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Synthesis of Some Conjugated Polyynes

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Received June 2, 1986

Several aryl substituted 1,3,5-hexatriynes were synthesized by the use of aryl containing trimethylsilylated 1,3-butadiyne intermediates. 1-Phenyl-1,3,5-heptatriyne, one of the naturally occurring phototoxic conjugated polyacetylenes, and 1-(1'-naphthyl)-1,3,5-heptatriyne were prepared by the use of 1-trimethylsilyl-1,3-pentadiyne which is a very stable precursor for the 1,3-pentadiyne at room temperature.

Introduction

Certain naturally occurring conjugated polyacetylenes such as 1-phenyl-1,3,5-heptatriyne(PHT) have been reported to be phototoxic to a variety of substrates.[1-5] However, little is known about the photochemistry of conjugated polyacetylenes. In connection with this problem, we needed a variety of conjugated polyynes -especially aryl containing conjugated polyynes which are similar to PHT- and study their photochemical and photophysical properties.

Synthesis of these compounds, therefore, was carried out and the schemes were devided into three parts:

Part-1: Synthesis of diyne units.
Part-2: Coupling of triple bonds(mono or diyne) with aryliodides.
Part-3: Extension of triple bond units and variation of the substituents of triple bond by coupling reactions.

In order to satisfy these purposes, considerably stable and asymmetrically substituted butadiynes such as trimethyl silylated 1,3-butadiynes were required. Generally, the base promoted elimination reaction of 1,4-dichloro-2-butyne was used for the preparation of diyne units.[6-10] But reaction condition is unfavorable for trimethylsilylation[11] and (Z)-1-methoxybut-1-en-3-yne as diyne source was used instead.[12]

Classical synthetic methods for the terminal arylacetylenes in general involve manipulation of preformed, two carbon side chains and include methods such as the Vilsmeier method,[13,14] the halogenation-dehydrohalogenation sequence of vinyl aromatics[15] and ketones,[16,17] and the dehydrohalogenation of β,β-dihalo olefins.[18,19] Terminal aryl butadiynes have also been prepared by the use of aryl-1,4-butandiol-2-ynes as a precursor through several steps[20] or coupling reactions between aryl acetylenes[11,21] and triethylsilylacetylenes. Trimethylsilyl group cannot be used in this case because of the sensitivity of the trimethylsilyl-acetylene bonds to base.[11] A recent innovation in the synthesis of arylacetylenic compounds has been the use of protecting groups.[22] Acetylenes, protected at one end, can be introduced onto an aromatic nucleus via coupling at the free end. Subsequent removal of the protecting group generates a terminal arylacetylene. The widely accepted procedure for the introduction of an acetylenic substituent onto an aromatic nucleus is the Stephens-Castro methods.[23-25] An elegant alternative to the Stephens-Castro methods rests in the coupling between arylcopper reagents and (iodoethynyl) trimethylsilane below ambient temperatures.[26] Recently, however, it was reported that the palladium-catalyzed coupling reaction between arylhalides and ethynyltrimethylsilane give trimethylsilylated arylacetylenes which yield ethynylated aromatic compounds after removal of the trimethylsilyl group with base, quantitatively.[27,28] These reactions can be proceeded at room temperature. Several trimethylsilyl arylacetylenes and arylbutadiynes were synthesized by the use of this reaction. Moreover various symmetric and asymmetric aryl containing conjugated polynes are synthesized through self or cross coupling reactions of them. Trimethylsilyl group plays an important role in synthesis as a protecting group and as one which enhances the stability of resulting butadiynes.

For the synthesis of the polyynes, present method offers some distinct advantages over methods using a copper acetylides, alkynylzinc, and aryl copper reagents in terms of

simplicity, efficiency, and wide range of applications.

Experimental

Instruments. ^{1}H-nuclear magnetic resonance spectra were run in $CDCl_3$ on a Varian T-60A, FT-80A, and Bruker AM-200-SY spectrometers. Infrared spectra were obtained on a Perkin-Elmer 283B spectrophotometer in KBr pellets and NaCl cell. UV-VIS spectra were recorded on a Cary-17 spectrophotometer. Mass spectra were determined at 70 eV with a Hewlett Packard 5985A GC/MS system by electron impact method.

Materials. Methyliodide, 3,3-dimethyl-1-butyne, n-butyllithium(1.6 M hexane solution), N,N,N′,N′-tetramethylethylene diamine, triphenylphosphine were purchased from Aldrich Chemical Co. and were used without further purification. (Z)-1-Methoxybut-1-en-3-yne was purchased from Fluka and was purified according to the literature procedure prior to use. Phenylacetylene, iodobenzene, 1-iodonaphthalene, trimethylsilylchloride were purchased from Fluka and were used without further purification. Palladium chloride was purchased from Inushio. Extra pure solvents were used as received or after purification by distillation of standard methods. The column chromatography was performed by using Kiesel gel 60(Merck, 70-230 mesh). Bis[triphenylphosphine]palladium dichloride was prepared by the reported method.[30]

1-Trimethylsilyl-1,3-pentadiyne(4). A solution of (Z)-1-methoxybut-1-en-3-yne(30 mmol) which was purified according to the literature procedure[31] in THF(60 ml) was treated with n-BuLi(30 mmol) at −78°C followed by Me_3SiCl(32 mmol). The mixture was warmed to 0°C and stirred for 2 hr to give **2**. Compound **4** was prepared by treatment of the mixture at −40 ∼ −45°C with n-BuLi(60 mmol) for 30 min followed by CH_3I(62 mmol). The resulting reaction mixture was warmed to room temperature and stirred for 2 hr. The reaction mixture of **4** was poured into saturated aqueous NH_4Cl, extracted with n-pentane and dried over $MgSO_4$. Crude product of **4** was purified by column chromatography using petroleum ether as an eluent to give **4** in 80 % yield. **4**: ^{1}H NMR($CDCl_3$) δ 1.86(*s*,3H), 0.1(*s*,9H); IR(NaCl) 2950, 2260, 2140, 1420, 1260, 1210, and 860 cm^{-1}; MS, m/e 136(M^+,13.2), 121(M^+-CH_3,100).

1,4-Ditrimethylsilyl-1,3-butadiyne(5). was prepared by the treatment of **2** at −40∼−45°C with n-BuLi(60 mmol) for 30 min followed by $(CH_3)_3SiCl$(62 mmol). The resulting reaction mixture was warmed to room temperature and stirred for 2 hr. The reaction mixture of **5** was poured into saturated aqueous NH_4Cl. After extraction with n-pentane, the combined organic phase was washed with saturated aqueous NaCl and dried over $MgSO_4$. The solvent was removed under the reduced pressure and the crude product of **5** was recrystalized from methanol in 80 % yield. **5**: ^{1}H NMR($CDCl_3$) δ 0.2(*s*,18H); IR(NaCl) 2980, 2080, 1420, 1360, 840, 770, 710, and 650 cm^{-1}; MS, m/e 194(M^+, 18.2), 179(M^+-CH_3, 100).

1-Trimethylsilyl-1,3-butadiyne(6). was prepared by treatment of the reaction mixture of **2** at −40∼−45 °C with n-BuLi(60 mmol) for 30 min followed by pouring into 1N HCl solution. After extraction with n-pentane, the combined organic layer was washed with saturated aqueous NaCl. The solvent was removed under the reduced pressure and the residue was purified by column chromatography on silica gel using n-pentane as an eluting solvent to give **6** in 80 % yield. **6**: ^{1}H NMR($CDCl_3$) δ 2.2(*s*,1H), 0.4(*2*,9H); IR(NaCl) 3310, 2240, 2180, 2150, 1460, 1390, and 840 cm^{-1}; MS, m/e 122(M^+, 14.5), 107(M^+-CH_3, 11.6), 73($C_3H_9Si^+$, 100).

1-Trimethylsilyl-2-(1′-naphthyl)acetylene(7) and 1-naphthylacetylene(8). To a mixture of trimethylsilylacetylene (11.76 g, 120 mmol) and iodonaphthalene(25.4 g, 100 mmol) in deaerated anhydrous triethylamine(500 ml) were added bis[triphenylphosphine]palladium dichloride(1.4 g, 2 mmol) and copper(I) iodide(190 mg, 1 mmol). The reaction mixture was stirred at 30°C for 40 min under nitrogen and then the solvent is removed under the reduced pressure. The residue is extracted charcoal and purified by column chromatography on silica gel using petroleum ether as an eluting solvent to give **7** in 94 % yield. The product(**7**, 21 g, 94 mmol) in 150 ml MeOH at 25 °C was treated with 100 ml of 1N NaOH(in MeOH) for 10 min. The mixture was acidified with 20 ml of 5N HCl(in MeOH) in ice bath and extracted with petroleum ether. The combined organic phase was washed with aqueous sodium bicarbonate and dried over $MgSO_4$. Removal of solvents yielded 14.28 g of **8**(100 %). **7**: ^{1}H NMR($CDCl_3$) δ7.4-8.6(*m*,7H), 0.3(*s*,9H); IR(NaCl) 3070, 2970, 2900, 2150, 1600, 1510, 1400, 1250, 850, 800, 770, 760, 730, 700, and 650 cm^{-1}; MS, m/e 224(M^+,35.2), 209(M^+-CH_3, 100). **8**: ^{1}H NMR($CDCl_3$) δ 8.4-7.6(*m*,7H), 3.4(*s*,1H); IR(NaCl) 3300, 3080, 2970, 2110, 1600, 1520, 1400, 1345, 840, 800, 770, and 735 cm^{-1}; MS, m/e 152(M^+, 100), 151(M^+-H, 23.1).

1-Trimethylsilyl-4-phenyl-1,3-butadiyne(9) and 1-trimethylsilyl-4-(1′-naphthyl)-1,3-butadiyne(10). A deaerated solution of 1-trimethylsilyl-1,3-butadiyne(**6**, 4.88 g, 40 mmol) and aryliodide(40 mmol) in deaerated anhydrous triethylamine(120 ml) were added bis[triphenylphosphine] palladium dichloride(400 mg, 1 mmol) and copper(I) iodide (95 mg, 0.5 mmol) under nitrogen. The mixture was heated to 30 °C and maintained at that temperature for 40 min. After evaporation of solvent, the reaction mixture was extracted with petroleum ether and decolourized with activated charcoal. The reaction mixture was filtered and the filtrate was concentrated. The concentrated filtrate was separated by chromatography on silica gel using petroleum ether as an eluent to give **9** and **10** in 72 % and 85 % yields, respectively. **9**: ^{1}H NMR($CDCl_3$) δ 7.1(*m*,5H), 0.2(*s*,9H); ^{13}C NMR($CDCl_3$) δ 133, 129.8, 129, 121.8, 90.5, 88.5, 77, 74.8, and 0; IR(NaCl) 3080, 2980, 2220, 2120, 1620, 1580, 1500, 1450, 1200, 860, 760, and 690 cm^{-1}; UV(methanol) λmax 297, 279, 263, 250, 229, and 215 nm; MS, m/e 198(M^+, 32.0), 183(M^+-CH_3, 100). **10**: ^{1}H NMR($CDCl_3$) δ7-8.2(*m*,7H), 0.77(*2*,9H); ^{13}C NMR ($CDCl_3$) δ135, 134.3, 133.5, 130.9, 129.5, 128.4, 128.1, 127, 126.1, 120, 92, 89, 79.7, and 75.9; IR(NaCl) 3080, 2980, 2900, 2220, 2115, 1600, 1515, 1470, 1350, 1120, 1065, 1025, 850, 770, 700 680, and 630 cm^{-1}; UV(methanol) λmax 334, 312, 300, 253, 232, and 221 nm; MS, m/e 248(M^+, 45.7), 233(M^+-CH_3, 100).

Bromophenylacetylene(11) and bromo-(1′-naphthyl) acetylene(12). Mercuryacetylides of phenylacetylene and α-naphthylacetylene were prepared by reported method. **11** was prepared by reported method using $CHCl_3$ as a solvent in 92 % yield. Mercury acetylide of the α-naphthylacetylene was obtained in 100 % yield. Exactly the same procedure for the preparation of **11** was followed starting with a solution of mercuryacetylide of the α-naphthylacetylene(5.03 g, 10 mmol) in $CHCl_3$(400 ml) to obtain **12** in 62% yield. **12**: ^{1}H

NMR($CDCl_3$) δ8.6-7.2(*m*,7H); IR(NaCl) 3080, 2210, 1600, 1520, 1410, 1020, 800, 775, 740, and 620 cm^{-1}; UV(methanol) λmax 313, 298, 287, and 227 nm; MS, m/e 232(M^++1, 11.5), 230(M^+-1, 10.9), 151(M^+-Br, 100).

5,5-Dimethyl-1-phenyl-1,3-hexadiyne(13) and 5,5-dimethyl-1-(1'-naphthyl)-1,3-hexadiyne(14). A solution of bromoarylacetylene(**11**, **12**) (5 mmol) in MeOH(5 ml) was added dropwise during 15 min to a rapidly stirred mixture of 3,3-dimethyl-1-butyne (0.5 g, 6 mmol), $NH_2OH \cdot HCl$ (50 mg), CuCl(50 mg) and $EtNH_2$(405 mg, 9 mmol) in MeOH(20 ml) maintained at 25 °C. The resulting solution was stirred for 30 min more at room temperature and the blue colour developed was discharged by addition of small quantities of $NH_2OH \cdot HCl$. For the preparation of **13**, the reaction mixture was acidified with 2N HCl and organic products were extracted with petroleum ether and the petroleum ether extracts were dried (Na_2SO_4). The solvent was removed under the reduced pressure and the residue was fractionated by column chromatography on silica gel using petroleum ether as an eluent to give **13** in 45 % yield. **14** was obtained by filtration of the reaction mixture. The solid precipitate was identified as 1,4-di(1'-naphthyl)-1,3-butadiyne. The filtrate was acidified with 2N HCl and extracted with n-pentane. The organic phase was dried over Na_2SO_4 and evaporated under the reduced pressure to give **14** in 40 % yield. **13**: ^1H NMR($CDCl_3$) δ 7.6-7.2(*m*,5H), 1.4(*s*,9H); ^{13}C NMR($CDCl_3$) δ131, 127.5, 127, 121, 91, 75.2, 74, 63.5, and 30; IR(NaCl) 3080, 2730, 2250, 2180, 2160, 1600, 1580, 1500, 1450, 1370, 1330, 750, and 690 cm^{-1}; UV(methanol) λmax 287, 270, 257, 243, 220, and 210 nm; MS, m/e 182(M^+, 73.2), 167(M^+-CH_3, 100), 152($M^+-C_2H_6$, 76.5). **14**: ^1H NMR($CDCL_3$) δ 8.4-7.2 (*m*,7H), 1.3(*s*,9H); ^{13}C NMR($CDCl_3$) δ 133.94, 133.05, 131.67, 129.17, 128.28, 126.91, 126.47, 125.07, 119.85, 93.15, 79.08, 74.32, 64.26, 30.52, and 28.32; IR(NaCl) 3080, 2930, 2250, 2240, 1600, 1515, 1490, 1465, 1410, 1370, 1340, 1320, 870, 800, 770, 740, and 700 cm^{-1}; UV(methanol) λmax 330, 328, 317, 310, 299, 260, 246, 232, and 217 nm; MS, m/e 232(M^+, 17.5), 217(M^+-CH_3, 57.1), 202($M^+-C_2H_6$, 100).

1-Phenyl-1,3-pentadiyne(15) and 1-(1'-naphthyl)-1,3-pentadiyne(16). Methyllithium(1.7 M ethyl ether solution, 14.12 ml) was added to a solution of 1-trimethylsilyl-4-aryl-1,3-butadiyne(**9**,**10**, 20 mmol) at −78 °C. The mixture was warmed to room temperature and stirred for 40 min. 1.4 Equivalent of CH_3I(4.26 g, 30 mmol) was added and stirred for 20 min at room temperature. The reaction mixture was extracted with n-pentane and the organic phase concentrated under the reduced pressure. The residue was fractionated by column chromatography on silica gel using n-pentane as an eluting solvent to give **15** and **16** in 89%, 85%, respectively. **15**: ^1H NMR($CDCl_3$) δ7.4(*m*,5H, 2.0(*s*,3H); ^{13}C NMR($CDCl_3$) δ132.13, 128.45, 128.03, 121.81, 80.01, 74.61, 73.89, 64.47, and 3.85; IR(NaCl) 3080, 2980, 2930, 2260, 2180, 1610, 1580, 1500, 1450, 1380, 1260, 750, and 690 cm^{-1}; UV(methanol) λmax 286, 269, 256, 242, 230, 220, and 210 nm; MS, m/3 140(M^+, 73), 139 (M^+-H, 100). **16**: ^1H NMR($CDCl_3$) δ7.2-8.4(*m*, 7H), 2.0(*s*,3H); ^{13}C NMR($CDCl_3$) δ135.3, 134.4, 133, 130.5, 129.5, 128.4, 128.1, 127.3, 126.4, 120, 82, 79.8, 73, 65, and 5.5; IR(NaCl) 3080, 2980, 2940, 2260, 2160, 1600, 1520, 1440, 1410, 1380, 1350, 1260, 910, 850, 800, 780, and 740 cm^{-1}; UV(methanol) λmax 329, 327, 316, 309, 298, 260, 246, 232, and 217 nm; MS, m/e 190(M^+, 100), 189(M^+-H, 67.3).

1,4-Di(1'-naphthyl)-1,3-butadiyne(17). was prepared on a 20 mmol scale by the Hay coupling method in 95 % yield. **17**: ^1H NMR($CDCl_3$) δ8.5-7.2(*m*, 14H); ^{13}C NMR($CDCl_3$) δ134.67, 133.89, 132.73, 130.43, 129.88, 127.91, 127.38, 126.85, 125.89, 120.32, 81.74, 79.49; IR(KBr) 3080, 2150, 1600, 1520, 1400, 1342, 1280, 1165, 1020, 800, and 770 cm^{-1}; UV(methanol) λmax 370, 345, 328, 322, 230, and 208 nm; MS, m/e 302(M^+, 100).

1-(1'-naphthyl)-4-phenyl-1,3-butadiyne(18). 20 mmole scale Cadiot-Chodkiewicz coupling of **8** with **11** gave **18**. The crude product was recrystallized from n-pentane in 62 % yield. **18**: ^1H NMR($CDCl_3$) δ 7.2-8.4(m, 12H); ^{13}C NMR($CDCl_3$) δ135.1, 134.4, 133.6, 133.4, 131, 130.5, 129.5, 128.5, 128, 127.4, 126.5, 122.8, 120.5, 84.5, 82, 80.5, and 79.1; IR(KBr) 3080, 2160, 1600, 1520, 1500, 1450, 1410, 1340, 1270, 870, 840, 920, 800, 770, 750, and 690 cm^{-1}; UV(methanol) λmax 350, 330, 317, 285, 280, 270, 262, 248, and 230 nm; MS, m/e 252(M^+, 100).

1,6-Diphenyl-1,3,5-hexatriyne(19) and 1,6-di(1'-naphthyl)-1,3,5-hexatriyne(20). A solution of 1-trimethylsilyl-4-aryl-1,3-butadiyne(**9**,**10**, 20 mmol) in methanol(5 ml) was treated with 30 ml of 1N NaOH(in MeOH) at room temperature. After 10 min the solution was treated with 6 ml of 5N HCl(in MeOH). The resulting NaCl was filtered and CuCl(0.2 g, 2 mmol), $NH_2OH.HCl$(0.2 g, 2.8 mmol), and $EtNH_2$(2.25 g, 50 mmol) were added to the filtrate. A solution of bromoarylacetylene(**11**, **12**, 20 mmol) in methanol(20 ml) was added dropwise in 15 min, and then the mixture was stirred at 20 °C for 1 hr under nitrogen. The mixture was acidified and extracted with n-pentane. The n-pentane extracts were dried and the solvent was removed under the reduced pressure and the residue was crystallized to give **19** and **20**, in 55 % and 76 % yields, respectively. **19**: ^1H NMR ($CDCl_3$) δ 7.4(m, 10H); ^{13}C NMR($CDCl_3$) δ 134, 131, 130, 122, 80, 76, and 68; IR(NaCl) 3080, 2260, 2200, 1600, 1585, 1505, 1450, 910, 755, and 687 cm^{-1}; UV(methanol) λmax 358, 332, 311, 283, 267, and 254 nm; MS, m/e 226(M^+, 100). **20**: ^1H NMR($CDCl_3$) δ 7.3-8.6(m, 14H); ^{13}C NMR($CDCl_3$) δ 134.93, 133.98, 132.75, 130.46 129.15, 127.92, 127.39, 126.86, 125.87, 119.41, 81.76, 79.83, 68.54: IR(KBr) 3060, 2200, 1600, 1515, 1420, 1400, 1340, 1265, 860, 800, and 760 cm^{-1}; UV(methanol) λmax 370, 365, 358, 350, 345, 338, 322, and 230 nm; MS, m/e 326(M^+, 100).

1-Phenyl-1,3-heptatriyne(21) and 1-(1'-naphthyl)-1,3,5-heptatriyne(22). Exactly the same procedure used for the preparation of **19** and **20** was followed starting with a solution of **4**(2.42 g, 20 mmol) in methanol (5 ml) to obtain **21** and **22** in 65 % and 79 % yields, respectively. **21**: ^1H NMR($CDCl_3$) δ 7.2(*m*, 5H), 2 (*s*, 3H); ^{13}C NMR($CDCl_3$) δ 133, 130, 129, 120.4, 79, 75.7, 75, 68, 65.4, 59.5, and 4.8; IR(NaCl) 3080, 2940, 2240, 1600, 1500, 1450, 1380, 760, 690 cm^{-1}; UV (methanol) λmax 330, 309, 289, 273, 249, 237 nam; MS, m/e 167(M^+, 100), 153(M^+-H, 51). **22**: ^1H NMR($CDCl_3$) δ 7.2-8.4(*m*, 7H), 2.1(*s*, 3H); ^{13}C NMR($CDCl_3$) δ 134.94, 133.78, 133.38, 130.69, 129.17, 128.01, 127.41, 126.65, 125.82, 119.52, 79.98, 79.59, 74.42, 69.36, 65.72, 59.86, 5.33; IR(KBr) 3070, 2230, 1595, 1515, 1430, 1410, 1380, 1340, 1330, 1270, 1220, 870, 800, 775, and 745 cm^{-1}; UV(methanol) λmax 351, 330, 319, 310, 309, 290, 278, 265, 241, and 232 nm; MS, m/e 214(M^+, 100), 213(M^+-H, 21.9).

1-(1'-Naphthyl)-6-phenyl-1,3,5-hexatriyne(23). **23** was prepared on a 20 mmole scale in a similar way used for **19**

and **20**. **10** and **11** were used as starting materials. The crude product was fractionated to give **23** in 55 % yield. **23**: ^{1}H NMR($CDCl_3$) δ 7.2-8.4(*m*, 12H); ^{13}C NMR($CDCl_3$) δ 134.15, 133.03, 132.94, 132.78, 130.23, 129.67, 128.47, 127.39, 126.76, 125.88, 125.12, 120.99, 118.59, 90.0, 80.1, 80.0, 74.5, 65.72, and 64.2; IR(NaCl) 3080, 2200, 1600, 1515, 1500, 1450, 1410, 1340, 1280, 1250, 1220, 1180, 1170, 970, 910, 840, 800, 770, 750, and 690 cm^{-1}; UV(methanol) λmax 377, 350, 327, 320, 315, 307, 303, 285, 272, 262, 250, 245, and 222 nm; MS. m/e 276(M^+, 100).

Results and Discussion

1,4-Disubstituted-1,3-butadiynes and 1,6-disubstituted-1,3,5-hexatriynes were prepared by the use of **1** as a diyne source. n-BuLi was used for preparing butadiynes from **1** in THF and the trimethylsilylated 1,3-butadiynes were directly introduced to the aryl iodides to give **9**, **10** using $PdCl_2(PPh_3)_2$ as a catalyst. These are very useful intermediates for the preparation of the aryl containing polyynes. The reaction conditions and yields for the synthesis of these intermediates and the polyynes are shown in Table 1.

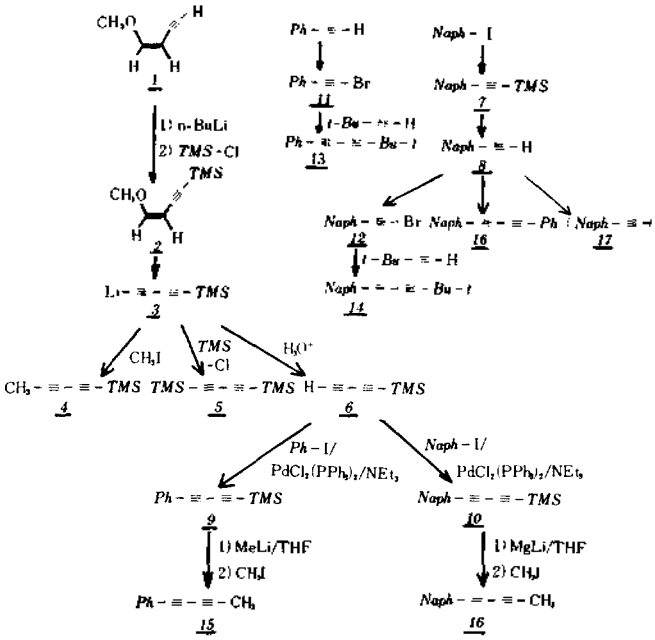
Synthesis of 1,4-disubstituted-1,3-butadiynes. In the synthesis of asymmetrically substituted 1,3-butadiynes and 1,3,5-hexatriynes, the use of 1,4-dichloro-2-butyne as a source of diyne unit is very unfavorable because of the following reasons. First, the reaction is required to use liquid ammonia and sodium. Second, the reaction yield is low and symmetrically disubstituted 1,3-butadiyne is obtained as a byproduct. Third, the stability of resulting mono-substituted 1,3-butadiyne is low. In addition, trimethylsilylating agent cannot be used due to the sensitivity of the trimethyl silylacetylene bonds to base. On the other hand, trimethylsilylated 1,3-butadiynes from **1** are easy to prepare and very useful and stable intermediates for the synthesis of polyynes.

Table 1. Some Conjugated Polyynes Synthesis by Various Processes

entry	R	R′	n	T(°C)	solvent	Yield[a](%)
4[a]	methyl	TMS	2	-78*	THF	80
5[a]	TMS	TMS	2	-78*	THF	80
6[a]	H	TMS	2	-78*	THF	80
7[b]	α-naphthyl	TMS	1	30	Et_3N	94
8	α-naphthyl	H	1	25	MeOH	100
9[b]	phenyl	TMS	2	30	Et_3N	72
10[b]	α-naphthyl	TMS	2	30	Et_3N	85
13[c]	t-Butyl	phenyl	2	25	MeOH	45
14[c]	t-Butyl	α-naphthyl	2	25	MeOH	40
15[a]	phenyl	methyl	2	-78*	THF	89
16[a]	α-naphthyl	methyl	2	-78*	THF	85
17[d]	α-naphthyl	phenyl	2	25	Acetone	95
18[c]	α-naphthyl	phenyl	2	25	MeOH	62
19[c]	phenyl	phenyl	3	25	MeOH	55
20[c]	α-naphthyl	α-naphthyl	3	25	MeOH	76
21[c]	methyl	phenyl	3	25	MeOH	65
22[c]	methyl	α-naphthyl	3	25	MeOH	79
23[c]	α-naphthyl	phenyl	3	25	MeOH	55

*see the experimental section.

Synthetic routes for symmetrical and asymmetrical 1,4-disubstituted-1,3-butadiynes through the coupling reaction and using **1** are shown in Scheme 1.



TMS: Trimethylsilyl, *Ph* : Phenyl, *Naph* : α-Naphthyl

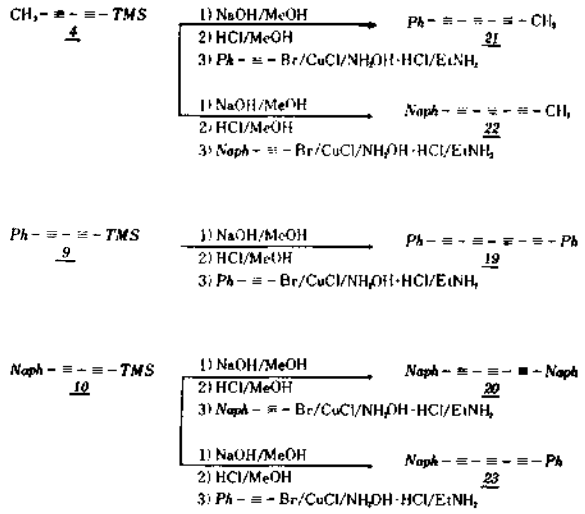
Scheme 1. Synthetic Routes for 1,4-Disubstituted-1,3-butadiynes.

The preparation of trimethylsilylated 1,3-butadiynes (**4**,**5**,**6**) from **1** were carried out using n-BuLi and trimethylsilylchloride in higher yields than the method of elimination of 1,4-dichloro-2-butyne by sodium amide in liquid ammonia because those syntheses are performed *via* **2**. Also trimethylsilyl group contribute to the stability of the trimethylsilylated 1,3-butadiynes(**4**,**5**,**6**) but it could not be used as a protecting group in the coupling reaction between the protected acetylenes because of its base sensitivity. But they can be used as good intermediates for the synthesis of the aryl containing conjugated polyynes. Compound **6** was directly introduced into phenyliodide and α-naphthyliodide to give **9** and **10**, respectively. The synthesis of the arylbutadiynes have been performed via several steps, whereas these reactions are one pot reaction. In this reaction, trimethylsilyl group was not only used as a protecting group but also stabilizes the aryl-1,3-butadiynes and is easily removed in situ in the higher polyynes synthetic reaction step. Moreover the trimethylsilyl groups of **9** and **10** were removed by MeLi followed by the treatment of CH_3I to give **15** and **16** in situ, respectively. Palladium(II) catalyzed reaction which was used for **9** and **10** was carried out to give **7** and desilylation gave **8**. **8** is used for preparing **12** via bromination of mercuryacetylide of **8** and Hay coupling[29] to give **17**. **18** was prepared by the Cadiot-Chodkiewicz coupling of **8** with **11**. Also, Cadiot-Chodkiewicz coupling of **11** and **12** with 3,3-dimethyl-1-butyne give **13** and **14** in moderate yields, respectively.

In overall synthetic routes of 1,4-disubstituted-1,3-butadiynes, the products could be identified primarily by the characteristic UV-absorption bands as shown in Figure 1. Conjugated polyynes exhibit characteristic electronic absorption spectra with the most prominent feature being a very high

intensity band with well-defined vibrational fine structure. Most of aryl substituted 1,3-butadiynes exhibit these typical polyyne bands but the case of α-naphthyl substituted 1,3-butadiynes the fine structure is diminished because of the increased conjugation of triple bonds with aromatic ring. Moreover the red shift of the λ max was observed in the aryl substituted 1,3-butadiynes following the order of alkyl < trimethylsilyl < phenyl < α-naphthyl.

Synthesis of 1,6-disubstituted-1,3,5-hexatriynes. 1,6-diaryl-1,3,5-hexatriynes(**19,20,23**) and 1-aryl-1,3,5-heptatriynes(**21,22**) were synthesized from **4**, **9**, and **10** as shown in Scheme 2.



TMS : Trimethylsilyl, *Ph* : Phenyl, *Naph* : α-Naphthyl

Scheme 2. Synthetic Routes for 1,6-Disubstituted-1,3,5-hexatriynes.

Compound **4** is coupled with **11** and **12** to give **21** and **22** in good yields *via* desilylation and Cadiot-Chodkiewicz coupling reaction, respectively. Coupling reaction between

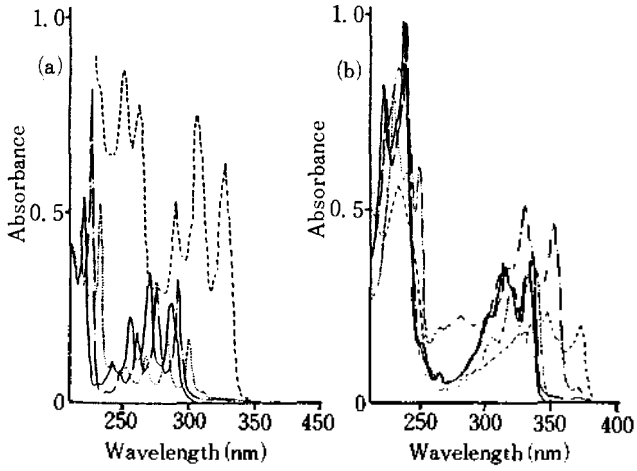


Figure 1. Ultraviolet absorption spectra of 1,4-disubstituted-1,3-butadiynes. (a) *Ph*-≡-≡-R [R = Me(—), t-Bu(- · -), *TMS* (···), *Ph* (——)]. (b) *α-Naph*-≡-≡-R[R = Me(—), t-Bu(- · -), *TMS*(···), *α-Naph* (---), *Ph* (- · · -)].

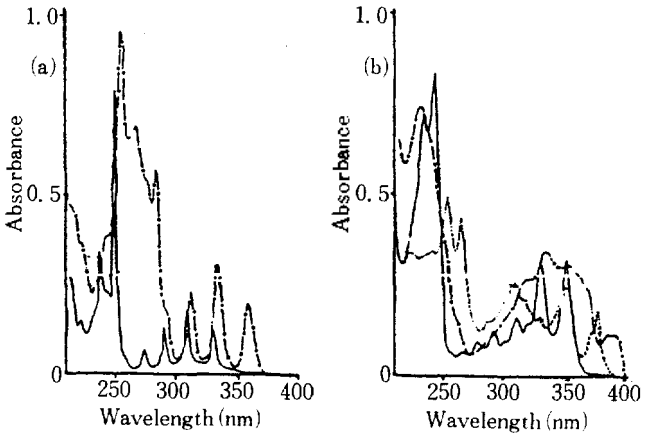


Figure 2. Ultraviolet absorption spectra of 1,6-disubstituted-1,3,5-hexatriynes. (a) *Ph*-≡-≡-≡-R[R = Me(—), *Ph*(- · -)]. (b) *α-Naph*-≡-≡-≡-R[R = Me(—), *α-Naph* (- · -), *Ph*(· · ·)].

desilylated **9** and **11** gives **19**. **20** and **23** were prepared by the coupling reaction of desilylated **10** with **12** and **11**, respectively. The use of trimethylsilylated 1,3-butadiynes on the coupling reaction requires mild condition and desilylation before the coupling reaction. These are the major advantages of the method. Trimethylsilyl group makes the handling of those compounds easy as a result of stabilization of the triple bonds. 1,6-Disubstituted 1,3,5-hexatriynes show the characteristic UV absorption band just like 1,4-disubstituted 1,3-butadiynes as shown in Figure 2. From these UV spectra, the red shift of the absorption maxima was observed in accordance with the same sequences as the arylsubstituted 1,3-butadiynes and fine structure was diminished even though very similar.

Acknowledgement. This investigation was supported by the Korean Traders Scholarship Foundation and the Korea Ad-Institute of Science and Technology.

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Reactions of Aryl Organometallic Reagents with Isomers of Phthalonitriles: Triaryl Diketimines and Diketones

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Synthesis and hydrolysis of aromatic diketimines of triaryl type were investigated by the action of aryl organometallics on the three isomers of phthalonitrile. The reactions of organometallic reagents, prepared from bromobenzene, *o*-bromotoluene and *o*-bromoanisol, with iso- and terephthalonitrile proceeded in normal way. Decomposition of the addition complex with dry ammonia, methanol or water gave six diketimines, which could be hydrolysed to the corresponding diketones. Reactions of phthalonitrile with the organometallic reagent were different from the other isomers, so that the decomposition and hydrolysis of the addition complex did not give diimines and the corresponding aromatic diketones.

Introduction

In spite of their frequent occurrence as intermediates in the synthesis of ketones from the reaction of organometallic reagents on nitriles, relatively a few ketimines appear to have been isolated and characterized. The production of ketimines as hydrochloride was described for the first time by Hantzch and Kraft,[1] in 1891, by the reaction between urethan and dihydrochlorides produced from ketones and phosphorus pentachloride. In 1920, Moureu and Mignonac[2] published a study of eleven ketimines prepared from aromatic nitriles and Grignard reagents. Other workers[3-9] also have since described the synthesis of ketimines or their salts by the action of organomagnesium reagents on nitriles. The hydrolysis of ketimines into corresponding ketones was also widely accomplished.

The systematic studies on ketimines, however, were done first by Pickard and his coworkers in early 1950s. They developed two methods for the preparation of ketimines by Grignard reaction on nitrile. The first method involves decomposition of the Grignard adduct with anhydrous hydrogen chloride to get an imine salt. This procedure, which parallels that of Moureu and Mignonac,[2] has proved feasible and afforded fair yields of products.

$$RMgX \xrightarrow{R'CN} \begin{matrix} R \\ R' \end{matrix}\!>C=NMgX \xrightarrow{HCl} \begin{matrix} R \\ R' \end{matrix}\!>C=NH\cdot HCl$$

The second involves decomposition of the Grignard adducts with anhydrous ammonia, which gives free imines. This modified procedure required less time and gave higher yield. By these methods, they prepared various ketimines of alkyl-aryl,[10,11] diaryl[12] and dialkyl types.[13-15]

$$\begin{matrix} R \\ R' \end{matrix}\!>C=NMgX \xrightarrow{\text{dry } NH_3} \begin{matrix} R \\ R' \end{matrix}\!>C=NH$$