Synthesis of Cyclopropane Derivatives from Electron-deficient Olefins and Dichloromethane *via* Copper(I) Catalysed Photochemical Addition followed by an Electroreductive Dehalogenation Reaction

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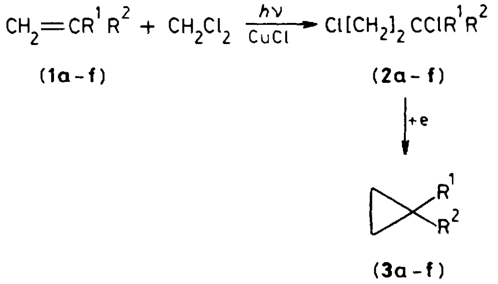
The CuCl-catalysed photochemical reaction of electron-deficient olefins with dichloromethane gave 1,3-dichloro compounds, which then afforded cyclopropane derivatives by electrochemical reduction.

The synthesis of cyclopropane derivatives by the transfer of a methylene group of di-iodomethane to olefins has been successful using the Simmons–Smith reaction[1] and some of its variations.[2] However, these methods are limited in that only electron-rich olefins are used because the intermediate metal–methylene carbenoid species are electrophilic and because di-iodomethane is more often used as the cyclopropanation reagent than dichloromethane which is less labile. We report here a reaction in which the methylene group of dichloromethane, although in a two-step process, can be transferred to electron-deficient olefins to give cyclopropane derivatives in a scheme that overcomes the limitation of, and complements, the Simmons–Smith type syntheses.



a; $R^1 = H, R^2 = CN$
b; $R^1 = H, R^2 = CO_2Et$
c; $R^1 = H, R^2 = COMe$
d; $R^1 = Me, R^2 = CN$
e; $R^1 = Me, R^2 = CO_2Et$
f; $R^1 = CH_2CO_2Et, R^2 = CO_2Et$

1 : 1 Adducts of dichloromethane and the electron-deficient olefins (**1a**—**f**) were obtained using a CuCl-catalysed photochemical procedure which we have developed for addition reactions of halogen compounds to olefins.[3] In a typical example of the complete sequence (**1**) → (**3**), a solution consisting of acrylonitrile (6 mmol), CuCl (0.4 mmol), CH_2Cl_2 (40 ml), and $Bu^n{}_4NBr$ (1.6 mmol) was irradiated using a low-pressure Hg lamp for 30 h under a nitrogen atmosphere. After work-up of the solution (addition of 10% aqueous HCl, extraction with Et_2O, washing with H_2O, drying over $MgSO_4$, and solvent removal), 2,4-dichlorobutanenitrile (**2a**) was obtained in an almost pure form.† A solution of (**2a**) (5 mmol) in Me_2SO (DMSO) (20 ml) containing $Et_4NO_3SC_6H_4Me$-*p* (0.2 M) as supporting electrolyte was electrolysed in an undivided cell with carbon rod electrodes as cathode and anode. After electrolysis had been carried out for 10 h at a constant voltage,‡ the DMSO solution was poured into water and the products extracted, first with n-pentane and then with Et_2O. After the Et_2O and n-pentane were carefully removed, the desired product was purified by silica gel chromatography (278 mg, 83%) and identified as cyclopropanecarbonitrile (**3a**) by spectroscopic analysis and by comparison of its i.r. and n.m.r. spectra with those of the authentic material.

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† By v.p.c. analysis, (**2a**) was the only volatile component in the residue in 90% yield. Oligo- or poly-(acrylonitrile) were possible impurities indicated by ^1H n.m.r. spectroscopy of the residue.

‡ The voltage between the anode and cathode was 8 V with an initial current of 50 mA and a final current of 30 mA.

Table 1

Olefin (1)	Yield (2), %	Yield (3), %
(a)	90	83
(b)	93	82
(c)	85	51[a]
(d)	90	90
(e)	65	73
(f)	70	62

[a] 5-Chloropentan-2-one was also produced (36% yield).

The results of the syntheses of the cyclopropane derivatives (**3**) from dichloromethane and the electron-deficient olefins (**1a—f**) *via* the chloro compounds (**2**) are summarized in Table 1. In the electroreduction of (**2a**) in dipolar solvents other than DMSO, *e.g.* dimethylformamide (DMF), MeCN, or hexamethylphosphoramide (HMPA), (**3a**) was produced in poorer yields (40, 35, and 3% in DMF, MeCN, and HMPA, respectively).

To introduce the chlorocyclopropane functionality into an olefin, 2,4,4-trichlorobutanenitrile (**4**) was produced in 91% yield by irradiation of a chloroform solution of acrylonitrile, CuCl, and $Bu^n{}_4NBr$; (**4**) was then electroreduced in DMSO. Unfortunately, 2-chlorocyclopropanecarbonitrile, the expected product, was obtained only in 7% yield.

$CHCl_2CH_2CHClCN$

(**4**)

Our methodology gives satisfactory results for the introduction of the cyclopropane group into compounds with terminal electron-deficient olefinic groups, but cannot be used to synthesise cyclopropane derivatives of compounds with non-terminal electron-deficient double bonds such as in diethyl maleate and ethyl crotonate because the addition reaction of dichloromethane could not be performed. We propose a tentative mechanism for the CuCl-catalysed reaction in which dichloromethane oxidatively adds to Cu^I to generate a Cu^{III} complex which adds to the olefins and then reductively eliminates to form the addition products. It might be expected from this that addition of ligands to stabilize the Cu^{III} intermediate may facilitate the reaction of dichloromethane with non-terminal olefins. Investigations are now in progress to see if this is true.

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