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APPLICATION OF NITROGEN-CONTAINING SIX-MEMBERED PSEUDO-BASE TYPE COMPOUNDS ON ORGANIC SYNTHESIS (IV) —SYNTHESIS OF SPIRO-CYCLOPROPANE RING COMPOUNDS FROM THE REACTION WITH DICHLOROCARBENE

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Quinaldine(1) was dissolved in chloroform not containing any ethanol, 50% sodium hydroxide was added, and was stirred at room temperature in the presence of triethylbenzylammonium chloride as a phase-transfer catalyst, by which 3'-formyl-2,2,1',1'-tetrachloro-1a',2',3',7b'-tetrahydro-spiro[cyclopropane-1,2'-1'H-cyclopropa[c]quinoline](2) was formed in high yield. Treatment of 2 with lithium aluminum hydride gave a 3'-methyl compound(3). Formation of 2 passes through the intermediate formation of 2,2-dichloro-1'-formyl-1',2'-dihydro-spiro[cyclopropane-1,2'-quinoline](4). Presence of a small amount of polar solvent in the reaction mixture during formation of 2 results in the formation of 2-(2-chlorovinyl)-1,1-dichloro-1a,7b-dihydro-1H-cyclopropa[c]quinoline(5) as a major product.

Reaction for the formation of compounds possesing a spiro ring, like 2 was found to be specific for quinoline derivatives having an active methylene in the 2-position and to have a fair general character. Spiro ring compounds were formed from 2-methyl(or ethyl)-x-methyl(or ethoxy)quinolines, 2,9-dimethyl-o-phenanthroline, 2,7-dimethyl-1,8-naphthyridine, 2,3-dimethylquinoxaline, 6-methyl(or ethyl)-phenanthridine, aceton-anil, a model compound of 1. But acetophenon-anil(6) did not give N-formyl derivative, and gave N-H derivative, 1,1-dichloro-N,2-diphenyl-cyclopropanecarboxylic acid amide. The difference of this reactivity is because aromatic C-N double bond, like 1, with dichlorocarbene forms N-ylide as a intermediate, and Schiff base's C-N double bond, like 6, with dichlorocarbene forms dichloroaziridine as a intermediate.

Spiro ring compound was not formed from 1-methylisoquinoline and gave 1,1-dichloro-3-ethoxy-2-formyl-3-methyl-1a,2,3,7b-tetrahydro-1H-cycloprop[c]isoquinoline.