AROMATIZED PROTONATION OF EXO-ELEMENT-SUBSTITUTED SEMIQUINOID SYSTEMS

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We recently showed that trienes of the exo-methylenedihydroarene type (I) can be aromatized by electrophilic agents E^+ (E = HgCl) with the formation of heteroorganic benzyl compounds (path A), and we advanced the hypothesis that this rearrangement takes place through an intermediate σ -complex (II) [1]. However, similar σ -complexes can also be generated in principle by a different path, namely, protonation of the corresponding exo-element-substituted alkylidenedihydroarenes such as (III), opening up the possibility of one more new path to the synthesis of heteroorganic benzyl compounds (path B):

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This type of reaction was first observed in our work with the exophosphorylated methylene dihydrobenzenes of the (III) type which we recently prepared ($E = POCl_2$) [2]. We showed that when treated with 18% aqueous HCl (20°C, 1 h), the triene (IV) is rearranged with a yield of 80% (with simultaneous hydrolysis of the dichlorophosphoryl group) to a dialkyl-substituted benzyl phosphonic acid (V) (mp 131°C), whose structure was established by elementary analysis, mass spectrometry (M⁺ 242), and PMR spectroscopy (a tri-spin system of ring protons and spin-spin splitting of the exomethylene-group protons with respect to the ³¹P nucleus with ²J = 22.7 Hz)*



The new acid-catalyzed skeletal isomerization of an unsaturated organophosphorus compound that we have discovered theoretically extends the circle of alkylidene dihydroarene ligands which can take part in electrophilic aromatization reactions and constitutes a new method of synthesizing arylmethyl derivatives of P(V).

*We cannot rule out the possibility that the compound obtained is a mixture of the 3,4- and 4,3-isomers.

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REACTION OF ETHYL TRIBUTYLSTANNYLACETATE WITH CARBONYL COMPOUNDS IN THE PRESENCE OF TRIBUTYLSTANNIC IODIDE

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We have found that Bu_3SnCH_2COOEt (I) reacts with PhCHO (II) in DMSO in the presence of Bu_3SnI (III) to form an addition product to the carbonyl group (IV). Compound (IV) is easily converted to a 3-hydroxy derivative (V) and a 3-acetoxy derivative (VI) of ethyl 3-phenyl-propionate:

 $\begin{array}{c} PhCHCH_{2}COOEt \\ Bu_{3}SnCH_{2}COOEt + PhCHO \rightarrow PhCHCH_{2}COOEt \\ & & & & \\ & &$

In the case of acetophenone (VII) a remetallization reaction takes place: $Bu_3SnCH_2COOEt + PhCOCH_3 \rightarrow CH_3COOEt + PhCOCH_2SnBu_3$

In the absence of (III), these reactions hardly occur. Without a catalyst, (I) is known to react only with activated aldehydes [1].

By analogy with the explanation given in [2] of the acceleration of electrophilic substitution of (I) in the presence of (III), we may assume that (III) catalyzes the enolization OEt

in the reactions of (I) with carbonyl compounds with the formation of $CH_2 = C$, which is $OSnBu_3$

an active intermediate [3]. The acceleration of the reactions in the presence of (III) (Lewis acid) may also be related to the increased electrophilic character of the carbonyl compound.

An equimolar solution of (I)-(III) in DMSO (1 M) was heated at 75°C. The course of the reaction was followed by PMR. After 6 h, (IV) was separated by distillation (85% yield), bp 145°C (0.02 mm). Hydrolysis of (IV) produced (V) (93%); reaction of (IV) with Ac₂O (50°C, 2 h) produced (VI) (75%). Under the same conditions, the reaction of (VII) for 36 h proceeded to the extent of \sim 80%. After treatment with bromine, gas-liquid chromatography (GLC) detected ethyl bromoacetate (10%), ethyl acetate (82%), α -bromoacetophenone (75%), and acetophenone (15%).

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