

DICHLOROCARBENE INSERTION REACTIONS

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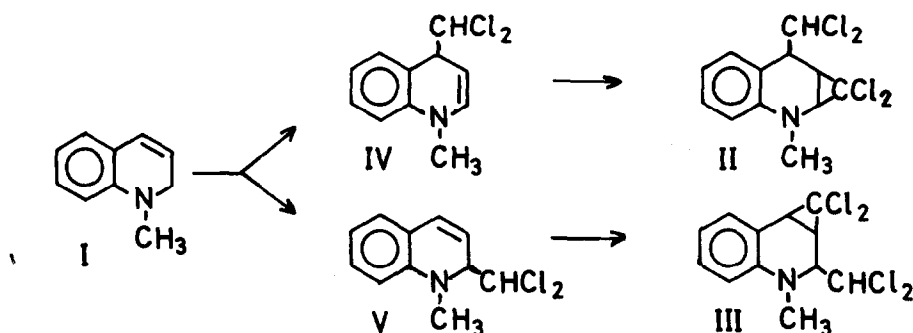
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The reactions of dihalocarbenes towards 1,2-dihydroquinolines have been examined. The relatively stable 1-methyl-2-phenyl-1,2-dihydroquinoline was reacted with dibromocarbene (from phenyl(tribromomethyl)mercury¹) with no result. Treatment with dichlorocarbene, from ethyl trichloroacetate² and from chloroform/50 % NaOH in water^{3,4} was negative too. The supposedly more reactive 1-methyl-1,2-dihydroquinoline(I)⁵ also was inert to the first two of these methods. The highly reactive dichlorocarbene⁶ from chloroform/50 % NaOH, however, reacted with I when stirred in an ice-bath for 6 hours, then at room temp. overnight. Isolation and chromatography on silica gel gave two products which decomposed upon heating. Chromatography on alumina gave the major component in 30 % yield by elution with hexane/benzene (10:1). The high resolution mass spectra of both compounds showed the same molecular ion corresponding to $C_{12}H_{11}Cl_4N$ and also a similar fragmentation. Thus a simple addition product, as found in a 4-alkoxy-1,2-dihydroquinoline^{7,8}, was not possible.

Both compounds were CH insertion products, for which the structures II and III are proposed. The minor compound which was eluted in 20 % yield had a NMR spectrum in $CDCl_3$ which together with the chemical evidence discussed below is in agreement with structure II. The proton from the dichloromethyl group resonated as a doublet at 3.80 τ and coupled to the 4-methine proton at 6.30 τ , while the 3-methine proton was found as a double doublet at 7.40 τ , the 2-methine proton as a doublet at 6.80 τ and the N-methyl singlet at 6.87 τ . The major component(III) had the dichloromethyl proton doublet at 4.10 τ , the 2-methine doublet at 6.05 τ the 3- and 4-methine protons falling together at 7.2 τ and the N-methyl singlet at 7.05 τ . Both had four aromatic protons at 2.7-3.5 τ .



In order to examine the formation of these compounds the dihydroquinoline (I) was reacted with 50 % NaOH in deuterated chloroform and the reaction followed in the NMR. After a few minutes at room temp. three products were found and identified as II, III and V. The NMR spectrum of V had the 4-vinyl proton at about 3.4 τ together with the four aromatic protons, the 3-vinyl proton at 4.15 τ , the 2-methine proton at 5.60 τ , the dichloromethyl proton at 4.40 τ and the N-methyl protons at 6.90 τ . On further reaction the proportion of III increased while V disappeared. The amount of II did not change. The formation of the intermediates IV and V is similar to the synthesis of 4-dichloromethyl-4H- and 2-dichloromethyl-2H-1-benzothiopyran from 2H-1-benzothiopyran⁹. The higher reactivity of IV compared to V towards addition of dichlorocarbene is similar to the reactivity of the benzothiopyrans, while the formation of III is explained by the highly reactive dichlorocarbene which has been used. Parham et al.⁹ also reported the formation of a diadduct, the structure of which was not resolved. The NMR spectrum of this diadduct agrees very well with the sulphur analogue of II having a dichloromethyl proton doublet at 3.65 τ , a 4-methine proton double doublet at 6.60 τ , a 2-methine proton doublet at 6.90 τ , a 3-methine proton double doublet at 7.38 τ , in addition to the aromatic protons at 2.8 τ . The origin of this compound must be the addition of dichlorocarbene to 4-dichloromethyl-4H-1-benzothiopyran.

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