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RADICAL FORMATION DURING REACTIONS OF GRIGNARD REAGENTS WITH QUINONES

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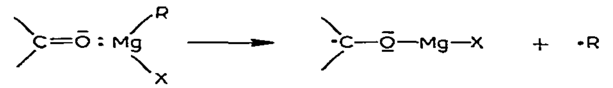
SUMMARY

In dilute solution the addition of phenylmagnesium bromide to acenaphthenequinone and phenanthrenequinone leads by single electron transfer to the formation of the corresponding semiquinones, which can be identified by ESR. Phenanthrenequinone yields ca. 20% 9-hydroxy-10-phenoxyphenanthrene, the formation of which is explained by combination of the initially formed semiquinone and phenyl radicals.

The analogy with photochemical reactions and the possible occurrence of similar reactions in organomagnesium and organozinc chemistry are briefly discussed.

INTRODUCTION

Radical formation during reactions of Grignard reagents with ketones and quinones has been detected with the aid of ESR spectroscopy[1-5]. It has been assumed[4] that after formation of a complex between the Grignard reagent and the ketone, one of the possible reaction paths is the transfer of a single electron from the carbon–magnesium bond in the Grignard compound to the ketone moiety in the complex under formation of an alkyl or aryl radical and an alkoxide according to eqn. (1).



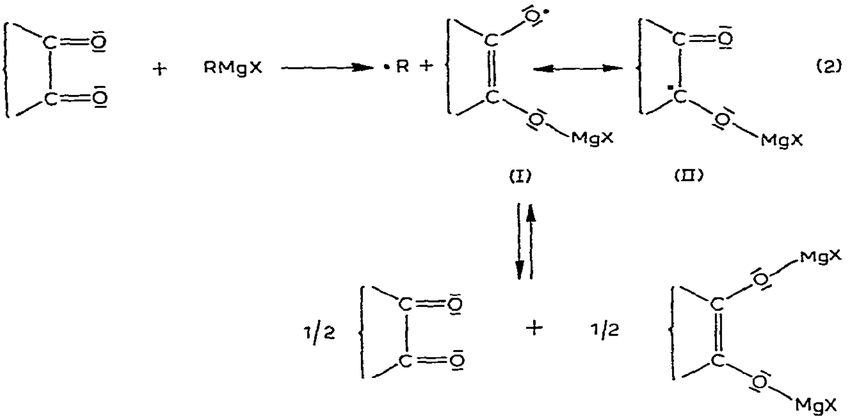
(1)

E.g. 20% of neopentane was detected in the products of interaction of neopentylmagnesium chloride and benzophenone in tetrahydrofuran[4], indicating that the reactive neopentyl radical had escaped from the solvent cage and had stripped a hydrogen atom from the solvent.

Recently Relles[6] investigated the reaction of arylmagnesium halides with *ortho*-substituted diphenoquinones [(bi-2,5-cyclohexadien-1-ylidene)-4,4′-dione]; he reported the formation of considerable amounts of products resulting from coupling of aryl radicals (within the solvent cage).

A third possible reaction path for the radical is formation of a bond with the ketyl carbon atom leading to the normal addition product. It is not clear at present to what extent this radical mechanism competes with the generally accepted carbanion mechanism[7,8a].

Interaction of a Grignard reagent with a quinone gives a variety of products, and among them reduction products are important. Thus, formation of quinhydrones has been reported several times[8b,9]. Although magnesium subhalides, formed by the combination of unreacted metallic magnesium and magnesium halides (from Wurtz-type side reactions during the preparation of the Grignard compounds) may be responsible for some of these reduction reactions[9], we now present evidence that reduction does, in fact, take place by reaction (2). It has been shown previously that the semiquinones can "comproportionate"[10,11].

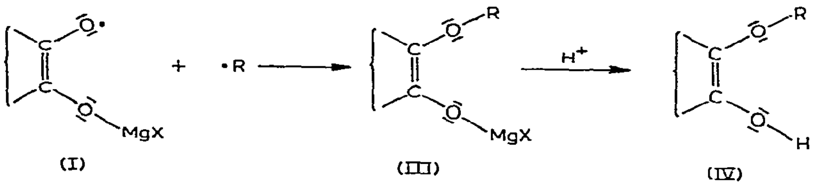


(2)

RESULTS AND DISCUSSION

Using high-vacuum techniques[12] and ultra-clean, water-white solutions of the Grignard reagent, we mixed equimolar amounts of phenylmagnesium bromide (0.04 *M*) and acenaphthenequinone or phenanthrenequinone in tetrahydrofuran and obtained brightly colored solutions (violet and green respectively), and recorded their ESR spectra. The spectra were identical with those reported in the literature for the semiquinones obtained by reduction of the quinones with metallic zinc[13]. Addition of more than two molar equivalents of phenylmagnesium bromide to the quinones resulted in the change of the bright color to yellow and no ESR signals could be detected from the solutions.

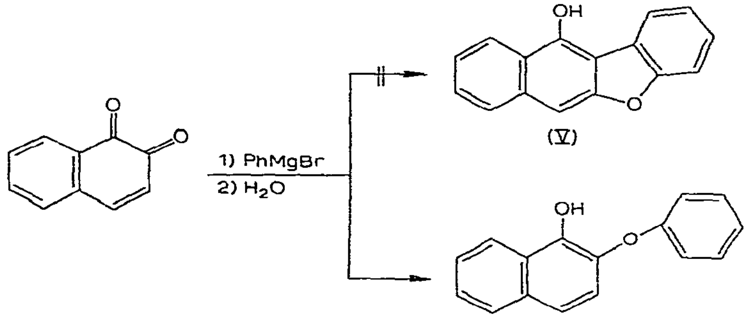
From a preparative point of view, it is noteworthy that when phenylmagnesium bromide and phenanthrenequinone were used in 0.65 *M* solution the expected product (9,10-dihydroxy-9,10-diphenyl-9,10-dihydrophenanthrene) could not be isolated, whereas it was obtained in reasonable yields (ca. 50%) under the conditions used by Acree[14] (*i.e.* 2.5 *M*). Instead, an unexpected product, the monophenylether of 9,10-phenanthrenediol [(IVa):(IV) with $R=C_6H_5$ and {$=o,o'$-biphenylene] was isolated in 20% yield. The formation of (IVa) can be rationalised by eqn. (3).



(3)

Reaction (3) is of great theoretical interest because it is an example of a fourth reaction path which is in principle open to the radical pair formed in reaction (2). This reaction implies at first sight a reversion of the direction of Grignard addition to carbonyl groups and obviously is only possible in the dicarbonyl series where conjugation of the ketyl grouping with the second carbonyl group leads to a relatively high spin density at an oxygen atom [compare (I)↔(II)]. Strong evidence for the proposed reaction path (3) is found in the reaction of photoactivated quinones with hydrocarbons. This photochemical reaction is assumed to proceed via the triplet state of the diketone which strips a hydrogen atom from the hydrocarbon, leading to a semiquinone and a hydrocarbon radical; these can, among other things, recombine to form hydroxy ethers[15]. A relevant example was recently presented by Maruyama who reported the formation of (IVa) from triplet-state phenanthrenequinone with benzene[16].

To our knowledge this novel type of radical reaction has not been reported in Grignard chemistry before. However, we note that Franssen[17] described the formation of a product (25% yield) from the reaction of phenylmagnesium bromide with 1,2-naphthoquinone to which he ascribed the rather unlikely structure (V). In view of our results we assume that the product was, in fact, one of the monophenyl ethers of 1,2-naphthalenediol [(VI) or its isomer]. This reaction is being reinvestigated.



(V)

(VI)

The formation of monoethers of hydroquinones from quinones has, however, been observed in reactions of quinones with organozinc compounds[18]. Although the participation of radicals was not demonstrated in those reactions, we suggest that a radical reaction such as we have postulated would explain satisfactorily the different course of the reaction for dimethyl- and diethylzinc.

EXPERIMENTAL

Use was made of high-vacuum techniques, as previously described[12], in preparing the Grignard solutions required for ESR measurements.

For all experiments the magnesium used was supplied by Johnson, Matthey and Co, Limited, London, and contained the following impurities (in ppm): Iron 20; Zinc 20; Manganese 8; Aluminium 5; Nickel 5; Copper 3; Calcium 2; Silicon 2; Sodium 1; Silver 1.

Performance of ESR measurements

By repeated crystallisation of phenylmagnesium bromide in sealed glass vessels a solution could be obtained which contained an excess of magnesium bromide. The Grignard concentration was 0.04 *M*. Small ampoules of this Grignard solution were sealed to ESR tubes (quartz) which contained one molar equivalent of the required quinone. The apparatus was evacuated (10^{-6} mm Hg) and sealed, after which the breakseals were opened and the Grignard solution poured on the quinones in the ESR tube. Measurements could be performed within one minute after the breaking of the seals. The ESR signals were unchanged for several days.

Preparation of 9-hydroxy-10-phenoxyphenanthrene (IVa)

In two different runs 50 ml of a solution of phenylmagnesium bromide (0.65 *M*) which was free from metallic magnesium and from excess magnesium bromide was pipetted under N_2 to either 3 g (ca. 14.5 mmoles) or 6 g (ca. 29 mmoles) of phenanthrenequinone. The first reaction mixture was yellow, the second dark green. The mixtures were then treated as follows: after four hours with stirring under reflux, the reaction mixture was added to ice, and the water layer was slightly acidified with acetic acid, separated from the organic layer, and extracted several times with ether. The combined organic layers were neutralized, dried on anhydrous magnesium sulphate, and evaporated to yield a thick, dark red syrup. This syrup was dissolved in hot petr.ether (b.p. 60–80°), and bright yellow needles crystallized on cooling. After repeated concentration of the petr.ether solutions, ca 2 g of crystals were isolated (the yields were 24% and 19% resp.). The crystals were purified by repeated crystallization to give material of m.p. 143° [reported[19] for (IVa) 141–142°].

The structure was confirmed unambiguously by mass spectrometry.

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REFERENCES

1 K. Maruyama, *Bull. Chem. Soc. Jap.*, 37 (1964) 879, 1013.
2 G. A. Russell, E. G. Janzen and E. T. Storm, *J. Amer. Chem. Soc.*, 86 (1964) 1807.
3a A. Rieker, *Angew. Chem.*, 76 (1964) 601.
3b E. Müller, A. Rieker, K. Scheffler and A. Moosmayer, *Angew. Chem.*, 78 (1966) 98; *cf.* p. 102.
4 C. Blomberg and H. S. Mosher, *J. Organometal. Chem.*, 13 (1968) 519.
5 J. F. Fauvarque and E. Rouget, *C. R. Acad. Sci., Ser. C*, 267 (1968) 1355.
6 H. M. Relles, *J. Org. Chem.*, 34 (1969) 3678.
7 E. C. Ashby, *J. Chem. Soc. D*, (1970) 330.
8 (a) A. N. Nesmeyanov and K. A. Kocheskov, *Methods of Elemento–Organic Chemistry*, Vol. 2, North-Holland Publ. Co, Amsterdam, 1967, p. 117. (b) *Ibid.*, p. 218.
9 M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Non-Metallic Substances*, Prentice Hall, New York, 1954, p. 529.
10 E. Müller, F. Günter, K. Scheffler, P. Ziemek and A. Rieker, *Justus Liebigs Ann. Chem.*, 688 (1965) 134.
11 A. G. Evans, J. C. Evans and E. H. Godden, *J. Chem. Soc. B*, (1969) 546.

12 A. D. VREUGDENHIL AND C. BLOMBERG, *Recl. Trav. Chim. Pays-Bas*, 82 (1963) 453.
13 M. ADAMS, M. S. BLOIS JR. AND R. H. SANDS, *J. Chem. Phys.*, 28 (1958) 774.
14 S. F. ACREE, *Amer. Chem. J.*, 33 (1905) 186.
15 M. B. RUBIN, *Fortschr. Chem. Forsch.*, 13 (1969) 251.
16 K. MARUYAMA, *Bull. Chem. Soc. Jap.*, 42 (1969) 3357.
17 A. FRANSSEN, *Bull. Soc. Chim. Fr.*, [4] 45 (1929) 1030.
18 B. EISTERT AND L. KLEIN, *Chem. Ber.*, 101 (1968) 900 and references given therein.
19 S. GOLDSCHMIDT, A. VOGT AND M. A. BREDIG, *Justus Liebigs Ann. Chem.*, 445 (1925) 123.