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THE DYE-SENSITIZED PHOTOOXIDATION OF CYCLOPENTADIENE

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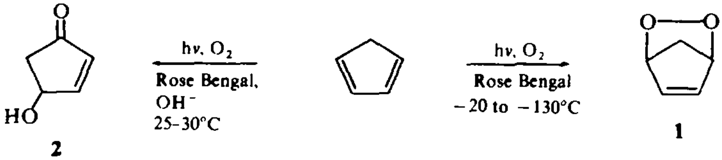
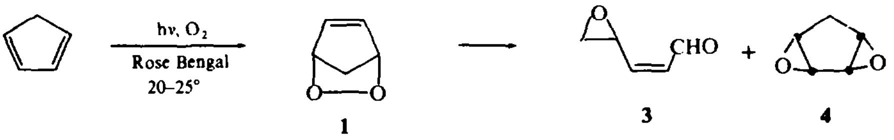
Abstract—The dye-sensitized photooxygenation of cyclopentadiene provides a novel one-step synthesis of 4,5-epoxy-*cis*-2-pentenal (**3**) and *cis*-1,2:3,4-diepoxycyclopentane (**4**) presumably via a facile thermal isomerization of the transannular peroxide (**1**). Spectrometric identification of the *cis*- and *trans*-epoxyaldehyde is presented. Some unique transformations of **3** are described. For example, 4,5-epoxy-*cis*-2-pentenal undergoes a facile acid-catalyzed rearrangement in aqueous solutions to furfuryl alcohol. As a dienophile, **3** produces an adduct with cyclopentadiene and ethyl vinyl ether. Hydrogenation of **3** with Raney nickel in methanol provides 5-hydroxypentanal (**8**) and 1,5-pentanediol. Hydrogenolysis of **3** with Raney nickel in aqueous solutions at higher pressure affords 1,5-pentanediol in 61% yield. In a novel thermal process, the epoxyaldehyde fragments to furan and formaldehyde.

RECENT work by Schulte-Elte and coworkers[1] concerning the dye-sensitized photooxygenation of cyclopentadiene prompts us to report similar results obtained simultaneously and independently in our laboratory. Original investigations[2–4] reported the isolation of a transannular peroxide (**1**) when the irradiations were carried out at −20° to −130°C, whereas 4-hydroxy-2-cyclopentenone (**2**) was allegedly formed when the reaction was conducted at ambient temperatures. Schulte-Elte and co-workers[1] prepared the hydroxyenone (**2**) in 20% yield by conducting the photooxygenation in dilute alkaline alcoholic solutions at room temperature but obtained 4,5-epoxy-*cis*-2-pentenal (**3**) and *cis*-1,2:3,4-diepoxycyclopentane (**4**) from comparable irradiations in neutral media.



In our hands, irradiation of a methanolic solution of cyclopentadiene at 20–25°C employing Rose Bengal as sensitizer gave (**3**) and (**4**) in 70% and 10% yields, respectively. Both products presumably arose from a thermal isomerization of intermediate (**1**).

The IR spectrum (cap film) of 4,5-epoxy-*cis*-2-pentenal had absorption bands at 2860, 2740 (aldehyde C-H), 1680 (carbonyl), 1245, 903, and 827 (epoxide), and 1635, 764 cm^{-1} (*cis*-CH=CH—). The NMR spectrum ($CDCl_3$) exhibited a one-proton multiplet centred at δ 10·18 (aldehyde proton), a two-proton multiplet centred at δ 6·14 (olefinic protons), a one-proton multiplet centred at δ 4·26 (methine proton),



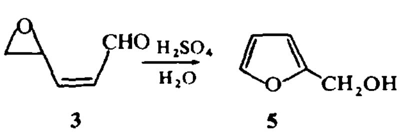
and two single-proton absorptions appearing as a doublet of doublets centred at δ 3·14, $J = 5·5, 4·2$ Hz, and δ 2·79, $J = 5·5, 2·5$ Hz (methylene protons).

The IR and NMR spectra of **4** were identical to spectra of *cis*-1,2:3,4-diepoxycyclopentane prepared by reaction of the corresponding dibromoglycol with aqueous alkali.[6,7]

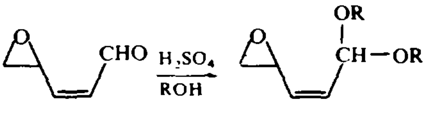
Distillation converted a portion of **3** to 4,5-epoxy-*trans*-2-pentenal, whose stereochemistry was delineated by triple resonance NMR spectroscopy (Figs 1 and 2). The spectrum exhibited a one-proton doublet associated with finer splitting at δ 9·50, $J = 6·0$ Hz (aldehyde proton), two single-proton quartets centred at δ 6·40 (olefin protons), a one-proton multiplet centred at δ 3·60 (methine proton), and two single-proton absorptions appearing as a doublet of doublets centred at δ 3·15, $J = 6·0$, 4·0 Hz, and δ 2·80, $J = 6·0, 2·2$ Hz (geminal methylene protons). Simultaneous irradiation of the aldehyde and methine protons collapsed the olefinic eight-line splitting pattern into an AB proton pattern. The 16 Hz coupling constant was consonant with a *trans* stereochemical assignment.[5] The irradiation technique further confirmed the structural assignment. Irradiating the methine proton collapsed the downfield methylene proton pattern into a AB quartet ($J = 6·0$ Hz).

The IR spectrum (cap film) of the *trans*-isomer gave absorption bands at 2820, 2730 (aldehyde C—H), 1675 (carbonyl), 1642, 974 (*trans*-CH=CH=), and 926, 847 and 827 cm^{-1} (epoxide).

The novel epoxyaldehyde (**3**) underwent facile transformations upon treatment with a variety of reagents. For example, treatment of an aqueous solution of **3** with 0·01% H_2SO_4 provided furfuryl alcohol (**5**) in 51% isolated yield.



Acidified alcoholic solutions of **3** afforded the dimethyl- and diethyl acetals in 11% and 20% yields respectively.



R = Me, Et

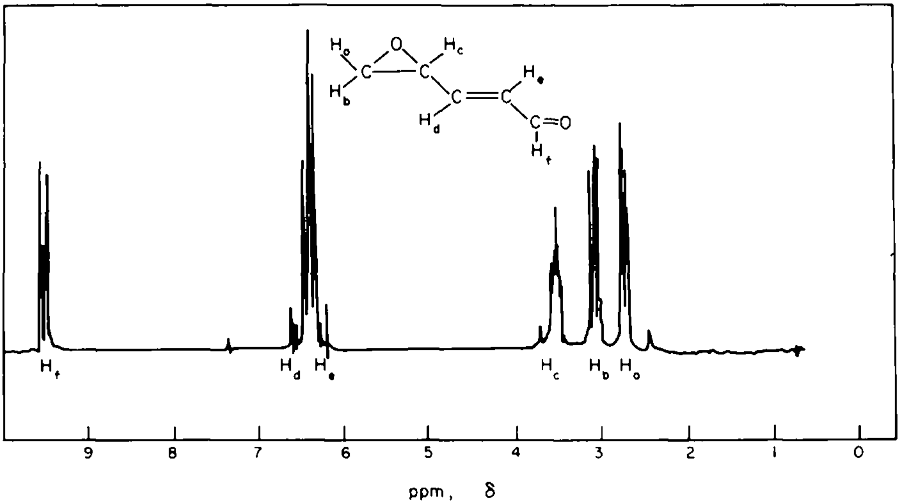


FIG. 1 100 MHz NMR spectrum of 4,5-epoxy-*trans*-2-pentenal

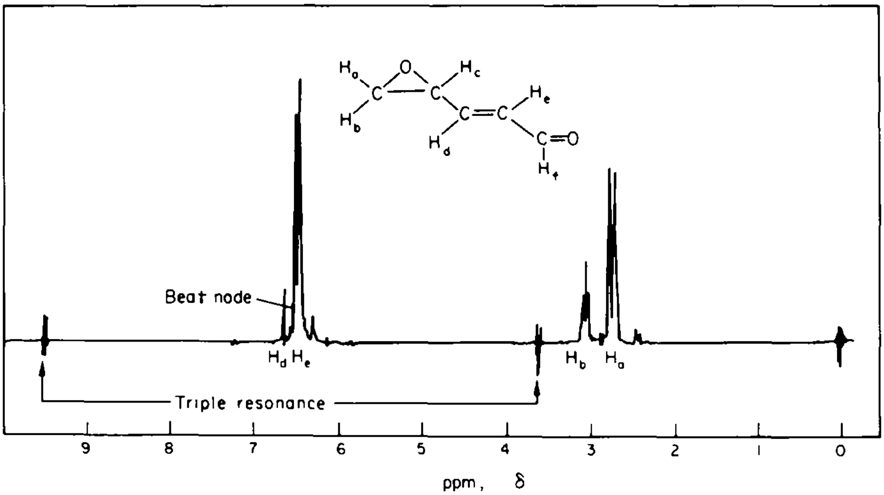
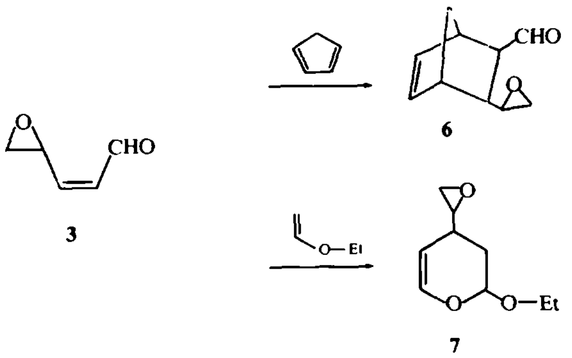


FIG. 2 Spin–spin decoupling by irradiation of protons H_c and H_f

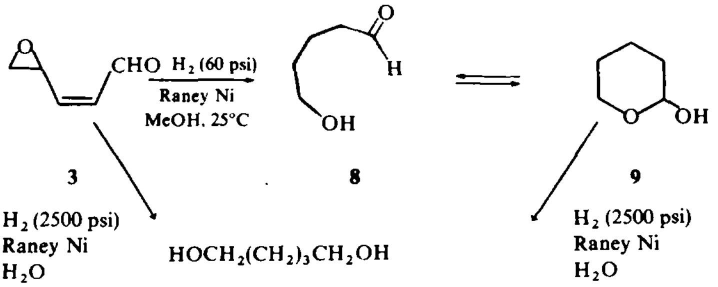
Although the epoxyaldehyde failed to condense with itself, it readily underwent Diels–Alder condensations with cyclopentadiene and ethyl vinyl ether.



Initial efforts concerning the catalytic hydrogenation of 4,5-epoxy-2-pentenal involved extensive screening of various catalysts under reduction conditions. Catalysts such as Ru on carbon, Pd on $CaCO_3$, Pt on C, PtO, Rh on C, basic Raney Ni, and W-2 (neutral) Raney Ni were examined. The pH of the catalyst support appeared to be a critical factor in the reduction reaction since the epoxyaldehyde underwent a concomitant acid rearrangement and appeared to polymerize under the influence of base. The W-2 (neutral) Raney Ni appeared to be the most selective catalyst under the conditions employed.

Reduction carried out at low H_2 pressures using Raney Ni as catalyst provided 5-hydroxypentanal (**8**) and 1,5-pentanediol in 44% and 33% yield, respectively. The intermediacy of the 5-hydroxypentanal (**8**) was shown by its isolation and subsequent reduction to 1,5-pentanediol.

It was found that 4,5-epoxy-*cis*-pentenal (**3**) could be converted directly to 1,5-pentanediol using the same catalyst at higher pressure in the presence of H_2O. The yield of the diol from initial experiments was found to be 30% to 40%. H_2O appeared to facilitate the reduction of the 2-hydroxytetrahydropyran (**9**) by directing the equilibrium toward the open-chain hydroxyaldehyde (**8**). In contrast, the reduction of (**3**) under similar conditions in MeOH was very sluggish.



Finally, the thermolysis of 3 at 180°C provided furan and formaldehyde in low yields.

EXPERIMENTAL

NMR spectra were recorded on a Varian Model HA-100 spectrometer (solvent was $CDCl_3$ with TMS as internal standard), IR spectra on a Perkin–Elmer Model 221 spectrophotometer, mass spectra on AE1-MS 9026 spectrometer and UV spectra in 95% EtOH on a Carey Model 14 spectrophotometer.

Photooxygenation of cyclopentadiene. A solution of cyclopentadiene (50·0 g, 0·76 mole) and Rose Bengal (0·5 g) in MeOH (500 ml) was irradiated in a Pyrex immersion vessel using a Hanovia Type A 450-watt lamp. Air (flow rate = 960 cc/min) was continuously bubbled through the solution throughout the irradiation. The reaction temperature (18–25°C) was maintained by regulating the flow of brine solution through the external cooling jacket and the water flow theough the immersion well. The uptake of cyclopentadiene and the formation of the epoxyaldehyde was followed by glc (12 ft × $\frac{1}{8}$ in. 10% Apiezon M on Chromasorb G column at 120°C) using *o*-dichlorobenzene as an internal standard. After 2·5 hr the diene was completely consumed. Glc analysis indicated that 3 was formed in 71% yield. Several runs with initial cyclopentadiene concentrations varying from 0·4 to 1·0 mole gave (3) in 70–75% yield. The solvent was removed under reduced pressure and the liquid residue distilled at 50–51°/0·5 mm giving 30·1 g (43% yield) of (3). Found: C, 61·16; H, 6·10. $C_5H_6O_2$ requires C, 61·22; H, 6·16%). The yield of *cis*-1,2,3,4-diepoxycyclopentane (4) varied from 5–10% and appeared to be temperature dependent. An analytical sample was collected on glc (12 ft × $\frac{1}{8}$ in. 10% Apiezon M on Chromasorb G column at 120°C) and the IR spectrum (neat) was superimposable on that of the authentic *cis*-diepoxide.[6,7]

The epoxyaldehyde was redistilled and ~10% of the distillate contained the *trans* isomer. An analytical sample of the *trans* compound was collected via glc (12 ft × $\frac{1}{8}$ in. 10% Apiezon M on Chromasorb G column at 120°C); IR(max) 2830, 2730, 1680, 1642, 974, 925, 848 and 828 cm^{-1}; NMR (see Fig. 1), λ max (95% EtOH) 227μ (15,700) 315 (33); mass spectrum, molecular ion *m/e* 98 with peaks at *m/e* 68 and 69.

Acid-catalyzed rearrangement of 3. In a 100-ml round-bottom flask equipped with a magnetic stirrer was placed 0·01% aqueous sulfuric acid (100 ml). 4,5-Epoxy-2-pentenal (10·0 g, 0·1 mole) was added over a period of 5 min. Aliquots were periodically removed from the reaction, neutralized with solid Na_2CO_3 and ether extracted. The samples were analyzed by vpc ($\frac{1}{8}$ in. × 12 ft. 10 ft. 10% Carbowax 20M on 60–80 Chromasorb G programmed from 150 to 200°C) using dibutyl Carbitol as an internal standard. After 2 hr the conversion of furfuryl alcohol had reached a maximum value of 57·6%. It was observed that a reaction period exceeding 2 hr appeared to destroy the furfuryl alcohol. For example, after 4 hr the yield of furfuryl alcohol had decreased to 23·3%.

In an experiment carried out exactly as described above, the reaction was quenched after 2 hr with Na_2CO_3 and extracted 3 times with 100 ml fractions of ether. The etheral extracts were combined, dried, and concentrated under reduced pressure. Distillation of the residue afforded furfuryl alcohol (5·1 g, 51% yield, bp 82–83°/25 mm). The IR spectrum (neat) was identical to an authentic sample of furfuryl alcohol.

4,5-*Epoxy-2-pentenal dimethyl acetal.* A solution of 4,5-epoxy-2-pentenal (20·0 g, 0·2 mole) and 0·01% methanolic sulfuric acid (200 ml) was placed in a 500 ml round-bottom flask equipped with a magnetic stirrer. Aliquots were periodically removed from the reaction and analyzed by vpc ($\frac{1}{8}$ in. × 12 ft. 10% Carbowax 20M on 60–80 Chromasorb G at 200°C). After 16 hr the reaction was quenched with Na_2CO_3 and concentrated under reduced pressure. Distillation of the residue afforded 4,5-epoxy-2-pentenal dimethyl acetal (6·9 g; bp 93–94°/30 mm). Unreacted 4,5-epoxy-2-pentenal (15·2 g) was recovered. The efficiency for the acetal production was 11%. No attempt to optimize the reaction conditions was made. (Found: C, 58·42; H, 8·41. $C_7H_{12}O_3$ requires C, 58·32; H, 8·39%). IR(max) 3010, 1460, 1405, 1320, 1270, 1190, 1110, 962, 913, 837 and 812 cm^{-1}; NMR ($CDCl_3$) δ 3·30 (s, OCH_3), 3·33 (s, OCH_3), 3·45 (m, 2 methylene H), 3·90 (m, epoxy methine H) 4·75 (d, J = 3·0 Hz, acetal methine H), 5·85 (m, J_{AB} = 11·0 Hz, J = 3·0 Hz, olefin H), 6·08 (m, J_{AB} = 11·0 Hz, J = 4·2 Hz, olefin H); mass spectrum, molecular ion *m/e* 144.

4,5-Epoxy-2-pentenal diethyl acetal. A solution of ammonium nitrate (2·0 g) in EtOH (25 ml) was added to a mixture of 4,5-epoxy-2-pentenal (30·0 g, 0·30 mole) and ethyl orthoformate (45·0 g, 0·30 mole). The mixture was allowed to react at room temperature for 12 hr. The red solution was filtered, Na_2CO_3 was added (*ca.* 2 g) and the mixture distilled affording 4,5-epoxy-2-pentenal diethyl acetal (24·9 g, 49%; bp 106–108°/12 mm). (Found: C, 62·83; H, 9·40. $C_9H_{16}O_3$ requires C, 62·77; H, 9·36%). IR (max) 2940, 1470, 1440, 1380, 1309, 1050, 918, 830 and 800 cm^{-1}; NMR ($CDCl_3$) δ 1·20 (t, $J = 7·0$ Hz, CH_3) 2·60 (q, $J = 2·5$ Hz, $J = 5·5$ Hz, epoxy methylene H), 2·90 (q, $J = 4·0$ Hz, $J = 5·5$ Hz, epoxy methylene H), 3·60 (m, $O\underline{CH_2}CH_3$), 3·80 (m, epoxy methine H), 5·15 (m, acetal methine H), 5·50 (m, $J = 11·0$ Hz, 2 olefin H); mass spectrum, molecular ion *m/e* 172.

Diels-Alder adduct of 3 *and cyclopentadiene.* To a round-bottom flask fitted with a magnetic stirrer and a condenser was added C_6H_6 (50 ml), cyclopentadiene (20·0 g, 0·30 mole) and 4,5-epoxy-*cis*-2-pentenal (30·0 g, 0·30 mole). The reaction was followed by periodically removing aliquots and analyzing on a ⅛ in. × 12 ft. 10% Apiezon M on 60–80 Chromasorb G column programmed from 70–200°C. After 4 hr the reaction mixture was cooled, the solvent removed, and the residue distilled giving the cyclopentadiene adduct (32·4 g, 21%; bp 112°/2 mm). (Found C, 73·25; H, 7·37. $C_{10}H_{12}O_2$ requires C, 73·15; H, 7·37%). IR(max) 2900, 1730, 1460, 1340, 1240, 867, and 724 cm^{-1}. The NMD was very complex due to the several *exo* and *endo* isomers which were present. Four aldehyde proton absorptions were observed as doublets at δ 9·38, 9·47, 9·70 and 9·83. Mass spectrum exhibited a molecular ion at *m/e* 164.

Diels-Alder adduct of 3 *and ethyl vinyl ether.* 4,5-Epoxy-*cis*-2-pentenal (50·0 g, 0·51 mole) and vinyl ethyl ether (70·0 g, 0·97 mole) were charged to a glass-lined stainless steel pressure reactor and heated at 140° for 12 hr. The liquid residual was distilled giving the adduct (7) (42·7 g, 25%; bp 54–56°/0·1 mm). (Found: C, 63·32; H, 8·26. $C_9H_{14}O_3$ requires C, 63·51; H, 8·29%). IR(max) 2980, 1650, 1230, 1120, 1045, 1000, 972 and 882 cm^{-1}; nmr ($CDCl_3$) δ 1·20 (2 overlapping t, $J = 7·0$ Hz, CH_3), 2·65 (m, epoxide H), 3·65 (m, ABX_3 pattern, $O\underline{CH_2}CH_3$), 4·60 (m, C-5 olefin H) 5·00, acetal methine H), 6·25 (m, C-6 olefin H). The mass spectrum exhibited a molecular ion at *m/e* 170.

*Hydrogenolysis of 4,5-epoxy-*cis*-2-pentenal* (3)

A. *Reduction in methanol*—A mixture of 4,5-epoxy-2-pentenal (30·0 g, 0·30 mole), W-2 Raney Ni (5·0 g) and MeOH (250 ml) was placed in a 500 ml thick-walled reaction bottle. The reduction was carried out using a low-pressure Parr Hydrogenator at 25°C. Air was removed from the reactor by alternately purging with H_2 and venting. The pressure was maintained at 60 psi throughout the course of the hydrogenation. After 12 hr approximately 0·6 moles of H_2 was absorbed. Analysis by glc (12 ft × ⅛ in. 20% Carbowax 20M on Chromasorb G column at 200°) indicated three compounds were present in the reaction mixture. The ratio of the three components was 3:46:50 and corresponded to unreacted 4,5-epoxy-2-pentenal, 5-hydroxypentanal (8), and 1,5-pentanediol, respectively. The yields of the 5-hydroxypentanal (44%) and 1,5-pentanediol (33%) were determined by using diphenyl ether as an internal standard. The solution was filtered and concentrated under reduced pressure affording a light yellow viscous liquid. The liquid was distilled on a 12 in. spinning band column giving 5-hydroxy-pentanal (12·0 g, 39% yield; bp 114–120°/15 mm) and 1,5-pentanediol (8·4 g, 26% yield, bp 118–120°/6 mm).

The IR spectrum of 5-hydroxypentanal was superimposable on that of an authentic sample. The 2,4-dinitrophenylhydrazone melted at 106–107°C (lit.[8] m.p. 107–109°C).

B. *Reduction in water.* A mixture of 4,5-epoxy-2-pentenal (50·0 g, 0·51 mole) W-2 Raney Ni (20·0 g) and H_2O (500 ml) was placed in a 3-l heavy-duty glass liner and inserted into a stainless steel 3-l bomb. The bomb was placed on a rocker assembly, purged with H_2 gas, and finally filled with H_2 to a pressure of 2000 psi. The temperature was held at 80°C and the pressure was maintained at 2000 psi throughout the reduction by intermittently adding H_2. After 45 hr the total H_2 uptake was 600 psi. The bomb was allowed to cool and the mixture was filtered. The filtrate was concentrated under reduced pressure giving a colorless viscous liquid (100 g). Analysis via glc (12 ft. × ⅛ in. 20% Carbowax 20M on Chromasorb G column at 150–200°C) using 1,6-hexanediol as a standard indicated a 36·4% yield of 1,5-pentanediol. The presence of unreacted 4,5-epoxy-2-pentenal was noted. The reaction mixture was fractionally distilled to isolate 1,5-pentanediol, (15·0 g) bp 118–120°/6 mm. The IR spectrum (neat) was superimposable on that of an authentic sample of 1,5-pentanediol.

Hydrogenation of 5-hydroxypentanal. Catalytic reduction 5-hydroxypentanal (5·0 g, 0·49 mole) with W-2 Raney Ni at 3000 psi and 90° required approximately one hr. 1,5-Pentanediol, after removal of the catalyst was distilled, bp 103–105°/3–4 mm, giving 49 g (96% yield).

*Thermal decomposition of 4,5-epoxy-*cis*-2-pentenal* (3). The epoxyaldehyde (0·1 g) in C_6H_6 was dropped onto a vertical glass column from a 5-ml syringe attached to the top and collected in a Dry Ice-cooled trap. The temperature of the furnace was 280°C. The system was flushed with N_2 for one hr and the material was allowed to drop into the column over a 30-minute period. The column was cooled and the helices were rinsed with C_6H_6. The solutions were combined and analyzed via glc (12 ft × $\frac{1}{8}$ in. 10% Apiezon M on 60–80 Chromasorb G column at 180°C), indicating three compounds. The ratio was 1 : 1 : 8; corresponding to formaldehyde, furan, and unreacted 4,5-epoxy-*cis*-2-pentenal. The peaks corresponding to formaldehyde and furan were collected and compared with authentic IR spectra.

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