

Radical Organometallic Phase-transfer Reactions

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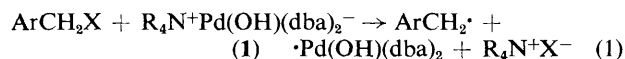
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The phase-transfer catalysed coupling reactions of benzylic halides, in the presence of catalytic quantities of bis(dibenzylideneacetone)palladium(0) or cobalt carbonyl, proceed *via* radical pathways.

A number of interesting metal-catalysed reactions can be effected under phase-transfer catalysis conditions.¹ The most versatile metal catalysts are those containing cobalt,^{2,3} ruthenium,⁴ and palladium.⁵ It has been suggested that free radicals may participate in certain organometallic phase-transfer processes effected under thermal conditions. In addition, the cobalt carbonyl catalysed carbonylation of aryl and vinyl halides, in the presence of ultraviolet light, has also been postulated to proceed *via* a radical pathway.⁶ We now present the first evidence for the occurrence of radical intermediates in organometallic phase-transfer reactions.

While tetrakis(triphenylphosphine)palladium(0) and Pd(diphos)₂ [diphos = 1,2-bis(diphenylphosphino)ethane] catalyse the selective carbonylation of benzylic halides to acids and esters, respectively, bis(dibenzylideneacetone)palladium(0) [Pd(dba)₂] induces coupling and/or dehalo-

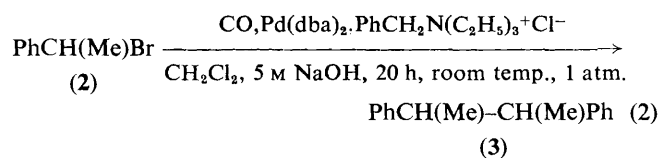
genation to give hydrocarbons.⁵ Radicals were believed to be involved in the latter process, a key step being the electron transfer reaction between an anionic palladium species (**1**) and the organic substrate (equation 1). Anion (**1**) is generated



by hydroxide ion attack on Pd(dba)₂, which would make one of the two dba ligands in (**1**) monodentate. Crown-ether catalysed nucleophilic displacement (*i.e.* cyanide ion) of neutral ligands has been described by Fakley and Pidcock.⁷

It seemed conceivable that the use of the secondary halide, α -phenethyl bromide (**2**), as the organic substrate would serve as a probe of the extent of radical character of the Pd(dba)₂ catalysed phase-transfer reaction, since the coupled product can exist as *meso* or racemic isomers. Treatment of (**2**) with carbon monoxide, methylene chloride, 5 M NaOH, benzyl-triethylammonium chloride as the phase-transfer agent, and

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Pd(dba)_2 as the metal catalyst [25.5/1.0 ratio of (2)/ Pd(dba)_2] afforded 2,3-diphenylbutane (3) as the only product (no acid or ester was formed) (equation 2). Since the n.m.r. spectra of the *meso* and racemic forms are easily distinguished,⁸ this method proved valuable for determining the proportion of stereoisomers. The ratio of *meso*/racemic forms was 1.00/1.10, indicating that the Pd(dba)_2 and phase-transfer catalysed reaction of benzylic halides is a radical process.

The coupling reaction of secondary halides, including (2), catalysed by cobalt carbonyl under phase-transfer conditions, has also been proposed to proceed *via* radical intermediates [$\text{PhCHMe}\cdot$ and $\cdot\text{Co(CO)}_4$]. Such radical species could be generated either by homolytic cleavage of $\text{PhCH(Me)Co(CO)}_4^3$ or by a single-electron transfer reaction of $\text{R}_4\text{N}^+\text{Co(CO)}_4^-$ and (2). We have now determined that 2,3-diphenylbutane (3) was formed in a 1.13/1.00 ratio of racemic/*meso* stereoisomers, by the reaction of (2) with carbon monoxide, toluene, 20% NaOH, benzyltriethylammonium chloride, and

cobalt carbonyl [23.8/1.0 ratio of (2)/ $\text{Co}_2(\text{CO})_8$] at room temperature and atmospheric pressure for 22 h. Therefore the largely radical nature of this coupling reaction is established. No acid was formed in this reaction, as in the Pd(dba)_2 catalysed process.

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References

- 1 H. Alper, *Adv. Organomet. Chem.*, 1981, **19**, 183.
- 2 H. Alper, J. K. Currie, and H. des Abbayes, *J. Chem. Soc., Chem. Commun.*, 1978, 311.
- 3 F. Francalanci and M. Foa, *J. Organomet. Chem.*, 1982, **232**, 59.
- 4 H. Alper and S. Amaratunga, *Tetrahedron Lett.*, 1980, 2603.
- 5 H. Alper, K. Hashem, and J. Heveling, *Organometallics*, 1982, **1**, 775.
- 6 J. J. Brunet, G. Sidot, and P. Caubere, *Tetrahedron Lett.*, 1981, **22**, 1013.
- 7 M. E. Fakley and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1977, 1444.
- 8 P. Bonn and G. Weill, *J. Chem. Phys.*, 1967, **64**, 253.