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SYNTHESIS OF THE FIRST PERCHLOROARYLACETYLENES

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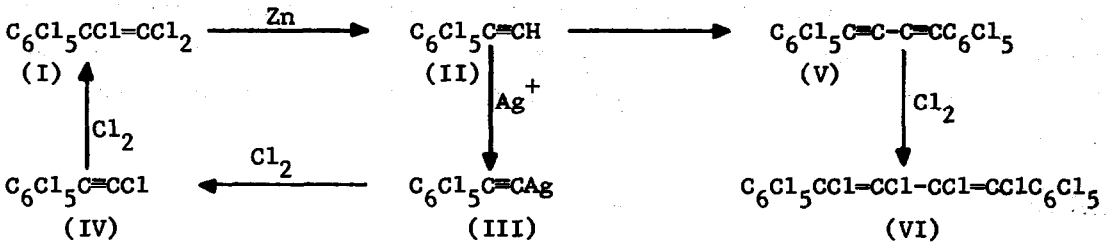
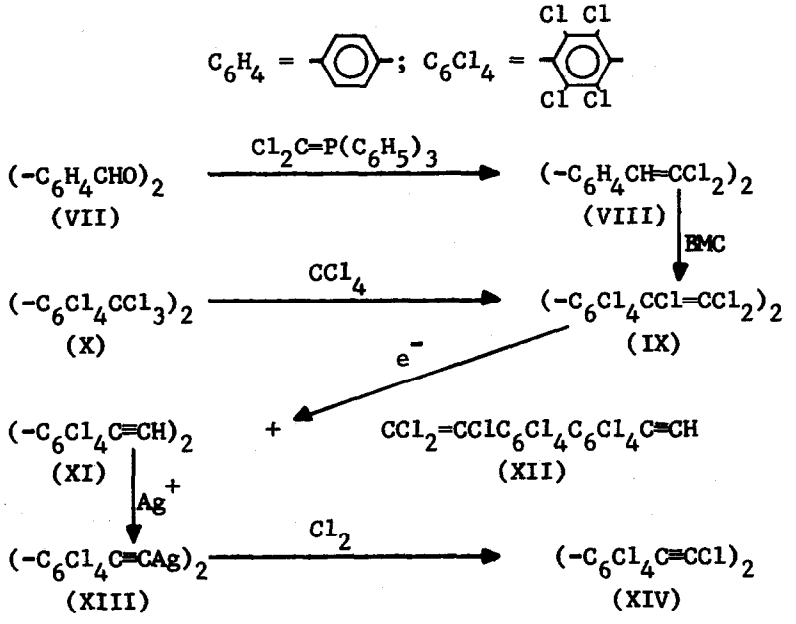
Some chlorocarbons, are excellent precursors which have extensively been used in Perchloro-Organic Chemistry.[1] For this purpose, it was desirable to synthesize and study perchloroarylacetylenes.

Perchlorostyrene[2] (I) reacts sluggishly with zinc in refluxing dioxane to give ω-H-pentachlorophenylacetylene (II; <85%), synthesized before by electrochemical reduction.[3] II, by treatment with $AgNO_3$ in aqueous THF (room temp.), gives the insoluble silver salt (III; 81%) (dec. ~280°). The reaction of III with Cl_2 in CCl_4 in the dark (room temp.) gives perchlorophenylacetylene (IV; 90%), mp 132-5°. IV chlorinated with Cl_2 in presence of sunlight in CCl_4 reverts to I (81%). II in pyridine with Cu_2Cl_2 and O_2, in the presence of TEMED,[4] yields perchlorodiphenylbutadiyne (V; 84%), mp 310-2° (dec.). Chlorination of V with Cl_2 and incandescent light, in CCl_4, gives trans,trans-perchloro-1,4-diphenylbutadiene (VI; 80%), mp 238-41°. VI does not change under ultraviolet light in CCl_4.



4,4'-Diformylbiphenyl (VII) reacts with dichloromethylenetriphenylphosphorane (from $CHCl_3$, $(CH_3)_3COK$ and $(C_6H_5)_3P$) giving 4,4'-bis(β,β-dichlorovinyl)biphenyl (VIII; 57%), mp 127.0-30.5°. VIII, with reagent BMC,[5] yields perchloro-4,4'-divinylbiphenyl (IX; 84%), mp 215.0-7.5°. IX can also be obtained by reducto-condensation between perchlorobi-p-tolyl[6] (X) and CCl_4 with diethyl hydrogen phos-

phonate and Cu_2Cl_2 (52%). Electrochemical reduction of IX by Seiber's method[4] results in a mixture of 4,4'-diethynyloctachlorobiphenyl (XI; max. 48%), dec.~220°, and ωH-undecachloro-4-vinyl-4'-ethynylbiphenyl (XII; max. 20%), mp 203-5° (dec.).



XI is converted into its silver salt (XIII; 91%), dec.~180°, with the silver-ammonia complex in aqueous THF. XIII with Cl_2, as in the synthesis of IV, yields the perchloro-4,4'-diethynylbiphenyl (XIV; 83%), dec. ~ 200°.

A remarkable result is the great stability of the silver salts reported above under heating or shock. It is concluded that the synthesis of perchloroarylacetylenes can contribute significantly to the development of Perchloro-Organic Chemistry.

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