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A CONVENIENT METHOD FOR SYNTHESIS OF 3,4,5-TRICHLORO-PYRIDAZINE

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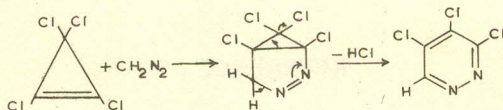
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Trichloropyridazines are highly reactive and have been used extensively for synthesis of pyridazinobenzothiazines [1-3], pyridazinobenzoxazines [3] and dipyridazinothiins [4].

In the course of our investigation on the reaction of tetrachlorocyclopropene with a variety of 1,3-dipolar compounds, we found that tetrachlorocyclopropene reacted with diazomethane at room temperature to give 3,4,5-trichloropyridazine in 70% yield. Our procedure simplifies the synthesis of 3,4,5-trichloropyridazine in the way that it avoids the use of copper catalyst and carrying out the reaction at -50° as has been mentioned by earlier workers [5]. Moreover, the yield is much higher than the reported 50% [5], and large quantity of the material can be prepared in much shorter time. The product obtained is pure enough for synthetic work.

Our study of the reaction of tetracyclopropene with various 1,3-dipolar compounds [6] strongly supports the mechanism in which 3,4,5-trichloropyridazine is probably formed via the intermediate formation of a strained ring II followed by ring opening with the loss of HCl.



Analogous mechanism has been proposed [7,8] for similar reactions of diphenylcyclopropenone and di-n-propylcyclopropenone with diazomethane.

A solution of diazomethane [9] (0.052 mole in 100 ml ether) was added dropwise, at room temperature, to a magnetically stirred solution of tetracyclopropene [10,11] (from 8.9 g, 0.05 mole, in 100 ml ether) over a period of 30 min. The solid mass, obtained after the removal of ether on a rotary evaporator at room temperature, on washing with petroleum ether ($30-40^{\circ}$) yielded 6.5 g (70%) of 3,4,5-trichloropyridazine mp $55-56^{\circ}$ (lit. [5] mp for the crude product $51-53^{\circ}$). A sample purified by sublimation had mp 61° . Structural evidences were obtained by spectral data.

We have also observed that solutions of 3,4,5-trichloropyridazine produces severe blisters on coming in contact with the skin [12].

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