Preparation and Photocyclisation of Bromomethyl 1,2-Diketones

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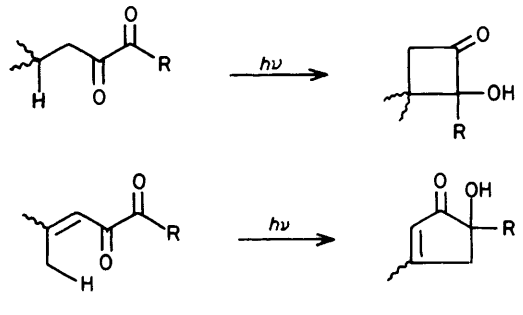
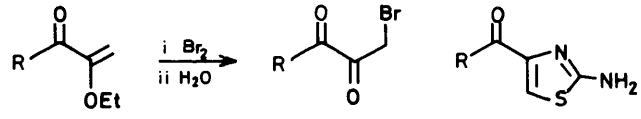
A simple preparative route to the title compounds is given involving bromine addition to α-ethoxyvinyl ketones and subsequent hydrolysis. These compounds undergo efficient photocyclisation with retention of the halogen to hydroxycyclobutanone and hydroxycyclopentanone derivatives.

Photocyclisation reactions of 1,2-diketones resulting from intramolecular γ-hydrogen abstraction may lead, depending on the structure of the diketone, to 2-hydroxycyclobutanones [1] or 5-hydroxycyclopent-2-enones [2] (Scheme) and are often extremely clean and efficient processes. However, with unsymmetrical diketones there may be competition from other γ-hydrogen abstractions [3] or intramolecular cycloaddition of one carbonyl group to an appropriately placed double bond.[4] For practical purposes in syntheses this restricts the reaction to symmetrical diketones or those where R is methyl or aryl (the latter not bearing an *o*-alkyl substituent). Since the latter groups cannot be readily removed or elaborated this imposes a serious limitation on the synthetic scope of the reaction. In the hope of removing, in part, this limitation we have examined the preparation and photochemical reactivity of α-bromomethyl 1,2-diketones.



Scheme



(1) (2) (3)

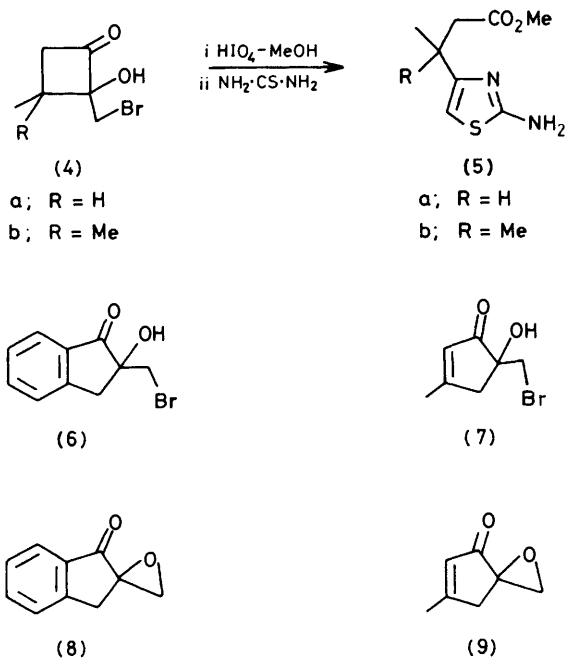
a; R = CH_2CH_2Me
b; R = CH_2CHMe_2
c; R = $CH_2C(Me)=CH_2$
d; R = Ph
e; R = *o*-MeC_6H_4
f; R = $CH=CMe_2$

No satisfactory general methods for the preparation of α-bromomethyl 1,2-diketones seem to have been reported. Acid-catalysed bromination of aryl methyl 1,2-diketones gives largely the mono-α-bromo-derivatives [5] but the reaction is slower and less clean than for the corresponding monoketones. However, unsymmetrical saturated diketones bearing hydrogen on both α-positions brominate preferentially at the more substituted site; *N*-bromosuccinimide behaves similarly.[6] In any event the procedures cannot be used for unsaturated diketones and we therefore investigated α-ethoxyvinyl ketones (1) as possible precursors. Compounds of this type were first reported [7] from the reaction of Grignards with the readily accessible α-alkoxyacrylonitriles, but details were sparse and subsequent workers have preferred to use methods based on elimination of alcohol from the monoacetals of 1,2-diketones as a route to these reportedly labile compounds.[8] Unfortunately this last method has no general utility but the original method provides a simple route to compounds (1) in good yield and in a high state of purity, without recourse to chromatography, provided the intermediate imine is extracted into aqueous acid and subsequently hydrolysed. The vinylic Grignard from 1-bromo-2-methylpropene [9] (prepared in TNF) gave a much poorer yield, but fortunately the diene (1c) was isomerised smoothly to (1f) by base in wet acetonitrile.

Bromine addition to compound (1) in dichloromethane gave the expected dibromide except in the case of compound (1c) when addition to the non-conjugated double bond competed giving rise to mixtures of products. It is possible that a more selective brominating agent would avoid this difficulty but since the non-conjugated bromo-ketones were not required in the present study this aspect was not pursued. Hydrolysis of the dibromides in aqueous acetonitrile gave excellent yields of the diones (2) which reacted with thiourea to give the expected 2-amino-4-acylthiazoles (3).[10]

Irradiation of the two saturated diketones (2a) and (2b) in benzene or methyl acetate solution through Pyrex caused rapid disappearance of the characteristic yellow colour with conversion into the appropriate 2-hydroxycyclobutanone (4) as sole products (t.l.c.). Their unambiguous characterisation presents a problem since the compounds very readily form hemiacetal dimers [11] and undergo a facile ketol rearrangement [12] in the presence of acid or base; in addition compound (4a) is a mixture of both epimers. However, their spectral data and periodic acid oxidation products [characterised after reaction with thiourea to the aminothiazoles (5)] establish the structures as those proposed. The conjugated diketones (1e) and (1f) were more sensitive to the conditions of photolysis and exclusion of light of wavelength $\lambda < 380$ nm was necessary to prevent darkening of the solution and evolution of hydrogen bromide. Methyl acetate was the solvent of choice and under these conditions the photocyclisation proceeded smoothly to give compounds (6) and (7) in 80—90% yield. On treatment with base these compounds gave, as expected, the epoxides (8) and (9); the indanone (6) was also reduced by zinc and acetic acid to 2-methylindan-1-one.

The retention of the halogen in these photocyclisations is in marked contrast to the photolytic behaviour of $n \longrightarrow \pi^*$ states of α-chloro-derivatives of monoketones where the primary photochemical process is generally fission of the C–Cl bond.[13] In the case of α-bromo-ketones the weaker C–Br bond energy makes it likely that this is the sole primary process, as seems to be borne out by the relatively few studies on such compounds.[14] Intramolecular H abstraction (analogous to the present example) is probably the initial step in the photoreaction of α-chloro-*o*-methylacetophenone [15] leading to indanone and photosolvolysis products, but on current evidence mechanisms involving C–Cl fission are not completely excluded. The difference in behaviour of α-halogenated mono- and di-ketones is no doubt partially attributable to the lower energy of the $N \longrightarrow \pi^*$ states (particularly S^1) but may



also reflect the greater stability of the semidione radicals, resulting from H abstraction, over the ketomethylene radicals, from halogen loss. However, the retention of the bromine in the photocyclisations reported here (a similar result may be expected for α-chloro-1,2-diketones) is gratifying from the point of view of synthesis since it provides a simple route to highly functionalised cyclobutanone and cyclopentenone derivatives.

Experimental

^{1}H N.m.r. spectra were obtained on a Varian HA100 spectrometer in carbon tetrachloride solution (unless otherwise stated) with tetramethylsilane as internal standard. I.r. spectra were obtained for Nujol mulls (solids) or liquid films. Preparative t.l.c. separations were conducted on Merck Kieselgel in acetone–hexane. Irradiations were carried out with a Philips 100-W medium-pressure Hg lamp cooled by a water jacket (Pyrex) using, where necessary, a filter solution (0.5 cm) of aqueous sodium nitrite solution (20%). 2-Ethoxyacrylonitrile was prepared from ethyl vinyl ether using the procedure of Rogers *et al.*[16] Ether refers to diethyl ether.

α-Ethoxyvinyl Ketones (1). *General Procedure.*—To a solution of the appropriate alkyl or aryl magnesium bromide (20 mmol) in ether (25 ml) was added 2-ethoxyacrylonitrile (14 mmol) in dry ether (5 ml) and the mixture was refluxed under N_2 with vigorous stirring for 18 h. After being cooled to 0 °C the resulting fine suspension was transferred rapidly to a vigorously stirred mixture of sulphuric acid (30 ml, 10%), crushed ice (100 g), and pentane (50 ml). Immediately the precipitate had dissolved (*ca.* 15 s) the aqueous layer was separated, the pH adjusted to 3.0—3.5 by the addition of aqueous disodium hydrogen phosphate, and pentane (50 ml) added. The mixture was stirred under N_2 at 25 °C until the aqueous layer became clear and then for a further 1 h after which time the organic layer was separated and the aqueous phase extracted with pentane (25 ml). The combined extracts were dried and evaporated under N_2 to give the products as pale yellow oils which darkened on exposure to air. ^{1}H N.m.r. spectroscopy indicated a purity >97%, and in view of the tendency of the neat liquids to oxidise and polymerise they were used without further purification. Yields and spectral data are as follows. 2-Ethoxyhex-1-en-3-one (1a) (65%), $\nu_{max.}$ 1 710 cm^{-1}; δ 0.9 (3 H, t, *J* 7 Hz), 1.0—1.5 (2 H, m), 1.4 (3 H, t, *J* 7 Hz) 2.6 (2 H, t, *J* 7 Hz), 3.75 (2 H, q, *J* 7 Hz), 4.2 (1 H, d, *J* 2 Hz), and 5.0 (1 H, d, *J* 2 Hz); 2-ethoxy-5-methylhex-1-en-3-one (1b) (78%), $\nu_{max.}$ 1 710 cm^{-1}; δ 0.9 (6 H, d, *J* 7 Hz), 1.4 (3 H, t, *J* 7 Hz), 2.1 (1 H, m), 2.4 (2 H, d, *J* 7 Hz), 3.75 (2 H, q, *J* 7 Hz), 4.2 (1 H, d, *J* 2 Hz), and 5.05 (1 H, d, *J* 2 Hz); 2-ethoxy-5-methylhexa-1,5-dien-3-one (1c) (81%), $\nu_{max.}$ 1 710 cm^{-1}; δ 1.4 (3 H, t, *J* 7 Hz), 1.8 (3 H, s), 3.3 (2 H, s), 3.75 (2 H, q, *J* 7 Hz), 4.2 (1 H, d, *J* 2 Hz), 4.75 (2 H, d, *J* 6 Hz), 5.2 (1 H, d, *J* 2 Hz), and 5.2 (1 H, d, *J* 2 Hz); 2-ethoxy-1-phenylprop-2-en-1-one (1d) (75%), $\nu_{max.}$ 1 690 cm^{-1}; δ 1.4 (3 H, t, *J* 7 Hz), 3.9 (2 H, q, *J* 7 Hz), 4.55 (1 H, d, *J* 2 Hz), 4.9 (1 H, d, *J* 2 Hz), 7.4 (3 H, m), and 7.8 (2 H, dd, *J* 6.5, 2 Hz); 2-ethoxy-1-*o*-methylphenylprop-2-en-1-one (1e) (63%), $\nu_{max.}$ 1 695 cm^{-1}; δ 1.4 (3 H, t, *J* 7 Hz), 2.4 (3 H, s), 3.75 (2 H, q, *J* 7 Hz), 4.55 (1 H, d, *J* 2 Hz), 4.9 (1 H, d, *J* 2 Hz), and 7.4 (4 H, m).

2-Ethoxy-5-methylhexa-1,4-dien-3-one (1f).—*Method A.* To magnesium turnings (0.50 g) and dry tetrahydrofuran (THF) (10 ml) under N_2 was added, dropwise with stirring, 1-bromo-2-methylprop-1-ene (2.7 g) in THF (25 ml) during 2 h followed, when reaction was complete, by 2-ethoxyacrylonitrile (1.3 g) in ether (5 ml). After 12 h at 50 °C the mixture was worked up as above to give the crude product which was purified by chromatography on silica to give a pale yellow oil (0.66 g), $\nu_{max.}$ 1 685 cm^{-1}; δ 1.4 (3 H, t, *J* 7 Hz), 1.8 (3 H, s), 2.2 (3 H, s), 3.75 (2 H, q, *J* 7 Hz), 4.2 (1 H, d, *J* 2 Hz), 5.0 (1 H, d, *J* 2 Hz), and 6.5 (1 H, s).

Method B. To a solution of the diene (1c) (1.5 g) in acetonitrile (6 ml) containing water (0.1 ml) was added 1,5-diazabicyclo[4.3.0]non-5-ene (0.30 g) and the mixture allowed to stand at room temperature until chromatography showed that isomerisation was complete (3—4 h). After addition of water (30 ml) the mixture was brought to pH 6 by the dropwise addition of dilute phosphoric acid and extracted with pentane (3 × 30 ml). The combined extracts were dried and evaporated to give the product (1.31 g) whose spectra were identical with the earlier sample.

1-Bromohexane-2,3-dione (2a).—To a solution of the olefin (1a) (2.0 g) in dry dichloromethane (25 ml) cooled to 0 °C was added, dropwise with stirring, a solution of bromine (1.0M) in dichloromethane until the brown colour persisted. Removal of the solvent at <10 °C gave a colourless oil which was taken up into acetonitrile (15 ml). After the addition of water (3.0 ml), the mixture was stirred at room temperature for 4 h, then diluted with water (40 ml) and extracted with pentane (5 × 20 ml). The combined extracts were dried and the solvent evaporated under reduced pressure to give the product as a bright yellow, lachrymatory oil (2.3 g) which was homogeneous on t.l.c., $\nu_{max.}$ 1 718 and 1 733 cm^{-1}; δ 0.9 (3 H, t, *J* 7 Hz), 1.1—1.7 (2 H, m), 2.7 (2 H, t, *J* 7 Hz), and 4.2 (2 H, s).

For analysis a sample was distilled, b.p. 76—78 °C at 11 mmHg (Found: C, 37.35; H, 4.7. $C_6H_9BrO_2$ requires C, 37.3; H, 4.6%). However with this and subsequent diketones the undistilled material was quite pure enough for the photolysis experiments.

A sample (100 mg) and thiourea (100 mg) in methanol (2 ml) was heated under reflux for 30 min, then poured into aqueous sodium hydrogen carbonate (10 ml of 2%) and the resulting solid recrystallised from chloroform–hexane to give 2-aminothiazol-4-yl propyl ketone (3a), m.p. 116—117 °C (Found: C, 49.25; H, 5.8; N, 16.3. $C_7H_{10}N_2OS$ requires C, 49.5; H, 5.9; N, 16.5%).

1-*Bromo*-5-*methylhexane*-2,3-*dione* (2b).—From the olefin (1b) (1.8 g), following a similar procedure, the product was obtained (2.05 g), b.p. 88—91 °C at 11 mmHg, $\nu_{max.}$ 1 716 and 1 733 cm^{-1}; δ 0.9 (6 H, d, *J* 7 Hz), 2.2 (1 H, m), 2.65 (2 H, d, *J* 7 Hz), and 4.2 (2 H, s) (Found: C, 40.15; H, 4.9. $C_7H_{11}BrO_2$ requires C, 40.55; H, 5.3%).

Reaction with thiourea as above gave 2-aminothiazol-4-yl isobutyl ketone (3b), m.p. 136—137 °C (Found: C, 52.6; H, 6.8; N, 15.6. $C_8H_{12}N_2OS$ requires C, 52.2; H, 6.5; N, 15.2%).

3-*Bromo*-1-*phenylpropane*-1,2-*dione* (2d).—From the olefin (1d) (2.5 g), following a similar procedure, the product was obtained (2.65 g), b.p. 118—121 °C at 3.0 mmHg (lit.,[5] 145 °C at 10 mmHg), $\nu_{max.}$ 1 690 and 1 728 cm^{-1}; δ 4.35 (2 H, s), 7.5 (3 H, m), and 8.0 (2 H, dd, *J* 8, 2 Hz).

Reaction with thiourea as above gave 2-aminothiazol-4-yl phenyl ketone (3d), m.p. 161—162 °C (lit.,[10] 161 °C).

3-*Bromo*-1-o-*methylphenylpropane*-1,2-*dione* (2e).—From the olefin (1e) (1.7 g) following the above procedure the product was obtained (1.9 g), b.p. 80—82 °C at 0.2 mmHg, $\nu_{max.}$ 1 690 and 1 730 cm^{-1}; δ 2.50 (3 H, s), 4.30 (2 H, s), and 7.6 (4 H, m) (Found: C, 50.1; H, 3.75. $C_{10}H_9BrO_2$ requires C, 49.8; H, 3.7%).

Reaction with thiourea gave 2-aminothiazol-4-yl 2-*o*-methylphenyl ketone (3e), m.p. 177—178 °C (Found: C, 60.4; H, 4.8; N, 12.8. $C_{11}H_{10}N_2OS$ requires C, 60.55; H, 4.6; N, 12.85%).

1-*Bromo*-5-*methylhex*-4-*ene*-2,3-*dione* (2f).—To compound (1f) (1.54 g) in dry, ethanol-free dichloromethane (15 ml) was added, dropwise with stirring during 15 min, a solution of bromine (1.60 g) in dichloromethane (20 ml), the temperature being maintained at 0 °C throughout the addition. The solvent was then evaporated off and the residue hydrolysed in aqueous acetonitrile as before to give the product (1.8 g), b.p. 85—88 °C at 10 mmHg, $\nu_{max.}$ 1 685 and 1 728 cm^{-1}; δ 2.0 (3 H, s), 2.25 (3 H, s), 4.2 (2 H, s), and 6.8 (1 H, s) (Found: C, 40.6; H, 4.8. $C_7H_9BrO_2$ requires C, 41.0; H, 4.4%).

Reaction with thiourea gave 2-aminothiazol-4-yl 2-methylprop-1-enyl ketone (3f), m.p. 125 °C (Found: C, 52.7; H, 5.4; N, 15.15. $C_8H_{10}N_2OS$ requires C, 52.7; H, 5.5; N, 15.4%).

2-*Bromomethyl*-2-*hydroxy*-3-*methylcyclobutanone* (4a).—A solution of the dione (2a) (2.0 g) in methyl acetate (150 ml) [with added 2,4,6-collidine (20 mg) to remove any traces of hydrogen bromide] was irradiated at 20 °C (external cooling) until the solution became colourless (30—40 min). Evaporation of the solvent gave a colourless gum (2.0 g), $\nu_{max.}$ 3 440 and 1 775 cm^{-1}; M^+ 192/194, whose ^1H n.m.r. spectrum was consistent with a mixture of the *cis*- and *trans*-isomers of the product, but which did not allow a detailed interpretation.

A sample (0.5 g) of the product was treated at 0 °C with a solution of periodic acid (0.6 g) in methanol (6 ml). After 5 min a solution of thiourea (0.5 g) in methanol (5 ml) was added, the mixture refluxed for 20 min, then poured into aqueous sodium hydrogen carbonate (25 ml of 4%). The resulting suspension was extracted with chloroform (3 × 45 ml), the combined extracts dried ($MgSO_4$), and the solvent removed under reduced pressure. Recrystallisation of the residue from carbon tetrachloride–hexane gave methyl 3-(2-aminothiazol-4-yl)butyrate (5a) (266 mg), m.p. 81—82 °C, δ 1.3 (3 H, d, *J* 7 Hz), 2.5, 2.75 (2 H, ABx, J_{AB} 15 Hz; J_{Ax} 8 Hz; J_{Bx} 6 Hz), 3.25 (1 H, m), 3.7 (3 H, s), 5.6 (1 H, br s), and 6.1 (1 H, s) (Found: C, 47.7; H, 6.1; N, 14.0. $C_8H_{12}N_2O_2S$ requires C, 48.0; H, 6.0; N, 14.0%).

2-*Bromomethyl*-2-*hydroxy*-3,3-*dimethylcyclobutanone* (4b).—A similar irradiation of compound (2b) (1.0 g) in methyl acetate (120 ml) gave, after evaporation of the solvent, a gum (1.0 g), $\nu_{max.}$ 3 445 and 1 775 cm^{-1}; M^+ 206/208; δ 1.25 (3 H, s), 1.35 (3 H, s), 2.65, 2.9 (2 H, ABq, *J* 17 Hz), 3.65 (2 H, s), and 2.9 (1 H, br s, exchange D_2O).

Oxidation of a sample (0.5 g) with periodic acid followed by reaction with thiourea as before gave methyl 3-(2-aminothiazol-4-yl)-3-methylbutyrate (5b) (296 mg), m.p. 115—116 °C; δ 1.3 (6 H, s), 2.6 (2 H, s), 3.55 (3 H, s), 5.25 (1 H, br s), and 6.1 (1 H, s) (Found: C, 50.45; H, 6.75; N, 12.75. $C_9H_{14}N_2O_2S$ requires C, 50.45; H, 6.55; N, 13.1%).

2-*Bromomethyl*-2-*hydroxyindan*-1-*one* (6).—A solution of the olefin (1e) (1.2 g) in methyl acetate (150 ml) containing 2,4,6-collidine (50 mg) was irradiated as before (using the sodium nitrite solution filter) until the yellow colour had faded, during which time a small amount of collidine hydrochloride separated. The solvent was then evaporated, the residue taken up in warm ether (25 ml), and washed with dilute hydrochloric acid (5 ml) and then aqueous sodium hydrogen carbonate (10 ml of 5%). After drying the ether was removed and the resulting solid recrystallised from carbon tetrachloride–hexane to give the product (0.88 g), m.p. 88—89 °C, $\nu_{max.}$ 3 385 and 1 715 cm^{-1}; δ 3.3, 3.5 (2 H, ABq, *J* 18 Hz), 3.45 (1 H, br s, exchanges D_2O), 3.6 (2 H, s), and 7.3—7.5 (4 H, m) (Found: C, 49.85; H, 4.05. $C_{10}H_9BrO_2$ requires C, 49.8; H, 3.75%).

From the mother liquors there was obtained by preparative t.l.c. a further 0.11 g of the product.

Indan-2-*spiro*-*oxiran*-1-*one* (8).—To a cooled solution of compound (6) (220 mg) in dry ether (10 ml) was added 1,5-diazabicyclo[4.3.0]non-5-ene (150 mg) and, after 5 min, sodium dihydrogen phosphate (10 ml, 10%). The organic layer was separated, the aqueous layer extracted with ether (2 × 20 ml), and the combined extracts dried and evaporated to give the crude product (121 mg) which was homogeneous on t.l.c. Recrystallisation from ether–hexane gave colourless crystals, m.p. 74—75 °C, $\nu_{max.}$ 1 720 cm^{-1}; δ 3.05, 3.15 (2 H, ABq, *J* 7 Hz), 3.30, 3.35 (2 H, ABq, *J* 18 Hz), and 7.3—7.8 (4 H, m) (Found: C, 74.8; H, 5.15. $C_{10}H_8O_2$ requires C, 75.0; H, 5.0%).

5-*Bromomethyl*-5-*hydroxy*-3-*methylcyclopent*-2-*en*-1-*one* (7).—Irradiation of a solution of compound (2f) (0.85 g) in methyl acetate (120 ml), following a similar procedure to that for (2e), gave after work-up the product (0.74 g) which, after recrystallisation from carbon tetrachloride–hexane, had m.p. 49—50 °C, $\nu_{max.}$ 1 710 cm^{-1}; δ 2.2 (3 H, s), 2.5, 2.6 (2 H, ABq, *J* 17 Hz), 3.55 (2 H, s), 3.6 (1 H, br s, exchanges D_2O), and 5.9 (1 H, br s) (Found: C, 41.05; H, 4.6; Br, 38.9. $C_7H_9BrO_2$ requires C, 41.0; H, 4.4; Br, 39.0%).

6-*Methyl*-1-*oxaspiro*[2.4]*hept*-5-*en*-4-*one* (9).—Treatment of compound (7) (520 mg) with DBN (400 mg) under similar conditions to those for compound (6) gave, after work-up as before, the crude product (310 mg) which was purified by distillation, b.p. 54—57 °C at 10 mmHg, $\nu_{max.}$ 1 720 cm^{-1}; δ 2.0 (3 H, s), 2.6 (2 H, br s), 2.75, 2.80 (2 H, ABq, *J* 7 Hz), and 5.8 (1 H, br s) (Found: C, 68.1; H, 6.7. $C_7H_8O_2$ requires C, 67.75; H, 6.45%).

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