CHEMISTRY LETTERS, pp. 13-16, 1980.

DIMERIZATION OF α-METHYLSTYRENE BY BINARY SOLID ACIDS

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Binary solid acids catalyze the dimerization of α-methylstyrene. The linear isomers are principal products among the reaction products.

α-Methylstyrene is known to give a mixture of isomeric dimers according to reaction conditions[1-2]. However, there is uncertainty on the reported structure[1] of the linear dimers. We have carried out the reaction of α-methylstyrene with catalytic amounts of binary solid acids at 30 °C, in which isomeric dimers are principal products among oligomeric products. The structure of dimers is elucidated. The effects of the preparation method and the composition of solid acids on the distribution of dimers have been studied, and comments on the dimer formation are given. The solid acids were prepared by calcining the binary metal hydroxides at 500 °C for 4 hr under nitrogen. The hydroxides were obtained by hydrolyzing the mixture of metal chlorides by conc. ammonium hydroxide, or by hydrolyzing the mixture of metal alkoxides by equimolar amounts of water in isopropanol. SiO_2-Al_2O_3 was prepared by calcining the kneaded mixture of SiO_2 and $Al(OH)_3$.

The catalytic activity of the solid acid and the molecular weight data are given in Table 1.

Table 1. Reaction of α-Methylstyrene in Bulk by Solid Acids

No.	Initiator	Time (h)	Yield (%) MeOH sol.	Yield (%) MeOH insol.	Molecular weight MeOH sol.	Molecular weight MeOH insol.
1	Al_2O_3-TiO_2 (9:1)[a]	90	88	2	dimer, trimer	10,000
2	Al_2O_3-TiO_2 (9:1)[b]	90	26	14	dimer - 1,000	10,000
3	Al_2O_3-TiO_2 (1:1)[b]	90	89	trace	dimer - 1,000	-
4	TiO_2 -ZrO_2 (1:1)[a]	90	10	trace	dimer	-
5	SiO_2 -Al_2O_3(4:1)[c]	90	14	4	dimer - 1,500	2,800
6	Acid Clay	1	71	23	dimer - 1,000	5,000

Three ml of the monomer was allowed to react with 5 wt% initiator in bulk at 30 °C.
a) prepared by hydrolysis of metal chlorides b) prepared by hydrolysis of alkoxides c) prepared by kneading SiO_2 with $Al(OH)_3$

Typical GPC traces of the methanol-soluble fraction are shown in Figure 1.

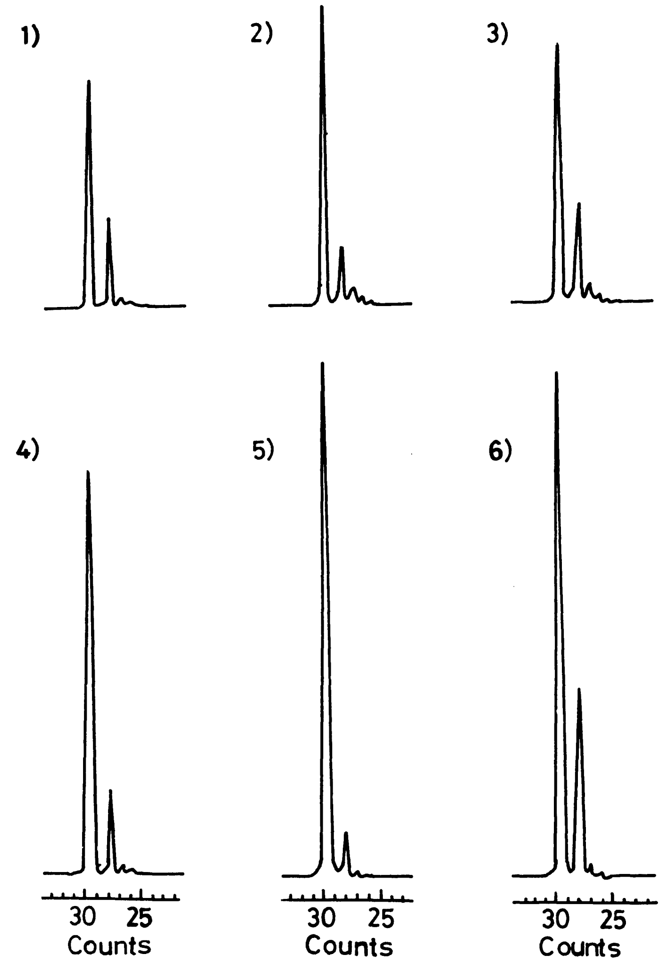


Fig. 1. GPC Traces of Oligo-(α-Methylstyrene) by Solid Acids.

1) Al_2O -TiO_2 (9:1)[a] 2) SiO_2-Al_2O_3 (4:1)

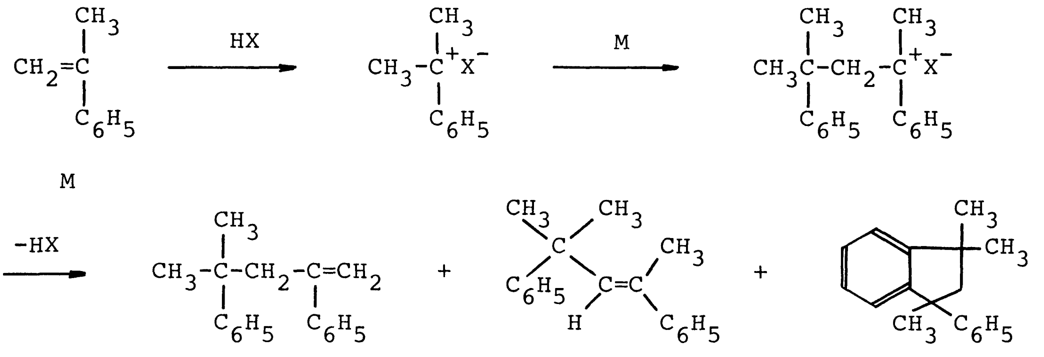
3) Acid Clay 4) Al_2O_3-TiO_2 (9:1)[b]

5) TiO_2-ZrO_2 (1:1) 6) Al_2O_3-TiO_2 (1:1)[b]

a) from chlorides b) from alkoxides

It can be seen that Al_2O_3-TiO_2 prepared from alkoxides tend to give relatively more dimers than that from chlorides. TiO_2-ZrO_2 gives dimers almost exclusively. On the other hand, acid clay, SiO_2-Al_2O_3 (4:1), and Al_2O_3-TiO_2 (9:1) from chlorides give a mixture of oligomers. The dimers can be separated by gas chromatography using 2 m polyethylene glycol 20 M containing 5 % $AgNO_3$ as a stationary phase at 210 °C with 25 ml/min helium as a carrier gas. Dimers were separated into three peaks, and isolated by preparative gas chromatography. Peak I (retention time 15.0 min) ^{1}H-NMR ($CDCl_3$) δ 1.03 (s, 3H, $C\underline{H}_3$), 1.37 (s, 3H, $C\underline{H}_3$), 1.72 (s, 3H, $C\underline{H}_3$), 2.16 (d, 1H, J=13Hz, $C\underline{H}_2$), 2.50 (d, 1H, J=13Hz, $C\underline{H}_2$), 7.26 (m, 9H, $C_6\underline{H}_5$ and $C_6\underline{H}_4$). This compound was assigned as 1,3,3-trimethyl-1-phenylindan (IND) by comparing its NMR spectrum with reported one. Peak II (retention time 23.0 min). Anal. Calcd for $C_{18}H_{20}$ (dimer): C, 91.46; H, 8.54. Found: C, 91.48; H, 8.53. ^{1}H-NMR ($CDCl_3$) δ 1.23 (s, 6H, $(C\underline{H}_3)_2C$), 2.85 (s, 2H, $C\underline{H}_2$), 4.83 (d, 1H, J=3.0Hz, $=C\underline{H}$), 5.18 (d, 1H, J=3.0Hz, $=C\underline{H}$), 7.10-7.43 (m, 10H, $C_6\underline{H}_5$). Peak III (retention time 26.4 min). Anal. Calcd for $C_{18}H_{20}$ (dimer): C, 91.46; H, 8.54. Found: C, 91.35; H, 8.31. ^{1}H-NMR ($CDCl_3$) δ 1.53 (s, 6H, $(C\underline{H}_3)_2C$), 1.58 (d, 3H, J=1.36Hz, $C\underline{H}_3$), 6.18 (q, 1H, J=1.36Hz, $=C\underline{H}$), 7.15-7.60 (m, 10H, $C_6\underline{H}_5$). II and III were assigned as 2,4-diphenyl-4-methyl-1-pentene (PT-1) and 2,4-diphenyl-4-methyl-2-pentene (PT-2), respectively. The NMR signals of PT-2 were reported at δ 1.15 (s, 3H, $C\underline{H}_3$), 1.43 (s, 3H, $C\underline{H}_3$), 1.48 (d, 3H, $C\underline{H}_3$), 5.88 (q, 2H), 6.90-7.10 (m, 10H)[1)]. Four signals for methyls were reported. However, our data show only three peaks for methyls. Reexamination of the reported synthesis of PT-2 by palladium sulfate proved that the product is a mixture of PT-1 and PT-2. The integral ratio between the signals at 1.58 and 1.53 is 3:6, which clearly indicate the signals at 1.58 (doublet) arise from same methyl. Moreover, the singals at 1.58 became a singlet on irradiation at 6.18. The reported signal at 1.15 for PT-2 should be assigned to methyl group of PT-1. The long-renge coupling constant

1.36Hz indicate that PT-2 is probably the trans isomer regarding phenyl and dimethylphenylmethyl groups. The reaction scheme for the formation of these three kinds of dimers by protonic acid can be written as reaction (1).



PT-1 PT-2 IND

--- (1)

The product distribution by various initiators is shown in Table 2.

Table 2. Product Distribution by Various Initiators[a)]

No.	Initiator	Time (h)	Wt % of Dimers and Oligomers				Yield[b)] (%)
			PT-1	PT-2	IND	Oligomers	
1	Al_2O_3-TiO_2 (9:1)[c)]	90	40	23	2	25	90
2	Al_2O_3-TiO_2 (9:1)[d)]	90	26	1	-	13	40
3	Al_2O_3-TiO_2 (1:1)[d)]	90	42	26	2	19	89
4	TiO_2 -ZrO_2 (1:1)[c)]	90	7	-	-	3	10
5	SiO_2-Al_2O_3 (4:1)[e)]	90	13	1	-	5	18
6	Acid Clay	1	4	2	65	23	94
7	CF_3SO_2H [f)]	1	0	0	83	13	96
8	BF_3 OEt_2 [f)]	1	16	38	10	34	98
9	$PdSO_4$ [g)h)]	4	20	42	1	17	80

a) 30 °C with 5 wt % initiator b) based on initial monomer concentration c) prepared by hydrolysis of metal chlorides d) prepared by hydrolysis of alkoxides e) prepared by kneading SiO_2 with $Al(OH)_3$ f) 0.6 mol % initiator to monomer was used. g) 2.0 mol % initiator to monomer was used. h) 95 °C in acetic acid.

It will be interesting to point out that the structure of the dimers is reported to be determined by the nature of the ion pair in the case of homogeneous initiators. The conversion of monomer and the ratio of the dimers PT-1 and PT-2 are shown in Table 3.

Table 3. Change in the Ratio of PT-1 and PT-2[a)]

No.	Time (h)	Conv. (%)	PT-1 (%)	PT-2 (%)
1	3	25	87	13
2	6	33	90	10
3	16	56	90	10
4	23	65	80	20
5	31	67	80	20
6	43	83	72	28
7	92	85	70	30

a) by 5 wt % Al_2O_3-TiO_2 (9:1) from chlorides.

The ratio decreases with increasing monomer conversion. The isomerization of PT-1 to PT-2 by solid acid is shown in Table 4. In the initiator systems TiO_2-ZrO_2(1:1) and SiO_2-Al_2O_3 (4:1), Al_2O_3-TiO_2 (9:1) prepared from alkoxides, which selectively gave PT-1, did not isomerize PT-1 to PT-2. On the other hand, Al_2O_3-TiO_2 (9:1), from chlorides, isomerized PT-1 to PT-2, a fact which coincides with that it gave a mixture of PT-1 and PT-2 (Table 2, No. 1). PT-1 is first formed kinetically, and then isomerized to PT-2.

Table 4. Isomerization of PT-1 to PT-2

No.	Initiator[a)]	Time (h)	PT-1 (%)	PT-2 (%)
1	none	0	93	7
2	none	48	94	6
3	Al_2O_3-TiO_2 (9:1)[b)]	48	81	19
4	Al_2O_3-TiO_2 (9:1)[c)]	48	92	8
5	TiO_2-ZrO_2 (1:1)[b)]	48	93	7
6	SiO_2-Al_2O_3 (4:1)	48	92	8

a) 7 wt % to dimer. b) from chlorides. c) from alkoxides.

Conclusion Binary solid acids are active in oligomerization of α-methylstyrene giving linear dimers as principal products. The ratio of the two linear dimers is controlled kinetically, and the distribution of three dimers seems to be determined by the structure of ion pair.

References

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(Received October 11, 1979)