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ACID-CATALYSED INTRAMOLECULAR CYCLISATION OF DIAZOMETHYL KETONES. SYNTHESIS OF BRIDGED TETRACYCLIC SYSTEMS RELATED TO DITERPENES

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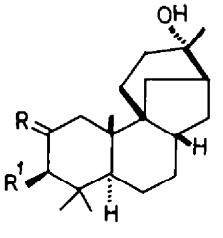
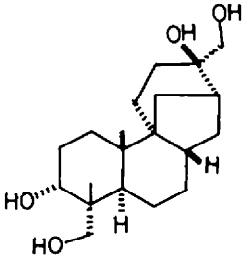
Abstract—Tetracyclo[10.3.1.0.^{1,10}.0^{2,7}]hexadeca-2(7),9-diene-8,14-dione **7** and tetracyclo[10.2.2.0^{1,10}.0^{2,7}]hexadeca-2(7),9-diene-8,13-dione **8** have been prepared through acid-catalysed intramolecular cyclisation of the diazomethyl ketones **19** and **25** respectively. The compound **7** is a skeletal representative of several tetracyclic diterpenes.

Acid-catalysed intramolecular reactions of diazomethyl ketones have provided[1] synthetic routes to many novel ring systems. Recently we have demonstrated[2] the utility of this reaction for the synthesis of several tricyclic bridged ring compounds related to sesquiterpenes. Utilising β-(8-methoxy-1, 2, 3, 4-tetrahydro-5-naphthyl)-propionic acid **10**[3] as a common starting material, we now wish to report convenient synthesis of two bridged tetracyclic dienediones **7** and **8** through acid-induced intramolecular cyclisation of the diazomethyl ketones **19** and **25** respectively. The basic tetracyclo[10.3.1.0^{1,10}.0^{2,7}]hexadecane skeleton of **7** is present in several tetracyclic diterpenes, e.g. stemodin **1**, stemodinone **2**, 2-desoxystemodinone **3**, maritimol **4** and aphidicolin **5**. Synthesis of the natural products **1**, **2**, **3**, **4** and **5** have been recently reported[4] from several laboratories. Bridged-ring compounds incorporating 13-oxo-tetracyclo[10.2.2.0^{1,10}.0^{2,7}]hexadecane framework (basic skeleton of **8**) have been utilised recently for the synthesis of the tetracyclic diterpenes stemarin **6**[5] and maritimol **4**.[4d] Although our immediate objective was to establish convenient routes for the bridged tetracyclic systems reported here, prior incorporation of substituents in the A-ring of the starting material **10** (for which methods are available[3]) and at later stages of the synthesis would lead to more useful products in future extension of this work. Recently we have been able to extend the present method for the synthesis of ring-A aromatic bridged tetracyclic compounds analogous to **7** and **8** (unpublished results).

For synthetic entry into the aphidicolin and related structures, Nicolaou *et al.*[6] recently performed stereocontrolled synthesis of the compound **9** through Lewis acid catalysed Diels–Alder reaction of tricy-



1 R = OH (H), R^1 = H
2 R = O, R^1 = H
3 R = H$_2$, R^1 = H
4 R = H$_2$, R^1 = OH



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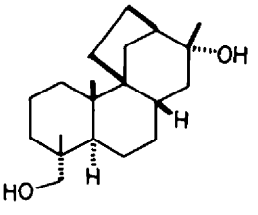

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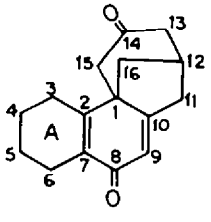

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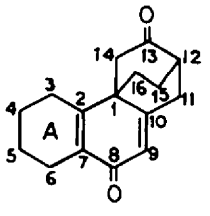

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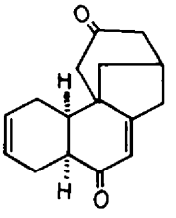

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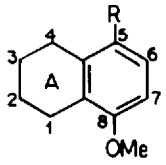
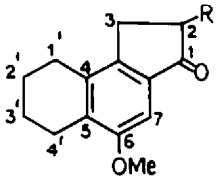
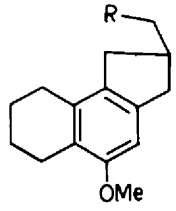
Scheme 1.



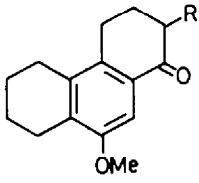
10 R = $CH_2CH_2CO_2H$
11 R = $CH_2CH_2COCHN_2$
12 R = $CH_2CH_2CH_2CO_2Me$
13 R = $CH_2CH_2CH_2CO_2H$



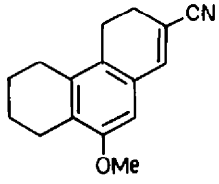
14 R = H
15 R = Br
16 R = $CH(CO_2Et)_2$
17 R = CH_2CO_2H



18 R = CO_2H
19 R = $COCHN_2$



20 R = H
21 R = CN



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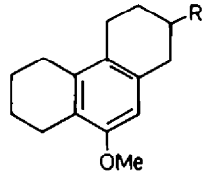

23 R = CN
24 R = CO_2H
25 R = $COCHN_2$

Scheme 2.

clo[6.3.1.0^{1,6}]dodeca-2,5-diene-4,10-dione[2,6] with butadiene. A synthesis of 4,5(1',2',3',4'-tetrahydrobenz)indane skeleton has been recently reported by Volhardt *et al.*[7]

β-(8-Methoxy-1,2,3,4-tetrahydro-5-naphthyl) propionic acid **10** was conveniently prepared[3] in 65% yield through Birch reduction of β-(4,6-dimethoxy-1-naphthyl)-propionic acid[8] with excess of Li and EtOH in liquid ammonia. Since the acid **10** was not readily soluble in polyphosphoric acid, cyclisation of **10** to the known ketone **14**[3] was carried out in a manner slightly different from the reported procedure (see Experimental). Monobromination of **14** with Br_2 at 10° in anhydrous Et_2O gave rise to **15** in 73% yield. Condensation of the bromoketone **15** with diethyl sodiomalonate in benzene afforded the keto-diester **16** in good yield. Alkaline hydrolysis of **16** followed by thermal decarboxylation of the resulting diacid furnished the keto-acid **17**. Reduction of the keto-acid **17** with $NaBH_4$ in aqueous NaOH followed by hydrogenolysis (H_2, 10% Pd–C) of the crude product in AcOH gave 77% yield of the acid **18**. The acid chloride, prepared from **18** using oxalyl chloride, was converted into the diazoketone **19** with CH_2N_2. On treatment with trifluoroacetic acid (TFA) in CH_2Cl_2 at −30°, the diazoketone **19** underwent intramolecular cyclisation to afford the tetracyclic bridged-ring dienedione **7** in 53% (based on **18**) yield.

For the synthesis of the dienone **8**, the acid **10** was converted into its higher homologue **13** through a modified Arndt–Eistert reaction developed by Hudlicky *et al.*[9] The diazoketone **11**, prepared from the acid chloride of **10** with CH_2N_2, was treated with silver benzoate in MeOH in the presence of Et_3N to give the ester **12**. Base hydrolysis of **12** led to the acid **13**. Cyclisation of **13** with PPA gave rise to the hydrophenanthrone **20** in 89% yield. The ketone **20** was converted into the β-ketonitrile **21** following the isoxazole procedure of Johnson *et al.*[10] for the conversion of 6-membered ring ketones to the corresponding β-ketonitriles. Reduction of the crystalline β-ketonitrile **21** with $NaBH_4$ and subsequent dehydration of the crude hydroxy-nitrile with toluene-p-sulphonic acid in benzene afforded the unsaturated nitrile **22** in good yield. The α,β-unsaturated nitrile **22** was conveniently reduced to the saturated nitrile **23** with Mg and MeOH (Corey procedure[11]). Alkaline hydrolysis of the saturated nitrile **23** furnished the corresponding acid **24** in good yield. The diazoketone **25**, prepared from the acid chloride of **24** with CH_2N_2, was treated with TFA in CH_2Cl_2 at −25° to give the desired dienedione **8**.

EXPERIMENTAL

M.ps were taken for samples in open capillaries in a H_2SO_4 bath UV spectra were recorded for solutions in 95% EtOH with a Beckmann DU spectrophotometer, and IR spectra with a Perkin-Elmer 298 instrument. NMR spectra were determined with a Varian T-60A spectrophotometer (TMS as internal standard). Extracts were dried over Na_2SO_4. Light petroleum refers to the fraction of b.p. 60–80°.

6-Methoxy-4,5-(1',2',3',4'-tetrahydrobenz)indan-1-one **14**. A mixture of P_2O_5 (10 g) and H_3PO_4 (6 ml, 89%) was heated at 100° for 1 h. To this mixture was added **10** (1.4 g) at 100° over a period of 15 min in ten small portions and the contents were mixed thoroughly after each addition. The viscous mass was then stirred at 100° for another 15 min and then poured into ice water. The precipitated solid was filtered, washed thoroughly with $NaHCO_3$ aq, and then with water. Crystallisation of the dry solid from a mixture of Et_2O-light petroleum furnished **14** (1.1 g, 85%), m.p. 148–149° (lit[3] m.p. 148–149°); spectral data identical with the reported values.

2-Bromo-6-methoxy-4,5-(1',2',3',4'-tetrahydrobenz)indan-1-one **15**. Br_2 (750 mg) was added at 10° during 30 min to a stirred soln of **14** (1 g) in anhyd Et_2O (150 ml) containing one drop of HBr (48%). The mixture was stirred at 10–15° for another 2 h and left at room temp. for 20 h. It was then washed with sat $NaHCO_3$ aq, water and dried. Evaporation of the solvent left a solid residue which was chromatographed over silica gel (30 g). Elution with Et_2O–light petroleum (1:5) afforded the desired bromoketone **15** (1 g, 73%), m.p. 120°; ν_{max}(KBr) 1700, 1590 cm^{-1}; δ ($CDCl_3$) 1.67–1.93 (m, 4H), 2.46–3.53 (m, 6H), 3.82 (s, 3H), 4.35–4.73 (m, 1H), 7.03 (s, 1H). Found: C, 56.67; H, 5.39. $C_{14}H_{15}O_2Br$ requires: C, 56.96; H, 5.12%.

Diethyl 6-methoxy-4,5-(1',2',3',4'-tetrahydrobenz)indan-1-one-2-malonate **16**. A soln of **15** (950 mg) in dry benzene (5 ml) was added dropwise with shaking to diethyl sodiomalonate [prepared from NaH (160 mg) and diethyl malonate (1.6 g)] in benzene (10 ml). The mixture was refluxed under N_2 for 12 h and then worked up with benzene. Removal of benzene and excess diethyl malonate left a residue which was evaporatively distilled at 220°/0.01 mm to furnish a solid product. Crystallisation of this material from light petroleum afforded **16** (850 mg, 70.5%), m.p. 114–115°; ν_{max} (KBr) 1752, 1730, 1700, 1595 cm^{-1}; δ ($CDCl_3$) 1.13 (t, 3H, J = 7 Hz), 1.30 (t, 3H, J = 7 Hz), 1.6–2.02 (m, 4H), 2.5–3.37 (m, 7H), 3.83 (s, 3H), 3.92–4.47 (m, 5H), 7.02 (s, 1H). Found: C, 67.66; H, 7.04. $C_{21}H_{26}O_6$ requires: C67.36; H, 7.00%.

2-Carboxymethyl-6-methoxy-1-oxo-4, 5-(1',2',3',4'-tetrahydrobenz) indane **17**. A mixture of **16** (800 mg), KOH (1 g), EtOH (9 ml) and water (1 ml) was refluxed under N_2 for 4 h. Usual work-up afforded a solid diacid which was decarboxylated by heating it at 210° (oil-bath) for 20 min under N_2. The product was crystallised from benzene to furnish **17** (500 mg, 85%), m.p. 218–219°; ν_{max} (KBr) 1705, 1600 cm^{-1}. Found: C, 70.21; H, 6.82. $C_{16}H_{18}O_4$ requires: C, 70.06; H, 6.61%.

The corresponding methyl ester (**17**, R=CH_2CO_2Me) had m.p. 120° (from Et_2O–light petroleum); ν_{max} (KBr) 1730, 1705, 1595 cm^{-1}; δ ($CDCl_3$) 1.58–2.05 (m, 4H), 2.13–3.45 (m, 9H), 3.7 (s, 3H), 3.83 (s, 3H), 7.0 (s, 1H). Found: C, 70.71; H, 7.20. $C_{17}H_{20}O_4$ requires: C, 70.81; H, 6.99%.

2-Carboxymethyl-6-methoxy-4, 5-(1', 2', 3', 4'-tetrahydrobenz)-indane **18**. To a stirred soln of the keto-acid **17** (450 mg) in NaOH aq (8 ml, 1.5N) was added $NaBH_4$ (100 mg) in small portions during 30 min. The mixture was stirred at r.t. for 24 h, cooled to 0° and acidified with HCl (6N). Extraction with ether afforded a gummy material (450 mg) [ν_{max} ($CHCl_3$) 1770, 1710, 1610 cm^{-1}] which was dissolved in AcOH (10 ml) and hydrogenated over Pd–C (10%, 100 mg) in the presence of a drop of perchloric acid. Uptake of H_2 (45 ml) ceased after 1 h. The mixture was filtered, diluted with water and extracted with chloroform. The extracts were washed with brine, water and dried. Evaporation of the solvent left a solid residue which was chromatographed over silica gel (15 g). Elution with Et_2O–light petroleum (1:4) afforded **18** (330 mg, 77%), m.p. 128–129° (Et_2O–light petroleum); ν_{max} (KBr) 1710, 1600 cm^{-1}; δ ($CDCl_3$) 1.6–1.97 (m, 4H), 2.25–3.33 (m, 11H), 3.8 (s, 3H), 6.6 (s, 1H). Found: C 73.57; H, 7.91. $C_{16}H_{20}O_3$ requires: C, 73.82; H, 7.74%.

Tetracyclo[10.3.1.$0^{2,7}$.$0^{1,10}$]hexadeca-2(7),9-diene-8,14-dione **7**. The acid **18** (300 mg) was converted into the corresponding diazomethyl ketone **19** (300 mg) [ν_{max} ($CHCl_3$) 2110, 1640 cm^{-1}] following the procedure of Ghatak *et al.*[12] To a stirred soln of TFA (12 ml) in dry CH_2Cl_2 (12 ml) at −30° was added under N_2 a son of the crude diazoketone (yellow solid) in CH_2Cl_2 (10 ml) over a period of 3 min. The mixture was stirred at −25° for another 3 min, diluted with CH_2Cl_2 (25 ml) and washed with water (3 × 20 ml). Evaporation of the solvent left a residue which was chromatographed over silica gel (10 g). Elution of the column with ether–light petroleum (3:7) afforded **7** (150 mg, 53.7%), m.p. 160° (from Et_2O–light petroleum); ν_{max} (KBr) 1712, 1662, 1615 cm^{-1}; λ_{max} 248 nm (log ε 4.17); δ ($CDCl_3$) 1.53–3.07 (m, 17H), 6.08 (t, 1H, small allylic coupling). Found: C, 79.52; H, 7.62. $C_{16}H_{18}O_2$ requires: C, 79.31; H, 7.49%.

Methyl γ-(8-methoxy-1,2,3,4-tetrahydro-5-naphthyl)butyrate **12**. Following usual procedure[12] the acid **10** (1 g) was converted into the corresponding diazoketone **11** (1 g, 90.7%), m.p. 88–89° (light petroleum); ν_{max} (KBr) 2110, 1634 cm^{-1}; δ ($CDCl_3$) 1.58–1.9 (m, 4H), 2.3–2.98 (m, 8H), 3.78 (s, 3H), 5.17 (s, 1H), 6.63 (d, 1H, J = 8 Hz), 6.97 (d, 1H, J = 8 Hz). Found: C, 70.06; H, 7.31. $C_{15}H_{18}N_2O_2$ requires: C, 69.74; H, 7.02%.

A soln of silver benzoate (100 mg) in Et_3N (3 ml) was added at r.t. during 30 min to a stirred soln of **11** (980 mg) in dry MeOH (20 ml). After the addition the mixture was stirred at room temp. for 1 h and then MeOH was removed. Usual[9] work-up afforded **12** as an oil (770 mg, 77%), b.p. 138–140° (bath)/0.1 mm; δ (CCl_4) 1.53–2.9 (m, 14H), 3.67 (s, 3H), 3.77 (s, 3H), 6.6 (d, 1H, J = 8 Hz), 6.93 (d, 1H, J = 8 Hz). Found: C, 73.22; H, 8.68. $C_{16}H_{22}O_3$ requires: C, 73.25; H, 8.45%.

Compound **12** (720 mg) was hydrolysed by refluxing for 4 hr with a soln of KOH (700 mg) in MeOH (6 ml) and water (1 ml). Usual work-up afforded **13** (620 mg, 91%), m.p. 122°; ν_{max} (KBr) 1700, 1590 cm^{-1}. Found: C, 72.59; H, 8.35. $C_{15}H_{20}O_3$ requires: C, 72.55; H, 8.12%.

9-Methoxy-1-oxo-1,2,3,4,5,6,7,8-octahydrophenanthrene **20**. The acid **13** (1.7 g) was added to PPA [prepared from P_2O_5 (12 g) and H_3PO_4 (7 ml, 89%)] at 100° in small portions during 10 min and the contents were mixed thoroughly after each addition. The mixture was stirred at 100° for another 15 min and then poured on ice. Usual work-up afforded **20** (1.4 g, 88.8%), m.p. 85° (Et_2O–light petroleum); ν_{max} (KBr) 1668, 1590 cm^{-1}; δ ($CDCl_3$) 1.6–2.87 (m, 14H), 3.85 (s, 3H), 7.38 (s, 1H). Found: C, 77.92; H, 8.09. $C_{15}H_{18}O_2$ requires: C, 78.23; H, 7.88%.

2-Cyano-9-methoxy-1-oxo-1, 2, 3, 4, 5, 6, 7, 8-octahydrophenanthrene **21**. A soln of ethyl formate (1.5 ml) in dry benzene (6 ml) was added under N_2 to an ice-cold stirred suspension of NaH (300 mg) in benzene (5 ml) containing one drop of abs EtOH. To this mixture was added a soln of **20** (1.3 g) in benzene (8 ml) during 30 min. After stirring at 0° for 2 hr, the mixture was left at room temp. for 16 h. Usual work-up[10] afforded the formyl derivative (1.4 g) which was used for the next step without further purification.

A soln of the above crude formyl compound in glacial AcOH (20 ml) was treated with powdered $NH_2OH \cdot HCl$ (900 mg) and the mixture was quickly heated (bath temp. 170°) to boiling for 10 min. AcOH was removed under reduced pressure. The residue was diluted with water and worked up to afford the isoxazole derivative (1.32 g) as a reddish solid.

To an ice-cold stirred soln of the above crude isoxazole derivative in dry THF (25 ml) was added during 20 min a cold soln of NaOMe, prepared from Na (250 mg) and dry MeOH (5 ml). The mixture was stirred at 0° for 2 h and then left at 10° for 16 h. Work-up[10] of the reaction mixture afforded the crude cyanoketone. Chromatography over silica gel (30 g) and elution with Et_2O–C_6H_6 (1:1) furnished **21** (1.06 g, 73.5%), m.p. 185–186° (from Et_2O–light petroleum); ν_{max} (KBr) 2245, 1685, 1590 cm^{-1}; δ ($CDCl_3$) 1.58–2.0 (m, 4H), 2.15–3.1 (m, 8H), 3.52–3.72 (t, 1H), 3.85 (s, 3H), 7.37 (s, 1H). Found: C, 75.15; H, 6.57; N, 5.30. $C_{16}H_{17}NO_2$ requires: C, 75.27; H, 6.71; N, 5.49%.

2-Cyano-9-methoxy-3,4,5,6,7,8-hexahydrophenanthrene **22**. $NaBH_4$ (300 mg) was added in small portions during 20 min to a cold (ice-bath) stirred soln of **21** (1 g) in MeOH (70 ml) and THF (30 ml). After the addition the mixture was stirred at 0° for 2 h and left at 10° for 10 h. The mixture was then diluted with water, acidified with AcOH and extracted with ether. After the removal of the solvent, the crude hydroxy-nitrile [ν_{max} (KBr) 3470, 2250, 1600 cm^{-1}] was dissolved in dry benzene (120 ml) and refluxed for 12 h under N_2 with toluene-p-sulphonic acid (80 mg). The mixture was cooled, washed with sat $NaHCO_3$ aq and then with water. Removal of benzene left a residue which was evaporatively distilled at 160°/0.01 mm to furnish a colourless solid product. Crystallisation of this material from Et_2O–light petroleum afforded **22** (700 mg, 74.7%), m.p. 150° (Et_2O–light petroleum); ν_{max} (KBr) 2200, 1622, 1595 cm^{-1}, δ ($CDCl_3$) 1.49–1.92 (m, 4H), 2.43–2.87 (m, 8H), 3.8 (s, 3H), 6.5 (s, 1H), 7.12 (s, 1H). Found C, 79.99; H, 7.02; N, 5.77. $C_{16}H_{17}NO$ requires: C, 80.3; H, 7.16; N, 5.85%.

2-Cyano-9-methoxy-1,2,3,4,5,6,7,8-octahydrophenanthrene **23**. To a stirred soln of **22** (600 mg) in dry MeOH (40 ml) was added Mg-turnings (3 g) at room temp. An exothermic reaction ensued after 45 min and was moderated with an ice-bath. The mixture was stirred in the cold (ice-bath) for 1 h and at room temp. for

5 h. The reaction mixture was then cooled, decomposed carefully with cold dil HCl (6N) and worked-up with benzene. The crude product was evaporatively distilled at 160°/0.01 mm to afford a solid material which on crystallisation from Et_2O–light petroleum furnished **23** (540 mg, 89%), m.p. 170°; ν_{max} (KBr) 2240, 1600 cm^{-1}; δ ($CDCl_3$) 1.58–3.18 (m, 15H), 3.78 (s, 3H), 6.43 (s, 1H). Found: C, 79.76; H, 7.76; N, 5.93. $C_{16}H_{19}NO$ requires: C, 79.63; H, 7.94; N, 5.80%.

2-Carboxy-9-methoxy-1,2,3,4,5,6,7,8-octahydrophenanthrene **24**. The compound **23** (500 mg) was hydrolysed by refluxing under N_2 for 24 h. with a soln of KOH (4 g) in MeOH (17 ml) and water (3 ml). The crude acidic product was chromatographed over silica gel (15 g). Elution with Et_2O–light petroleum furnished **24** (440 mg, 81.5%), m.p. 168–169° (Et_2O–light petroleum); ν_{max} (KBr) 1700, 1600 cm^{-1}, δ ($CDCl_3$) 1.55–3.15 (m, 15H), 3.77 (s, 3H), 6.48 (s, 1H). Found: C, 73.66; H, 7.94. $C_{16}H_{20}O_3$ requires: C, 73.82; H, 7.74%.

Tetracyclo[10.2.2.0^{2,7}.0^{1,10}]hexadeca-2(7),9-diene-8,13-dione **8**. A soln of the crude diazoketone **25** [prepared in the usual[12] manner from **24** (400 mg) as a yellow solid] in CH_2Cl_2 (12 ml) was added during 3 min at −25° to a stirred mixture of TFA (12 ml) and CH_2Cl_2 (15 ml). The mixture was stirred at −25° for another 3 min, diluted with CH_2Cl_2 (30 ml) and washed with water. The solvent was dried and evaporated off. The crude product on chromatography over silica gel (10 g) and elution with Et_2O–light petroleum (3:7) furnished **8** (90 mg, 24%), m.p. 126–127° (from Et_2O–light petroleum); λ_{max} 248 nm (log ϵ 4.18); ν_{max} (KBr) 1720, 1662, 1620 cm^{-1}; δ ($CDCl_3$) 1.4–2.98 (m, 17H), 6.25 (t, 1H, small allylic coupling). Found: C, 79.20; H, 7.67. $C_{16}H_{18}O_2$ requires: C, 79.31; H, 7.49%.

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