

REACTION OF AROMATIC CARBONYL COMPOUNDS WITH  
TRIMETHYLCHLOROSILANE/MAGNESIUM IN HEXAMETHYLPHOSPHORAMIDE

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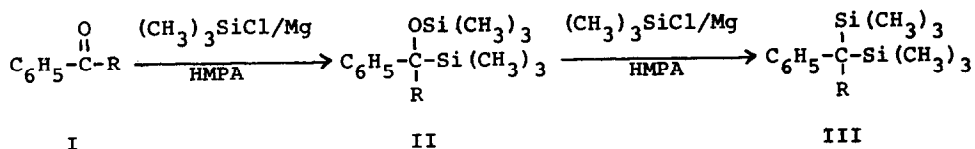
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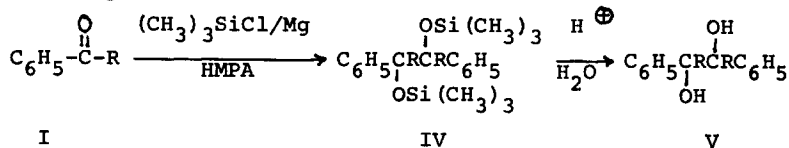
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Recently, Calas et al (1) reported a facile method for the formation of carbon-silicon bond by the reaction of aromatic carbonyl compounds with trimethylchlorosilane and magnesium in hexamethylphosphoramide (HMPA) according to the following equation:

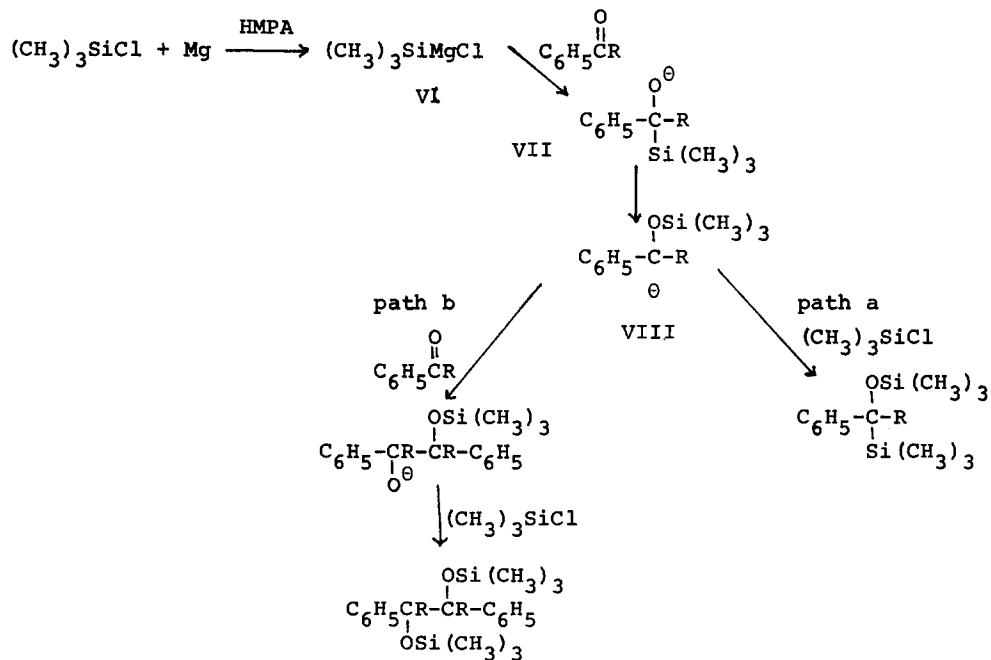


Our experiences showed that the reaction yielded, under slightly modified conditions, entirely different products via a novel type of pinacol formation. Thus, a mixture of benzaldehyde (I, R=H, 0.1 mole), magnesium turning (0.1 mole) and trimethylchlorosilane (0.1 mole) in 100 ml of HMPA was stirred at 95° for 22 hrs and the mixture was hydrolysed with saturated aqueous ammonium chloride (100 ml) at room temperature. The product, isolated in greater than 90% yield (2), was found to be a mixture of *d,l*- and meso-1,2-diphenyl-1,2-ethanediol (V, R=H, ratio of *d,l* to meso = 3:1). Similarly, acetophenone (I, R=CH<sub>3</sub>) gave an equal mixture of *d,l*- and meso-2,3-diphenyl-2,3-di-(trimethylsiloxy)-butane (IV, R=CH<sub>3</sub>) (3) in 88% yield. The identities of these compounds were confirmed

by hydrolysis to the corresponding diols (V, R=CH<sub>3</sub>) (4) under stronger acidic conditions (0.6 N hydrochloric acid)



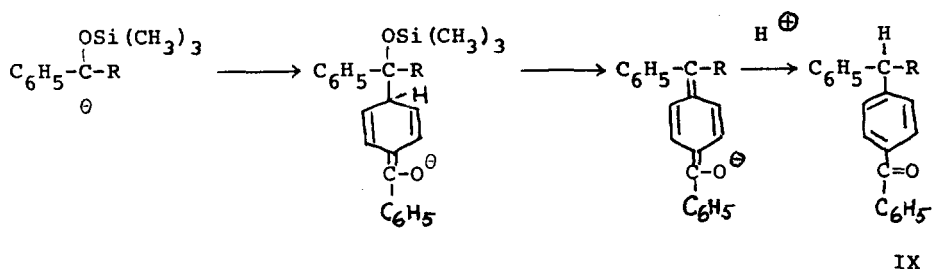
The reaction may proceed through the intervention of trimethylsilyl-magnesium chloride (VI), a species postulated by Gilman (5) and others (6). It then attacked the carbonyl compound to give the oxyanion VII which is prone to rearrange to the siloxycarbanion VIII. This rearrangement has been documented by Brook (7) and recently amplified by West *et al* (8). Under the reaction conditions reported by Calas (1), where there was a deficient amount of I in the reaction mixture, VIII was silylated by the excess trimethylchlorosilane (Scheme I, path a). Under our reaction conditions, nucleophilic attack of VIII on another molecule of I prevailed and yielded the silylated diols (path b) (9).



Scheme I

The novel feature about this mode of pinacol formation is that it does not

assume a role for ketyl radical. This is based on the following observations. Firstly, the reaction does not proceed in the absence of trimethylchlorosilane, thus the possibility of magnesium-promoted reductive coupling can be ruled out. Secondly, benzophenone (I,  $R=C_6H_5$ ) gave, under similar conditions, p-benzoylphenyldiphenylmethane (IX,  $R=C_6H_5$ , 65% yield) (10), a product entirely unexpected on the basis of normal pinacol reduction(11,12). Control experiments indicated that neither benzpinacol nor benzpinacolone would give IX under the reaction conditions. A possible mode of formation for IX is outlined below:



We are actively investigating the mechanism and synthetic potential of this reaction.

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References and Footnotes

- (1) R. Calas, C. Biran, J. Dunoguès and N. Duffant, C.R. Acad. Sci., Ser. C, 269 412 (1969)
- (2) This method of pinacolic reduction of aromatic carbonyl compound appears to give higher yield than other known metal reduction, see A.A.P. Schreibmann, *Tetrahedron Letters* 4271 (1970)
- (3) The mixture showed the following nmr (CDCl<sub>3</sub>, τ) 2.4 (m, C<sub>6</sub>H<sub>5</sub>-C); 8.05 (s, CH<sub>3</sub>-C, d, l) 8.40 (s, CH<sub>3</sub>-C, meso) 9.9 (s, CH<sub>3</sub>-Si, d, l) 10.0 (s, CH<sub>3</sub>-Si, meso). By fractional recrystallization, analytical sample of the meso-isomer could be obtained. It had m.p. 109-111° Anal. Calcd. C = 68.1%; H = 8.8% Found C = 68.3%; H = 8.9%
- (4) J.H. Stocker, D.H. Kern and R.M. Jenevein, *J. Org. Chem.* 33 412 (1968)
- (5) M.V. George, D.J. Peterson and H. Gilman, *J. Amer. Chem. Soc.* 82 403 (1960)
- (6) T.G. Selin and R. West, *Tetrahedron* 5 97 (1959)
- (7) A.G. Brook, *J. Amer. Chem. Soc.* 80 1886 (1958); 81 981 (1959) A.G. Brook and B. Iachia, *ibid* 83 827 (1961); A.G. Brook, *Pure Appl. Chem.* 13 215 (1966)
- (8) R. West, R. Lowe, H.F. Stewart and A. Wright, *J. Amer. Chem. Soc.* 93 282 (1971)
- (9) When methyl benzoate was allowed to react under our conditions, the products obtained were identical to those reported by J.P. Picard, R. Calas, J. Dunoguès and N. Duffant, *J. Organometal. Chem.* 26 183 (1971)
- (10) Identity was confirmed by comparison with authentic sample prepared by Friedel-Craft benzoylation of triphenylmethane according to C. Merritt and C.E. Braun, *Org. Synthesis*, Coll vol. IV, p. 8 (1963). The compound was also synthesized by G. Wittig, L. Gonsior and H. Vojel, *Ann.* 688 1 (1965)
- (11) M. Gomberg and W.E. Bachmann, *J. Amer. Chem. Soc.* 49 241 (1927)
- (12) A.G. Beaumont, R.W. Bott, C. Eaborn and R.A. Jackson, *J. Organometal. Chem.* 6 671 (1966) reported that trimethylsilyl radical (from pyrolysis of Bis(trimethylsilyl)mercury) reacted with ketones to give normal pinacols.