

## Dichlorocarbene Addition by Phase Transfer Catalysis: Optimization Experiments and Mechanistic Considerations†

ECKEHARD V. DEHMLOW\* and MANFRED LISSEL

*Institut für Organische Chemie, Technische Universität Berlin, Strasse des 17 Juni 135, D-1000 Berlin 12*

*J. Chem. Research (S), 1978, 310  
J. Chem. Research (M), 1978, 4163-4193*

Dichlorocarbene generated from concentrated aqueous sodium hydroxide, chloroform, and a phase transfer catalyst<sup>1</sup> has been used extensively,<sup>2</sup> but the pertinent reaction variables have never been investigated in a systematic way. Such a study is, however, the prerequisite of preparative success in critical cases and the deduction of a mechanistic model. We have therefore investigated the effects of the following 10 reaction variables: amounts of chloroform and sodium hydroxide (relative to olefin), concentration of aqueous sodium hydroxide, concentration of catalyst, reaction time and temperature, nature of stirring, type of olefin, type of catalyst, and cosolvents.

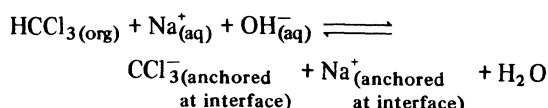
The results obtained do not exhibit simple, easy to analyse pseudo-first-order kinetics. As reproducibility of the heterogeneous reactions was only of the order of ~1.0% (relative) and as the mechanistic scheme developed (see below) turned out to be very complex, no detailed kinetic analysis was attempted.

The following conditions were found to be optimal for dichlorocarbene additions: 4 molar excess each of chloroform and 50% aqueous sodium hydroxide over alkene, 1 mol % catalyst, mixing at 0–5 °C, stirring at >800 rev. min<sup>-1</sup> for 1–2 h at room temperature, then heating for 2–4 h at 50 °C.

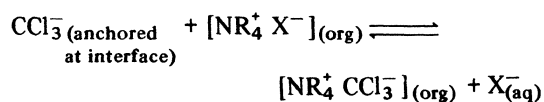
Of about 50 catalysts tested, most quaternary ammonium chlorides were suitable, although some differences became apparent.<sup>1,3</sup> Some phosphonium salts and crown ethers, as well as tetraphenylarsonium chloride may also be used, but non-ionic surfactants performed poorly. Even the ammonium salts do not show any correlation between detergent property and catalytic activity. On a cost/efficiency basis the following catalysts are the most useful: TEBA (benzyltriethylammonium chloride), tetra-n-butylammonium chloride or hydrogen sulphate, Aliquat 336 (methyltrioctylammonium chloride), and tri-n-propylamine. Preferably the anions of the catalysts should be hydrogen sulphate or chloride.

A mechanistic scheme was deduced that seems to be applicable to all known reactions of CCl<sub>2</sub>:

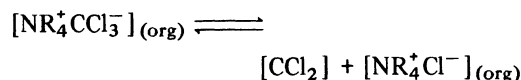
(1) Non-catalysed deprotonation at the phase interface leads to ions that cannot move, as their counter-ions are in the other phase:



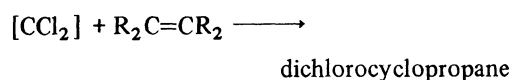
(2) The catalyst ion pair detaches the anchored trihalomethylidene ion, and the catalyst anion migrates into the aqueous phase. This equilibrium is displaced very much to the left, thereby stabilizing the system of subsequent steps:



(3) Reversible formation of dichlorocarbene:



(4) Irreversible adduct formation:



Alternative side reactions include hydrolysis, halide exchange, and formation of pentachloroethane and polymers. These processes are of minor importance with 'good' carbene acceptors, and the net reaction rate is strongly dependent on the nucleophilicity of the alkene.

Full text in German

References: 28

Figures 1–4: Dependence of the yield of 7,7-dichloronorcarane on (1) the relative amount of chloroform, (2) the relative amount of 50% aqueous NaOH, (3) the relative amount of catalyst TEBA (time 4 h), (4) the relative amount of catalyst TEBA (time 1 h)

Figures 5 and 6: Time dependence of the yield of 7,7-dichloronorcarane under various conditions [(5) 0.1 mol cyclohexene, 0.2 mol 50% NaOH, 0.4 mol chloroform, 1 or 0.1 mmol TEBA; (6) 50 or 23 °C, with or without Vibromixer]

Figure 7: Time dependence of the yields of dichlorocyclopropanes (1,1-dichloro-2,2,3-trimethylcyclopropane, 7,7-dichloronorcarane, 1,1-dichloro-2-n-butylcyclopropane, 1,1-dichloro-2-t-butylcyclopropane)

Table 1: Time dependence of the yield of 7,7-dichloronorcarane

Table 2: Time dependence of the yield of 7,7-dichloronorcarane related to the kind and speed of stirring

Table 3: Relative rates of dichlorocarbene addition under phase transfer conditions

Tables 4 and 5: Dependence of the yield of 7,7-dichloronorcarane on catalyst structure

Table 6: Dependence of the yield of 7,7-dichloronorcarane on the anion of the catalyst

Table 7: Experiments for optimization of the addition of CCl<sub>2</sub>

Paper: G/015/78

Received: 5th June 1978

References cited in this synopsis:

<sup>1</sup> M. Makosza and M. Wawrzyniewicz, *Tetrahedron Letters*, 1969, 4659.

<sup>2</sup> Reviews: (a) E. V. Dehmlow, *Angew. Chem.*, 1974, 86, 187; *Angew. Chem. Internat. Edn.*, 1974, 13, 170; (b) E. V. Dehmlow, *Angew. Chem.*, 1977, 89, 521; *Angew. Chem. Internat. Edn.*, 1977, 16, 493; (c) E. V. Dehmlow, 'Phase Transfer Catalysis', Verlag Chemie, in the press.

<sup>3</sup> E. V. Dehmlow and M. Lissel, *Chem. Ber.*, in the press.

<sup>1,3</sup> For preliminary results see E. V. Dehmlow and M. Lissel, *Tetrahedron Letters*, 1976, 1783.

† Applications of Phase Transfer Catalysis, Part 7. For Part 6 see reference 3.

\*To receive any correspondence.