



Science of Synthesis

Houben–Weyl Methods of Molecular Transformations

Sample Contribution

Category		Organometallics
Volume	5	Compounds of Group 14 (Ge, Sn, Pb)
Product Subclass	5.1.22	Aryl- and Heteroarylgermanes
Written by		A. C. Spivey and C. M. Diaper



Science of Synthesis

Houben-Weyl Methods of Molecular Transformations

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Biographical Sketches



Alan Spivey received his BSc in chemistry in 1988 from the University of Nottingham, UK and his DPhil in 1991 from the University of Oxford under the guidance of Prof. Sir Jack Baldwin. After postdoctoral work at the Université de Genève, Switzerland with the late Prof. Wolfgang Oppolzer, and at the University of Cambridge with Prof. Sir Alan Battersby, he moved to a lectureship at the University of Sheffield. In January 2003 he moved to Imperial College London as a reader. Research in his group is focused on the development of new catalysts for asymmetric acylation, new linkers for solid phase organic synthesis, chemical aspects of signal transduction, and total synthesis of bioactive natural products.



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5.1.22 Product Subclass 22: Aryl- and HeteroarylgermanesA. C. Spivey and C. M. Diaper

5.1.22	Product Subclass 22: Aryl- and Heteroarylgermanes	6
	Synthesis of Product Subclass 22	8
5.1.22.1	Method 1: From Halogermanes by Substitution with Arylmetals	8
5.1.22.1.1	Variation 1: Using Preformed Arylmetals	8
5.1.22.1.2	Variation 2: Using Barbier-Type Reactions	9
5.1.22.2	Method 2: From Aryl Halides by Palladium(0)-Mediated Coupling with Digermanes	9
5.1.22.3	Method 3: From Aryl Halides by Insertion of Dichlorogermylene	10
5.1.22.4	Method 4: Heteroarylgermanes by Cycloaddition	11
	Applications of Product Subclass 22 in Organic Synthesis	12
5.1.22.5	Method 5: Arylgermanes as Linkers for Solid-Phase Synthesis	12

for references see p 13

Product Subclass 22: Aryl- and Heteroarylgermanes

A. C. Spivey and C. M. Diaper

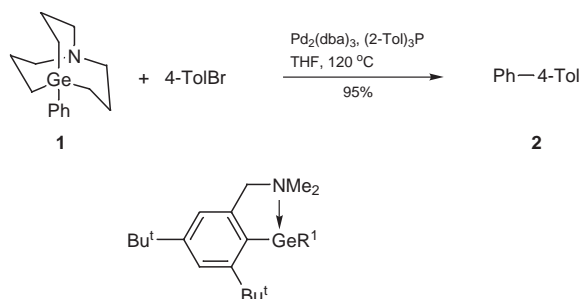
General Introduction

Previously published information regarding aryl- and heteroarylgermanes can be found in *Comprehensive Organic Functional Group Transformations*,^[1] *The Chemistry of Organic Germanium, Tin and Lead Compounds*,^[2] *Houben–Weyl, Vol. 13/6*, and *The Organic Compounds of Germanium*.^[3]

Arylgermanes are thermally stable and amenable to purification by chromatographic techniques. In addition to spectroscopic studies,^[4] reports dealing with the structural properties of germatriptycenes,^[5] germametallocyclophanes,^[6] tri-,^[7] and tetrasubstituted arylgermanes have appeared,^[8] focusing on the geometry and bonding of the sterically congested ligands around germanium. In addition, germanium congeners of triphenylmethyl radicals,^[9] cations^[10,11] (e.g., tropylium-type ions)^[12] have been investigated. The photochemistry of arylgermanes has also been investigated.^[13–15]

A number of hypervalent derivatives of germanium have been synthesized. These include triarylgermanes with heteroatom functionality at the *ortho* position on the aromatic ring,^[16–18] and germatranes.^[19] Arylgermatranes such as **1** participate in Stille-type cross-coupling reactions giving, for example, biphenyl **2**, presumably because hypervalent germanium is particularly susceptible to transmetalation with palladium(II) intermediates (Scheme 1).^[20] In addition, aryl(trifuryl)germanes undergo fluoride-mediated Stille-type couplings, presumably via the hypervalent germanium species $[\text{ArGe}(\text{OH})_3\text{F}]^-$.^[79] Chelation to germanium has also been used to stabilize thermodynamically highly reactive metallogermene,^[21] germene,^[22,23] germacumulene,^[24] and germylene^[25] derivatives. Sterically demanding aromatics are also commonly used to stabilize these reactive functionalities kinetically. 2,4-Di-*tert*-butyl-6-[(dimethylamino)methyl]phenyl (Mamx) groups combine both these features, facilitating isolation of germylene structures such as **3**.^[26]

Scheme 1 Intramolecular Chelation Involving Arylgermanes^[20,26]



3 R¹ = O-*t*Bu, O-*i*Pr, OEt, OMe, C≡CPh, C≡CH, *t*Bu, Bu, Me

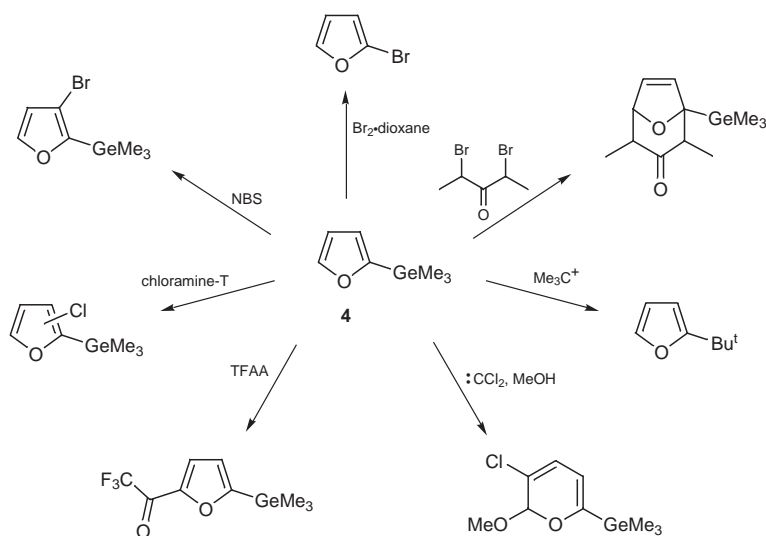
Although silane-based polymers are well-documented,^[27] the corresponding germanium-based materials have only recently been subjected to detailed investigation. This interest is a consequence of the physical properties of these materials common to the group 14 based polymers, namely their electroluminescence and conductivity when doped, typi-

cally with antimony(V) fluoride.^[28] As with related polymers, these materials are susceptible to photodegradation.^[29]

A number of methods have been utilized successfully to synthesize polymeric aryl- and heteroarylgermanes. These include Wurtz coupling,^[30] coupling of Grignard reagents with dihalogermanes,^[31] treatment of organolithiums with dichlorogermylene-dioxane complex,^[28] zirconium-mediated dehydrogenative coupling^[32] and ruthenium-mediated demethanative coupling.^[33]

The reactivity of heteroarylgermanes^[34] has been investigated only to a limited extent. Cycloadditions involving furans **4** (Scheme 2)^[35,36] and thiophene 1,1-dioxides^[37] have been reported. In these examples, the presence of germanium does not affect the expected course of the reactions. Although the electrophilic chemistry of arylgermanes has been well-documented,^[38–43] the reactivity of heteroarylgermanes in this respect remains to be established except in the case of furylgermanes **4** (Scheme 2).^[44]

Scheme 2 Reactions of Furylgermanes^[44]



Redistribution reactions between aryl- and halogermanes can readily be achieved using Lewis acid catalysis and microwave irradiation.^[45] This process requires strict stoichiometric control and often results in complex mixtures, detracting from its use as a preparative technique. Attempts to synthesize arylgermanes from simple aromatics by direct Friedel–Crafts germylation,^[45] or high temperature condensation with trichlorogermane^[46] generally result only in low yields of the desired products. In contrast, polyfluorinated arenes readily react with halogermanes in the presence of tris(diethylamino)phosphine to give the corresponding polyfluoroarylgermanes in moderate to good yields.^[47]

SAFETY: Appropriate safety precautions and procedures should be taken when handling and disposing of germanium compounds. For further information about the toxicity of organogermanium compounds please see Section 5.1.

Synthesis of Product Subclass 22

5.1.22.1

Method 1:

From Halogermanes by Substitution with Arylmetals

Ge–C bonds are usually formed by reaction of halogermanes with organometallics. This process generally provides the most efficient and convenient entry into this class of compound, and remains the standard method for their synthesis where applicable.

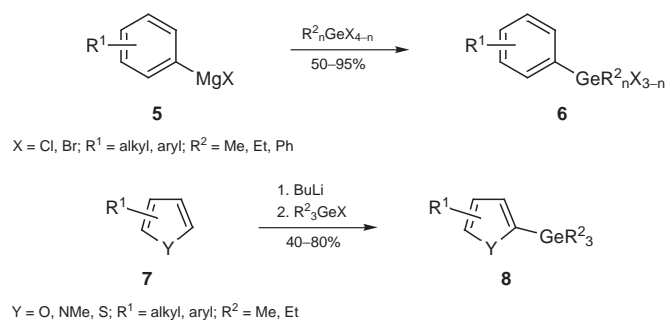
5.1.22.1.1

Variation 1:

Using Preformed Arylmetals

The use of preformed aryl Grignard reagents **5** and organolithium reagents (e.g., those generated from **7** and butyllithium) with halogermanes is the most common method for the introduction of aromatic ligands around germanium (Scheme 3).^[1] Attempts to effect selectively monoarylation of polyhalogenated germanium substrates can be achieved using stoichiometric quantities of reagent,^[48] although this process can be substrate dependent.^[49] Synthesis of fully arylated germanes using a large excess of Grignard reagent requires forcing conditions, otherwise the reaction stops at the triarylated stage when employing hindered aromatics.^[1] Moreover, a total absence of free magnesium from the reaction mixture is required under thermal conditions to avoid the competitive formation of hexaaryldigermanes.^[3] Use of organolithium reagents is often found to be inferior to the use of the corresponding Grignard reagents,^[1] but can give superior results in specific cases.^[49] Pyrrolyl-, furyl-, and thienylgermanes **8** are synthesized predominantly using organolithium precursors due to their ease of preparation by selective deprotonation at the 2-position using alkylolithiums (Scheme 3).^[34,50,51]

Scheme 3 Use of Preformed Organometallics in the Synthesis of Aryl- and Heteroarylgermanes^[1,34,50,51]



(Chloromethyl)methylphenyl(2-tolyl)germane [**6**, R¹ = 2-Me; GeR²_nX_{3-n} = Ge(CH₂Cl)MePh]; **Typical Procedure:**^[52]

CAUTION: Inhalation, ingestion, or absorption of iodomethane (MeI) through the skin may be fatal. It affects the central nervous system, causes irritation to the skin, eyes, and respiratory tract, and is a suspected carcinogen. Appropriate safety precautions and procedures should be taken during all stages of its handling and disposal.

2-Tolylmagnesium bromide prepared from 2-bromotoluene (13.5 g, 79 mmol) and Mg (2.1 g, 87 mmol) in Et₂O (80 mL) was added to a mixture of dichloro(chloromethyl)phenylgermane (21.3 g, 79 mmol) in Et₂O (50 mL) at 0 °C with stirring. The mixture was stirred at rt for 3 h. The Grignard reagent prepared from MeI (13.3 g, 87 mmol) and Mg (2.3 g, 95 mmol) in Et₂O (70 mL) was added to the mixture at 0 °C with stirring. The mixture was

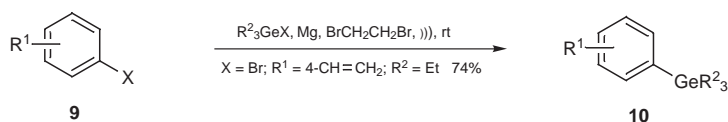
stirred at rt for 3 h, and then refluxed for 1 h. Aq 3 M HCl (40 mL) was added to the mixture at 0°C. The organic layer was separated and the aqueous layer extracted with Et₂O (2 × 30 mL). The combined organic layer and extracts were dried (Na₂SO₄), and evaporated. Distillation of the residue gave the product as a colorless oil; yield: 17.2 g (71%); bp 141 °C/0.18 Torr.

5.1.22.1.2 Variation 2: Using Barbier-Type Reactions

Attempts to synthesize monoarylgermanes using stoichiometric quantities of tetraethoxygermane or germanium(IV) halides with aryl halides and magnesium metal (Barbier conditions) generally result in poor yields, often due to low selectivity.^[4] This can be improved in some instances by switching to copper, with the best results being achieved using germanium(IV) chloride and aryl bromides under forcing conditions.^[53] Synthesis using Barbier conditions under thermal conditions are also plagued by competitive formation of hexaphenyldigermanes, although yields can be improved using hexacoordinate tris(benzene-1,2-diolato)germanates in place of germanium(IV) halides when preparing tetraarylgermanes.^[54] Although Wurtz–Fittig coupling using sodium (or lithium) has been used in the synthesis of tetraarylgermanes,^[55] treatment with zinc also results in modest conversion of germanium(IV) iodide to tetraphenylgermane.^[56]

Ultrasound has been used successfully to induce Barbier reactions involving trialkylhalogermanes,^[36] and gives superior yields and avoids digermene side products often observed under thermal conditions.^[57]

Scheme 4 Synthesis of Arylgermanes Using Barbier Conditions^[36]



4-(Triethylgermyl)styrene (**10**, R¹ = 4-CH=CH₂; R² = Et); Typical Procedure:^[57]

A Schlenk tube containing Mg turnings (0.60 g, 25 mmol), 1,2-dibromoethane (0.54 mL, 6.22 mmol), Et₃GeBr (3.0 g, 12.5 mmol), and 4-bromostyrene (**9**, X = Br; R¹ = 4-CH=CH₂; 2.28 g, 12.5 mmol) in THF (25 mL) was placed in a commercial ultrasonic cleaning bath (Branson B1200 E1, working frequency: 47 kHz) and sonicated for 2 h. The mixture was washed with brine (20 mL) and extracted with Et₂O (2 × 20 mL). The organic layers were dried (MgSO₄), the solvents removed in vacuo, and the residue purified by column chromatography (silica gel, petroleum ether/Et₂O 95:5) to give the product as an oil; yield: 2.4 g (74%); ¹H NMR (CDCl₃, δ): 0.9–1.2 (m, 15H), 2.24 (dd, J = 2, 11 Hz, 1H), 5.79 (dd, J = 2, 11 Hz, 1H), 6.73 (dd, J = 11, 17.5 Hz, 1H), 7.39 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H); ¹³C NMR (CDCl₃, δ): 4.4, 9.0, 113.8, 125.9, 134.6, 137.3, 140.1.

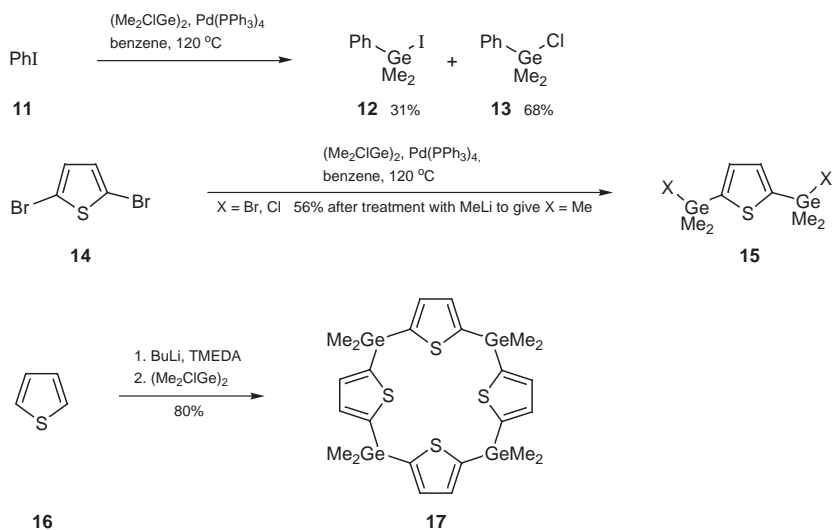
5.1.22.2 Method 2: From Aryl Halides by Palladium(0)-Mediated Coupling with Digermanes

Initial studies carried out by Eaborn demonstrated that hexaalkyldigermanes, like other group 14 metal analogues,^[58] undergo palladium(0)-mediated coupling with aryl bromides, albeit in low-to-modest yields due to competing formation of the corresponding biaryl derivatives.^[59] This problem was resolved by the use of aryl iodides such as iodobenzene (**11**) and 1,2-dichloro-1,1,2,2-tetramethyldigermene,^[60] which resulted in excellent yields of the desired germylated aromatics, in this case iododimethylphenylgermane (**12**) and chlorodimethylphenylgermane (**13**) (Scheme 5).^[61] This method is also suitable

for references see p 13

for the synthesis of derivatives such as bis(halodimethylgermyl)thiophene **15** synthesized from 2,5-dibromothiophene (**14**),^[30] which can be difficult to synthesize using conventional organometallic procedures due to their tendency to participate in oligomerization i.e. reaction of **16** to give **17** (Scheme 5).^[62] The major drawback with this methodology is the availability of 1,2-dichloro-1,1,2,2-tetramethyldigermane,^[63] which is currently not commercially available and requires synthesis before use.

Scheme 5 Palladium(0)-Mediated Coupling of Digermanes with Aryl Halides^[30,61,62]



Iodobenzene (**11**) and Chlorodimethylphenylgermane (**13**);

Typical Procedure:^[61]

A soln of iodobenzene (**11**; 82 mg, 0.4 mmol) in benzene (0.8 mL) (**CAUTION: carcinogen!**) was treated with 1,2-dichloro-1,1,2,2-tetramethyldigermane (0.4 mmol) in the presence of $\text{Pd}(\text{PPh}_3)_4$ (23 mg, 0.02 mmol) at 120 °C for 5 h. Purification by fractional distillation led to the isolation of **12**; yield: 38 mg (31%) and **13**; yield: 59 mg (68%) (yields calculated by GC).

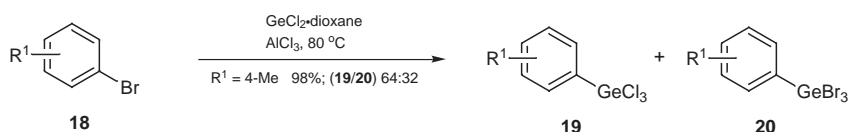
5.1.22.3

Method 3:

From Aryl Halides by Insertion of Dichlorogermylene

Insertion of germynes into aryl carbon–halogen bonds of simple aromatics generally proceeds in moderate yield using elevated temperatures (>150 °C) and sealed reaction vessels.^[64,65] A modification of this procedure involving the use of the most readily accessible dichlorogermylene source, dichlorogermylene–dioxane complex,^[66] and catalytic quantities of anhydrous aluminum trichloride allows these reactions to be conducted under relatively mild conditions (~80 °C, atmospheric pressure) giving insertion in excellent yields (Scheme 6).^[4] The tolerance of this methodology towards other functionalities however remains to be established.

Scheme 6 Germylene Insertion into Aromatic Halides^[4]



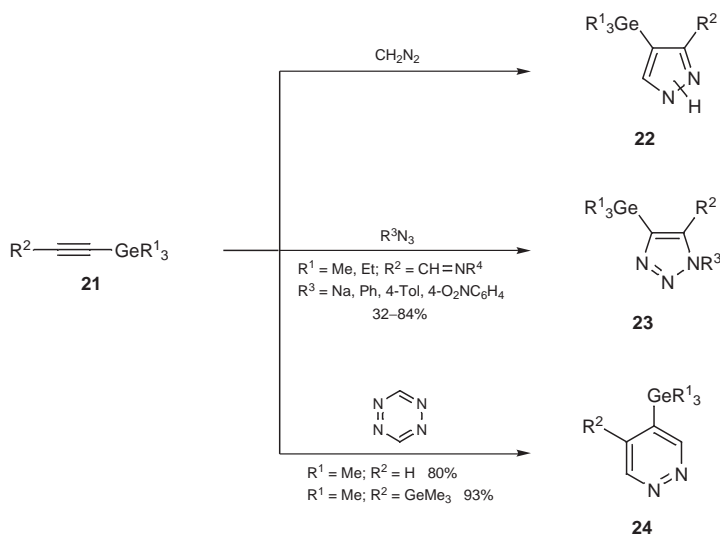
Trichloro(4-tolyl)germane (19, R¹ = 4-Me) and Tribromo(4-tolyl)germane (20, R¹ = 4-Me);**Typical Procedure:**^[4]

A mixture of 4-bromotoluene (250 mL), GeCl₂•dioxane (10 g, 43.2 mmol), and anhyd AlCl₃ (0.29 g, 2.17 mmol) was heated to 80 °C for 24 h with continuous stirring. After the mixture was cooled to rt, it was filtered, the dioxane removed in vacuo, and the unreacted 4-bromotoluene removed by vacuum distillation (43 °C/5 × 10⁻⁴ Torr) to leave the product as a white solid; yield: 13.33 g (98%); ratio **19/20** 64:32 (by GC/MS).

5.1.22.4 Method 4: Heteroarylgermanes by Cycloaddition

Cycloaddition reactions involving alkynylgermanes (Section 5.1.20) are generally analogous to those observed using nonmetalated alkynes. Hence, nitrogen-based heterocycles such as pyrazoles **22**, triazoles **23**, and pyridazines **24** can be readily accessed in high yield by treatment of alkynylgermanes **21** with diazomethane,^[67] azides,^[68] or tetrazines,^[69] respectively (Scheme 7).

Scheme 7 Nitrogen Heterocycles from Alkynylgermanes by Cycloaddition^[67-70]

**4-(Trimethylgermyl)pyridazine (24, R¹ = Me; R² = H); Typical Procedure:**^[70]

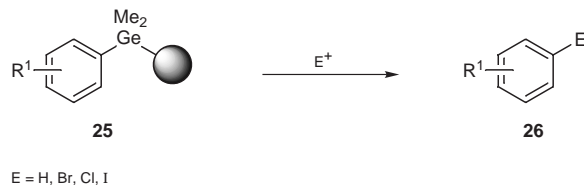
Tetrazine (82.0 mg, 1.0 mmol) and (ethynyl)trimethylgermane (**21**, R¹ = Me; R² = H; 300 mg, 1.80 mmol, contains approx. 20% THF) in MeCN were heated to reflux for 90 min. The resulting pale yellow soln was concentrated in vacuo. The residual brown liquid was purified by column chromatography (silica gel, Et₂O) to afford the product as colorless oil (which turned yellow quite rapidly in air); yield: 158 mg (80%); ¹H NMR (CDCl₃, δ): 0.45 (s, 9H), 7.50 (dd, *J* = 4.9, 1.8 Hz, 1H), 9.06 (dd, *J* = 4.9, 1.4 Hz, 1H), 9.17 (dd, *J* = 1.8, 1.4 Hz, 1H); ¹³C NMR (CDCl₃, δ): -2.43, 131.29, 142.43, 150.64, 154.98.

Applications of Product Subclass 22 in Organic Synthesis

5.1.22.5

Method 5:**Arylgermanes as Linkers for Solid-Phase Synthesis**

Group 14 metals have been utilized as key functional elements in a number of linker strategies for solid-phase organic synthesis.^[71] Arylsilane linkers have been shown to be stable towards a relatively wide range of reaction conditions and can be cleaved via *ipso*-protodesilylation with acid to liberate aromatics from the resin in a traceless fashion.^[72] Cleavage with concomitant diversification has also been achieved via *ipso*-halodesilylation using bromine and iodine chloride to liberate aryl bromides and iodides, respectively.^[73] However, one limitation to the use of arylsilane linkers for solid-phase organic synthesis is the necessity for harsh conditions (e.g., neat HF) when cleaving electron-deficient aromatics. One tactic that addresses this problem involves increasing the susceptibility towards electrophilic *ipso*-demetalation by exchanging silicon for germanium (Scheme 8).^[74] This is as a result of the increasing β -effect observed down the periodic group (i.e., Si < Ge < Sn) in the rate-determining electrophilic *ipso*-addition step.^[10,38,75-77] Treatment of the arylgermanium linkers **25** with halogen sources also permits diversification at the point of cleavage giving **26**,^[78] and these linkers have been used to synthesize chemical libraries based on benzodiazapines^[74] and pyrazoles.^[49]

Scheme 8 Arylgermanes as Diversification Linkers for Solid-Phase Organic Synthesis^[78]

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