International Conference on Natural Products and Physiologically Active Substances (ICNPAS-2004)
September 12-17, 2004, Novosibirsk, Russia
Poster Presentation

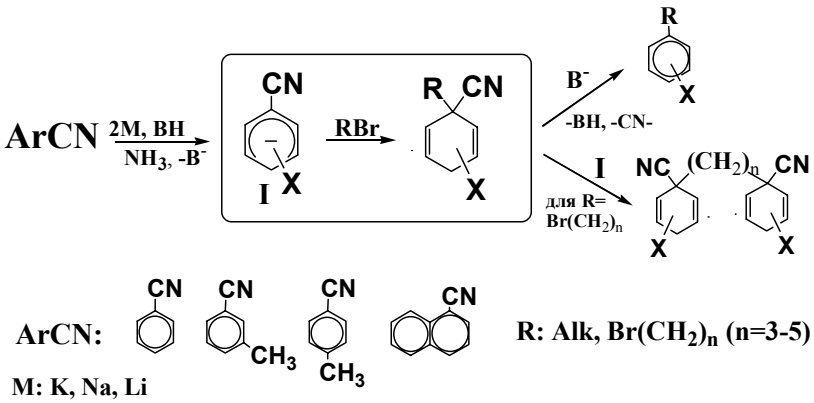
Synthesis of the Functionalized Cyclohexadienes Based on the Reactions of Cyanodihydroaryl Anions with Electrophiles

Tamara A. Vaganova[1], Pavel S. Yuferov[2], Vitalij D. Shteingarts[1]

[1]*N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry SB RAS*
Novosibirsk 630090, Lavrent'ev Avenue 9
e-mail: vaganova@nioch.nsc.ru
[2]*Novosibirsk State University, Novosibirsk 630090, Pirogova Street 2*

Substituted cyclohexadienes are widely used as precursors of fungicides and insecticides (H. Schepanski et al, PCT Int. Appl. WO 9929700 A2 1999), spirocompounds (G. Gavrilova et al, Bull. Rus. AS, 1997) and functionalized cyclopropane derivatives (J. Salaun, M. Bard, Curr. Med. Chem. 1995) endowed with a large spectrum of biological activity. One of the perspective approaches to the development of a convenient method of functionalized cyclohexadienes synthesis is based on employment of stable cyanodihydroaryl anions, being the products of two-electron reduction of arenecarbonitriles by alkaline metals in liquid ammonia, as anionic synthons for cyanodihydroarylation of electrophiles.

In the present work investigated has been the dependence of a structure and a ratio of the products of arenecarbonitriles reductive alkylation – cyanoalkyldihydroarenes and alkylarenes – on factors, such as the metal and protonating additives nature, co-solvent, temperature, and the order of reagents mixing. On this base the conditions allowing to prevent base initiated transformations of the reaction products and to prepare 1-cyano-1-alkyl-1,4-dihydroarenes in 80-90% yield have been found.



The interaction of sodium and lithium salts of cyanodihydroaryl anions with α,ω-dibromalkanes has been studied and the factors determining the degree of dehydrocyanation of the primary products and replacement of their bromine atom are revealed. The reaction of $Br(CH_2)_nBr$ with cyanodihydroaryl anions, generated by the action of lithium on benzonitrile, *m*- and *p*-tolunitriles, 1-naphthonitrile in NH_3/THF mixture at the presence of t-butanol, has been found to give selectively 1-cyano-1-bromalkyl-1,4-dihydroarenes, being the precursors of physiologically active substances.