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THE FIRST REPORTED EVIDENCE OF SINGLE ELECTRON TRANSFER IN THE 1,2-ADDITION OF PRIMARY GRIGNARD REAGENTS TO KETONES.[1]

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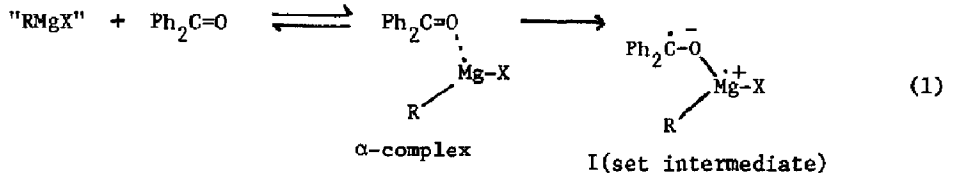
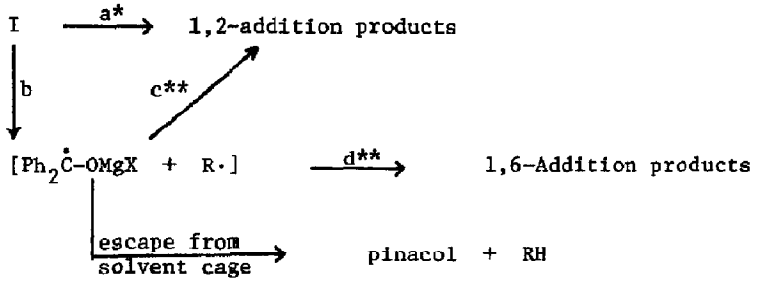
Abstract: The first evidence to support the electron transfer nature of the reaction of primary Grignard reagents with aromatic ketones is presented.

In continuing our investigation of the nature of alkyl transfer in reactions of Grignard reagents with ketones, we have previously presented data[2,3] which supports a modification of an electron transfer mechanism (eq. 1) first postulated by others[4-6] for the reaction of Grignard reagents with benzophenone. More recently Holm and Crossland have suggested that the electron transfer mechanism, although in effect for tertiary Grignard reagents, is not in effect for primary Grignard reagents.[6] We would like to suggest here that possibly all Grignard reactions with aromatic ketones proceed through an electron transfer pathway described by eq. 1. Our data sug-



(1)



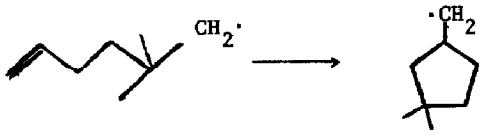
* = precludes observation of free radical

** = free radical character observable

gest that if primary Grignard reagents react via an electron transfer mechanism, pathway a* (collapse of the radical anion-radical cation pair to 1,2-addition product without observation of free radical character) is the usual course of reaction due to the instability of the incipient

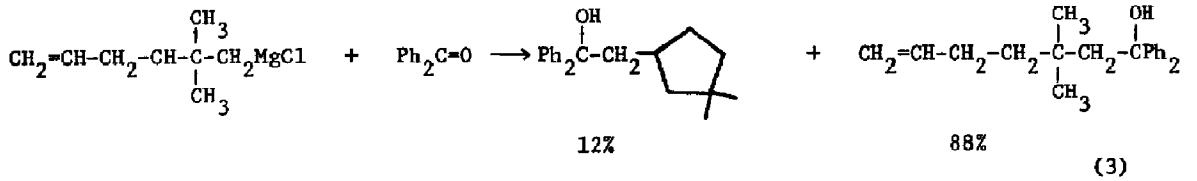
free radical formed from complex (I), when R is primary. Thus, if electron transfer were to be observed in the reaction of a primary Grignard reagent with benzophenone, pathway a* would have t be slowed sufficiently in order to allow at least partial reaction through pathway b.

With this in mind, a sterically hindered probe (a neopentyl Grignard derivative, eq. 2) was incorporated into the R-group of a Grignard reagent such that free-radical character would be observed as a cyclization of the probe in the reaction products. 2,2-Dimethyl-5-hexenylmagnesium



(2)

chloride was prepared and allowed to react with benzophenone in ether at room temperature in a Grignard to ketone ratio of 2:1. The resulting product consisted of 100% 1,2-addition products with cyclization observed in 12% of the product (eq. 3). This experiment has been repeated sever times and the results verified within experimental error. The Grignard reagent used in these experiments was shown to be devoid of any cyclized product as determined by hydrolysis of the Grignard and isolation of only 2,2-dimethyl-5-hexane.



12% 88%

(3)

These data are the first reported indication that electron transfer may occur in the reactio of a primary Grignard reagent with a ketone. Thus, the increase in steric bulk of the R-group of 2,2-dimethyl-5-hexenylmagnesium chloride slowed down the collapse of the radical cation-radical anion pair in complex (I) such that reaction through path b and c** were observed.

References

1. The authors gratefully acknowledge the support of the National Science Foundation Grant No. MPS-7504127.

2. E. C. Ashby and J. S. Bowers, Jr., J. Amer. Chem. Soc., 99, 8504 (1977).
3. E. C. Ashby and T. L. Wiesemann, J. Amer. Chem. Soc., 100, 189 (1978).
4. C. Blomberg, R. Salinger, and H. Mosher, J. Org. Chem., 34, 2385 (1969).
5. J. F. Fauvarque and E. Rouget, C. R. Acd. Sci., Ser. C., 267, 1355 (1968).
6. T. Holm and I. Crossland, Acta Chem. Scand., 25, 59 (1971).

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