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

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Quinaldine(1) was dissolved in chloroform not containing any ethanol, 50% so-
dium 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-cyclo-
propa[c]quinoline](2) was formed in high yield. Treatment of 2 with lithium alu-
minum 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-cyclopropan[c]quinoline(5) as a major product.

Reaction for the formation of compounds possessing 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-phenanthro-
line, 2,7-dimethyl-1,8-naphthyridine, 2,3-dimethylquinoxaline, 6-methyl( or ethyl)-
phenanthridine, acetan-anil, a model compound of 2. But acetophenon-anil(6)
did not give N-formyl derivative, and gave N-H derivative, 1,1-dichloro-N,2-diphe-
nyl-cyclopropane-carboxylic acid amide. The difference of this reactivity is be-
cause aromatic C-N double bond, like 1, with dichlorocarbene forms N-ylide as a in-
termediate, 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.

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