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DICHLOROMETHYLATION OF XYLENES

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This invention relates to a process for the dichloromethylation of xylenes. More particularly, this invention relates to a process for the conversion of xylenes to dichloromethyl xylenes with high yield and high selectivity.

In copending application Ser. No. 717,225 for H. W. Earhart et al., filed February 24, 1958, and entitled "Chloromethylation Process," now abandoned, there is disclosed a process for chloromethylating aromatic hydrocarbons in a manner to minimize the formation of unwanted alkyl diphenyl methane by-products. While highly beneficial results are obtainable with the process disclosed in the said copending application, problems are encountered in dichloromethylating xylenes when the desired product is to be composed primarily of the dichloromethylated product.

It has now been surprisingly discovered that maximized yields and selectivities of dichloromethyl xylenes

are obtainable when the xylene is reacted with about 12 to 15 mols of hydrochloric acid, about 1.5 to 2.5 mols of zinc chloride, about 4.5 to 5.5 mols of formaldehyde, and about 55 to 65 mols of water per mol of xylene at a temperature of about 90° to 100° C. for a reaction time of about 1 to 3 hours.

The invention will be further illustrated by the following specific examples which are given by way of illustration and not as limitations on the scope of this invention.

EXAMPLE I

A plurality of samples of orthoxylenes were chloromethylated under a variety of chloromethylation conditions. The chloromethylation conditions employed and the results obtained are set forth in the following table.

Table I

DICHLOROMETHYLATION OF o-XYLENE

Experiment No.	1	2	3	4	5	6	7	8	9
Mols HCl/Mol o-Xylene	2	10	4⅔	7	3	14	5	3⅓	6
Mols $ZnCl_2$/Mol o-Xylene	⅔	3	1	½	1½	2	1	⅓	1
Mols CH_2O/Mol o-Xylene	2	6	1⅓	3	2½	5	2	1⅔	4
Mols H_2O/Mol o-Xylene	11	70	20	30	25	60	35	23	50
Time, Hr	1	1	½	1	1½	1½	½	1½	½
Temperature, ° C	95	85	85	75	85	95	95	75	75
Product, Percent:									
o-Xylene	69.7	31.8	34.7	28.0	56.2	0.4	69.1	64.7	87.9
Chloromethyl-o-xylene	22.1	42.7	38.8	59.9	25.1	48.7	27.1	5.9	5.6
Dichloromethyl-o-xylene	2.1	10.6	------	4.5	2.5	38.3	1.1	1.9	------
Trichloromethyl-o-xylene	0.1	------	------	0.4	------	------	------	1.8	------
Tetrachloromethyl-o-xylene	------	------	------	------	------	------	------	3.1	------

It will be observed from Table I that a high yield of dichloromethyl-ortho-xylene was obtained only in the case of Experiment 6 which was conducted in accordance with the present invention. It will be further observed that there was a high selectivity to the dichloromethylated products.

While not reported in the table, it is to be observed that the dichloromethylated product that was formed was a mixture of the three possible isomeric forms of dichloromethyl-ortho-xylene.

EXAMPLE II

A plurality of samples of paraxylene were subjected to chloromethylation under a wide variety of reactions. The conditions employed and the results obtained are set forth in Table II.

Table II

DICHLOROMETHYLATION OF p-XYLENE

Experiment No.	1	2	3	4	5	6	7	8	9
Mols HCl/Mol p-Xylene	2	10	4⅔	7	3	14	5	3⅓	6
Mols $ZnCl_2$/Mol p-Xylene	⅔	3	1	½	1½	2	1	⅓	1
Mols CH_2O/Mol p-Xylene	2	6	1⅓	3	2½	5	2	1⅔	4
Mols H_2O/Mol p-Xylene	11	70	20	30	25	60	35	23	50
Time, Hr	1	1	½	1	1½	1½	½	1½	½
Temperature, ° C	95	85	85	75	85	95	95	75	75
Product, Percent:									
p-Xylene	83.2	47.4	42.9	36.2	70.4	1.2	79.3	88.0	93.9
Chloromethyl-p-xylene	14.6	43.6	31.9	56.2	21.0	66.0	19.2	6.0	2.8
Dichloromethyl-p-xylene	2.2	9.0	5.2	5.7	4.8	28.2	1.5	1.1	0.7
Trichloromethyl-p-xylene	------	------	------	------	------	------	------	0.5	0.4
Tetrachloromethyl-p-xylene	------	------	------	------	------	------	------	0.5	------

From Table II it will be observed again that the only experiment providing for a material yield of dichloromethyl-paraxylene was Experiment 6, conducted in accordance with the present invention. It will further be observed that there was a high selectivity to the dichloromethylated product and that, in addition, a maximized yield of the monochloromethylated product was obtained.

EXAMPLE III

A plurality of samples of metaxylene were subjected to a variety of chloromethylation conditions. The experimental conditions employed and the results obtained are set forth in Table III.

Table III

DICHLOROMETHYLATION OF m-XYLENE

Experiment No.	1	2	3	4	5	6	7	8	9
Mols HCl/Mol m-xylene	7	6	14	4.7	10	3.3	5	2	3
Mols $ZnCl_2$/Mol m-xylene	0.5	1	2	1	3	0.3	1	0.7	1.5
Mols CH_2O/Mol m-xylene	3	4	5	1.3	6	1.7	2	2	2.5
Mols H_2O/Mol m-xylene	30	50	60	20	70	23	35	11	25
Time, Hr.	1	0.5	1.5	0.5	1	1.5	0.5	1	1.5
Temperature, ° C.	75	75	95	85	85	75	95	95	85
Product, Percent:									
Monochloromethyl	79.0	45.4	2.0	64.5	43.5	44.2	58.9	36.0	25.0
Dichloromethyl	15.7	41.9	84.9	21.1	33.4	1.8	8.8	7.9	13.6
Diphenylmethanes and Trichloromethyl	0.5	3.1	8.5	7.2	19.4	1.4	6.6	29.2	51.7

From Table III it will again be observed that a maximized yield of the dichloromethyl product was obtained only in the case of Run No. 3 conducted in accordance with the present invention. The results obtained with metaxylene are particularly surprising. Note that with metaxylene the chloromethylation product that is obtained consists essentially of dichloromethyl-meta-xylene and that only minor amounts of monochloromethyl-meta-xylene are formed.

Having described our invention, what is claimed is:

1. A method for the dichloromethylation of a xylene which comprises contacting said xylene with about 12 to 15 mols of hydrochloric acid, about 1.5 to 2.5 mols of zinc chloride, about 4.5 to 5.5 mols of formaldehyde, and about 55 to 65 mols of water per mol of xylene at a temperature of about 90° to 100° C. for a reaction time within the range of about 1 to 3 hours and thereafter recovering a dichloromethyl xylene from said product.

2. A method as in claim 1 wherein the xylene is orthoxylene.

3. A method as in claim 1 wherein the xylene is metaxylene.

4. A method as in claim 1 wherein the xylene is paraxylene.

References Cited in the file of this patent

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