Dehydroannulenes. VII. Synthesis of 3,7,10,14-Tetrasubstituted 1,8-Bisdehydro[14]annulenes

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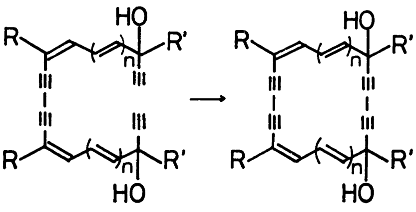
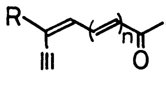
It was found that dienyne ketones such as 2,2-dimethyl-7-*t*-butyl-4,6-nonadien-8-yn-3-one, 2,2-dimethyl-7-phenyl-4,6-nonadien-8-yn-3-one and 1,5-diphenyl-2,4-heptadien-6-yn-1-one give the corresponding tetrasubstituted 14-membered cyclic glycols on treatment with a suspension of potassium hydroxide in liquid ammonia. Reactions of the cyclic glycols with tin(II) chloride in organic solvent saturated with hydrogen chloride afforded strongly diatropic tetrasubstituted bisdehydro[14]annulenes.

Oxidative coupling of polyentetrayne glycols (**1** or **2**) with copper(II) acetate in pyridine–methanol–ether in high dilution[1] yielded the corresponding 18-membered (**3**) or 22-membered cyclic glycols (**4**), precursors of tetrakisdehydro[18]-[2] and [22] annulenes,[3] in unexpectedly high yields. This seems to be a reflection of the favorable configuration of the acyclic glycols (**1** and **2**) on intramolecular oxidative coupling, suggesting the possibility of cyclic dimerization of polyenyne ketones (**5**) to give cyclic polyendiyne glycols under suitable conditions. The cyclic glycols may be transformed into bisdehydro[4n+2]annulenes by the reductive dehydroxylation reaction adopted in the conversion of the cyclic tetrayne glycols (**3** and **4**) into tetrakisdehydro[18]- and [22]annulenes.[2,3]



1: n=1 **3**: n=1
2: n=2 **4**: n=2



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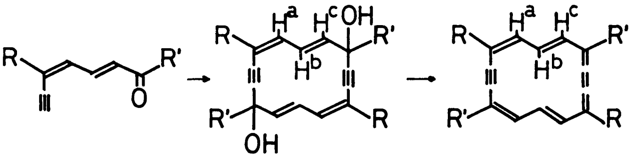
In this paper we wish to report on the cyclic dimerization of dieyne ketones (**6**) to 14-memberd cyclic glycols (**7**) and their transformation into 3,7,10,14-tetrasubstituted 1,8-bisdehydro[14]annulenes (**8**).[4] The parent compound 1,8-bisdehydro[14]annulene (**8d**) was obtained by Sondheimer and his co-workers by prototropic rearrangement accompanied by an unexpected dehydrogenation by atmospheric oxygen in the course of synthesis of monodehydro[14]annulene.[5] The present studies have opened an efficient route to the synthesis of 1,8-bisdehydro[14]annulenes.

Synthesis. Ethynylation of carbonyl compounds with acetylene or monosubstituted acetylenes in organic solvent in the presence of alkali hydroxide, carbonate or alcoholate is well-known (Favorskii method).[6] Formation of a trace of the cyclic glycol (**7c**) could be recognized on treatment of the diphenyldienyne ketone (**6c**) with potassium hydroxide in tetrahydrofuran or pyridine. No indication of the formation of **7c** could be obtained with alkali amide in liquid ammonia, sodium hydroxide in tetrahydrofuran or pyridine, potassium hydroxide in *N,N*-dimethylformamide or in ether, or sodium hydroxide and calcium carbide in tetrahydrofuran. It was found that slow addition of a solution of **6** in tetrahydrofuran to a stirred suspension of finely powdered potassium hydroxide in liquid ammonia caused the cyclic dimerization of **6** to give a diastereomeric mixture of the desired cyclic glycol (**7**) in a high yield. In the case di-*t*-butyl ethynyl ketone (**6a**), an amorphous solid with an unidentified structure was obtained in addition to the desired cyclic glycol (**7a**).



6 **7** **8**

a: R=R'=*t*-Bu: b: R=Ph, R'=*t*-Bu;
c: R=R'=Ph ; d: R=R'=H

The cyclic glycols (**7a**—**c**) in an organic solvent were mixed with tin(II) chloride in ether saturated with hydrogen chloride. The resulting deeply colored

Table 1. Yields and melting points of **7** and **8** and color of crystals of **8**

	Glycol			Annulene		
	Yield (%)	Mp (°C)		Yield (%)	Color	Mp (°C)
7a	19	230.9—232.4 (dec)	**8a**	64	red	298.0—229.0 (dec)
	50	220.0—222.2 (dec)	**8b**	83	brown violet	284.0—284.5 (dec)
7b	96	241.0—243.0 (dec)	**8c**	83	deep violet	>300 (dec)
7c	93	236.0—237.0 (dec)				

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TABLE 2. 60 MHz ^{1}H NMR PARAMETERS OF BISDEHYDRO[14]ANNULENES (**8**) (τ-VALUES)

	8a	**8b**	**8c**	**8d**
Outer protons	H^a, H^c 0.58 d J=13.5	H^a 0.12 d J=13.5 H^c 0.47 d J=13.5	H^a, H^c 0.06 d J=13.5	H^a, H^c 0.45 dd J=13.3, 8 R,R′ 1.57 d J=13.3
o-Protons of phenyl		1.2—1.5 m	1.1—1.5 m	
m,p-Protons of phenyl		2.2—2.8 m	2.1—2.6 m	
Protons of *t*-butyl	8.10 s	8.02 s		
Inner protons	14.39 t J=13.5	13.42 t J=13.5	12.56 t J=13.5	15.54 t J=13.3
Solvent	THF-d_8	THF-d_8	THF-d_8	$CDCl_3$

reaction mixtures were worked up in the usual way to give the tetrasubstituted 1,8-bisdehydro[14]annulenes (**8a**—**c**). The yields and melting points of cyclic glycols (**7a**—**c**) and annulenes (**8a**—**c**) together with the color of crystals of the annulenes are given in Table 1.

Properties. The tetrasubstituted 1,8-bisdehydro-[14]annulenes (**8a**—**c**) were found to be quite stable, no decomposition being observed in the air at room temperature under diffused daylight for a long time. The ^{1}H NMR spectra of **8a**—**c** indicate that they sustain fairly strong diamagnetic ring current as evidenced by low-field and high-field signals of the outer and inner protons, respectively. The ^{1}H NMR parameters are summarized in Table 2 together with those of the parent compound (**8d**).[5] As a representative example, the ^{1}H spectrum of the tetra-*t*-butyl derivative (**8a**) is shown in Fig. 1. The di-*t*-butyl-diphenyl derivative (**8b**) exhibits two outer proton signals as doublets at τ 0.12 and 0.47. The lower field signal (τ 0.12) could be assigned H^a which undergoes the deshielding effect of the ring current both of the annulene ring and the phenyl groups. The multiplets observed at τ 1.1—1.5 and 2.2—2.8 in the spectra of **8a** and **8c** could be assigned to *o*- and *m,p*-protons of the phenyl groups, since the protons of the phenyl groups are disposed in the deshielding region of diamagnetic ring current of the annulene ring, and lower field shift of the *o*-protons can be attributed to their proximate position to the 14-membered ring. The most remarkable feature of ^{1}H NMR spectra is the marked low-field shift of signals of inner protons in the tetrasubstituted derivatives (**8a**—**c**) as compared with that of the parent compound (**8d**). A slight low-field shift of the outer protons of phenyl substituted derivatives (**8b, c**) was also observed.

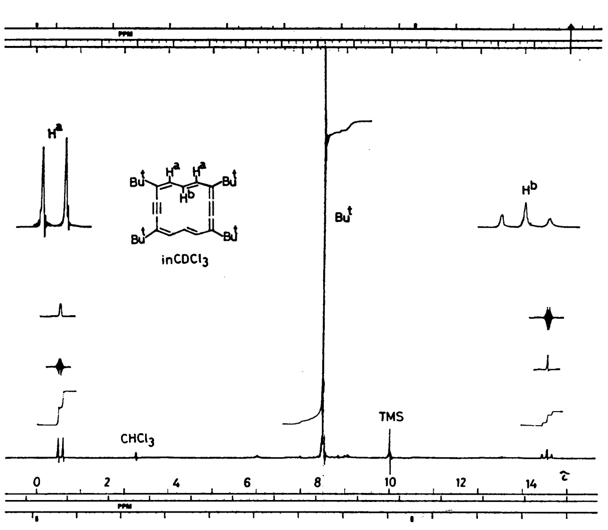
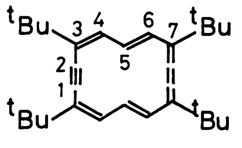
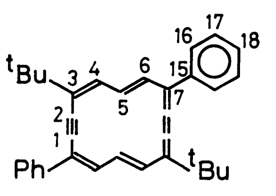


Fig. 1. 100 MHz ^{1}H NMR spectrum of tetra-*t*-butyl-bisdehydro[14]annulene (**8a**) in $CDCl_3$.



8a



8b

TABLE 3. ^{13}C NMR PARAMETERS OF **8a** AND **8b** IN $CDCl_3$ (ppm FROM TMS)

8a		**8b**	
t-Bu	32.2(CH_3), 37.8(C)	*t*-Bu	32.3(CH_3), 37.8(C)
C^1,C^2	116.7	C^1,C^2	114.7, 115.7
C^3	131.3	C^3,C^7,C^{15}	119.8, 113.7, 139.9
C^4	130.4	C^4,C^6	130.3, 130.7
C^5	129.0	C^5	132.3
		C^{16},C^{17}	128.0, 128.7
		C^{18}	127.3

Carbon-13 NMR spectral parameters of **8a** and **8b** are given in Table 3. The spectrum of **8c** could not be obtained owing to the poor solubility in NMR solvents. Assignment was made on the basis of chemical shift, off resonance technique and the magnitude of NOE. However, the signals of tertiary carbon atoms (C^3, C^7 and C^{15}) and *o,m*-carbons of phenyl groups (C^{16} and C^{17}) could not be discriminated. The sp-hybridized carbon atoms in symmetrical **8a** exhibits only one signal at an intermediate region of acetylene[7,8] and cumulene[8] carbon atoms, suggesting strongly the identity of acetylenic and cumulenic linkages incorporated in aromatic $[4n+2]\pi$-electron system.[2g,h] On the other hand, two signals were observed in the corresponding region in the spectrum of **8b**. This seems to be ascribable to the difference in electron density between C^1 and C^2 caused by the different inductive effect of *t*-butyl and phenyl groups.

TABLE 4. ELECTRONIC SPECTRA OF **8a**—**c** IN THF
λ_{max} IN nm (ε)[a)]

8a	228.5(6670), 301 sh(28100), 329(272000), 432 sh (11900), 452(24600) 500 sh(150), 525(100), 548 (210), 567 sh(240), 590(920)
8b	226 sh(12300), 234(14300), 260(13400), 272 sh (10800), 315 sh(27900), 332 sh(41100), 345 sh (76300), 354(195000), 508(50), 571(570), 623(1640)
8c	224 sh(13400), 246(26000), 268(23200), 274.5 (24700), 282.5(24400), 326(18100), 343(30900), 372 sh(68100), 388(289000), 521(26300), 549(53200), 600 sh(830), 658(2520)

a) The absorption curves were given in a preliminary report.[4)]

The electronic spectra of the tetrasubstituted 1,8-bisdehydro[14]annulenes (**8a**—**c**) consist of three main absorption bands characteristic of aromatic [4*n*+2]-annulenes. The numerical data are given in Table 4. Increase in the number of phenyl substitution causes a progressive bathochromic shift of the main three absorption bands and appreciable intensification of the medium and the longest wavelength bands indicating electronic perturbation of phenyl groups on the annulene ring. The same trend has been observed in the electronic spectra of tetrakisdehydro[18]-[2e)] and [22]annulenes.[3)]

Tetra-*t*-butyl- (**8a**) and di-*t*-butyl-diphenyl derivatives (**8b**) formed 1:1 CT complexes with 2,4,7-trinitrofluorenone. On the other hand, the tetraphenyl analogue (**8c**) gave CT complex with 2 moles of the nitro compound.

Experimental

All melting points are uncorrected. The IR spectra were measured with a Hitachi EPI-2 or EPI-3G spectrophotometer, the weak, medium and strong absorptions being indicated by w, m and s, respectively. The electronic spectra obtained on a Hitachi EP-3T spectrophotometer were recorded in nm. The ε-values are given in parentheses, the shoulder being denoted by sh. The mass spetra were measured with a Hitachi RM-50 spectrometer (ionization potential 70 eV). The ^{1}H NMR spectra were obtained on a Varian T-60 or a Varian XL-100 spectrometer, and are recorded in τ-values with respect to TMS as an internal standard. The coupling constants (J) are given in Hz. The ^{13}C NMR spectra were measured with an XL-100 spectrometer operated at 25.2 MHz using pulse FT technique with a deuterium internal lock, and given in ppm from TMS as an internal standard. Silica gel (Merck, Kiesel Gel 60) or alumina (Merck, Act. II—III) was used for column chromatography, unless otherwise stated.

*1,4,8,11-Tetra-*t*-butyl-4,6,11,13-cyclotetradecatetraen-2,9-diyn-1,8-diol (7a).* A solution of 2,2-dimethyl-7-*t*-butyl-4,6-nonadine-8-yn-3-one (**6a**, 0.21 g, 0.96 mmol)[2d),e)] in THF (50 ml) was added over a period of 8 h to a stirred suspension of finely powdered potassium hydroxide (1.5 g, 27 mmol) in liquid ammonia (200 ml) at −40—−50 °C. After the mixture had been stirred for 5—6 h at −30—−40 °C, powdered ammonium chloride (3.0 g, 56 mmol) was added at −40 °C, and the ammonia was allowed to evaporate. Water was added to the residue and the mixture was extracted with ether. The ethereal solution, after being washed with water and dried (sodium sulfate), was evaporated under reduced pressure. The residue was chromatographed on silica gel (Wako, 15 g). Elution with hexane–benzene gave colorless crystals, mp 202—205 °C (dec), 65 mg, 31%. The IR, NMR and mass spectral data indicate that the colorless srystals are oligomeric, presumably trimeric, cyclic alcohol. However, no further studies on the structure have been performed. Further elution with benzene and benzene–ether (9:1) yielded a diastereomer of **7a**, colorless crystals, mp 230.9—232.4 °C (dec), 39 mg, 19%; Mass (*m/e*) 436 (M+). Elution with a solvent of increased polarity (benzene–ether) gave another diastereomer of **7c**, colorless crystals, mp 220.0—222.2 °C (dec), 105 mg, 50%; IR(KBr-disk) 3600, 3455 m (OH), 1633 w (C=C), 975 s (*trans* –CH=CH–) cm^{-1}; NMR (CDCl$_3$) 2.34 (dd, 2, J=10.5, 16.0, H^b), 3.67 (d, 2, J=10.5, H^c), 4.06 (d, 2, J=16.0, H^a), 8.45 (s, 2, OH, disappeared on addition of D_2O), 8.85 (s, 18, *t*-butyl adjacent to OH), 8.94 (s, 18, *t*-butyl).

Found: C, 82.75; H, 10.40%; M+ 436. Calcd for $C_{30}H_{44}O_2$: C, 82.51; H, 10.16%; M 436.

*3,7,10,14-Tetra-*t*-butyl-1,8-bisdehydro[14]annulene (**8a**).* A diastereomeric mixture of **7a** (59 mg, 0.14 mmol) in ether (50 ml) was mixed at −60 °C with the same solvent saturated with hydrogen chloride (10 ml) and finely powdered tin(II) chloride dihydrate (200 mg). After being stirred for 15 min, the resulting deep red solution was worked up in the usual way. Red crystals (57 mg) obtained on evaporating the solvent were dissolved in hexane and chromatographed on alumina (20 g) to give pure **8a**, red crystals, mp 298.0—299.0 °C (dec), 36 mg, 64%; IR(KBr-disk) 963 (*trans* –CH=CH–) 2000 (–C≡C–↔=C=C=) cm^{-1}; NMR(CDCl$_3$) 0.65 (d, J=13.5, outer-H), 14.50 (t, J=13.5, inner-H), 8.10 (s, *t*-butyl).

Found: C, 89.49; H, 10.53%; M+ 402. Calcd for $C_{30}H_{42}$: C, 89.42; H, 10.63%; M 402.

The reaction product obtained on treatment of **6a** with potassium hydroxide in liquid ammonia could be converted without purification under similar reaction conditions into **8a** (67%).

*CT Complex of **8a** with 2,4,7-Trinitrofluorenone.* Brown crystals of CT complex of **8a** with 2,4,7-trinitrofluorenone were obtained on admixing a solution of the nitro compound (9 mg, 0.029 mmol) in ethanol (4 ml) with a hot solution of **8a** (9 mg, 0.022 mmol) in cyclohexane (3 ml).

Found: C, 72.19; H, 6.65; N, 5.91%. Calcd for $C_{30}H_{42}\cdot C_{13}H_5N_3O_5$: C, 71.94; H, 6.60; N, 5.85%.

1,8-Di-t-butyl-4,11-diphenyl-4,6,11,13-cyclotetradecatetraen-2,9-diyn-1,8-diol (7b). 2,2-Dimethyl-7-phenyl-4,6-nonadien-8-yn-3-one (**6b**) was prepared by a slight modification of the reported method[2g),h)] (mp 77.5—76.0 °C, 52% based on 3-phenyl-2-penten-4-ynal). A solution of **6b** (0.500 g, 2.22 mmol) in THF (60 ml) was added over a period of 7 h to a stirred suspension of potassium hydroxide (2.0 g) in liquid ammonia (1000 ml) at the boiling point of the solvent. After the mixture had been stirred overnight at the same temperature, finely powdered ammonium chloride (6 g) was added to the reaction mixture at −65 °C, and then the ammonia was allowed to evaporate. Ethereal extract (500 ml) of the residue was evaporated to yield crystalline material. An examination with TLC indicated predominant formatiom of one of the diastereomers. The material was washed successively with hexane–benzene (9:1) and hexane. Colorless fine crystals (0.480 g, 96%), thus obtained, were recrystallized twice from benzene to give pure **7b**, colorless crystals, mp 241—243 °C (dec); IR(KBr-disk) 970 s (*trans* –CH=CH–), 2220 w (–C≡C–), 3440 w, 3560 m (OH) cm^{-1}; NMR (acetone-d_6) 1.96—2.23 (m, 6, H^b and *o*-H of phenyl), 2.49—2.76 (m, 8, H^a and *m, p*-H of phenyl), 3.65 (d, 2, J=15, H^c), 5.23 (s, 2, OH, disapppeared on addition of D_2O), 8.85 (s, 18, *t*-butyl).

Found: C, 85.60; H, 7.58%. Calcd for $C_{34}H_{36}O_2$: C, 85.67; H, 7.61%.

*7,14-Di-*t*-butyl-3,11-diphenyl-1,8-bisdehydro[14]annulene (**8b**).* To a stirred solution of **7b** (0.110 g, 0.23 mmol) in ether (100 ml) kept at −60 °C was added a solution of tin(II) chloride dihydrate (0.40 g) in the same solvent saturated with hydrogen chloride (20 ml). The cooling bath was removed and the reaction mixture was stirred for 20 min. The mixture was worked up in the usual way. Ethereal extract of the product was evaporated under reduced pressure and the crystalline residue was washed thoroughly with hexane to give fairly pure **8b**, reddish brown fine crystals, 85 mg, 83%, which were recrystallized from benzene–ethanol to give an analytical specimen of **8b**, brown violet crystals, mp 284.0—284.5 °C (dec); IR(KBr-disk) 962 (*trans* –CH=CH–), 2020 (–C≡C–↔=C=C=); NMR($CDCl_3$, 60 MHz) 0.12 (d, 2, J=13.5, H^a), 0.53 (d, 2, J=13.5, H^c), 1.2—1.6 (m, 4, *o*-H of phenyl), 2.2—2.7 (m, 6, *m,p*-H of phenyl), 8.07 (s, 18 *t*-butyl), 13.58 (t, 2, J=13.5, H^b); (THF-d_8, 100 MHz) 0.16 (d, 2, J=13, H^a), 0.49 (d, 2, J=13, H^c), 1.39 (m, 4, *o*-H of phenyl), 2.3—2.7 (m, 6, *m,p*-H of phenyl), 8.05 (s, 18, *t*-butyl), 13.45 (*t*, 2, J=13, H^b).

Found: C, 91.96; H, 7.70%. Calcd for $C_{34}H_{34}$: C, 92.26; H, 7.74%.

*CT Complex of **8b** with 2,4,7-Trinitrofluorenone.* A hot solution of 2,4,7-trinitrofluorenone (15.0 mg) in ethanol (6 ml) was mixed with a hot solution of **8b** (15.0 mg) in benzene (2 ml). On cooling the mixture the CT complex was obtained as violet brown crystals.

Found: C, 74.27; H, 5.16; N, 5.57%. Calcd for $C_{34}H_{34}\cdot C_{13}H_5N_3O_7$: C, 74.49; H, 5.19; N,5.54%.

*1,8,4,11-Tetraphenyl-4,6,11,13-cyclotetradecatetraen-2,9-diyn-1,8-diol (**7c**).* A solution of 1,5-diphenyl-2,4-heptadien-6-yn-1-one (**6c**, 396 mg, 1.53 mmol)[2c,d,e)] in THF (25 ml) was added over a period of 17 h to a suspension of potassium hydroxide (1.6 g, 29 mmol) in liquid ammonia (600 ml) at −55—−65 °C. After the mixture had been stirred at −55 °C for 4 h, ammonium chloride (4 g) was added to the reaction mixture, and the ammonia was allowed to evaporate. The residue was digested with ether by decantation. The insoluble material was dissolved in water, and the aqueous solution was extracted with ether. The combined organic layer was worked up in the usual way. Crystalline solid obtained on evaporating the solvent was dissolved in THF and passed through a short column of silica gel (10 g). The filtrate was concentrated under reduced pressure to give pale brown crystals, which were washed with hexane-benzene to give slightly impure **7c** (369 mg, 93%). The material was recrystallized from THF to give colorless crystals, and was found to contain half mole of THF as a solvent of crystallization, mp 236—237 °C (dec); IR(KBr-disk) 974 s (*trans* –CH=CH–), 2210 w (–C≡C–), 3550 w, 3340 broad (OH) cm^{-1}; NMR(THF) 2.23—2.92 (m, 24, H^a, H^b, and phenyl), 3.69 (d, 2, J=15.0, H^c).

Found: C, 85.47; H, 5.72%. Calcd for $C_{38}H_{28}O_2$–1/2 C_4H_8O: C, 85.68; H, 5.75%.

*3,7,10,14-Tetraphenyl-1,8-bisdehydro[14]annulene (**8c**).* Finely powdered tin(II) chloride dihydrate (600 mg) was added under nitrogen atmosphere to a solution of **7c** (45.0 mg, 0.087 mmol) in dimethoxyethane (40 ml) at −60 °C. To the stirred mixture was added ether saturated with hydrogen chloride (4 ml) at −50—−55 °C. After the mixture had been stirred for 10 min at −55—−60°C, the resulting deep purple solution was poured into water and extracted with ethyl acetate. The extract was worked up in the usual way. Deep purple crystals obtained on evaporating the solvent under reduced pressure were washed with hexane–ether (1: 1) to give pure **8c**, deep purple crystals, mp >300 °C (dec.), 35 mg, 83%; IR(KBr-disk) 945 s (*trans* –CH=CH–) cm^{-1}.

Found: C, 94.57; H, 5.43%. Calcd for $C_{38}H_{26}$: C, 94.26; H, 5.45%.

*CT Complex of **8c** with 2,4,7-Trinitrofluorenone.* The bisdehydro[14]annulene (**8c**, 10.0 mg, 0.032 mmol) was dissolved in hot toluene (20 ml), and the solution was mixed with a solution of 2,4,7-trinitrofluorenone (10.0 mg, 0.032 mmol) in ethanol (5 ml) and toluene (5 ml). After addition of ethanol (10 ml), the mixture was kept in a refrigerator to give 1: 2 CT complex as violet crystals.

Found: C, 68.87; H, 3.23; N, 7.59%. Calcd for $C_{38}H_{26}\cdot 2C_{13}H_5N_3O_7$: C, 69.06; H, 3.26; N, 7.55%.

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