BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(4), 1327—1328 (1975)

Abnormal Grignard Reaction of 2,4,6-Trimethylbenzophenone: An Electron-transfer Mechanism

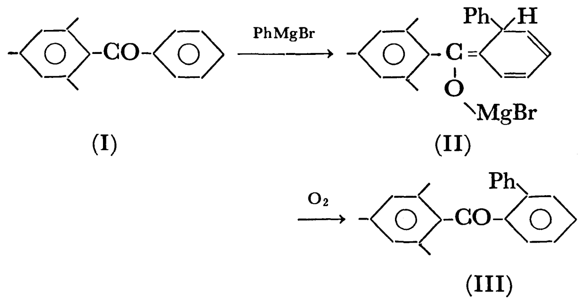
Masao Ōkubo

Department of Chemistry, Faculty of Science and Engineering, Saga University, Honshō-chō, Saga 840

(Received June 24, 1974)

Synopsis. The reaction of 2,4,6-trimethylbenzophenone with phenyl-MgBr in tetrahydrofuran was examined by ESR technique. A high amount of the ketyl radical was detected. An electron-transfer mechanism was proposed to explain the formation of *o*-biphenylyl mesityl ketone.

2,4,6-Trimethylbenzophenone(I) undergoes nuclear phenylation in the reaction with phenyl-MgBr as reported by Fuson *et al.*[1] They explained the formation of *o*-biphenylyl mesityl ketone(III) in terms of 1,4-addition followed by air-oxidation.

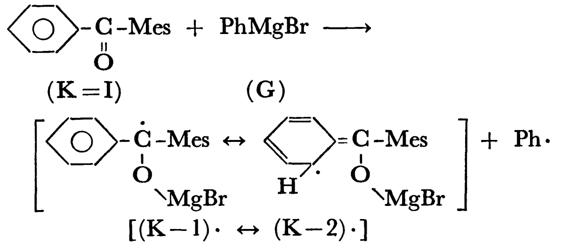


However, aeration of the ether extract of the hydrolyzed reaction mixture did not improved the yield of III. Intense red-coloration of the reaction solution seemed to indicate the presence of the ketyl radical derived from I. These results led the author to re-examine the reaction by means of ESR spectroscopy.

When ketone I was treated with five moles of phenyl-MgBr in tetrahydrofuran (THF) under vacuum at room temperature, the colorless solution turned to wine-red. A radical species was detected, its concentration increasing gradually and becoming *ca.* 30 mol% of the original ketone after four days. When the colored solution was sufficiently diluted, ESR spectrum A (Fig. 1) consisting of ninety lines evenly spaced at an interval of 0.23 gauss (total width 20.9 gauss) was obtained. When the dilution was not sufficient, the spectrum turned to one consisting of four broad lines (splitting constant 4.87 gauss, relative strength 1 : 3 : 3 : 1). Spectrum A was observed even after the solution had been allowed to stand for thirty days at room temperature.

The magnesium-ketyl prepared by the treatment of I with Mg-amalgum in THF gave a spectrum consisting of four broad lines, ascribable to the equivalent coupling of *o*- and *p*-hydrogen atoms of phenyl group with free spin.[2] However, when the treatment with amalgum was not sufficient, a spectrum identical with A was obtained. Since insufficient treatment left the original ketone mostly unchanged, spectrum A can be ascribed to a particular form of the ketyl radical existing as a dimeric or an oligomeric "aggregate" in which other neutral ketone molecules coordinate to the "monomeric" ketyl. The result of a recent work on the Grignard-ketyl of *o*-methylbenzophenone[3] suggests that "aggregate-formation" suppresses the twisting vibration of mesityl group out of the plane of benzoyl group, making it possible to observe the hyperfine splittings. The Grignard-ketyl of d_5-phenyl mesityl ketone gave a spectrum with the very small total width of 3.45 gauss, which indicates that almost all the free spin of Grignard-ketyl of I is delocalized on the phenyl group.[4] This can be explained in terms of the inhibition of conjugation due to the large twisting angle between the plane of the mesityl group and that of the benzoyl group.

As the observed radical concentration is high, most part of the original ketone may be involved in the "aggregate-formation." The main reaction should proceed in the agregate *via* an electron-transfer mechanism. The following processes can elucidate the formation of the identified products: the 1,4-adduct (II, AdH),[1] III(Ad)[1] and 2,4,6-trimethylbenzhydrol (KH).[5]

i)


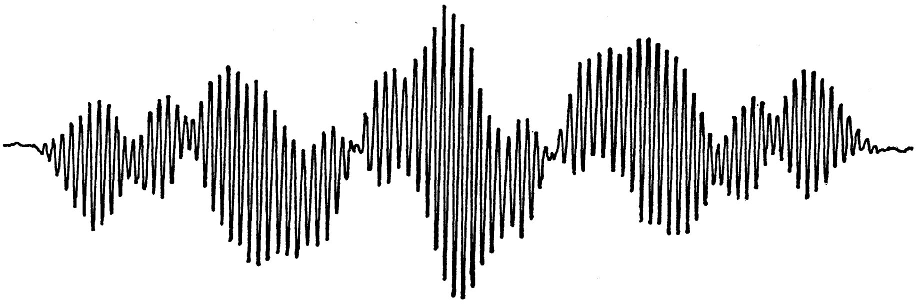
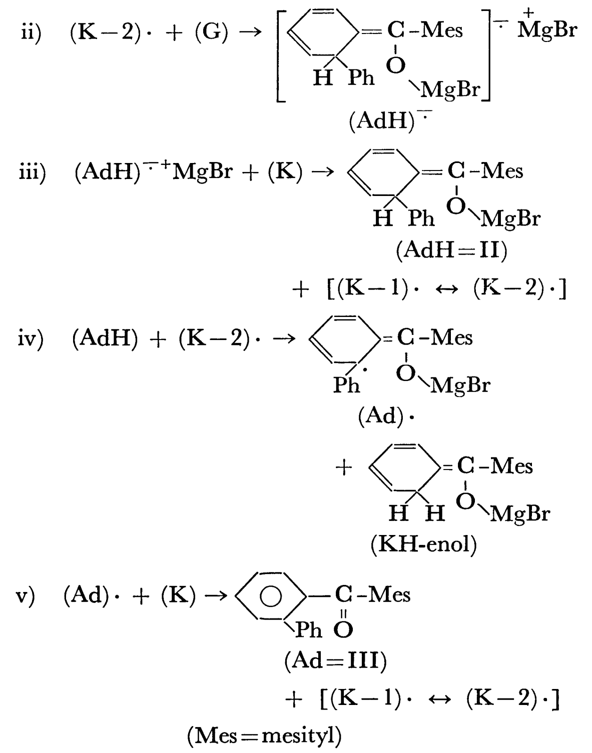


Fig. 1. ESR spectrum A obtained from the reaction of 2,4,6-trimethylbenzophenone and phenyl-MgBr.



The five processes can explain the fact that product III(Ad) was obtained in a fair yield even if the reaction was carried out in the absence of air. Processes i), iii) and v) can also explain the presence of the high amount of ketyl radical throughout the course of reaction. The ketyl radical can be represented mainly by formula (K–2)· on the basis of the extremely high spin density on the phenyl group. The phenyl radical produced in process i) probably abstracts hydrogen from the solvent molecule.⁽⁶⁾ Radical (K–2)·, which can be regarded as a neutral radical because of covalency of the O–Mg linkage, might reveal affinity towards another molecule of phenyl-MgBr, a nucleophile⁽⁷⁾ (process ii). No *para*-phenylated product (*p*-biphenylyl mesityl ketone) was detected. Thus the attack of the carbanion on the *ortho*-position is favored because the position is nearer to the carbonyl-oxygen coordinating to the Mg-atom. The benzpinacol⁽⁸⁾ was absent possibly due to the steric hindrance of the mesityl group.

Experimental

2,4,6-Trimethylbenzophenone was prepared from mesitylene and benzoyl chloride by the Friedel-Crafts method. d_5-Phenyl mesityl ketone was prepared by the same method with the use of d_5-benzoyl chloride. *o*-Biphenylyl mesityl ketone was prepared according to the reported method,⁽¹⁾ and *p*-biphenylyl mesityl ketone by the Friedel-Crafts method. 2,4,6-Trimethylbenzhydrol was obtained by reduction of the corresponding ketone.⁽⁵⁾ *sym*-Diphenyldimesitylpinacol was prepared according to the method of Kharasch, Morrison and Urry.⁽⁸⁾ The reaction products were compared with authentic samples by means of column- and thin-layer-chromatography.

The evacuated samples for ESR measurements were prepared according to the method previously reported.⁽⁹⁾ The radical concentration was determined by the overmodulation technique with a THF solution of galvinoxyl as a standard in the same sample tube.

References

1) R. C. Fuson, M. D. Armstrong, and S. B. Speck, *J. Org. Chem.*, **7**, 297 (1942).
2) K. Maruyama, R. Tanikaga, and R. Gotō, This Bulletin, **36**, 1141 (1963).
3) M. Ōkubo, *ibid.*, **48**, 1057 (1975).
4) H. M. McConnell, *J. Chem. Phys.*, **24**, 632, 764 (1956).
5) K. Elbs, *J. Prakt. Chem.*, [ii] **35**, 472 (1887).
6) In the reaction of benzophenone with mesityl-MgBr, evidence was obtained for hydrogen-abstraction from THF molecule by the mesityl radical.
7) R. A. Rossi and J. F. Bunnett, *J. Org. Chem.*, **38**, 3020 (1973).
8) M. S. Kharasch, R. Morrison, and W. H. Urry, *J. Amer. Chem. Soc.*, **66**, 368 (1944).
9) K. Maruyama, This Bulletin, **37**, 1013 (1964).