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THE REACTION OF HYPOCHLOROUS ACID WITH OLEFINS. A CONVENIENT SYNTHESIS OF ALLYLIC CHLORIDES

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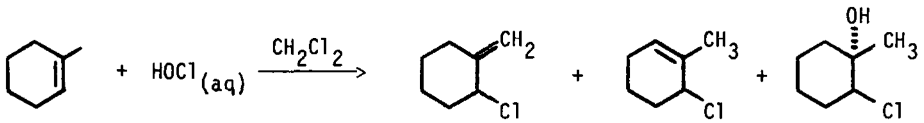
Summary: The reaction of HOCl with more highly substituted olefins in methylene chloride affords allylic chlorides in 60-80% isolated yields. The utility of the reaction is illustrated with the synthesis of Rose oxide and α-monoterpenes.

We wish to report a synthetically important reaction of hypochlorous acid with more highly substituted olefins leading to allylic chlorides rather than chlorohydrins.[1] This modification involves the trivial use of methylene chloride as solvent for the olefin.[2] The reaction is easily performed by adding dry ice slowly to a mixture of 4.1 g of "70%" calcium hypochlorite (40 mmol of HOCl), 20-40 mL of water, 40 mmol of olefin and 200 mL of methylene chloride. In this manner 1-methylcyclohexene[3] affords 2-chloro-1-methylenecyclohexane (1)[5] and 3-chloro-2-methylcyclohexene (2) in 60% yield and only 25% of chlorohydrin 3. In the absence of methylene chloride chlorohydrins[6] are obtained exclusively from 1-methylcyclohexene.



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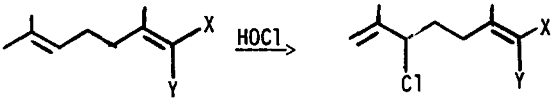
Employing these conditions, olefins such as 1-octene, cyclooctene and cyclohexene yield chlorohydrins exclusively or predominantly[7] suggesting this addition-elimination reaction is limited to more highly substituted olefins.

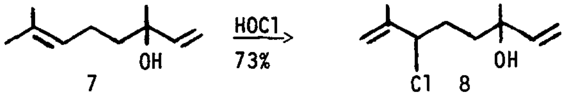
The reactions of HOCl appear to be regiospecific and in many of the cases examined to date

HOCl discriminates readily between two or more double bonds. Furthermore, functional groups such as alcohols, aldehydes, epoxides, ethers, esters, ketones and nitriles are not altered in competition with an olefin. Thus citral (4a), methyl geranate (4b), geraniol (4c), geranyl acetate (4d), nerol (4e), dimethyl ester (4f) and dinitrile (4g) afford the corresponding allylic chlorides (5a-g)[8] in 60-80% isolated yields.



4a: X = CHO
4b: X = CO_2Me
4c: X = CH_2OH
4d: X = CH_2OAc
4e: Y = CH_2OH
4f: X = Y = CO_2Me
4g: X = Y = CN
5a-g

The absence of participation of an alcohol function is not only observed with geraniol (4c), nerol (4e) and citronellol (6), but with linalool (7) and isopulegol (9) as well.



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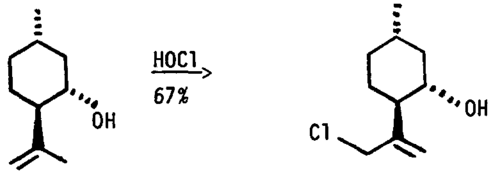

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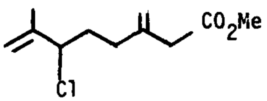
The selectivity of HOCl toward the terminal trisubstituted double bond in acyclic terpenes is further demonstrated[9] in the reaction with methyl γ-geranate,[11] myrcene, citral enol acetate, farnesol[12] and nerolidol where allylic chloride 11 (83%), 12 (60%), 13 (66%), 14 (78%) and 15 (76%), respectively, are obtained.



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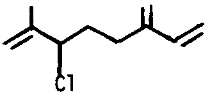

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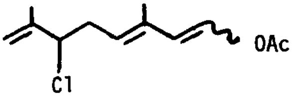

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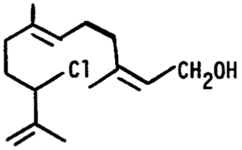

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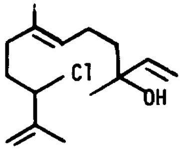

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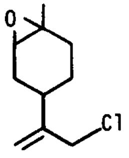
Limonene monoxide and carvone react cleanly at the isopropenyl group to afford 16 and 17 in high yield. The reaction with Δ^3-carene is uneventful yielding (68%) chlorides 18 and 19 in a 3:1 ratio.



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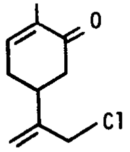

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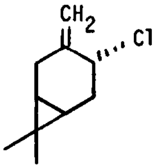

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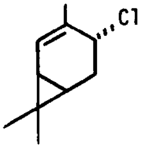

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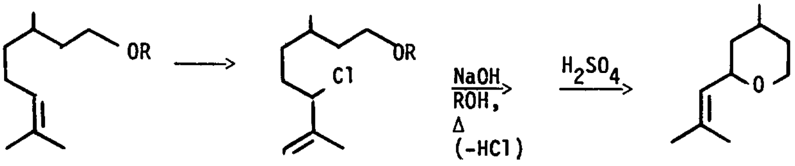
Finally, we illustrate the utility of the HOCl reaction with the syntheses of Rose oxide (20)[14] (*ca.* 50% overall yield) and α-monoterpenes 21a-c[15] as outlined below.



6: R = H or Ac

20

5a-c

21a-c: X = CHO, CO_2Me or CH_2OH

Further studies of the reaction of unsaturated compounds with HOCl and the use of the resulting allylic chlorides as synthetic intermediates are in progress.

REFERENCES AND FOOTNOTES

1. For examples of the reaction of HOCl with olefins see: (a) A. Michael and V. L. Leighton Ber., 39, 2157 (1906); (b) A. Wohl and H. Schweitzer, ibid., 40, 92 (1907) (c) G. G. Henderson and C. A. Kerr, ibid., 125, 102 (1924); (d) A. Kotz and G. Busch, J. Prakt. Chem., 119, 1 (1928); (e) E. H. Farmer and C. G. B. Hose, J. Chem. Soc., 962 (1933); (f) J.Colonge and L. Cumet, Bull. Soc. Chim. Fr., 838 (1947); (g) J. A. McRae, R. Y. Moir, J. W. Haynes and L. G. Ripley, J. Org. Chem., 17, 1621 (1952); (h) D. A. Craw, J. Chem. Soc., 2515 (1954); (i) A. Chung and C. Israel, ibid., 2667 (1955); (j) P. B. D. de la Mare and A. Salama, ibid., 3337 (1956); (k) A. Guyer, A. Bieler and E. Pedrazzetti, Helv. Chim. Acta, 39, 423 (1956); (l) J. G. Traynham and O. S. Pascual, Tetrahedron, 7, 165 (1959); (m) B. Blouri, M. Laroche and P. Rumpf, Bull. Soc. Chim. Fr., 1240 (1964); (n) J. R. Shelton and L. Lee, J. Org. Chem., 24, 1271 (1959); (o) J. A. Hopwood and D. L. H. Williams, J. Chem. Soc (B), 718 (1968); (p) M. Muhlstadt, K. Schulze and G. Winkler, J. Prakt Chem., 317, 166 (1975).

2. For the reaction of highly hindered olefins with HOCl in acetone to form vinyl chlorides see: S. Marmor and J. G. Maroski, J. Org. Chem., 31, 4278 (1966).

3. Essentially identical results are observed using HOCl generated from calcium hypochlorite and boric acid, distilled HOCl[4] or an ether solution of HOCl in the presence of a drying agent. When conducted in the absence of a drying agent the proportion of chlorohydrin increases markedly.

4. R. L. Taylor and C. Bostock, J. Chem. Soc., 444 (1912).

5. 2-Chloro-1-methylenecyclohexane (1) undergoes considerable rearrangement to 1-chloromethylcyclohexene during glc at 150°C.

6. H. Bodot, J. Jullien and M. Mousseron, Bull. Soc. Chim. Fr., 1097 (1958).

7. The reaction with cyclohexene under these conditions affords approximately 10% of 3-chlorocyclohexene.

8. Allylic chloride 5a-g, 8, 11, 12 and 13 can be distilled in vacuo with no sign of allylic rearrangement. The $CH_2=C(CH_3)-CH-Cl$ group in these compounds is characterized by NMR signals at δ 4.3-4.4 ppm ($-CH-Cl$) and 4.95 and 5.05 ppm for the terminal methylene group.

9. Limonene affords a mixture of monochlorides where reaction of the internal double bond appears to predominate somewhat over reaction at the terminal double bond. α and β-Pinene mainly undergo ring opening[10] to yield menthyl chlorides along with other products.

10. J. Wolinsky and M. K. Vogel, J. Org. Chem., 42, 249 (1977).

11. R. H. Bedoukian and J. Wolinsky, J. Org. Chem., 40, 2154 (1975).

12. The farnesol used in this work was a mixture of E and Z isomers.

13. B. A. Arbuzov, Z. G. Isaeva and G. S. Bikbulatova, Proc. Acad. Sci U.S.S.R., 195, 804 (1970).

14. For syntheses of Rose oxide see E. H. Eschinasi, J. Org. Chem., 35, 1097 (1970) and references cited therein.

15. See J. L. Simonsen, "The Terpenes", Vol. 1, University Press, Cambridge, for historical references to these compounds.

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