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In our recent papers on the alkylation of aromatic hydrocarbons with styrene (eq 1),^{1,2} we have shown that solid polymeric oxo acids as catalysts can bring about higher yields of 1-phenyl-1-arylethane (**I**) than the corresponding soluble oxo acids [e.g., poly(styrenesulfonic acid) (Amberlyst 15) vs. *p*-CH₃C₆H₄SO₃H; perfluorinated resinsulfonic acid (Nafion-H) vs. CF₃SO₃H]. In view of the easy separation of the product from the catalyst, the use of these effective polymeric oxo acids should be industrially more advantageous than homogeneous processes using soluble acidic catalysts.

This article deals with the alkylation of aromatic hydrocarbons (toluene and *m*-xylene) with divinylbenzene (DVB) catalyzed by solid polymeric oxo acids (Nafion-H and Amberlyst 15). If the two vinyl groups in DVB, as in the case of styrene, react independently with aromatic hydrocarbons (eq 2), the product will be bis(1-arylethyl)benzene (**II**), a tri-nuclear aromatic compound. DVB in conjunction with a solid polymeric oxo acid as catalyst has not yet been used in the Friedel-Crafts alkylation, although the synthesis of **II** using bis(chloromethyl)benzene³ or aryl chlorides⁴ has been reported. Alkylation with DVB catalyzed by soluble oxo acids and Lewis acids was also investigated for comparison.

EXPERIMENTAL

Materials

The DVB used in most experiments was an isomeric mixture (*m*-DVB/*p*-DVB = 70/30, purity $\geq 98\%$) separated from a commercial mixture of DVB (60%) and ethylvinylbenzene (40%) by preparative liquid chromatography.⁵ *p*-DVB and *m*-DVB were isolated from the commercial mixture by the method of Storey *et al.*⁶ Catalysts and aromatic hydrocarbons, toluene and *m*-xylene, were purified and used as reported.^{1,2}

Procedure

Reactions were initiated under dry nitrogen by the addition of DVB to an aromatic substrate (toluene and *m*-xylene) containing a catalyst.^{1,2} When the DVB was completely consumed (checked by gas chromatography), methanol containing a small amount of aqueous ammonia was added to

Table I. Alkylation of toluene and *m*-xylene with DVB by acid catalysts at 70°C^a

Catalyst	[Catalyst] ₀	Aromatic substrate	Yield of II
	mM		wt%
Nafion-H	3.0 ^c	Toluene	42.6
CF ₃ SO ₃ H	0.50	Toluene	5.0
BF ₃ OEt ₂ ^b	20	Toluene	trace
Nafion-H	3.0 ^c	<i>m</i> -Xylene	61.8
Amberlyst 15	10 ^d	<i>m</i> -Xylene	54.7
CF ₃ SO ₃ H	0.50	<i>m</i> -Xylene	45.4
<i>p</i> -CH ₃ C ₆ H ₄ SO ₃ H	30	<i>m</i> -Xylene	40.4
AcClO ₄	1.0	<i>m</i> -Xylene	40.0
BF ₃ OEt ₂ ^b	20	<i>m</i> -Xylene	trace

^a [DVB]₀ = 0.10 M (*m/p* = 70/30); reaction time, 12 hr for BF₃OEt₂ and 1 h for the other catalysts; conversion of DVB = 100%.

^b With 10 mM of added water.

^c 3.3 mg cm⁻³.

^d 2.0 mg cm⁻³.

stop the reaction. After removing the catalyst residue by filtration or extraction with water, the product was recovered by evaporation of the volatile compounds. The yield of **II** was determined by liquid chromatography (JASCO TRIOTAR chromatography with a refractive index detector, JSP-101 polystyrene gel column, chloroform solution). The alkylation products were isolated from the crude products by liquid chromatography. The structure of each product was analyzed by ¹H NMR (JEOL FX90Q, CDCl₃ solution).

RESULTS AND DISCUSSION

Effect of Catalysts

Alkylation of toluene and *m*-xylene with DVB (*m/p* = 70/30) was carried out at 70°C with a variety of catalysts including solid polymeric oxo acids and their soluble counterparts. The concentration of DVB was kept low (0.10 M) so as to suppress its polymerization. The yields of **II** are summarized in Table I. The remainder of the products was confirmed to be DVB oligomers capped with toluene and *m*-xylene by ¹H NMR.⁵

In the alkylation of toluene, Nafion-H gave **II** in a 43% yield. However, CF₃SO₃H and BF₃OEt₂ promoted the polymerization of DVB, resulting in very low yields of **II**.²

In the reaction of *m*-xylene, a more basic substrate, the yield of **II** was always higher than that for

toluene with the same catalyst. Nafion-H and Amberlyst 15 gave higher yields of **II** than the corresponding soluble acids.² Other soluble oxo acid such as AcClO₄ also produced **II** as well as CF₃SO₃H and *p*-CH₃C₆H₄SO₃H, but BF₃OEt₂ (metal halide) gave only a trace amount of **II**. These catalyst effects are similar to those obtained for alkylation with styrene,^{1,2} suggesting a strong interaction between the carbocation and oxo acid anion.¹ The effectiveness of the solid polymeric oxo acids (Nafion-H and Amberlyst 15) as alkylation catalysts was also demonstrated in this work.²

¹H NMR spectra of the alkylation products isolated from the products by liquid chromatography were independent of the kind of catalysts and showed the following signals:

Toluene/DVB system: phenyl (δ 6.96 ppm, s, 12H); methine (3.96 ppm, q, 2H); aromatic methyl [2.23 (*p*-CH₃) and 2.13 (*o*-CH₃) ppm, s, 6H; *p/o* = 95/5]; and aliphatic methyl (1.25 ppm, d, 6H).

m-Xylene/DVB system: phenyl (δ 7.06 ppm, t, 10H); methine (4.24 ppm, q, 2H); aromatic methyl [2.29 (*p*-CH₃) and 2.18 (*o*-CH₃) ppm, s, 12H]; and aliphatic methyl (1.56 ppm, d, 6H).

These data indicate that the alkylation products obtained with toluene and *m*-xylene were mainly **II-a** and **II-b**, though **II-a** contained 5% of an *o*-substituted product.

Table II. Effect of reaction conditions and the isomeric structure of DVB on the alkylation of *m*-xylene^a

Catalyst ^b	Temp	[DVB] ₀	<i>m</i> -DVB/ <i>p</i> -DVB in feed	Yield of II-b
	°C	M		wt%
Nafion-H	70	0.10	70/30	61.8
Nafion-H	120	0.10	70/30	73.2
Nafion-H	120	0.50	70/30	60.8
Nafion-H	120	0.10	90/10	79.3
CF ₃ SO ₃ H	70	0.10	70/30	45.4
CF ₃ SO ₃ H	120	0.10	90/10	70.5
CF ₃ SO ₃ H	120	0.10	70/30	66.0
CF ₃ SO ₃ H	120	0.10	0/100	14.5

^a Reaction time, 1 h; DVB conversion, 100%.^b [Catalyst]₀: Nafion-H, 3.0 mM (3.3 mg cm⁻³); CF₃SO₃H, 0.50 mM.

attained even at a high DVB concentration (0.50 M) at 120°C. DVB feeds richer in the *m*-isomer led to higher yields of **II-b**, which can be explained on the basis of the higher polymerizability of *p*-DVB than that of *m*-DVB.⁵ Thus, **II-b** can be prepared selectively (~80% yield) in the *m*-xylene/*m*-DVB/Nafion-H system at a higher temperature.

Effect of Reaction Conditions on Alkylation of *m*-Xylene

To prepare **II-b** in high yield, the effects of the reaction condition and the isomeric structure of DVB were investigated in the alkylation of *m*-xylene with Nafion-H and CF₃SO₃H catalysts (Table II).

The yield of **II-b** was higher at a higher temperature (120°C) or at a lower DVB concentration (0.10 M), since under these conditions the oligomerization of DVB was suppressed.^{5,7} However, with the Nafion-H catalyst, a high yield of **II-b** (60.8%) was

1. H. Hasegawa and T. Higashimura, *Polym. J.*, **11**, 737 (1979).
2. H. Hasegawa and T. Higashimura, *Polym. J.*, **12**, 407 (1980).
3. N. Grassie and I. G. Meldum, *Eur. Polym. J.*, **5**, 195 (1969).
4. P. Finocchiaro, *Tetrahedron*, **27**, 581 (1971).
5. H. Hasegawa and T. Higashimura, *Macromolecules*, **13**, 1350 (1980).
6. B. T. Storey, *J. Polym. Sci., A*, **3**, 265 (1965).
7. T. Higashimura, M. Hiza, and H. Hasegawa, *Macromolecules*, **12**, 217 (1979).