On the Crystal and Molecular Structure of 1,4-Diphenylbuta-1,2,3-triene in Connection with its Stereospecific Synthesis from (*Z*)-2-Phenyl-1-(methylthio)vinyl Cuprate and its Conversion into (1*Z*,3*E*)-2-Ethyl-1,4-diphenylbuta-1,3-diene

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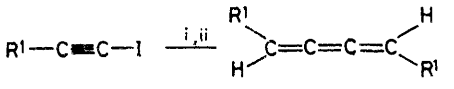
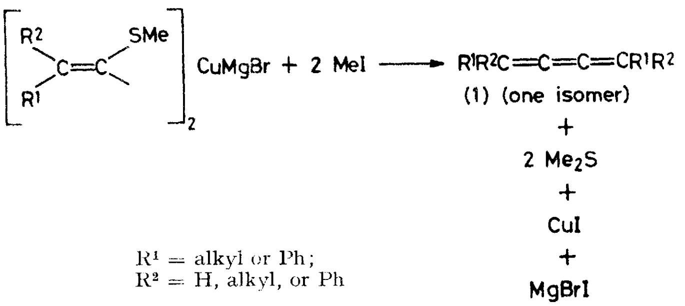
The crystal and molecular structure of the title compound (1) has been determined by single-crystal *X*-ray diffraction. Crystals are orthorhombic, space group *Pcab*, with cell dimensions $a = 8.029(7)$, $b = 13.032(6)$, $c = 22.09(2)$ Å, and $Z = 8$. The structure was solved by direct methods and refined by block-diagonal least-squares to R 0.038 for 690 observed reflections. The molecular configuration is *cis*, which is of significance for establishing the stereochemistry of additions to the inner double bond. Parallel butatriene chains with a mean distance of 3.7 Å are stacked in planes parallel to (010).

A NUMBER of methods have been developed for the synthesis of buta-1,2,3-trienes C=C=C=C, but most of them have led to a mixture of (*E*)- and (*Z*)-isomers.[1] Hitherto, two methods have appeared in the literature dealing with a stereospecific preparation of these compounds. One involves hydroboration of 1-iodoalk-1-ynes:[2]



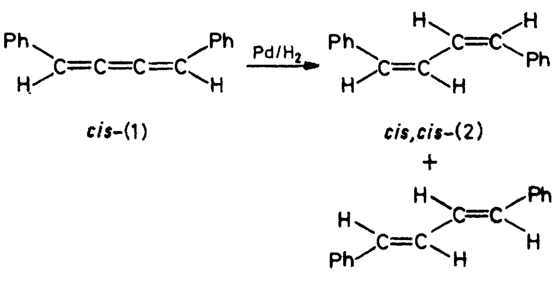
Reagents: i, R^2BH_2; ii, NaOMe. $R^{1,2}$ = alkyl

Hydroboration studies point to a *trans*-configuration of these cumulenes (*cf.* ref. 2). Recently,[3] we found another stereospecific route to buta-1,2,3-trienes was found by starting from specific substituted α-(methylthio)vinyl cuprates:



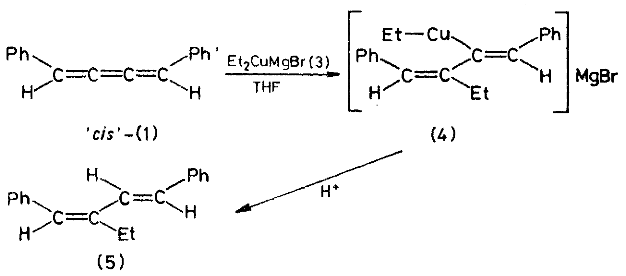
R^1 = alkyl or Ph;
R^2 = H, alkyl, or Ph

The configuration of the butatrienes thus obtained was suggested to be *cis*, based on hydrogenation studies on (1) (R^1 = Ph, R^2 = H) [*cf.* ref. 3]. Two 1,3-dienes were obtained upon hydrogenation of (1) with Pd/$CaCO_3$–H_2 in chloroform, *viz. cis,cis*- and *trans,trans*-1,4-diphenylbuta-1,3-diene (2). As hydrogenation reactions generally proceed in a *cis*-manner, the formation of *cis,cis*- and *trans,trans*-(2) is indicative of a *cis*-configuration of the starting cumulene (1):



cis-(1) *cis,cis*-(2) + *trans,trans*-(2)

There were some reasons, however, which made the assignment of a *cis*-configuration to (1) somewhat uncertain. For instance, the reaction of '*cis*'-(1) with the diethyl cuprate (3) in tetrahydrofuran (THF) furnished exclusively (1*Z*,3*E*)-2-ethyl-1,4-diphenylbuta-1,3-diene (5) upon protonolysis:



'*cis*'-(1) (4) (5)

If one assumes a direct formation of (4) from (1) and (3), adduct (5) can only arise by *trans*-addition of the cuprate on (1). The *trans*-addition of organocuprates on *sp* hybridized carbon–carbon multiple bonds is very uncommon, however.[4-8] It must be noted that the protonolysis of (4) into (5) will most likely take place with retention of configuration (*cf.* refs. 6—8). On the other hand, compound (4) [and thus (5)] could also be formed by a direct *cis*-addition of (3) on *trans*-(1), but this would necessarily imply that hydrogenation of the inner double bond in (1) occurs by a *trans*- rather than a *cis*-mechanism. A *trans*-hydrogenation cannot *a priori* be ruled out, as in a few cases partial *trans*-hydrogenation has been observed.[9-11]

An unequivocal determination of the configuration of the title compound, 1,4-diphenylbuta-1,2,3-triene, was therefore imperative, and we now report results of an *X*-ray study.

EXPERIMENTAL

1,4-Diphenylbuta-1,2,3-triene (1), synthesized from (*Z*)-2-phenyl-1-(methylthio)vinyl cuprate and methyl iodide,[3] was crystallized from toluene as yellow, plate-like crystals which are thermally unstable and light-sensitive.

Addition of Diethylcuprate (3) *to* (1).—To a well-stirred suspension of $Et_2CuMgBr$ (0.0100 mol), prepared from EtMgBr (0.0200 mol) and a 1 : 1 complex of CuBr–LiBr (0.0100 mol) in tetrahydrofuran (30 ml),[8] was added (1) (0.0100 mol) at −50 °C. Stirring was continued, the temperature of the reaction mixture being raised slowly (30 min) to 20 °C. The reaction mixture was then poured into a saturated solution of NH_4Cl in water (100 ml) containing some NaCN (0.5 g). The product was isolated by extracting with pentane (3 × 50 ml). After washing the combined extracts (water) and drying ($MgSO_4$), solvent was removed *in vacuo*. The crude (1*Z*,3*E*)-2-ethyl-1,4-diphenylbuta-1,3-diene (5) was analyzed by n.m.r. spectroscopy and further purified by column chromatography (Al_2O_3 + 5% aqueous hexane) giving pure (5) as a colourless oil (yield 80%). N.m.r. data for $PhCH^1{=}C(CH_2{}^4{-}CH_3{}^5){-}CH^2{=}CH^3{-}Ph$ (5) (δ values from $SiMe_4$, solvent $CDCl_2$): 7.47 (2Ph, m), 7.36 (2-H, d, $J_{2,3}$ 15.0 Hz), 6.80 (3-H, d, $J_{2,3}$ 15.0 Hz), 6.65 (1-H, s), 2.58 (4-H, q, $J_{4,5}$ 7.5 Hz), and 1.27 (5-H, t, $J_{4,5}$ 7.5 Hz). The orientation of H-1 and the ethyl group was deduced from the CH coupling constant ${}^3J(H^1, CH_2)$ which is 6.2 Hz, characteristic for a *cis*-orientation.[12]

Crystal Data.—$C_{16}H_{12}$, M = 204.27. Orthorhombic, a = 8.029(7), b = 13.032(6), c = 22.09(2) Å, U = 2 312 Å^3, Z = 8, D_c = 1.174 g cm^{-3}, $F(000)$ = 864. Mo-K_α radiation, λ = 0.7107 Å, μ(Mo-K_α) = 0.72 cm^{-1}. Space group $Pcab$ (No. 61, D_{2h}^{15} *) from systematic absences.

Cell dimensions were measured and data collected on a four-circle automatic Nonius diffractometer by means of Zr-filtered Mo-K_α radiation. A single crystal of dimensions 0.1 × 0.3 × 0.4 mm was used and data collected by the moving-crystal–moving-counter technique with a variable scan angle (0.8 + 0.35tanθ)°. In the range of 2θ 0.2—44°, 1 416 reflexions were measured, of which 690 having $I \geq 2.5\sigma(I)$ were considered observed. Data were corrected for Lorentz and polarisation effects, but not for absorption or extinction. All calculations were carried out with the *X*-Ray '76 system of crystallographic programs[13] implemented and extended by the local versions.

The structure was solved by use of MULTAN.[14] The phase set with the highest COMB FOM (2.693) gave an electron-density map from which all carbon atoms could be identified. The structure was refined by block-diagonal least-squares, first isotropically (R 0.113) then anisotropically (R 0.087). The 12 hydrogen atoms, located from a difference-Fourier map, were added; their co-ordinates were included in the refinement, but their thermal parameters were restricted to a value of B 8 Å^2. Refinement was continued until convergence: R 0.038 for 690 observed data. The maximum shift in the last cycle was 1.4σ; the maximum peak height in the final difference-Fourier map was 0.10 eÅ^{-3}.

Thermal parameters for the carbon atoms and observed and calculated structure factors have been deposited as Supplementary Publication No. SUP 22379 (10 pp., 1 microfiche).* Scattering factors for carbon were taken from ref. 15, and for hydrogen from ref. 16. Final positional parameters for the C atoms are listed in Table 1, H atoms in Table 2.

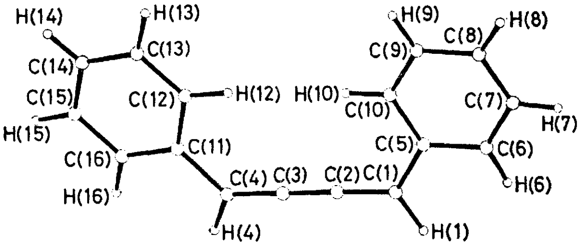


FIGURE 1 Key to the atomic numbering in the *cis*-diphenylbutatriene molecule (1)

TABLE 1

Final fractional co-ordinates of the carbon atoms (× 10^4), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
C(1)	−45(5)	2 619(4)	193(2)
C(2)	−610(5)	2 611(3)	765(2)
C(3)	−1 203(5)	2 581(4)	1 291(2)
C(4)	−1 903(5)	2 542(4)	1 832(2)
C(5)	963(5)	3 418(3)	−76(2)
C(6)	1 324(5)	3 374(3)	−696(2)
C(7)	2 280(6)	4 127(4)	−963(2)
C(8)	2 889(6)	4 933(3)	−631(2)
C(9)	2 541(6)	4 988(3)	−16(2)
C(10)	1 593(5)	4 237(3)	256(2)
C(11)	−1 732(5)	3 296(3)	2 319(2)
C(12)	−755(5)	4 175(3)	2 247(2)
C(13)	−584(6)	4 867(3)	2 716(2)
C(14)	−1 426(6)	4 709(3)	3 252(2)
C(15)	−2 405(6)	3 850(3)	3 328(2)
C(16)	−2 562(6)	3 146(3)	2 863(2)

RESULTS AND DISCUSSION

The atom numbering scheme is shown in Figure 1 and the molecular packing in Figures 2 and 3, viewed in the direction of *a* and *b* respectively. It can be seen that the molecule is in a *cis*-configuration. It is concluded that the coupling of the two vinyl groups of (*Z*)-2-phenyl-1-(methylthio)vinylcuprate occurs *via* an extremely stereospecific mechanism with the formation of *cis*-1,4-diphenylbutatriene. The *cis*-geometry of (1) shows that catalytic hydrogenation of the inner double bond of this cumulenic system occurs in a *cis*-manner. The addition

TABLE 2

Final fractional co-ordinates for the hydrogen atoms (× 10^3)

Atom	*x*	*y*	*z*
H(1)	−44(5)	198(3)	−9(2)
H(4)	−272(5)	194(3)	195(2)
H(6)	71(4)	279(3)	−91(2)
H(7)	257(5)	405(3)	−141(2)
H(8)	368(4)	546(3)	−83(2)
H(9)	314(4)	556(2)	23(1)
H(10)	125(4)	426(3)	69(2)
H(12)	−3(4)	424(3)	183(2)
H(13)	18(4)	554(3)	264(2)
H(14)	−121(4)	518(3)	360(2)
H(15)	−324(4)	372(3)	370(2)
H(16)	−339(4)	254(3)	291(2)

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* The space-group setting used is obtained from the standard one by interchanging *b* and *c*; equivalent positions, apart from those generated by the centre of symmetry, are: x,y,z; $\frac{1}{2}+x$, $-y$, $\frac{1}{2}-z$; $\frac{1}{2}-x$, $\frac{1}{2}+y$, $-z$; $-x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$.

* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1978, Index issue.

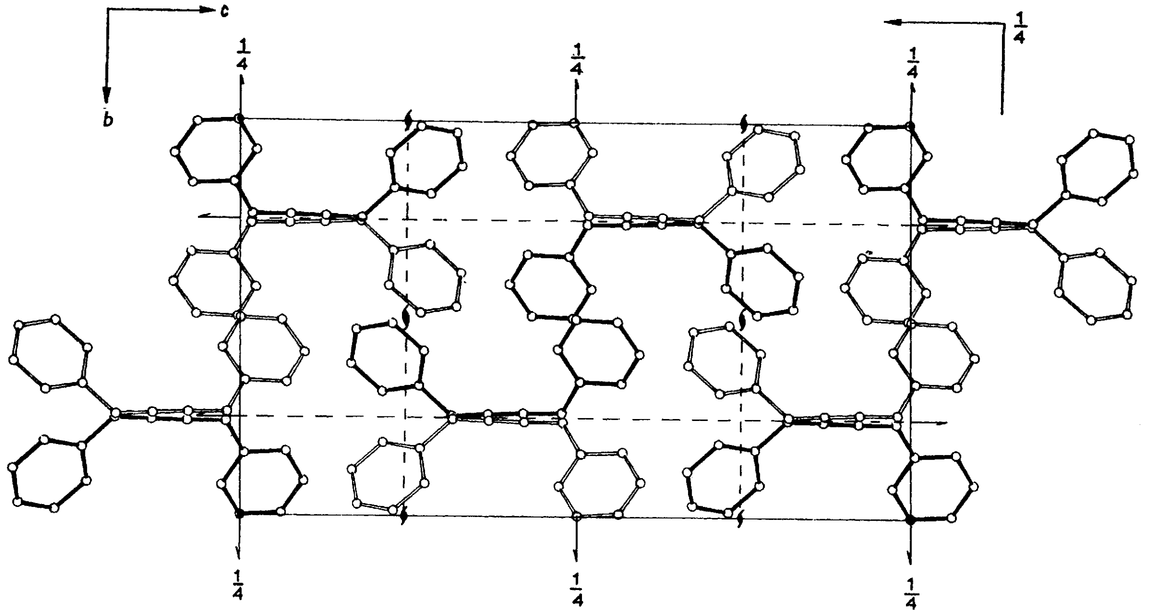

FIGURE 2 Projection of the structure of (1) along *a*. Molecules with centres of gravity on the same *x* level are drawn similarly

TABLE 3

Interatomic distances (Å)

(*a*) Involving C			
C(1)–C(2)	1.343(6)	C(2)–C(3)	1.256(6)
C(3)–C(4)	1.322(6)	C(1)–C(5)	1.446(6)
C(5)–C(6)	1.402(6)	C(6)–C(7)	1.379(7)
C(7)–C(8)	1.372(7)	C(8)–C(9)	1.388(7)
C(9)–C(10)	1.377(6)	C(10)–C(5)	1.390(6)
C(4)–C(11)	1.462(6)	C(11)–C(12)	1.397(6)
C(12)–C(13)	1.381(6)	C(13)–C(14)	1.379(7)
C(14)–C(15)	1.378(6)	C(15)–C(16)	1.383(6)
C(16)–C(11)	1.389(6)		
(*b*) Involving H			
C(1)–H(1)	1.09(3)	C(4)–H(4)	1.06(4)
C(6)–H(6)	1.02(3)	C(7)–H(7)	1.03(4)
C(8)–H(8)	1.04(3)	C(9)–H(9)	1.04(3)
C(10)–H(10)	1.00(3)	C(12)–H(12)	1.08(3)
C(13)–H(13)	1.08(3)	C(14)–H(14)	0.99(4)
C(15)–H(15)	1.08(4)	C(16)–H(16)	1.04(4)

of ethyl cuprate (3) must be either *trans* or must follow another route leading to the adduct (4).

Bond distances are listed in Table 3 and bond angles in Table 4. In the butatriene chain the central C=C (*sp*–*sp*) bond is 1.256(6) Å, the terminal C=C (*sp*–sp^2) bonds are 1.343(6) and 1.322(6) Å. These values compare reasonably well with 1.260(2) and a mean value of 1.348(3) Å respectively, found in a low-temperature *X*-ray diffraction study on tetraphenylbutatriene (6) [17] and with data for other butatrienes quoted in ref. 17. The chain, as can be inferred from the bond angles, deviates significantly from linearity and is bent. Also a slight departure from planarity of the butatriene skeleton is found (a planar D_{2h} configuration is adopted in an electron-diffraction and spectroscopic study on tetrafluorobutatriene [18,19]). These distortions are also present

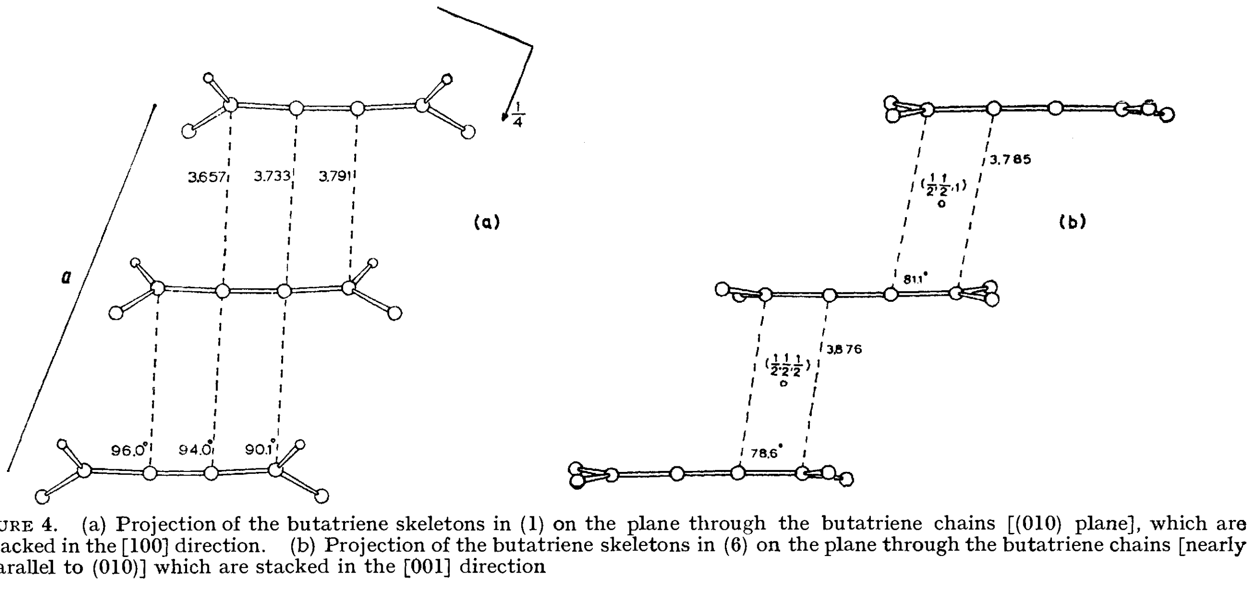

FIGURE 4. (a) Projection of the butatriene skeletons in (1) on the plane through the butatriene chains [(010) plane], which are stacked in the [100] direction. (b) Projection of the butatriene skeletons in (6) on the plane through the butatriene chains [nearly parallel to (010)] which are stacked in the [001] direction

in (6).[17] The phenyl groups are rotated out of the C(5),C(1)—(4),C(11) plane; pertinent torsion angles are 6.2° for the C(5)—(10) phenyl ring and 0.4° for the C(11)—(16) ring. Corresponding torsion angles in (6) are appreciably larger owing to intramolecular overcrowding. In spite of this difference in the molecular shape in the structures of (1) and (6), the butatriene chains are arranged similarly, *viz.* mutually parallel. In (1) the central C=C bond makes contacts with the terminal C=C bonds, while in (6) only contacts between the terminal C=C bonds are present. These arrangements can best be inferred from Figure 4. The crystal structure of the photodimer product of (6) is known [20] and the formation of this compound can be understood from the packing of the butatriene chains. There is only one independent plane-to-plane contact between phenyl rings C(5) · · · C(10) at x,y,z and C(5′) · · · C(10′) at $-x, 1-y, -z$ with an interplanar distance of 3.38 Å and a centre-to-centre distance of 4.08 Å. Other phenyl-group interactions consist of C · · · C, C · · · H, and H · · · H contacts with normal values.

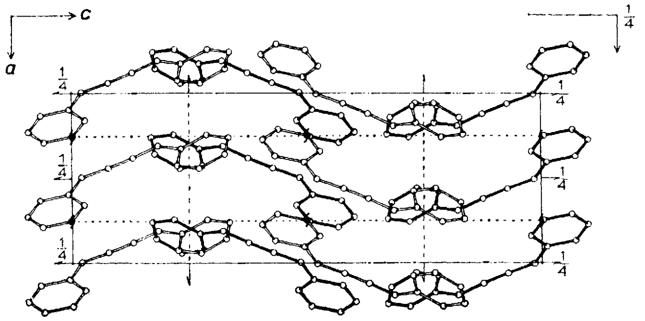

FIGURE 3 Projection of the structure of (1) along *b*. Molecules with centres of gravity on the same *y* level are drawn similarly

TABLE 4

Bond angles (°)

(*a*) Involving C

C(5)–C(1)–C(2)	125.5(4)	C(1)–C(2)–C(3)	177.1(5)
C(2)–C(3)–C(4)	177.0(5)	C(3)–C(4)–C(11)	126.8(4)
C(1)–C(5)–C(6)	119.2(4)	C(5)–C(6)–C(7)	120.3(4)
C(6)–C(7)–C(8)	120.9(4)	C(7)–C(8)–C(9)	119.4(4)
C(8)–C(9)–C(10)	120.1(4)	C(9)–C(10)–C(5)	121.2(4)
C(10)–C(5)–C(1)	122.7(4)	C(10)–C(5)–C(6)	118.1(4)
C(4)–C(11)–C(12)	121.3(4)	C(11)–C(12)–C(13)	120.4(4)
C(12)–C(13)–C(14)	119.9(4)	C(13)–C(14)–C(15)	120.3(4)
C(14)–C(15)–C(16)	120.1(4)	C(15)–C(16)–C(11)	120.4(4)
C(16)–C(11)–C(4)	119.8(4)	C(16)–C(11)–C(12)	118.9(4)

(*b*) Involving H

C(5)–C(1)–H(1)	119(2)	H(1)–C(1)–C(2)	116(2)
C(3)–C(4)–H(4)	122(2)	H(4)–C(4)–C(11)	112(2)
C(5)–C(6)–H(6)	113(2)	H(6)–C(6)–C(7)	126(2)
C(6)–C(7)–H(7)	118(2)	H(7)–C(7)–C(8)	121(2)
C(7)–C(8)–H(8)	120(2)	H(8)–C(8)–C(9)	120(2)
C(8)–C(9)–H(9)	117(2)	H(9)–C(9)–C(10)	122(2)
C(9)–C(10)–H(10)	123(2)	H(10)–C(10)–C(5)	115(2)
C(11)–C(12)–H(12)	117(2)	H(12)–C(12)–C(13)	122(2)
C(12)–C(13)–H(13)	118(2)	H(13)–C(13)–C(14)	122(2)
C(13)–C(14)–H(14)	119(2)	H(14)–C(14)–C(15)	121(2)
C(14)–C(15)–H(15)	125(2)	H(15)–C(15)–C(16)	115(2)
C(15)–C(16)–H(16)	119(2)	H(16)–C(16)–C(11)	121(2)

[8/246 *Received*, 13*th February*, 1978]

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