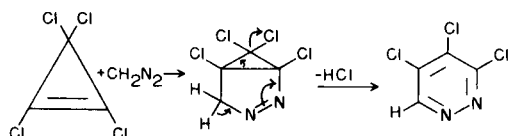


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A Novel Synthesis of 3,4,5-Trichloropyridazine

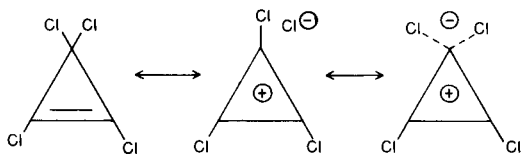
Harvey M. Cohen

In the course of our investigation on the reaction of tetrachlorocyclopropene with carbenes and methylene transfer reagents, we found that tetrachlorocyclopropene reacted with diazomethane to give 3,4,5-trichloropyridazine in 51% yield. The mechanism is believed analogous to that proposed (1,2) for similar reactions of diphenylcyclopropenone and di-*n*-propylcyclopropenone with diazomethane. The 3,4,5-tri-



chloropyridazine was found to crystallize explosively on removal of solvent indicating that a strained ring intermediate such as shown above rearranged only on attempted isolation.

It is interesting to note that tetrachlorocyclopropene is inert to phenyltrichloromethylmercury in refluxing benzene solution indicating that it is less reactive than tetrachloroethylene (3) despite its lower steric hindrance at the double bond. This lack of reactivity could be explained by assuming ionic resonance contributions similar to those written for cyclopropenones.



Tetrachlorocyclopropene is rapidly decomposed by iodomethylzinc iodide in ether, zinc iodide in ether and sodium iodide in acetone. Since tetrachlorocyclopropene is stable to zinc chloride (4), decomposition probably proceeds via an iodinated cyclo-

propene. The initial reaction would be analogous to the rapid reaction of boron tribromide with tetrachlorocyclopropene to yield tetrabromocyclopropene (5).

EXPERIMENTAL

Elemental analysis was done by Dr. S. M. Nagy, Microchemical Laboratory, Massachusetts Institute of Technology, Cambridge, Mass. All reactions were performed under an atmosphere of purified nitrogen.

Reaction of Tetrachlorocyclopropene With Diazomethane.

A solution of diazomethane (6,7) (0.15 mole) in 170 ml. of diethyl ether was added dropwise (90 minutes) to a stirred mixture of 26.7 g. (0.15 mole) of tetrachlorocyclopropene, and 0.7 g. of copper powder maintained at -50° . After addition was complete, the yellow diazomethane color persisted. The mixture was allowed to warm to room temperature overnight, then filtered. The filtrate was concentrated by distillation until the pot temperature reached 55° and about 75 ml. of liquid remained. The heating mantle was removed. Within 30 minutes, the residual liquid had crystallized explosively (completely covering the inside of the flask and forcing its way out the joints onto the outside apparatus). The solid was dried *in vacuo* then extracted with pentane. Evaporation of the pentane yielded 14 g. (51%) of 3,4,5-trichloropyridazine (m.p. $51-53^\circ$) purified by sublimation ($40-50^\circ/1\text{ mm.}$) (m.p. 60.5°), (lit. (8) m.p. 61°).

Anal. Calcd. for $\text{C}_4\text{HCl}_3\text{N}_2$: C, 26.19; H, 0.55; Cl, 57.99; N, 15.27. Found: C, 25.92; H, 0.44; Cl, 58.00; N, 14.93.

Conclusive identification was made by comparison (infrared spectrum and mixed melting point) with authentic material prepared from 4,5-dichloropyridazone (8). As indicated by Castle and Kaji (9), solutions of 3,4,5-trichloropyridazine are strongly vesicating.

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