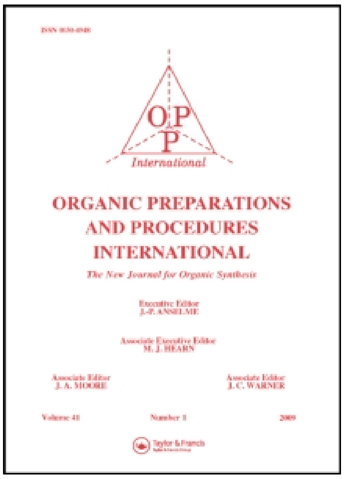

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SYNTHESIS OF CHLOROALKANE-α,ω-DIOIC ACIDS

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SYNTHESIS OF CHLOROALKANE-α,ω-DIOIC ACIDS

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Chloroalkanedioic acids can readily be converted by dehydrochlorination to the corresponding alkenedioic acids which are of some biological importance.[1] We now report a convenient synthesis of some chlorodicarboxylic acids by the following scheme.

$$\underset{\text{I}}{CH_2{=}CR(CH_2)_nCOOR'} + CCl_4 \xrightarrow{RuCl_2(PPh_3)_3} \underset{\text{II}}{CCl_3CH_2CClR(CH_2)_nCOOR'}$$

$$\xrightarrow{H_2O} \underset{\text{III}}{HOOCCH_2CClR(CH_2)_nCOOH}$$

a) R=H, R'=Me, n=0
b) R=R'=Me, n=0
c) R=H, R'=Me, n=1
d) R=R'=H, n=8

Addition of carbon tetrachloride to unsaturated acid or esters catalyzed by dichlorotris(triphenylphosphine)ruthenium[2] gave (II) in excellent yields. Hydrolysis of the tetrachloro compounds (II) was carried out with fuming nitric acid[3,4] or ferric chloride,[5] and yields of the chlorodicarboxylic acids were also very satisfactory.

Recently, Rao and Nayak obtained 3-chlorododecanedioic acid by hydrolysis of 10,12,12,12-tetrachlorododecanoic acid prepared by the benzoyl peroxide catalyzed addition of carbon tetrachloride to 10-undecenoic acid in 61% overall yield.[3] The present method involving the ruthenium (II) complex catalyzed addition of carbon tetrachloride and subsequent hydrolysis of the adduct with fuming nitric acid in the presence of phosphorus pentoxide afforded the same acid in 92% overall yield.

EXPERIMENTAL

Melting points and boiling points were uncorrected. IR spectra were recorded on a Hitachi Model EPI-G3 spectrophotometer. NMR spectra were obtained using a Varian A-60D instrument. GLPC analyses were performed with an Ohkura Model 802 gas chromatograph. All starting materials were purchased and distilled before use.

Methyl 2,4,4,4-tetrachlorobutanoate (IIa).- A mixture of 43.1 g (500 mmol) of methyl acrylate, 769 g (5 mol) of carbon tetrachloride and 1.4 g (1.4 mmol) of dichlorotris(triphenylphosphine)ruthenium was heated at reflux for 13 hrs. After dilution of the mixture with n-hexane and removal of the catalyst by filtration, vacuum distillation gave 79 g (66%) of methyl 2,4,4,4-tetrachlorobutanoate(IIa) as a colorless liquid, bp. 57-58°/2.5 mm, lit.[6] 111°/20 mm. Its NMR and IR spectra were in good agreement with those previously reported.[7]

Methyl 2-methyl-2,4,4,4-tetrachlorobutanoate (IIb).- A sample of 50.1 g (0.5 mol) of methyl methacrylate was mixed with 769 g (5 mol) of carbon tetrachloride and 1.44 g (1.5 mmol) of the ruthenium(II) complex and the mixture was heated at reflux for 5 hrs. Essentially the same work-up as above gave 99.4 g (78%) of tetrachloro compound(IIb), bp. 73-76°/3 mm, lit.[6] 76-78°/2 mm, as a colorless liquid. Its NMR and IR spectra were in complete agreement with those previously reported.[7]

Methyl 3,5,5,5-tetrachloropentanoate (IIc).- A mixture of 16.5 g (165 mmol) of methyl 3-butenoate, 254.7 g (1.66 mol) of carbon tetrachloride and 1.4 g (1.4 mmol) of the ruthenium(II) complex was refluxed for 5 hrs. Work-up gave 29.2 g (70%) of methyl 3,5,5,5-tetrachloropentanoate(IIc), bp. 92-93°/2 mm.

^{1}NMR(CCl_4): δ 2.93 (quin., 2H, $\underline{CH_2}CO_2Me$), δ 3.33 (d, 2H, CH_2CCl_3), δ 3.73 (s, 3H, CO_2Me), δ 4.63 (m, 1H, -CHCl-)

IR(neat): 1749(C=O) and 790, 700 cm^{-1}(C-Cl).

Anal. Calcd for $C_6H_8Cl_4O_2$: C, 28.38; H, 3.18; Cl, 55.84.

Found: C, 28.62; H, 3.28; Cl, 55.85.

10,12,12,12-Tetrachlorododecanoic acid (IId).- In a 500 ml three-necked round-bottomed flask equipped with a stirrer and a reflux condenser were placed 152 g (900 mmol) of carbon tetrachloride, 60 g (326 mmol) of 10-undecenoic acid and 0.63 g (0.6 mmol) of the ruthenium(II) complex. The mixture was refluxed for 1 hr with stirring and the course of the reaction was monitored by GLPC analysis. The resultant mixture was diluted with n-hexane and the precipitated catalyst was removed by filtration. Evaporation of volatile materials gave 110 g (100%) of 10,12,12,12-tetrachlorododecanoic acid(IId) as a yellowish liquid which was identified by comparing its NMR and IR data with reported values.[3]

2-Chlorobutanedioic acid (IIIa).- A mixture of (IIa) (26.1 g, 109 mmol) and anhydrous ferric chloride (3.5 g, 21 mmol) was stirred at 53° for 1.5 hrs and the resulting mixture was poured into ice-water. After ether extraction, the extract was washed with water and dried over anhydrous sodium sulfate. Concentration of the solution resulted in the separation of crude solid which was recrystallized from benzene to give 9.1 g (69%) of white crystals, mp. 148-149°, lit.[5] 150-152°. Structure of the product was further confirmed by its NMR and IR spectra.

2-Methyl-2-chlorobutanedioic acid (IIIb).- A mixture of (IIb) (60 g, 236 mmol) and anhydrous ferric chloride (4 g, 25 mmol) was stirred at room temperature for 2 hrs and the resulting mixture was poured into ice-water. After ether extraction, the extract was washed with water and dried over anhydrous sodium sulfate. Distillation gave 36.3 g (92%) of (IIIb). mp. 130-131.5°, lit.[5] 130-131.5°. Its NMR and IR spectra were in good agreement with those previously reported.[5]

3-Chloropentane-1,5-dioic acid (IIIc).- (IIc) (10 g, 39 mmol) was added to a mixture of phosphorus pentoxide (1 g, 7 mmol) and 60 ml of fuming nitric acid (d: 1.52) at 60° with stirring for 0.5 hr. Then, the mixture was stirred for 18 hrs at 75°. The resulting mixture was poured into ice-water ans extracted with ether. The ethereal extract was washed with water and dried with anhydrous sodium sulfate. Removal of the solvent afforded 3.0 g (58%) of solid (IIIc). Recrystallization from glacial acetic acid gave a pure sample of (IIIc), mp. 123-125°.

^{1}NMR(d_8-dioxane): δ 2.77 (d, 4H, $\underline{CH_2}CO_2H$), δ 4.54 (q, 1H, -CHCl-), δ 6.83 (s, 2H, CO_2H). IR(neat): 1730 and 1710 cm^{-1} (C=O).

Anal. Calcd for C_5H_7ClO: C, 36.06; H, 4.24; Cl, 21.3
: C, 36.27; H, 4.17; Cl, 21.8

3-Chlorododecane-1,12-dioic acid (IIId).- In a 300 ml round bottomed flask were placed 19.3 g (57 mmol) of (IId) and 3 g (21 mmol) of phosphorus pentoxide. Fuming nitric acid (d: 1.52) 36 ml was added in portion to the mixture with stirring over a period of 1 hr. The solution was then heated to 80° and allowed to stand for an additional 2 hrs. After pouring the mixture into ice-water, precipitated solid was collected by filtration. The yield after recrystallization from benzene was 15.3 g (92%), mp. 106-107°, lit.[3] 105-107°.

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