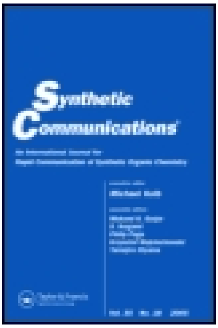

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Synthesis of Herbicides Using Polymer Supported 2, 4-Dichlorophenoxy Acetic Acid Anion

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SYNTHESIS OF HERBICIDES USING POLYMER SUPPORTED 2, 4-DICHLOROPHENOXY ACETIC ACID ANION[1]

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ABSTRACT : 2, 4-Dichlorophenoxy acetic acid anion supported on anion exchange resin (Tulsion A-27 Chloride form) was treated with appropriate dihalide in acetonitrile at 25°C or 80 - 85°C to give corresponding diesters of 2, 4-dichlorophenoxy acetic acid as effective herbicides.

The esters of 2,4-dichlorophenoxy acetic acid (2,4-D) are widely used as herbicides[2]. They are generally prepared by the following three methods; (a) by refluxing the appropriate alcohol with 2, 4-D in the presence of acid catalyst[3,4] (b) by the reaction of the appropriate alcohol with the acid chloride of 2,4-D[5] and (c) by the reaction of 2,4-dichlorophenol with the corresponding chloroacetic acid ester in acetone in the presence of potassium carbonate.[6] As mono esters of 2,4-D are effective herbicides, we believe that diester of 2,4-D would be more active herbicides. Therefore, we are interested in the synthesis of diesters of 2,4-D.

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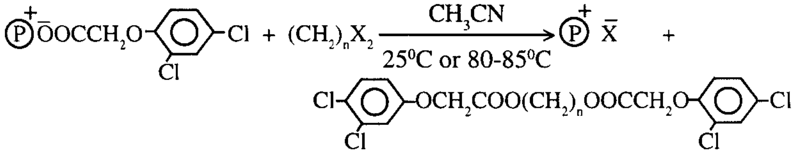
The treatment of polymer supported 2,4-D anion with the appropriate dihalide, $(CH_2)_nX_2$ in acetonitrile at 25⁰C or 80-85⁰C gave product which was isolated by simple filtration of the resin and removal of the solvent under reduced pressure (scheme).



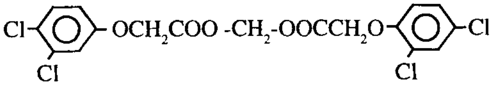
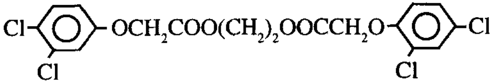
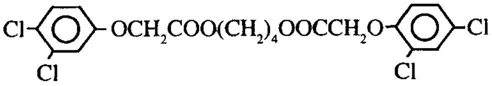
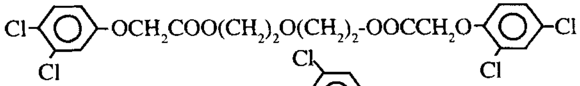
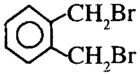
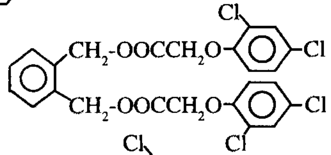
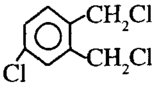
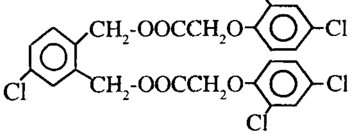
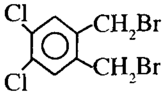
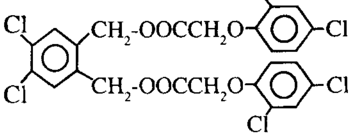
The products were obtained in a state of high purity. The results are summarised in table 1. When sodium salt of 2,4-D in ethanol was treated with appropriate dihalide at 25⁰C or 80- 85⁰C, the yields of corresponding diesters were very low as compared with the yields of present methodology. This indicates that the nucleophilicity of polymer supported 2,4-D anion is more than that of sodium salt of 2,4-D. After completion of the reaction, the resin could be regenerated to its initial activity. Herbicidal activity of all diesters was found to be much more than that of corresponding mono esters of 2,4-D.

Experimental: Solvents were distilled before use. All chemicals were of analytical grade. Tulsion A-27 ($\bar{Cl}$ form) was obtained from Thermax Chemicals, Pune.

General Procedure for the preparation of polymer supported 2,4-D anion: 2,4-D (50 mmol) was dissolved in 100 ml aqueous solution of NaOH (50 mmol). Tulsion A-27 ($\bar{Cl}$) (10 g) was added in above solution of sodium salt of 2,4-D and the reaction mixture was stirred for 1 h and kept overnight. The resin was filtered and washed with distilled water till filtrate was free from chloride ions and excess of 2,4-D sodium salt. Then resin was washed with alcohol and ether. The resin was then dried under vacuum at 50⁰C for 2 h. The capacity of the resin was found to be 2 mmol/gm.

General procedure for the synthesis of diesters of 2,4-D: A dihalide (5 mmol) was dissolved in acetonitrile (20 ml) and 2,4-D anion supported resin (10 g) was added

Table 1 : Synthesis of 2,4-D in acetonitrile

Entry	Dihalide	Product	Reaction time (h)	Yield %
1	$Cl\text{-}CH_2\text{-}Cl$		16	37
2	$Br\text{-}(CH_2)_2\text{-}Br$		5.5	60
3	$Br\text{-}(CH_2)_4\text{-}Br$		4	62
4	$Br(CH_2)_2O(CH_2)_2Br$		6.5	43
5			8	69
6			7	81
7			6	80

in above solution. Then the reaction mixture was stirred at 25°C or refluxed at 80-85°C for the specified period (table). The reaction was monitored by TLC. After the reaction was complete, the resin was removed by filtration and washed with diethyl ether (3x10 ml). Removal of the solvent under reduced pressure gave product in almost pure form. The products were characterised by IR and PMR.

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References and footnotes:

1. This paper has been dedicated to Prof. M. S. Wadia (University of Pune) on occasion of his 60th birthday. This paper is in the series of solid supported reagents and reactions part 20. For part 19, see Gajare, A. S.; Shingare, M. S. and Bandgar, B. P. Communicated.
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