

## Reactions of $\alpha\omega$ -Dodecatrienediylnickel with Dimethyl Acetylenedicarboxylate and Methyl Propiolate

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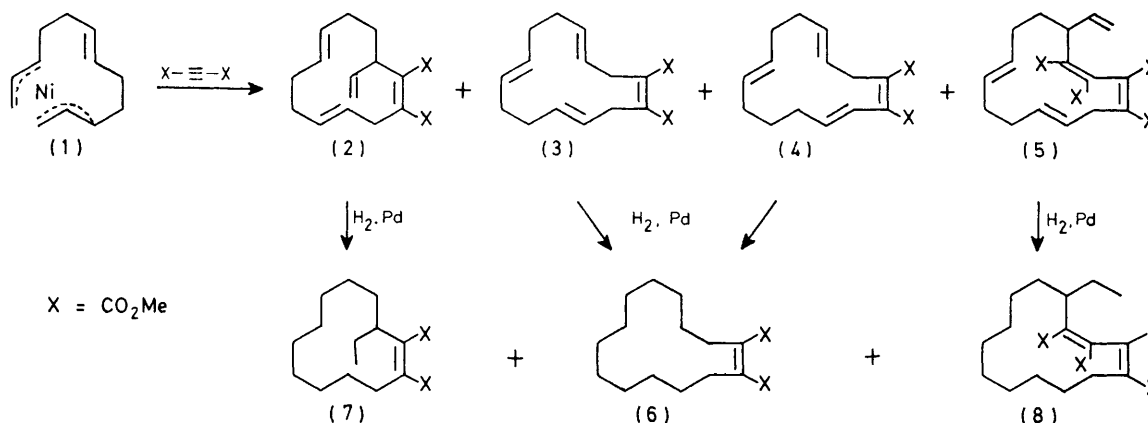
The reaction of  $\alpha\omega$ -dodecatrienediylnickel with dimethyl acetylenedicarboxylate at 0 °C yields approximately equal amounts of twelve- and fourteen-membered ring products, whereas, at -78 °C, 80% of the product has the larger ring. The reaction of  $\alpha\omega$ -dodecatrienediylnickel with methyl propiolate yields exclusively methyl 12-vinylcyclo-dodeca-1,4,8-trienecarboxylate. A similar insertion reaction of dimethyl acetylenedicarboxylate into a bis( $\eta$ -allyl)-nickel complex, derived from  $\alpha\omega$ -dodecatrienediylnickel and allene, has been shown to give a reasonable yield of dimethyl 14-methylenecyclohexadeca-1,4,8,12-tetraene-1,2-dicarboxylate.

THE formation of  $\alpha\omega$ -dodecatrienediylnickel (1) from the oligomerisation of buta-1,3-diene with bis(cyclo-octa-1,5-diene)nickel [ $\text{Ni}(\text{cod})_2$ ] is well established,<sup>1,2</sup> and a number of reactions of this nickel complex have been published. Thus, although carbonylation of (1) at 20 °C yields only *trans,trans,trans*-cyclododeca-1,5,9-triene, reaction with carbon monoxide at -60 °C yields an 8:1 mixture of 2-vinylcycloundeca-5,9-dienone and cyclotrideca-3,7,11-trienone in over 75% yield.<sup>3-5</sup> Similar products have also been obtained by hydrolysis of the imines produced by reaction of (1)

products, and a similar reaction of a bis( $\eta$ -allyl)nickel complex derived from (1) and allene.

### RESULTS AND DISCUSSION

Dimethyl acetylenedicarboxylate (32 mmol) was added to a solution of (1) (32 mmol) and the mixture stirred at -60 °C for 1½ h. Carbon monoxide was then passed through the solution overnight to remove the nickel, and the ether and nickel carbonyl were removed by distillation. G.l.c. analysis indicated the presence of cyclododeca-1,5,9-triene (21%), 11-vinylcycloundeca-3,7-dienone (17%),



with alkyl isocyanides.<sup>6</sup> In these reactions variation of the alkyl group was found to affect the ratio of the products. Thus with *t*-butyl and cyclohexyl isocyanide the major products were the eleven- and the thirteen-membered ring ketones, respectively. Long-chain organic compounds have been obtained by the reaction of acetaldehyde, acetyl chloride, or acrylaldehyde at one of the  $\pi$ -allyl groups of (1). In the presence of two reagents such as acetaldehyde and allyl bromide, addition to both  $\pi$ -allyl groups of (1) occurs, giving products of increased chain length.<sup>7</sup> We now report the reactions of (1) with dimethyl acetylenedicarboxylate and methyl propiolate which yield medium-sized ring

formed by insertion of carbon monoxide into (1), and four products [(2) (11%), (3) (20%), (4) (20%), and (5) (5%)] obtained from reaction of the diester with  $\alpha\omega$ -dodecatrienediylnickel. These products were characterised from their n.m.r., i.r., and mass spectra (Table 1), after separation by column chromatography and final purification by preparative g.l.c. For (2), (3), and (4), the disubstituted double bonds were assigned *trans* on the basis of  $\nu_{\text{max}}$  at 965 cm<sup>-1</sup>. Only (3) was obtained as a solid but, after hydrogenation, separation of the major product (6) (35% yield based on Ni) was easily achieved since it crystallised conveniently from the solution of hydrogenated esters (spectral details, Table 2). The specificity of the reaction of (1) with dimethyl acetylenedicarboxylate varied with

<sup>1</sup> B. Bogdanovic, P. Heimbach, H. Hey, E. Muller, and G. Wilke, *Annalen*, 1969, **727**, 161.

<sup>2</sup> G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Kein, M. Kroner, W. Oberkirch, K. Tanaka, E. Steinrucke, D. Walter, and H. Zimmerman, *Angew. Chem. Internat. Edn.*, 1966, **5**, 151.

<sup>3</sup> B. Bogdanovic, P. Heimbach, M. Kroner, and G. Wilke, *Annalen*, 1969, **727**, 143.

<sup>4</sup> G. Wilke, *Angew. Chem. Internat. Edn.*, 1963, **2**, 105.

<sup>5</sup> R. Baker, R. C. Cookson, and J. R. Vinson, unpublished results.

<sup>6</sup> H. Breil and G. Wilke, *Angew. Chem. Internat. Edn.*, 1970, **9**, 367.

<sup>7</sup> R. Baker, B. N. Blackett, R. C. Cookson, R. C. Cross, and D. P. Madden, *J.C.S. Chem. Comm.*, 1972, 343.

temperature; whereas the ratio of fourteen- to twelve-membered ring product was 4 : 1 at  $-78^{\circ}\text{C}$ , a 1 : 1 ratio was found at  $0^{\circ}\text{C}$ .

The yield of the tetraester product (5), obtained by reaction of (1) with 2 mol of dimethyl acetylenedicarboxylate could be increased by a longer reaction time and by using

Extensive studies have been made on the reactions of butadiene and alkynes in the presence of nickel complex catalysts and organophosphorus ligands.<sup>8</sup> The main products were the result of co-oligomerisation of 2 mol of butadiene with 1 mol of alkyne; 2,5-dimethyl-*cis,cis,trans*-cyclodeca-1,4,7-triene was obtained by reaction of butadiene

TABLE 1

Spectral data for products of reaction of (1) with dimethyl acetylenedicarboxylate			
	<sup>1</sup> H N.m.r. ( $\delta$ )	Mass spectrum ( <i>m/e</i> )	$\nu_{\text{max.}}$ /cm <sup>-1</sup>
(2)	4.9—6.0(7 H, m, olefinic) 3.66(3 H, s, OCH <sub>3</sub> ) 3.62(3 H, s, OCH <sub>3</sub> ) 3.15—3.4(1 H, m, doubly allylic) 2.6—3.05(2 H, m, doubly allylic) 1.8—2.5(6 H, m, allylic) 1.4—1.7(2 H, m, methylene)	304 (1.5%, <i>M</i> ), 273 (12%), 272 (15%), 91 (78%), 41 (100%)	1 725, 1 625, 1 260, 1 195, 1 155, 995, 965, 915
(3)	5.0—5.6(6 H, m, olefinic) 3.67(6 H, s, OCH <sub>3</sub> ) 2.9—3.02 (4 H, br d, doubly allylic) 2.0—2.2(8 H, br s, allylic)	304 (4%, <i>M</i> ), 273 (43%), 272 (80%), 91 (100%)	1 725, 1 640, 1 260, 1 195, 1 155, 965
(4)	5.0—6.0(6 H, m, olefinic) 3.5—3.8(6 H, m, OCH <sub>3</sub> ) 2.8—3.1(2 H, m, doubly allylic) 1.9—2.2(8 H, m, allylic) 1.2—1.4(2 H, m, methylene)		1 725, 1 630, 1 590, 1 260, 1 195, 1 155, 965
(5)	4.9—6.0(7 H, m, olefinic) 3.77, 3.75, 3.69, 3.66(12 H, 4 s, OCH <sub>3</sub> ) 3.2(1 H, m, doubly allylic) 2.6—3.1(2 H, m, doubly allylic) 1.8—2.5(2 H, m, methylene) 1.9—2.2(6 H, m, allylic)	446 (2%, <i>M</i> ), 415 (30%), 414 (33%), 387 (90%), 41 (100%)	1 720, 990, 965, 910

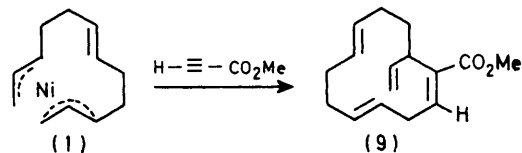
TABLE 2

Spectral data for products of hydrogenation (6)—(8)			
	<sup>1</sup> H N.m.r. ( $\delta$ )	Mass spectrum ( <i>m/e</i> )	$\nu_{\text{max.}}$ /cm <sup>-1</sup>
(6)	3.63(6 H, s, OCH <sub>3</sub> ) 2.18—2.4(4 H, m, allylic) 1.36(20 H, br s, methylene)	310 (3%, <i>M</i> ), 279 (18%), 278 (23%), 55 (56%), 41 (100%)	1 725, 1 630
(7)	3.62(3 H, s, OCH <sub>3</sub> ) 3.59(3 H, s, OCH <sub>3</sub> ) 2.0—2.8(3 H, m, allylic) 1.1—1.9(18 H, br s, methylene) 0.84 (3 H, t, <i>J</i> = 7 Hz, methyl)	310 (5%, <i>M</i> ), 279 (29%), 278 (44%), 161 (35%), 79 (69%), 41 (100%)	1 725, 1 630
(8)	3.74, 3.72, 3.66, 3.62(12 H, 4 s, OCH <sub>3</sub> ) 2.1—2.4(3 H, m, allylic) 1.1—1.9(18 H, br s, methylene) 0.82(3 H, t, <i>J</i> = 7 Hz, methyl)	452 (5%, <i>M</i> ), 421 (20%), 420 (27%), 393 (72%), 55 (52%), 41 (100%)	

a 2 : 1 ratio of the latter to (1). Even so, the best that could be achieved was that (5) was *ca.* 50% of the total diester products. There was no evidence for the formation of a sixteen-membered ring product.

The reaction of methyl propiolate with (1) at  $0^{\circ}\text{C}$  has also been studied; a 29% yield of (9) was obtained by a similar procedure. No other isomeric product could be isolated even when the temperature of the reaction was varied from  $-78^{\circ}\text{C}$  to room temperature.

and but-2-yne.<sup>9-12</sup> Whilst this reaction has been the most widely studied, the reactions of other substituted alkynes



with butadiene have also been investigated and have been the source of good yields of substituted cyclodecatrienes.<sup>13-15</sup>

<sup>12</sup> W. Brenner, P. Heimbach, K.-J. Ploner, and F. Thomel, *Annalen*, 1973, 1882.

<sup>13</sup> W. Brenner and P. Heimbach, *Annalen*, 1975, 660.

<sup>14</sup> K.-J. Ploner and P. Heimbach, *Annalen*, 1976, 54.

<sup>15</sup> P. Heimbach and W. Brenner, *Angew. Chem.*, 1966, 78, 983.

<sup>8</sup> P. W. Jolly and G. Wilke, 'The Organic Chemistry of Nickel,' vol. 2, Academic Press, New York, 1975, pp. 167—184.

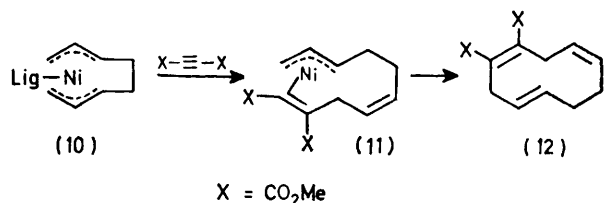
<sup>9</sup> W. Brenner, P. Heimbach, and G. Wilke, *Annalen*, 1969, 727, 194.

<sup>10</sup> W. Brenner, P. Heimbach, K.-J. Ploner, and F. Thomel, *Angew. Chem.*, 1969, 81, 744.

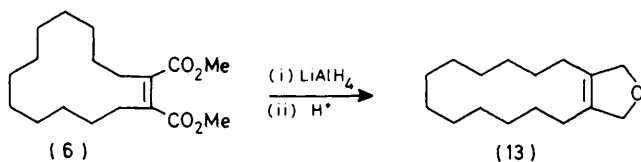
<sup>11</sup> P. Heimbach, P. W. Jolly, and G. Wilke, *Adv. Organometallic Chem.*, 1970, 8, 29.

All these reactions were assumed to proceed through the bis( $\eta$ -allyl)nickel complex (10). Evidence for this was obtained from an experiment in which (12) was obtained from reaction of butadiene with diethyl acetylenedicarboxylate; the intermediate (11) was isolated as a yellow solid from the reaction in 30% yield.<sup>16</sup>

The present reactions almost certainly proceed in a similar manner although an intermediate analogous to (11) has not been isolated. The insertion of dimethyl



acetylenedicarboxylate into (1) has been confirmed to occur in a *cis*-manner since (6) has been converted into (13) by a

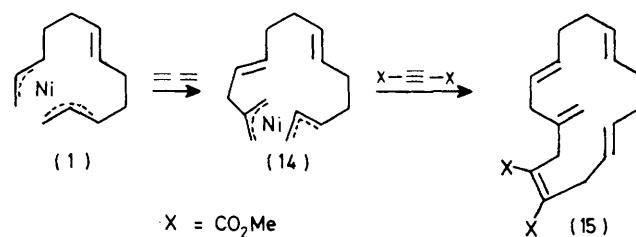


sequence of reactions.<sup>17</sup> A general *cis*-insertion reaction has also been found in the formation of cyclodecatrienes from (10). The presence of an electron-withdrawing group on the acetylene seems important since only a very small extent of reaction of (1) was found with acetylene and methylacetylene and no reaction with olefins such as dimethyl maleate, tetracyanoethylene, methyl vinyl ether, styrene, and acrylonitrile. Whilst similar in some ways, differences in reactivity between (1) and the bis( $\eta$ -allyl)nickel complex (10) have been found. For example, butadiene has been shown to yield products with a range of alkyl-substituted alkynes and olefins under conditions in which (10) must be formed.<sup>18</sup>

This difference in reactivity could be a consequence of a number of factors but might simply be the result of the difference in temperature at which the reactions are conducted. With (1), room temperatures and below are used for the reactions to avoid the formation of cyclododeca-1,4,7-triene. Temperatures in the range 40–80 °C are commonly used to obtain (10) and for its subsequent reaction. Additionally, the mixtures used to obtain (10) always contain an organophosphorus ligand and this must also affect the reactivity of this bis( $\eta$ -allyl)nickel complex.

In an additional experiment, the bis( $\eta$ -allyl)nickel complex (14) was formed by the addition of 1 mol of allene to (1) at 10 °C.<sup>19</sup> Dimethyl acetylenedicarboxylate was added to a solution of (14) at –78 °C and, after stirring for 1 h, carbon monoxide was bubbled into the solution and the products were extracted. A 30% yield of a mixture (2) (10%), (3) (23%), (4) (12%), and (15) (53%) was obtained.

The first three of these products were formed by reaction of dimethyl acetylenedicarboxylate with (1) which remained



unconverted into (14). The major product (15) was formed by insertion of the diester into (14).

#### EXPERIMENTAL

Solutions of the dodecatrienediylnickel complex (1) were prepared from bis(cyclo-octa-1,5-diene)nickel<sup>20</sup> as previously described.<sup>21</sup> The reactions were carried out in an atmosphere of high-purity argon and all solvents were dried over sodium wire.

*Reaction of  $\alpha\omega$ -Dodecatrienediylnickel (1) with Dimethyl Acetylenedicarboxylate.*—Dimethyl acetylenedicarboxylate (4.6 g, 32 mmol) was added dropwise to a dark red solution of (1) [from nickel acetylacetonate (8.1 g, 32 mmol)] in ether at –60 °C. The solution turned dark red-brown and was stirred at –60 °C for 1½ h before carbon monoxide was passed through for 6 h at –78 °C. The tetracarbonylnickel formed was removed by bubbling nitrogen through the mixture and destroyed by passage through bromine traps.

Distillation of the ethereal layer and extraction with light petroleum gave a pale yellow oil (4.84 g) which was shown by g.l.c. (5 ft 10% SE30; 140–240 °C at 12 °C min<sup>-1</sup>) to contain cyclo-octa-1,4-diene, cyclododeca-1,5,9-triene (21%), 11-vinylcycloundeca-3,7-dienone (17%), and the esters (2) (11%), (3) (20%), (4) (20%), and (5) (5%). The products were separated on a 30 cm silica (100–120 mesh) column. Light petroleum eluted the hydrocarbons; 10% ether–light petroleum eluted the ketone and then the diesters [in the order (2), (3), (4)]; the tetraester (5) was eluted with 15% ether–light petroleum. Final purification was achieved by preparative g.l.c. (10 ft, 25% SE30; 230 °C, 100 ml min<sup>-1</sup>) but only (3) was obtained as a solid, m.p. 67 °C (recrystallised from light petroleum).

In a duplicate experiment the crude product mixture was dissolved in ethanol, 10% Pd–C (300 mg) was added, and the solution was stirred under hydrogen at room temperature until uptake ceased. The catalyst was removed and the solution evaporated. Column chromatography as before gave a 4 : 1 mixture of (6) and (7) (0.98 g, 35%) on elution with light petroleum–diethyl ether (20 : 1), and further elution with light petroleum–ether (10 : 1) afforded (8) (0.57 g, 14%). The major product *dimethyl cyclootetradeca-1-ene-1,2-dicarboxylate* (6) was easily separable from (7) by filtration and crystallised from light petroleum, m.p. 83–84 °C (Found: C, 69.9; H, 9.6; O, 20.5. C<sub>18</sub>H<sub>30</sub>O<sub>4</sub> requires C, 69.65; H, 9.75; O, 20.6%).

<sup>16</sup> B. Bussemeier, P. W. Jolly, and G. Wilke, *J. Amer. Chem. Soc.*, **1974**, **96**, 4726.

<sup>17</sup> R. Baker, P. C. Bevan, and R. C. Cookson, *J.C.S. Chem. Comm.*, **1975**, 752.

<sup>18</sup> Ref. 8, pp. 172–184.

<sup>19</sup> R. Baker, B. N. Blackett, and R. C. Cookson, *J.C.S. Chem. Comm.*, **1972**, 802.

<sup>20</sup> 'Inorganic Synthesis,' vol. XV, ed. G. W. Parshall, McGraw-Hill, New York, **1974**, p. 5.

<sup>21</sup> R. Baker and A. H. Copeland, *J.C.S. Perkin I*, **1977**, 2560.

*Reaction of  $\alpha\omega$ -Dodecatrienediylnickel (1) with Methyl Propiolate.*—Methyl propiolate (2.3 g, 28 mmol) was added dropwise to a solution of (1) [from nickel acetylacetonate (12 g, 46.3 mmol)] in ether at 0 °C. The mixture changed immediately from dark red to brown and was stirred at 0 °C for 2 h. After warming to room temperature, carbon monoxide was bubbled into the solution for 5 h. G.l.c. analysis indicated the formation of a 66 : 34 mixture of cyclododeca-1,5,9-triene and methyl 12-vinylcyclododeca-1,4,8-triene-carboxylate (9), which was separated by column chromatography as an oil (1.8 g, 29% yield) (Found: C, 78.25; H, 9.0; O, 12.75.  $C_{16}H_{22}O_2$  requires C, 78.0; H, 9.0; O, 13.0%;  $\delta(CCl_4)$ ; 6.36 (1 H, t,  $J$  11 Hz,  $-C=CH-$ ), 5.3—5.8 (1 H, m,  $-CH=CH-$ ), 4.7—5.2 (6 H, m,  $-CH=CH-$ ), 3.68 (3 H, s,  $-CH_3$ ), 3.0—3.44 (2 H, m,  $=C-CH_2-C=$ ), 2.5—2.8 (1 H, m, methine), 1.9—2.4 (6 H, m,  $-CH_2-C=$ ), and 1.4—1.6 (2 H, m,  $-CH_2-$ ). Double resonance of this compound was carried out and irradiation at  $\delta$  3.27 of the doubly allylic methylene protons caused collapse of the triplet at  $\delta$  6.36. The structure assigned is consistent with these facts and also with the i.r. [ $\nu_{max}$ , 1 725, 1 640, 990, 965, and 910  $cm^{-1}$ ] and the mass spectrum [ $m/e$  246(5%,  $M$ ), 187(39%), 186(17%), 145(28%), 131(40%), 119(40%), 117(44%), 105(50%), 93(37%), 91(100%), 79(68%), 77(55%), 67(48%), and 41(89%)].

*Reaction of (14) with Dimethyl Acetylenedicarboxylate.*—To Ni(cod)<sub>2</sub> (8.75 g, 32 mmol), cooled in an ice-salt bath, was added butadiene (excess; 50 ml) and the solution allowed to reflux at ca. 0 °C for 4 h. A red solution resulted and excess of butadiene was removed on the water pump. The residue was dissolved in sodium-dried ether (200 ml) and cooled to -78 °C. Allene (2.5 ml) was distilled into the mixture which was allowed to warm to -10 °C and kept between -10 and +10 °C for 2 h. After cooling to -78 °C a solution of dimethyl acetylenedicarboxylate (4.6 g, 32 mmol) in ether (10 ml) was added and the solution stirred at -78 °C for 16 h. Carbon monoxide was bubbled into the solution for 6 h at -78 °C and the tetracarbonylnickel

formed was removed by bubbling nitrogen through the mixture and destroyed by passage through bromine traps.

Removal of solvent left a green gelatinous material to which ethanol was added and the precipitated green solid removed by filtration. Evaporation gave a green oil (9.72 g) which by g.l.c. (10 ft, 10% SE30, 100—230 °C at 16 °C  $min^{-1}$ ) was indicated to contain cyclo-octa-1,5-diene, cyclododeca-1,5,9-triene, and 11-vinylcycloundeca-3,7-dienone. Further g.l.c. (10 ft, 10% OVI, 150—290 °C at 16 °C  $min^{-1}$ ) showed the presence of four diester products in the relative yields (2) (10%), (3) (23%), (4) (12%), and (15) (53%).

Column chromatography on silica (100—200 mesh) separated the product mixture into the following fractions; hydrocarbons (light petroleum eluent),  $C_{13}$ -ketone (10% ether-light petroleum), (2), (3), and (15) (10% ether-light petroleum), and (4) (20% ether-light petroleum). The total weight of diester products was 3.18 g (30% conversion based on dimethyl acetylenedicarboxylate). Bulb-to-bulb distillation of the mixture of (2), (3), and (15) separated (2) and (3) (ca. 120 °C, 1 mmHg) from an almost pure sample of (15) as a viscous oil (1.4 g, ca. 130 °C, 1 mmHg). The oil solidified on standing and was recrystallised from ether-light petroleum to give dimethyl 14-methylenecyclohexadeca-1,4,8,12-tetraene-1,2-dicarboxylate (15), m.p. 105—107 °C (Found: C, 73.0; H, 8.1.  $C_{21}H_{28}O_4$  requires C, 73.25; H, 8.2%;  $\delta(CCl_4)$  5.1—5.5 (6 H, m, olefinic), 4.8—4.6 (2 H, br d,  $=CH_2$ ), 3.61 (3 H, s,  $-OCH_3$ ), 3.59 (3 H, s,  $-OCH_3$ ), 2.6—2.9 (6 H, m, doubly allylic), and 1.9—2.2 (8 H, m, allylic);  $\nu_{max}$ , 1 725, 965, and 890  $cm^{-1}$ ,  $m/e$  344(24%,  $M$ ), 313(25%), 312(55%), 285(11%), 225(28%), 129(41%), and 91(100%).

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