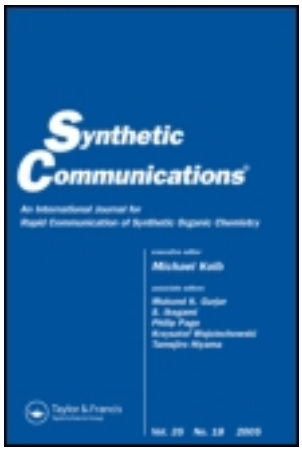

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Oxidation of Aliphatic 2,2-Dichloroalkanals by HNO_3 in CH_2Cl_2: An Easy and Eco-friendly Route to the Corresponding 2,2-Dichloroalkanoic Acids

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ABSTRACT

A simple, economically convenient, and eco-compatible procedure for the oxidation of 2,2-dichloroalkanals to the corresponding alkanoic

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acids has been set up, employing HNO_3 in CH_2Cl_2, in the presence of $NaNO_2$ as catalyst.

Key Words: Alkanals; Alkanoic acids; Oxidations; Nitric acid; Radical reactions.

INTRODUCTION

2,2-Dichloroalkanoic acids and their derivatives are valuable and versatile substrates in synthetic organic chemistry.[1–8] The bifunctional arrangement CCl_2COY, which provides these molecules with a number of interesting features, can be secured by "classical" connective approaches,[9–13] starting from dichloroacetic or trichloroacetic acids derivatives and exploiting ionic[10,11] or radical[9,12] or even pericyclic[13] routes; nevertheless, in the overwhelming majority of cases these methods also insert a third functional group at the β-carbon on the ensuing molecular skeleton. In comparison, the nonconnective strategy, more appropriate for large scale production of 2,2-dichloroalkanoic acids and derivatives bearing no additional function on the aliphatic chain, has received much less attention so far. The Viehe's direct chlorination of amides with $COCl_2/Cl_2$,[5] as well as the oxidation–chlorination of 2-alkyl-4,5-dimethyl-1,3-dioxolanes with trichloroisocyanuric acid[14] are viable syntheses, but the excessive complexity make these protocols tedious and thus less attractive for a potential scale-up. Chlorination by the classical Hell–Volhard–Zelinskii reaction is unsuitable for the preparation of α,α-dihalocarboxylic acids, being only useful for the introduction of a single Cl atom (see for example Ref.[15]).

Currently, the more convenient way to obtain 2,2-dichloroalkanoic acids (**2**) involves the oxidation of 2,2-dichloroalkanals (**1**), starting materials smoothly obtainable by direct chlorination of aldehydes or even one-pot chlorination–oxidation of alcohols.[16–19] Final oxidation to the corresponding acids has been performed with $KMnO_4$,[16,17] $K_2Cr_2O_7$,[16] $H_2O_2/NaHCO_3$,[16,17] and, more recently, with Cl_2/2-picoline · HCl.[18] To date, alkaline permanganate remains the reagent of choice for the oxidation step, but the actual need to minimize the amounts of toxic wastes and by-products from chemical processes makes urgent the development of alternative and more environmentally compatible synthetic protocols.[20,21]

RESULTS AND DISCUSSION

Nitric acid in CH_2Cl_2 solution proves to be a very versatile and mild-in-nature reagent, having recently found many useful synthetic applications

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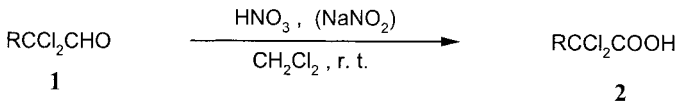
in organic chemistry;[21–26] on the other hand, the special ability of HNO_3 in smoothly performing the oxidation of aldehydes to the corresponding carboxylic acids is well known.[27–29] Therefore, we decided to consider the possibility of using the HNO_3–CH_2Cl_2 system for the oxidation of some 2,2-dichloroalkanals (**1**) to the corresponding alkanoic acids (**2**), also taking into account the safe, easy availability,[30] and low cost of the chemicals to be employed, in addition to the advantages of operating in an organic solvent.

When 2,2-dichlorohexanal (**1e**) was treated with HNO_3 (1 : 2 up to 1 : 3 molar ratio) in CH_2Cl_2 at room temperature, no conversion was observed even after prolonged reaction times (^{1}H NMR analysis of the intact reaction mixture after dilution with $CDCl_3$), probably as a consequence of the presence of two electron-withdrawing α-Cl atoms causing a marked inhibition of the oxidation process. We strongly deemed that the observed inertness towards HNO_3 attack had to be correlated to an ineffective generation of NO_2, the latter being considered responsible of the oxidation under the present conditions.[26]

The catalytic role of HNO_2 as initial source of the active species NO_2 in the HNO_3 oxidation of aldehydes to acids is well documented.[27,31] Therefore, we reasoned that the drawback could be circumvented by simply adding $NaNO_2$ (1% mol per mol of substrate) to the reaction mixture. As expected, in the presence of nitrite the oxidation took place and **1e** was smoothly converted into acid **2e** within 8 d at room temperature. The method was extended to a series of aliphatic 2,2-dichloroalkanals, affording the corresponding acids generally in good yields (Sch. 1, Table 1).

The efficiency of the oxidation proved to be independent with respect to the length of the aliphatic chain and only in the case of 2,2-dichloro-3-phenylpropanal (**1i**), the reaction gave poor yields (Table 1, entry 10) owing to competitive ring nitration. The productivity of the method can be considerably enhanced by heating: in fact, the oxidation of 2,2-dichlorooctanal (**1f**), at 60°C under moderate pressure, was complete within 24 hr, affording the corresponding acid **2f** in yields comparable to those obtained at room temperature (Table 1, entries 6 and 7).

The mechanism of the reaction, also in accordance with previous reports,[31,32] appears to be definitively of radical nature (Sch. 2), with HNO_3 playing the role of a convenient source of the active species NO_2, as such or in its protonated form, responsible of the oxidation.



Scheme 1.

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Table 1. Oxidation of 2,2-dichloroalkanals (**1**) to the corresponding alkanoic acids (**2**) with HNO_3 in CH_2Cl_2 (Sch. 1).

Entry	Substrate (**1**)	R	Conversion (%)[a]	Product (**2**)	Yield (%)[b]
1	**a**	CH_3	>99	**a**	66
2	**b**	C_2H_5	>99	**b**	78
3	**c**	$(CH_2)_2CH_3$	>99	**c**	87
4	**d**	$CH(CH_3)_2$	98[c]	**d**	72
5	**e**	$(CH_2)_3CH_3$	98	**e**	80
6	**f**	$(CH_2)_5CH_3$	97	**f**	92
7	**f**	$(CH_2)_5CH_3$	98[d]	**f**	92
8	**g**	$(CH_2)_9CH_3$	97	**g**	88
9	**h**	$(CH_2)_{13}CH_3$	98	**h**	93
10	**i**	CH_2Ph	98	**i**	47[e]

[a]Determined by ^1H NMR on intact reaction mixture, after suitable dilution with $CDCl_3$. Acid **2** was the sole reaction product. Unless otherwise stated, the oxidation was performed in 8 d at room temperature.
[b]Isolated product.
[c]Longer reaction time (15 d) was required.
[d]Reaction carried out in 24 hr at 60°C.
[e]Not isolated; the reaction mixture contained in addition some 51% of ring-nitrated products.

In conclusion, the procedure described above may represent a valuable alternative to the existing methods for the oxidation of aliphatic α,α-dichloroalkanals to the corresponding alkanoic acids in terms of simplicity, economicity, and eco-compatibility, especially in the case of large scale processes. Furthermore, the operation in CH_2Cl_2 offers evident advantages on respect to previous similar oxidations performed in aqueous environment.[33,34]

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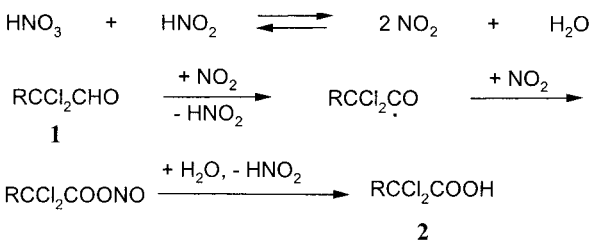

Scheme 2.

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EXPERIMENTAL

Unless otherwise specified, reagents, solvents, and products were commercially available. 2,2-Dichloroalkanals were prepared according to literature procedures.[17,19] Commercial 100% HNO_3 ($d = 1.51$) was purchased from Hydro Chemicals France (Nanterre, France) and kept at 4°C in the dark to avoid decomposition; the acid was freshly distilled and its titre, averaging ca. 24 M, alkalimetrically checked prior to use. Reported boiling points refer to the central cut of small scale distillations and are uncorrected. Melting points were obtained with a Mettler FP 61 automatic apparatus and are uncorrected. IR spectra were recorded on a Nicolet FTIR Magna 550 spectrophotometer using the KBr technique. ^{1}H- and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AC-200 spectrometer at 200 and 50 MHz, respectively. GC analyses were carried out using a 0.25 mm i.d. × 30 m SPB5^{TM} fused silica capillary column (Supelchem, Milano, Italy). MS measurements were performed with a Fisons TRIO-2000 apparatus, working in the positive-ion electron impact mode (70 eV).

General Procedure for the Oxidation of 2,2-Dichloroalkanals

In a typical procedure, a solution of the selected dichloroalkanal (**1**, 50.0 mmol) in CH_2Cl_2 (10 mL) was admixed with finely grinded $NaNO_2$ (0.5 mmol), treated with a solution of HNO_3 ($d = 1.51$, 150.0 mmol) in CH_2Cl_2 (10 mL), and kept under stirring for 8 d at room temperature (or 24 hr at 60°C under moderate pressure) in a well sealed flask. After that time, the reaction mixture was diluted with CH_2Cl_2 (30 mL), washed with 10% aqueous Na_2SO_4 (2 × 30 mL), dried over anhydrous Na_2SO_4, filtered, and the solvent evaporated off. The obtained acids **2** were isolated after conventional distillation or crystallized when suitable (Table 1).

2,2-Dichlorobutanoic acid (2b). Colorless liquid, b.p. 124°C/4000 Pa (106–108°C/1867 Pa).[16] ^{1}H NMR ($CDCl_3$) δ (TMS): 1.22 (t, 3H, CH_3), 2.49 (q, 2H, CH_2), 11.90 (br s, 1H, COOH). ^{13}C NMR ($CDCl_3$) δ (TMS): 9.40 (CH_3), 38.35 (CH_2), 84.92 (CCl_2), 171.97 (COOH).

2,2-Dichloropentanoic acid (2c). Colorless liquid, b.p. 131°C/4000 Pa (65–67°C/10 Pa).[17] ^{1}H NMR ($CDCl_3$) δ (TMS): 1.02 (t, 3H, CH_3), 1.56–1.78 (m, 2H, CH_2), 2.36–2.49 (m, 2H, CH_2), 11.94 (br s, 1H, COOH). ^{13}C NMR ($CDCl_3$) δ (TMS): 13.33 (CH_3), 18.55 (CH_2), 46.83 (CH_2), 83.93 (CCl_2), 172.01 (COOH).

2,2-Dichloro-3-methylbutanoic acid (2d). Colorless liquid, b.p. 125°C/4000 Pa (109–111°C/1467 Pa).[16] ^{1}H NMR ($CDCl_3$) δ (TMS): 1.18 (d, 6H,

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CH_3), 2.75 (heptet, 1H, CH), 11.44 (br s, 1H, COOH). ^{13}C NMR ($CDCl_3$) δ (TMS): 17.57 (CH_3), 40.38 (CH), 90.20 (CCl_2), 172.02 (COOH).

2,2-Dichlorohexanoic acid (2e). Colorless liquid, b.p. 141 °C/4000 Pa (66–67°C/1 Pa).[17] ^1H NMR ($CDCl_3$) δ (TMS): 0.96 (t, 3H, CH_3), 1.32–1.52 (m, 2H, CH_2), 1.53–1.70 (m, 2H, CH_2), 2.39–2.51 (m, 2H, CH_2), 11.84 (br s, 1H, COOH). ^{13}C NMR ($CDCl_3$) δ (TMS): 13.71 (CH_3), 22.02 (CH_2), 27.11 (CH_2), 44.67 (CH_2), 84.13 (CCl_2), 171.97 (COOH).

2,2-Dichlorooctanoic acid (2f). Pale yellow liquid, b.p. 116°C/133 Pa (93–96°C/2 Pa).[17] ^1H NMR ($CDCl_3$) δ (TMS): 0.90 (t, 3H, CH_3), 1.24–1.48 (m, 6H, CH_2), 1.52–1.72 (m, 2H, CH_2), 2.37–2.50 (m, 2H, CH_2), 11.97 (br s, 1H, COOH). ^{13}C NMR ($CDCl_3$) δ (TMS): 13.94 (CH_3), 22.44 (CH_2), 24.99 (CH_2), 28.50 (CH_2), 31.40 (CH_2), 44.91 (CH_2), 84.12 (CCl_2), 172.01 (COOH).

2,2-Dichlorododecanoic acid (2g). Pale yellow liquid, b.p. 135°C/4 Pa (135–136°C/4 Pa).[17] ^1H NMR ($CDCl_3$) δ (TMS): 0.88 (t, 3H, CH_3), 1.18–1.51 (m, 14H, CH_2), 1.51–1.78 (m, 2H, CH_2), 2.33–2.48 (m, 2H, CH_2), 11.91 (br s, 1H, COOH). ^{13}C NMR ($CDCl_3$) δ (TMS): 14.22 (CH_3), 22.84 (CH_2), 25.61 (CH_2), 29.31 (CH_2), 29.52 (CH_2), 29.57 (CH_2), 29.66 (CH_2), 29.74 (CH_2), 32.11 (CH_2), 45.49 (CH_2), 84.94 (CCl_2), 171.03 (COOH).

2,2-Dichlorohexadecanoic acid (2h). Pale yellow solid, m.p. 32°C (hexane) [(33–35°C (hexane)].[17] ^1H NMR ($CDCl_3$) δ (TMS): 0.88 (t, 3H, CH_3), 1.17–1.50 (m, 18H, CH_2), 1.50–1.82 (m, 2H, CH_2), 2.34–2.49 (m, 2H, CH_2), 9.92 (br s, 1H, COOH). ^{13}C NMR ($CDCl_3$) δ (TMS): 14.10 (CH_3), 22.68 (CH_2), 25.04 (CH_2), 28.85 (CH_2), 29.25 (CH_2), 29.35 (CH_2), 29.44 (CH_2), 29.56 (CH_2), 29.65 ($4 \times CH_2$), 31.91 (CH_2), 44.93 (CH_2), 84.29 (CCl_2), 171.23 (COOH).

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