Phenylcarbene from Benzaldehyde, Zinc, and Boron Trifluoride. A New Route to Phenylcyclopropanes

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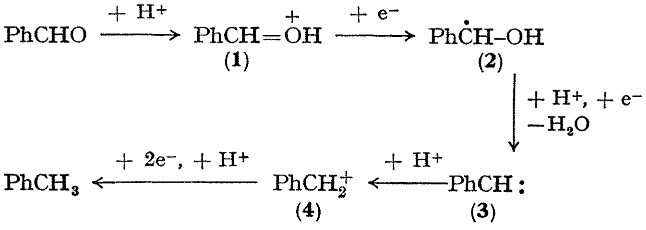
Summary Benzaldehyde, zinc, boron trifluoride and ethylenic compounds afford phenylcyclopropanes (using simple olefins) and phenylcyclopropyl acetates (using enol acetates).

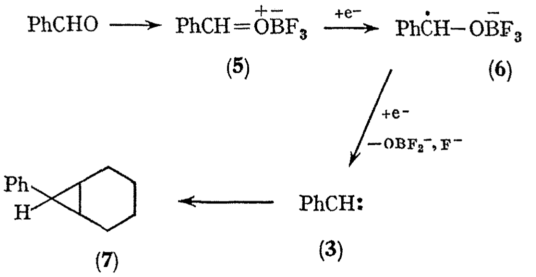
ONE possible mechanism[1] for the Clemmensen reduction, exemplified in Scheme 1 for the case of benzaldehyde, involves a carbene (or carbenoid) intermediate (**3**). This intermediate, the formation of which requires either one



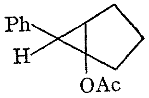
SCHEME 1

two-electron transfer, or two successive one-electron transfers as illustrated in Scheme 1 (**1** → **2** and **2** → **3**), then undergoes protonation, and the resulting carbonium ion (**4**) is reduced to toluene, two further electrons and one proton being required.

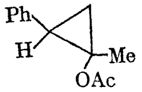
We have found that the intermediate carbene (**3**) (or carbenoid: see below) can be trapped by various ethylenic compounds when the zinc reduction of benzaldehyde is carried out in dry ether using boron trifluoride as the acid, *i.e.*, under conditions under which protonation of the intermediate (**3**) to the carbonium ion (**4**) cannot occur. Thus, when benzaldehyde (1 g.), boron trifluoride etherate (1·3 g.), cyclohexene (5 g.), and amalgamated zinc powder (5 g.) were stirred in dry ether (20 ml.) at room temperature for 24 hr., 7-phenylnorcarane[2] (**7**) (0·6 g.; 35% based on benzaldehyde; *endo* : *exo* = 8 : 1) was formed.† Similarly, 1-acetoxycyclopentene gave 6-phenylbicyclo[3,1,0]hexyl acetate[3] (**8**) (24%; *endo* : *exo* = 3 : 2), 2-acetoxypropene gave 1-methyl-2-phenylcyclopropyl acetate[4] (**9**) (26%; *cis* : *trans* = 1 : 2), and allyl methyl ether gave 1-methoxymethyl-2-phenylcyclopropane‡ (**10**) (25%; *cis*: *trans* = 1 : 1).



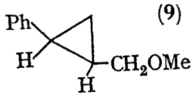
SCHEME 2



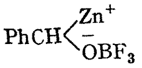
(**8**)



(**9**)



(**10**)



$\mathrm{PhCH}\langle^{\mathrm{Zn}^+}_{\bar{\mathrm{O}}\mathrm{BF}_3}$

(**11**)

We are currently investigating the scope of this new route to cyclopropanes from olefins and carbonyl compounds. A variety of mechanisms is possible, one of which is illustrated in Scheme 2. This involves two successive one-electron transfers, *via* the intermediates (**5**) (*cf.* **1**), (**6**) (*cf.* **2**), and (**3**). It may, however, well be that a *free* carbene (**3**) is not an intermediate, and that the reaction goes through a carbenoid such as (**11**); this could be formed from (**5**) in one step on the surface of the metal.

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† When the reaction was run in cyclohexene as solvent (30 ml.), the yield of **7** was 60%.

‡ B.p. 114—116°/22 mm.; identified through independent synthesis from *cis*- and *trans*-methyl cinnamyl ethers by the Simmons–Smith reaction.

[1] D. Staschewski, *Angew. Chem.*, 1959, **71**, 726.

[2] F. R. Jensen and D. B. Patterson, *Tetrahedron Letters*, 1966, 3837.

[3] The same acetates are formed by Zn–Ac_2O-reduction of 2-phenylcyclohex-2-enone (I. Elphimoff-Felkin and P. Sarda, *Tetrahedron Letters*, 1969, in the press).

[4] J. P. Freeman, *J. Org. Chem.*, 1964, **29**, 1379.