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A NEW METHOD OF RING EXPANSION

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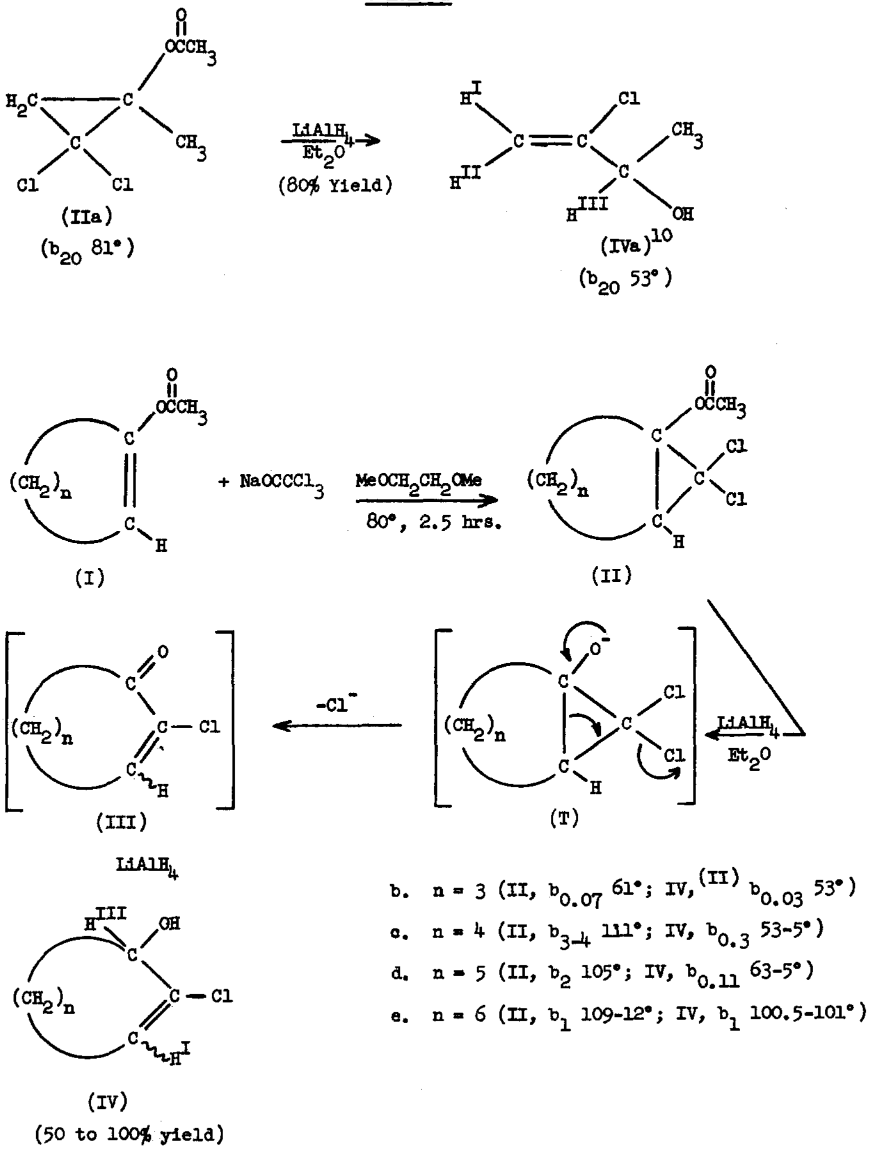
General methods of carbocyclic ring synthesis have been the subject of considerable study.(1) The advent of carbene(2) and related(3) syntheses of three-membered rings has focused recent attention in this area on the utilization of these intermediates to expand rings by one-carbon units. None of the three-membered ring expansion methods thus far developed could be considered as being of general synthetic utility due to competing side reactions,(4) difficulty in preparation of starting materials,(5) or inherent limitations in their chemistry.(6)

We now report a new method of three-membered ring opening and one-carbon, ring enlargement. The procedure employs mild conditions, proceeds in a predictable manner, and as far as it has been investigated is not subject to the above-mentioned limitations. Scheme I exemplifies the method with the examples we have studied.

Readily available ketones were easily converted to the enol esters (I) by the method of Hagemeyer and Hull.(7) Previous reactions of dichlorocarbene with enol esters have been rather discouraging.(8) However, we were able to obtain yields of 25 to 50% in the present instances without attempts of optimization.(9) The acetoxy-gem-dichlorocyclopropanes, II, on treatment with a slight excess of lithium aluminum hydride in ether at

Scheme I



b. n = 3 (II, $b_{0.07}$ 61°; IV,(11) $b_{0.03}$ 53°)
c. n = 4 (II, b_{3-4} 111°; IV, $b_{0.3}$ 53-5°)
d. n = 5 (II, b_{2} 105°; IV, $b_{0.11}$ 63-5°)
e. n = 6 (II, b_{1} 109-12°; IV, b_{1} 100.5-101°)

room temperature readily gave the ring expanded α-haloalkenyl carbinols, IV, in good yields.

The carbinols IV were free of contaminants and side products as evidenced by GLC. Simple distillation at reduced pressure in each case gave the analytically pure product. The infrared and NMR spectra were consistent with all assigned structures. Unsaturation and hydroxyl absorptions occurred at 1630-70 and 3400-3570 cm^{-1}, respectively, in the infrared spectra of the neat liquids.

The NMR spectrum of IVa yielded unequivocal proof of its structure. At 60 Mc in CCl_4 (TMS) the following absorptions were in evidence: CH_3, a doublet at 1.34δ (J = 6.6 cps); H^{III}, a quadruplet at 4.33δ (J = 6.6 cps); H^{I}, a doublet at 5.50δ (J = 1.3 cps); H^{II}, a doublet at 5.23δ (J = 1.3 cps); and O-H, a broad absorption centered at 4.15δ. All absorptions integrated for the correct number of protons.

The NMR spectra of the remaining four compounds, IVb-e, were observed at 100 Mc of CCl_4 (TMS) solutions. The spectra of IVb and IVc were straightforward with the following respective absorptions: H^{I}, triplets at 5.80δ (J = 4.0 cps) and 5.90δ (J = 6.6 cps); H^{II}, triplets at 4.01δ (J = 4.0 cps) and 4.27δ (J = 4.8 cps); $(CH_2)_n$, complexes at 1.4-2.2 and 1.4-2.3δ; OH, sharp singlets at 4.22 and 4.18δ. Although, the spectra of IVd and IVe were consistent with the assigned structures, they were complicated by the presence of both the cis and trans isomers and could not be conveniently presented in detail here.

The intricacies of this reaction were not studied. However, it seemed that the mechanism could readily be explained by describing a path through the transient anion T or some complexed equivalent. The other proposed intermediate III was not isolated since partial reduction experiments yielded mixtures containing only II and IV. It was therefore concluded that if III had existed, it must have reacted with lithium aluminum hydride at a much faster rate than the corresponding II.

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