Tetrahedron Letters,Vol.23,No.51,pp 5475-5478,1982 0040-4039/82/515475-04$03.00/0
Printed in Great Britain

ELECTRON TRANSFER FREE RADICAL MECHANISM IN THE REACTIONS OF ARENEDIAZONIUM CATIONS WITH GRIGNARD REAGENTS

P.R. Singh,* R.K. Khanna and B. Jayaraman[1]
Department of Chemistry,
Indian Institute of Technology, Kanpur 208 016, U.P., India

Summary: The major pathway in the reactions of arenediazonium cations with certain Grignard reagents is found to involve an electron transfer from the latter to the π-system of the former reactant and radicals are the immediate precursors of the final products.

Reactions of arenediazonium cations with certain nucleophiles,earlier believed to occur by ionic mechanisms are now known to proceed via electron transfer free radical pathways.[2-4] A few reports have appeared on the reactions of arenediazonium cations with organometallics,[5-7] but the mechanistic details are obscure.[8] We now present the results of our studies on the reactions of some arenediazonium cations with Grignard reagents which demonstrate that the major reaction pathway involves a single electron transfer from the latter to the former reactant, subsequently producing radicals which serve as the immediate precursors of the final products.

The reactions of arenediazonium fluoroborates, $p\text{-R-}C_6H_4\text{-}N_2^+BF_4^-$ (1, where R=H, Me, OMe, NO_2, COMe) with benzylmagnesium chloride 2a and tert.butyl magnesium chloride 2b, carried out under carefully varied conditions in THF solvent/N_2 atmosphere at 30°C proceeded with vigorous evolution of nitrogen gas and yielded other products as listed in the Table. The reactivity of arenediazonium cations in the sequence: 1 (R = OMe) < 1 (R = H) < 1 (R = NO_2) as seen from the speeds of nitrogen evolution, disfavours the existence of otherwise conceivable aryl cation intermediates in these reactions.[9] Also, the formation of dediazoniation products, $R\text{-}C_6H_5$ in high yields, eliminates the possibility of bimolecular nucleophilic displacement of nitrogen. These facts coupled with the inhibition of the reactions observed in the presence of α-methylstyrene, strongly suggest the intervention of free radicals. Indeed, strong esr signals observed by us[10] in the reaction of 1 (R = NO_2) with 2a confirm the existence of radicals. The formation of radicals by thermal homolytic dissociation of covalent azo compounds is ruled out because the product distribution obtained in these reactions remained essentially unaltered on extending the reaction time. Furthermore, azo compounds similar to those likely to be encountered in these reactions are known[11,12] to be stable under our conditions. It is also known that radicals

TABLE: Reactions[a] of arenediazonium fluoroborates, p-R-C_6H_4-$\overset{+}{N_2}\overset{-}{BF_4}$, <u>1</u> with alkyl magnesium chlorides <u>2</u>

Run	R	R'MgCl	Rxn. Time (sec)	% Yield of Products[b]					
				N_2	R-C_6H_5	p-R-C_6H_4-R'	p-R-C_6H_4-C_6H_4-R (Isomeric mixture)	R'-R'[c,d]	R'-H[c]
1	H	<u>2a</u>	50	85	60	9	4	30	24[d]
2[e]	H	<u>2b</u>	120	85	70	5	3	13	50
3[e]	H	<u>2b</u>	1800	85	71	5	3	14	50
4[e,f]	H	<u>2b</u>	2400	20	10	-	-	-	6
5	OMe	<u>2a</u>	60	80	57	13	3	27	22[d]
6	OMe	<u>2a</u>	1800	80	59	12	3	28	23[d]
7[e]	OMe	<u>2b</u>	180	80	66	8	4	11	48
8[e]	OMe	<u>2b</u>	1800	80	65	8	4	12	50
9[e,f]	OMe	<u>2b</u>	2400	10	6	-	-	-	4
10	NO_2	<u>2a</u>	35	90	65	12	3	30	27[d]
11	NO_2	<u>2a</u>	1800	90	67	12	3	32	28[d]
12[e]	NO_2	<u>2b</u>	90	90	74	7	4	14	50
13[e,f]	NO_2	<u>2b</u>	2400	25	15	-	-	-	10
14	CH_3	<u>2a</u>	50	85	61	10	3	32	25[d]
15	COMe	<u>2a</u>	45	90	66	14	2	31	28[d]

a) Grignard reagents were prepared by refluxing the organic halide (0.015 mol) over cleaned magnesium ribbon (0.015 g-atom) in THF (30ml) until all the metal dissolved. On chemical[14] and GLC analyses, <u>2a</u> (66.7%, ca. 0.01 mol), toluene (18.3%) and bibenzyl (15%) were found to have formed from benzyl chloride; and <u>2b</u> (86.7%, ca. 0.013 mol) and Me_3C-CMe_3 (4.5%) along with an unestimated amount of Me_3CH were found in the case of tert.butyl chloride. Equimolar quantities of <u>1</u> taken in THF (30 ml) were then reacted with the Grignard reagent thus obtained, at 30°C/N_2 atmosphere. Reaction mixtures were worked up soon after the N_2 evolution stopped excepting in runs 3, 6, 8 and 11 where work up time was extended by 30 min.

b) Percentages based on arenediazonium fluoroborates unless otherwise specified. In addition, benzaldehyde phenyl hydrazone (ca. 8%) in run 1; benzene-azo-α,α-dimethylethane (ca. 7%) each in runs 2 and 3, besides a trace amount in run 4; N-benzyl benzaldehyde p-methoxyphenyl hydrazone, <u>4</u> (ca. 12%) each in runs 5 and 6; p-methoxybenzene-azo-α,α-dimethylethane (ca. 10%) each in runs 7 and 8, besides a trace amount in run 9 were also obtained. Additional coloured product mixtures could not be analysed.

c) Percentages based on alkyl magnesium chloride.

d) Yields have been corrected after taking into account the amounts of these products formed during the preparation of Grignard reagents.[15]

e) Mixture of nitrogen and methylpropane was analysed by G.C.

f) In presence of α-methylstyrene (0.1 mol).

---

do not induce decomposition of covalent azo compounds.[13] These facts along with the observed low yields of azo compounds (or the isomeric hydrazones) where identified among the products, lead us to conclude that the formation of azo compounds by the expected ionic coupling does not constitute the major mechanistic path of the title reactions. It is noteworthy that while arenediazonium cations $\underline{1}$ act as good one electron oxidants in many reactions,[2-4] Grignard reagents are capable of reacting with appropriate substrates as single electron reductants.[15,16]

In view of the foregoing arguments, we propose a single electron transfer free radical mechanism outlined in the Scheme as the major pathway satisfactorily accounting for all the observations.

SCHEME

$$\underset{\underline{1}}{p\text{-}R\text{-}C_6H_4\text{-}N_2^+} + \underset{\underline{2}}{R'MgCl} \xrightarrow{SET} [p\text{-}R\text{-}C_6H_4\text{-}N_2]^{\bullet} + R'\bullet + {}^{+}MgCl \quad ..(1)$$

$$[p\text{-}R\text{-}C_6H_4\text{-}N_2]^{\bullet} \longrightarrow p\text{-}R\text{-}C_6H_4^{\bullet} + N_2 \quad ..(2)$$

$$p\text{-}R\text{-}C_6H_4^{\bullet} \xrightarrow{THF} R\text{-}C_6H_5 \quad ..(3)$$

$$p\text{-}R\text{-}C_6H_4^{\bullet} + R\text{-}C_6H_5 \xrightarrow{-H^{\bullet}} p\text{-}R\text{-}C_6H_4\text{-}C_6H_4\text{-}R \quad ..(4)$$

$$2\ p\text{-}R\text{-}C_6H_4^{\bullet} \longrightarrow p\text{-}R\text{-}C_6H_4\text{-}C_6H_4\text{-}R\text{-}p \quad ..(5)$$

$$p\text{-}R\text{-}C_6H_4^{\bullet} + R'\bullet \longrightarrow p\text{-}R\text{-}C_6H_4\text{-}R' \quad ..(6)$$

$$R'\bullet \xrightarrow{THF} R'\text{-}H \quad ..(7)$$

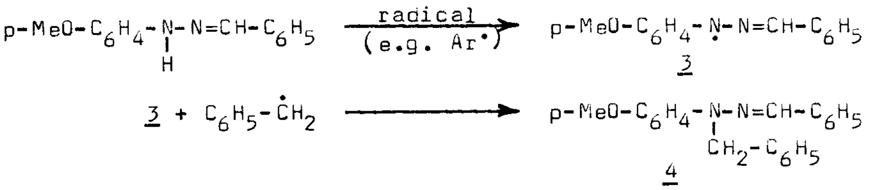
$$R'\bullet + R'\bullet \longrightarrow R'\text{-}R' \quad ..(8)$$

The reaction is initiated by a single electron transfer from the polar C-Mg bond of the Grignard reagent $\underline{2}$ to the arenediazonium cation $\underline{1}$, via the formation of a π-complex.[4] The resulting diazenyl radical may decompose by the heterolysis of the C-N bond,[2] yielding gaseous nitrogen and a stable σ-aryl radical, $p\text{-}R\text{-}C_6H_4^{\bullet}$ via an electrophilic π-aryl radical. This aryl radical may then abstract a hydrogen atom from the solvent (step 3) and attack $R\text{-}C_6H_5$ (step 4) or couple with another radical (steps 5 and 6). Because of the high reactivity and non-selectivity of aryl radicals,[13] step (3) is preferred over all other steps consuming these. Benzyl and tert.butyl radicals being more stable than the aryl radicals, dimerize to a larger extent, besides abstracting hydrogen atoms from the solvent. The observed difference in the reactivities of the two Grignard reagents may also be related to the difference in stabilities of the alkyl radicals formed in step (1). The reactivity sequence of the arenediazonium cations $\underline{1}$, may be related to their oxidation potentials[17] and the ease of heterolysis[2] of the C-N bond in the diazenyl radical. α-Methylstyrene inhibits the reaction presumably by scavenging the radicals[18] formed in step (1).

Minor amounts of azo compounds formed, may either result by the coupling of the diazenyl radical with the alkyl radical, before the former radicals undergo fragmentation or by a minor ionic pathway. The azo compounds formed in the reactions with 2a isomerize to yield the corresponding substituted phenyl hydrazones.

$$p\text{-}R\text{-}C_6H_4\text{-}N{=}N\text{-}\underset{H}{C}H\text{-}C_6H_5 \longrightarrow p\text{-}R\text{-}C_6H_4\text{-}\underset{H}{N}\text{-}N{=}CH\text{-}C_6H_5$$

The N-benzylated hydrazone 4 obtained in runs 5 and 6 might arise by the coupling of a benzyl radical with the radical 3 derived from the corresponding phenyl hydrazone:



$$p\text{-}MeO\text{-}C_6H_4\text{-}\underset{H}{N}\text{-}N{=}CH\text{-}C_6H_5 \xrightarrow[\text{(e.g. Ar}^\bullet)]{\text{radical}} p\text{-}MeO\text{-}C_6H_4\text{-}\dot{N}\text{-}N{=}CH\text{-}C_6H_5 \quad \underline{3}$$

$$\underline{3} + C_6H_5\text{-}\dot{C}H_2 \longrightarrow p\text{-}MeO\text{-}C_6H_4\text{-}\underset{CH_2\text{-}C_6H_5}{N}\text{-}N{=}CH\text{-}C_6H_5 \quad \underline{4}$$

Apparently, the presence of a p-MeO group in the phenyl ring, in contrast to other substituents, has a stabilising effect on the radical 3, which couples with a stable benzyl radical.

Acknowledgement: We thank the C.S.I.R., New Delhi, for the award of a research fellowship to RKK.

REFERENCES AND NOTES

(1) Present address: Department of Chemistry, Vivekananda College, Madras, India.
(2) Ramesh Kumar and P.R. Singh, Tetrahedron Lett., 613 (1972).
(3) P.R. Singh and Ramesh Kumar, Aust. J. Chem., 25, 2133 (1972).
(4) P.R. Singh, B. Jayaraman and H.K. Singh, Chem. & Ind., 311 (1977).
(5) D.Y. Curtin and J.A. Ursprung, J. Org. Chem., 21, 1221 (1956).
(6) Y. Nomura, Bull. Chem. Soc. Jpn., 1648 (1961).
(7) Y. Nomura, Bull. Chem. Soc. Jpn., 111 (1962).
(8) K.U. Ingold and B.P. Roberts, in "Free Radical Substitution Reactions," Wiley-Interscience, New York, 1971, Chap. III.
(9) E.S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, 1959, pp. 457-58.
(10) ESR signals were absent in pure reactants.
(11) P.T. Uemura and Y. Inamura, Bull. Chem. Soc. Jpn., 10, 169 (1935).
(12) M.G. Alder and J.E. Leffler, J. Am. Chem. Soc., 76, 1425 (1954).
(13) W.A. Pryor, "Free Radicals," McGraw-Hill Book Company, 1966, pp. 128-29.
(14) H. Gilman, Z.A. Zoellner and J.B. Dickey, J. Am. Chem. Soc., 51, 1576 (1929).
(15) P.R. Singh, S.R. Tayal and Alok Nigam, J. Organomet. Chem., 42, C9 (1972).
(16) E.C. Ashby and A.B. Goel, J. Am. Chem. Soc., 103, 4983 (1981).
(17) R.M. Elofson and F.F. Gadallah, J. Org. Chem., 34, 854 (1969).
(18) T. Holm and I. Crossland, Acta Chem. Scand., B 33, 421 (1979).

(Received in UK 11 October 1982)