**, 1432) also has been unable to obtain diphenyloxen from desyl chloride.

We found little evidence of coupling of desyl chloride molecules in any of these Grignard reactions along the lines indicated by McKenzie, Drew, and Martin (J., 1915, **107**, 26), who found that phenylchloroacetic acid and phenylmagnesium bromide gave derivatives of diphenylsuccinic acid. The substitution of the $\cdot$COPh group for the $\cdot CO_2H$ group evidently inhibits this type of action. In the action of *o*- and *m*-tolylmagnesium bromides on desyl chloride, however, we did obtain a solid, m. p. 185°, which was probably a derivative of dioxan (see experimental section). We also effected the coupling of desyl chloride molecules by the action of silver hydroxide in ethylene glycol solution, bidesyl being formed.

## EXPERIMENTAL.

(a) *Desyl Chloride and Phenylmagnesium Bromide.*—(1) *Addition of desyl chloride to phenylmagnesium bromide.* Desyl chloride (20 g.; 1 mol.) in dry ether was added to phenylmagnesium bromide (from bromobenzene, 34 g.; 1½ mols.). The mixture became dark green and finally dark yellow. After boiling for 2 hours, the solution was decomposed with ice and dilute sulphuric acid. The white solid obtained had m. p. 230·5° (3·5 g.) after recrystallisation from chloroform–alcohol (Found: C, 89·0; H, 6·4. Calc.: C, 89·1; H, 6·4%) and was identical with the 1 : 1 : 2 : 2-tetraphenylethanol described by McKenzie and Boyle (*loc. cit.*). Wegler (*Ber.*, 1934, **67**, 35) records m. p. 236° and discusses the existence of two forms of this compound.

From the ethereal layer a mixture of oil and solid was obtained; the oil was dissolved in a small amount of ether. The undissolved solid (1·5 g.) proved to be more 1 : 1 : 2 : 2-tetraphenylethanol. From the ethereal washings a solid (2 g.), m. p. 120—130°, was obtained, m. p. 136—137° alone (after several recrystallisations from alcohol), or mixed with phenyldeoxybenzoin. It gave an emerald-green coloration with concentrated sulphuric acid.

(2) *Addition of phenylmagnesium bromide to desyl chloride.* This reaction gave the same two compounds as in (1). Their separation was much more difficult, however, and the yields were much smaller. The 1 : 1 : 2 : 2-tetraphenylethanol was submitted to scission with alcoholic potash and the only disruption product obtained was benzhydrol, m. p. 67—68°.

(b) *Desyl Chloride and* m-*Tolylmagnesium Bromide.*—(1) *Addition of* m-*tolylmagnesium bromide to desyl chloride.* *m*-Tolylmagnesium bromide (from *m*-bromotoluene, 30 g.; 2 mols.) was added to an ethereal solution of desyl chloride (20 g.; 1 mol.) and a vigorous action ensued. A white precipitate formed, but disappeared. After boiling for 5 hours, the mixture was decomposed with ice and ammonium chloride. A solid (A) which separated between the layers was removed and the ethereal portion of the filtrate was separated. The oil left after evaporation of the ether was distilled in a high vacuum, two fractions being obtained: (1) b. p. 100—200°, (2) 205—208°. The second fraction was dissolved in light petroleum, and a solid (2 g.), m. p. 80—82°, isolated. After several recrystallisations from light petroleum colourless prisms were obtained, m. p. 82·5—83·5°, identical with the *m*-tolyldeoxybenzoin obtained by the dehydration of *m*-tolylhydrobenzoin (α-form) (Roger and McKay, *loc. cit.*).

The solid (A) (0·25 g.), recrystallised several times from chloroform–alcohol, separated in fine needles, m. p. 185° (Found : C, 82·4; H, 5·8%). It gave a light green–dark green coloration with concentrated sulphuric acid (see action of *o*-tolylmagnesium bromide on desyl chloride).

(c) *Desyl Chloride and* o-*Tolylmagnesium Bromide.*—(1) *Addition of the Grignard reagent to desyl chloride.* *o*-Tolylmagnesium bromide (from *o*-bromotoluene, 40 g.; 2 mols.) was added to an ethereal solution of desyl chloride (25 g.; 1 mol.); a vigorous action ensued and eventually a dark green solid was deposited. The mixture was boiled for 7 hours and decomposed with ice and dilute sulphuric acid. The solid then obtained was recrystallised from chloroform–alcohol, separating as fine needles, m. p. 185°, identical with the compound (A) above (Found : C, 82·4; H, 5·8. $C_{28}H_{22}O_3$ requires C, 82·7; H, 5·5%). When heated in a vacuum at 130°, it suddenly decomposed into a yellow oil, which set to a cheese-like mass (m. p. 45—75°) and after recrystallisation from light petroleum gave benzil (m. p. 93—94°) and a solid, m. p. (after several further recrystallisations from light petroleum) 55—56° (alone or mixed with deoxybenzoin).

The ethereal layer from the Grignard reaction yielded a dark brown oil, which was distilled in a high vacuum. A first fraction, b. p. up to 120°, gave a small amount of solid, m. p. 119—120°. A second fraction, b. p. 120—240°, was redistilled : fraction (a), b. p. 120—200°, gave a small amount of benzil. Fraction (b), b. p. 200—220°, was a viscous yellow oil, which was redistilled, giving a fraction, b. p. 210—217°. This (2 g.), submitted to scission with alcoholic potash, gave 0·2 g. of benzoic acid and a neutral liquid, b. p. 156—160°/20 mm. (Found : C, 91·8; H, 7·4%), and therefore would seem to consist partly of *o*-tolyldeoxybenzoin.

Several fractions of this kind were collected and treated with more *o*-tolylmagnesium bromide; a small amount of *o*-toluoyldiphenylcarbinol (Roger and McGregor, this vol., p. 442), m. p. 115—116°, was obtained.

(2) *Addition of desyl chloride to the Grignard reagent.* Several experiments were carried out and in each case an oil was obtained which gave no identifiable product.

*Experiments on the Preparation of Diphenyloxen.*—Two experiments, on the preparation of diphenyloxen from desyl chloride by the action of solid potassium hydroxide, were replicas of Madelung and Oberwegner's experiments as far as possible. In neither case was a trace of diphenyloxen obtained. The only products were benzilic acid and deoxybenzoin, the latter as colourless, thick, striated plates, m. p. 55—56° (m. p.'s were obtained between 53° and 56°) (Found : C, 85·8; H, 6·3. Calc. for deoxybenzoin : C, 85·7; H, 6·1%. Calc. for diphenyloxen : C, 86·6; H, 5·2%). The action of semicarbazide on it gave clusters of fine colourless needles, m. p. 146—147° alone or mixed with the authentic semicarbazone (Rupe and Oestreicher, *Ber.*, 1912, **45**, 35). The action of *p*-tolylmagnesium bromide gave *phenyl*-p-*tolylbenzylcarbinol*, m. p. 89·5—90·5° (Found : C, 87·2; H, 7·3. $C_{21}H_{20}O$ requires C, 87·4; H, 6·9%), identical with the compound obtained by the action of *p*-tolylmagnesium bromide on authentic deoxybenzoin. In the mother-liquors of crystallisation of the solid, m. p. 55—56°, no trace of diphenyloxen could be found.

*Other attempts to prepare diphenyloxen.* (1) Distillation of desyl chloride with calcium carbonate gave no definite result.

(2) A mixture of desyl chloride (5 g.), ethylene glycol (50 c.c.), and moist silver oxide (10 g.) was heated on a water-bath for 3 hours and then boiled for 2 hours. A yellow solid which separated was recrystallised from benzene, m. p. 254—255° (bidesyl has m. p. 254—255°). From the ethylene glycol solution a small amount of benzoin was obtained, m. p. and mixed m. p. 132—133° after several recrystallisations from light petroleum.

(3) (Compare Madelung and Oberwegner, *loc. cit.*). α-Methoxy-αβ-diphenyloxan (20 g.), freshly prepared, was distilled from a metal bath in a current of carbon dioxide at atmospheric pressure. A little methyl alcohol, b. p. 63°, was collected. The main fraction, b. p. 310—315°, was a yellow oil which, on cooling, deposited crystals of benzil, m. p. (after recrystallisation from light petroleum) and mixed m. p. 93—94°. The residual oil was steam-distilled from concentrated alkali, and the oil, b. p. 178—181°/13 mm., in the distillate was dissolved in light petroleum and kept in ice for several weeks; the colourless hard crystals obtained had m. p. 48—49° after several recrystallisations from light petroleum (Found : C, 75·7; H, 6·4. Calc. for diphenyloxen, $C_{14}H_{10}O$ : C, 86·6; H, 5·2%), gave no coloration in the cold with concentrated sulphuric acid but a yellow colour on gentle warming, and markedly depressed the m. p. of deoxybenzoin. A large amount of oil was left after removal of the compound, m. p. 48—49°.

The action of *p*-tolylmagnesium bromide on the compound, m. p. 48—49°, and on the residual oil, gave a solid, m. p. **139—141°**, and **142—143°** after several recrystallisations from light petroleum (Found : C, 81·8; H, 6·85%). A trace of this product gave a yellow coloration with concentrated sulphuric acid.

If the compound, m. p. 48—49°, were diphenyloxen, it ought to have given *p*-tolyldeoxybenzoin with *p*-tolylmagnesium bromide, and 1 : 2-diphenyl-1 : 2-di-*p*-tolylethanol by further reaction.

*p*-Tolyldeoxybenzoin (3 g.) was boiled with *p*-tolylmagnesium bromide for 8 hours. An oil was obtained from the ethereal layer which yielded a solid (0·5 g.), m. p. 191—194°. 1 : 2-*Diphenyl*-1 : 2-*di*-p-*tolylethanol* crystallised from light petroleum in rectangular prisms, m. p. 195—196° (Found : C, 88·6; H, 7·3. $C_{28}H_{26}O$ requires C, 88·8; H, 6·9%). A trace of this compound gave a yellow coloration with concentrated sulphuric acid.

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