Registry No.—1, 66793-10-0; *syn*-10, 66793-11-1; *anti*-10, 66808-40-0; *syn*-11, 66793-12-2; *anti*-11, 66808-41-1; 12, 66788-12-3; 13, 66793-13-3; 14, 66793-14-4; 15, 66793-15-5; 16, 66793-16-6; 17, 66808-42-2; 18, 66793-17-7; 19, 66793-18-8; 20, 66793-19-9; *anti*-20, 66808-43-3; 21, 66808-44-4; 22, 66808-45-5; 23, 66793-20-2; 24, 66793-21-3; 26, 66793-22-4; 27, 66792-72-1; 28, 66793-23-5; 2,6-bis(mercaptomethyl)-4-methoxytoluene, 66793-24-6; 2,6-bis(bromomethyl)-4-methoxytoluene, 14542-73-5.

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(16) Elemental and mass spectral analyses were determined by Dr. R. Wielesek, University of Oregon Microanalytical Laboratories. Melting points are uncorrected and were taken with a Mel-Temp apparatus, visible and ultraviolet spectra were measured with a Cary 15, NMR spectra were measured using deuteriochloroform with tetramethylsilane as an internal standard and were obtained with a Varian HA-100 or XL-100 instrument, and all mass spectra were taken using a CEC Model 21-110 spectrometer at 70 eV.
(17) We thank Dr. F. Häfliger and the Geigy Research Laboratories for a generous gift of 2,6-bis(bromomethyl)-4-methoxytoluene.
(18) At present there is no accepted system of nomenclature for the multilayered cyclophanes. The name given to compounds **24**, **26**, and **1** follow from the system proposed by H. Lehner (*Monatsh. Chem.*, **107**, 565 (1976)). However, Lehner did not provide for the conformational isomerism possible in the triple-layered [2.2]metacyclophane, and so to his system we have added the use of superscripts u and o to designate whether that aromatic ring is under or over the previous ring. This follows the pattern of up–down nomenclature used by Misumi (*Mem. Inst. Sci. Ind. Res., Osaka Univ.*, **33**, 53 (1976).

Chemical Behavior of *cis*-15,16-Dimethyldihydropyrene

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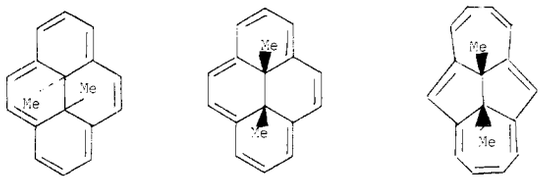
The synthesis of *cis*-15,16-dimethyldihydropyrene derivatives has been reexamined and 2-nitro-*cis*-15,16-dimethyldihydropyrene (**8**) has been prepared both by nitration of *cis*-15,16-dimethyldihydropyrene (**2**) and by independent synthesis. Acetylation of *cis*-15,16-dimethyldihydropyrene gives both the 1- and 2-acetyl derivatives (**10** and **11**) in a ratio of 2:1. In contrast to the trans series, *cis*-15,16-dimethyldihydropyrene (**2**) readily reacts with oxygen to give a nonaromatic diepoxide.

The development of the dithiacyclophane–sulfur extrusion route for the synthesis of *trans*-15,16-dimethyldihydropyrene (**1**) made possible the concomitant synthesis of *cis*-15,16-dimethyldihydropyrene (**2**), albeit in poor yield.[1] For purposes of comparing the chemical properties of the *cis*-



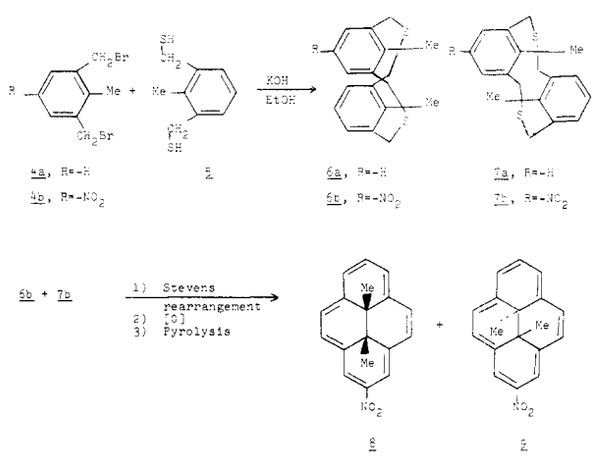
1 2 3

and *trans*-15,16-dimethyldihydropyrenes, as well as making a comparison of the physical and chemical properties of **2** with 1,6:8,13-ethanediylidene[14]annulene (**3**),[2,3] where both types of molecules have the same saucer-shaped geometry but different perimeter contours, we needed additional quantities of *cis*-15,16-dimethyldihydropyrene.

The difficulty in the previous synthesis was the coupling reaction of **4a** and **5** which, although it proceeds in about 75% overall yield, gives the syn and anti isomers of 9,18-dimethyl-2,11-dithia[3.3]metacyclophane (**6a** and **7a**) in a ratio of about 1:7.[1] For the synthesis of **2** only the syn isomer is useful and so the unfavorable syn to anti isomer distribution in the coupling reaction is a severe disadvantage. Subsequently, it was found that substituents present in **4** or **5** affect the ratio of syn to anti isomers formed and the role of substituents in such coupling reactions is discussed in an accompanying paper.[5] On the assumption that the presence of a nitro group, as in **4b**, would improve the syn to anti isomer ratio and that the nitro group could be removed as a final step, we undertook the synthesis of 2-nitro-*cis*-15,16-dimethyldihydropyrene (**8**), as shown in Scheme I.

To obtain the requisite 2,6-bis(bromomethyl)-4-nitrotoluene (**4b**), 2-methylisophthalaldehyde was nitrated and then converted by standard procedures to **4b**. The coupling reaction of **4b** and **5** proceeded in 47% overall yield, giving a mixture whose NMR spectrum showed the ratio of syn to anti isomers (**6b**/**7b**) to be 1:1. Since the Stevens rearrangement

Scheme I



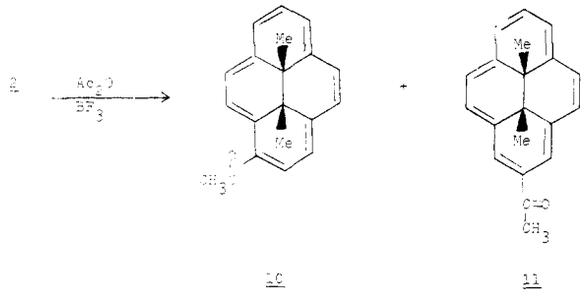
4a, R=H; 4b, R=NO_2 5 6a, R=H; 6b, R=NO_2 7a, R=H; 7b, R=NO_2

6b + 7b 8 9

of *syn*-2,11-dithia[3.3]metacyclophanes gives mixtures of both the syn and anti isomers of the corresponding [2.2]metacyclophanes,[1] separation was not attempted at this stage but, instead, the mixture was carried through the complete sequence of Stevens rearrangement, oxidation of the product to the corresponding disulfoxide, and pyrolysis of this to give the cis and trans isomers of 2-nitro-15,16-dimethyldihydropyrene (**8** and **9**).

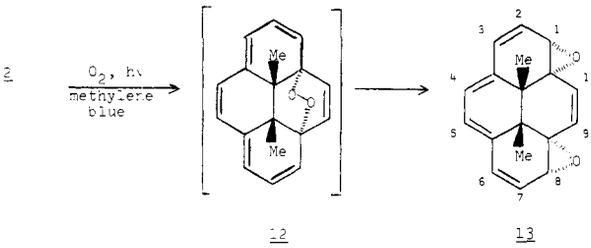
Although **8** and **9** could readily be separated and characterized, they were obtained in exceedingly poor yield and this is not a useful route for preparing *cis*-15,16-dihydropyrenes. In order to obtain samples of **2** for study, we then repeated the original synthesis.[1] As expected, nitration of **2** proceeded smoothly in 88% yield to give **8**, identical in all respects with the specimen obtained previously by independent synthesis.

However, in contrast to *trans*-15,16-dimethyldihydropyrene, which undergoes initial electrophilic substitution only at the 2 position,[6] *cis*-15,16-dimethyldihydropyrene (**2**) reacts with acetic anhydride in the presence of boron trifluoride etherate to give a mixture of the 1-acetyl and 2-acetyl derivatives **10** and **11** in a ratio of 2:1. The correct assignment of structure in each case was readily apparent from its ^{1}H NMR spectrum.



10 11

Also, in contrast to *trans*-15,16-dimethyldihydropyrene, the cis isomer **2** slowly reacts with air, and to be preserved it must be stored in the dark under vacuum. Since the reaction of **2** with oxygen is promoted by light, it seemed probable that singlet oxygen was involved. When a solution of **2** in chloroform containing methylene blue was irradiated with an ordinary tungsten lamp in the presence of oxygen, conversion of **2** to a new product containing two oxygen atoms was complete in 180 s. The composition, molecular weight, and spectra of this new oxygenated product, formed in essentially quantitative yield, are in full accord with its assignment of structure **13**. This is also a logical result. Attack on **2** by singlet oxygen would be expected to give **12** which, in turn, by thermal rearrangement would lead to **13**.



12 13

The ultraviolet absorption spectrum of **13** has a long wavelength band at 333 nm (ϵ 7750), as would be expected for such a conjugated tetraene.[7] In the NMR spectrum of **13** the symmetry of the molecule is evidenced by the fact that the protons of the internal methyl groups appear as a singlet (τ 8.61) as do the vinyl protons at the 4 and 5 positions and at the 9 and 10 positions (τ 3.56 and 4.09). The protons at the 1 and 8 positions appear as a doublet of doublets at τ 6.53, in good analogy to other examples of cyclic vinyl epoxides.[8]

Under the same reaction conditions used for the conversion of **2** to **13**, *trans*-15,16-dimethyldihydropyrene (**1**) remains unchanged. Apparently, the internal methyl groups of **1** provide sufficient steric hindrance that reaction with singlet oxygen does not occur. In the case of the cis isomer **2** approach of singlet oxygen from the side anti to the methyl groups is free of steric hindrance.

Experimental Section[9]

2,6-Bis(bromomethyl)-4-nitrotoluene (4b). A. 2-Methyl-5-nitroisophthalaldehyde. A solution of 4.82 g of 2-methylisophthalaldehyde[1] in 29 mL of concentrated sulfuric acid was added dropwise with stirring to a solution of 17.3 g of ammonium sulfate and 5.8 mL of 90% nitric acid in 28 mL of concentrated sulfuric acid held at 0 °C. When the addition was complete, the mixture was stirred for an additional 3.5 h and then was poured onto 250 g of ice. After the mixture had warmed to room temperature, the precipitate was collected by filtration, washed with water, and dried. This gave 5.63 g (90%) of a cream-colored solid, mp 98–100 °C. A sample, after recrystallization from a dichloromethane–hexane mixture, gave crystals: mp 101–101.5 °C; NMR, singlets at τ −0.50 (2 H, –CHO), 1.15 (2 H, ArH), and 6.95 (3 H, $-CH_3$). Anal. Calcd for $C_9H_7NO_4$: C, 55.96; H, 3.65; N, 7.25. Found: C, 55.72; H, 3.69; N, 7.62.

B. 2,6-Bis(hydroxymethyl)-4-nitrotoluene. A solution of 170 mg of 2-methyl-5-nitroisophthalaldehyde in 5 mL of tetrahydrofuran was added with stirring to a suspension of 75 mg of sodium borohydride in 10 mL of tetrahydrofuran. After the resulting mixture had been stirred at room temperature for 6 h, it was decomposed by addition of 3 mL of dilute hydrochloric acid followed by 5 mL of brine. The organic layer was extracted with ether, washed with water, dried, and concentrated. The residual solid was recrystallized from 2-propanol to give 87 mg (50%) of pale yellow crystals: mp 140–142 °C; NMR, singlets at τ 1.73 (2 H, ArH), 5.17 (4 H, $-CH_2OH$), and 7.64 (3 H, $-CH_3$); mass spectrum *m/e* 197.070 (calcd for $C_9H_{11}NO_4$: 197.069). Anal. Calcd for $C_9H_{11}NO_4$: C, 54.82; H, 5.62; N, 7.10. Found: C, 54.75; H, 5.82; N, 6.96.

C. 2,6-Bis(bromomethyl)-4-nitrotoluene. A solution of 2.61 g of 2,6-bis(hydroxymethyl)-4-nitrotoluene in 15 g of a 30% solution of hydrogen bromide in acetic acid was stirred at room temperature for 16 h. The suspension was diluted with water and the precipitate was collected by filtration. The resulting dry solid was chromatographed over silica gel using a 1:1 mixture of benzene–hexane as eluent. The main fraction of eluate gave 1.91 g (45%) of colorless crystals: mp 154–155 °C; NMR, singlets at τ 1.80 (2 H, ArH), 5.44 (4 H, $-CH_2Br$), and 7.47 (3 H, $-CH_3$); mass spectrum *m/e* 325, 323, and 321. Anal. Calcd for $C_9H_9NO_2Br_2$: C, 33.44; H, 2.79. Found: C, 33.25; H, 3.01.

Coupling of 4b and 5 to Give the Syn and Anti Isomers 6b and 7b. A solution of 2.92 g of 2,6-bis(mercaptomethyl)toluene[1] and 5.14 g of 2,6-bis(bromomethyl)-4-nitrotoluene (**4b**) in 750 mL of benzene was added dropwise with stirring to a boiling solution of 2.7 g of potassium hydroxide in 3 L of ethanol. When the addition was complete (5 days), the solution was concentrated and the residual solid was extracted with dichloromethane. After the dichloromethane extract had been washed with water and dried, it was concentrated and the residual solid was chromatographed over silica gel using a 1:1 mixture of dichloromethane–petroleum ether (30–60 °C) as eluent. The main fraction of eluate gave 2.55 g (47%) of a colorless solid melting over a broad range. The NMR spectrum of the mixture showed the signals of the syn and anti isomers (**6b** and **7b**) sufficiently separated so that the spectrum of each could be individually analyzed. The syn isomer **6b** showed a singlet at τ 2.50 (2 H, ArH), a singlet at 3.35 (3 H, ArH), a doublet at 5.97 (4 H, J = 15 Hz, $ArCH_2$–), a doublet at 6.09 (4 H, J = 15 Hz, $ArCH_2$), and singlets at 6.36 and 7.48 (3 H each, CH_3–). The anti isomer **7b** showed a singlet at τ 1.81 (2 H, ArH), a multiplet at 2.62–2.90 (3 H, ArH), a singlet at 6.28 (8 H, $ArCH_2$–), and singlets at 8.59 and 8.71 (3 H each, $-CH_3$). The integration values indicated the syn to anti isomer ratio to be 1:1. The mass spectrum of the mixture showed *m/e* 313.115 (calcd for $C_{18}H_{19}NO_2S_2$: 313.114).

2-Nitro-*cis*-15,16-dimethyldihydropyrene (8) and 2-Nitro-*trans*-15,16-dimethyldihydropyrene (9). A. Stevens Rearrangement of 6b and 7b. A solution of 2.55 g of the 1:1 mixture of **6b** and **7b** in 74 mL of dichloromethane was added dropwise with stirring to a suspension of 3.20 g of dimethoxycarbonium fluoroborate[10] in 10 mL of dry dichloromethane held at −20 °C under a nitrogen atmosphere. After the mixture had been stirred for 5 h, 40 mL of methyl formate was added with stirring and the precipitate was collected by filtration. This gave 3.75 g (92%) of the bis(sulfonium fluoroborate) as a tan solid, mp 220 °C dec. The bis(sulfonium fluoroborate) was added in one portion with stirring to a suspension of 500 mg of sodium hydride in 300 mL of tetrahydrofuran. After the mixture had been stirred at room temperature for 9 h, it was decomposed by the addition

of water and aqueous hydrochloric acid. The organic layer was extracted with ether, washed with water, dried, and concentrated. Chromatography of the residue over silica gel using a 1:1 mixture of dichloromethane–petroleum ether (30–60 °C) as eluent gave 2.4 g (93%) of a yellow oil. The NMR spectrum of the oil was complicated, but appropriate for the expected mixture of isomers. The protons for the internal methyl groups of the *anti*-[2.2]metacyclophane isomers appeared in the region of τ 8.96–9.42, whereas the corresponding methyl protons of the syn isomers appeared in the region of τ 7.2–7.6. The comparative integration values for these areas indicated the ratio of syn to anti isomers to be 1:3. Since attempts to separate the individual isomers were not fruitful, the mixture was employed directly in the next step.

B. Oxidation of the Stevens Rearrangement Product. To a solution of 110 mg of the mixture of isomers from the Stevens rearrangement in 10 mL of dichloromethane was added 125 mg of *m*-chloroperbenzoic acid and the mixture was stirred at room temperature for 16 h. The solution was then decanted from the solid, washed with water, dried, and concentrated. The residual oil was again taken up in dichloromethane, washed with aqueous base followed by water, dried, and concentrated. This gave 124 mg (100%) of a pale yellow oil. The complicated NMR spectrum of the oil showed the protons of the internal methyl groups of the anti isomers at τ 9.0–9.4 and those of the syn isomers at τ 7.5–8.0, with the integration values for these regions indicating again a ratio of syn to anti isomers of 1:3.

C. Pyrolysis of the Disulfoxide Mixture. The pyrolysis was conducted in the normal apparatus used for sulfone pyrolyses with the preheater set at 150 °C and the oven at 500 °C.[11] A sample of 100 mg of the disulfoxide mixture from the above experiment was placed in the pyrolysis apparatus and the pressure was reduced to 1 Torr. After 2 h the pyrolysate was collected and purified by preparative thin-layer chromatography over silica gel (silica gel PF254) using a 1:1 mixture of benzene–petroleum ether (30–60 °C) for elution.

The first purple band (R_f 0.35) gave 4.6 mg of deep purple crystals: mp 172–173 °C; identical in all respects with an authentic sample of 2-nitro-*trans*-15,16-dimethyldihydropyrene (**9**).[6]

The second purple band (R_f 0.20) gave 2 mg of 2-nitro-*cis*-15,16-dimethyldihydropyrene (**8**) as deep purple crystals: mp 140–145 °C; NMR, singlet at τ 0.72 (2 H, ArH), two doublets at 0.90 and 1.90 (2 H each, J = 7.5 Hz, ArH), doublet at 1.61 (2 H, J = 8 Hz, ArH), a triplet at 2.23 (1 H, J = 8 Hz, ArH), and singlets at 11.89 and 11.98 (3 H each, $-CH_3$); UV (cyclohexane), maxima at 288 (ϵ 5400), 342 (35 200), 378 (17 400), 484 (12 700), 562 (1170), and 617 nm (1370); mass spectrum *m/e* 277, 262, 247, and 201. Anal. Mol wt calcd for $C_{18}H_{15}NO_2$: 277.110. Found (high-resolution mass spectrum): 277.108.

2-Nitro-*cis*-15,16-dimethyldihydropyrene was also prepared independently. A solution of 1.8 mg of *cis*-15,16-dimethyldihydropyrene[1] and 1.9 mg of cupric nitrate trihydrate in 0.5 mL of acetic anhydride was stirred at 0 °C for 1 h. Ice (2 g) was then added and the mixture was allowed to warm to room temperature with stirring. After extraction of the mixture with ether, the ether extract was washed successively with aqueous bicarbonate solution and water, dried, and concentrated. The residue was chromatographed over silica gel using dichloromethane as eluent to give 2.1 mg (88%) of deep purple crystals, identical in all respects with the specimen of 2-nitro-*cis*-15,16-dimethyldihydropyrene (**8**) described above.

1- and 2-Acetyl-*cis*-15,16-dimethyldihydropyrene (10 and 11). To a solution of 2.0 mg of *cis*-15,16-dimethyldihydropyrene (**2**)[1] in 1 mL of acetic anhydride held at 0 °C was added 5 drops of boron trifluoride etherate with stirring. After the mixture had been stirred for 10 min, 2 mL of water was added and the mixture was allowed to warm and was stirred at room temperature for 2 h. The organic constituents were extracted with dichloromethane and the dichloromethane extract was washed successively with aqueous bicarbonate solution and water, dried, and concentrated. The residual green solid was purified by thin-layer chromatography over silica gel using dichloromethane for elution.

The first band (R_f 0.4) gave 1 mg (40%) of 1-acetyl-*cis*-15,16-dimethyldihydropyrene (**10**) as deep green crystals: NMR, doublets at τ 0.35 and 1.13 (1 H each, J = 8 Hz, ArH), a singlet at 1.17 (2 H, ArH), an AB pattern at 1.73 and 1.91 (2 H, J = 8 Hz, ArH), a doublet at 1.67 (2 H, J = 8 Hz, ArH), a triplet at 2.37 (1 H, J = 8 Hz, ArH), a singlet at 7.06 (3 H, $-C(=O)CH_3$), and singlets at 11.94 and 11.97 (3 H each, $-CH_3$); (cyclohexane), maxima at 358 (ϵ 12 000), 423 (1200), 442 (1000), 570 (100), and 616 nm (100). Anal. Mol wt calcd for $C_{20}H_{18}O$: 274.136. Found (high-resolution mass spectrum): 274.139.

The second band (R_f 0.3) gave 0.5 mg of 2-acetyl-*cis*-15,16-dimethyldihydropyrene as deep green crystals: NMR, a singlet at τ 1.04 (2 H, ArH), an AB pattern at 0.98 and 1.20 (4 H, J = 8 Hz, ArH), a doublet at 1.69 (2 H, J = 8 Hz, ArH), a triplet at 2.32 (1 H, J = 8 Hz, ArH), a singlet at 7.06 (3 H, $-C(=O)CH_3$), and singlets at 11.85 and 11.96 (3 H, each, $-CH_3$); UV (cyclohexane), maxima at 262 (ϵ 12 000), 333 (13 000), 367 (9300), 467 (2600), 570 (100), and 617 nm (200). Anal. Mol. wt calcd for $C_{20}H_{18}O$: 274.136. Found (high-resolution mass spectrum): 274.138.

Oxidation of *cis*-15,16-Dimethyldihydropyrene (2) to 13. A stream of oxygen was slowly bubbled through a solution of 1.0 mg of *cis*-15,16-dimethyldihydropyrene (**2**)[1] in 0.2 mL of chloroform containing a trace of methylene blue while the solution was irradiated with an ordinary 250-W incandescent lamp. After 180 s the solution was removed and chromatographed over silica gel. From the main fraction of eluate there was isolated 1.1 mg (100%) of a yellow oil: NMR, a singlet at τ 3.56 (2 H, –CH=C<), a doublet of doublets at 3.70 (2 H, J = 2 Hz, J^1 = 9 Hz, –CH=C<), a doublet of doublets at 4.03 (2 H, J = 2 Hz, J^1 = 9 Hz, –CH=C<), a singlet at 4.09 (2 H, –CH=CH–), a doublet of doublets at 6.53 (2 H, J = 2, J^1 = 4 Hz, C–CHOC<), and a singlet at 8.61 (6 H, $-CH_3$); UV (ethanol), maxima at 207 (ϵ 10 300), 223 (8720), 230 (10 700), 239 (14 800), 249 (7300), 261 (8250), 272 (9940), 303 (3550), 317 (5230), and 333 nm (7750). Anal. Mol wt calcd for $C_{18}H_{16}O_2$: 264.115. Found (high-resolution mass spectrum): 264.114.

The same product was obtained when oxygen was bubbled through a chloroform solution of **2** in the absence of methylene blue, but the reaction required hours for completion.

Acknowledgment. We thank the National Science Foundation for their support of this investigation.

Registry No.—**2,** 52028-44-1; **4b,** 66901-98-2; **5,** 41563-67-1; **6b,** 66901-99-3; **6b** bis-*S*-Me derivative tetrafluoroborate salt, 66966-28-7; **6b** bissulfoxide bis-*S*-Me derivative tetrafluoroborate salt, 66902-32-7; **6b** Stevens rearrangement product, 66902-31-6; **7b,** 66966-21-0; **7b** bis-*S*-Me derivative tetrafluoroborate salt, 66902-07-6; **7b** bissulfoxide bis-*S*-Me derivative tetrafluoroborate salt, 66902-33-8; **7b** Stevens rearrangement product, 66966-22-1; **8,** 66902-00-9; **9,** 13979-82-3; **10,** 66902-01-0; **11,** 66902-02-1; **13,** 66902-03-2; 2-methyl-5-nitroisophthalaldehyde, 66902-04-3; 2-methylisophthalaldehyde, 51689-50-0; 2,6-bis(hydroxymethyl)-4-nitrotoluene, 66902-05-4; dimethoxycarbonium fluoroborate, 18346-68-4.

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