Tetrahedron Letters No.22, pp. 1749-1752, 1965. Pergamon Press Ltd.
Printed in Great Britain.

CONVERSION OF OLEFINS TO DIHALOCYCLOPROPANES WITH SODIUM HYDROXIDE AND HALOFORMS

Gene C. Robinson
Ethyl Corporation, Baton Rouge, La., U. S. A.

(Received 1 April 1965)

We wish to report that in appropriate solvents anhydrous sodium hydroxide and haloforms react with olefins to give dihalocyclopropanes in excellent yields (1). Typically 0.25 mole olefin, 0.25 mole haloform, 1.0 mole anhydrous pelletized sodium hydroxide and 25 ml tetraethylene glycol dimethyl ether ("tetraglyme") are put in a flask fitted with a high shear stirrer. The stirrer is activated and the mixture is stirred vigorously while being warmed rapidly in a water bath to 95°. An ice condenser is used to retain chloroform and volatile olefins in the reaction mixture. The mixture is kept at 95° for two hours. With heat sensitive materials prolonged stirring at 25° gives good results. Dilution with water, separation of the organic phase, and distillation is usually an effective workup procedure. In Table I are listed some typical yields along with the highest reported yield from the literature by alternative dichlorocyclopropanation procedures. Yields reported using trihalomercurials were not used in this compilation because of the inconvenience of this method in large scale preparations.

The data in Table I demonstrate that the procedure described is as effective in dichlorocyclopropanation of olefins as any method currently used for large scale syntheses. In simplicity of application and availability of reactants the sodium hydroxide-chloroform method is superior to other published procedures.

TABLE I

Dichlorocyclopropanation Yields

Olefin	Yield	Alternate Process	Yield	Ref.
ethylene[a]	17	KOt-Bu + $CHCl_3$	0	2
ketene dimethyl-acetal	62	KOt-Bu + $CHCl_3$	68[b]	3
allyl chloride	23	CCl_3CO_2Na	60	4
styrene	86	KOt-Bu + $CHCl_3$	84	5
cyclohexene	83	$CCl_3CO_2CH_3$ + $NaOCH_3$	79-88	6
hexene-1[c]	45	$KOC(CH_3)_2C_2H_5$ + $CHCl_3$	16	7
heptene-1	-	KOt-Bu + $CHCl_3$	69	5
propylene[a]	65[d]	-	-	-

(a) Pressure reaction.

(b) Ketene diethyl acetal.

(c) Triethylene glycol dimethyl ether solvent.

(d) New compound, 1,1-dichloro-2-methylcyclopropane, characterized by elemental analysis, infrared spectrum and nuclear magnetic resonance spectrum.

Application of the reaction conditions to other haloforms has been briefly explored. Products of dihalocyclopropanation have been obtained from bromoform, chlorodifluoromethane, and fluorodichloromethane. Some of the results are summarized in Table II. As yet, insufficient comparative yield data have been obtained to permit a judgement about the preparative value of this procedure relative to published alternative procedures with these haloforms.

TABLE II

Dihalocyclopropanation with Other Haloforms

Haloform	Olefin	% Yield
$CHBr_3$	Cyclohexene	54[a]
$CHCl_2F$	Tetramethylethylene	43[b]
$CHClF_2$	Tetramethylethylene	6[c]

(a) Triethylene glycol dimethylether solvent.

(b) New compound, analysis and infrared spectrum satisfactory for 1-chloro-1-fluoro-2,2,3,3-tetramethylcyclopropane.

(c) Analysis and infrared spectrum agree with 1,1-difluoro-2,2,3,4-tetramethylcyclopropane (8).

In order to establish that the dichlorocyclopropanating moiety generated by chloroform and sodium hydroxide did not differ significantly from that generated by chloroform and potassium tert-butoxide relative reactivity data were obtained. These data are summarized in Table III along with comparative literature data. Allowing for temperature differences the relative reactivities are identical within their limits of error.

TABLE III

Reactivities Relative to Cyclohexene

Substrate	Rel. Reactivity (80°, tetraglyme)	Rel. Reactivity* (-10°, excess olefin)
Trimethylethylene	14	24
Cyclohexene	1.0	1.0
Hexene-1	0.3	0.2
t-butyl alcohol	<0.6	-

*From Ref. 2.

Data on tert-butyl alcohol reactivity toward the dichlorocyclopropanation conditions is included in Table III. Although such data have not been published a low reactivity of tert-butyl alcohol relative to cyclohexene is implicit in the results of Doering and Hoffmann (7). The low relative reactivity of tert-butyl alcohol taken with the work of E. A. Robinson (9), who found the phenolate ion to be one hundred times more reactive toward "dichloromethylene" than water, suggests that the sensitivity of the dichlorocyclopropanation reaction to water has been exaggerated (10). The excellent yields from the new dichlorocyclopropanation conditions described in this paper almost demand that this be true. We propose to discuss this question in depth in a subsequent paper.

REFERENCES

1. French Patent 1,363,460, June 12, 1964.
2. W. von E. Doering and W. A. Henderson, Jr., J. Am. Chem. Soc., **80**, 5274 (1958).
3. S. M. McElvain and P. L. Weyna, J. Am. Chem. Soc., **81**, 2579 (1959).
4. W. M. Wagner, H. Kloosterziel, and S. van der Ven, Rec. Trav. Chim., **80**, 740 (1961).
5. O. M. Nefedov, N. N. Novitskaya, and A. D. Petrov, Dokl. Akad. Nauk. SSR, **152**, 629 (1963).
6. W. E. Parham and E. E. Schweitzer, J. Org. Chem., **24**, 1733 (1959).
7. W. von E. Doering and A. K. Hoffman, J. Am. Chem. Soc., **76**, 6162 (1954).
8. D. Seyferth, J. Y. Mui, M. E. Gordon, and J. M. Burlitch, J. Am. Chem. Soc., **87**, 681 (1965).
9. E. A. Robinson, J. Chem. Soc., 1633 (1961).
10. W. Kirmse, "Carbene Chemistry", Academic Press, New York and London (1964), p. 152.