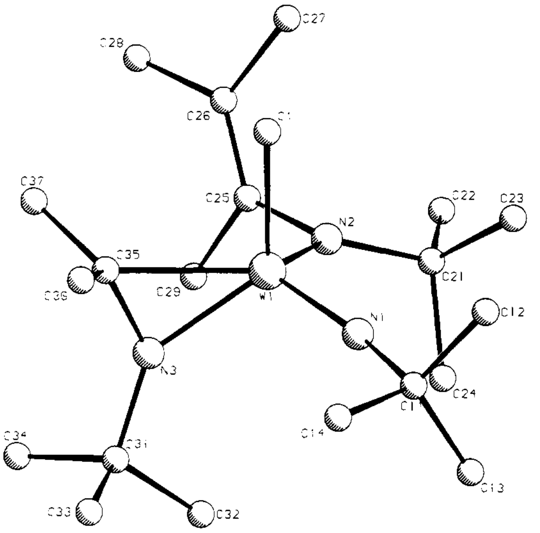
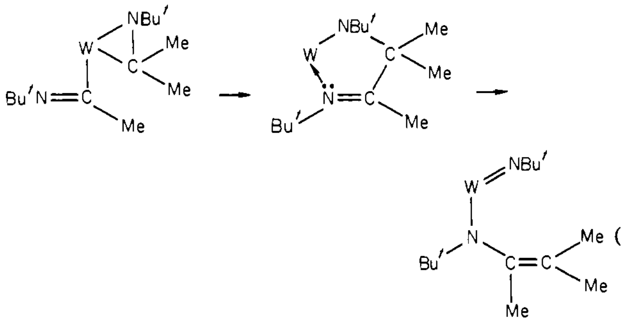


Figure 1. Molecular structure of **1**. Bond lengths (Å) and angles (deg) in the coordination sphere are as follows: W–N(1) = 1.74 (1), W–N(2) = 1.94 (1), W–N(3) = 1.92 (1), W–C(35) = 2.19 (1), W–C(1) = 2.14 (1), W···C(25) = 2.79 (1); N(1)–W–C(1) = 99 (1), N(1)–W–N(2) = 109 (1), N(1)–W–N(3) = 110 (1), N(1)–W–C(35) = 123 (1), N(2)–W–C(1) = 106 (1), N(2)–W–N(3) = 110 (4), N(2)–W–C(35) = 126 (1), N(3)–W–C(35) = 40 (1).

(1)

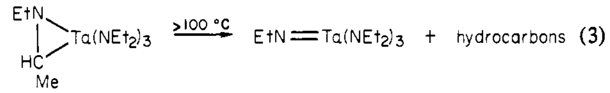
A similar $\overline{\text{WN(Et)CHMe}}$ group has been detected in the reaction products from WCl_6 and $LiNEt_2$.[8] Migration of two methyl groups to coordinated carbon monoxide to give acetone via the acyl has been demonstrated in reactions of CO with $(\eta^6\text{-}C_6H_6)Mo(CO)(PR_3)Me_2$[9] and $CoMe_3(PMe_3)_3$,[10] while $(\eta^5\text{-}C_5Me_5)TaMe_4$ gives an (η^2-acetone)(oxatantallacyclopropane) complex, $(\eta^5\text{-}C_5Me_5)TaMe_2(\eta^2\text{-}OCMe_2)$,[11] which provides an analogue for the $\eta^2\text{-}NBu^tCMe_2$ group.

Further methyl transfer to isocyanide and intramolecular rearrangement of adjacent azacyclopropane and $WC(Me){=}NBu^t$ groups with C–C bond formation could then lead to the dialkylamido and *tert*-butylimido groups (eq 2). Note that the reaction of $(\eta^5\text{-}C_5Me_5)Me_2Ta(\eta^2\text{-}OCMe_2)$ with a second CO molecule yields a product which appears to contain Ta=O and $TaOC(Me){=}CMe_2$ groups—analogous to the $W{=}NBu^t$ and $WN(Bu^t)C(Me){=}CMe_2$ units found in **1**.[11]



(2)

Although thermolysis of an azatantallacyclopropane complex has been reported to yield an organomido group[12] it seems unlikely that a similar process occurs in our case since **1** is formed in high yield under mild conditions and no gaseous hydrocarbons are evolved.



(3)

Further reaction of two of the remaining WMe groups with 1 mol of Bu^tNC would then give rise to the final $\overline{\text{WC(Me)}_2\text{NBu}^t}$ group. Steric factors may be responsible for the retention of one WMe group in the molecule which does not react with the excess Bu^tNC present under the reaction conditions employed.

Hexamethyltungsten reacts with CO (3 atm) in isopentane to give $W(CO)_6$ and acetone (NMR, GLC).

Acknowledgment. We thank the S.R.C. (U.K.) for support.

Supplementary Material Available: Tables of fractional coordinates and anisotropic thermal parameters (2 pages). Ordering information is given on any current masthead page.

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(8) Airoldi, C.; Bradley, D. C.; Vuru, G. *Transition Met. Chem.* **1979**, *4*, 64.

(9) Carmona-Guzman, E.; Wilkinson, G., *J. Chem. Soc., Dalton Trans.* **1978**, 1139.

(10) Klein, H. F.; Karsch, H. H. *Chem. Ber.* **1976**, *109*, 1453. The complex $(\eta^5\text{-}C_5H_5)CoMe_2(PPh_3)$ also gives acetone on treatment with CO: Bergman, R. G. *Acc. Chem. Res.* **1980**, *13*, 113 and references therein.

(11) Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5431.

(12) Takahashi, Y.; Onoyama, N.; Ishikawa, Y.; Motojirna, S.; Sugiyama, K. *Chem. Lett.* **1978**, 525.

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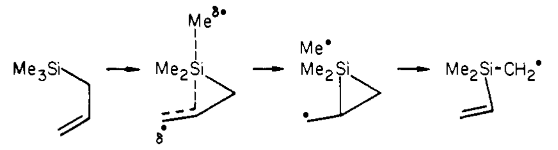
Radical Rearrangements in the Pyrolysis of Allyldisilanes

Sir:

Jones[1] has recently presented surprising evidence that a major mode of thermal decomposition of allyltrimethylsilane, to ultimately afford trimethylvinylsilane, is through direct loss of the methyl radical. As simple homolysis of Si–Me rather than Si–allyl bonds should not be at all competitive,[2] we would suggest that these results argue for π participation in the loss of methyl radical.



Since the Si–Si bond is almost 10 kcal/mol weaker than the Si–Me bond,[3] alkylsilyl should be a considerably better leaving group than methyl. Thus, in order to favor the formation of the silahomoallyl/silacyclopropylcarbinyl radical, we undertook the thermolysis of 1,2-diallyl-1,1,2,2-tetramethyldisilane (**1**).[4,5] However, we were surprised to find that vacuum-flow pyrolysis of **1** (800° C, 10^{-4} torr, 1-ft quartz-packed horizontal tube) cleanly produces 1,1,3,3-tetramethyl-1,3-disilacyclopentene (**2**)[7] in 51%

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(1) Neider, S. M.; Chambers, G. R.; Jones, M., Jr. *Tetrahedron Lett.* **1979**, 3793.

(2) Assuming that ΔE_{act} for Me· loss vs. C_3H_5· loss is simply $\Delta\Delta H$, then Me· loss would be ~16 kcal/mol > E_{act} for allyl loss. Thus, even at the reported 600 °C, allyl radicals should be produced more than 3000 times faster than methyl radicals. Of course this argument is only necessary if the process is unimolecular. No evidence has been presented to date which rules out a bimolecular origin of trimethylvinylsilane.

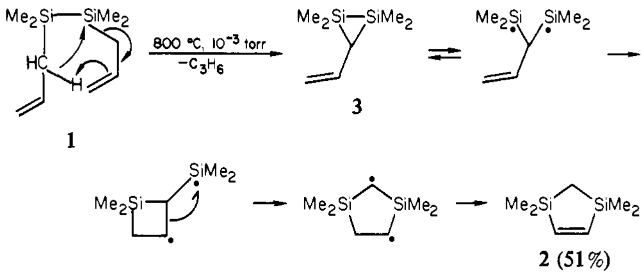
(3) Sakurai, H. "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2, Chapter 25.

(4) All starting materials and products reported here were established by both their mass and NMR spectra.

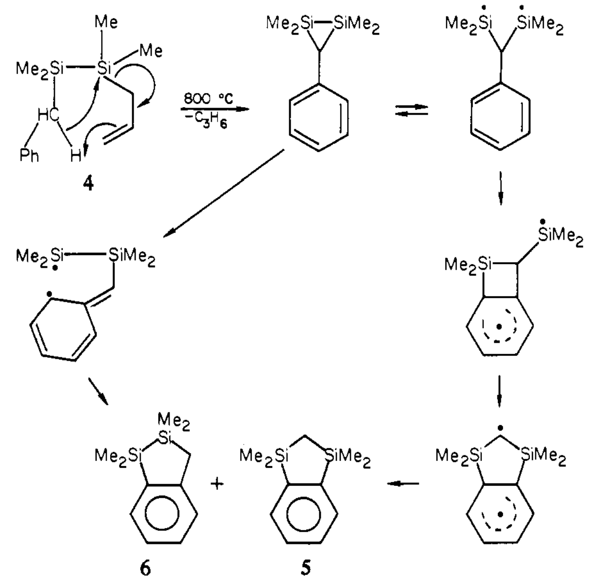
(5) Prepared in 77% yield from the coupling of 1,2-dichlorotetramethyldisilane and excess allylmagnesium bromide; bp 95–100° (34 mm) [lit. bp 86 °C (24 mm)].[6]

(6) Sakurai, H.; Hosomi, A.; Kumada, M. *Tetrahedron Lett.* **1968**, *20*, 2469.

Scheme I



Scheme II

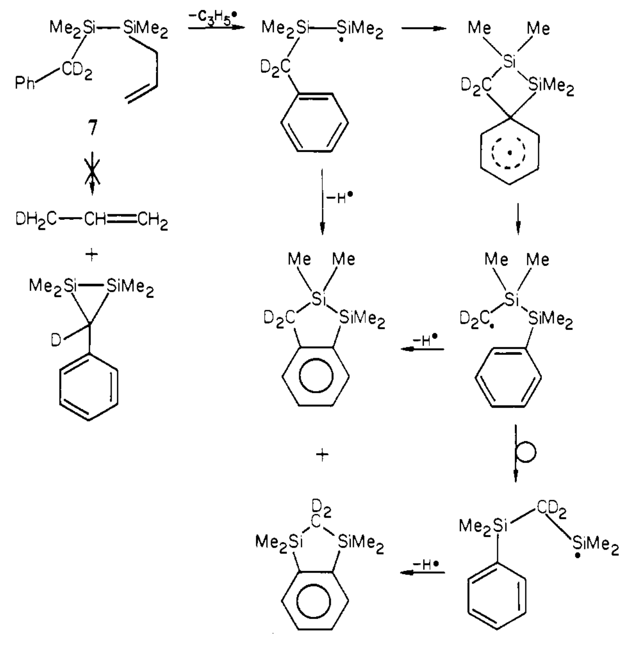


yield. A rationalization for this extraordinary behavior was that we were observing an unprecedented homoretroene (HRE) elimination of propene, where one of the silicon atoms was bypassed to achieve the six-electron process (Scheme I). The resulting disilacyclopropane, **3**,[8] could now undergo the initially desired homolysis of the strained Si-Si bond, cyclize, and ring expand to the five-membered ring. Ample precedent for such a ring expansion is found in the gas-phase reactions between silylenes and cycloalkenes.[11]

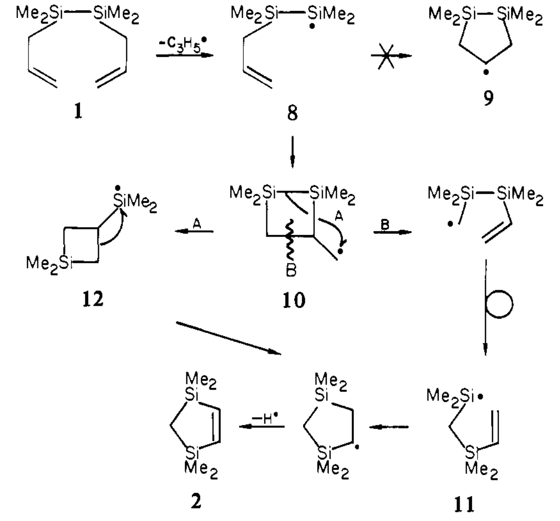
To put this mechanistic reasoning to a test, we replaced one of the allyl groups of **1** with a benzyl group. Since the benzylic methylene should possess similar lability to the allylic methylene, the same general mechanistic pathway would be expected. The synthesis of 1-allyl-2-benzyl-1,1,2,2-tetramethyldisilane (**4**)[4] was accomplished in 60% yield by sequential addition of benzyl- and allylmagnesium bromides to 1,2-dichlorotetramethyldisilane. Pyrolysis of **4** (800 °C, 10^{-4} torr) produced as the two major products disilaindans **5**[12] and **6**[13] in respective yields of 21% and 29%. Both of these products can be rationalized as originating from an initial HRE elimination of propene as illustrated in Scheme II.

However, careful examination of GC/MS of the product mixture from thermolysis of **4** revealed that **2** (<5%) was also a product of this reaction. This observation demands consideration

Scheme III



Scheme IV



of an alternative mechanism for the **1** → **2** transformation and suggests that the observed products **2**, **5**, and **6** arise from simple homolysis of benzyl- and allyl-silicon bonds. In the case of **4** a mechanistic distinction can be experimentally made by examination of the thermolysis products from the dideuterio derivative **7**. In a HRE elimination, one deuterium would be removed by the extrusion of propene in the initial step. However, in the totally free-radical process of Scheme III, it is possible to maintain the integrity of the CD_2 unit. Mass spectral and NMR analysis of the disilaindans formed in the pyrolysis of **7** revealed no significant loss of deuterium.[14] Further confirmation of the all-radical pathway was obtained when 1,2-dibenzyltetramethyldisilane was pyrolyzed to also afford **5** and **6** as the only major products. Thus, the HRE process is not operative in the pyrolysis of **4**, and there is no reason to suspect it in the thermochemistry of **1**.

There are several important ramifications to the discovery that these processes proceed by initial homolysis (other than the inconsistency with the results from allyltrimethylsilane[1]). First, it would appear that the initially formed disilanyl radical **8** (from **1**, Scheme IV) must cyclize in an endo fashion to afford **10**, as we see no products with the ring system of **9**. This would fit the general rules for carbon radical cyclization recently adumbrated

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(7) Barton, T. J.; Wulff, W. D. *J. Organomet. Chem.* **1979**, *168*, 23.

(8) While disilacyclopropanes have never been observed, they have been postulated as transient intermediates in other gas-phase[9] and solution[10] processes.

(9) Wulff, W. D.; Goure, W. F.; Barton, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 6236.

(10) Seyferth, D.; Duncan, D. P. *J. Organomet. Chem.* **1976**, *111*, C21.

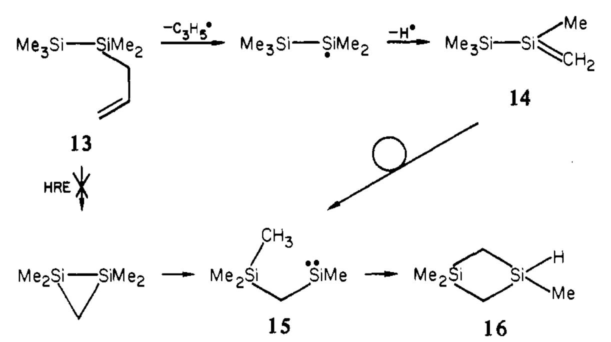
(11) Gaspar, P. P.; "Reactive Intermediates"; Wiley Interscience: New York, 1978; pp 249-255.

(12) Chernyshev, E. A.; Komalenkova, N. G.; Bashkirova, S. A.; Zhavoronkova, T. A. *Zh. Obshch. Khim.* **1976**, *46*, 1278. [NMR (CCl_4) δ -0.05 (s, 2 H), 0.30 (s, 12 H), 7.1-7.56 (m, 4 H).]

(13) Tsui, F. P.; Zon, G. *J. Organomet. Chem.* **1974**, *70*, C3. [NMR (CCl_4) δ 0.22 (s, 6 H), 0.30 (s, 6 H), 2.27 (s, 2 H), 7.60 -6.97 (m, 4 H).]

(14) No evidence for deuterium loss in the isotopic analogues of **5** and **6** could be detected by NMR. Mass spectral analysis allowed up to 2% **5**-*d* and 6% **6**-*d*.

Scheme V



by Beckwith.[15] However, we are unaware of any published studies on the cyclization of 4-pentenyl radicals.

It is interesting to note (Scheme IV) that ultimate formation of **2** from **10** could involve either endo closure of radical **11** or ring expansion of cyclobutylcarbinyl radical **12**. Neither of these processes has precedent in carbon-radical chemistry.

Lastly, the elimination of the HRE mechanism presents a problem in the interpretation of the thermolysis results from allylpentamethyldisilane (**13**). We initially undertook the pyrolysis (840 °C, 10^{-3} torr)[16] of **13** as a test for the necessity of C–H activiation in the proposed HRE elimination. Thus, we predicted (Scheme V) and observed the formation of the major product, 1,1,3-trimethyl-1,3-disilacyclobutane (**16**, 18%).[18] Key features in this route are the now precedented[19] disproportionation of a methylsilicon radical to a silene (**14**) and the rearrangement of a silene (**14**) to a silylene (**15**). To our knowledge, this latter process has never before been observed or proposed. Silylene **15** has been generated before in our laboratory, and shown to cyclize to **16**.[9] Experiments are currently under way to unambiguously generate silene **14** as well as radicals such as **11** and **12**.

Acknowledgment. We thank Dow Corning Corporation for partial support of this work.

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(15) Beckwith, A. L. J.; Easton, C. J.; Serelis, A. K. *J. Chem. Soc., Chem. Commun.* **1980**, 482.

(16) Prepared in 71% yield from the coupling of chloropentamethyldisilene and allylmagnesium bromide; bp 80 °C (55 mmHg) [lit. bp 155 °C (760 mm)].[17]

(17) Chernyshev, E. A.; Tolstikova, N. G.; Ivashenko, A. A.; Zelenetskaya, A. A.; Leites, L. A. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* **1963**, 660.

(18) Also obtained in the pyrolysis of **13** were allyltrimethylsilane (5%), trimethylvinylsilane (2%) (possibly from α elimination of Me$_2$Si: and decomposition of Me$_3$SiC$_3$H$_5$, respectively, although both products could arise from addition of Me$_3$Si· to **13**), and **2** (10%, presumably from initial loss of methyl radical, perhaps with π assistance?).

(19) Tokach, S. K.; Koob, R. D., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 376. Cornett, B. J.; Choo, K. V.; Gaspar, P. P. *Ibid.* **1980**, *102*, 377. Gammie, L.; Safarik, I.; Strausz, O. P.; Roberge, R.; Sandorfy, C. *Ibid.* **1980**, *102*, 378.

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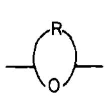
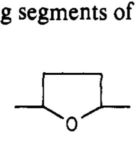
A New Family of Cation-Binding Compounds: *threo*-α,ω-Poly(cyclooxalkane)diyl

Sir:

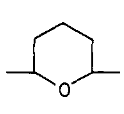
α,ω-Poly(cyclooxalkane)diyl (**1**) constitutes a new generic family of polymers in which cyclic ether units are bonded together along the main chain. Specifically, separate polymers have been made which contain long segments of recurring 2,5-tetrahydrofurandiyl (**2**), 2,6-tetrahydropyrandiyl (**3**), and 2,4-bicyclo[3.2.1]-3-oxaoctanediyl (**4**) units.



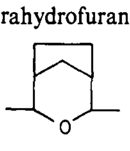
1



2

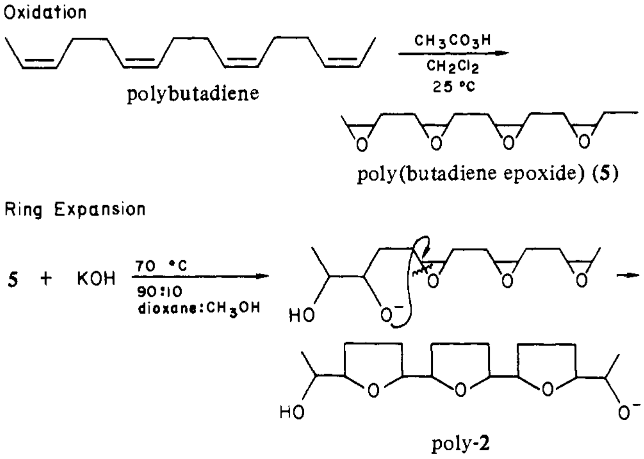


3

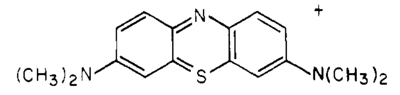


4

Scheme I



Certain of these polymers bind cations in a manner similar to that of the crown ethers. However, unlike the crowns, whose complexing ability is determined to a large extent by the relative cation and macrocycle cavity dimensions,[1-3] a given **1** compound can effectively bind cations of widely varying sizes, e.g., Li$^+$, Ba^{2+}, and methylene blue. Cation binding properties of **1** are particularly manifest when the average segment length of cyclic ether units is sufficient (at least 6 units) and the ring junctures are of threo configuration.



methylene blue

The syntheses of polymers of **2**, **3**, and **4** involve the essentially complete oxidation[4] and subsequent ring expansion of the oxiranes thus derived from the polymers of butadiene, cyclopentene,[5] and norbornene,[6] respectively. Scheme I gives the synthesis of poly-**2** by using Ameripol CB220 as starting material (B. F. Goodrich Co.), a poly butadiene of 100 000 mol wt having 98% *cis*-olefin and 2% pendent vinyl contents.

The following features characterize the overall synthesis of poly-**2**: (a) Assignment of all polymer functional groups can be made by ^{1}H and ^{13}C NMR. (b) The complete conversion of main chain olefins to oxirane units is readily achieved under conditions which leave vinyl groups intact. (c) The rate-controlling step in the ring expansion reaction is the initiation step, which amounts to the random nucleophilic cleavage of an oxirane unit. (d) The propagation reaction which gives rise to poly-**2** segments is a chain reaction. (e) Termination of the reaction involves proton transfer when the propagating alkoxide ion encounters a "defect" unit, i.e., a separation of oxirane units by other than two or three carbon atoms.

Polymers having essentially all *cis*- and all *trans*-olefin configurations were used as precursors for **1** in separate experiments. Products derived from cis precursors were discovered to be effective complexing agents for a large variety of cations as measured by phase-transfer experiments of the type used to determine the binding efficiencies of crown ethers,[2] whereas those made from

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(1) C. J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017–7036 (1967).

(2) C. J. Pedersen and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, **11**, 16–25 (1972).

(3) J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, **74**, 351–384 (1974).

(4) The oxidation of diene polymers with peracids is the subject of a review article: E. M. Fettes, Ed., "High Polymers", Vol. 19, Chemical Reactions of Polymers, Interscience Publishers, New York, 1964, pp 152–172 (F. P. Greenspan).

(5) N. Calderson, *J. Macromol. Sci.*, Rev. *Macromol. Chem.*, **C7**, 105–159 (1972).

(6) K. J. Ivin, D. T. Laverty, and J. J. Rooney, *Makromol. Chem.*, **178**, 1545–1560 (1977).

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