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# DIMESITYLBORYL COMPOUNDS

## V *. ARYL, ETHENYL, ALLENYL, PHENYLETHYNYL AND ALLYL DERIVATIVES

N.M.D. BROWN, F. DAVIDSON and J.W. WILSON **
*School of Physical Sciences, The New University of Ulster, Coleraine (Northern Ireland)*

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## Summary

Trimesitylborane, five aryldimesitylboranes, ethenyl, allenyl, phenylethynyl and allyldimesitylboranes have been synthesised and characterised by their $^{1}H$, $^{11}B$ and $^{13}C$ NMR spectra.

A set of $^{13}C$ chemical shift shielding parameters for the dimesitylboryl group have been obtained which allow the assignment of $^{13}C$ resonances in *meta*- and *para*-substituted aryldimesitylboranes.

On the basis of $^{13}C$ and $^{11}B$ chemical shift data it is concluded that the unsaturated ligands stabilise these systems by $\pi$ electron back-donation to the empty $p$ orbital on boron in the order aryl $\ll$ allenyl $<$ alkenyl $<$ alkynyl.

Allyldimesitylborane does not undergo the expected intramolecular allylic rearrangement in solution at temperatures below 140°C.

## Introduction

In Part I of this series chemical and physical properties of a set of substituted alkyldimesitylboranes $Mes_2BR$ (I) were reported [2]. These studies have now been extended to include a simple series of compounds where R is an unsaturated organic ligand. Availability of data on such a series is significant for several reasons. The study of a closely related series of compounds has obvious advantages with regard to the understanding of substituent effects and to problems of spectral assignment etc. in $^{13}C$ NMR spectroscopy. In addition it has already been shown that $^{13}C$ NMR spectroscopy provides a useful technique for detecting possible $\pi$ electron back-donation to boron from unsaturated organic ligands

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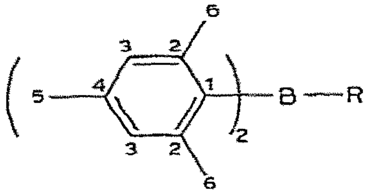
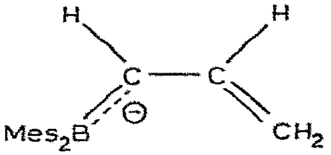
* For Part IV see ref. 1.

** Author to whom correspondence should be addressed.

[3]. Finally, the structurally interesting and synthetically useful carbanion (II) can be readily prepared from allyldimesitylborane [4] and it was therefore desirable to characterise this and closely related compounds as fully as possible.



(I)



(II)

## Results

All the compounds are crystalline with the exception of the vinyl derivative which is a waxy solid at room temperature. The aliphatic derivatives are sensitive to atmospheric oxygen over a period of several hours, especially in solution, whereas the aryl compounds remain unaffected.

### *NMR data for aryldimesitylboranes*

The $^1H$ spectra of the aryldimesitylboranes are of a routine nature and are of little interest other than for identification purposes. The $^{13}C$ chemical shifts of the fully proton noise-decoupled spectra have been assigned as follows (for notation see structure I and Table 1): with the exception of the C(1) carbons, the mesityl aromatic carbons are readily assigned by comparison with other systems and the fact that they occur in very narrow ranges; C(2) (140—141 ppm), C(3) (128—129 ppm) and C(4) (138—139 ppm). In each of these compounds the C(1) and C(a) carbon atoms give rather broad signals of low intensity whose relative peak areas are, to a first approximation, in a ratio of 2 : 1. They have been assigned on this basis.

The phenyl carbons in dimesitylphenylborane have been assigned with the help of the fully undecoupled spectrum gated to give the Overhauser enhancement. In this spectrum the C(2) and C(4) signals appear as quartets in a ratio of 2 : 1. The C(3) and C(c) signals appear as doublets, each component of which is a complex multiplet. This is caused by the fact that these C(3) and C(c) carbons have very similar chemical shifts (128.0 ± 0.2 ppm) and $^1J(^{13}C^1H)$ coupling constants (~161.5 Hz). The expected doublet of doublets for the C(c) carbons is therefore complicated by the seven line spectrum due to $^3J(^{13}CCC^1H_3)$ coupling of the C(3) carbons. The two remaining signals due to the phenyl C(b) and C(d) carbons appear as triplets of doublets. The signal at 136.2 ppm has been assigned to the C(b) carbons by virtue of its greater intensity.

These assignments give rise to a set of shielding parameters for the dimesitylboryl group when substituted on benzene ($\delta^{13}C = 128.7$ ppm). They are C(a) + 17.2; C(b) + 7.5; C(c) —0.8; and C(d) + 3.2 ppm. These values have been used to assign the chemical shifts to the substituted phenyl derivatives, assuming that a simple additivity relationship exists for the shielding parameters of the $Mes_2B$ group and the second substituent when they are *meta* or *para* to each other [5]. The results of this procedure are presented in Table 1. The $^{11}B$ spectra of these compounds are single broad peaks. The chemical shifts are given in Table 1.

*NMR data for ethenyl, phenylethynyl, allyl and allenyl dimesitylboranes*

In $CCl_4$ the signals due to the mesityl protons in all these compounds appear as a set of three singlets (ratio 2 : 3 : 6) in the ranges $\delta$ 6.67—6.75 (*meta* aromatics), 2.22—2.24 (*p*-methyls) and 2.14—2.17 ppm (*ortho* methyls).

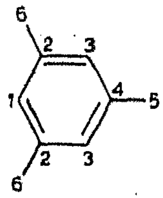
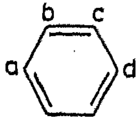
The protons of the vinyl group appear as a poorly resolved multiplet centred at $\delta$ 6.00 ppm. The allenyl derivative shows a doublet at $\delta$ 4.45 ppm ($C\underline{H}_2$) and a triplet at $\delta$ 6.04 ppm ($C\underline{H}$). The allyl compound shows the expected spectrum for a $\sigma$-bonded allyl group [6] i.e. a doublet at $\delta$ 2.28 ppm,($C\underline{H}_2$), a poorly resolved multiplet centred at $\delta$ 4.90 ppm ($=C\underline{H}_2$) and an asymmetric multiplet centred at $\delta$ 5.81 ppm ($=C\underline{H}$). This pattern does not change significantly at temperatures below 140°C in 1-bromonaphthalene.

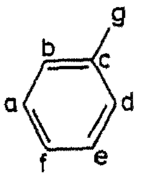
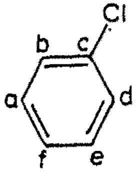
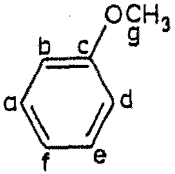
The assignments for the $^{13}C$ spectra of these compounds are given in Table 2 together with those for appropriate saturated derivatives [2]. With the exception of the C(1) carbons the mesityl carbon atoms are readily assigned from the decoupled spectra. The carbons of the third substituent have been assigned with the aid of undecoupled spectra.

The decoupled spectrum of 7 showed two broad low intensity signals at 147.6 and 142.5 ppm and a sharp signal at 139.4 ppm. In the completely undecoupled spectrum the signals at 147.6 and 139.4 ppm appear as complex multiplets, the details of which led to their assignment as C(7) and C(8), respectively. The decoupled spectrum of 9 showed a fairly broad signal at 40.4 and two sharp signals at 135.8 and 114.0 ppm. In the off-resonance undecoupled spectrum these appear as a triplet, a doublet, and a triplet, respectively. They are therefore readily assigned in turn to C(7), C(8) and C(9). The decoupled spectrum of 10 showed a broad singlet at 96.0 and two sharp singlets at 68.6 and 221.8 ppm. The fully undecoupled spectrum showed these signals in order as: a doublet $\{^1J(CH) \sim 152$ Hz$\}$, each component of which is a relatively broad line due to long-range coupling with the methylene protons and broadening caused by the boron quadrupole; a triplet of doublets $\{^1J(CH_2) = 168.5$ Hz, $^3J(^{13}C{=}C{=}C^1H) = 7.3$ Hz$\}$ and finally a symmetrical five line multiplet (ratios 1 : 3 : 2 : 3 : 1) which arises from the fact that $^2J(^{13}C{=}C^1H)$ is by chance exactly twice $^2J(^{13}C{=}C^1H_2)$ and equals 5.86 Hz. Complete assignment of 8 was only achieved with some difficulty. The fully decoupled spectrum, obtained using standard settings (see Experimental section), showed only resonances due to the mesityl and phenyl parts of the molecule. The C(1), C(7) and C(8) carbon signals were not visible. Use of a 30 $\mu$s pulse (tip angle of 90°) and a pulse interval of 20 s produced a spectrum which showed, in addition to the mesityl and phenyl signals, a low intensity signal at 126.9 ppm and two very low intensity broad signals at 137.7 and 102.4 ppm. To confirm the origin of the latter signals several spectra were recorded at low temperature (—75°C, $CH_2Cl_2$, $^7Li$ external lock) under noise decoupling conditions known, when optimised, to enhance the signals of tertiary carbons at the expense of those coupled to protons [7]. The required confirmatory enhancements were obtained using suitable decoupling frequency offsets with both narrow-band, high power noise and broad-band, low power procedures.

TABLE 1

THE CHEMICAL SHIFTS $\delta^{13}C$ AND $\delta^{11}B$ OF ARYLDIMESITYLBORANES [a]

| No. | R | $\delta^{13}C$ (ppm) | | | | | | | | | | | | | $\delta^{11}B$ (ppm) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | a | b | c | d | e | f | g | |
| 1 |  | 144.1 | 140.5 | 128.6 | 139.0 | 21.2 | 22.8 | | | | | | | | 79.0 |
| 2 |  | 141.7 | 140.7 | 128.2 | 138.6 | 21.2 | 23.4 | 145.9 | 136.2 | 127.9 | 131.9 | | | | 79.5 |

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 4 |  | 141.8 | 140.7 | 128.1 | 138.4 | 21.2 | 23.4 | 145.9<br>(145.7) | 136.6<br>(136.8) | 137.2<br>(137.0) | 132.7<br>(132.5) | 127.9<br>(127.7) | 133.5<br>(133.1) | 21.3 | 77.0 |
| 5 |  | 141.2 | 140.8 | 128.3 | 139.0 | 21.2 | 23.4 | 148.1<br>(146.9) | 135.3<br>(136.4) | 134.4<br>(134.3) | 131.6<br>(132.1) | 129.5<br>(128.9) | 134.0<br>(134.2) | | 74.5 |
| 6 |  | 141.7 | 140.7 | 128.1 | 138.5 | 21.1 | 23.3 | 147.6<br>(145.9) | 120.8<br>(120.7) | 159.2<br>(158.1) | 117.3<br>(116.4) | 129.0<br>(127.9) | 128.7<br>(127.3) | 55.1 | 75.5 |

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[a] Values given in parentheses are calculated values obtained using assumed additivity of substituent shielding parameters (see text).

TABLE 2

THE CHEMICAL SHIFTS $\delta^{13}C$ AND $\delta^{11}B$ FOR UNSATURATED ALIPHATIC DIMESITYLBORANES

| No. | R | $\delta^{13}C$ (ppm) | | | | | | | | | $\delta^{11}B$ (ppm) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | |
| — | $-\overset{7}{C}H_2\overset{8}{C}H_3$ | 142.6 | 138.9 | 128.4 | 138.1 | 21.1 | 22.6 | 26.3 | 9.2 | | 85.0 |
| 7 | $-\overset{7}{C}H=\overset{8}{C}H_2$ | 142.5 | 140.6 | 128.2 | 138.6 | 21.2 | 23.3 | 147.6 | 139.4 | | 70.0 |
| 8 | $-\overset{7}{C}\equiv\overset{8}{C}Ph$ [a] | 137.7 | 141.1 | 128.6 | 139.5 | 21.2 | 23.1 | 102.4 | 126.9 | | 64.0 |
| — | $-\overset{7}{C}H_2\overset{8}{C}H_2\overset{9}{C}H_3$ | 142.9 | 138.9 | 128.3 | 138.1 | 21.1 | 22.6 | 37.3 | 19.1 | 17.5 | 84.5 |
| 9 | $-\overset{7}{C}H_2\overset{8}{C}H=\overset{9}{C}H_2$ | 141.9 | 139.1 | 128.4 | 138.5 | 21.1 | 22.9 | 40.4 | 135.8 | 114.0 | 87.5 |
| 10 | $-\overset{7}{C}H=\overset{8}{C}=\overset{9}{C}H_2$ | 141.1 | 140.1 | 128.2 | 138.5 | 21.1 | 22.9 | 96.0 | 221.8 | 68.6 | 77.5 |

[a] $C_1$ = 123.4 (122.2); $o$ = 132.5 (132.1); $m$ = 128.4 (128.2); $p$ = 129.7 (128.7) values in parenthesis are for phenylacetylene measured under the same conditions.

The $^{11}B$ spectra consisted of single broad peaks, these chemical shifts are also given in Table 2.

## Discussion

Triarylboranes are known to adopt propeller conformations in the solid state [8]. Their solution properties have also been interpreted on this basis [9] and this has led to the conclusion that barriers to rotation in arylboranes are mainly steric in origin and that conjugative effects play only a minor role [8a]. Furthermore $\pi$-electron donation from a phenyl group to boron does not appear to be very efficient even under favourable conditions since the barrier to internal rotation about the phenyl—boron bond in dihalogenophenylboranes is only ~13.6 kJ mol$^{-1}$ [10]. The $^{13}C$ chemical shift values given in Table 1 can be taken therefore as typical values for phenyl groups carrying a boryl substituent under conditions of negligible $\pi$ back-donation. The dimesitylboryl group shielding parameters should also be of some value in the identification, by $^{13}C$ NMR, of arylboranes of unknown structure such as those generated by photochemical methods [11].

The effects of substituting a dimesitylboryl group for an $\alpha$-hydrogen in unsaturated aliphatic hydrocarbons are summarised in Table 3. This table gives the changes in $^{13}C$ chemical shifts of the relevant carbons in the dimesitylboryl compound relative to the parent hydrocarbon i.e. $\Delta\delta^{13}C = \delta^{13}C$ (dimesitylboryl compound) — $\delta^{13}C$ (parent hydrocarbon). The values of $\delta^{13}C$ for the hydrocarbons are given in Table 4.

It is seen from Table 3 that substitution at the $\alpha$-carbon causes a deshielding of about 20 ppm which is due in the main to the inductive effect of the boryl group. As such, this rapidly attenuates along the saturated hydrocarbon chains. However when the $\gamma$ carbon is $sp^2$ hybridised it is shielded by ~5 ppm. Since in the allyl case the $\pi$ system is "insulated" from the empty $p$ orbital on the boron atom by the saturated $\alpha$-carbon, this effect is not caused directly by any kind of $\pi$ electron charge delocalisation.

Most information on the electronic structures of these unsaturated systems

TABLE 3

SUBSTITUENT EFFECTS ON THE CHEMICAL SHIFTS $\delta^{13}C$ OF DIMESITYLBORYL-SUBSTITUTED ALIPHATIC HYDROCARBONS

| Hydrocarbon | $\Delta\delta^{13}C$ (ppm) | | |
|---|---|---|---|
| | $\alpha$ | $\beta$ | $\gamma$ |
| $H_2\overset{\alpha}{C}-\overset{\beta}{C}H_3$ | 20.4 | 3.3 | — |
| $H\overset{\alpha}{C}=\overset{\beta}{C}H_2$ | 24.8 | 16.6 | — |
| $\overset{\alpha}{C}\equiv\overset{\beta}{C}Ph$ | 25.1 | 43.3 | — |
| $\overset{\alpha}{C}H_2-\overset{\beta}{C}H_2\overset{\gamma}{C}H_3$ | 21.7 | 3.0 | 1.9 |
| $\overset{\alpha}{C}H_2\overset{\beta}{C}H=\overset{\gamma}{C}H_2$ | 18.0 | −1.0 | −4.6 |
| $H\overset{\alpha}{C}=\overset{\beta}{C}=\overset{\gamma}{C}H_2$ | 22.5 | 9.2 | −4.9 |

TABLE 4

THE CHEMICAL SHIFTS $\delta^{13}C$ OF RELEVANT ALIPHATIC HYDROCARBONS [a]

| Hydrocarbon | $\delta^{13}C$ (ppm) | | | Ref. |
|---|---|---|---|---|
| | $\alpha$ | $\beta$ | $\gamma$ | |
| $H_3C{-}CH_3$ | 5.9 | 5.9 | — | 5 |
| $H_2C{=}CH_2$ | 122.8 | 122.8 | — | 5 |
| $HC{\equiv}CPh$ | 77.3 | 83.6 | — | 12 |
| $CH_3CH_2CH_3$ | 15.6 | 16.1 | 15.6 | 5 |
| $CH_3CH{=}CH_2$ | 22.4 | 136.8 | 118.6 | 13 |
| $H_2C{=}C{=}CH_2$ | 73.5 | 212.6 | 73.5 | 14 |

[a] W.r.t. to internal TMS.

comes from observing changes in chemical shifts at the $\beta$ carbons [3]. It is here that the effects of any $\pi$ electron back-donation to the boron should be most evident. In the vinyl system the C($\beta$) is deshielded by 16.6 ppm and this fits into the pattern observed for $X_2B$ alkenyl derivatives [3] which have $\Delta\delta^{13}C$ (X) values of 11.3 (alkoxy) 17.4 (alkyl) and ~22.7 (halogeno). In fact it is seen that the Lewis acidity of the boron atom in these compounds, as measured by $\Delta\delta^{13}C(\beta)$, mimics the established acidity order of $BX_3$ systems i.e. alkoxy < alkyl < halogen. The difference in $\Delta\delta^{13}C(\beta)$ observed for $(Bu^nO)_2B$ (11.3) and $C_6H_4O_2B$ (20.4) alkenyls is also consistent with the greater Lewis acidity of aryloxyboranes [15].

The corresponding carbon in the alkynyl derivative is deshielded by 43.3 ppm which is some 20 ppm more than is observed for dialkylamino- and dialkoxy alkynylboranes [3b,c] where nitrogen and oxygen atoms are competitive $\pi$ Lewis bases. The deshielding of the C($\beta$) atom is not transmitted to the phenyl group in 8 since the chemical shifts of this group are very similar to those in the parent hydrocarbon (see Table 2). This situation contrasts with that in corresponding carbocations [3c] and confirms the observation that trigonal boron is a worse $\pi$ acceptor than the equivalent carbon in a carbocation [16]. The C($\beta$) *sp*-hybridised atom in the allenyl compound is only deshielded by 9.2 ppm, which reflects the appreciable electron deficiency of this atom in the parent molecule.

These results indicate that stabilisation due to $\pi$ electron back-donation from the unsaturated ligand to boron follows the order aryl << allenyl < alkenyl < alkynyl. This trend is also seen in the $^{11}B$ chemical shift values although in the case of 8 the situation is complicated by a shielding contribution due to the anisotropy of the triple bond [17].

Finally the inability of the allyl derivative to undergo the usually observed intramolecular allylic rearrangement [6] at temperatures below 140°C is attributed to the steric effects of the mesityl groups which prevent the formation of the necessary four-coordinate intermediate but do, however, permit the synthesis of II.

## Experimental

$^{13}C$ and $^{11}B$ NMR spectra were recorded under the same conditions used in earlier studies [18]. Routine $^1H$ spectra were recorded on a Perkin-Elmer R12A instrument in $CCl_4$ with internal TMS as reference. The variable temperature measurements on 9 were carried out on a Perkin-Elmer R32 instrument with an upper limit for the variable temperature attachment of 140°C. All manipulations involving the aliphatic derivatives were carried out in a dry nitrogen filled glove box or in modified Schlenk tubes.

Except where otherwise stated the compounds were synthesised from 0.005 mole of fluorodimesitylborane and the stoichiometric quantity of the appropriate lithium or Grignard reagent. Dry nitrogen atmospheres and anhydrous oxygen-free solvents were used during the preparative stages of the syntheses. Reagent grade solvents were used without further purification for recrystallisations etc. The products were characterised by $^1H$ and $^{13}C$ NMR spectroscopy and precise mass spectrometric measurements. The relevant details are given below.

*Trimesitylborane (1).* 1 was synthesised in 60% yield, after two recrystallisations from ethyl acetate, by the published method [19] m.p. 192—195°C (Lit. [19] 195—197°C).

*Dimesitylphenylborane (2) and dimesitylboranes (3 and 4).* Fluorodimesitylborane in ether (30 ml) was added dropwise to an ethereal solution of phenyllithium or the appropriate tolylmagnesium bromide. The mixture was refluxed for 2 h, cooled to room temperature and poured into cold water. The organic layer was separated and dried ($MgSO_4$). Removal of the solvent gave a solid product which after one recrystallisation from ethyl acetate or ethanol/ethyl acetate (3) gave well-formed colourless crystals (yield, m.p.) of 2 (74%, 177—180°C), 3 (70%, 168—169°C) and 4 (65%, 136—138°C).

*Dimesityl(m-chlorophenyl)borane (5).* 5 was prepared from *m*-chlorophenyllithium [20] in pentane and fluorodimesitylborane in ether (30 ml) at —30°C. The reaction mixture was allowed to warm up to room temperature and stirred for 2.5 h. The work up procedure was as described above to yield a yellow solid which after one recrystallisation from ethanol/ethyl acetate gave colourless crystals of 5 (73%, 146—148°C).

*Dimesityl(m-methoxyphenyl)borane (6).* 6 was prepared from *m*-anisylmagnesium bromide in an ether/THF mixture (70 : 20) using the procedure described for 2 above, except that instead of refluxing for 2 h.the mixture was stirred at room temperature for 15 h. Work-up, as described above, gave a viscous yellow oil, which gave a white solid on triturating with methanol. One recrystallisation from ethanol gave colourless crystals of 6 (45%, 97—99°C).

*Ethenyldimesitylborane (7).* 7 was prepared by dropwise addition of an ether solution of freshly-prepared solid ethenyllithium [21] and fluorodimesitylborane in ether (25 ml) at —78°C. The solution was allowed to warm to room temperature and stirred for 2 h. Removal of the solvent gave a viscous yellow oil which was extracted with pentane. The mixture was filtered under nitrogen to give a colourless solution. A small amount of a yellow polymeric material remained on the filter. Evaporation of the pentane in vacuo gave a pale yellow oil which solidified at 0°C to form a waxy solid.

Attempts to make 7 from ethenyl magnesium bromide were frustrated by the fact that the product polymerised rapidly as the reaction mixture warmed to above —25°C. The use of ethenyllithium solution prepared directly from phenyllithium and tetraethenylstannane in ether was unsatisfactory since it proved impossible to separate the product from the trace amounts of tetraphenylstannane present in the solution of ethenyllithium [21].

*Dimesityl(phenylethynyl)borane (8).* 8 was prepared by adding fluorodimesitylborane in hexane (30 ml) to a suspension of phenylethynyllithium in hexane (120 ml) and stirring the mixture for 2 days, during which time ether (75 ml) was added. The mixture was filtered under nitrogen and evaporation of the solvent gave a yellow oil which solidified on tituration with pentane. Recrystallisation from ethanol gave pale yellow crystals of 8 (42%, 100—104°C). The infra-red spectrum of 8, as a KBr disc, showed a strong absorption at 2135 $cm^{-1}$ (—C≡C— stretch).

*Allyldimesitylborane (9).* 9 was prepared from allylmagnesium bromide and fluorodimesitylborane in ether according to the procedure used for 2 above. The solid product was recrystallised from ethanol to give colourless crystals of 9 (85%, 68°C).

*Allenyldimesitylborane (10).* 10 was prepared by the dropwise addition of a solution of "propargyl magnesium bromide" [22] in ether to fluorodimesitylborane in ether (40 ml) at —50°C. The mixture was stirred at —50°C for 1 h and then overnight at room temperature. Filtration under nitrogen gave a clear yellow solution. Removal of the solvent in vacuo gave a viscous yellow oil which slowly crystallised. One recrystallisation from hexane gave yellow crystals of 10 (26%, 89—92°C).

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