

할로겐화 아릴 화합물들의 팔라듐 촉매화 비닐화 반응을 이용한
p-Phenylene Diacrylic Acid 유도체들의 합성.
4-Bromiodobenzene의 선택적인 비닐화반응

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Synthesis of *p*-Phenylene Diacrylic Acid Derivatives by
Palladium Catalyzed Vinylation of Aryl Halides.
Selective Vinylation of 4-Bromiodobenzene

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요 약. 4-Bromiodobenzene 또는 4-diiodobenzene 과 2 당량의 아크릴산 유도체들간의 트리에틸아민 존재하의 팔라듐 촉매를 이용한 비닐화 반응에 의해 (E, E)-*p*-phenylene diacrylic acid 유도체들을 비교적 좋은 수득율로 쉽게 얻을 수 있었다. 이들 반응에서 4-diiodobenzene 이 4-bromiodobenzene 보다 더 좋은 반응성을 나타냈으며 이들 반응들은 입체특이성있게 진행되었다. 또한, 사용된 촉매에 다른 4-bromiodobenzene 의 선택적인 비닐화 반응을 이용하여 (E, E)-*p*-phenylene diacrylic acid 유도체들과 이외의 몇가지 1,4-diolefinic aromatic compounds 를 편리하게 합성할 수 있었다.

ABSTRACT. (E, E)-*p*-Phenylene diacrylic acid derivatives were prepared in moderate to good yields by the palladium catalyzed vinylation of 4-bromiodobenzene or 4-diiodobenzene with 2 equiv of acrylic acid derivatives in the presence of triethylamine. 4-Diiodobenzene was more reactive than 4-bromiodobenzene in the above reactions and the reactions were proceeded stereospecifically. (E, E)-*p*-Phenylene diacrylic acid derivatives and several other 1,4-diolefinic aromatic compounds were also synthesized by utilizing the selective vinylation of 4-bromiodobenzene.

INTRODUCTION

Four-center type photopolymerization in the solid state of *p*-phenylene diacrylic acid derivatives produces high molecular weight linear polymers having cyclobutane rings in the main chain and high crystallinity¹⁻⁴. Polymerization of dicarboxylic acids such as *p*-phenylene diacrylic acid with polyols also produces photosensitive polyesters^{5,6}.

Notwithstanding increased interest in the polymerization of various diolefinic aromatic compounds, there are only several methods available for the preparation of *p*-phenylene diacrylic acid derivatives in the literature^{7,8}. These monomers might be prepared by means of new process employing palladium catalyzed vinylation of aryl halides with acrylic acid derivatives. The palladium catalyzed vinylation of aryl halides with olefins provides a convenient method

for the preparation of 1-aryl olefins⁹⁻¹¹. The catalyst required for the vinylation is determined by what kind of halides present. Aryl iodides require only palladium acetate, whereas aryl bromides do not react unless a triarylphosphine is also present. Therefore, it is possible that reactants containing both iodo and bromo groups, such as bromiodobenzene, undergo vinylation reaction selectively either at the iodo position only or at both iodo and bromo positions.

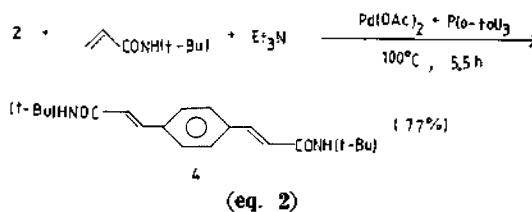
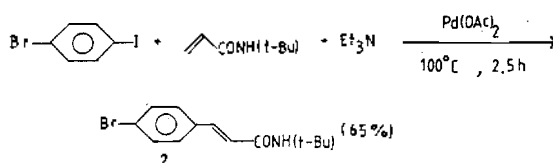
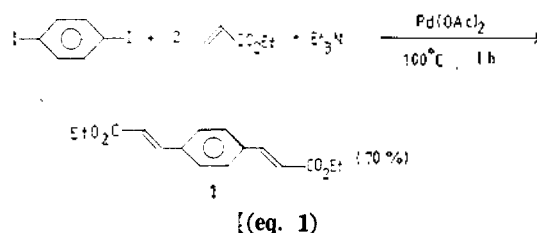
In the present study, *p*-phenylene diacrylic acid derivatives were synthesized by palladium catalyzed vinylation of 4-diiodobenzene or 4-bromiodobenzene with acrylic acid derivatives, and the selective vinylation of 4-bromiodobenzene was utilized for the preparation of several other 1,4-diolefinic aromatic compounds.

RESULTS AND DISCUSSION

p-Phenylene diacrylic acid derivatives were readily obtained by the palladium catalyzed vinylation of aryl halides with acrylic acid derivatives in the presence of triethylamine at 100°C. 4-Diiodobenzene and 4-bromiodobenzene as aryl halides reacted with ethyl acrylate and *N-t*-butylacrylamide. In the above reaction, it was found that 4-diiodobenzene was more reactive than 4-bromiodobenzene and that reaction of 4-diiodobenzene with 2 equiv of ethyl acrylate in the presence of 6 equiv of triethylamine and 2 mol% palladium acetate in DMF produced within 1 hr (E,E)-*p*-phenylene diacrylic acid ethyl ester(1) in 70% yield (eq. 1).

Reaction of 4-bromiodobenzene with 2 equiv of ethyl acrylate under 2 mol% palladium acetate-4 mol% triorthotolylphosphine catalyst in acetonitrile for 2 hr produced 1 in 35% yield only.

p-Phenylene diacrylic acid derivatives were also obtained by utilizing the selective vinylation of 4-bromiodobenzene. At first, the reaction


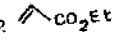

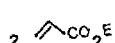



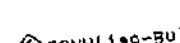

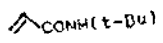


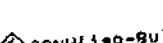
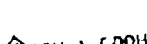
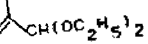


of 4-bromiodobenzene with *N-t*-butylacrylamide has been carried out in the presence of 1 mol % palladium acetate and 3 equiv of triethylamine to selectively produce (E)-*N-t*-butyl-4-bromocinnamamide(2) in 65% yield. Compound 2 was then reacted with *N-t*-butylacrylamide under 1 mol % palladium acetate-2 mol % triorthotolylphosphine to form 4 in 77% yield (eq. 2).

Results are summarized in Table 1.

Further reaction of 2 with other olefins such as ethyl acrylate, *N*-isobutylacrylamide, 10-undecenoic acid and methacrolein diethyl acetal in the presence of 3 equiv of triethylamine and 1 mol % palladium acetate-2 mol % triorthotolylphosphine catalyst in DMF at 100°C produced (E,E)-1,4-diolefinic aromatic compounds. Results are also summarized in Table 1. Reaction of 2 with ethyl acrylate under the condition described above produced (E,E)-1,4-diolefinic aromatic compound 5 in 75% yield. In the

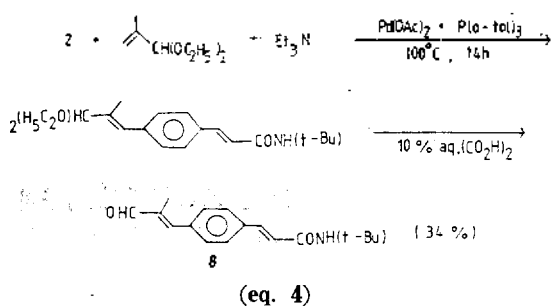
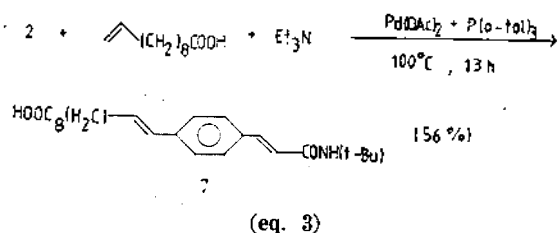
Table 1. Palladium Catalyzed Vinylation of Aryl Halides with Olefins^a

Aryl Halide	Olefin	Catalyst ^b Pd(OAc) ₂ P(o-tol) ₃	Time, h	Product (% yield of isolated product)
			2	1 (70)
			2/4	1 (35)
			1	2 (55)
			1	3 (50)
			1/2	4 (77)
			1/2	5 (75)
			1/2	6 (65)
			1/2	7 (56)
			1/2	8 (34)

^a All reactions were carried out by employing triethylamine as the base at 100°C. ^b Mol% based upon the aryl halide. ^c 10ml of DMF was added as solvent. ^d Palladium acetate was used only as the catalyst. ^e C retained after treatment of reaction product with 10% aqueous oxalic acid.

same manner, 2 and N-isobutylacrylamide reacted to give 6 in 65% yield. 10-Undecenoic

acid as a long chain olefin also reacted with 2, and compound 7 was obtained in 5



yield (eq. 3).

Methacrolein diethyl acetal was less reactive than other olefins, and produced 8 in only 34% yield on treatment of the reaction product with 10% aqueous oxalic acid at room temperature for 4 hr (eq. 4).

In conclusion, (E,E)-*p*-phenylene diacrylic acid derivatives were synthesized readily by one step reaction of palladium catalyzed vinylation of 4-diiodobenzene with 2 equiv of acrylic acid derivatives in good yields. The selective vinylation of 4-bromiodobenzene with olefins was demonstrated as the convenient route for the preparation of various (E,E)-1,4-diolefinic aromatic compounds.

EXPERIMENTAL SECTION

The ^1H NMR spectra were obtained on Varian Model S-60T and Varian Model FT-80 spectrometer, with tetramethylsilane as internal standard. Infrared spectra were obtained on Beckman Model 18-A spectrometer. Gas chromatographic analyses were carried out on Shimadzu Model GC-6A using 10% SE-30/Chromosorb W NAW, $2\text{m} \times 1/4$ in. column and heli-

um as a carrier gas.

Reagents. Ethyl acrylate (Tokyo Kasei Co.), acetonitrile (Tokyo Kasei Co.) N,N-dimethylformamide (Tokyo Kasei Co.), 10-undecenoic acid (Hayashi Pure Chemical Ind.), triethylamine (Junsei Chemical Co.) and palladium acetate (Aldrich Chemical Co.) were commercial products and used without further purification. The following reagents used in this study were prepared according to literature methods; tri-*o*-tolylphosphine¹³, 4-diiodobenzene¹⁴, 4-bromiodobenzene¹⁵, N-*t*-butylacrylamide¹⁶, N-*iso*-butylacrylamide¹⁶ and methacrolein diethyl acetal¹⁷.

Preparation of (E,E)-*p*-phenylene diacrylic acid ethyl ester(1). A mixture of 4.65g (15 mmol) of 4-diiodobenzene, 3.3g (33 mmol) of ethyl acrylate, 8.9g (90 mmol) of triethylamine, 0.0672g (0.3 mmol) of palladium acetate and 10ml of DMF was placed in a reaction bottle and the bottle was capped. After the catalyst was dissolved by shaking, the solution was maintained at 100°C for 1hr. After cooling, the reaction mixture was stirred with 10% aqueous hydrochloric acid and the product was filtered. Recrystallization from *n*-hexane gave 2.88g (70%) of pure (E,E)-*p*-phenylene diacrylic acid ethyl ester(1). mp 91~92°C (Lit³. 92.7°C); ^1H NMR (DMSO- d_6) δ 1.2 (=t, J=7Hz, 6H), 4.15 (q, J=7Hz, 4H), 6.8 (d, J=16Hz, 2H), 7.8~8.2 (m, 6H); IR (KBr) 3040, 2990, 1710, 1635, 980, 835 cm^{-1}

Preparation of (E)-N-*t*-butyl-4-bromocinnamamide(2). A mixture of 7.07g (25 mmol) of 4-bromiodobenzene, 3.56 g(28 mmol) of N-*t*-butylacrylamide, 7.59g(75 mmol) of triethylamine, 0.056g(0.25mmol) of palladium acetate and 10ml of acetonitrile was prepared in a reaction bottle. The bottle was capped with a self-sealing rubber-lined cap with a small hole in the metal crown for inserting a syringe

needle. Gas chromatographic analysis of the reaction mixture indicated that 4-bromiodobenzene had been completely consumed after 2.5h at 100°C. After being cooled, the reaction mixture was stirred with 10% aqueous hydrochloric acid. The insoluble solid was separated, and recrystallization from ethanol gave 4.58g (65%) of pure (E)-N-*t*-butyl-4-bromocinnamamide(2). mp 201~202°C; ¹H NMR (CDCl₃) δ 1.4 (s, 9H), 5.8(bs, 1H), 6.5(d, J=16Hz, 1H), 7.2~7.8(m, 5H); IR (KBr) 3290, 3080, 1660, 1630, 975, 815cm⁻¹

General procedure for the preparation of 1,4-diolefinic aromatic compounds from 2.

A mixture of 15mmol of 2, 18 mmol of olefins, 45 mmol of triethylamine, 0.15mmol of palladium acetate, 0.3mmol of triorthotolylphosphine and 10ml of DMF was shaken until becoming homogeneous in a capped bottle and then heated at 100°C in water bath. The reaction was concluded after determining the remaining olefin in the reaction mixture by means of GLC analysis. After being cooled, the reaction mixture was diluted with 10% aqueous hydrochloric acid and filtered. Resultant crude products were purified by recrystallization.

The 1,4-diolefinic aromatic compounds prepared by employing the above procedure have following spectral data.

(E)-N-isobutyl-4-bromocinnamamide(3). mp 179~180°C; ¹H NMR (CDCl₃) δ 1.0(s, 3H), 1.1(s, 3H), 1.7~2.1(m, 1H), 3.28(t, J=7Hz, 2H), 6.1(bs, 1H), 6.46(d, J=16Hz, 1H), 7.2~7.5(m, 5H); IR(KBr) 3280, 3065, 1645, 1613, 980, 805cm⁻¹

4: mp 285~287°C (dec.); ¹H NMR(CF₃COOD) δ 1.0(s, 18H), 5.62(bs, 2H), 6.28(d, J=16Hz, 2H), 7.08(s, 4H), 7.32(d, J=16Hz, 2H); IR(KBr) 3290, 3090, 1665, 1630, 980, 820 cm⁻¹.

5: mp 143~145°C; ¹H NMR(DMSO-d₆) δ

0.8(t, J=7Hz, 3H), 1.05(s, 9H), 3.8(q, J=7Hz, 2H), 5.8~6.4(m, 3H), 6.8~7.5(m, 6H); IR (KBr) 3280, 3070, 1710, 1655, 1625, 975, 815cm⁻¹.

6: mp 277°C (dec.); ¹H NMR (CF₃COOD) δ 1.0(s, 12H), 1.12(s, 3H), 1.8~2.15(m, 1H), 3.38(t, J=7Hz, 2H), 5.76(bs, 1H), 6.1(bs, 1H), 6.38(d, J=16Hz, 2H), 7.2~7.7(m, 8H); IR (KBr) 3300, 3080, 1660, 1630, 980, 835cm⁻¹.

7: mp 119~119.5°C; ¹H NMR(DMSO-d₆) δ 0.8(bs, 12H), 1.1(s, 9H), 1.85(bs, 4H), 5.8(bs, 1H), 6.16(d, J=16Hz, 2H), 6.9~7.5(m, 6H), 9.85(s, 1H); IR(KBr) 3370, 3050, 1710, 1660, 1615, 965, 815cm⁻¹.

8: mp 143.5~144°C; ¹H NMR(DMSO-d₆) δ 1.05(s, 9H), 3.15(s, 3H), 5.8(bs, 1H), 6.25(d, J=16Hz, 1H), 6.75~7.5(m, 6H), 9.95(s, 1H); IR(KBr) 3310, 3060, 1680, 1625, 980, 830cm⁻¹.

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