

- (21) Application No. 19989/77 (22) Filed 12 May 1977
 (23) Complete Specification filed 10 May 1978
 (44) Complete Specification published 14 Oct. 1981
 (51) INT CL³ C07C 23/20 23/04 69/743
 (52) Index at acceptance

C2C 1173 121X 123X 125X 200 220 225 226 227 22X 22Y 304
 305 313 314 31Y 338 366 368 37X 466 562 564 565 628
 65X 668 69Y 73Y 776 BN FJ HG

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(54) PREPARATION OF DIHALOCYCLOPROPANE
 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 a process for the preparation of dihalocyclopropane derivatives.

A method for the addition of a dihalomethylene to an unsaturated compound to form a dihalo-cyclopropane derivative has been described in British Patent Specification 983,203; it involves using an initially substantially-anhydrous mixture comprising an alkali metal hydroxide, a haloform containing at least one chlorine or bromine atom, and an unsaturated compound. The reactants may be employed in equimolar amounts, but it is usually advantageous to employ an excess of the unsaturated compound. A disadvantage of this known process is that insufficient haloform is available for reaction with the unsaturated compound; hence, the resulting cyclopropane derivatives are obtained in a correspondingly low yield. Most of the experiments described in the examples of the last mentioned specification have been carried out at temperatures of at least 90°C. At such high temperatures much of the dihalomethylene formed in situ enters into undesired side reactions. This, of course, involves an inefficient use of the haloform.

The Applicant has tried to apply the above-mentioned known process to the conversion of esters of 2-alkenoic acids into esters of 2,2-dihalocyclopropanecarboxylic acids, but has found that this conversion did not take place.

The above-mentioned specification states that the use of an ether solvent or a cycloparaffin sulphone solvent increases the yield of cyclopropane derivatives. The Applicant has found that in the presence of such solvents esters of 2-alkenoic acids are converted to a very low extent only, even after prolonged reaction time.

According to British Patent Specification 1,432,540 gem-dihalo-cyclopropane derivatives are prepared by contacting an aqueous phase containing an alkali metal hydroxide, with an organic phase containing a haloform and an ethylenically-unsaturated compound, in the presence of certain onium compounds as catalysts. The reaction mixture obtained in this process contains a liquid organic phase, an aqueous phase and a solid inorganic phase. The dihalocyclopropane derivative may be isolated from this reaction mixture by the addition of water until the solid inorganic phase has been dissolved, followed by separation of the organic phase from the aqueous phase and distillation of the separated organic phase. However, this procedure requires the use of large quantities of water and, consequently, large vessels. Moreover, it may give rise to emulsion problems. Alternatively, the solid inorganic phase is filtered off, the organic phase is separated from the aqueous phase and the separated organic phase is subjected to distillation. This filtration is often rather difficult, as is the separation of the organic phase from the aqueous phase. Furthermore, this process often requires a relatively large molar ratio of the alkali metal hydroxide to the olefin—for example from 4 to 10—to enhance the yield of the di-halocyclopropane derivative.

The present invention allows the formation of dihalocyclopropane derivatives

in a considerably enhanced yield at a relatively high rate in a reaction mixture from which they can easily be isolated.

The invention provides a process for the preparation of a dihalocyclopropane derivative which comprises reacting under substantially anhydrous conditions an unsaturated compound with a haloform, in the presence of a solid alkali metal hydroxide and an onium catalyst to promote the formation of dihalo-methylene radicals from the haloform.

The reaction mixture obtained in the process according to the present invention comprises an organic phase containing the dihalocyclopropane derivative prepared, a solid inorganic phase and the onium catalyst. A simple decantation of the organic phase and distillation of the decanted organic phase affords the dihalocyclopropane derivative in a usually high yield. Any excess of haloform, obtained by this distillation, may be re-used. A preferred class of unsaturated compound comprises ethylenically-unsaturated compounds, particularly those having up to 30 carbon atoms per molecule and 1 to 3 carbon-carbon double bonds. Monomers and polymers of ethylenically unsaturated compounds may be used.

A very attractive feature of the present invention is that it allows the preparation of esters of 2,2 - dihalocyclopropanecarboxylic acids in high yield, starting from esters of 2 - alkenoic acids. These esters may be derived from primary, secondary or tertiary alcohols. Esters of tertiary alcohols are very suitable. Examples of tertiary alcohols are tert - butyl alcohol 2 - methyl - 2 - butanol and 3 - methyl - 3 - pentanol. Very good results have been obtained with tert - butyl 3 - methyl - 2 - butenoate. It has been observed that the addition of an ether solvent or a cycloparaffin sulphone solvent usually decreases the yield of the 2,2 - dihalocyclopropanecarboxylates. If desired, however, the process according to the invention may be carried out in the presence of aliphatic hydrocarbon solvents such as pentane, hexane or heptane.

Another group of very suitable ethylenically-unsaturated compounds are ethylenically unsaturated hydrocarbons, particularly those containing one to three carbon-carbon double bonds per molecule, for example alkenes, cycloalkenes and cycloalkatrienes. The alkene may be linear or branched, may have a terminal or an internal double bond and may have a *cis* or *trans* structure. Examples of alkenes are ethylene, propylene, 1 - butene, isobutene, 1 - pentene, 1 - hexene, 1 - heptene, 1 - octene, 1 - nonene, 3 - methyl - 1 - butene, 3 - methyl - 1 - hexene, 1 - decene, 2 - pentene, 2 - hexene, 3 - heptene, 2 - methyl - 2 - butene, 2 - octene and 3 - nonene. Examples of cycloalkenes are cyclohexene, Δ^3 -carene, cycloheptene, cyclooctene, cyclononene, cyclodecene, cycloundecene, cyclotridecene, cyclotetradecene and the 1 - methyl and 1 - ethyl derivatives thereof. Examples of cycloalkatrienes are 1,3,5 - cyclononatriene and 1,5,9 - cyclododecatiene. The latter compound is particularly suitable. Other examples of ethylenically-unsaturated compounds are alkapolyenes, in which the double bonds may be conjugated or non-conjugated. Examples of alkapolyenes are butadiene, isoprene and 1,4 - pentadiene.

The process according to the invention is carried out in the substantial absence of an aqueous phase, which allows the use of a reactor of correspondingly smaller size.

The formation of an aqueous phase in the reaction mixture is preferably prevented by using a water-binding agent; for example by the use of the solid alkali metal hydroxide in excess. The molar ratio of the alkali metal hydroxide to the unsaturated compound can be relatively low, preferably in the range of from stoichiometric to 10 times stoichiometric and particularly from 1.5 times stoichiometric to 4 times stoichiometric, the excess being such that the formation of an aqueous phase is prevented. The stoichiometric ratio refers to the number of dihalomethylene radicals to be accepted by one molecule of the unsaturated compound. For example, this stoichiometric ratio is one when alkenes, and may be three when cycloalkatrienes are used as unsaturated compounds.

Examples of other water-binding agents which may be additionally employed are anhydrous sodium sulphate, anhydrous sodium carbonate, anhydrous potassium carbonate and silica gel.

The use of an initially substantially-anhydrous mixture helps to prevent the formation of an aqueous phase, thus enhancing the yield of the dihalocyclopropane derivative. An initially substantially-anhydrous mixture can be obtained by removing water, if present, from the unsaturated compound, the haloform, and, if

used, the solvent, for example by drying with anhydrous magnesium sulphate, and by using a dry alkali metal hydroxide.

The molar ratio of the haloform to the unsaturated compound can advantageously be greater than 1, the excess haloform enhancing the yield of the dihalocyclopropane derivative and serving as a solvent. The process may be carried out at a temperature in the range of from 0°C to 100°C, but is preferably carried out at relatively-low temperatures, preferably in the range of from 15°C to 45°C. At these relatively-low temperatures the tendency of the dihalomethylene formed in situ to enter into side reactions is substantially reduced. This involves an efficient use of the haloform. Ambient temperatures are usually very suitable.

Among the alkali metal hydroxides, i.e. lithium hydroxide, sodium hydroxide, potassium hydroxide, rubidium hydroxide and cesium hydroxide, sodium hydroxide is preferred, because it usually allows the dihalo-cyclopropane derivative to be obtained in the highest yield.

Examples of onium catalysts, capable of forming a dihalomethylene in situ, are described in Tetrahedron Letters 53 (1969) 4659—4662, and British Patent Specification 1,432,540. Such catalysts comprise a wide variety of onium compounds. Preferred groups of onium compounds are quaternary onium compounds of an element of Group VA of the Periodic Table of the Elements (see e.g. The Merck Index, 9th Edition), i.e. nitrogen, phosphorus, arsenic and antimony, and tertiary onium compounds of an element of Group VI A of the Periodic Table of the Elements having an atomic number of at least 16, i.e. sulphur, selenium and tellurium. The atoms of the elements of these two groups may be surrounded by hydrocarbyl groups, selected from, for example, alkyl, cycloalkyl, aryl, aralkyl or alkaryl groups, and in which, in the case of quaternary nitrogen compounds, the surrounding groups can be additionally a hydroxy group.

Very good results have been obtained with quaternary ammonium and tertiary sulphonium compounds in which the surrounding groups are selected from alkyl groups individually containing 1 to 20 carbon atoms, the compounds being in the form of hydroxides, chlorides, bromides, iodides, sulphates or alkylsulphates. Examples of catalysts are methyltri(1 - methylheptyl)ammonium chloride, tetrabutylammonium chloride, hydroxytrimethylammonium hydroxide, diethylhydroxymethylammonium iodide, diethylhydroxymethylammonium iodide, triethylhydroxyammonium hydroxide, ethyldi(1 - methylundecyl)sulphonium ethyl sulphate, ethylhexadecylundecylsulphonium ethyl sulphate, triethylsulphonium iodide, methyldi(1 - methylnonyl)sulphonium chloride, hexadecyldimethylsulphonium methyl sulphate, ethyl - 1 - methylpentadecyl - 1 - methylundecylsulphonium ethyl sulphate, dimethyl - 1 - methylpentadecylsulphonium iodide, ethylmethyl - 1 - methylpentadecylsulphonium tosylate, dimethyl - 1 - methylpentadecylsulphonium tosylate, trimethylsulphonium bromide and dibutylmethylsulphonium iodide.

The molar ratio of the catalyst to the haloform is not critical and may vary within a wide range; usually the catalyst is present in an amount which may be indicated by the expression "catalytic amount". The molar ratio of the catalyst to the haloform is preferably in the range of from 0.1:1 to 0.0001:1, excellent results have been obtained in the range of from 0.01:1 to 0.0005:1.

The haloform preferably has at least one atom of chlorine or bromine. Examples of haloforms are chloroform, bromoform, chlorodifluoroform, dichlorofluoroform, dibromofluoroform, dibromiodoform, bromochloriodoform, bromodichloroform, dibromochloroform, chlorodiodoform, dichloriodoform, bromodiodoform, chlorofluoriodoform and bromofluoriodoform. Very good results have been obtained with bromoform and chloroform.

The Examples further illustrate the invention.

Each of the experiments described hereinafter was carried out in a three-necked, round-bottomed flask, placed in a water bath, and provided with a stirrer, thermometer, reflux condenser and calcium chloride tube. In the Comparative Experiments and in Examples I, II, III, VII and VIII a magnetic stirrer and in the other Examples a paddle stirrer was used. The starting materials were placed in the flask, stirring was started and samples of the contents of the flask were taken as indicated in the Tables. These samples were analysed by means of gas-liquid chromatography. A dash in the tables means that the analysis has not been carried out. The experiments were carried out at a temperature between 20°C and 25°C, unless otherwise stated.

Examples I—III and Comparative Experiments A and B

Preparation of 13,13-dichlorobicyclo(10,1,0)tridecane

Table I states the amounts of the starting materials used. The cyclododecene contained 7%*m* of cyclododecane. The starting materials were initially anhydrous.

5	TABLE I							5
			Comparative Experiment		Example			
	Starting Material	Unit	A	B	I	II	III	
	Cyclododecene	mmol	100	100	100	100	100	
10	Powdered sodium hydroxide	mmol	200	200	200	200	100	10
	Chloroform	mmol	500	500	500	500	500	
	Methyltri(1-methylheptyl)- ammonium chloride	mmol	0	0	0.2	0.2	0	
	Tetrabutylammonium chloride	mmol	0	0	0	0	0.3	
15	Anhydrous sodium sulphate	mmol	0	0	0	100	100	15
	Bis(2-methoxyethyl) ether	ml	0	5	0	0	0	

Table II presents the results. The reaction mixtures obtained in the two Comparative Experiments and in the three Examples did not contain an aqueous phase.

20		TABLE II					20
		Yield of Title Compound, %					
	Sample Taken . . . Hours	Comparative Experiment		Example			
	After Start of Stirring	A	B	I	II	III	
	0.5	1.5	13	10	22	9	
25	1.3	1.7	25	19	36	17	25
	2	—	33	29	44	24	
	4	—	48	51	56	28	
	6	—	51	88	—	—	
	18	—	—	—	—	57	
30	45	—	65	—	—	—	30

Comparison of Example I with Comparative Experiment A shows that methyltri(1 - methylheptyl)ammonium chloride considerably enhances the yield of the title compound.

Comparison of Example I with Comparative Experiment B shows that the methyltri(1 - methylheptyl)ammonium chloride has enhanced the yield of the title compound to a larger extent than the bis(2 - methoxyethyl) ether. After 45 hours' stirring the reaction mixture of comparative Experiment B had become such a thick slurry that stirring had to be stopped.

Comparison of Example II with Example I shows that the presence of anhydrous sodium sulphate slightly enhances the yield of the title compound.

Comparison of Example III with Comparative Experiment A shows that tetrabutylammonium chloride also considerably enhances the yield of the title compound.

Comparison of Example III with Example II shows that a molar ratio of sodium hydroxide to cyclododecene of 2:1 instead of 1:1 gives a higher yield of the title compound, assuming that the two different quaternary ammonium chlorides exert the same influence.

Examples IV—VI and Comparative Experiment C

Preparation of 13,13-dichlorobicyclo(10,1,0)tridecane

Table III states the amounts of the starting materials used. The cyclododecene contained 7%*m* of cyclododecane. The starting materials of Examples V and VI were initially anhydrous.

TABLE III
Comparative
Experiment

	Starting Material	Unit	C	IV	Example V	VI	
5	Cyclododecene	mmol	26	26	26	301	5
	Sodium hydroxide	mmol	62.4 ¹⁾	62.4 ²⁾	62.4 ²⁾	723 ²⁾	
	Chloroform	mmol	250	250	250	1810	
	Methyltri(1-methyl- heptyl)ammonium chloride	mmol	0.10	0.10	0.10	1.12	
10	Pentane	ml	10	10	10	350	10
	Water	ml	2.5	0.5	0	0	

1) present in 5 g of a 50%w aqueous solution

2) powdered sodium hydroxide was added.

15 Table IV presents the results. The reaction mixtures obtained in the three Examples did not contain an aqueous phase. 15

TABLE IV
Yield of the Title Compound, %

	Sample Taken . . . Hours After Start of Stirring	Comparative Experiment C	IV	Example V	VI	
20	1.5	29	—	71	—	20
	2	31	50	77	—	
	3	37	60	84	more than 90	
	4	42	70	90	—	
25	5	50	—	—	—	25
	8	—	—	—	100	

Comparison of Example IV with Comparative Experiment C shows that the yield of the title compound is considerably increased when the amount of water is decreased to such an extent that no aqueous phase is present.

30 Comparison of Example V with Example IV shows that when water is initially absent the yield of the title compound is even more enhanced. 30

After 8 hours' stirring the liquid phase in the reaction mixture of Example VI was separated from the solid phase by decantation and boiled down at a pressure of 12 mm Hg to yield a residue consisting of the title compound, the yield thereof being 99.0%.

35 35

Examples VII and VIII and Comparative Experiments D and E

Preparation of tert-butyl 2,2-dichloro-3,3-dimethylcyclopropanecarboxylate

Table V states the amounts of the starting materials used.

TABLE V
Comparative Experiment

	Starting Material	Unit	D	E	Example VII	VIII	
40	Tert-butyl 3-methyl- 2-butenate	mmol	25	25	25	25	40
	Powdered sodium hydroxide	mmol	50	50	50	50	
45	Chloroform	mmol	125	125	125	125	45
	Ethyl-di(1-methylunde- cyl)sulphonium ethyl sulphate	mmol	0	0	0.25	0.25	
50	Anhydrous sodium sulphate	mmol	25	0	25	25	50
	Bis(2-methoxyethyl)ether	ml	0	1.2	0	1.2	

The starting materials were initially anhydrous.

55 Table VI presents the results. The reaction mixtures obtained in the two Comparative Experiments and the two Examples did not contain an aqueous phase. 55

TABLE VI

TABLE VI										
5	Sample Taken ... Hours After Start of Stirring	Conversion of tert-butyl 3-methyl-2-butenate, %				Selectivity to tert-butyl 2,2- dichloro-3,3-dimethylcyclopro- panecarboxylate ⁺¹ %				5
		Comparative Experiment		Example		Comparative Experiment		Example		
		D	E	VII	VIII	D	E	VII	VIII	
	0.5	0	1	16	26	—	100	100	54	
	2	0	3	37	32	—	100	95	62	
10	4	0	5	44	41	—	100	95	57	10
	24	0	9	—	—	—	89	—	—	
	68	—	—	62	46	—	—	82	52	

+) See Example XI for the definition of the selectivity to a certain compound.

15 Comparison of Example VII with Comparative Experiment D shows that the presence of ethyldi(1-methylundecyl)sulphonium ethyl sulphate has brought about a considerable conversion of tert-butyl 3 - methyl - 2 - butenoate with a high selectivity to the title compound. 15

20 Comparison of Comparative Experiment D with E shows that the presence of bis(2 - methoxyethyl) ether has only led to a low conversion of tert-butyl 3 - methyl - 2 - butenoate, neglecting the absence of the anhydrous sodium sulphate in Comparative Experiment E. 20

Comparison of Examples VII and VIII shows that in the absence of bis(2 - methoxyethyl) ether a higher conversion of tert-butyl 3 - methyl - 2 - butenoate and a considerably higher selectivity to the title compound can be obtained.

25 Example IX 25

Preparation of 15,15-dichlorodicyclo(12,1,0)pentadecane
The starting materials were:

30	Cyclotetradecene	21.6 mmol	
	Powdered sodium hydroxide	54 mmol	
	Chloroform	195 mmol	30
	Methyltri(1-methylheptyl)ammonium chloride	0.16 mmol	
	Pentane	40 ml	

The starting materials were initially anhydrous. The temperature of the contents of the flask was kept at 35°C.

35 After four hours' stirring the cyclotetradecene was fully converted and the reaction mixture did not contain an aqueous phase. The liquid phase in the reaction mixture obtained was separated from the solid phase by decantation and boiled down at a pressure of 12 mm Hg to yield a residue consisting of the title compound, the yield thereof being 97%. 35

40 Example X 40

Preparation of 9,9-dichloro-1-methylbicyclo(6,1,0)nonane
The starting materials were:

45	1-methylcyclooctene	15 mmol	
	Powdered sodium hydroxide	22.5 mmol	
	Chloroform	60 mmol	45
	Methyltri(1-methylheptyl)ammonium chloride	0.05 mmol	
	Anhydrous sodium sulphate	10.5 mmol	
	Pentane	20 ml	

The starting materials were initially anhydrous.

50 After 2.5 hours' stirring the yield of the title compound was quantitative and the reaction mixture did not contain an aqueous phase. 50

Example XI

Preparation of 5,5,10,10,15,15-hexachlorotetracyclo(12,1,0,0^{4,6},0^{9,11})pentadecane
The starting materials were:

55	1,5,9-cyclododecatriene	255 mmol	
	Powdered sodium hydroxide	535 mmol	
	Chloroform	5000 mmol	
	Methyltri(1-methylheptyl)ammonium chloride	2.55 mmol	55

The starting materials were initially anhydrous. The temperature of the contents of the flask was kept at 40°C. More powdered sodium hydroxide and onium compound were added at the times and in the amounts indicated in Table VII. Table VII also presents the results. The reaction mixture did not contain an aqueous phase.

TABLE VII

Sample Taken ... Hours After Start of Stirring	Molar Equivalents ¹⁾ Added of		Conversion of 1,5,9- cyclodode- catriene, %	Selectivity to, %, Adduct ⁴⁾ No.		
	NaOH (cumulative)	Onium Compound (separately)		I	II	III
0	2.1	0.01 ²⁾	0	—	—	—
2	2.1	0	95	57	41	2
13	6.3	0.008 ²⁾	100	0	23	77
15	17	0.005 ³⁾	100	0	16	84
40	8.4	0.01 ³⁾	100	0	11	89
100	9.0		100	0	6	94

1) calculated on 1,5,9-cyclododecatriene

2) methyltri(1-methylheptyl)ammonium chloride

3) tetrabutylammonium chloride

4) the Roman numerals indicate the following adducts:

I: 13,13-dichlorobicyclo(10.1.0)trideca-4,8-diene

II: 5,5,14,14-tetrachlorotricyclo(11.1.0.0^{4,6})tetradeca-9-ene

III: 5,5,10,10,15,15-hexachlorotetracyclo(12.1.0.0^{4,6}.0^{9,11})pentadecane

The selectivity to a certain compound, expressed in a percentage, is defined as

$$\frac{a}{c} \times 100$$

wherein "a" is the molar amount of dihalocyclopropane derivative formed and "c" is the molar amount of the converted unsaturated compound.

The liquid phase in the reaction mixture obtained was isolated from the solid phase by decantation and boiled down at a pressure of 12 mm Hg to yield a residue containing adducts III and II in yields of 93% and 6%, respectively.

Example XII

Preparation of 2,2-dichloro-3,3-dimethylcyclopropane

A stirred suspension of sodium hydroxide (2.4 mol) and anhydrous sodium sulphate (1 mol) in pentane (1 litre) was saturated at atmospheric pressure with isobutene. After addition of methyltri(1-methylheptyl)ammonium chloride (0.00135 mol), chloroform (6 mol) was added dropwise over a period of 1.5 hours. The reactants and the pentane were initially anhydrous. After 2.5 hour's stirring a second quantity of methyltri(1-methylheptyl)ammonium chloride (0.00135 mol) was added and simultaneously the addition of isobutene was terminated. Stirring was continued for ten hours after stopping the addition of isobutene. The reaction mixture did not contain an aqueous phase. The liquid phase was isolated from the solid phase by decantation and boiled down to give the title compound (0.35 mol).

Example XIII

Preparation of tert-butyl 2,2-dichloro-3,3-dimethylcyclopropanecarboxylate

The starting materials were:

Tert-butyl 3-methyl-2-butenolate	12.8 mmol
Powdered potassium hydroxide	60.7 mmol
Chloroform	150 mmol
Tetrabutylammonium chloride	0.25 mmol

The starting materials were initially anhydrous. The temperature of the contents of the flask was kept at 45°C. The potassium hydroxide was added over a period of one hour to the other starting materials. At the end of this hour the

conversion of the tert-butyl 3 - methyl - 3 - butenoate was 80%, with a selectivity to the title compound of 31%. An aqueous phase was absent.

Example XIV

Preparation of tert-butyl 2,2-dichloro-3,3-dimethylcyclopropanecarboxylate

5 The starting materials were: 5

Tert-butyl 3-methyl-2-butenate	12.8 mmol
Powdered potassium hydroxide	60.7 mmol
Chloroform	150 mmol
Ethylhexadecylundecylsulphonium ethyl sulphate	0.25 mmol

10 The starting materials were initially anhydrous. The potassium hydroxide was added over a period of one hour to the other starting materials, keeping the temperature at 45°C. At the end of this period the yield of the title compound was 50%.

15 Then, stirring was continued for four hours at a temperature of 22°C. At the end of these four hours the conversion of tert-butyl 3 - methyl - 2 - butenoate was 90%, with a selectivity to the title compound of 100%. An aqueous phase was absent. 15

Comparison with Example XIII shows that the sulphonium compound affords the title compound in a higher yield than the quaternary ammonium compound.

20 Example XV 20

Preparation of 13,13-dibromobicyclo(10,1,0)tridecane

The starting materials were:

Cyclododecene	26 mmol	
Powdered sodium hydroxide	62.4 mmol	
25 bromoform	171 mmol	25
Methyltri(1-methylheptyl)ammonium chloride	0.11 mmol	
Water	0.5 ml	

30 The reaction mixture did not contain an aqueous phase. After two hours' stirring the yield of the title compound was 66%. Then, a second amount of methyltri(1 - methylheptyl)ammonium chloride (0.055 mmol) was added. After a further five hours' stirring the yield of the title compound was more than 95%. 30

Example XVI

Preparation of 15,15-dibromobicyclo(12,1,0)pentadecane

The starting materials were:

35 Cyclotetradecene	5.2 mmol	35
Powdered sodium hydroxide	10.4 mmol	
Bromoform	114 mmol	
Methyltri(1-methylheptyl)ammonium chloride	0.054 mmol	
Water	0.1 ml	

40 The reaction mixture did not contain an aqueous phase. 40

The yield of the title compound was 50% after one hour and 73% after 2.5 hours' stirring. After 3.5 hours' stirring an additional quantity of powdered sodium hydroxide (15.6 mmol) and of methyltri(1 - methylheptyl)ammonium chloride (0.054 mmol) were added. The yield of the title compound was more than 95% after 45 a total stirring time of 20 hours. 45

Example XVII

Preparation of 3,8,8-trimethyl-4,4-dichloro-tricyclo[5,1,0,0^{3,5}]octane

The starting materials were:

50 (+) 3-carene	294 mmol	
Chloroform	678 mmol	50
methyltri(1-methylheptyl)ammonium chloride	0.9 mmol	

Powdered sodium hydroxide (525 mmol) was added over a period of one hour in such a manner that the temperature was maintained at 40°C. When after an

additional 0.5 hours' stirring the temperature dropped to 35°C the cooling bath was removed. This caused an increase of the temperature to 49°C within 30 minutes; then the temperature dropped to 20°C within five hours. Then, anhydrous sodium sulphate (10 g) was added and the solid material was filtered off. The filtrate was washed with dichloromethane (50 ml) and the solvent was evaporated from the washed filtrate to give a residue 62.2 g) fully consisting of the title compound, the yield being 97%.

Example XVIII

Preparation of 2,2-dichloro-1-phenylcyclopropane

The starting materials were:

Styrene	400 mmol
Powdered sodium hydroxide	680 mmol
Chloroform	1200 mmol
Methyltri(1-methylheptyl)ammonium chloride	4 mmol
Sodium sulphate	400 mmol

The yield of the title compound was 100% after 0.5 hours' stirring at 65°C.

WHAT WE CLAIM IS:—

1. Process for the preparation of a dihalocyclopropane derivative which comprises reacting under substantially anhydrous conditions an unsaturated compound with a haloform, in the presence of a solid alkali metal hydroxide and an onium catalyst to promote the formation of dihalo-methylene radicals from the haloform.

2. Process according to Claim 1 wherein the solid alkali metal hydroxide is present in a molar ratio to the unsaturated compound in the range 1:1 to 10:1.

3. Process according to Claim 2 wherein the molar ratio of solid alkali metal hydroxide to unsaturated compound is in the range 1.5:1 to 4:1.

4. Process according to any one the preceding claims wherein the reaction temperature is in the range 15°C to 45°C.

5. Process according to any one of the preceding claims wherein the alkali metal hydroxide is sodium hydroxide.

6. Process according to any one of the preceding claims wherein the onium catalyst is a quarternary onium compound of nitrogen, phosphorus, arsenic or antimony, or a tertiary onium compound of sulphur, selenium or tellurium and which the groups surrounding these atoms are hydrocarbyl groups selected from alkyl, cycloalkyl, aryl, aralkyl, or alkaryl group, and in which in the case of quaternary ammonium compounds one of the surrounding groups can be additionally a hydroxy group.

7. Process according to Claim 6 wherein the onium catalyst is a quaternary ammonium compound or a tertiary sulphonium compound in which the surrounding groups are selected from alkyl groups individually containing 1 to 20 carbon atoms and wherein the onium catalyst is in the form of a hydroxide, chloride, bromide, iodide, sulphate or alkyl sulphate.

8. Process according to any one of the preceding claims wherein the molar ratio of onium catalyst to haloform is in the range 0.01:1 to 0.0005:1.

9. Process according to any one of the preceding claims wherein the haloform is bromoform or chloroform.

10. Process according to any one of the preceding claims wherein the unsaturated compound is an ethylenically-unsaturated compound containing 1 to 3 carbon-carbon double bonds and up to 30 carbon atoms per molecule.

11. Process according to Claim 10 wherein the unsaturated compound is an ester of a 2-alkenoic acid in which the ester is derived from a tertiary alcohol.

12. Process according to Claim 10 wherein the unsaturated compound is an alkene, cycloalkene or cycloalkatriene.

13. Process according to Claim 1 substantially as hereinbefore described and with reference to any one of Examples I to XVI.

14. Process according to Claim 1 substantially as hereinbefore described and with reference to Example XVII or XVIII.

15. Dihalo-cyclopropane derivatives prepared by a process claimed in any one of the preceding claims.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1981
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.