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ROLE OF THE POLYMER BACKBONE ON THE REACTIVITY OF POLYMER-SUPPORTED (DICHLOROIODO)BENZENE

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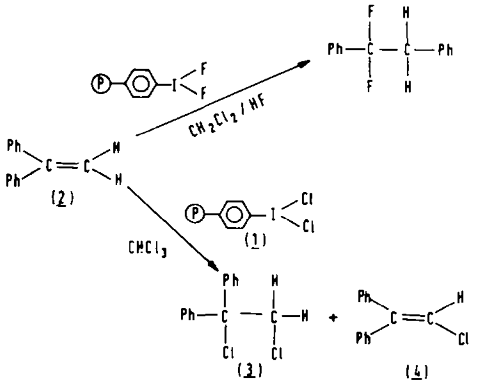
Abstract—Chlorination of iodinated crosslinked polystyrene with Cl_2 gave polyaryliododichloride containing 1.1 mmol of active chlorine per gram of resin, while fluorination of the same iodinated resin with XeF_2 gave polyaryliododifluoride, containing 1.05 mmol of active fluorine per gram of resin. Both resins reacted with 1,1-diphenylethylene, reaction with polyaryliododifluoride giving rearranged 1,1-difluoro-1,2-diphenylethane, while polyaryliododichloride gave 1,2-dichloro-1,1-diphenylethane and 1,1-diphenyl 2-chloroethene. The stereochemistry of chlorine addition with polyaryliododichloride to cis or trans-1-phenylpropene is very similar to that observed in the reaction with Cl_2 under ionic conditions, and its reactivity differs markedly from (dichloroiodo)benzene, which reacts via radical intermediates. Similar studies with 1-phenylalkynes and norbornene are described.

Polymeric resins can be chemically transformed so that they can act as reagents, and besides offering a simpler experimental technique, the chemical reactivity can also be changed when the reagent is attached to a polymer backbone.[1] Katchalski and coworkers have pointed out the important role of the polymeric backbone observed in chlorination and bromination of alkyl substituted benzene derivatives with N-chloropolymaleimide[2] and N-bromopolymaleimide,[3] where chlorination of toluene was directed towards the benzene nucleus.[2]

(Dichloroiodo)benzenes react with alkenes and alkynes mainly via radical intermediates to give dichloro products. Halensleben has prepared a polymer supported analogue from polystyrene and found that reaction with cyclohexene gave only trans products.[4] We have already found that iodination of "popcorn" polystyrene resulted in a polymer containing 32% of iodine, while further reaction with xenon difluoride in the presence of HF in methylene chloride at 25° gave polyaryliododifluoride, the amount of active fluorine on the polymer resin depending on the amount of XeF_2 used.[5,6] In experiments where 3.04 mmol of XeF_2 per gram iodinated "popcorn" polystyrene was used, the reagent contained 2.19 mmol of active fluorine.

We now wish to report the synthesis and properties of crosslinked polymer supported aryliododichloride and aryliododifluoride. Iodination of crosslinked polystyrene (2% DVB), which was prepared by emulsion polymerization, contained 26.2% of iodine after iodination, which means that more than one quarter of the phenyl rings was functionalized. However, further reaction of 1 g of polymer resin with 3 mmols of XeF_2 gave polyaryliododifluoride containing only one half of the amount of active fluorine compared to that prepared in the reaction with iodinated "popcorn" polystyrene. Introduction of chlorine at 0° in a chloroform suspension of iodinated crosslinked polystyrene gave polyaryliododichloride containing 1.1 mmol of active chlorine per gram of polymer resin. Further, we studies the reactivity of both reagents with 1.1-diphenylethene (**2**). Polyaryliododifluoride in methylene chloride in the presence of a catalytic amount of HF gave rearranged 1,1-difluoro 1,2-diphenylethane as sole product in high yield, while reaction with polyaryliododichloride, besides addition, also resulted in the elimination product (Scheme 1). Conversion of the starting olefin (**2**) in chloroform, and the ratio between 1,2-dichloro 1,1-diphenylethane (**3**) and 1,1-diphenyl 2-chloroethene (**4**) depended on the reaction temperature and reaction time, and is presented in Scheme 1.



VARIATION OF PRODUCT DISTRIBUTION WITH TEMPERATURE AND REACTION TIME IN THE CHLORINATION OF 1,1-DIPHENYLETHENE (2) IN CHLOROFORM

T [°C]	REACT TIME [MIN]	2 [%]	3 [%]	4 [%]
20	60	24	46	30
20	240	8	37	55
62	60	–	53	47
62	240	–	23	77

Scheme 1.

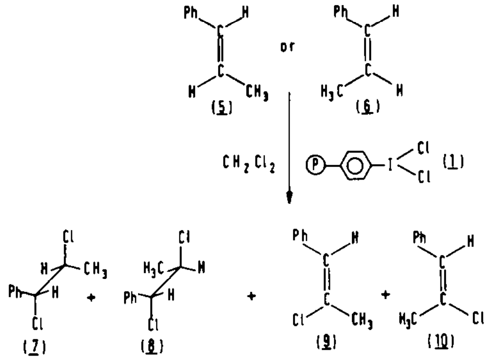
Being interested in the effect of a polymer backbone on the reactivity of a polymer supported dichloroiodo reagent (**1**), we studied the stereochemistry of chlorine addition to cis and trans-1-phenylpropene-1, where it is known that the reaction with (dichloroiodo)benzene occurs through radical intermediates[7] and with Cl_2 through ionic intermediates,[8] the different pathways for the two reactions being strongly reflected in the stereochemistry of addition (Scheme 2). A 2 h reaction of 1 mmol of alkene **5** or **6** with 1 g of **1** in methylene chloride under reflux gave four products in the case of E-alkene (**5**), and in the case of Z-alkene (**6**), three products. Conversion of starting olefin under the mentioned conditions was more than 70%. The structures of the products were determined on the basis of spectroscopic data and by comparison to compounds prepared by independent synthesis.[8] The results presented in Scheme 2 show that the polymer backbone significantly changed the course of chlorination, while the stereochemistry of chlorine addition is very similar to that observed in chlorination with Cl_2. The presence of oxygen as radical scavenger also had no significant effect on the stereochemistry of addition.

Reactions with norbornene have often been used to differentiate the ionic or radical character of various reactions. It was also confirmed in reactions with norbornene that chlorination with (dichloroiodo) benzene[9] occurred via a radical pathway, thus forming only 2-exo-3-endo-dichloronorborane, and exo-2,3-dichloronorborane, while reaction with chlorine in the presence of oxygen led to four products via ionic intermediates, whereas chlorination with Cl_2 in a nitrogen atmosphere resulted in six products, which was explained by a course of reaction partially radical in nature. A 2 h reaction of 1 mmol of norbornene (**11**) in 20 ml of methylene chloride under reflux with **1** (1 g) resulted in more than 80% conversion of the starting olefin and four products were isolated by preparative GLC (Scheme 3). The structures of the products were established on the basis of spectroscopic data and by comparison with compounds synthesized independently. The product distribution stated in Scheme 3 was determined by analytical GLC and represents average data from three experiments, (with a maximum error ±0.5%) and again confirms the similarity of the reactions of the polymer-supported dichloroiodo derivative to those of Cl_2.

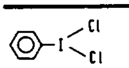
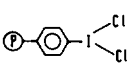
The stereochemistry of chlorine addition to acetylenes strongly depends on the reagent used, and the structure of the acetylene. First we studied the effect of the amount of 1-phenylpropyne and the reaction time on the conversion of starting acetylene, and on the stereochemistry of chlorine addition with polyaryliododichloride. Reaction time and the amount of halogenating agent (**1**) affected the degree of conversion, but little influence on the stereochemistry of addition was observed (Scheme 4). The influence of the reagent on the stereochemistry of chlorine addition to 1-phenylpropyne is evident from Scheme 4, and again the similarity of reactivity of polyaryliododichloride with Cl_2 is confirmed.

Further, we investigated the effect of the structure of the acetylene on the stereochemistry of chlorine addition with polyaryliododichloride. Reaction of (**1**) with phenylacetylene, besides the cis and trans adduct, also gave 57% of 1-phenyl-2-chloro acetylene, while addition of chlorine with (**1**) to 1-phenyl-2-t-butylacetylene occurred predominantly cis. The presence of oxygen had no significant effect on the stereochemistry of addition (Scheme 5].

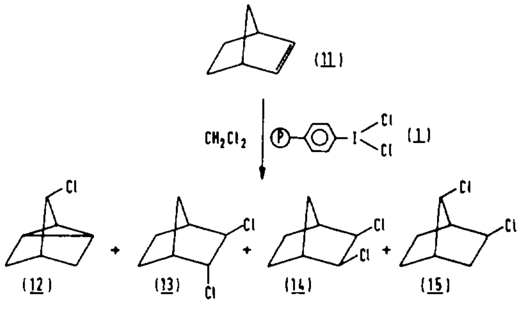
All these results once again indicate the important



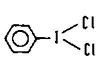
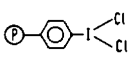
STEREOCHEMISTRY OF CHLORINE ADDITION TO 1-PHENYLPROPENE-1

REAGENT	ALKENE	7+8 [%]	7 8	9 [%]	10 [%]	REF
	5	100	15 7	–	–	7
	6	100	15 7	–	–	7
	5	88	3 6	3	9	
	6	84	2 2	16	–	
	5 [O_2]	84	2 5	12	4	
	6 [O_2]	79	2 2	21	–	
Cl_2	5	84	2	2	14	8
	6	84	2 8	10	6	8

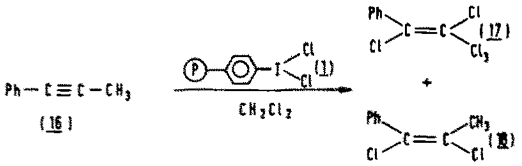
Scheme 2.



PRODUCT DISTRIBUTION IN THE CHLORINATION OF NORBORNENE (11)

REAGENT	SOLVENT	12 [%]	13 [%]	14 [%]	15 [%]	REF
	$CHCl_3$	–	75	25	–	9
	CH_2Cl_2	52	12	10	26	
$Cl_2(N_2)$	CCl_4	50	8	16	22	10
$Cl_2(O_2)$	CCl_4	65	6	3 5	25.5	10

Scheme 3.



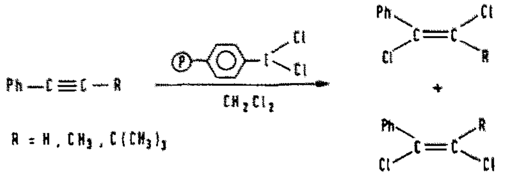
EFFECTS OF VARIABLES ON STEREOCHEMISTRY OF CHLORINE ADDITION TO 1-PHENYLPROPYN (16) IN CH_2Cl_2 (20ml) UNDER REFLUX

(1) (gram)	(16) (mmol)	REACT TIME (min)	CONVERSION OF (16) (%)	E Z
2	1	60	32	1 56
2	1	120	55	1 56
2	1	180	67	1 70
2	1	300	100	1 78
1	0 5	300	80	1 86
1	1	300	45	1 63
1	2	300	30	2 13
1	3	300	24	2 23

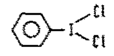
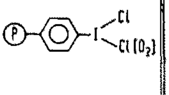
STEREOCHEMISTRY OF CHLORINE ADDITION TO 1-PHENYLPROPYN

REAGENT	SOLVENT	TEM (°C)	E Z	Ref
$CuCl_2$	CH_3CN	82	49	11
$C_6H_5ICl_2$	$CHCl_3$	refl	9	12
(1)	CH_2Cl_2	refl	1 7	
Cl_2	CCl_4	25	2	13
$SbCl_5$	CCl_4	76	0 28	13

Scheme 4.



EFFECTS OF SUBSTITUENTS ON STEREOCHEMISTRY OF CHLORINE ADDITION TO ACETYLENES

	R = H	R = CH_3	R = $C(CH_3)_3$
REAGENT	Z / E	Z / E	Z / E
	0 12	0 11	
	1 5 1 4	0 59 0 59	10 1 11
Cl_2	1 04	0 5	6 7

Scheme 5.

influence ofthe polymer backbone on the reactivity of the supported reagent.

EXPERIMENTAL

Iodination of crosslinked polystyrene

In a 2-L three necked flask, equipped with reflux condenser, glass stirrer, and thermometer, 83 ml of 50% H_2SO_4, 330 ml of nitrobenzene, 50 g of iodine, 16.6 g of HIO_3, 125 ml of CCl_4, and 50 g of polystyrene (2% of DVB, prepared by emulsion polymerisation and activated with various solvents) were stirred for 160 h at 110°. Polymer resin was filtered off, washed with ethanol, then placed in a Soxhlet apparatus and extracted for 24 h with methylene chloride and after drying in air at room temperature, 62 g of iodinated product was isolated. For elemental analysis, 1 g of product was dried in vacuo at 62° to constant weight and 0.9 g of product containing 26.2% of iodine was obtained.

Crosslinked polyaryliododifluoride

5 g of air-dried iodinated polystyrene, 2.7 g of XeF_2 and 60 ml of methylene chloride were placed in a 100 ml polyethylene flask and under stirring the reaction was initiated with a catalytic amount of HF. After 1 h polymer the beads were filtered off, washed with methylene chloride and dried for 24 h in air at room temperature and 6.2 g of polyaryliododifluoride was isolated. 1 g of air dried product, when dried in vacuo at 62° to constant weight, gave 0.97 g of product. 1 g of polymer resins contained 1.05 mmol of active fluorine, determined by titration of the iodine liberated from a solution of KI.

Crosslinked polyaryliododichloride (**1**)

6 g of air dried iodinated polystyrene and 120 ml of chloroform were placed in a 250 ml glass flask and under stirring at 0° chlorine was introduced until the reaction mixture remained yellow-green in colour, and was then stirred at room temperature for an additional hour. The polymer beads were filtered off, washed with chloroform, dried in air at room temperature for 24 h, and 7.5 g of polyaryliododichloride was obtained. 1 g of air dried product when dried in vacuo at 62° to constant weight, gave 0.89 g of product. 1 g of polymer resins contained 1.1 mmol of active chlorine, determined by titration of the iodine liberated from a solution of KI.

Fluorination of 1,1-*diphenylethene*

15 ml of methylene chloride, 1 mmol of 1,1-diphenylethene, and 1 g of polyaryliododifluoride were placed in a polyethylene vessel and under stirring a catalytic amount of HF was introduced in the reaction mixture, which was stirred for 2 h at room temperature. Insoluble polymer beads were filtered off, washed twice with methylene chloride, and the combined filtrate was washed with aqueous $NaHCO_3$, water, and dried over Na_2SO_4. The solvent was evaporated in vacuo and 210 mg of crude product was obtained which was analysed by NMR spectroscopy; it was found that all the olefin was converted to 1,1-difluoro-1,2-diphenylethane.

Chlorination of 1,1-*diphenylethene*

Chloroform (15 ml), 1 mmol of 1,1-diphenylethene and 1 g of polyaryliododichloride were placed in a glass vessel. The reaction mixture was stirred at room temperature or heated at 62° for 1 to 4 h. The polymer beads were filtered off, the solvent evaporated *in vacuo* and 200–220 mg of reaction mixture were obtained. The products were isolated by preparative GLC and identified on the basis of their spectroscopic data. Product distributions were determined by ^1H NMR and data are presented in Scheme 1.

Chlorination of cis or trans-1-*phenylpropene*-1 (**6** *or* **5**)

Alkene (1 mmol), 1 g of polyaryliododichloride and 20 ml of methylene chloride were heated under reflux for 2 h, the polymer beads were filtered off, the solvent evaporated in vacuo and the crude reaction mixture analysed by ^1H NMR and GLC. In Scheme 2 average data for the product distribution from three experiments, obtained by ^1H NMR are presented. The structures of the products were established on the basis of spectroscopic data and by comparison with those synthesized independently.

Chlorination of norbornene (**11**)

Norbornene (1 mmol), 1 g of polyaryliododichloride and 20 ml of methylene chloride were heated under reflux for

2 h, the polymer beads were filtered off, the solvent evaporated in vacuo and the crude reaction mixture analysed by GLC. The averaged data of three experiments are presented in Scheme 3. Pure products were isolated by preparative GLC and their structure was determined on the basis of spectroscopic data and by comparison with compounds synthesized independently.

Chlorination of 1*-phenylpropyne* (**16**)

Various amounts of acetylene and polyaryliododichloride were heated under reflux for various time (see Scheme 4). After the usual work-up, the crude reaction mixture was analysed by ^{1}H NMR; the product distributions are presented in Scheme 4. products were isolated by preparative GLC and their structures determined on the basis of spectroscopic data and by comparison with those synthesized independently.

Chlorination of phenylacetylene and 1*-phenyl-*2*-t-butylacetylene*

The acetylene (1 mmol), 1 g of polyaryliododichloride and 20 ml of methylene chloride were heated under reflux for 5 h, and the crude reaction mixture analysed by ^{1}H NMR after the usual work-up procedure. Product distributions determined by ^{1}H NMR are presented in Scheme 5. In chlorination of phenylacetylene with **1**, beside E and Z-1,2-dichloro-1-phenylethene, 1-phenyl-2-chloroacetylene in 57% relative yield, as determined by GLC, was also formed.

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