

CHEMISTRY OF GEM-DIHALOCYCLOPROPANES VIII

A CONVENIENT PREPARATION OF GEM-DIBROMOCYCLOPROPANES

L. Skattebøl, G. Aziz Abskharoun and T. Greibrokk

Department of Chemistry, University of Oslo, Oslo 3, Norway

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The method described by Makosza and Wawrzyniewicz^{1,2,3} is a most useful addition to the arsenal of dihalocarbene-generating reactions⁴. The two-phase reaction system consisting of the olefins, chloroform, and 50% aqueous sodium hydroxide with a tetraalkylammonium chloride as catalyst provides a particularly reactive dichlorocarbene^{2,3} that results in high yields of gem-dichlorocyclopropanes. It has been reported² that the exchange of chloroform with bromoform resulted in poor yields of the corresponding gem-dibromocyclopropanes. Depending on the structure, the latter can be converted with alkyllithium into allenes⁵, bicyclobutanes⁶ and other strained hydrocarbons⁷. These reactions would be the more valuable from a preparative point of view if the starting material could be prepared by the Makosza method, and in the present communication we want to report that under the proper conditions good yields of gem-dibromocyclopropanes were obtained from various olefins by that procedure.

The reactions were carried out essentially as described previously^{1,2} for the dichlorocarbene generating reactions using benzyltriethylammonium chloride as catalyst. The results of some of our experiments are recorded in the Table. The amount of bromoform necessary for obtaining a good yield clearly depends on the structure of the olefin; in the case of styrene a one molar excess is sufficient while in the reaction of 2-methyl-2-butene a considerably larger excess of bromoform was required in order to obtain a comparable yield. The reaction time is another important factor; less than twentyfour hours resulted

in decreased yields. On the other hand the amount of catalyst appears to be less critical. Our experience also suggests that efficient stirring is required. The use of benzene as solvent did not improve the yields.

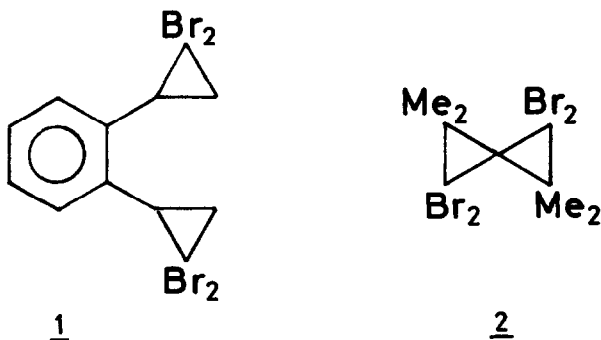
Table

Reactions of Olefins with Bromoform, 50% aqueous Sodium Hydroxide and Catalyst

Olefin	CHBr ₃ : Olefin ^x	Catalyst ^f	Time (hrs)	Product	Yield %
Styrene	3	1	72	1,1-Dibromo-2-phenylcyclopropane	66
"	3	1	48	"	64
"	3	1	24	"	66
"	2	1	48	"	65
"	2	1	24	"	66
"	1	1	24	"	26 ^Δ
"	2	3	24	"	65
Cyclohexene	3.5	2	96	7,7-Dibromobicyclo(4.1.0)-heptane	72
"	2	2	24	"	65
Cyclooctene	2	1	48	9,9-Dibromobicyclo(6.1.0)-nonane	51 ^Δ
"	2	1	24	"	37
"	2	2.5	24	"	47
"	3	1	48	"	70
2-Methyl-2-butene	4	2	72	1,1-Dibromo-2,2,3-trimethylcyclopropane	73
"	2	1	72	"	40

^xmolar ratio ^fg benzyltriethylammonium chloride per mole olefin ^ΔAddition of benzene as solvent in a molar amount equivalent to that of the alkene had insignificant effect on the yield.

The reaction is also useful for preparing diadducts from dienes; for example *o*-divinylbenzene gave under the above conditions the corresponding spiro-pentane(1)⁸ in 50% yield, and tetramethylallene yielded 10% of the diadduct(2)⁹.



Our results indicate that styrene is more reactive than 2-methyl-2-butene contrary to that which has been observed previously with other dibromocarbene-generating reagents¹⁰. According to the postulated¹ mechanism the reaction takes place at the phase boundary; the haloform anion reacts with the catalyst which then becomes soluble in the organic phase where dihalocarbene is liberated. Clearly, properties other than the nucleophilicity of the olefin will have to play an important role according to the above mechanism; for instance, the olefin will exert an effect on the solubility of the catalyst-haloform ion complex and thereby influence the reaction.

Our preliminary results show that the Macosza method is quite useful for the preparation of gem-dibromocyclopropanes. The maximum yield obtained from each of the olefins in the present work compares well with those obtained by other methods. In our view the inconvenience of the long reaction time is more than compensated for by the extreme experimental simplicity, and the reaction should be the method of choice in many cases. Our results indicate, however, that there is no general set of conditions that will result in optimum yield for any kind of olefin.

References

1. M. Makosza and W. Wawrzyniewicz, Tetrahedron Lett., 4659 (1969).
2. E.V. Dehmlow and J. Schönefeld, Ann. Chem., 744, 42 (1971).
3. E.V. Dehmlow, Tetrahedron, 27, 4071 (1971);
E.V. Dehmlow, ibid., 28, 175 (1972);
G.C. Joshi, N. Singh, and L.M. Pande, Tetrahedron Lett., 1461 (1972).
4. W. Kirmse, "Carbene Chemistry", Acad. Press, London 1971.
5. L. Skattebøl and S. Solomon, Org. Synthesis 49, 35 (1969) and references therein.
6. W.R. Moore and H.R. Ward, J. Am. Chem. Soc., 83, 2019 (1961);
W.R. Moore, K.G. Taylor, P. Müller, S.S. Hall, and Z.L.F. Gaibel, Tetrahedron Lett., 2365 (1970); L. Skattebøl ibid., 2361 (1970).
7. L. Skattebøl, J. Org. Chem., 31, 2789 (1966).
8. L. Skattebøl and Naser-ud-din, unpublished work; L. Skattebøl, J. Org. Chem. 29, 2951 (1964).
9. L. Skattebøl, Tetrahedron Lett., 2175, (1965).
10. P.S. Skell and A.Y. Garner, J. Am. Chem. Soc., 78, 5430 (1956).