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Linear Conjugated Systems Bearing Aromatic Terminal Groups. III. The Synthesis and the Electronic Spectra of 1,1′-Dinaphthyl- and 2,2′-Dinaphthylpoly-ynes

Kazuhiro NAKASUJI, Shuzo AKIYAMA, Kazuko AKASHI and Masazumi NAKAGAWA

Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka

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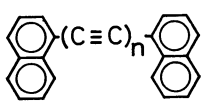
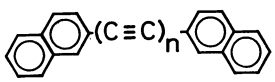
1,1′-Dinaphthylpoly-ynes (I_n, $n=1$—6) and 2,2′-dinaphthylpoly-ynes (II_n, $n=1$—6) were synthesized, and their electronic spectra were measured. The I_n-series gave an excellent agreement with the $\lambda_{max} \propto n^{1.5}$ relationship, and the II_n-series followed a straight line, $\lambda_{max} \propto n^{1.3}$. These relationships are different from those of 1,1′-dianthryl- and 9,9′-dianthrylpoly-ynes, in which the plots of λ_{max} *versus* n^2 give excellent straight lines (*Bull. Chem. Soc. Jap.*, **39**, 2320 (1966); **40**, 340 (1967)). The new linear relationships found in the dinaphthyl-series offer further evidence of the prominent effect of the terminal groups upon the electronic spectral properties of the conjugated poly-yne system.

In previous papers,[1,2] two of the present authors (S. A and M. N.) have reported the novel electronic spectral properties of 1,1′-dianthryl- and 9,9′-dianthrylpoly-ynes. In the two series of dianthrylpoly-ynes, the variation in λ_{max} with an increase in the number of acetylenic bonds (n) is expressed by the linear relation: $\lambda_{max}=An^2+B$.

We now hoped to synthesize the poly-ynes bearing different types of aromatic terminal groups in order to clarify the role of terminal groups on the electronic spectral regularity of the poly-yne system.



I_n



II_n

$n=1, 2, 3, 4, 5, 6$

Synthesis. The synthesis of the mono-, di-, tri-, and tetra-acetylenes (I_{1-4} and II_{1-4}) has been carried out according to the reaction sequence outlined in Scheme 1. The dinaphthylacetylenes (I_1 and II_1) were prepared according to the method of Curtius.[3] The dinaphthyldi-, tri-, and tetra-acetylenes (I_{2-4} and II_{2-4}) were synthesized employing 1- and 2-naphthaldehydes as the starting materials. As is shown in Scheme 2, the naphthylpropargylaldehydes (XVII and XVII′), which had been derived from the acetylnaphthalenes (XV and XV′), were used as the starting materials for the synthesis of the penta- and the hexa-acetylenes (I_5, I_6 and II_5 and II_6). It was found that the replacement reaction of the hydroxyl group in the acetylenic alcohol or glycol by the chlorine atom by means of the action of thionyl chloride and pyridine in tetrahydrofuran was rather sensitive to the reaction conditions, a good result was obtained only under limited reaction conditions (see, the Experimental section).

The colors, the melting points, and the wave-numbers of the IR absorptions due to $\nu_{C\equiv C}$ are summarized in Tables 1 and 2.

Table 1. Physical properties of 1,1′-dinaphthylpoly-ynes (I_n)

n	Color of crystals	Mp (°C)	$\nu_{C\equiv C}$(cm^{-1})
1	colorless	129	—
2	light yellow	175—177	2130
3	yellow	192—193	2190
4	deep yellow	205—207	2205
5	orange yellow	*ca.* 195 (dec.)	2180
6	orange	*ca.* 175 (dec.)	2155

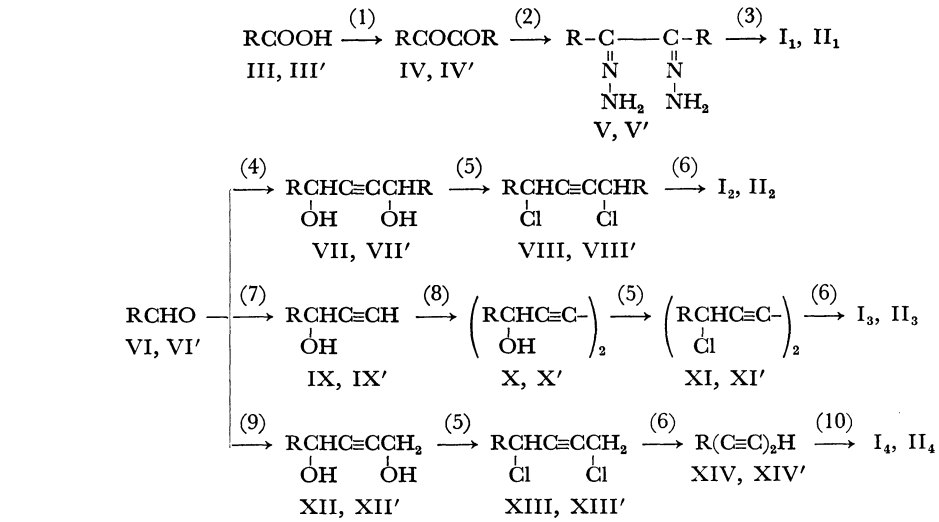
Table 2. Physical properties of 2,2′-dinaphthylpoly-ynes (II_n)

n	Color of crystals	Mp (°C)	$\nu_{C\equiv C}$(cm^{-1})
1	colorless	228—229	—
2	colorless	202—203	—
3	faint yellow	173—174	2190
4	light yellow	*ca.* 172 (dec.)	2185
5	yellow	*ca.* 180 (dec.)	2170
6	orange yellow	*ca.* 200 (dec.)	2140

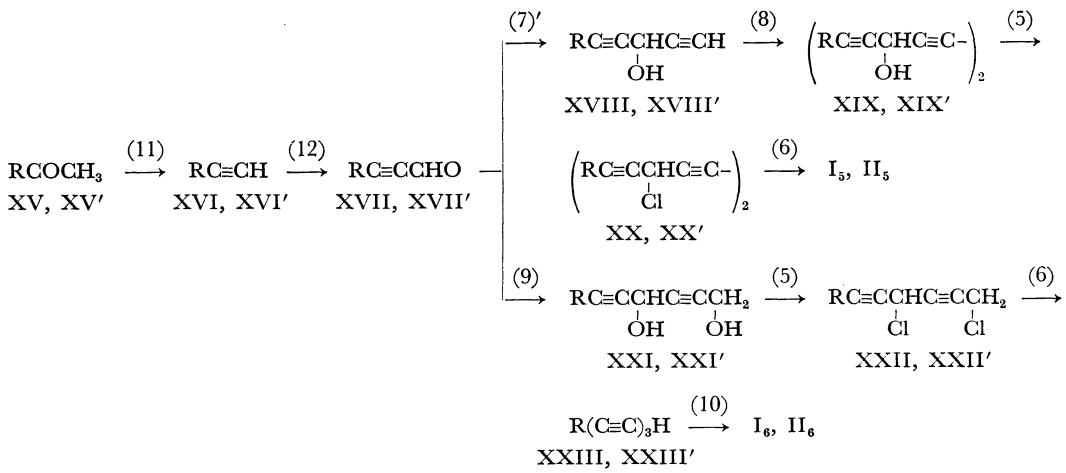
1) S. Akiyama and M. Nakagawa, This Bulletin, **40**, 340 (1967); K. Nishimoto, S. Akiyama, M. Nakagawa and R. Fujishiro, *ibid.*, **39**, 2320 (1966).

2) The preceding paper.

3) Th. Curtius and K. Thun, *J. Prakt. Chem.*, [2] **44**, 171 (1891).



Scheme 1. Synthesis of Dinaphthylpoly-ynes (I_{1-4}, II_{1-4})



Scheme 2. Synthesis of Dinaphthylpenta- and hexa-acetylenes

R means a 1- or 2-naphthyl group, and the prime on the Roman figure indicates that R is a 2-naphthyl group.

(1) i. Mg-MgI_2, ii. $Cu(OAc)_2$, NH_4NO_3; (2) $H_2NNH_2 \cdot H_2O$/*n*-PrOH; (3) HgO; (4) BrMgC≡CMgBr/THF; (5) $SOCl_2$-Pyridine/THF; (6) $NaNH_2$/liq.NH_3; (7) HC≡CLi/liq.NH_3; (7)′ HC≡CMgBr/THF; (8) CuCl-NH_4Cl-O_2/MeOH or Hay's method[4]; (9) BrMgC≡CCH$_2$OMgBr/THF; (10) $Cu(OAc)_2$/pyridine; (11) i. PCl_5, ii. $NaNH_2$/liq.NH_3; (12) i. C_2H_5MgBr/THF, ii. dimethylformamide/THF, iii, dil.H_2SO_4. THF=tetrahydrofuran.

Electronic Spectra. The absorption curves and the numerical data of the electronic spectra of the two series of dinaphthylpoly-ynes (I_n and II_n) are shown in Figs. 1 and 2 and in Tables 3 and 4. In both series, the spectra can be regarded as consisting of two groups of absorption bands, *i. e.*, the short-wavelength absorption bands and the long-wavelength absorption bands. The most characteristic feature of the spectra of I_n and II_n is found in the pronounced vibrational structure in the long-wavelength band, which is more distinct than that of the dianthrylpoly-ynes.[1,2]

The long-wavelength band can reasonably be attributed to the interaction of the polyacetylenic chromophore with the ^1L_a-band of the naphthalene nucleus. As the direction of the polarization of the ^1L_a-band is parallel to the short axis of the naphthalene nucleus, the red shift of the long-wavelength bands in the 1,1′-dinaphthyl-series (I_n) as compared with that in the 2,2′-series (II_n) can be ascribed to the more effective extension of conjugation by the polyacetylenic substituent in the 1,1′-series, which extends parallel to the short axis of the nucleus. The difference in wavelength of

4) A. S. Hay, *J. Org. Chem.*, **27**, 3320 (1962).

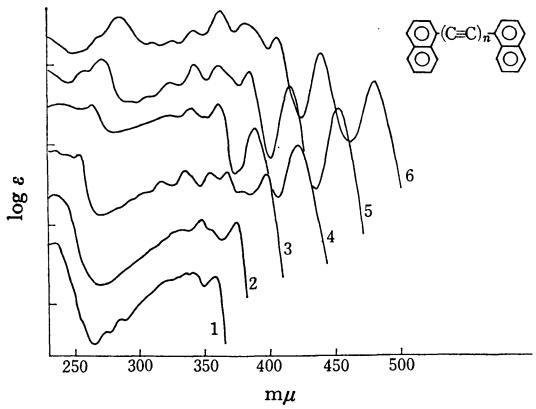


Fig. 1. The absorption curves of 1,1′-dinaphthylpoly-ynes (I_1–I_6). The curves, with the exception of the monoacetylene at the bottom, have been displaced upward on the ordinate axis by 0.5 log ε unit increments from the curve immediately below (in tetrahydrofuran).

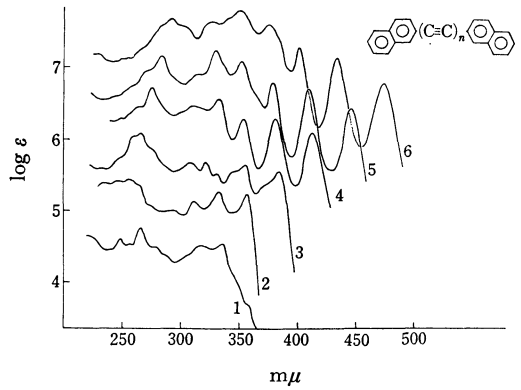


Fig. 2. The absorption curves of 2,2′-dinaphthylpoly-ynes (II_1–II_6). The curves, with the exception of the monoacetylene at the bottom, have been displaced upward on the ordinate axis by 0.5 log ε unit increments from the curve immediately below (in tetrahydrofuran).

Table 3. The electronic spectral data of 1,1′-dinaphthylpoly-ynes (I_n)

n	λ_{max} in mμ and log ε (in parentheses) in tetrahydrofuran										
1	235.5 (4.83)	273.5 (3.65)	284.5 (3.81)	322* (4.31)	336 (4.40)	342 (4.41)	359 (4.36)				
2	234 (4.89)	326* (4.42)	333 (4.44)	348 (4.57)	375 (4.54)						
3	235 (4.92)	244 (4.87)	255.5 (4.87)	285* (3.17)	307* (3.10)	317 (3.12)	336 (4.71)	355 (4.63)	367 (4.64)	378 (3.37)	397 (4.60)
4	238.5 (4.90)	265 (4.86)	286* (4.28)	324 (4.64)	340 (4.80)	361 (4.86)	389 (4.70)	422 (4.49)			
5	259.5 (4.95)	272.5 (5.09)	310 (4.61)	325 (4.74)	343 (4.96)	362 (4.94)	385 (4.85)	415 (4.69)	452 (4.42)		
6	285.5 (5.11)	301 (4.79)	326 (4.80)	343 (4.93)	363 (5.16)	382 (5.00)	407 (4.83)	440 (4.62)	479 (4.27)		

The asterisks indicate shoulders.

Table 4. The electronic spectral data of 2,2′-dinaphthylpoly-ynes (II_n)

n	λ_{max} in mμ and log ε (in parentheses) in tetrahydrofuran						
1	257 (4.54)	267 (4.77)	317 (4.56)	336 (4.59)	358* (3.89)		
2	236 (4.81)	248 (4.83)	257 (4.85)	294.5 (4.44)	312 (4.56)	333 (4.70)	357 (4.66)
3	261 (5.06)	267 (5.09)	308 (4.67)	322 (4.69)	332 (4.53)	356 (4.64)	384 (4.57)
4	264.5 (4.90)	276 (5.16)	311 (4.91)	332 (4.99)	354 (4.72)	381 (4.74)	413 (4.54)
5	284.5 (5.18)	330 (5.24)	353 (5.08)	379 (4.80)	409 (4.71)	445 (4.43)	
6	292 (5.00)	327.5 (4.97)	350 (5.12)	374 (4.91)	401 (4.68)	434 (4.54)	473 (4.21)

The asterisk indicates the shoulder.

the longest-wavelength maxima between I_n and II_n was found to decrease with an increase in the number of n (Table 5). This fact seems to indicate a diminishing contribution of the terminal groups with an increase in the length of the polyacetylenic chain. The intensities of the strongest sub-bands in the long-wavelength absorption increase with an

Table 5. The bathochromic shift of thf longest-wavelength maxima in I_n (mμ)

n	1	2	3	4	5	6
I_n	359	375	397	422	452	479
II_n	336	357	384	413	445	473
$\Delta\lambda$	23	18	13	9	7	6

increase in the number of n. However, the intensities of the longest-wavelength sub-bands reach their maxima at $n=3$ in the 1,1′-series (I_n) and at $n=2$ in the 2,2′-series (II_n), and then decrease monotonously with an increase in the number of n. As is summarized in Table 6, the spacing between the longest-wavelength sub-band and the second-longest-wavelength sub-band diminishes with an increase in the number of n. This tendency seems to reflect the decrease in the triple-bond character, *i. e.*, the increasing contribution of a cumulene-type structure in the excited state with an increase in the length of the poly-yne chain. The short wavelength bands in I_n and II_n clearly relate to the ^1B_b-band of naphthalene. The direction of the polarization of the ^1B_b-band has been known to be parallel to the long axis of the naphthalene nucleus. Therefore, the introduction of a poly-acetylene chain at the 2-position, thus extending the conjugation of the naphthalene nucleus, should exert a more prominent effect than such an introduction at the 1-position. In fact, as is summarized in Table 7, we observed a remarkable bathochromic shift of the absorption maximum in the short-wavelength band in II_n as compared with that in I_n. Just as in the case of the ^1L_a-band, the extent of the bathochromic shift decreases with an increase in the number of the acetylenic linkage, suggesting a diminishing contribution of the terminal groups.

Table 6. Spacing of the vibrational sub-band (cm^{-1})

n	2	3	4	5	6
I_n	2070	2060	2010	1980	1850
II_n	2020	2040	2010	1980	1900

Table 7. The bathochromic shift of the maxima in the short-wavelength band in II_n (mμ)

n	1	2	3	4	5	6
II_n	267	264	267	276	285	292
I_n	236	234	256	265	273	286
$\Delta\lambda$	31	30	11	11	12	6

In the previous series of this series,[1,2] it was pointed out that the plots of λ_{max} against the square of the number of the acetylenic bond (n^2) gave an excellent straight line in the cases of 1,1′-dianthryl- and 9,9′-dianthrylpoly-ynes. In the case of 1,1′-dinaphthylpoly-ynes (I_n), it was found that the variation in the wavelength of the longest-wavelength maximum (λ_{max}) with an increase in the number of the acetylenic bond (n) can be expressed by the linear relation:

$$\lambda_{max} = 9\, n^{1.5} + 350 \text{ (tetrahydrofuran)}$$

The plots of λ_{max} *versus* $n^{1.5}$ are illustrated in Fig. 3. The observed and the calculated values of λ_{max} are compared in Table 8.

Table 8. The longest-wavelength maxima of I_n (mμ)

n	1	2	3	4	5	6
Calcd.	359	375	397	422	452	479
Obs.	359	375	397	422	451	482
$\Delta\lambda$	0	0	0	0	−1	3

A good correlation between the wavelength of the longest-wavelength maxima (λ_{max}) and $n^{1.3}$ was observed in the case of 2,2′-dinaphthylpoly-ynes (II_n). The linear relation is well expressed by the empirical formula:

$$\lambda_{max} = 15.5\, n^{1.3} + 319 \text{ (tetrahydrofuran)}$$

The observed and the calculated values of λ_{max} are listed in Table 9, while the plots of λ_{max} against $n^{1.3}$ are shown in Fig. 4. As is shown by the B lines in Figs. 3 and 4, the second-longest-wavelength peaks of I_n and II_n also gave straight lines when plotted against $n^{1.5}$ and $n^{1.3}$ respectively.

Table 9. The longest-wavelength maxima of II_n (mμ)

n	1	2	3	4	5	6
Calcd.	335	357	384	413	445	478
Obs.	336	357	384	413	445	473
$\Delta\lambda$	−1	0	0	0	0	5

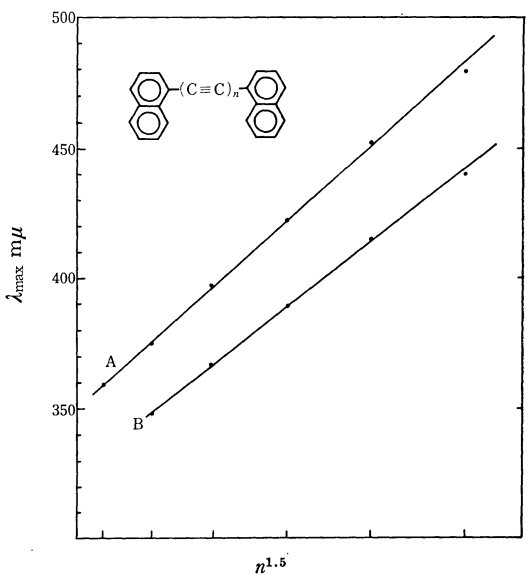


Fig. 3. Plot of λ_{max} *vs.* $n^{1.5}$ for 1,1′-dinaphthylpoly-ynes (I_1–I_6).
A: longest-wavelength maxima
B: second-longest-wavelength maxima

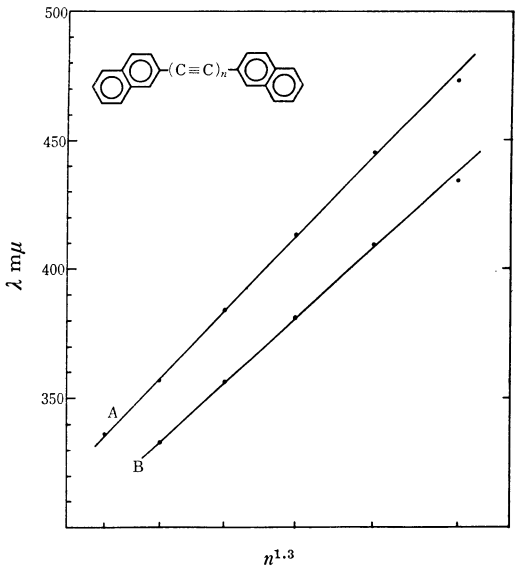


Fig. 4. Plot of λ_{max} *vs.* $n^{1.3}$ for 2,2′-dinaphthylpoly-ynes (II_1–II_6).
A: longest-wavelength maxima
B: second-longest-wavelength maxima

In both series, the deviation from the straight line is distinct in the case of $n=6$. This fact seems to indicate that the diminishing contribution of the terminal groups to the electronic excitation as the number of n increases causes a gradual change in the spectral properties of these diarylpoly-ynes. If the length of the poly-yne chains in these diarylpoly-ynes is large enough, the spectral shift might be similar to that of simple poly-yne or dialkylpoly-yne. However, it is evident that the regularities in the relationship between λ_{max} and the length of the conjugated polyacetylene chain (n) are markedly influenced by the nature of the aromatic terminal groups, at least in the range of a small number of n. Further studies along this line are now in progress.

Experimental

All the melting points are uncorrected. The electronic spectra were obtained on a Hitachi EPS-3T Spectrophotometer at room temperature using a well-matched pair of 1-cm cells. The infrared spectra were determined with a Hitachi EPI-2 Infrared Spectrophotometer.

1,1′-Naphthil Dihydrazone (V). A mixture of 1,1′-naphthil[5] (IV, 3.10 g, 0.01 mol), 80% hydrazine hydrate (3.10 g, 0.05 mol), and *n*-propanol (80 m*l*) was refluxed for 43.5 hr. The mixture was then cooled in an ice-bath. The crystalline solid which was thus separated was collected by filtration and washed with a small amount of methanol to yield V as fine colorless crystals; 1.15 g; mp 270—275°C (dec.). The mother liquor was refluxed for a further 48 hr to afford additional V; 0.5 g (total yield, 49%).

Found: C, 78.25; H, 5.31; N, 16.14%. Calcd for $C_{22}H_{18}N_4$: C, 78.08; H, 5.36; N, 16.56%.

1,1′-Naphthil Monohydrazone (colorless cubes; 0.35 g; 11%; mp 173—175°C) was obtained by concentrating the filtrate.

Found: C, 81.12; H, 5.06; N, 8.69%. Calcd for $C_{22}H_{16}N_2O$: C, 81.46; H, 4.97; N, 8.64%.

1,1′-Dinaphthylacetylene (I). A mixture of the dihydrazone (V, 1.52 g, 4.5 mmol), yellow mercuric oxide (4.0 g, 0.018 mol), sodium sulfate (0.9 g), powdered potassium hydroxide (0.8 g), and toluene (200 m*l*) was refluxed for 3.5 hr and then filtered. The concentration of the filtrate under a reduced pressure yielded light brown needles; 1.03 g (82%); mp 120—126°C. The crystals were dissolved in benzene and percolated through a small column of alumina (10 g). The filtrate was then concentrated to yield colorless needles; 0.99 g (79%); mp 127—128°C. The crystals were recrystallized twice from methanol to give pure I; mp 129°C*1.

Found: C, 95.00; H, 5.04%. Calcd for $C_{22}H_{14}$; C, 94.93; H, 5.07%.

1,4-Di(1-naphthyl)-1,4-dihydroxy-2-butyne (VII). A solution of 1-naphthaldehyde (VI, 6.20 g, 0.04 mol) in tetrahydrofuran (30 m*l*) was added to a stirred and ice-cooled solution of acetylene dimagnesium bromide [from magnesium 1.92 g, 0.08 g atom and ethyl bromide 8.72 g, 0.08 mol] in benzene - tetrahydrofuran (60 m*l*) over a period of 15 min. After this mixture had been stirred overnight at room temperature, a saturated aqueous solution of ammonium chloride was added under cooling with an ice-salt bath. The aqueous layer was removed and extracted with ether. The extract was combined with the organic layer and dried (magnesium sulfate). It was concentrated under reduced pressure to yield an oily material which crystallized on standing. The crude material was treated with a small amount of benzene to give colorless crystals; 4.80 g (71%). Two recrystallizations of the crystals from benzene gave pure VII; mp 186.5—187.5°C.

Found: C, 85.61; H, 5.38%. Calcd for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36%. IR (in Nujol): 3300—3400 (O–H), 1010 (C–O) cm^{-1}.

1,1′-Dinaphthyldiacetylene (I_2). *The Preparation of the Dichloride (VIII).* To an ice-cooled and stirred mixture of the glycol (VII, 1.01 g, 3 mmol), pyridine (0.95 g, 0.012 mol), and tetrahydrofuran (10 m*l*), there was added a solution of thionyl chloride (1.40 g, 0.012 mol) in tetrahydrofuran (3 m*l*) over a period of 30 min, then the mixture was warmed to 40°C over a period of 1 hr, after which it was stirred an additional hour at that temperature. Cracked ice was added to the reaction mixture, and it was extracted with benzene. The extract was washed with water and aqueous sodium hydrogen carbonate successively, and then dried (magnesium sulfate). The crude dichloride (VIII, 1.00 g, 90%) which was obtained as a yellowish-brown mass by evaporating the solvent *in vacuo* was used in the following reaction without purification.

The Dehydrochlorination of VIII. A solution of the above-mentioned crude chloride (VIII) in tetrahydro-

5) M. Gomberg and W. E. Bachmann, *J. Amer. Chem. Soc.*, **50**, 2762 (1928).

*1 It should be noted that the description of 1,1′-dinaphthylacetylene in Beilstein, Bd. V, p. 735, is erroneous. It concerns the 2,2′-isomer.

furan (7 ml) was added over a period of 5 min to a stirred suspension of sodium amide [from sodium 0.7 g, 0.03 g atom] in liquid ammonia (50 ml) at −70°C. After 4 hr, ammonium chloride (2.5 g) was added to the reaction mixture, and the ammonia was allowed to evaporate. The residue was repeatedly digested with benzene (total 250 ml), and the benzene solution was concentrated to 50 ml and passed through a short column of alumina (15 g). The yellow crystals [0.28 g, (31% based on VII), mp 171—175°C] which were obtained by concentrating the filtrate under a reduced pressure were recrystallized twice from benzene to give pure I_2; mp 175—177°C. [lit. value, mp 171°C[6]].

Found: C, 95.32; H, 4.69%. Calcd for $C_{24}H_{14}$: C, 95.33; H, 4.67%.

The Oxidative Coupling of 1-Ethynylnaphthalene (XVI). The diacetylene (I_2) was obtained in a quantitative yield by stirring a mixture of 1-ethynylnaphthalene (XVI, 0.86 g, 5.7 mmol), cupric acetate monohydrate (3.0 g), pyridine (8 ml), and methanol (0.5 ml) at 30°C overnight. The crystals thus obtained were recrystallized 3 times from benzene and once from acetone to give pure I_2; mp 175—177°C.

Found: C, 95.42; H, 4.79%. Calcd for $C_{24}H_{14}$: C, 95.33; H, 4.67%.

1-(1-Naphthyl)-2-propyn-1-ol (IX). A solution of 1-naphthaldehyde (VI, 56 g, 0.36 mol) in tetrahydrofuran (300 ml) was added to a stirred solution of lithium acetylide [from lithium 7.45 g (1.08 g atom)] in liquid ammonia (1.2 l) at −70°C over a period of 30 min. Stirring was then continued for 28 hr at −60——65°C. After the addition of ammonium chloride (36 g), the ammonia was allowed to evaporate. The organic layer was separated, and the residue was digested with benzene. The combined organic layer was evaporated *in vacuo*, resulting in a viscous red oil which crystallized on standing. The crude material was treated with benzene - cyclohexane (2 : 5), filtered, and washed with the same solvent to yield a light brown, crystalline powder; 45.4 g (69%). This was recrystallized 5 times from the same solvent to give pure IX as colorless needles; mp 61—63°C.

Found: C, 85.68; H, 5.37%. Calcd for $C_{13}H_{10}O$: C, 85.69; H, 5.53%. IR (Nujol): 3200—3300 (OH), 3300 (≡CH), 2100 (C≡C), 1060 (C–O) cm^{-1}.

1,6-Di(1-naphthyl)-1,6-dihydroxy-2,4-hexadiyne (X). A mixture of the ethynyl carbinol (IX, 6.90 g, 0.038 mol), *N,N,N',N'*-tetramethylethylenediamine (0.22 g, 0.002 mol), cuprous chloride (0.19 g, 0.002 mol), and acetone (50 ml) was vigorously stirred in an atmosphere of oxygen for 2 hr at room temperature and then for 4 hr at 40°C.[4] The oily material which was obtained by evaporating the solvent was dissolved in tetrahydrofuran (100 ml). Benzene (25 ml) was added to the solution, and it was washed with a saturated aqueous solution of sodium chloride, diluted sulfuric acid, a sodium chloride solution and an aqueous sodium hydrogen carbonate solution successively, and then dried (magnesium sulfate). The residue obtained by evaporating the solvent *in vacuo* was mixed with benzene (30 ml), resulting in crude brown crystals; 5.76 g(80%). Five recrystallizations from benzene and two from ethanol - benzene yielded pure X as fine colorless needles; mp 156—176°C.[7]

Found: C, 85.89; H, 4.97%. Calcd for $C_{26}H_{18}O_2$: C, 86.16; H, 5.01%. IR (Nujol): 3200—3300 (OH), 1065 (C–O) cm^{-1}.

1,1'-Dinaphthyltriacetylene (I_3). *The Preparation of the Dichloride (XI).* To a stirred mixture of the glycol (X, 1.09 g, 3 mmol), pyridine (0.71 g, 9 mmol), and tetrahydrofuran (10 ml), there was added a solution of thionyl chloride (1.07 g, 9 mmol) in tetrahydrofuran (3 ml) over a period of 30 min at 0°C. After further stirring for 1 hr at room temperature and then 30 min at 40°C, cracked ice was added to the reaction mixture and it was extracted with benzene. The extract was washed with water, a sodium hydrogen carbonate solution, and water successively, and then dried (magnesium sulfate). The crude dichloride (XI), which was obtained as a deep brown oil by evaporating the solvent *in vacuo*, was subjected to the subsequent reaction without purification.

The Dehydrochlorination of XI. A solution of the crude dichloride (XI) in tetrahydrofuran (10 ml) was added, over a period of 5 min, to a suspension of sodium amide [from sodium 0.41 g, 0.018 g atom] in liquid ammonia (50 ml) at −70°C. After 1 hr, ammonium chloride (2 g) was added to the mixture, and the ammonia was allowed to evaporate. The residue was repeatedly digested with petroleum benzine (total 300 ml). The extract was concentrated under reduced pressure to yield crude I_3, as yellow crystals; 0.26 g (27% based on X). This was dissolved in benzene and percolated through a short column of alumina. The crystals obtained by concentrating the filtrate *in vacuo* were recrystallized twice from acetone to afford pure I_3 as yellow needles; mp 192—193°C.

Found: C, 95.56; H, 4.30%. Calcd for $C_{26}H_{14}$: C, 95.68; H, 4.32%.

1-(1-Naphthyl)-2-butyne-1,4-diol (XII). A solution of propargyl alcohol (11.20 g, 0.2 mol) in tetrahydrofuran (30 ml) was added, over a period of 30 min, to a stirred and water-cooled solution of ethylmagnesium bromide [from magnesium 9.60 g (0.40 g atom) and ethyl bromide 43.9 g (0.40 mol)] in the same solvent (150 ml). After it had refluxed for 1 hr, the mixture was cooled in an ice-bath. 1-Naphthaldehyde (VI, 15.60 g, 0.1 mol) in the same solvent (80 ml) was introduced to the cooled mixture, and it was stirred overnight at 20°C. After refluxing for 1.5 hr, the reaction mixture was then mixed with 4N sulfuric acid (100 ml) and extracted with ether. The extract was washed successively with a saturated solution of sodium chloride and a sodium hydrogen carbonate solution, and then dried (magnesium sulfate). The removal of the solvent *in vacuo* resulted in a dark red oil which crystallized on standing. The crude crystals were treated with a small amount of benzine - cyclohexane (1 : 1), collected by filtration, and washed with the same mixed solvent to yield fine pale yellow cubes; mp 120—123°C; 14.20 g (67%). The crystals were recrystallized 4 times from benzene to give pure XII as colorless needles; mp 125—126°C.

Found: C, 78.97; H, 5.70%. Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70%. IR (KBr-disk): 3200—3300 (OH), 1020 (C–O) cm^{-1}.

1-Butadiynylnaphthalene (XIV). *The Preparation*

6) V. Grignard and H. Perrichon, *Ann. Chim. et Phys.*, **5**, 5 (1926).

7) This is a mixture of meso- and rac-isomers of X. *Cf.* I. Iwai and T. Konotsune, *Yakugaku Zasshi*, **78**, 505 (1958).

of the Dichloride (XIII). To an ice-cooled mixture of the glycol (XII, 4.24 g, 0.02 mol), pyridine (4.80 g, 0.06 mol), and tetrahydrofuran (50 m*l*), we added, drop by drop, a solution of thionyl chloride (7.20 g, 0.06 mol) in tetrahydrofuran (10 m*l*) over a period of 30 min. The temperature of the reaction mixture was gradually raised to 40°C in 60 min. After stirring for 30 min at that temperature, crushed ice was added to the ice-cooled reaction mixture. The reaction product was extracted with ether. The extract was washed with water, and aqueous sodium hydrogen carbonate successively, and then dried (magnesium sulfate). The crude dichloride (XIII) obtained by evaporating the solvent *in vacuo* was subjected to the following dehydrochlorination without further purification.

The Dehydrochlorination of XIII. A solution of the above-mentioned crude dichloride (XIII) in tetrahydrofuran (10 m*l*) was added, over a 5-min period to a suspension of sodium amide [from sodium 3.5 g, 0.152 g atom] in liquid ammonia (150 m*l*) at −70°C. The mixture was stirred for 1.5 hr, and then the ammonia was allowed to evaporate after the addition of ammonium chloride (9.0 g). The organic solvent was removed under reduced pressure. The residue was extracted with petroleum ether (400 m*l*). The concentrated extract (*ca.* 150 m*l*) was passed through a short column of alumina (5 g). The light yellow filtrate was concentrated under reduced pressure to yield crude XIV as yellow leaflets; 1.39 g (40%); mp *ca.* 40°C. The crude XIV was dissolved in petroleum ether and passed through a thin-layer of alumina (4 g). The filtrate was chilled in a dry ice-ethanol-bath to yield analytically pure XIV as pale yellow leaflets; mp 44—45°C. XIV gave orange yellow cuprous and pale yellow silver acetylide. XIV was found to be a fairly unstable substance. The crystals rapidly changed to an insoluble brown substance.

Found: C, 95.11; H, 4.55%. Calcd for $C_{14}H_8$: C, 95.42; H, 4.58%. IR (Nujol): 3270 (≡CH), 2190, 2205 (C≡C) cm^{-1}.

1,1′-Dinaphthyltetraacetylene (I_4). Cupric acetate monohydrate (4.0 g) was added to a solution of the diacetylene (XIV, 0.50 g, 2.8 mmol) in pyridine (20 m*l*), after which the mixture was stirred for 1 hr at 45°C.[8] The stirring was continued overnight at room temperature. The reaction mixture was then chilled in an ice-bath, and the insoluble material was collected by filtration, and washed successively with a small amount of methanol and with water, thus affording crude I_4 as fine greenish-yellow needles; 0.37 g (77%); mp *ca.* 200°C (dec.). A second crop of I_4 (0.07 g) was obtained from the filtrate. A benzene solution of the crude I_4 was passed through a short column of alumina. The crystals obtained by concentrating the filtrate were recrystallized twice from acetone to yield pure I_4 as yellow needles; mp 205—206°C (dec.).

Found: C, 95.70; H, 4.04%. Calcd for $C_{28}H_{14}$: C, 95.97; H, 4.03%.

1-Ethynylnaphthalene (XVI). Phosphorus pentachloride (168 g, 0.81 mol) was added to a solution of 1-acetylnaphthalene (134 g, 0.79 mol) in dry benzene (250 m*l*). After the vigorous reaction had subsided, the mixture was gradually heated and refluxed for 1.5 hr. The reaction mixture was poured onto ice water, and the organic layer was separated. The aqueous layer was extracted with benzene. The combined benzene layer was washed successively with water and with aqueous sodium hydroxide, and then dried (sodium sulfate). After the solvent had been removed under reduced pressure, the residue was distilled *in vacuo* to yield 1-(α-chlorovinyl)-naphthalene; 141.3 g (95%); bp 113—114°C/3 mmHg.

Found: C, 76.33; H, 4.79; Cl, 19.02%. Calcd for $C_{12}H_9Cl$: C, 76.40; H, 4.81; Cl, 18.79%.

The chloride thus obtained (75.5 g, 0.40 mol) was dissolved in ether (100 m*l*), and the solution was added, drop by drop, to a suspension of sodium amide [from sodium 33 g, 1.44 g atom] in liquid ammonia (1.2 *l*) at −70°C over a period of 1 hr. After stirring for a further 2.5 hr, the ammonia was allowed to evaporate. Petroleum benzine (350 m*l*) and then a saturated solution of ammonium chloride were added to the residue at −40°C. The organic layer was separated, and the aqueous layer was extracted with the same solvent. The combined benzine solution was dried (sodium sulfate), and the solvent was removed under reduced pressure. The residue was distilled *in vacuo* to yield XVI; 56.3 g (92%); bp 76—77°C/0.1 mmHg [lit. values: bp 143°C/25 mmHg;[9] bp 45°C/0.25 mmHg;[10] bp 92°C/4 mmHg[11]].

Found: C, 94.78; H, 5.30%. Calcd for $C_{12}H_9$: C, 94.70; H, 5.30%.

3-(1-Naphthyl)-prop-2-ynal (XVII). Into an ice-cooled solution of ethylmagnesium bromide [from magnesium (10.8 g, 0.44 g atom) and ethyl bromide (57.8 g, 0.53 mol)] in tetrahydrofuran (300 m*l*), there was added, drop by drop, a solution of XVI (56 g, 0.37 mol) in tetrahydrofuran (100 m*l*) under stirring, the mixture was then refluxed for 1 hr. *N,N*-Dimethylformamide (84 m*l*) in the same solvent (100 m*l*) was added in one portion to the mixture chilled in an ice-salt-bath. After 30 min stirring, the cooling bath was removed and the stirring was continued for a further 2 hr at 30°C. The reaction mixture was then mixed with 5% sulfuric acid (2 *l*) under vigorous agitation, after which the stirring was continued overnight. The mixture was then extracted with benzene. The extract was washed with water and aqueous alkali, and dried. The viscous liquid obtained by evaporating the solvent under reduced pressure was mixed with cyclohexane - ether (2 : 1). The solution was then cooled, yielding crude XVII, 35 g (52%). This was recrystallized twice from the same solvent to afford pure XVII; mp 20.5—21.5°C; colorless needles.

Found: C, 86.22; H, 4.37%. Calcd for $C_{13}H_8O$: C, 86.65; H, 4.48%. [lit. value: bp 85—86°C/0.5 mmHg[10]].

1-(1-Naphthyl)-1,4-pentadiyne-3-ol (XVIII). A solution of the aldehyde (XVII, 4.68 g, 0.026 mol) in tetrahydrofuran (30 m*l*) was added to a stirred and ice-cooled solution of ethynylmagnesium bromide[12] [from magnesium (1.37 g, 0.057 g atom) and ethyl

8) G. Eglinton and A. R. Galbraith, *J. Chem. Soc.*, **1959**, 889.

9) R. E. Atkinson, R. E. Curtis, D. M. Jones and J. A. Taylor, *Chem. Commun.*, **1967**, 718.

10) Idem., *J. Chem. Soc., C.*, **1969**, 2173.

11) D. Bertin, *Ann. Chim. (Paris)*, **8**, 296 (1953).

12) E. R. H. Jones, L. L. Skattebøl and M. C. Whiting, *J. Chem. Soc.*, **1956**, 4765; "*Org. Synth.*" Vol. 39, p. 56 (1959).

bromide (6.6 g, 0.06 mol)] in tetrahydrofuran (100 ml), after which the mixture was stirred for a further hour at the same temperature. Then the cooling-bath was removed and the mixture was stirred overnight at room temperature. The ice-cooled reaction mixture was then treated with a saturated aqueous solution of ammonium chloride and extracted with benzene. The extract was dried (magnesium sulfate), and the solvent was removed *in vacuo*, resulting in crude crystals. A benzene solution of the crude material was percolated through a short column of alumina (10 g). The filtrate was concentrated under reduced pressure, and the residue was treated with charcoal in methanol. Recrystallization from benzene - petroleum ether (1 : 3) gave XVIII; 3 g (56%). An analytical specimen was obtained by recrystallizing the crystals 3 times from the same solvent; mp 86—87°C.

Found: C, 87.09; H, 4.85%. Calcd for $C_{15}H_{10}O$: C, 87.35; H, 4.89%. IR (KBr-disk): 3280 (≡CH), 2100 2220 (C≡C), 1015 (C–O) cm^{-1}.

1,10-Di(1-naphthyl)-1,4,6,9-decatetrayne-3,8-diol (XIX). A solution of the diyne-ol (XVIII, 1.03 g, 0.005 mol) in methanol (15 ml) was mixed with cuprous chloride (0.1 g, 0.001 mol) and ammonium chloride (0.075 g, 0.0014 mol); then one drop of concentrated hydrochloric acid was added. The mixture was vigorously stirred at 32°C in an atmosphere of oxygen under a slightly elevated pressure until the uptake of oxygen ceased (4 hr). The inorganic material was removed by filtration, and the filtrate was concentrated under reduced pressure. The residue was mixed with ether and treated with 2N hydrochloric acid. The organic layer was washed successively with water, aqueous sodium hydrogen carbonate, and water, and then dried (magnesium sulfate). The crude crystals obtained by evaporating the solvent under reduced pressure were recrystallized from benzene, resulting in XIX; 0.80 g (80%). This was recrystallized 3 times from the same solvent to yield pure XIX; mp 165°C (dec.).

Found: C, 87.34; H, 4.42%. Calcd for $C_{30}H_{18}O_2$: C, 87.78; H, 4.42%. IR (KBr-disk): 3100—3300 (≡CH, OH), 2220 (C≡C), 1005 (C–O) cm^{-1}.

1,1′-Dinaphthylpentaacetylene (I_5). *The Preparation of the Dichloride (XX).* To a cooled (ice-salt-bath) mixture of the tetraacetylene glycol (XIX, 0.62 g, 0.0015 mol), pyridine (0.36 g, 0.0045 mol), and tetrahydrofuran (10 ml), there was added, over a period of 20 min, a solution of thionyl chloride (0.54 g, 0.0045 mol) in tetrahydrofuran (10 ml). After stirring for an additional hour at the same temperature, crushed ice was added to the reaction mixture. The organic layer was washed successively with water and with aqueous sodium carbonate, and then dried. The organic layer was concentrated *in vacuo* to *ca.* 10 ml. The solution of XX thus obtained was used immediately for the following reaction.

The Dehydrochlorination of XX. The above-mentioned solution of XX was added, drop by drop and over a 5-min period, into a suspension of sodium amide [from sodium 0.20 g (0.0087 g atom)] in liquid ammonia (30 ml) at −70°C. After stirring for 1 hr at that temperature, ammonium chloride (1.0 g) was added to the reaction mixture; then the ammonia was allowed to evaporate. The residue was repeatedly digested with petroleum benzine. The crude crystals obtained by removing the solvent under reduced pressure were dissolved in benzene. The benzene solution was passed twice through a thin-layer of alumina (each 6 g). The filtrate was then concentrated, yielding I_5 as orange yellow crystals; 114 mg (20% based on XIX). This was recrystallized twice from benzene to give pure I_5; mp *ca.* 195°C (dec.).

Found: C, 96.14; H, 3.81%. Calcd for $C_{30}H_{14}$: C, 96.23; H, 3.77%.

1-(1-Naphthyl)-1,4-hexadiyne-3,6-diol (XXI). Propargyl alcohol (11.20 g, 0.2 mol) in tetrahydrofuran (30 ml) was added, over a period of 30 min, into a stirred solution of ethylmagnesium bromide [from magnesium (9.60 g, 0.40 g atom) and ethyl bromide (43.9 g, 0.40 mol)] in tetrahydrofuran (150 ml) at a temperature lower than 30°C. The mixture was refluxed for 1 hr, and then greatly cooled in an ice-salt-bath. A solution of the aldehyde (XVII, 18 g, 0.1 mol) in tetrahydrofuran (80 ml) was then added, drop by drop, to the cooled mixture. The cooling bath was removed, and the reaction mixture was stirred overnight. A saturated aqueous solution of ammonium chloride was added to the ice-cooled reaction mixture. The organic layer was separated, and the aqueous layer was repeatedly extracted with benzene. The combined organic layer was dried (magnesium sulfate). The crystals obtained by evaporating the solvent *in vacuo* were recrystallized from benzene to yield XXI; 15.6 g (66%). The crude material was recrystallized 3 times from benzene, thus affording pure XXI; mp 113—114°C.

Found: C, 80.93; H, 5.14%. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12.% IR (KBr-disk): 3100—3400 (OH), 2220 (C≡C), 1025 (C–O) cm^{-1}.

1,1′-Dinaphthylhexaacetylene (I_6). *The Preparation of the Dichloride (XXII).* A solution of thionyl chloride (3.1 g, 0.026 mol) in tetrahydrofuran (10 ml) was added, drop by drop and over a 30-min period, into a cooled (in an ice-salt-bath) and stirred mixture of the diacetylenic glycol (XXI, 2.04 g, 0.0086 mol), pyridine (2.06 g, 0.026 mol), and tetrahydrofuran (25 ml). The temperature of the reaction mixture was gradually raised to room temperature, and then the mixture was stirred at 40°C for 30 min. Cracked ice was added to the ice-cooled reaction mixture, and the product was extracted with benzene. The extract was washed successively with water and with aqueous sodium hydrogen carbonate, and then dried (magnesium sulfate). The extract was concentrated to *ca.* 10 ml under reduced pressure and immediately subjected to the following reaction.

The Preparation of 1-Naphthyltriacetylene (XXIII). To a suspension of sodium amide [from sodium 1.2 g (0.052 g atom)] in liquid ammonia (50 ml), there was added the above-mentioned solution of XXII over a period of 5 min at −70°C. After the mixture had been stirred for 1.5 hr at the same temperature, ammonium chloride (3.6 g) and petroleum benzine (120 ml) were added and the ammonia was allowed to evaporate. The organic layer was then separated, and the residue was digested with petroleum benzine. The orange-yellow organic layer was concentrated to *ca.* 200 ml under reduced pressure and passed through a short column of alumina (3.5 g), thus yielding a colorless filtrate. As the triacetylene was found to be a fairly unstable substance, the colorless filtrate was used in the subsequent reaction without isolation. UV (measured with an uncertain concentration in petroleum benzine): λ_{max} 350, 329, 308 and 296 mμ.

The Oxidation Coupling of XXIII. To a stirred solution of cupric acetate monohydrate (3.0 g) in pyridine (15 m*l*), there was added a 30 m*l* portion of the above-mentioned solution of the triacetylene (XXIII), and then the petroleum benzine was removed under reduced pressure at room temperature; the second portion (30 m*l*) of the solution was then added, and the benzine was removed again *in vacuo*. The entire benzine solution was added, portion by portion to the oxidizing reagent, repeating the above procedure. After the addition of the solution and the removal of the benzine had been completed, the mixture was stirred for 1.5 hr at 40°C. The reaction mixture was greatly chilled in an ice-salt-bath, and the precipitated solid was collected by filtration and washed with a small amount of cold pyridine. The brown crystals which were obtained by washing the solid thoroughly with water were dissolved in benzene and percolated through a short column of alumina (8 g). The filtrate was concentrated *in vacuo*, thus yielding orange crystals; 118 mg (14% based on XXI). They were recrystallized from benzene to give pure I_6; mp 175°C (dec.).

Found: C, 96.15; H, 3.54%. Calcd for $C_{32}H_{14}$: C, 96.46; H, 3.54%.

2,2′-Naphthil (IV′). The compound IV′ was prepared according to the method used in the case of the 1,1′-isomer (IV).

2,2′-Naphthil Dihydrazone (V′). The method used in the preparation of the 1,1′-isomer (V) was applied successfully in this case. mp 187—188°C. Yield, 83%.

Found: C, 77.86; H, 5.46; N, 16.51%. Calcd for $C_{22}H_{18}N_4$: C, 78.08; H, 5.36; N, 16.56%.

2,2′-Dinaphthylacetylene (II_1). Exactly the same procedure used in the preparation of I_1 was followed, yielding 0.95 g (77%) of crude light yellow II_1. This crude material was recrystallized successively from benzene - ethanol and from benzene, thus yielding pure II_1; colorless needles; mp 228—229°C. [lit. value: mp 225°C[13]].

Found: C, 94.55; H, 5.30%. Calcd for $C_{22}H_{14}$: C, 94.93; H, 5.37%.

1,4-Di(2-naphthyl)-1,4-dihydroxy-2-butyne (VII′). 2-Naphthaldehyde (VI′, 6.20 g, 0.04 mol) gave 5.3 g (85%) of slightly crude VII′ when treated by the method described in the case of the 1-naphthyl isomer. The crude material was recrystallized 3 times from benzene-ethanol to give pure VII′ as fine colorless crystals; mp 159—160°C.

Found: C, 85.33; H, 5.41%. Calcd for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36%. IR (KBr-disk): 3100—3400 (OH), 1000 (C–O) cm^{-1}.

2,2′-Dinaphthyldiacetylene (II_2). The acetylene glycol (VII′, 1.0 g, 3 mmol) was treated according to the procedure used in the case of VII, thus yielding crude II_2; 297 mg (33%). A benzene solution of the crude material was passed through a thin-layer of alumina. The crystals obtained from the filtrate were recrystallized twice from benzene, thus affording pure II_2 as colorless fine leaflets; mp 202—203°C.

Found: C, 95.44; H, 4.75%. Calcd for $C_{24}H_{14}$: C, 95.33; H, 4.67%.

1-(2-Naphthyl)-2-propyn-1-ol (IX′). 2-Naphthaldehyde (VI′, 12.5 g, 0.08 mol) was treated with lithium acetylide in liquid ammonia according to the procedure described in the case of IX; this afforded slightly impure IX′; 7.7 g (52%); mp 58—62°C.

IR (KBr-disk): 3300—3400 (OH), 3290 (≡CH), 2110 (C≡C), 1015 (C–O) cm^{-1}.

1,6-Di(2-naphthyl)-1,6-dihydroxy-2,4-hexadiyne (X′). A mixture of the ethynyl carbinol (IX′, 4.6 g, 0.025 mol), cuprous chloride (0.5 g, 0.005 mol), ammonium chloride (0.375 g, 0.007 mol), and methanol (75 m*l*) containing 3 drops of concentrated hydrochloric acid was vigorously stirred at room temperature under an oxygen atmosphere at a slightly elevated pressure for 9 hr. An inorganic material was then removed by filtration and washed with a small amount of methanol. The combined filtrate and washings were concentrated *in vacuo*. The residue was dissolved in ether containing a small amount of tetrahydrofuran and treated with 2N hydrochloric acid to remove the inorganic material. The organic layer was washed with water and dried. The crystals, 4.1 g (90%) obtained by evaporating the solvent under reduced pressure were recrystallized 3 times from benzene - methanol to afford pure X′ as colorless cubes; mp 170°C (dec.).

Found: C, 86.28; H, 5.20%. Calcd for $C_{26}H_{18}O_2$: C, 86.16; H, 5.01%. IR (KBr-disk): 3200—3400 (OH), 1010 (C–O) cm^{-1}.

2,2′-Dinaphthyltriacetylene (II_3). *The Preparation of the Dichloride (XI′).* Thionyl chloride (1.07 g, 0.009 mol) in tetrahydrofuran (5 m*l*) was added, drop by drop, into a cooled (in an ice-salt-bath) and stirred mixture of the diacetylene glycol (X′, 1.09 g, 0.003 mol), pyridine (0.71 g, 0.009 mol), and tetrahydrofuran (15 m*l*). After 1 hr, the cooling bath was removed, after which the stirring was continued for an additional hour at room temperature. Then the ice-cooled reaction mixture was mixed with cracked ice and extracted with benzene. The extract was washed successively with water and sodium carbonate, and dried. The crude dichloride (XI′, a deep-brown liquid) obtained by evaporating the solvent *in vacuo* was immediately subjected to the following reaction without purification.

The Dehydrochlorination of XI′. The above-mentioned crude XI′ was treated according to the procedure used in the case of XI, thus affording crude II_3; 246 mg (25% based on X′). The crude material was recrystallized 4 times from acetone to give pure II_3; pale yellow needles; mp 173—174°C.

Found: C, 95.40; H, 4.42%. Calcd for $C_{26}H_{14}$: C, 95.68; H, 4.32%.

1-(2-Naphthyl)-2-butyne-1,4-diol (XII′). The procedure used in the synthesis of XII was employed. 2-Naphthaldehyde (VI′, 10 g, 0.064 mol) gave 9.7 g (71%) of XII′. Three recrystallizations of the crystals from benzene gave pure XII′ as colorless leaflets; mp 74—75°C.

Found: C, 78.91; H, 5.68%. Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70%. IR (KBr-disk): 3100—3300 (OH), 1005 (C–O) cm^{-1}.

2-Butadiynylnaphthalene (XIV′). The acetylene glycol (XII′, 8.0 g, 0.038 mol) gave 2.4 g (36%) of XIV′ according to the method used in the preparation of the 1-isomer (XIV). This was recrystallized from petroleum ether to give pure XIV′ as colorless needles; mp 58—60°C (dec.).

Found: C, 95.20; H, 4.70%. Calcd for $C_{14}H_8$: C, 95.42; H, 4.58%. IR (KBr-disk): 3270 (≡CH), 2200 (C≡C) cm^{-1}.

13) J. Grabowsky, *Ber.*, **11**, 298 (1878).

2,2'-Dinaphthyltetraacetylene (II_4). The oxidative coupling of 2-butadiynylnaphthalene (XIV', 1.3 g, 7.4 mmol) according to the method used for the 1-isomer (I_4) afforded crude II_4; 680 mg (53%). The crude material was recrystallized twice from acetone - benzene to yield pure II_4 as fine pale yellow crystals; mp 172°C (dec.).

Found: C, 95.90; H, 4.07%. Calcd for $C_{28}H_{14}$: C, 95.97; H, 4.03%.

2-Acetylnaphthalene (XV'). A solution of 2-naphthoic acid chloride (190 g, 1 mol) in benzene (500 m*l*) was added, drop by drop, to a solution of ethoxymagnesiomalonate [prepared from magnesium (44.3 g, 1.7 g atom), diethyl malonate (315.4 g, 1.7 mol), dry ethanol (156.4 g, 3.4 mol) and dry benzene (500 m*l*). The excess of the ethanol was removed by azeotropic distillation with benzene] in benzene (500 m*l*) at 20°C, and then the mixture was refluxed for 3.5 hr. Aqueous sulfuric acid (concentrated sulfuric acid 50 m*l*, water 350 m*l*) was added, drop by drop, to the mixture under cooling. The organic layer separated was washed with water and dried (magnesium sulfate). The crude keto-malonate obtained by evaporating the solvent *in vacuo* was mixed with propionic acid (500 m*l*) and concentrated sulfuric acid (5 m*l*), and the mixture was gradually heated. After 2 hr refluxing, 4N sulfuric acid (500 m*l*) was added and the mixture was refluxed for a further 6 hr. The organic layer was separated after the addition of water, and the aqueous layer was extracted with benzene. The combined benzene layer was washed successively with aqueous sodium hydroxide and with water, and then dried. The residue obtained by removing the solvent under reduced pressure was distilled *in vacuo*, thus affording XV'; 128 g (75%); bp 120—123°C/3 mmHg, mp 52—54°C. [lit. value: mp 53°C[14]].

2-Ethynylnaphthalene (XVI'). The methyl ketone (XV', 68 g, 0.4 mol) was converted to XVI' (32 g (52%), mp 40.5—41.5°C) according to the method used in the preparation of XVI.

Found: C, 94.82; H, 5.41%. Calcd for $C_{12}H_8$: C, 94.70; H, 5.30%.

3-(2-Naphthyl)-prop-2-ynal (XVII'). According to the procedure used in the synthesis of XVII, the 2-ethynyl compound (XVI', 30 g, 0.198 mol) gave XVII' (25 g (70%)). Recrystallization from cyclohexane - ether (2 : 1) afforded pure XVII' as colorless leaflets; mp 52—53°C.

Found: C, 86.77; H, 4.50%. Calcd for $C_{13}H_8O$: C, 86.65; H, 4.48%.

1-(2-Naphthyl)-1,4-pentadiyne-3-ol (XVIII'). The procedure used in the case of XVIII was followed. XVII' (9.4 g, 0.052 mol) gave XVIII' (7.0 g (65%)). This was then recrystallized from cyclohexane - benzene (1 : 1) to give pure XVIII'; mp 91—92°C.

Found: C, 87.25; H, 4.93%. Calcd for $C_{15}H_{10}O$: C, 87.35; H, 4.89%. IR (KBr-disk): 3290 (≡CH), 2110, 2230 (C≡C), 1000—1040 (C–O) cm^{-1}.

1,10-Di(2-naphthyl)-1,4,6,9-decatetrayne-3,8-diol (XIX'). The oxidative coupling used in the synthesis of XIX was applied to XVIII' (3.1 g, 0.015 mol), thus yielding XIX', 1.4 g (45%). An analytical specimen was obtained by recrystallizing the crystals 3 times from benzene; fine needles; mp 150°C (dec.).

Found: C, 87.91; H, 4.60%. Calcd for $C_{30}H_{18}O_2$: C, 87.78; H, 4.42%. IR (KBr-disk): 3200—3300 (OH), 2220 (C≡C), 1000—1030 (C–O) cm^{-1}.

2,2'-Dinaphthylpentaacetylene (II_5). The same reaction sequence under the same reaction conditions as were used in the synthesis of I_5 from XIX were employed. The tetraacetylene glycol (XIX', 0.5 g, 1.2 mmol) gave 110 mg of II_5 (22% based on XIX'). Pure II_5, mp 180°C (dec.). Yellow needles were obtained by recrystallizing the crystals twice from benzene.

Found: C, 96.27; H, 3.82%. Calcd for $C_{30}H_{14}$: C, 96.23; H, 3.77%.

1-(2-Naphthyl)-1,4-hexadiyne-3,6-diol (XXI'). The reaction of the Grignard derivative of propargyl alcohol with the aldehyde (XVII', 8.0 g, 0.044 mol) according to the method used in the preparation of XXI afforded XXI'; 6.0 g (58%). This was recrystallized from benzene - ethanol to yield pure XXI'; mp 126—127°C; fine needles.

Found: C, 81.45; H, 5.15%. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12%. IR (KBr-disk): 3200—3400 (OH, ≡CH), 2200 (C–C), 1010—1035 (C≡O) cm^{-1}.

2,2'-Dinaphthylhexaacetylene (II_6). *The Preparation of 1-(2-Naphthyl)-1,3,5-hexatriyne (XXIII').* According to the procedure described in the case of XXIII, the diacetylenic glycol (XXI', 2.7 g, 0.0113 mol) was converted to the dichloride (XXII') and dehydrochlorinated to yield the triacetylene (XXIII'). Because of the unstable nature of XXIII', the petroleum benzine solution of the crude XXIII' was immediately used in the following reaction. UV (measured with an uncertain concentration in petroleum benzine): λ_{max} 339, 318, 296 and 285 mμ.

The Oxidative Coupling of XXIII'. The oxidative coupling of the above-mentioned crude XXIII' according to the procedure used in the synthesis of I_6 gave 120 mg of II_6 (11% based on XXI'). This was recrystallized 3 times from benzene to give pure II_6 as orange yellow needles; mp 200°C (dec.).

Found: C, 96.25; H, 3.51%. Calcd for $C_{32}H_{14}$: C, 95.46; H, 3.54%.

14) T. Immediata and A. R. Day, *J. Org. Chem.*, **5**, 516 (1940).