Addition of carbenes derived from aryldiazoacetates to arenes using chloro(tetraphenylporphyrinato)iron as catalyst

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Abstract

Chloro(tetraphenylporphyrinato)iron, Fe(TPP)Cl, is an active catalyst for the Büchner addition of para-substituted methyl 2-phenyldiazoacetates, 1a–d, to substituted benzenes. Yields greater than 70% have been achieved at temperatures ranging from 60–100°C. Reactions of substituted methyl 2-phenyldiazoacetates with benzene gave rapidly equilibrating mixtures of norcaradiene-cycloheptatriene valence isomers, 2a–d/2’a–d, in yields over 70%. Treatment of chlorobenzene with methyl 2-phenyldiazoacetate produced a regio-isomeric mixture of 7-carbomethoxy-2-chloro-7-phenylnorcaradiene/7-carbomethoxy-2-chloro-7-phenylcycloheptatriene, 3a/3’a, and 7-carbomethoxy-3-chloro-7-phenylnorcaradiene/7-carbomethoxy-3-chloro-7-phenylcycloheptatriene, 4a/4’a. When p-methylanisole was treated with methyl 2-phenyldiazoacetate at 80°C, a product that largely favored a fused cyclopropane structure, 7-carbomethoxy-2-methoxy-5-methyl-7-phenylnorcaradiene, 12a, was obtained along with the benzylic C–H insertion product methyl 3-(p-methoxyphenyl)-2-phenylpropionate, 13a. Heating the norcaradiene product 12a at 110°C yielded the ring-opened diarylacetate, 14a. The diene forms of the fluxional norcaradiene-cycloheptatriene systems were trapped with benzyne to give one stereoisomer of 3,3-disubstituted benzhomobarralenes, 18a–d. The norcaradiene-cycloheptatriene valence isomers were quantitatively converted into ring-opened diarylacetate products upon acidification in acetonitrile. Rates for the addition of methyl (p-chlorophenyl)diazoacetate to benzene were first order with respect to the diazo reagent. A concerted mechanism involving an iron carbene complex is proposed for these iron porphyrin-catalyzed Büchner reactions.