557. *Reduced Cyclic Compounds. Part XII.* Further Diels–Alder Reactions of* 1-1′-*Acetoxyvinylcyclohexene.*

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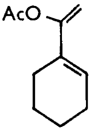
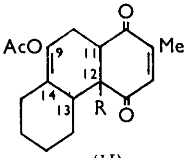
The Diels–Alder reaction of 1-1′-acetoxyvinylcyclohexene with toluquinone, 2,5-xyloquinone, and 6- and 5-methoxytoluquinone are reported. Except in the last case the structures of the products obtained were determined. The aromatisation of certain Diels–Alder adducts in boiling methanol is reported.

The recorded[1,2] Diels–Alder reactions of 1-1′-acetoxyvinylcyclohexene (I) include only one example,[1] 2,6-xyloquinone, of the use of an unsymmetrically substituted *p*-benzoquinone as a dienophil. We now report the reaction of this diene with toluquinone, 2,5-xyloquinone, and 5- and 6-methoxytoluquinone.

The diene (I) reacted with toluquinone exclusively at the unsubstituted double bond, to give a mixture of the adducts (II; R = H) and (III; R = H, R′ = Me). The structure of the former was established by reduction with lithium aluminium hydride (two reductions were necessary; cf. ref. 1), followed by dehydration and dehydrogenation to 2-methylphenanthrene. The ultraviolet spectrum of this adduct had its main maximum at 240 mμ, which is identical with the main maximum[1] for the compound (III; R = R′ = Me), an ene-dione of the same substitution type. The second adduct (III; R = H, R′ = Me) was not obtained pure, but its structure was shown by degradation to 3-methylphenanthrene.



(I)



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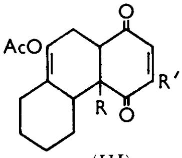

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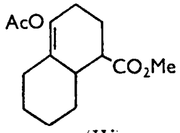

(IV)

The reaction between 2,5-xyloquinone and 1-1′-acetoxyvinylcyclohexene yielded a homogeneous product which was shown by degradation to 2-methylphenanthrene to be 9-acetoxy-$\Delta^{2,9(14)}$-decahydro-2,12-dimethylphenanthrene (II; R = Me). Thus 2,5-xyloquinone and, as previously reported,[1] 2,6-xyloquinone react with the acetoxy-diene (I) to yield only adducts containing an angular methyl group at $C_{(12)}$. The factors controlling this specificity are not clear. From simple polarity considerations, in which $C_{(2)}$ of the diene is positively charged, a conclusion consistent with its known [2c,e] reaction with methyl acrylate to yield the bicyclic ester (IV), both xyloquinones would be expected to yield products containing an 11-methyl group. If (i) we expect the maximum accumulation of unsaturation in the transition state,[3] (ii) a methyl group is considered as more unsaturated than hydrogen,[4] and (iii) the diene and the xyloquinones react by *endo*-addition, then the substituent on the non-reacting ene-dione system would be expected to influence the structure of the product by its interaction with the enol-acetate moiety. Thus neither of the two principles used in predicting the course of the Diels–Alder reaction is applicable in these cases. The principle of maximum accumulation of unsaturation is also violated

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* Part XI, *J.*, 1961, 206.

[1] Ansell and Brooks, *Chem. and Ind.*, 1955, 916; *J.*, 1956, 4518.

[2] (*a*) Nazarov, Kucherov, Andreyv, and Segal, *Doklady Akad. Nauk S.S.S.R.*, 1955, **104**, 729; (*b*) Nazarov, Kucherov, and Segal, *Bull. Acad. Sci. U.S.S.R.*, 1956, 1241 (U.S. translation); (*c*) Nazarov, Kucherov, and Andreev, *ibid.*, 1957, 345; (*d*) Nazarov, Kucherov, Andreev, and Segal, *Proc. Acad. Sci.* (*U.S.S.R.*), 1958, **119**, 277 (U.S. translation); (*e*) Winternitz and Balmossiere, *Tetrahedron*, 1958, **2**, 100; (*f*) Bergmann and Becker, *J. Amer. Chem. Soc.*, 1959, **81**, 221.

[3] Alder and Stein, *Angew. Chem.*, 1937, **50**, 510; Alder and Windemuth, *Ber.*, 1938, **71**, 1948.

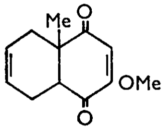
[4] Cf. Alder and Vogt, *Annalen*, 1949, **564**, 120.

in the addition of methyl acrylate to the acetoxy-diene (I). This is attributed [2c] to interaction of the enol-acetate group of the diene with the methoxycarbonyl group of the dienophil.

Condensation of the diene (I) with 6-methoxytoluquinone (Me = 2) resulted in exclusive formation of the adduct (III; R = Me, R′ = MeO) whose ultraviolet spectrum had its main maximum at 272 mμ, similar to that [5] (269 mμ) for the compound (V), indicating that addition had occurred at the methyl-ethene linkage, as was proved by the following degradation. Methanolysis of the adduct (III; R = Me, R′ = OMe) gave the triketone (VI), which after ozonolysis, followed by oxidation with hydrogen peroxide and Clemmensen reduction, gave the acid (VII). This acid was dehydrogenated with concomitant decarboxylation to 1-methylnaphthalene.

In contrast to the specificity of the reaction of 6-methoxytoluquinone with the diene (I), 5-methoxytoluquinone afforded a complex mixture. Three products were isolated by chromatography and fractional crystallisation, each having the analysis of a normal adduct and a maximum in its ultraviolet absorption spectrum consistent with a methoxy-substituted ene-dione system. None of these compounds was obtained in amount sufficient for its structure to be established. The presence of other products, possibly modified adducts, was inferred from the light-absorption characteristics of the unresolved mixtures.

The reaction between 1-1′-acetoxyvinylcyclohexene (I) and 2,6-xyloquinone is reported [1] to give a greater yield in ethanol than in benzene. A similar effect was observed with this diene and 5-methoxytoluquinone, which did not react in boiling benzene during 96 hr.; this is in contrast to the recorded [5] addition of 6-methoxytoluquinone to butadiene at *ca.* 105°. When, however, toluquinone and the diene (I) were allowed to react in methanol the only isolable product was the quinol (VIII; R = Me), which was also formed when a methanolic solution of the normal adduct (II; R = H) was boiled. The reaction between the diene and benzoquinone in ethanol yields [2e] the adduct (III; R = R′ = H) in a 63% yield after 72 hr. at room temperature, but the yield falls to 30% if the solution is boiled for 5 hr. and then left overnight; we have found that the initial reaction in methanol solution afforded the expected adduct (III; R = R′ = H) after a short reaction time, but on prolonged heating the aromatic compound (VIII; R = H) together with the related quinone (IX) was formed. Aromatisation of the ene-dione (III; R = R′ = H) also occurs at (or above) its melting point, for it is reported [1,2e] that this compound melts initially at 118—120°, resolidifies at *ca.* 155°, and melts again at *ca.* 225° [the quinol (VIII; R = H) has m. p. 228—231°]. Previous cases of aromatisation of ene-diones fall into two classes; those [6] in which the reaction is catalysed by alkali or mineral acid and those [6b,7] in which the ene-dione is heated alone or in water or acetic acid. Aromatisation under the mild conditions of boiling methanol has not been previously reported, although partial enolisation of the ketone (V) on recrystallisation from methanol is recorded (ref. 5, footnote 14).



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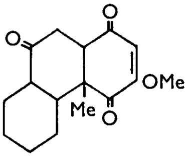

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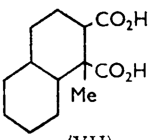

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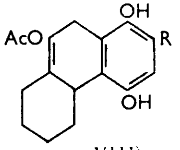
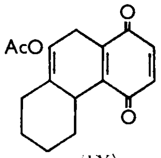


(VIII)



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[5] Woodward, Sondheimer, Taub, Hensler, and McLamore, *J. Amer. Chem. Soc.*, 1952, **74**, 4223.

[6] *Inter al.*, (*a*) Fieser and Chang, *J. Amer. Chem. Soc.*, 1942, **64**, 2043; (*b*) Tomayo and Leon, *J.*, 1948, 1499; (*c*) Robins and Walker, *J.*, 1952, 642.

[7] *Inter al.*, Ostrozhinskaya, *Zhur. obshchei Khim.*, 1946, **16**, 1053.

EXPERIMENTAL

Ultraviolet absorption spectra were measured for 96% ethanol solutions unless otherwise stated.

Reaction of 1-1′-*Acetoxyvinylcyclohexene with Toluquinone.*—A solution of 1-1′-acetoxyvinylcyclohexene (20 g.) and toluquinone [8] (12·2 g.) in benzene (150 ml.) was kept at room temperature for 4 days. Most of the benzene was then removed under reduced pressure and light petroleum (b. p. 40—60°) was added to the warm residue until the mixture was just cloudy. This solution, on cooling, deposited crude 9-*acetoxy*-$\Delta^{2,9(14)}$-*decahydro*-2-*methyl*-1,4-*dioxophenanthrene* (II; R = H) (7·8 g.), m. p. 123—134°. Recrystallisation from benzene–light petroleum (b. p. 60—80°) gave the pure compound, m. p. 136—139·5°, $\lambda_{\text{max.}}$ (in hexane) 240, 359 mμ (log ε 4·07, 1·78), $\lambda_{\text{infl.}}$ 284 mμ (log ε 1·97) (Found: C, 70·8; H, 7·0. $C_{17}H_{20}O_4$ requires C, 70·85; H, 6·9%). Concentration of the mother-liquors from the first crystallisation gave material (12·6 g.), m. p. 95—120°, which on fractional crystallisation from methanol yielded a further quantity (2·5 g.) of the above adduct, m. p. 134—138°, and an impure sample (3·1 g.), m. p. 113—123°, of 9-acetoxy-$\Delta^{2,9(14)}$-decahydro-1,4-dioxo-3-methylphenanthrene.

Degradation of 9-*Acetoxy*-$\Delta^{2,9(14)}$-*decahydro*-2-*methyl*-1,4-*dioxophenanthrene.*—The compound (0·023 mole) was added *via* a Soxhlet extraction apparatus (3·5 hr. required) to a stirred suspension of lithium aluminium hydride (4·0 g.) in dry ether (300 ml.). After cooling, water was cautiously added and the ethereal solution decanted from the precipitated solids which were washed with ether. The residue left on evaporation of the dried ($MgSO_4$) ethereal solutions contained ketonic material (that formed a 2,4-dinitrophenylhydrazone) and was dissolved in ether (75 ml.) and added to a suspension of lithium aluminium hydride (4·0 g.) in ether (200 ml.). After being boiled for 6 hr., this mixture was worked up as before. The resulting non-ketonic material (5·0 g.) was dehydrated at 180° for 45 min., in a stream of nitrogen, with powdered fused potassium hydrogen sulphate (5 g.). After addition of water the product was extracted with ether and dried (K_2CO_3). The solvent was then removed and the residue (4 g.) heated with 5% palladium–charcoal (2 g.) at 290° ±5° for 2 hr. The organic product (extracted with benzene) was chromatographed in light petroleum (b. p. <40) on alumina (Peter Spence, type H) to yield 2-methylphenanthrene (1 g.), m. p. and mixed m. p. 55—57°. The derived picrate had m. p. 118·5—120°. Haworth [9] records m. p. 55—56° (picrate, m. p. 118—119°).

Degradation of 9-*Acetoxy*-$\Delta^{2,9(14)}$-*decahydro*-3-*methyl*-1,4-*dioxophenanthrene.*—This compound (0·016 mole) was degraded as in the previous experiment except that the dehydrogenation was effected in boiling diphenylamine for 20 hr. The cooled mixture was extracted with ether; the ethereal solution was filtered and saturated with dry hydrogen chloride. The precipitated diphenylamine hydrochloride was filtered off, the filtrate evaporated, and the residue chromatographed in light petroleum (b. p. $<40°$) on alumina to yield a colourless oil from which was derived 3-methylphenanthrene picrate, m. p. 135—137° undepressed in admixture with an authentic specimen,[1] m. p. 138—139·5°.

9-*Acetoxy*-$\Delta^{2,9(14)}$-*decahydro*-2,12-*dimethyl*-1,4-*dioxophenanthrene.*—A solution of 1-1′-acetoxyvinylcyclohexene (12 g.) and 2,5-xyloquinone * (8·5 g.) in ethanol (200 ml.) was boiled under reflux for 40 hr. and the solvent then removed under reduced pressure. After treatment of the residue with light petroleum (b. p. 40—60°) the solid product was filtered off and washed with a little ether, to yield 9-*acetoxy*-$\Delta^{2,9(14)}$-*decahydro*-2,12-*dimethyl*-1,4-*dioxophenanthrene* (II; R = Me) (8·8 g., 46%), m. p. 154—158°. Recrystallisation from ethanol gave the pure adduct as needles, m. p. 157—159°, $\lambda_{\text{max.}}$ 243, 352 mμ (log ε 3·87, 2·41) (Found: C, 71·6; H, 7·3. $C_{18}H_{22}O_4$ requires C, 71·5; H, 7·3%).

Degradation of 9-*Acetoxy*-$\Delta^{2,9(14)}$-*decahydro*-2,12-*dimethyl*-1,4-*dioxophenanthrene.*—Degradation of this compound (0·023 mole) was effected as for 9-acetoxy-$^{2,9(14)}$-decahydro-2-methyl-1,4-dioxophenanthrene except that the final dehydrogenation was carried out with selenium (12 g.) at 320—350° for 20 hr. Distillation at $<190°/0·1$ mm. of the organic dehydrogenation product afforded a pale yellow oil (0·8 g.) from which was obtained 2-methylphenanthrene

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* Obtained in low yield by the oxidation of 2,5-xylidine as described [8] for oxidation of *o*-toluidine.

[8] Hickinbottom, " Reactions of Organic Compounds," Longmans, Green and Co. Ltd., London, 1957, p. 423.

[9] Haworth, *J.*, 1932, 1125.

picrate, m. p. 116—119°, which was not depressed in admixture with an authentic specimen of m. p. 118—119°.

9-*Acetoxy*-$\Delta^{2,9(14)}$-*decahydro*-3-*methoxy*-12-*methyl*-1,4-*dioxophenanthrene*.—A solution of 6-methoxytoluquinone (15 g.) and 1-1′-acetoxyvinylcyclohexene (22 g.) in methanol (500 ml.) was heated under reflux for 73 hr. and the solvent then evaporated (reduced pressure). Ether was added to the residue, and the solid product was filtered off and washed with a little ether, to yield 9-*acetoxy*-$\Delta^{2,9(14)}$-*decahydro*-3-*methoxy*-12-*methyl*-1,4-*dioxophenanthrene* (III; R = Me, R′ = OMe) (26 g., 82%), m. p. 178—188°. Recrystallisation from ethanol gave colourless octahedra (24 g.), m. p. 185—190°, $\lambda_{max.}$ 272 mμ (log ε 3·91), whose m. p. was not improved on further crystallisation (Found: C, 68·1; H, 7·0. $C_{18}H_{22}O_5$ requires C, 67·9; H, 7·0%)

Δ^2-*Dodecahydro*-3-*methoxy*-12-*methyl*-1,4,9-*trioxophenanthrene*.—A solution of 9-acetoxy-$\Delta^{2,9(14)}$-decahydro-3-methoxy-12-methyl-1,4-dioxophenanthrene (35 g.) in anhydrous methanol (1 l.) containing 98% sulphuric acid (12 ml.) was boiled for 30 min., then concentrated to *ca.* 250 ml. under reduced pressure and cooled. The precipitated crystals were filtered off and washed with a little methanol, to give Δ^2-*dodecahydro*-3-*methoxy*-12-*methyl*-1,4,9-*trioxophenanthrene* (VI) (14·1 g.), m. p. 195—197°, which on recrystallisation from methanol–chloroform gave the triketone (11 g.), m. p. 207—212°, $\lambda_{max.}$ 275 mμ (log ε 3·92). The analytical sample had m. p. 209·5—214·5° (Found: C, 69·6; H, 7·4. $C_{16}H_{20}O_4$ requires C, 69·6; H, 7·3%). This material showed no infrared absorption at 5·7—5·75 μ, indicating the absence of the enol-acetate group.

Degradation of Δ^2-*Dodecahydro*-3-*methoxy*-12-*methyl*-1,4,9-*trioxophenanthrene*.—A solution of the triketone (11 g.) in acetic acid (110 ml.) and chloroform (110 ml.) was treated with ozonised air for 12 hr. Water (12 ml.) and 30% hydrogen peroxide were then added and the solution was boiled for 30 min. The chloroform and most of the acetic acid were removed by steam-distillation, and the residual solution, when cooled, deposited starting material (1·4 g.) which was filtered off. The filtrate was made alkaline with sodium carbonate and extracted with ether. Sodium hydroxide (15 g.) and 30% hydrogen peroxide (100 ml.) were added to the aqueous phase, and the mixture was boiled for 10 min. The hot brown solution was decolorised by the addition of 30% hydrogen peroxide (*ca.* 30 ml.), then acidified with hydrochloric acid and extracted with ether. The residue (8 g.) obtained on evaporation of the ether extract was dissolved in toluene (150 ml.) and acetic acid (60 ml.), and the mixture together with amalgamated zinc wool (90 g.), hydrochloric acid (150 ml.), and water (60 ml.) was heated under reflux for 24 hr. Further additions (3 × 60 ml.) of hydrochloric acid were made during this time. The toluene and most of the acetic acid were removed by steam-distillation and the aqueous solution was decanted from the zinc. This solution, on cooling, deposited an acidic solid which was filtered off and twice recrystallised from benzene–ethanol to yield *perhydro*-1-*methylnaphthalene*-1,2-*dicarboxylic acid* (VII) (0·7 g.), m. p. 203—209·5° (Found: C, 65·4; H. 8·7. $C_{13}H_{20}O_4$ requires C, 65·0; H, 8·4%).

This solid together with 10% palladium–charcoal (0·8 g.) and acetone (14 ml.) was heated in a metal tube at 350° for 12 hr. The resulting solution was filtered and evaporated and the residual oil chromatographed in light petroleum (b. p. 30—40°) on alumina. Vapour-phase chromatography of the eluted oil at 150° on a " Pye Argon Chromatograph " with Apiezon " L " as the stationary phase showed it to be almost entirely 1-methylnaphthalene (1- and 2-methylnaphthalene are separable under these conditions). This result was confirmed by the infrared spectrum of the eluted oil which was essentially that of 1-methylnaphthalene.

Reaction of 1-1′-*Acetoxyvinylcyclohexene with* 5-*Methoxytoluquinone*.—This reaction was carried out as for the analogous reaction of 6-methoxytoluquinone, the reaction time being 96 hr. The use of benzene as a solvent (96 hr./b. p.) afforded only unchanged quinone. Thus was obtained material (A) (17 g.), m. p. 125—135°. Crystallisation from ether of the residue obtained on evaporation of the filtrate at 100°/1 mm. gave material B (2·5 g.), m. p. 125—135° (some sintering at 80—100°). Chromatography, in ether–benzene on silica gel, of the residue from the crystallisation of (B) gave several fractions (C) (2·3 g.). Recrystallisation of (A) from methanol yielded: (D) (2·4 g.), m. p. 145—172° (mainly quinone); (E) (7·0 g.), m. p. 135—164° (contaminated with quinone); and (F) (3·6 g.), m. p. 126—195°. Extraction (Soxhlet) of (E) with boiling water (to remove quinone) followed by recrystallisation from methanol gave an *adduct* (white prisms), m. p. 164—165°, $\lambda_{max.}$ 274 mμ (log ε 3·96) (Found: C, 67·8; H, 6·7. $C_{18}H_{22}O_5$ requires C, 67·9; H, 7·0%). Recrystallisation of the fractions (C) from methanol afforded another *adduct* (yellow prisms), m. p. 176—181°, $\lambda_{max.}$ 272 mμ (log ε 4·04) (Found: C, 68·3; H, 7·1; OMe, 10·1%; *M*, 308. $C_{18}H_{22}O_5$ requires C, 67·9; H, 7·0; OMe, 9·75%; *M*, 318), together with a third *adduct* (300 mg.) (stout plates from methanol), m. p. 172—175°, $\lambda_{max.}$ 271 mμ (log ε 4·04) (Found: C, 68·3; H, 6·8. $C_{18}H_{22}O_5$ requires C, 67·9; H, 7·0%). The "second" adduct was also obtained (2·5 g. in all) by recrystallisation of material (B) from benzene.

The mixture (F) had $\lambda_{max.}$ 252 mμ, 336—342 mμ (log ε 3·66, 3·43). Its infrared spectrum showed strong absorption at 5·76 (enol acetate), 6·24 (double bond of enol ether), 6·4 (conjugated polyene), and *ca.* 3·3br (OH) but only weak absorption at 5·85, 6·00, and 6·08 μ (C=O region). This suggests the presence of an enolic compound, possibly 10-acetoxy-1,2,3,4-tetrahydro-5,8-dihydroxy-7-methoxy-13-methylphenanthrene.

Reaction of 1-1′-*Acetoxyvinylcyclohexene with Benzoquinone.*—A solution of *p*-benzoquinone (2·2 g., 0·02 mole) and 1-1′-acetoxyvinylcyclohexene (3·5 g., 0·021 mole) in anhydrous methanol (30 ml.) was boiled for 2 hr., then cooled, and light petroleum (b. p. 30—40°) (30 ml.) was added. This solution, when left overnight at 0°, deposited 9-acetoxy-$\Delta^{2,9(14)}$-decahydro-1,4-dioxophenanthrene (1·8 g., 32%), m. p. 106—120°, raised to 117—120° (lit.,[1] 118—120°) on recrystallisation from ether.

This experiment was repeated, but with a reaction time of 18 hr., after which time the solvent was removed under reduced pressure and a mixture of light petroleum (b. p. 40—60°) (20 ml.) and ethanol (10 ml.) was added. The precipitate was filtered off and washed with a little ethanol, to yield 10-*acetoxy*-1,2,3,4,9,12-*hexahydro*-5,8-*dihydroxyphenanthrene* (VIII; R = H) (1·9 g., 34%), m. p. 196—220°. Repeated recrystallisation from benzene–ethanol raised the m. p. to 228—231° [$\lambda_{max.}$ 292 mμ (log ε 3·36)] (Found: C, 69·7; H, 6·55. $C_{16}H_{18}O_4$ requires C, 70·1; H, 6·6%). Slow evaporation of the mother-liquors deposited 9-*acetoxy*-5,6,7,8,10,13-*hexahydro*-1,4-*phenanthraquinone* (IX) (1 g.) as yellow needles, m. p. 135—142°. Recrystallisation raised the m. p. to 137—145° [$\lambda_{max.}$ 250, 350—355 mμ (log ε 3·95, 2·81)] which was not further improved by repeated crystallisation (Found: C, 70·7; H, 5·8. $C_{16}H_{16}O_4$ requires C, 70·6; H, 5·9%).

10-*Acetoxy*-1,2,3,4,9,12-*hexahydro*-5,8-*dihydroxy*-7-*methylphenanthrene.*—A solution of 9-acetoxy-$\Delta^{2,9(14)}$-decahydro-2-methyl-1,4-dioxophenanthrene (1·8 g) in methanol (50 ml.) was boiled for 18 hr. and the solvent then removed at reduced pressure. The semisolid residue was extracted with benzene, and the nearly insoluble 10-*acetoxy*-1,2,3,4,9,12-*hexahydro*-5,8-*dihydroxy*-7-*methylphenanthrene* (VIII; R = Me) (1 g. 55%), m. p. 200—205° (decomp.), was collected. Recrystallisation from benzene–ethanol gave the pure compound, m. p. 207—212°, $\lambda_{max.}$ 289 mμ (log ε 4·35) (Found: C, 70·5; H, 7·0. $C_{17}H_{20}O_4$ requires C, 70·85; H, 7·0%). This same compound was also isolated after reaction between toluquinone and 1-1′-acetoxyvinylcyclohexene in boiling methanol.

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