

Synthesis of 1,6,7-Triphenyltricyclo[4.1.0.0^{2,7}]heptan-3-one and Rearrangement of 3-(1,2,3-Triphenylcycloprop-2-enyl)propanoic Acid

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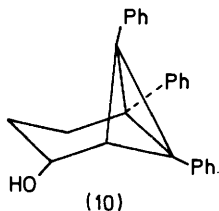
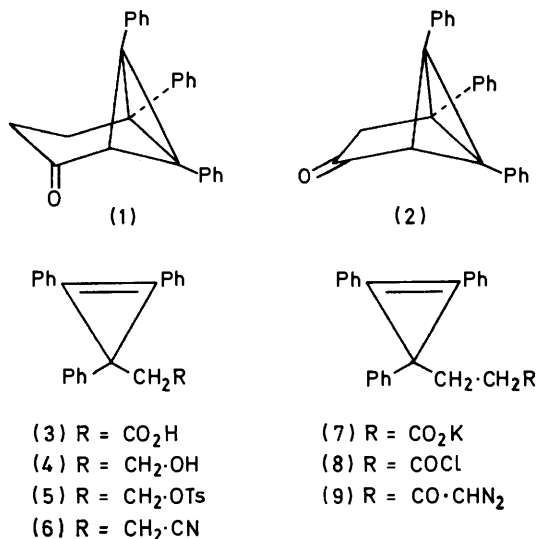
Copper-catalysed thermal decomposition of 1-diazo-4-(1,2,3-triphenylcycloprop-2-enyl)butan-2-one (9), synthesised by conventional procedures from (1,2,3-triphenylcycloprop-2-enyl)acetic acid, produced 1,6,7-triphenyltricyclo[4.1.0.0^{2,7}]heptan-3-one (1). The reaction of 3-(1,2,3-triphenylcycloprop-2-enyl)propanoic acid with oxalyl chloride gave 2,3,4-triphenylphenol, which was also prepared by an independent synthesis.

SYNTHESES of 1,5,5-trimethyltricyclo[4.1.0.0^{2,7}]heptan-3-one¹ and tetracyclo[6.1.0.0^{2,9}.0^{4,7}]non-5-en-3-one² by photochemical rearrangement have been reported. Our synthesis of the analogous 1,6,7-triphenyltricyclo[4.1.0.0^{2,7}]heptan-3-one (1) involves an intramolecular carbene addition reaction similar to the one used to prepare 1,5,6-triphenyltricyclo[3.1.0.0^{2,6}]hexan-3-one (2).³

When the diazo-ketone (9), prepared by a classical chain extension of the known (1,2,3-triphenylcycloprop-2-enyl)acetic acid (3) (see Experimental section), was heated in benzene in the presence of copper powder a 42% yield of ketone (1) was obtained. The i.r. spectrum

and was similar to the spectra of the known phenylated tricyclo[3.1.0.0^{2,6}]hexan-3-ones. For example, the ketone (2) showed a shoulder at 243 nm ($\log \epsilon$ 4.23)³ and 1,6-diphenyltricyclo[3.1.0.0^{2,6}]hexan-3-one showed a maximum at 255 nm ($\log \epsilon$ 4.08).⁴ The n.m.r. spectrum had a 15-proton multiplet centred at δ 7.2 (3 Ph), a one-proton singlet at 3.4 [bridgehead proton; cf. 3.2 for (2)], and a four-proton sextet (two superimposed triplets, J 5 Hz) centred at 2.7 [methylene protons; cf. 2.6 for (2)]. Further evidence for the structure (1) is based on its reduction with lithium aluminium hydride to the alcohol (10), which showed the expected spectroscopic properties.

3-(1,2,3-Triphenylcycloprop-2-enyl)propanoic acid (11) rearranged in the presence of an excess of oxalyl chloride to 2,3,4-triphenylphenol. No attempt was made to optimize the yield (ca. 50%). The phenol was also synthesised independently by a route (Scheme 1) based on phenol syntheses by Zimmerman and his co-workers.⁵ A formal mechanism for the rearrangement is given in Scheme 2. We cannot say exactly what kind of cation is interacting with the three-membered ring or whether it is the ring single bond or double bond which is interacting with the positive centre. However, this ready rearrangement may be compared with the work of Moerck and Battiste on the reaction of 2*H*-azirines with cyclopropenyl cations.⁶ These authors have substantiated a mechanism for pyridine formation (Scheme 3) which involves a cyclopropenylcarbinyl-cyclobutenyl cation type ring expansion (path *a*) rather than attack on the ring by a γ -cation (path *b*) as proposed by Stehouwer and Longone for the reaction of cyclopropenyl cations with cyclopropenes.⁷ In our case, where the former mechanism is not possible, ready cyclization still occurs.



showed a peak at 1 710 cm⁻¹ typical of a six-membered ring ketone. (Ipaktschi's ketone¹ had a peak at 1 700 cm⁻¹; Yano's² at 1 695 cm⁻¹). The u.v. spectrum showed maxima at 255 ($\log \epsilon$ 4.15) and 223 nm (4.34),

EXPERIMENTAL

M.p.s were determined with a Mel-temp apparatus. N.m.r. spectra were run on a Varian A-60 spectrometer, u.v. spectra on a Cary 14 spectrophotometer, i.r. spectra on a Perkin-Elmer 127 Infracord, and mass spectra on an A.E.I. MS12 spectrometer.

2-(1,2,3-Triphenylcycloprop-2-enyl)ethanol (4).—To a stir-

⁵ H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, 1962, **84**, 4527; H. E. Zimmerman and J. O. Grunewald, *ibid.*, 1967, **89**, 5163.

⁶ R. E. Moerck and M. A. Battiste, *Tetrahedron Letters*, 1973, 4421.

⁷ D. M. Stehouwer and D. T. Longone, *Tetrahedron Letters*, 1969, 5311.

¹ J. Ipaktschi, *Chem. Ber.*, 1972, **105**, 1996.

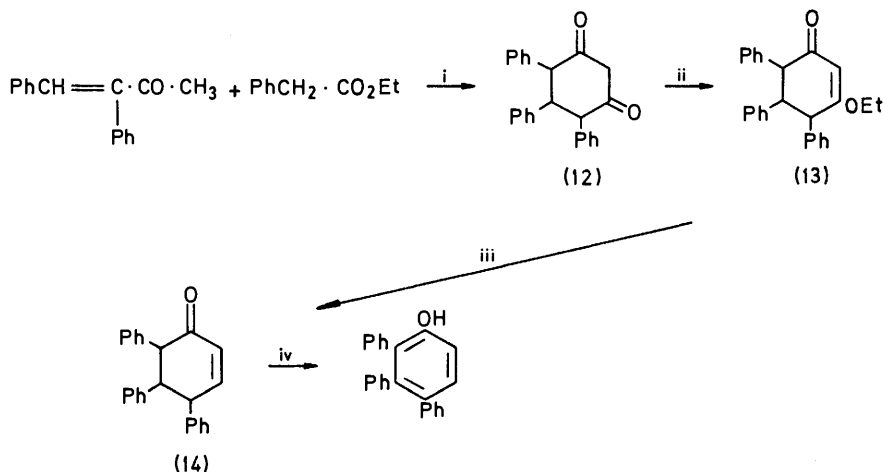
² K. Yano, *Tetrahedron Letters*, 1974, 1861.

³ A. S. Monahan, *J. Org. Chem.*, 1968, **33**, 1441.

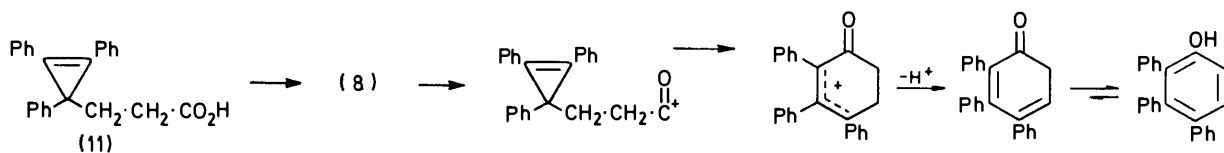
⁴ S. Masamune, *Tetrahedron Letters*, 1965, 945.

red solution of lithium aluminium hydride (1.2 g, 32 mmol) in anhydrous ether (50 ml) was added, in small portions, (1,2,3-triphenylcycloprop-2-enyl)acetic acid (3) (5.0 g, 15 mmol). The mixture was refluxed for 1 h and decomposed with water followed by 6*N*-hydrochloric acid. The mixture was extracted twice with ether, and the extract was washed twice with water, dried (MgSO₄), filtered, and evaporated *in vacuo* to give the alcohol (4) (4.21 g, m.p. 103–105°, and a second crop (0.86 g; total 5.07 g, 102%). Recrystallization twice from ethanol–heptane gave material with m.p.

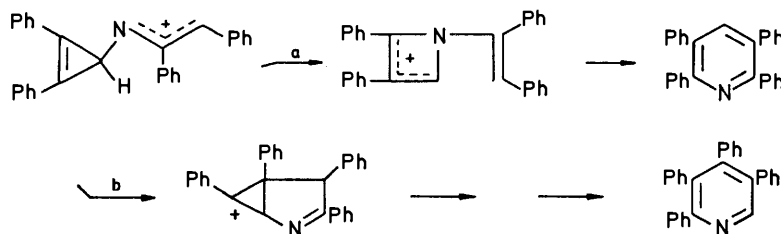
111–111.5° after drying under vacuum. A sample for analysis had m.p. 112.5–114.5°; ν_{\max} (KBr) 3 610 (O–H) and 1 820 cm⁻¹ (diphenylcyclopropene); δ (CDCl₃) 7.0–8.1 (15 H, m, Ph), 3.7 (2 H, t, *J* 7 Hz, CH₂–OH), 2.7 (2 H, t, *J* 7 Hz, CH₂–CH₂–OH), and 1.5 (1 H, s, OH); λ_{\max} (EtOH) 332 (log ϵ 4.33), 312 (4.42), 229 (4.41), and 302sh nm (4.32) (Found: C, 88.8; H, 6.7%; *M*⁺, 312.1514. C₂₃H₂₀O requires C, 88.4; H, 6.45%; *M*, 312.1514).



SCHEME 1 Reagents: i, NaOEt; ii, TsOH, EtOH; iii, LiAlH₄; iv, Br₂, AcOH



SCHEME 2



SCHEME 3

111–111.5° after drying under vacuum. A sample for analysis had m.p. 112.5–114.5°; ν_{\max} (KBr) 3 610 (O–H) and 1 820 cm⁻¹ (diphenylcyclopropene); δ (CDCl₃) 7.0–8.1 (15 H, m, Ph), 3.7 (2 H, t, *J* 7 Hz, CH₂–OH), 2.7 (2 H, t, *J* 7 Hz, CH₂–CH₂–OH), and 1.5 (1 H, s, OH); λ_{\max} (EtOH) 332 (log ϵ 4.33), 312 (4.42), 229 (4.41), and 302sh nm (4.32) (Found: C, 88.8; H, 6.7%; *M*⁺, 312.1514. C₂₃H₂₀O requires C, 88.4; H, 6.45%; *M*, 312.1514).

2-(1,2,3-Triphenylcycloprop-2-enyl)ethyl Toluene-*p*-sulphonate (5).—To toluene-*p*-sulphonyl chloride (2.56 g, 13 mmol) dissolved in pyridine (35 ml) was added the alcohol (4) (4.21 g, 13 mmol). The mixture was swirled until the alcohol had dissolved and then left in the refrigerator overnight. The resulting mixture was poured into dilute

(EtOH) 330 (log ϵ 4.37), 313 (4.47), 225 (4.61), and 300sh nm (4.36) (Found: C, 77.0; H, 5.8. C₃₀H₂₆O₃S requires C, 77.2; H, 5.6%).

3-(1,2,3-Triphenylcycloprop-2-enyl)propanonitrile (6).—To dimethyl sulphoxide (45 ml; freshly distilled *in vacuo* from calcium hydride) was added the tosylate (5) (1.60 g, 3.4 mmol). The stirred solution was heated to 40 °C, then sodium cyanide (0.30 g, 6.1 mmol; dried at 110 °C for 2 days) was added. The heat was removed and the temperature of the mixture rose to 75 °C. The mixture was allowed to cool to room temperature and poured into water (400 ml). The dimethyl sulphoxide–water layer was extracted three times with ether and the combined ether layers were washed three times with water, dried (MgSO₄), and evaporated *in*

vacuo yielding white crystals (1.1 g), m.p. 151–154°. Recrystallization from ethanol gave material (1.0 g, 91%), m.p. 154–155°; ν_{\max} (KBr) 2 220 (C≡N) and 1 820 cm⁻¹ (diphenylcyclopropene); δ (CDCl₃) 7.3 (15 H, m, Ph), 2.8 (2 H, t, *J* 7.5 Hz, CH₂·CN), and 2.2 (2 H, t, *J* 7.5 Hz, CH₂·CH₂·CN); λ_{\max} (MeCN) 331 (log ϵ 4.38), 314 (4.45), and 300sh nm (4.32) (Found: C, 89.95; H, 6.15; N, 4.15. C₂₄H₁₉N requires C, 89.7; H, 5.96; N, 4.35%).

3-(1,2,3-Triphenylcycloprop-2-enyl)propanoic Acid (11).—To a solution of potassium hydroxide (38 g, 0.56 mol) in aqueous 30% ethanol was added the nitrile (6) (0.50 g, 1.5 mmol). The mixture was stirred under reflux for 20 h. The resulting solution was poured into water (600 ml) and extracted three times with ether. To the basic water layer was slowly added an excess of ice-cold 40% hydrochloric acid. Then the mixture was extracted three times with ether and these extracts were washed three times with water, dried (MgSO₄), and evaporated *in vacuo*. The product was crystallized from ethanol–water yielding white crystals (0.22 g), m.p. 152–154° (second crop 0.20 g). Recrystallization twice from 95% ethanol gave material (0.35 g, 69%), m.p. 157–158°; ν_{\max} (KBr) 2 850–2 000 (CO₂H), 1 820 (diphenylcyclopropene), 1 700 (C=O), and 1 270 cm⁻¹ (C–O); δ (CDCl₃) 10.2 (1 H, s, CO₂H), 7.3 (15 H, m, Ph), and 2.2–2.7 (4 H, m, CH₂·CH₂); λ_{\max} (MeCN) 332 (log ϵ 4.29) 315 (4.36), and 300sh nm (4.25) (Found: C, 84.6; H, 6.0. C₂₄H₂₀O₂ requires C, 84.7; H, 5.9%).

Potassium 3-(1,2,3-Triphenylcycloprop-2-enyl)propanoate (7).—The work-up of the hydrolysis of the nitrile (6) was altered as follows: the reflux condenser was replaced with a distillation head and all the ethanol was distilled off. The solution was allowed to cool to room temperature, during which time a brownish white solid appeared; this was collected by suction filtration, then washed with ice-cold water. The material was broken up and kept at 110 °C for 24 h; m.p. 237–239° (decomp.); ν_{\max} (KBr) 1 820 (diphenylcyclopropene), 1 600, and 1 410 cm⁻¹ (CO₂⁻).

1-Diazo-4-(1,2,3-triphenylcycloprop-2-enyl)butan-2-one (9).—To a stirred suspension of the salt (7) (1.05 g, 2.8 mmol) in dry benzene (200 ml) was added oxalyl chloride (3.6 g, 28 mmol); then the flask was stoppered with a drying tube (CaCl₂). The solution was stirred for 20 min; then the excess of oxalyl chloride and benzene were removed *in vacuo*. The residue was washed with dry benzene (10 ml); the benzene was removed *in vacuo*. This procedure was repeated twice. The white residue showed ν_{\max} (CHCl₃) 1 790 cm⁻¹ (C=O).

The crude acid chloride was dissolved in dry benzene (20 ml) and added dropwise to a stirred solution of diazomethane (two-fold excess) in anhydrous ether at room temperature. The flask was covered with aluminium foil and the mixture stirred for 3 h at room temperature. The solvent was removed *in vacuo* (no heat) yielding a yellow oil. Treatment with a small amount of anhydrous ether caused crystallization. The crude solid was recrystallized from dichloromethane–hexane, yielding a powdery yellow solid (0.68 g, 67%); ν_{\max} (KBr) 2 100 (diazo-ketone), 1 820 (diphenylcyclopropene), and 1 640 cm⁻¹ (C=O); λ_{\max} (MeCN) 333 (log ϵ 4.30), 316 (4.38), 299 (4.32), 285 (4.29), and 230 nm (4.46); (CDCl₃) 7.1–7.9 (15 H, m, Ph), 5.0 (1 H, s, CH), and 2.1–3.0 (4 H, m, CH₂·CH₂).

1,6,7-Triphenyltricyclo[4.1.0.0^{2,7}]heptan-3-one (1).—To a refluxing mixture of copper powder (0.8 g) and dry benzene (40 ml) under nitrogen was added dropwise (35 min) the diazo-ketone (9) (0.507 g, 1.4 mmol) dissolved in dry benzene

(40 ml). The mixture was refluxed for another 1.5 h, then cooled to room temperature, and filtered. The benzene was removed *in vacuo* yielding a dark greenish-yellow oil. Upon addition of a small amount of anhydrous ether, the oil dissolved and a yellow solid was precipitated (0.222 g), m.p. 136–142°. After four recrystallizations from 95% EtOH the m.p. was 136–142° and the yield 0.202 g (42%); ν_{\max} (KBr) 1 710 cm⁻¹ (six-membered ring C=O); λ_{\max} (MeCN) 255 (log ϵ 4.15) and 223 nm (4.34); δ (CDCl₃) 7.2 (15 H, m, Ph), 3.4 (1 H, s, CH), and 2.7 (4 H, m, CH₂·CH₂) (Found: C, 89.0; H, 6.05. C₂₅H₂₀O requires C, 89.25; H, 5.9%).

1,6,7-Triphenyltricyclo[4.1.0.0^{2,7}]heptan-3-ol (10).—To anhydrous ether (25 ml) and lithium aluminium hydride (200 mg, 5.9 mmol) cooled in an ice-bath was added with stirring the ketone (1) (0.17 g, 0.49 mmol). The mixture was stirred for 20 min at ice-bath temperature, then hydrolysed with water. The two layers were separated and the aqueous layer extracted three times with ether. The ethereal portions were combined, dried (MgSO₄), and concentrated *in vacuo* yielding a pale yellow oil which could be crystallized with difficulty, affording white flowers, m.p. 128.5–131° (from dichloromethane–hexane). Two recrystallizations gave material (0.073 g, 43%) of m.p. 130.5–131.5°; ν_{\max} (KBr) 3 300 (O–H) and 1 060 cm⁻¹ (C–OH); λ_{\max} (MeCN) 227 (log ϵ 4.09) and 243sh nm (4.06); δ (CDCl₃) 7.0 (15 H, m, Ph), 4.0 (1 H, m, CH·OH), 3.2 (1 H, d, *J* 3 Hz, CH·CH·OH), 2.1 (2 H, m, CH₂·CH·OH), and 1.8 (3 H, m, CH₂·CH₂·CH·OH and OH); *m/e* 338 (*M*⁺) and 320 (*M* – 18). Because of difficulties in separation from impurities, a satisfactory analysis was not obtained.

Rearrangement of the Acid (11) to 2,3,4-Triphenylphenol.—A mixture of an excess of oxalyl chloride and the acid (11) (0.50 g, 1.4 mmol) was kept at room temperature for 12 h protected from moisture (CaCl₂). The excess of oxalyl chloride was removed *in vacuo*, leaving a yellow solid which was recrystallized from benzene–hexane giving white crystals (0.28 g), m.p. 152–154°. A sample recrystallized from dichloromethane–hexane (yield 0.23 g, 51%) had m.p. 156.0–156.5°; ν_{\max} (KBr) 3 450 (OH) and 1 190 cm⁻¹ (phenolic C–O); δ (CDCl₃) 7.2 (17 H, m, Ph) and 4.7 (1 H, s, OH); λ_{\max} (MeCN) 236 nm (log ϵ 4.72); (Found: C, 89.2; H, 5.6. C₂₄H₁₈O requires C, 89.4; H, 5.65%).

4,5,6-Triphenylcyclohexane-1,3-dione (12).—To a solution of sodium (2.4 g, 0.10 mmol) in absolute ethanol (50 ml) was added absolute ethanol (50 ml) containing 3,4-diphenylbut-3-en-2-one⁸ (14.2 g, 63 mmol) and ethyl phenylacetate (10.2 g, 63 mmol). The mixture was refluxed for 24 h and cooled to room temperature; then water (300 ml) was added. The brown precipitate was filtered off and the filtrate was concentrated *in vacuo*. To the filtrate was added glacial acetic acid (50 ml), producing an orange gum which was extracted three times with ether. The ethereal layer was shaken with 10% sodium hydrogen carbonate, then water, dried (MgSO₄), and evaporated *in vacuo* leaving a white solid, m.p. 191–198°. Recrystallization several times from dichloromethane–hexane gave material (5.8 g, 29%), m.p. 207–208° (decomp.); ν_{\max} (KBr) 2 000–2 800 (H-bonded enol) and 1 550–1 625 cm⁻¹ (enolic β -diketone); λ_{\max} (95% EtOH) 260 nm (log ϵ 4.19) (Found: C, 85.0; H, 5.65%; *M*⁺, 340.1465. C₂₄H₂₀O₂ requires C, 84.7; H, 5.9%; *M*, 340.1462).

3-Ethoxy-4,5,6-triphenylcyclohex-2-enone (13).—A solution of the ketone (12) (2.5 g, 7.3 mmol) and toluene-*p*-sulphonic

⁸ R. A. Abramovitch and A. Obach, *Canad. J. Chem.*, 1959, **37**, 502.

acid monohydrate (0.14 g, 7.3 mmol) in dry benzene (90 ml) and absolute ethanol (15 ml) was refluxed for 3.5 h with collection of water by azeotropic distillation. The mixture was concentrated to 20 ml and diluted with ether. The ethereal solution was washed with water, 5% sodium hydrogen carbonate, then water again, dried (MgSO_4), and evaporated *in vacuo*, leaving a dark yellow oil. From ether, white crystals were formed, m.p. 155–167°; total yield 1.42 g (53%); ν_{max} (KBr) 1 650 (C=O) and 1 600 cm^{-1} (C=C); δ (C_6D_6) 7.1 (15 H, m, Ph), 5.8 (1 H, s, =CH), 4.0 (5 H, m, PhCH and CH_2), and 1.2 (3 H, t, J 7 Hz, CH_3); λ_{max} (MeCN) 253 nm ($\log \epsilon$ 4.32) (Found: C, 84.75; H, 6.55. $\text{C}_{26}\text{H}_{24}\text{O}_2$ requires C, 84.75; H, 6.55%).

4,5,6-Triphenylcyclohex-2-enone (14).—To anhydrous ether (20 ml) and lithium aluminium hydride (50 mg, 1.3 mmol) under nitrogen was added dropwise (20 min) a solution of the ketone (13) (0.50 g, 1.3 mmol) in anhydrous ether (20 ml) and dry benzene (2 ml). The mixture was stirred for an additional 2 h at room temperature and then hydrolysed with 10% sulphuric acid. The layers were separated and the aqueous layer extracted three times with ether. The combined extracts were washed with water, dried (MgSO_4), and concentrated *in vacuo* leaving a yellow oil which was used directly.

A small amount of the oil was retained and crystallized

from ether–hexane; m.p. 129–130°; ν_{max} (film) 1 680 cm^{-1} (C=C=O); λ_{max} (95% EtOH) 265 nm ($\log \epsilon$ 4.00) (Found: C, 88.65; H, 6.2. $\text{C}_{24}\text{H}_{20}\text{O}$ requires C, 88.85; H, 6.2%).

2,3,4-Triphenylphenol.—The oil from the previous reaction was dissolved in 97% acetic acid (1 ml) and heated to 90 °C. Part (1.6 ml) of a solution of bromine (1.8 g, 22.5 mmol) in 97% acetic acid (10 ml) was added. The resulting solution was heated at 105 °C for 2 h, then allowed to cool to room temperature, and made basic to litmus by careful addition of saturated aqueous sodium hydrogen carbonate. During the addition, a brown solid appeared which was insoluble in the aqueous layer. The solid was taken up by extracting the aqueous layer three times with dichloromethane. The organic layer was washed three times with water, dried (MgSO_4), then concentrated *in vacuo* to yield a brown solid. Recrystallization twice from dichloromethane–hexane gave white crystals, m.p. 151–155°, mixed m.p. with the compound obtained from the reaction of the acid (11) with oxalyl chloride 153.5–155°. The i.r. spectra of the two samples were identical.

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