

observed on admixture with authentic sample prepared from 4-hydroxycinnoline with POCl_3 , and the IR spectra of the two samples were identical.

The authors express their gratitudes to Prof. E. Ochiai, the Director of Itsuu Laboratory, for his helpful advices, and to Drs. H. Kano and M. Ogata of Shionogi Research Laboratory, who kindly sent the IR spectra of **VII** to us. They are also indebted to members of microanalytical center of the University of Tokyo for the analysis data and to Dr. T. Ōba for his co-operation in IR absorption measurements.

Summary

Cinnoline 1-oxide (**I**) gave 4-nitrocinnoline 1-oxide (**II**) and a small amount of 5-nitrocinnoline 1-oxide (**V**) on warming with nitric and sulfuric acids, and gave 4,5-dinitrocinnoline 1-oxide (**IV**) by using fuming nitric acid in sulfuric acid. The nitration of **I** with benzoyl nitrate afforded 3-nitrocinnoline 1-oxide (**VII**). **I** was converted into 4-chlorocinnoline (**VIII**) on the treatment with phosphoryl chloride.

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152. Issei Iwai and Junya Ide : Studies on Acetylenic Compounds. XXXVIII.*¹ The Novel Cyclization Reaction of Diacetylenic Compounds to Naphthalene Derivatives involving Prototropic Rearrangement.

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Recently much attention has been drawn to the reaction of making carbon-carbon bond linkage between triple bond and carbanion^{1~3)} or carbene^{4,5)} in the field of acetylenic chemistry. Above all, it seemed to be more important to use non-activated triple bond for this reaction. Raphael and co-workers⁶⁾ reported that various diacetylenic hydrocarbons gave benzene derivatives by means of a 10% solution of potassium *tert*-butoxide in boiling bis(2-methoxyethyl) ether. Furthermore, isomerization of *cis*-4-octene-1,7-diyne with potassium *tert*-butoxide in *tert*-butyl alcohol was found to give rise to two aromatic dimers: the spiro-compound and dibenzo[*a, e*]cyclooctadiene by Sondheimer and Ben-Efraim.⁷⁾

This paper deals with the cyclization reaction of 1,7-diphenyl-1,6-heptadiyne and other diyne derivatives with potassium *tert*-butoxide in *tert*-butyl alcohol to naphthalene derivatives under a remarkably mild condition. Treatment of 1,7-diphenyl-1,6-heptadiyne (**I**) with 14% solution of potassium *tert*-butoxide in *tert*-butyl alcohol at 62~63° for

*¹ Part XXXVII : This Bulletin, 12, 813 (1964).

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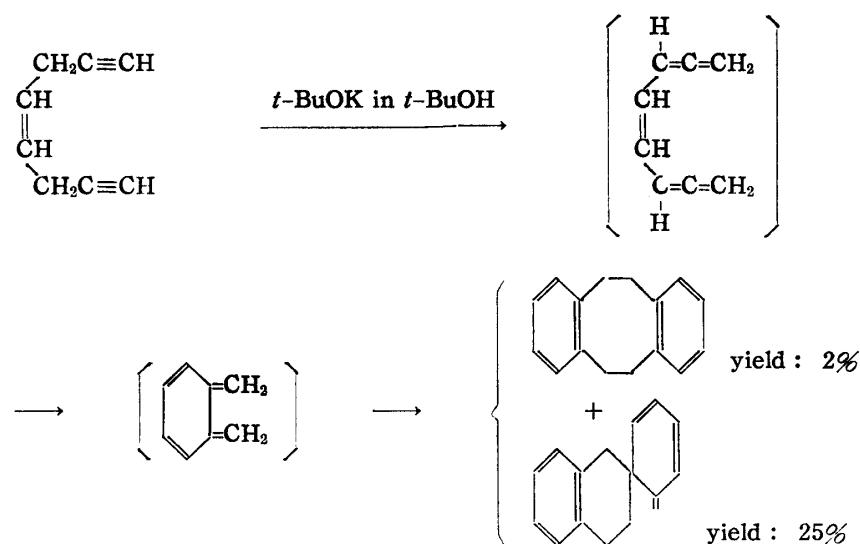
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4.5 hours afforded colorless prisms (II), m.p. $81.5\sim82.5^\circ$, in 35% yield after alumina column chromatography, whose elemental analysis gave $C_{19}H_{16}$ corresponding to the starting material. This compound (II) showed no infrared absorption maximum at 2100 cm^{-1} region corresponding to that of triple bond, but ultraviolet absorption of II showed maxima at 229, 277.5 (shoulder), 286, 296 (shoulder) and $323\text{ m}\mu$ (shoulder). These absorption maxima of II is very similar to that of 1-phenylnaphthalene. From these results, it is evident that the migration of unsaturated bonds proceeding aromatisation has involved several carbon atoms and presumably takes place by successive base-catalysed prototropic rearrangements.

In accordance with the empirical formulas supposedly obtained from ultraviolet, infrared spectra and elemental analysis, integration data of this compound in nuclear magnetic resonance spectra account for sixteen protons; ten aromatic protons due to naphthalene and benzene rings and six due to three methylene groups. The peak at τ 7.96 is present in the most high field comparing with other two signals, indicating that these protons are consequently assigned to the (c)-methylene group (at C-2). The signals at τ 6.90 (center) are slightly broader, which means that these protons are slightly spin-spin coupled to the adjacent proton (at C-9), and is consequently assigned to the (b)-methylene group (at C-1). The signals at τ 7.18 (center) are considered to be assigned to (a)-methylene group (at C-3), which is located in slightly higher field than (b)-methylene group (at C-1) due to anisotropic effect of phenyl group.⁸⁾ From these results, the compound (II) is confirmed to be 4-phenyl-2,3-dihydro-1H-benz[f]indene.

This novel reaction is extended to other diyne molecules including nitrogen, oxygen, and sulphur atom.

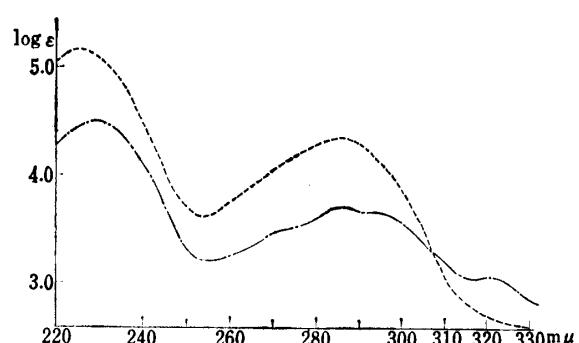
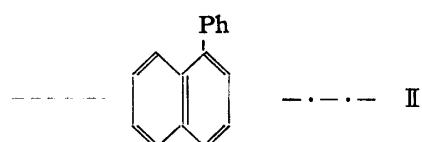


Fig. 1. Ultraviolet Spectra in Ethanol



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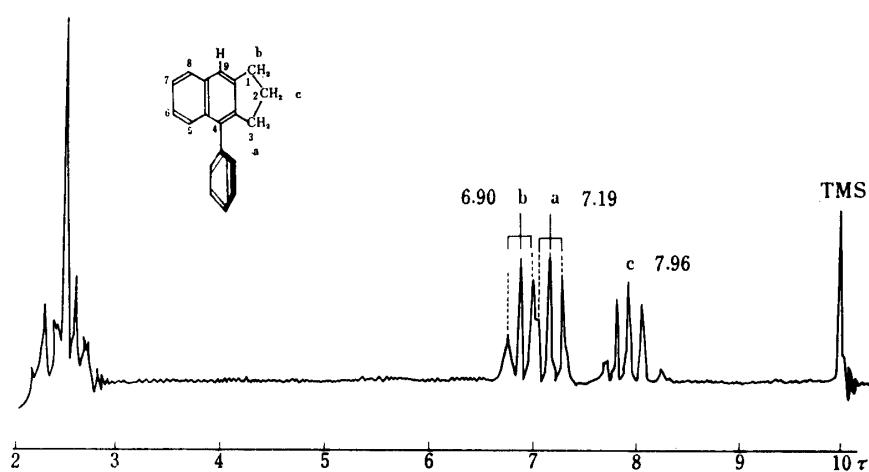
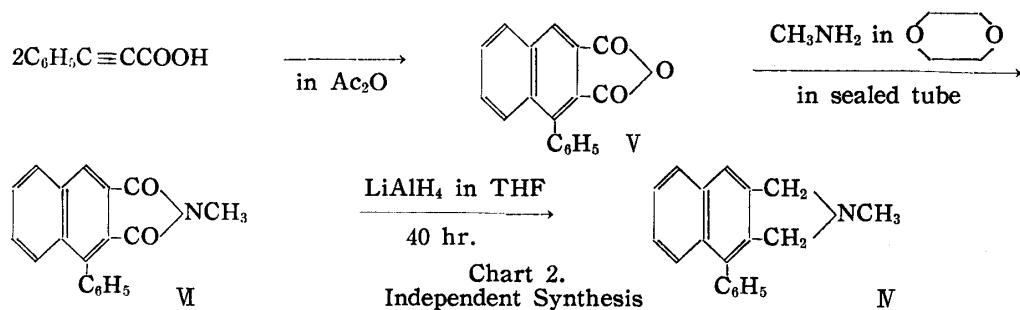


Fig. 2. Nuclear Magnetic Resonance Spectrum of II

N,N-Bis(3-phenyl-2-propynyl)methylamine (III) which was prepared from *N,N*-bis(butoxymethyl)methylamine and phenylethynyl magnesium bromide in tetrahydrofuran according to the method of Yura, *et al.*,⁹⁾ gave pale yellow needles (IV), m.p. 141~143°, under similar condition in good yield (85%). In this case, the reaction time took 75 minutes until the ultraviolet absorption maximum completely changed into a different pattern from that of starting material. Then, it was planned to synthesize the compound (IV) starting from phenylpropionic acid. Refluxing of phenylpropionic acid with acetic anhydride according to the known method¹⁰⁾ gave 1-phenyl-3,3-naphthalenedicarboxylic anhydride (V). Treatment of V with equimolecular amount of methylamine in dioxane in sealed tube at 200° for 4 hours gave corresponding *N*-methylimide derivative (VI), which was reduced with lithium aluminum hydride in tetrahydrofuran for forty hours into *N*-methyl-4-phenyl-1,3-dihydro-2*H*-benz[f]isoindole (IV). By infrared, ultraviolet, and nuclear magnetic resonance spectra, and mixed melting point determination the compound (IV) obtained from III was identical with obtained from V.



Analogously, bis(3-phenyl-2-propynyl) sulfide (VII) also underwent cyclization reaction affording 4-phenyl-1,3-dihydronaphtho[2,3-*c*]thiophene (VIII), m.p. 131~132°, in 40% yield, whose structure confirmed by elemental analysis, infrared, ultraviolet, and nuclear magnetic resonance spectra. Furthermore, bis(3-phenyl-2-propynyl) ether (IX) prepared from phenylpropargyl bromide and sodium phenylpropargylalcolate, gave 4-phenyl-1,3-dihydronaphtho[2,3-*c*]furan (X), m.p. 121.5~122.5° in 97% yield under similar conditions.

Extension of this intramolecular cyclization to diacetylenic derivatives was found to be surprisingly general reaction which was effected by means of 14% solution of potassium *tert*-butoxide in *tert*-butanol at low temperature.

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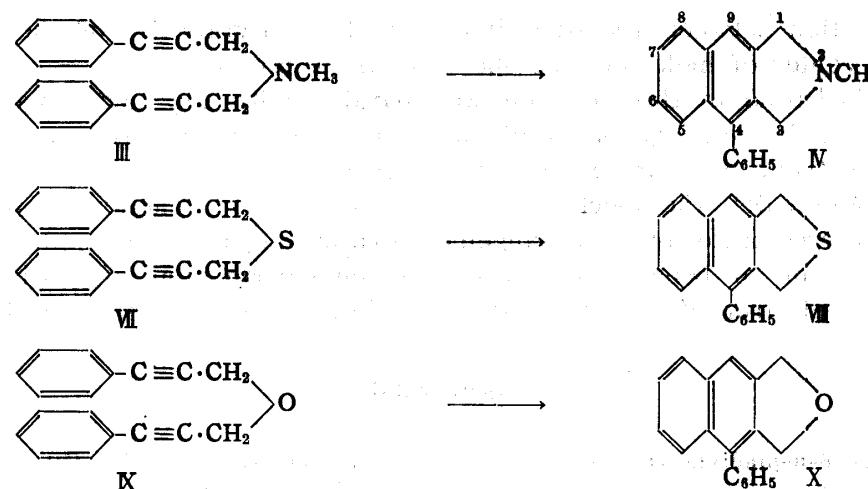
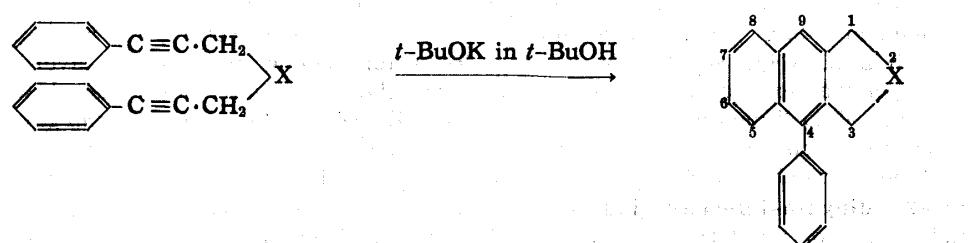


Chart 3.



X	Reaction time (min.)	Electronegativities (Pauling)	Yield (%)
-C-	210	2.5	35
-S-	240	2.5	40
>NCH ₃	75	3.0	85
-O-	20	3.5	97

Chart 4. Correlation between Reaction Time and Electronegativities

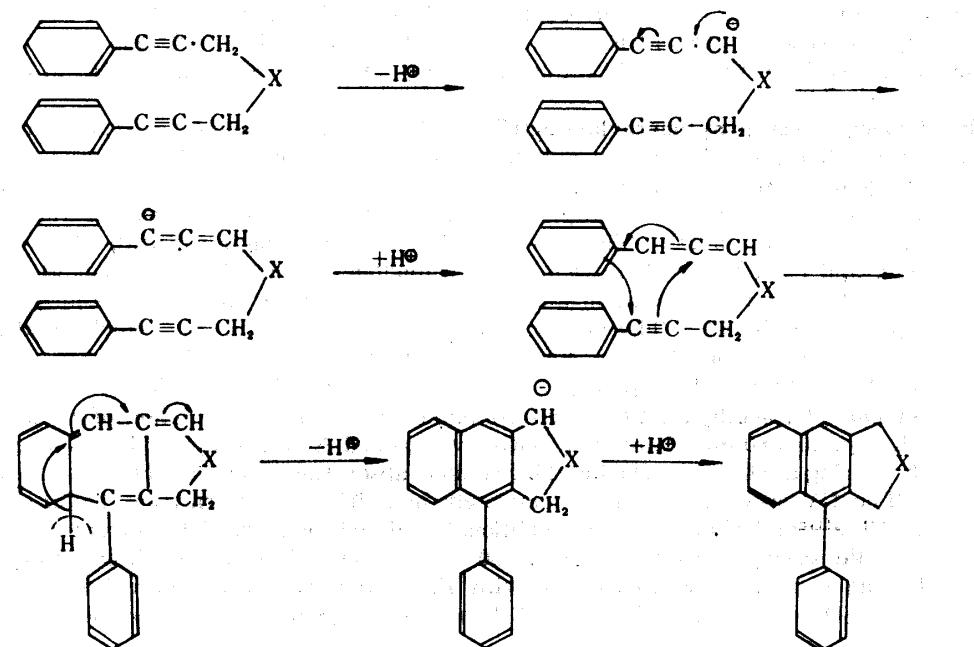


Chart 5.

The correlation between reaction time and electronegativities of the atoms which located at the center of molecule was shown in the Chart 4.

The reaction time in this reaction was parallel with the electronegativity of the hetero atom. This fact suggests that the proton abstraction from methylene group located between triple bond and hetero atom was first step in this cyclisation reaction.

From these results, the mechanism of this cyclisation reaction proposed involves initial base catalysed prototropic rearrangement to allenic system, followed by a cyclisation involving π -electron of benzene ring attacking on carbon atom of another triple bond and involving π -electron of the triple bond attacking on allenic center carbon atom.

Experimental*³

1,7-Diphenyl-1,6-heptadiyne (I)—To NaNH_2 prepared from 17.2 g. of Na , 450 ml. of liquid NH_3 and small amount of $\text{Fe}(\text{NO}_3)_3$ (0.5 g.) was added phenylacetylene (76 g., 0.746 mol.) in 80 ml. of abs. Et_2O at -40° to -37° under chilling with dry-ice-acetone and stirred for 1.5 hr. Then, to the reaction mixture was added dropwise trimethylene dibromide (75 g., 0.373 mol.) in 100 ml. of abs. Et_2O under controlling temperature from -40° to -35° with stirring during 75 min. The reaction mixture was continued stirring overnight at -35° . After evaporation of NH_3 at room temperature, the reaction mixture was decomposed with satd. NH_4Cl solution (56 g.) under ice-water cooling and organic layer was separated. The aqueous layer was extracted with Et_2O , combined ethereal solution was washed with satd. NaCl solution until neutral to litmus and dried over Na_2SO_4 . Evaporation of Et_2O in *vacuo* gave a liquid (28 g.) which was distilled in *vacuo* to afford a viscous oil (17 g.), b.p._{0.001} 144~146°. *Anal.* Calcd. for $\text{C}_{19}\text{H}_{16}$: C, 93.40; H, 6.60. Found: C, 93.05; H, 6.49. UV $\lambda_{\text{max}}^{\text{EtOH}}$ $\text{m}\mu$ ($\log \varepsilon$): 241.5 (4.53), 251 (4.45).

4-Phenyl-2,3-dihydro-1H-benz[f]indene (II)—To a solution of *t*-BuOK in *t*-BuOH prepared from K (4.0 g.) and 100 ml. of *t*-BuOH, was added 1,7-diphenyl-1,6-heptadiyne (I) (2 g.) with stirring at 62~63°. During the reaction, absorption maximum of UV spectra was checked every 15 min. After 3.5 hr. changing of the pattern of UV spectra stopped and further more the reaction-mixture was stirred for 1 hr. The solvent was evaporated in *vacuo* and to the residue was added H_2O and Et_2O . The ethereal layer was separated and aqueous layer was extracted with Et_2O . The combined ethereal solution was washed successively with H_2O , satd. NaCl solution and then dried over Na_2SO_4 . Evaporation of the solvent gave a colorless residue (2.5 g.) which dissolved in minimum amount (6 ml.) of benzene-hexane (1:3). The solution was absorbed in Al_2O_3 (70 g.) (Woelm, grade I) and eluting with benzene-hexane (1:3) gave 1.00 g. of colorless liquid from fraction No. 2 (each 100 ml. of eluting solvent was corrected) and 0.207 g. of pale yellow liquid from fraction No. 3. The former fraction was rechromatographed on Al_2O_3 (30 g.) (grade I) to give 700 mg. of colorless solid. Recrystallization from 99% of EtOH afforded colorless prisms, m.p. 81.5~82.5°. *Anal.* Calcd. for $\text{C}_{19}\text{H}_{16}$: C, 93.40; H, 6.60. Found: C, 93.05; H, 6.49. UV $\lambda_{\text{max}}^{\text{EtOH}}$ $\text{m}\mu$ ($\log \varepsilon$): 229 (4.509), 277.5 (3.453) (shoulder), 287 (3.712), 296 (3.604) (shoulder), 323 (3.133) (shoulder). NMR (in CCl_4) τ : 7.94 (quartet) ($-\text{CH}_2-$ at C_2), 7.18 (triplet) ($-\text{CH}_2-$ at C_3), 6.87 (triplet) ($-\text{CH}_2-$ at C_1).

N,N-Bis(3-phenyl-2-propynyl)methylamine(III)—This material was prepared according to the method of Iwai and Yura:⁸⁾ To a solution of phenylethynyl magnesium bromide in tetrahydrofuran (prepared from 11.6 g. phenylacetylene, 12.4 g. of EtBr , 2.38 g. of Mg and 130 ml. of anhyd. tetrahydrofuran), a solution of 11.5 g. of N,N-bis(butoxymethyl)methylamine and 20 ml. of tetrahydrofuran was added and stirred on a steam bath for 15 hr. The reaction mixture was decomposed with 10% of HCl solution under ice-cooling, and extracted with Et_2O to remove unchanged material. The acidic aqueous solution made alkaline with 10% of K_2CO_3 solution and filtered off to remove MgCO_3 . The filtrate was extracted with Et_2O and dried over K_2CO_3 . The evaporation of Et_2O gave viscous oil, which distilled in *vacuo* to afford 7.8 g. of pale yellow oil, b.p._{0.0002} 135~136°. *Anal.* Calcd. for $\text{C}_{19}\text{H}_{17}\text{N}$: C, 87.99; H, 6.61; N, 5.40. Found: C, 87.62; H, 6.97; N, 5.62. UV $\lambda_{\text{max}}^{\text{EtOH}}$ $\text{m}\mu$ ($\log \varepsilon$): 242.5 (4.57), 253 (4.53).

N-Methyl-4-phenyl-1,3-dihydro-2H-benz[f]isoindole (IV)—To the solution of *t*-BuOK in *t*-BuOH prepared from K (4 g.) and 80 ml. of anhyd. *t*-BuOH, was added N,N-Bis(3-phenyl-2-propynyl)methylamine (III) (2.0 g.) with stirring at 50~51°. During the reaction, absorption maximum of UV spectra was checked every 15 min. The UV spectrum changed completely into different pattern from that of starting material after 75 min. and the reaction mixture was additionally stirred for 2 hr. The solvent was removed under reduced pressure, the residue was dissolved in 150 ml. of H_2O and 100 ml. of Et_2O and organic layer was separated. The aqueous layer was extracted with Et_2O , and combined ethereal solution was washed successively with H_2O , satd. NaCl solution, and dried over Na_2SO_4 . The evaporation of Et_2O gave semi

*³ All melting points are uncorrected.

crystalline (1.96 g.). Recrystallization either from MeOH, EtOH or hexane did not succeed in affording fine crystallines. The semicrystalline substance (1.96 g.) was dissolved in benzene-hexane (1:3) and adsorbed on Al_2O_3 (70 g.) (Woelm, grade III). Elution with benzene-hexane (1:3) gave crystalline (1.76 g.) which recrystallized from EtOH to afford pale yellow leaflets, m.p. $141\sim143^\circ$. *Anal.* Calcd. for $\text{C}_{19}\text{H}_{17}\text{N}$: C, 87.99; H, 6.61; N, 5.62. Found: C, 87.52; H, 6.64; N, 5.55. UV $\lambda_{\text{max}}^{\text{EtOH}}$ $\text{m}\mu$ ($\log \varepsilon$): 266 (4.87), 275 (3.86) (shoulder), 285 (3.96), 292.5 (3.94) (shoulder), 322.5 (2.88) (shoulder). NMR (in CS_2) τ : 5.97 (singlet) ($-\text{CH}_2-$ at C_1), 6.25 (singlet) ($-\text{CH}_2-$ at C_3), 7.48 (singlet) ($-\text{NCH}_3$). Picrate of N showed m.p. $209\sim210^\circ$ after recrystallization from EtOH. *Anal.* Calcd. for $\text{C}_{25}\text{H}_{20}\text{O}_7\text{N}_4$: C, 61.47; H, 4.13; N, 11.47. Found: C, 61.14; H, 4.08; N, 11.61. Quaternary ammonium iodide of II prepared from CH_3I in abs. EtOH showed m.p. $240\sim241^\circ$ after recrystallization from EtOH. *Anal.* Calcd. for $\text{C}_{20}\text{H}_{20}\text{NI}$: C, 59.85; H, 5.02; N, 3.49. Found: C, 59.99; H, 5.18; N, 3.39.

N-Methyl-4-phenyl-1,3-dihydro-2-benz[f]isoindole (IV) from VI—A solution of 1.52 g. (0.04 mol.) of LiAlH_4 in 150 ml. of anhyd. tetrahydrofuran was placed in a 300 ml. of three necked flask equipped with Soxlet extractor in which 2.9 g. (0.011 mol.) of 1-phenyl-2,3-naphthalenedicarboxylic acid N-methyl-imide (VI) was placed, and refluxed for 18 hr. To the stirred reaction mixture there was added 10 ml. of AcOEt under cooling and then sodium potassium tartarate (10 g.) solution. Organic layer was separated and aqueous layer was extracted with Et_2O and combined organic layer was washed with H_2O and dried over Na_2SO_4 . Evaporation of solvent gave crude solid (IV) which recrystallized from EtOH affording pale yellow leaflets, m.p. $141\sim142^\circ$. A part of IV was converted into quaternary ammonium iodide with CH_3I furnishing colorless prisms, m.p. $240\sim241^\circ$ from EtOH.

1-Phenyl-2,3-naphthalenedicarboxylic Acid N-Methylimide (VI)—In sealed tube was placed 0.7 g. (0.022 mol.) of CH_3NH_2 and 4.2 g. (0.0154 mol.) of 1-phenyl-2,3-naphthalenedicarboxylic anhydride and 10 ml. of anhyd. dioxane and heated in oil bath at $300\sim320^\circ$ for 2 hr. and then at $180\sim190^\circ$ for 3.5 hr. After cooling, crystallines appeared from reaction mixture. Recrystallization from large amount of dioxane gave pale yellow needles, m.p. $260\sim262$. *Anal.* Calcd. for $\text{C}_{19}\text{H}_{13}\text{O}_2\text{N}$: C, 79.43; H, 4.56; N, 4.88. Found: C, 79.28; H, 4.51; N, 4.70. IR $\lambda_{\text{max}}^{\text{Nujol}}$ μ : 5.65, 5.84 (-CO-N-CO-).

Bis(3-phenyl-2-propynyl) Sulfide (VII)—To a solution of 3-phenyl-2-propynyl bromide (20.0 g., 0.1025 mol.) in 20 ml. of MeOH was added a solution of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (12 g., 0.0502 mol.) in 60 ml. of MeOH with controling at 15 to 17° under ice-water cooling. After completing the addition, the reaction mixture was stirred at room temperature overnight. The reaction mixture separated into two layers the upper layer of which concentrated under reduced pressure followed by extracting with Et_2O . The lower layer was dissolved in Et_2O . The combined ethereal solution was washed with satd. NaCl solution until neutral to litmus and dried over Na_2SO_4 . After evaporation of solvent, *vacuo* distillation of the residue gave a yellow liquid, b.p._{0.001} $169\sim170^\circ$. (9.0 g.). *Anal.* Calcd. for $\text{C}_{18}\text{H}_{14}\text{S}$: C, 82.39; H, 5.37. Found: C, 81.82; H, 5.22. UV $\lambda_{\text{max}}^{\text{EtOH}}$ $\text{m}\mu$ ($\log \varepsilon$): 245 (4.63), 262 (4.59).

4-Phenyl-1,3-dihydronaphtho[2,3-c]thiophene (VIII)—To a stirred solution of *t*-BuOK in *t*-BuOH prepared from K (4.0 g.) and 80 ml. of *t*-BuOH was added bis(3-phenyl-2-propynyl) sulfide (2.0 g.) at $59\sim60^\circ$ and continued to stir for 10 hr. During the reaction, absorption maximum of UV spectra was checked every 15 min. After stirring for 7.5 hr., the pattern of UV became constant and further more the reaction mixture was continued stirring for 2.5 hr. The solvent was evaporated in *vacuo* and H_2O and Et_2O was added. The ethereal layer was separated and aqueous layer was extracted with Et_2O . The combined ethereal solution was washed successively with H_2O , satd. NaCl solution and then dried over Na_2SO_4 . Evaporation of the solvent gave a gummy substance (1.99 g.) which was dissolved in minimum amount (7 ml.) of benzene-hexane (1:3). The solution was adsorbed on Al_2O_3 (100 g.) (Woelm, grade III) and eluting with benzene-hexane (1:3) afforded 1.511 g. of viscous fluorescened liquid from fraction No. 2 (each 100 ml. of eluting solvent was collected). This oily substance was submitted to rechromatography on Al_2O_3 (80 g.) (grade III) to give a fluorescened oily substance (665 mg.) from fraction No. 3 and crystalline (375 mg.) from No. 4 (each 100 ml. of eluting solvent (hexane only) was collected). The UV spectra of these two fractions gave the same pattern. The oily substance was purified by rechromatography on Al_2O_3 by the same procedure as above. The crystalline substance was recrystallized from EtOH to give colorless prisms, m.p. $131\sim132^\circ$. *Anal.* Calcd. for $\text{C}_{18}\text{H}_{14}\text{S}$: C, 82.39, H, 5.37. Found: C, 82.25; H, 5.21. UV $\lambda_{\text{max}}^{\text{EtOH}}$ $\text{m}\mu$ ($\log \varepsilon$): 229 (4.94), 277 (3.84), (shoulder), 287 (3.93), 296 (3.85) (shoulder), 322 (2.83). NMR (in CCl_4) τ : 5.98 (singlet) ($-\text{CH}_2-$ at C_3), 5.62 (singlet) ($-\text{CH}_2-$ at C_1).

Bis(3-phenyl-2-propynyl) Ether (IX)—Na (3.3 g., 0.144 mol.) in 3-phenyl-2-propyn-1-ol (36.5 g., 0.276 mol.) was warmed at $55\sim60^\circ$ for 20 hr. under stirring. To the above solution was added 1-phenyl-3-bromo-1-propyne (19.5 g., 0.1 mol.) and then warmed at 60° for 10 hr. under stirring. The reaction mixture was poured into ice-water and extracted with Et_2O . The combined ethereal extracts were washed with H_2O and dried over Na_2SO_4 . After evaporation of solvent the residue was submitted to *vacuo* distillation to give colorless liquid, b.p._{0.003} $170\sim180^\circ$ (bath temp.) (10 g. yield). *Anal.* Calcd. for $\text{C}_{16}\text{H}_{14}\text{O}$: C, 87.77; H, 5.73. Found: C, 87.34; H, 5.61.

4-Phenyl-1,3-dihydronaphtho[2,3-c]furan (X)—To a stirred solution of *t*-BuOK in *t*-BuOH prepared from K (4.0 g.) and 80 ml. of *t*-BuOH was added bis(3-phenyl-2-propynyl) ether (IX) (2.0 g.) at $51\sim52^\circ$ and

continued to stir for 3 hr. During the reaction, absorption maximum of UV spectra was checked every 15 min. After stirring for 15 min. the pattern of UV became constant and furthermore the reaction mixture was continued stirring for 2.25 hr. The solvent was evaporated *in vacuo* and H₂O and Et₂O was added. The ethereal layer was separated and aqueous layer was extracted with Et₂O. The combined ethereal solution was washed with H₂O, satd. NaCl solution and then dried over Na₂SO₄. Evaporation of solvent gave crystalline substance (1.9 g.) which was recrystallized from EtOH affording m.p. 121.5~122.5° colorless prisms. *Anal.* Calcd. for C₁₈H₁₄O: C, 87.77; H, 5.73. Found: C, 87.69; H, 5.81. UV $\lambda_{\text{max}}^{\text{EtOH}}$ m_μ (log ε): 228 (4.75), 275 (3.80) (shoulder), 284 (3.93), 294 (3.91) (shoulder), 321 (2.96) (shoulder). NMR (in CCl₄) τ: 4.93 (singlet) (-CH₂- at C₃), 4.67 (singlet) (-CH₂- at C₁).

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Summary

Diacetylenic compounds; 1,7-diphenyl-1,6-heptadiyne (I), N,N-bis(3-phenyl-2-propynyl)methylamine (III), bis(3-phenyl-2-propynyl) sulfide (VII) and bis(3-phenyl-2-propynyl) ether (IX) underwent intramolecular cyclization reaction by means of 14% solution of potassium *tert*-butoxide in *tert*-butyl alcohol in remarkably mild condition to afford naphthalene derivatives; 4-phenyl-2,3-dihydro-1H-benz[f]indene (II), N-methyl-4-phenyl-1,3-dihydro-2H-benz[f]isoindole (IV), 4-phenyl-1,3-dihydroneaphtho[2,3-c]thiophene (VIII) and 4-phenyl-1,3-dihydroneaphtho[2,3-c]furan (X) respectively. The reaction mechanism of this cyclization was proposed.

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