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HEMIACETAL FORMATION IN SULPHURIC ACID HYDROLYSIS OF A CHLORO OLEFIN

E.P.Woo, K.T. Mak, and H.N.C. Wong
Department of Chemistry, The Chinese University of Hong Kong
Shatin, Hong Kong.

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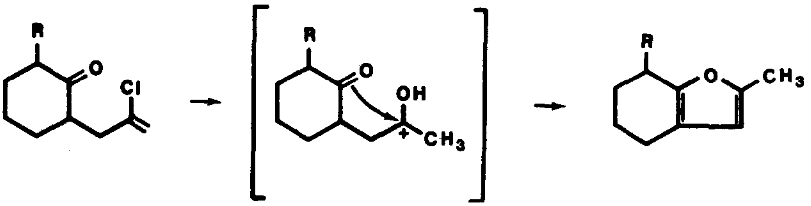
The well established behaviour of vinyl chlorides as masked carbonyl functions has been applied to the syntheses of cyclic compounds. Although still lacking unequivocable evidences, it is generally believed that sulphuric acid converts vinyl chlorides into the corresponding carbonyl compounds before further reactions take place[1]. In relation to syntheses of natural products, cycloalkanones bearing β-chloroene side chain have been widely studied. Products from these substrates appear to be largely determined by the nature of the side chain and, to a lesser degree, by the size of the ring. Four categories emerge from available literatures.

(1) When the side chain is derived from 2,3-dichloropropene, furans are generated[2] from the nucleophilic attack of one carbonyl oxygen at the other carbonyl carbon(eq 1).

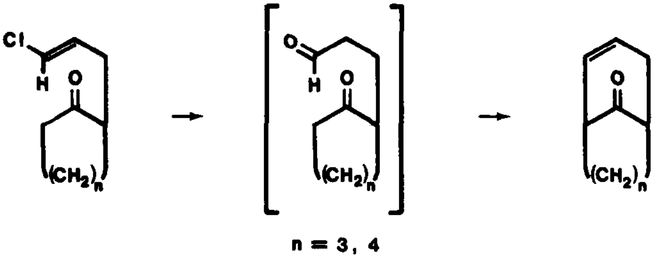
(2) When the side chain is derived from 1,3-dichloropropene, the products are bicyclo[n.3.1]alkenones[3]. The reaction presumably proceeds via the ketoaldehyde(eq 2).

(3) With 1,3-dichloro-2-butene as alkylating agent, the resulting 2-(3'-chlorocroty)cycloalkanones can give bicyclo[n.3.1]alkenones or bicyclo [(n+1).4.0]alkenones[4,5]. The direction of the aldol condensation depends on the nature of the substituents at the 2-position(eq 3).

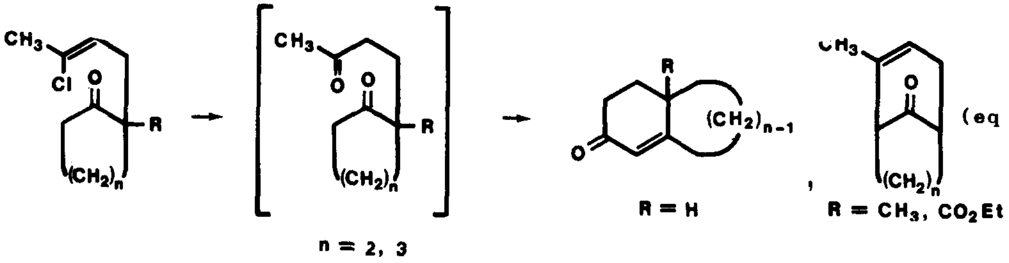
(4). The last reported pathway[5] with 3-chlorocrotyl side chain is the nucleophilic attack of the enol at the chlorocarbonium ion. This is analogous to the chloro olefin annelation[6](eq 4).



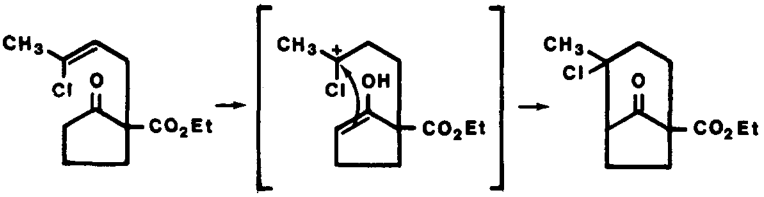
(eq 1)



(eq 2)

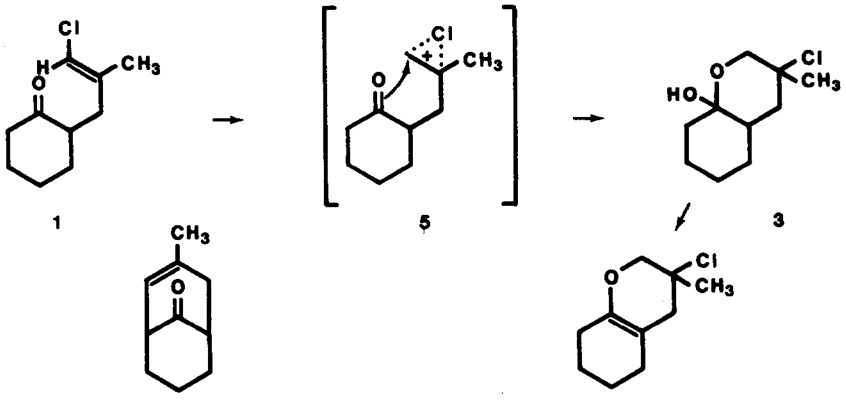


(eq 3)



(eq 4)

We now wish to report that reaction of 2-($2'$-methyl-$3'$-chloroallyl)-cyclohexanone^7(1)—— which according to the above classification should give 3-methylbicyclo [3.3.1] non-2-en-9one(2)—— proceeds by a hitherto unknown path in conc. sulphuric acid(eq 5). The only product isolated(85%, m.59-61°) was a hydroxy compound whose molecular formula represents the net addition of one molecule of water. A hemiacetal structure(3) is indicated from spectral analysis. Its ir spectrum shows only OH absorptions at 3600



1 2 5 3 4 (eq 5)

3420, and 1050cm^{-1}; its mass spectrum[8] exhibits ions at m/e 206, 204(M$^+$), 188, 186(M$^+$ - H_2O), 173, 171(M$^+$ - H_2O-CH_3), and 151(M$^+$ - H_2O-Cl). The nmr spectrum[8](220MHz) consists of a singlet(τ6.36, 1H, O-H), an AB quartet (τ6.45, J=10Hz, 2H, -CH_2O-), and a broad envelope(τ7.9-8.4, 14H, including a sharp singlet of ca. 3H).

The hemiacetal 3 dehydrates readily at temperatures above its melting point[9] to the enolether 4(b.61°/0.2mm). The structural assignment[10] is based on its spectral data [nmr: singlet, τ6.6, 2H(-CH_2O-); multiplet, τ7.2-8.2, 6H(allylic H); multiplet, τ8.2-8.5, 4H(-CH_2-); singlet, τ8.6, 3H(-CH_3); ir: 1700(w), 1200cm^{-1} (C=C-O); mass spect: M$^+$ at m/e 188, 186 remaining portion very similar to that of 3] . The formation of the same 2,4-dinitrophenylhydrazone from both 3 and 4 lends further support to the structures assigned.

The formation of 3 is unusual in that it does not follow any of the known routes. A plausible rationalization lies in the intervention of a chloronium ion(5) which then suffers nucleophilic attack by the carbonyl oxygen. In contrast to the formation of furans (eq 1), the vinyl chloride moiety of 1 is not hydrolyzed. There is, however, a certain relationship between the present reaction and that depicted in eq 4: the former may be regarded as an O-alkylation, whereas the latter, a C-alkylation.

A further investigation on the scope and limitation of this reaction is underway.

Acknowledgements

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Notes and References

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(9) Dehydration is complete in 15 min at 90°.

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