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Technical Notes

A Liquid−Liquid Process for Production of 2,4-Diphenyl-4-methyl-1-pentene by Dimerization of α-Methylstyrene

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Abstract:

A liquid−liquid process for the dimerization of α-methylstyrene (AMS) in order to produce selectively the commercially useful 2,4-diphenyl-4-methyl-1-pentene has been developed. The aqueous phase contained sulfuric acid as a catalyst and methanol as an additive, and the organic phase was 97% α-methylstyrene (AMS). An AMS conversion of 55% was achieved in 7 h when the dimerization was conducted at 80 °C. The product dimer contained 93% 2,4-diphenyl-4-methyl-1-pentene and only 0.06% 1,1,3-trimethyl-3-phenylindan, the saturated dimer. The liquid−liquid process can be used commercially to produce selectively 2,4-diphenyl-4-methyl-1-pentene at locations where cation-exchange resins are not readily available.

Introduction

The acid-catalyzed dimerization of α -methylstyrene (AMS) is an organic reaction of commercial importance and academic interest. Chaudhuri and Sharma (1989) have reported a comprehensive study on this system. A number of products are formed in the acid-catalyzed dimerization of AMS. These products include 2,4-diphenyl-4-methyl-1-pentene (UD1), 2,4-diphenyl-4-methyl-2-pentene (UD2), and 1,1,3-trimethyl-3-phenylindan, also called saturated dimer (SD). Under certain conditions, one more saturated dimer, *cis*- and/or *trans*-1,3-dimethyl-1,3-diphenylcyclobutane (CB) may also be formed. Figure 1 gives the reaction scheme of the dimerization of AMS. The unsaturated dimers of AMS are useful as chain-transfer agents or molecular weight regulators in the production of polymers such as polystyrene, SAN resin, ABS resin, SBR, and the like.[1] Of the unsaturated dimers, UD2 is not preferred as a molecular weight regulator since it hinders the initiating reaction and accordingly requires an undesirably longer induction period. Furthermore, the saturated indanic dimer, SD, and higher oligomers, e.g., trimers and tetramers, are of no value as molecular weight regulators, and their presence in the product dimer unnecessarily reduces the effective concentration of UD1. In order that the unsaturated dimers of AMS can function effectively as molecular weight regulators, the purity of UD1 in the product dimer should be as high as possible, preferably above 93%.

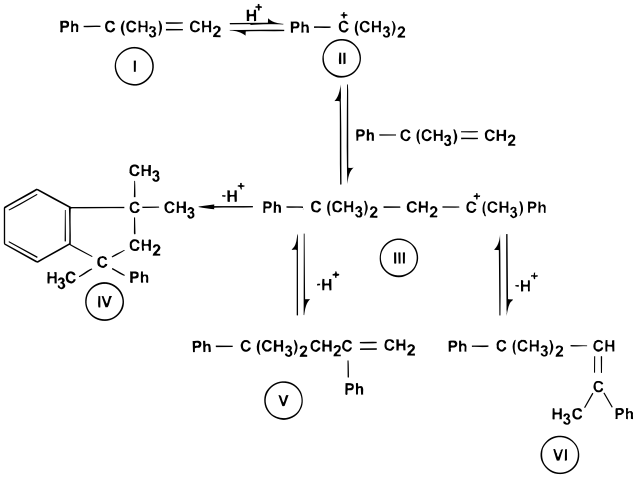

Figure 1. **Dimerization of AMS: reaction network/mechanism. I, α-methylstyrene; II and III, carbocations; IV, 1,1,3-trimethyl-3-phenylindan (SD); V, 2,4-diphenyl-4-methyl-1-pentene (UD1); and VI, 2,4-diphenyl-4-methyl-2-pentene.**

In their paper Chaudhuri and Sharma[2] have described a method of producing commercially UD1 of purity greater than 92% by conducting the dimerization in the presence of solid acid catalysts such as ion-exchange resins under carefully controlled conditions and also with aqueous sulfuric acid as a catalyst in a heterogeneous liquid−liquid (L−L) system. The problem with the heterogeneous L−L system with aqueous sulfuric acid as a catalyst was that, at low levels of conversion of AMS, the purity of UD1 in the product was 92% as desired, but as the fractional conversion of AMS increased beyond 20%, the selectivity for UD1 decreased, thus rendering the L−L operation unsuitable for production of UD1 of 92+% purity at high conversion level of AMS. The end users of AMS dimer now prefer UD1 purity of 93% (minimum) in the product. The objective of the present investigation was to explore an aqueous medium with sulfuric acid as the acidic material that would give a product dimer having UD1 at a concentration higher than 93% at high levels of conversion of AMS. It was also thought that the L−L operation would allow the aqueous phase to be reused again and again in the process. The use of such an aqueous medium

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[1] *Encyclopedia of Chemical Technology*; Kirk and Othmer, Wiley-Interscience: New York, 1978; Vol. 21, p 819.

[2] Chaudhuri, B.; Sharma, M. M. Some Novel Aspects of the Dimerization of α-Methylstyrene with Acidic Ion Exchange Resins, Clays and Other Acidic Materials as Catalysts. *Ind. Eng. Chem. Res.* **1989**, *28*, 1757−1763.

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Table 1. **Product Distribution in the Dimerization of AMS in L−L Mode (Aqueous Sulfuric Acid Catalyst)**[a]

H_2SO_4 concentration (% w/v) in aqueous phase	time (h)	AMS conversion (%)	product distribution (GC area %)				UD1:UD2 ratio
			UD1	UD2	SD	PDMC	
65	0.58	25	20.9	5.5	2.0	0.75	79.1:20.9
	1.5	55	47.3	12.2	4.4	0.68	79.4:20.6
	2.0	65	53.9	14.4	5.8	0.42	78.9:21.1
49	1.16	7.4	4.3	0.63	0.35	1.8	87.2:12.8
	2.16	14.0	9.9	1.6	0.25	1.8	86.0:14.0
	4.32	25.7	21.3	3.6	0.35	1.7	85.5:14.5
	10.0	52.0	40.7	7.4	0.61	2.0	84.6:15.4
36.7	2.0	3.6	1.8	0.15	0.08	1.8	92.3:7.7
	4.75	8.0	3.9	0.32	0.09	3.5	92.4:7.6
	8.0	13.0	9.0	0.80	0.07	4.2	91.8:8.2
	12.0	18.0	11.4	1.01	0.05	5.6	91.9:8.1

[a] Conditions: aqueous phase, 300 mL; AMS, 345 mL; temperature, 80 °C; speed of agitation, 2000 rpm.

for dimerization of AMS will obviate the need to restrict the conversion level of AMS to within 10−12% in a process employing only aqueous sulfuric acid as a catalyst. There will also be a substantial saving on separation as it will no longer be necessary to distill out a large quantity of unreacted AMS from the organic phase and recycle it back into the process. The results of the investigation are reported in this paper.

Previous Studies

It has been stated in the Introduction that Chaudhuri and Sharma[2] (1989) have reported a detailed study on the dimerization of AMS. Various aspects of the reaction, such as kinetics of the dimerization and selectivities for the different products in the presence of cation-exchange resins Amberlyst 15, K2661, Lewasorb AC 10 FT, etc., were investigated in the work. A method to produce selectively UD1 of purity greater than 92% was presented by Chaudhuri and Sharma.[2] Recently, Sun et al.[3] reported the dimerization of AMS on Amberlyst 15, and also on Nafion perfluoro sulfonic acid resin in three different microstructures: gel type Nafion NR50, a carbon-supported Nafion resin, and a Nafion resin/Silica composite material. Supported Nafion on carbon and Amberlyst 15 were found to be more active than pure Nafion. To compare the efficiencies of different catalysts in nonpolar media such as cumene and polar media such as *p*-cresol, Sun et al. used techniques such as temperature-programmed desorption and thermogravimetric analysis.

We find that practically no attempt has been made so far to find an aqueous medium having H_2SO_4 as a catalyst that can be used in L−L mode to dimerize AMS to obtain 93% pure UD1 at a reasonably high conversion of AMS. Our focus on H_2SO_4 is due to the fact that the material is readily available almost everywhere in the world. Secondly, the L−L mode of operation does not allow run-away reaction to occur, as experienced for the dimerization of 99% pure AMS in the presence of solid acid catalysts. In this paper, we present a methodology for producing 93+% UD1 by dimerizing AMS in the L−L mode at a reasonably high conversion of AMS, that is, at conversions of AMS of the order of 55−60%. Such a method is not reported in the open literature. The present technique will be an addition to the existing methods for production of 93+% pure UD1 by the dimerization of AMS.

Results and Discussion

Dimerization with Aqueous Sulfuric Acid. The rates of dimerization of AMS and the product selectivities were determined by conducting the dimerization reaction in L−L mode with aqueous H_2SO_4 solutions containing different quantities of H_2SO_4 in them, and the results are given in Table 1. With a catalyst concentration of 65% (w/v) H_2SO_4 in the aqueous phase, the rate of dimerization was quite fast: an AMS conversion of 65% was achieved in only 2 h. The product dimer did not meet the quality specification of a chain terminator, as the ratio of UD1:UD2 was only 79:21 and the concentration of SD in the product was also substantially high. At an intermediate catalyst concentration of 49% (w/v) H_2SO_4 in the aqueous phase, moderately high rates of dimerization were realized, and the selectivity of UD1 in the product dimer was around 85% at an AMS conversion level of 52%. When the catalyst concentration in the aqueous phase was 36.7% (w/v) H_2SO_4, the rate of dimerization was slow: only 18% conversion of AMS was realized in 12 h. The product dimer was rich in UD1, the ratio of UD1:UD2 being around 92:8. The concentration of SD in the product dimer was the lowest with the catalyst concentration of 36.7% (w/v). The results delineated above brought out two important points. (1) The higher the concentration of H_2SO_4 in the aqueous phase, the higher was the rate of dimerization. This was because of the high acidity of the aqueous phase with increased H_2SO_4 concentration. (2) The larger the concentration of water in the aqueous phase, the smaller was the concentration of SD in the product dimer. Other than the dimers, phenyl dimethyl carbinol (PDMC) was the byproduct formed by the acid-catalyzed hydration of AMS. In the range of H_2SO_4 concentrations (in the aqueous phase) investigated, the formation of PDMC was favoured when the aqueous phase contained the largest amount of water.

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(3) Sun, Q.; Farneth, W. E.; Harmer, M. A. Dimerization of α-Methylstyrene (AMS) Catalyzed by Sulfonic Acid Resins: A Quantitative Kinetic Study. *J. Catal.* **1996**, *164*, 62−69.

Table 2. **Product Distribution in the Dimerization of AMS in L−L Mode (Aqueous Sulfuric Acid Catalyst and Methanol)**[a]

quantity of methanol (mL) added to 300 mL of aqueous phase	time (h)	AMS conversion (%)	product distribution (GC area %)					UD1:UD2 ratio
			UD1	UD2	SD	CME	PDMC	
75	1	9.8	4.0	0.3	0.04	4.1	1.5	93.0:7.0
(20% v/v)	2.5	18.9	13.5	1.1	0.04	3.8	1.6	92.4:7.6
	7	45.0	37.4	3.0	0.05	3.3	1.2	92.6:7.4
100	1	19	3.35	0.21	0.03	12.9	2.6	94.0:6.0
(25% v/v)	2.66	28	13.67	0.92	0.03	11.3	2.6	93.6:6.4
	7	55	43.74	3.27	0.03	7.2	1.7	93.0:7.0
	10	67	57.0	4.6	0.03	6.9	1.4	92.5:7.5
125	1	22	4.4	0.3	0.05	14.7	2.5	93.6:6.4
(29.4% v/v)	2.6	33	18.1	1.5	0.05	13.9	2.5	92.3:7.7
	7	64	47.8	3.8	0.05	13.8	2.5	92.6:7.4

[a] Conditions: aqueous phase, 49% (w/v) H_2SO_4, 300 mL; methanol, as given in the table; AMS, 345 mL; temperature, 80 °C; speed of agitation, 2000 rpm.

Effect of Addition of Alcohol on the Dimerization of AMS in L−L Mode. Chaudhuri and Sharma[2] have reported that alcohols such as methanol and *tert*-butyl alcohol acted as inhibitors for the dimerization of AMS in the presence of cation-exchange resin catalysts. To examine the role of alcohol in the L−L mode of operation, the dimerization of AMS was conducted in the presence of methanol. In all experiments, 300 mL of 49% (w/v) aqueous H_2SO_4 solution and 345 mL of AMS were contacted, with varying quantities of methanol added to the two-phase system. The quantity of methanol was varied from 75 to 125 mL, and its addition into the aqueous phase enhanced the volume of the aqueous phase and, therefore, reduced the catalyst concentration. Results obtained on addition of methanol into the two-phase system are given in Table 2. When 100 mL of methanol was used along with 300 mL of 49% (w/v) aqueous H_2SO_4 solution, the effective concentration of H_2SO_4 was around 36.7% (w/v). On comparison of results given in Table 1 for the sulfuric acid concentration of 36.7% (w/v) and those given in Table 2 for 100 mL of methanol added to the aqueous phase, it is found that the presence of methanol improved the selectivity for the desired dimer UD1, and this improvement was the highest when the aqueous phase contained 25% (v/v) methanol. Under otherwise uniform conditions, a higher or lower dosage of methanol gave poorer selectivity for the desired UD1 in the product dimer.

There was practically no effect of the speed of agitation in the range of 1000−3000 rpm on the rates of dimerization in L−L mode (with or without methanol). We concluded, therefore, that the dimerization was kinetically controlled. For a L−L reaction for which the locale of the reaction is the aqueous phase, an increase in the volume of the aqueous phase would proportionately increase the rate of reaction in moles per hour. In Table 1, results on the dimerization of AMS are reported for 36.7% (w/v) H_2SO_4, and for this case an aqueous phase volume of 300 mL was used. For an aqueous phase volume of 400 mL, the rate would be 400/300, that is, 1.33 times the rate for the 300-mL aqueous phase. This would mean an AMS conversion of around 25% in 12 h for an aqueous phase volume of 400 mL of 36.7% (w/v) H_2SO_4. Results given in Table 2 for 400 mL of aqueous phase [consisting of 300 mL of 49% (w/v) aqueous H_2SO_4 + 100 mL of methanol] show that an AMS conversion of 67% was attained in 10 h. Therefore, the addition of methanol in the aqueous phase enhanced the rate of dimerization at the same effective H_2SO_4 concentration in addition to the improvement in selectivity with respect to UD1. The enhancement in rate in the presence of methanol in the aqueous phase was probably due to the enhanced solubility of AMS in the aqueous medium.

Other than the dimers UD1, UD2, and SD, the products formed in the dimerization of AMS with aqueous H_2SO_4 and methanol were phenyldimethyl carbinol (PDMC), formed by the hydration of AMS, and methyl cumyl ether (CME), formed by the reaction of methanol with AMS. These byproducts are very useful. PDMC is an important perfumery compound and has a potential of replacing phenylethyl alcohol as a perfumery material. CME has properties of enhancing octane number of gasoline like methyl *tert*-butyl ether (MTBE) and ethyl *tert*-butyl ether (ETBE). It is interesting to note that, for 25% (v/v) methanol used (Table 2), the concentration of CME in the product increased to as high as 12.9% in a reaction time of 1 h; CME then gradually decomposed as the reaction proceeded. Similarly, the concentration of PDMC decreased from 2.6% to 1.4% as the reaction continued from 1 to 10 h. These are some notable features of the dimerization of AMS with aqueous H_2SO_4 and methanol in L−L mode of operation.

We also checked the reusability of the aqueous phase [300 mL of 49% (w/v) H_2SO_4 + 100 mL of methanol] by conducting the dimerization of AMS with the same aqueous medium (that is, by separating the aqueous phase by simple phase separation and carrying out the dimerization in the medium) five times, and the same results as those reported in Table 2 were obtained in each experiment.

The UD1:UD2 ratio obtained on the dimerization of AMS with 300 mL of 49% (w/v) H_2SO_4 and 100 mL of methanol are reported in Table 2. At an AMS conversion of 19%, the ratio of UD1:UD2 was found to be 94:6, and this ratio reduced to 93:7 at an AMS conversion of 55%. The ratio fell below 93:7 as the AMS conversion increased beyond 55%. It is remarkable that the concentration of SD in the product dimer was as low as 0.06%. To the best of our knowledge, no report published in the open literature has claimed such a low concentration of SD in the product dimer; the large quantity of water present in the system probably suppressed the cyclization reaction, leading to the formation of SD.

In a typical experiment, the product mixture (organic phase) was subjected to distillation under reduced pressure (15−20 mm) after the organic phase was washed with an aqueous alkali solution. Unreacted AMS, PDMC, and CME were flashed off, and they were then recycled in the dimerization reaction. Recycling of the byproducts did not give any distortion in the selectivity of UD1, and practically no difference in the rates of dimerization was observed.

Chaudhuri and Sharma[2] reported that they produced UD1 of purity of 93+% by conducting the dimerization of AMS in the presence of cation-exchange resin as a catalyst and also 4% (w/w) of isopropyl alcohol as an additive (with AMS). It was thought that the alcohol became adsorbed on the surface of the cation-exchange resin, thereby deactivating some of the acid sites of the catalyst and reducing its activity. It is interesting to note that the aqueous medium consisting of 300 mL of 49% (w/v) H_2SO_4 and 100 mL of methanol used in this work gave 93+% UD1 in the product, comparable with that reported by Chaudhuri and Sharma.[2] This similarity in product distribution between solid−liquid and liquid−liquid heterogeneous reactions leads us to believe that the role of alcohol in controlling the rates of dimerization and in improving the selectivity of UD1 is more fundamental. Probably the mechanism of the reactions leading to the formation of the different dimers becomes affected in the presence of alcohol. It is also probable that the microenvironment created in the resin bead in the presence of isopropyl alcohol is the same as that created in the aqueous phase containing H_2SO_4 and methanol, as used in this work. For both cases, therefore, the selectivities for UD1 are identical at values of around 93%. More work is necessary to justify these similarities between solid−liquid and liquid−liquid heterogeneous reactions beyond any shadow of doubt.

Scale-Up Study. To check whether the dimerization of AMS with 300 mL of 49% (w/v) H_2SO_4 and 100 mL of methanol scaled up, an experiment was performed in which 1035 mL of AMS was contacted with 900 mL of 49% (w/v) H_2SO_4 and 300 mL of methanol at 80 °C in a 4-L fully baffled reactor. The reaction was conducted for 7 h, and an AMS conversion of 54% was achieved. This was comparable with the results reported in Table 2 for 300 mL of 49% (w/v) H_2SO_4 and 100 mL of methanol. The product distribution was the same as that reported in Table 2, and the UD1:UD2 ratio was 93:7. The experiments reported in this paper could, therefore, be scaled up without difficulty.

Conclusions

A L−L process using H_2SO_4 as a catalyst to produce 93% 2,4-diphenyl-4-methyl-1-pentene by the dimerization of AMS was developed. The concentration of UD1 in the product dimer was as high as 93% at an AMS conversion of 55% achieved in 7 h; the concentration of SD in the product dimer was only 0.06%. The aqueous phase could be repeatedly used for the dimerization. The present process can replace the process based on ion-exchange resins, particularly for those cases where the resin is not locally available and the supply of the resin does not occur regularly. The present work also demonstrates that it is, indeed, possible to produce 93% UD1 with H_2SO_4 as a catalyst in L−L mode of operation at a reasonably high conversion level of AMS.

Experimental Section

Experiments were conducted in a 0.10-m-i.d. fully baffled mechanically agitated contactor. A six-bladed glass-disk turbine impeller was used for agitation. All the experiments were carried out at the desired temperature by placing the reactor in a constant-temperature bath.

At first, a known volume of the aqueous phase was placed in the reactor and was slowly heated to the reaction temperature. For reactions where methanol was used, the mixture of aqueous acid phase and methanol was placed in the reactor. The organic phase, which was basically AMS, was heated to the same temperature in a separate vessel. Subsequently, the organic phase was carefully transferred with the help of a long funnel into the reactor, and the agitation of the liquid−liquid system was started. This was taken as the starting time of the reaction. Actual quantities of aqueous and organic phases used are given in Tables 1 and 2.

The liquid−liquid system readily separated into two distinct phases as soon as the agitation was stopped. Samples (2 mL) from the organic phase were collected at definite time intervals and analyzed on a Chemito model 9A gas chromatograph. A 4-m-long column, OV-17 on chromosorb L, was used for analysis. Typical conditions employed for analysis were as follow: injector and detector temperatures, 250 °C each; oven temperature, 100 °C (zero isothermal time), raised to 250 °C with a ramp rate of 4 °C/min; carrier gas, N_2 gas;and rate of flow of N_2, approximately 20 mL/min.

AMS of purity greater than 99% was procured from Lancaster Synthesis Ltd., U.K. A commercial variety having 97% AMS and cumene and *tert*-butylbenzene as impurities, manufactured by Herdillia Chemicals Ltd., Navi Mumbai, India, was procured through a local agent. In most experiments reported in this paper, this commercial grade AMS was used. It was confirmed that rates of the dimerization and product selectivities were practically the same for both grades of AMS. Sulfuric acid and methanol, both of AR grade, were procured from S.D. Fine. Chem. Pvt. Ltd., Mumbai, India. Aqueous acidic solutions were made of distilled water; it was confirmed, however, that the dimerization reactions conducted with aqueous acidic solutions prepared from tap water gave the same rates and product selectivities as those conducted with aqueous acidic solutions prepared from distilled water.

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