PATENT SPECIFICATION

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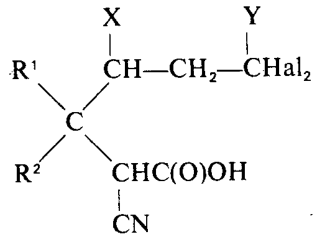
(54) 2-CYANOHEXANOIC ACID DERIVATIVES

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to 2-cyanohexanoic acid derivatives which are useful intermediates in the preparation of insecticidally-active compounds.

Accordingly the invention provides 2-cyanohexanoic acid derivatives of the general formula:—

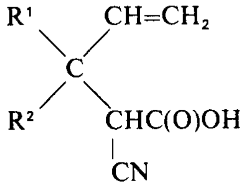


(I)

wherein X and Y each represent a chlorine or bromine atom, each Hal independently represents a fluorine, chlorine or bromine atom and R^1 and R^2 each independently represent an alkyl group of one to four carbon atoms or a salt thereof, preferably an alkali metal or ammonium salt.

A particularly preferred novel compound is 4,6,6,6 - tetrachloro - 2 - cyano - 3,3 - dimethylhexanoic acid, together with its alkali metal and ammonium salts. These compounds are useful intermediates in the preparation of 2 - (2,2 - dichlorovinyl) - 3,3 - dimethylcyclopropanecarboxylic acid, certain esters of which possess insecticidal activity.

The invention also relates to a process for the preparation of the 2-cyanohexanoic acid derivatives of the general formula I, which comprises reacting a pentenoic acid compound of the general formula:—



(II)

wherein R^1 and R^2 have the same meaning as in the general formula I, with a tetrahalomethane compound of the general formula

$CHal_2XY$ (III)

wherein Hal, X and Y have the same meaning as in the general formula I, in the presence of a catalyst, preferably a compound of copper iron, and a solvent capable of dissolving the reactants and the catalyst.

R^1 and R^2 in the general formula II preferably represent methyl groups. Carbon tetrachloride is the preferred compound of the general formula III.

Suitable solvents for the reaction are polar solvents, for example, acetonitrile, methylene chloride and benzene, and tetrahalomethane compounds of the general formula III; in order to use tetrahalomethane compound as a solvent in the process according to the invention it will have to be used in excess over the amount required as reactant. Mixtures of solvents may also be used.

Examples of suitable catalysts are ferric, cupric or ruthenium chloride, naphthenate, stearate or acetylacetonate. Very good results have been obtained with ferric or cupric chloride.

The process is preferably conducted in the presence of a solubilizer for the catalyst and/or reducing agent. Examples of compounds which enhance the solubility of the catalyst in the solvent are alkylammonium halides, for example diethylammonium chloride, di - *n* - butylammonium bromide, diethylpropylammonium chloride and trioctylammonium chloride. Examples of reducing agents are benzoin, hydroquinone, aldehydes, stannous chloride and alkali metal sulphites.

The molar ratios of solubilizer to compound of the general formula II and of catalyst to compound of the general formula II may vary within wide limits. Very good yields of compounds of the general formula I are usually obtained when these molar ratios are between 0.001 and 0.2.

An attractive feature of the process according to the invention is that the carboxylic acids of the general formulae I and II do not undergo decarboxylation reactions to any appreciable extent.

The following Examples further illustrate the invention.

EXAMPLE I

A 250 ml glass autoclave was charged with 0.3 mol of 2 - cyano - 3,3 - di - methyl - 4 - pentenoic acid, 0.9 mol of carbon tetrachloride, 0.6 mol of acetonitrile, 0.03 mol of ferric chloride, $6H_2O$, 0.03 mol of benzoin and 0.018 mol of diethylammonium chloride. The contents of the autoclave were stirred with a turbine stirrer (620 revolutions per minute), first for two hours at 105°C and then for 18 hours at 75°C. Subsequently, the contents of the flask were cooled to 22°C, 150 ml of diethyl ether was added and the solution formed was washed four times with 50 ml portions of 10% w aqueous hydrochloric acid to remove most of the iron salt. Then the organic phase was contacted with a 50 ml bed of grains of silica gel for further removal of iron salt. The organic phase thus obtained was boiled down at 30°C and 12 mm Hg. The NMR spectrum of the residue showed that no starting acid and no decarboxylation products were present. The yield of 4,6,6,6 - tetrachloro - 2 - cyano - 3,3 - dimethylhexanoic acid was more than 85%, calculated on starting acid.

The NMR spectrum of the product acid measured at 60 MHz in deuterochloroform solution showed the following absorptions relative to a tetramethylsilane standard. On the basis of the spectrum it was established that the acid consisted of two geometric isomers, configuration 1 and configuration 2.

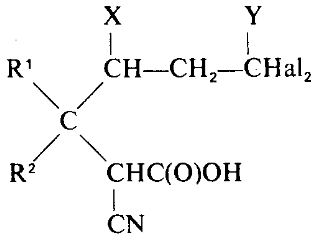
			δ, ppm, configuration	
			1	2
CH_2	1H	doublet	3.42	3.18
CH_2	1H	singlet	4.23	4.33
CHCl	1H	quartet	4.57	4.90
HCCN	1H	doublet	3.58	3.58
CH_3	3H	singlet	1.40	1.40
CH_3	3H	singlet	1.53	1.53
COOH	1H	singlet	8.92	8.92

EXAMPLE II

The experiment of Example I was repeated, but 0.1 mol of 2 - cyano - 3,3 - dimethyl - 4 - pentenoic acid, 0.01 mol of ferric chloride $6H_2O$, 0.01 mol of benzoin and 0.006 mol of diethylammonium chloride were used. The contents of the autoclave were stirred for 20 hours at 98°C. The yield of 4,6,6,6 - tetrachloro - 2 - cyano - 3,3 - dimethylhexanoic acid was more than 90%, calculated on starting acid.

WHAT WE CLAIM IS:—

1. 2-Cyanohexanoic acid derivatives having the general formula:—

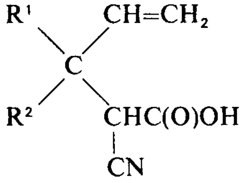


(I)

wherein X and Y each represent a chlorine or bromine atom, each Hal independently represents a fluorine, chlorine or bromine atom and R^1 and R^2 each independently represent an alkyl group of one to four carbon atoms, or a salt thereof.

2. The compound 4,6,6,6 - tetrachloro - 2 - cyano - 3,3 - dimethylhexanoic acid and its alkali metal and ammonium salts.

3. A process for the preparation of 2-cyanohexanoic acid derivatives of the general formula I, which comprises reacting a pentenoic acid compound of the general formula:—



(II)

wherein R^1 and R^2 have the same meaning as in the general formula I, with a tetrahalomethane compound of the general formula:—

$CHal_2XY$ (III)

wherein Hal, X and Y have the same meaning as in the general formula I, in the presence of a catalyst and a solvent capable of dissolving the reactants and the catalyst.

4. A process according to claim 3 wherein the tetrahalomethane compound of general formula III is carbon tetrachloride.

5. A process according to claim 3 or 4 wherein the solvent is a polar solvent.

6. A process according to claim 3 or 4 wherein the solvent is acetonitrile, methylene chloride, benzene, or a tetrahalomethane compound of general formula III.

7. A process according to any one of claims 3 to 6 wherein the catalyst is ferric, cupric or ruthenium chloride, napthenate, stearate or acetylacetonate.

8. A process according to claim 7 wherein the catalyst is ferric or cupric chloride.

9. A process according to any one of claims 3 to 8 wherein the reaction is carried out in the presence of a solubilizer for the catalyst and/or a reducing agent.

10. A process according to claim 9 wherein the solubilizer is an alkylammonium halide.

11. A process according to claim 9, wherein the reducing agent is benzoin, hydroquinone, an aldehyde, stannous chloride or an alkali metal sulphite.

12. A process according to claim 3 substantially as hereinbefore described and with reference to Example I or II.

13. 2-Cyanohexanoic acid derivatives prepared by the process claimed in any one of claims 3 to 12.

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