EXOPHOSPHORYLATION OF METHYLENEDIHYDROBENZENES

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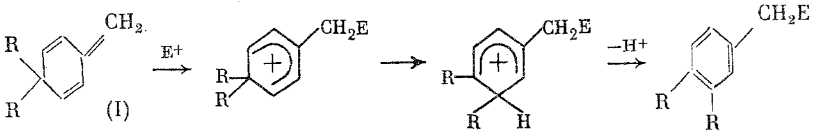
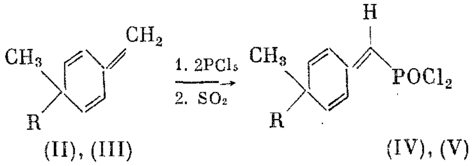
A characteristic property of trienes of the exomethylene cyclohexadiene type containing two alkyl substituents in a geminal unit (I) is their ability to undergo skeletal rearrangement when acted upon by electrophilic reagents (protonic acids, metal salts) with a transition to stable benzyl-type aromatic derivatives [1, 2].



We found in this work that this type of unsaturated compound can theoretically undergo another type of transformation on reaction with PCl_5, replacement of the exocyclic proton with conservation of the semiquinone π-bond system. In order to emphasize the difference between this reaction and aromatization processes, we call it exophosphorylation of methylenedihydrobenzenes



R = n-C_4H_9 (II), (IV), CCl_3 (III), (V)

We found that the reaction of two equivalents of freshly sublimed PCl_5 with trienes (II) [2] and (III) [3] in benzene (20°C, 1-2 h) after having treated the reaction mixture with gaseous SO_2 results in the formation of the dichloroanhydrides of semiquinoid phosphonic acids (IV) and (V) with a high yield (mp 67-68°C), whose structure was demonstrated by mass spectrometry [molecular ions with m/e 278 (IV) and 338 (V)] and PMR spectroscopy (a system of four nonequivalent ring protons and spin–spin splitting of the resonance absorption signal of the exocyclic proton with respect to the ^{31}P nucleus with ^2J = 31-33 Hz).

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