

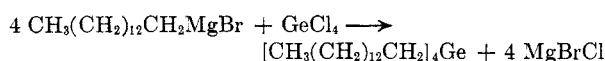
## Some Symmetrical Tetraalkyl- and Tetraaralkyl-germanes

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A group of symmetrical  $R_4Ge$  compounds has been synthesized where R represents either a long chain *n*-alkyl (8, 10, 12, 14, 16, or 18 carbon atoms), an aralkyl (*beta*-phenylethyl or *gamma*-phenylpropyl), a branched chain (2-ethylhexyl), or an alicyclic (2-cyclohexylethyl) group. The melting points, boiling points under reduced pressure, mixture melting points, and infrared spectra have been determined and compared with these properties of analogous organosilicon compounds. The molar refractions of the  $R_4Ge$  liquids have been determined. The applicability of various methods for calculating these molar refractions is discussed.

In the past the preparation of symmetrical tetra-*n*-alkylgermanes has been generally limited to compounds containing *n*-alkyl groups of six or fewer carbon atoms.<sup>2</sup> The complete series of  $R_4Ge$  compounds where R represents an even-numbered straight-chained radical containing from eight to eighteen carbon atoms has now been prepared. In addition, a branched-chained compound, *tetrakis*(2-ethylhexyl)germane, and an alicyclic compound, *tetrakis*(2-cyclohexylethyl)germane, have been prepared. The general reaction employed in all cases was the interaction of an organometallic compound, either a Grignard reagent or an alkyllithium compound, with germanium tetrachloride. The Grignard reagents seem to give slightly better yields in the *n*-alkyl series. A typical reaction is shown below:



In 1927, Orndorf, Tabern, and Dennis<sup>3</sup> reported the preparation of tetrabenzylgermane from benzylmagnesium chloride and germanium tetrachloride by use of a reaction similar to the one shown. We prepared two similar compounds, *tetrakis*(*beta*-phenylethyl)- and *tetrakis*(*gamma*-phenylpropyl)-germanes, by the reactions of *beta*-phenylethylmagnesium bromide and *gamma*-phenylpropylmagnesium bromide and *gamma*-phenylpropylmagnesium bromide and *gamma*-phenylpropylmagnesium bromide, respectively, with germanium tetrachloride.

Most of the compounds show quite high thermal stability in preliminary screening tests. Some physical properties (melting points, boiling points, molar refractions, mixture melting points with related compounds, and infrared spectra) were measured and most of these properties are compared in the Discussion to the properties of the analogous organosilicon compounds.

EXPERIMENTAL<sup>4</sup>

The three typical preparations recorded below represent

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(2) See Johnson, *Chem. Revs.*, **48**, 259 (1951) for a comprehensive review. For more recent work see Anderson, *J. Am. Chem. Soc.*, **73**, 5800 (1951); **75**, 814 (1953).

(3) Orndorf, Tabern, and Dennis, *J. Am. Chem. Soc.*, **49**, 2512 (1927).

(4) All melting points are uncorrected.

the reactions of an *n*-alkylmagnesium bromide, an aralkylmagnesium bromide, and an alkyllithium compound, respectively, with germanium tetrachloride. Pertinent data on all the preparations mentioned in the Introduction are found in Table I. Many of the reactions required a period of refluxing in high-boiling solvent such as xylene or toluene to complete the reaction of the fourth mole of  $\text{RMgBr}$  or  $\text{RLi}$  with germanium tetrachloride. The Grignard reagents were used in from 50 to 150% excess of the theoretical amount and were prepared from the alkyl or aralkyl bromide in all instances.

*Tetra-n-tetradecylgermane.* An ethereal solution of 0.33 mole of myristylmagnesium bromide was prepared from 96.5 g. (0.348 mole) of myristyl bromide and 8.46 g. (0.348 g.-atom) of magnesium turnings. This was placed in a 500-ml. round-bottomed flask equipped with a stirrer, a reflux condenser with a nitrogen inlet tube, and a dropping-funnel. Stirring was commenced and 12.5 g. (0.058 mole) of germanium tetrachloride dissolved in 80 ml. of dry xylene was slowly dropped into the flask. After the addition was complete, an additional 80 ml. of dry xylene was dropped into the flask and most of the ether was distilled from the mixture. The remaining xylene solution was heated at 100° for three days and then was hydrolyzed with 10% hydrochloric acid in water. A small amount of ether was added to complete dissolution of the solid which formed and the layers were separated. The organic layer was concentrated on a water-bath under a water aspirator vacuum and the liquid residue thus obtained was distilled under reduced pressure. The hydrocarbons formed by hydrolysis and coupling of the Grignard reagent distilled in two fractions below 105°/0.03 mm. The organogermanium compound then was distilled through a molecular distillation apparatus using a bath temperature of 360–370° and a pressure of 0.0005 mm. There was obtained 18.85 g. (37.6%) of a clear yellow liquid.

*Tetrakis(beta-phenylethyl)germane.* In a flask were placed 24.3 g. (1.0 g.-atom) of magnesium turnings and 300 ml. of anhydrous ether. To this was added 10 ml. of a solution of 185 g. (1.0 mole) of 2-bromoethylbenzene in 200 ml. of anhydrous ether. The mixture was stirred and the reaction began immediately. The remaining bromide solution was added dropwise over several hours during which time spontaneous refluxing occurred. The mixture then was heated at reflux for several hours and allowed to stand overnight. Acid titration showed 0.935 mole (93.5%) of the Grignard reagent to be present.

To the ice-cooled Grignard reagent solution described above was added a solution of 9.1 ml. (0.080 mole) of germanium tetrachloride in 80 ml. of dry toluene. The solution was stirred for five hours and then was allowed to stand overnight. More toluene, 100 ml., was added and 350 ml. of solvent, mainly ether, was distilled until the reflux temperature reached 85°. The mixture then was cooled in an ice-bath and hydrolyzed by the dropwise addition of 100 ml. of water. A little dilute hydrochloric acid solution was added to dissolve the magnesium salt. The layers were separated and the organic layer was washed with sodium

TABLE I  
 YIELDS AND ANALYSES OF R<sub>4</sub>Ge COMPOUNDS

RM COMPOUND	Solvent	Yield, <sup>a</sup> %	Analyses						
			Germanium <sup>c</sup>		Carbon		Hydrogen		
			Calc'd	Found	Calc'd	Found <sup>b</sup>	Calc'd	Found	
Beta-Phenylethylmagnesium bromide	Toluene	21.6	14.7	14.8	14.9				
gamma-Phenylpropyllithium	Toluene	33.0	13.2	12.6	12.7				
2-Ethylhexyllithium	—	27.0	13.8	13.7	14.0				
2-Cyclohexylethyllithium	Benzene	5.0	14.0	14.2	14.2				
n-Octyllithium	—	21.3	13.8	13.6	13.6				
n-Decyllithium bromide	—	18.0	11.4	11.3	11.2				
n-Dodecylmagnesium bromide	Xylene	47.0	9.9	9.7	9.6	76.8	76.6	13.4	13.5
n-Tetradecylmagnesium bromide	Xylene	37.6	8.4	8.0	8.0	78.0	77.8	13.6	13.5
n-Hexadecylmagnesium bromide	Xylene	36.0	7.5	7.6	7.8	78.9	78.5	13.7	13.6
n-Octadecylmagnesium bromide	Xylene	24.0	6.7	6.8	6.8	79.6	78.4	13.7	13.8

<sup>a</sup> The yield of the R<sub>4</sub>Ge compound is based on the amount of the germanium tetrachloride employed. <sup>b</sup> The low carbon analyses are ascribed (by Dr. Huffman of the Huffman Microanalytical Laboratories, Denver, Colorado) to the possible formation of germanium carbide during the ignition thus not giving a quantitative yield of CO<sub>2</sub>. <sup>c</sup> The germanium analyses were carried out by the procedure of Gilman and Gerow, *J. Am. Chem. Soc.*, **77**, 5740 (1955).

carbonate solution. The solvent then was removed, using a water aspirator. After standing several days, crystals separated from the oily liquid. Filtration gave 9.5 g. of crude material which was recrystallized from 95% ethanol giving 8.5 g. (21.6%) of the desired product, m.p. 53–54°.

*Tetakis(2-cyclohexylethyl)germane.* Germanium tetrachloride (8 ml., 0.07 mole) and 50 ml. of anhydrous ether were placed in a three-necked flask equipped with a stirrer, reflux condenser with a nitrogen inlet, and a dropping-funnel. Into the stirred ice-cooled, solution was slowly dropped 224 ml. of 2-cyclohexylethyllithium solution containing 0.357 mole of reagent (prepared in ether from 8.3 g. (1.2 g.-atoms) of lithium wire and 95.5 g. (0.50 mole) of 2-bromoethylcyclohexane in 73% yield at –15 to 0°). The reaction mixture was stirred overnight and then the ether was distilled with subsequent addition of ca. 80 ml. of benzene. The vapors soon reached 80° and heating was continued at the same rate for 2 hours. The flask was cooled in an ice-bath and 100 ml. of ice-water was added. Additional ether was needed to aid in the separation of the layers. The ether layer was dried over magnesium sulfate and the solvents were distilled.

The residue was distilled through a Vigreux column. Cyclohexylethyl bromide was removed at 12 mm.; then the remaining liquid was distilled at 0.1 mm. 1,4-Bis-(cyclohexyl)butane came over at 110° and the organogermanium compound at 244–254°. The product solidified in the condenser and a considerable amount of solid resin did not distill even when transferred to a molecular distillation apparatus and heated to 350–360° at a pressure of 0.02 mm. The solid in the condenser was washed out with hot benzene and then was recrystallized three times from methyl ethyl ketone giving 1.8 g. (15%) of organogermanium product, m.p. 137.5–138.5°.

The 1,4-bis-(cyclohexyl)butane melted at 10.5°. Reported melting points are 9°<sup>5</sup> and 12°.<sup>6</sup>

#### DISCUSSION

*Melting point and boiling point data.* In Table II there have been arranged the melting points and

boiling points under reduced pressure of the organogermanium compounds listed in Table I as well as the same data for the analogous organosilicon compounds. It may be noted from the table that the solid organogermanium compounds are generally slightly lower melting than the corresponding organosilicon compounds. The liquid and solid compounds in the organosilicon series have corresponding liquid and solid counterparts in the organogermanium series. In general the expected changes of melting points and boiling points with changes of molecular structure are observed. In the two series containing aralkyl groups, large decreases in melting points are noted with increased numbers of methylene groups. Most of the compounds are very high-boiling even at reduced pressures, and present indications are that most of the compounds are quite stable at high temperatures especially in the absence of air.<sup>7</sup>

*Anomalous mixture melting points.* Recently, it has been noted in this laboratory<sup>8</sup> that tetra-n-octadecyl- and tetra-n-hexadecyl-silanes when mixed do not give a depression in melting point, but rather melt over a moderately wide range between the melting points of the two compounds. In the present study there was observed no depression in any mixture melting points of the solid organogermanium compounds prepared above and the corresponding organosilicon compounds, but a wide melting range between the melting points of the pure compounds was observed. A mixture melt-

(7) See Gilman and Ingham, *J. Am. Chem. Soc.*, **77**, 1680 (1955) for a brief discussion of thermal properties of related silanes.

(8) Ingham and Gilman, unpublished studies. See also, Merten and Gilman, *J. Am. Chem. Soc.*, **76**, 5798 (1954).

(5) Sabatier and Murat, *Compt. rend.*, **156**, 1431 (1913).

(6) Kuhn and Winterstein, *Helv. Chim. Acta*, **11**, 137 (1928).

TABLE II  
 M. P. AND B. P. DATA OF SILICON AND GERMANIUM COMPOUNDS

R Group	M.P., °C.		Silicon Analogs		Germanium Analogs	
	Si	Ge	B.P., °C.	mm.	B.P., °C.	mm.
<i>n</i> -Octyl	Liquid <sup>a</sup>	Liquid	187-191 <sup>a</sup>	0.07	210-213	0.1
<i>n</i> -Decyl	<sup>b</sup>	<i>ca.</i> -15	<sup>b</sup>	—	230-240 <sup>c</sup>	0.015
<i>n</i> -Dodecyl	<i>ca.</i> -15 <sup>d</sup>	Liquid	253-255 <sup>d</sup>	0.06	330-340 <sup>c</sup>	0.0005
<i>n</i> -Tetradecyl	Liquid <sup>d</sup>	Liquid	240-258 <sup>d</sup>	0.06	360-370 <sup>c</sup>	0.0005
<i>n</i> -Hexadecyl	38.5-40 <sup>e</sup>	37-38	—	—	—	—
<i>n</i> -Octadecyl	50-51 <sup>e</sup>	43-45	—	—	—	—
2-Ethylhexyl	Liquid <sup>a</sup>	Liquid	135-143 <sup>a</sup>	0.04	193-196	0.15
2-Cyclohexylethyl	146-147 <sup>a</sup>	137.5- 138.5	—	—	—	—
Benzyl	127.5 <sup>f</sup>	107-108 <sup>g</sup>	—	—	—	—
<i>beta</i> -Phenylethyl	76-76.5 <sup>d</sup>	53-54	—	—	—	—
<i>gamma</i> -Phenylpropyl	Liquid <sup>d</sup>	Liquid	230-240 <sup>d</sup>	0.1	240-250 <sup>c</sup>	0.05

<sup>a</sup> Meen, unpublished studies. <sup>b</sup> Not yet prepared. <sup>c</sup> Bath temperature. <sup>d</sup> Miles and Moore, unpublished studies. <sup>e</sup> Gilman and Ingham, *J. Am. Chem. Soc.*, **77**, 1680 (1955). <sup>f</sup> Smith and Kipping, *J. Chem. Soc.*, **101**, 2553 (1912). <sup>g</sup> Cf. ref. 3.

ing point of tetra-*n*-hexadecyl- and tetra-*n*-octadecyl-germane also was not depressed.

*Molar refractions.* The molar refractions have been determined where possible for the new organogermanium compounds. These are compiled in Table III along with the calculated values using the bond refractions of Cresswell, *et al.*<sup>9</sup> The error using these values is less than one percent in all cases except *tetrakis*(*gamma*-phenylpropyl)germane. A value for the Ge—C bond refraction reported recently<sup>10</sup> is low and the reported calculations based on the bond refractions of Denbigh<sup>11</sup> appear to be in error. No agreement is found with our compounds. Laubengayer and Tabern's<sup>12</sup> atomic refraction for

*Infrared analyses.* The infrared spectra of all the new organogermanium compounds as well as most of the organosilicon compounds mentioned in the preceding tables were recorded, either in the liquid state or in carbon disulfide solutions, by means of a Baird recording spectrophotometer. In general, the spectra correlate well with the expected bands based on Colthup's chart.<sup>14</sup> We have reproduced in Figure 1 the spectra of the two *n*-octyl compounds in carbon disulfide solution. The most noticeable difference is in the 13 to 16 micron region. Both of these compounds have a band at 13.9  $\mu$  which is very likely due to the C—H rocking modes of the methylene chains. The silane has a

 TABLE III  
 MOLAR REFRACTIONS OF R<sub>4</sub>Ge COMPOUNDS

COMPOUND (R Group)	$n_{D1}^2$	$t_1$	$d_2^2$	$t_2$	MR		Difference, %
					Found	Calc'd <sup>a</sup>	
2-Ethylhexyl	1.4688	24	0.909	26	160.5	162.0	0.9
<i>n</i> -Octyl	1.4630	28	0.891	24	161.7	162.0	0.2
<i>n</i> -Decyl	1.4643	25	0.879	31	200.3	199.2	0.5
<i>n</i> -Dodecyl	1.4654	31	0.879	31	235.2	236.4	0.5
<i>n</i> -Tetradecyl	1.4640	31	0.880	31	271.4	273.6	0.8
<i>gamma</i> -Phenylpropyl	1.5704	20	1.106	25	163.0	166.6	2.1

<sup>a</sup> Using bond refractions from ref. 9.

the germanium atom in germanium tetrachloride cannot be applied to R<sub>4</sub>Ge compounds. They report a value of 7.597 while the average value required by our compounds would be *ca.* 9.2 if the atomic refractions of Auwers and Eisenlohr<sup>13</sup> are used for the other atoms in the compounds.

(9) Cresswell, Leicester, and Vogel, *Chemistry & Industry*, **19** (1953).

(10) Osthoff and Rochow, *J. Am. Chem. Soc.*, **74**, 845 (1952).

(11) Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

(12) Laubengayer and Tabern, *J. Phys. Chem.*, **30**, 1047 (1926).

(13) Auwers and Eisenlohr, *Ber.*, **43**, 806 (1910).

band at 13.2  $\mu$ , while the germane has a band at 14.5  $\mu$ . Similar bands were noted for all the *n*-alkyl compounds. In the spectra of branched chain compounds (2-ethylhexyl-), these bands did not appear.

Two more spectra, *tetrakis*(2-cyclohexylethyl)-silane and *tetrakis*(2-cyclohexylethyl)germane in carbon disulfide solution, are shown in Figure 2. Again the two spectra are nearly identical except for the bands at 13.3-13.4  $\mu$  for the silane and

(14) Colthup, *J. Opt. Soc. Amer.*, **40**, 397 (1950).

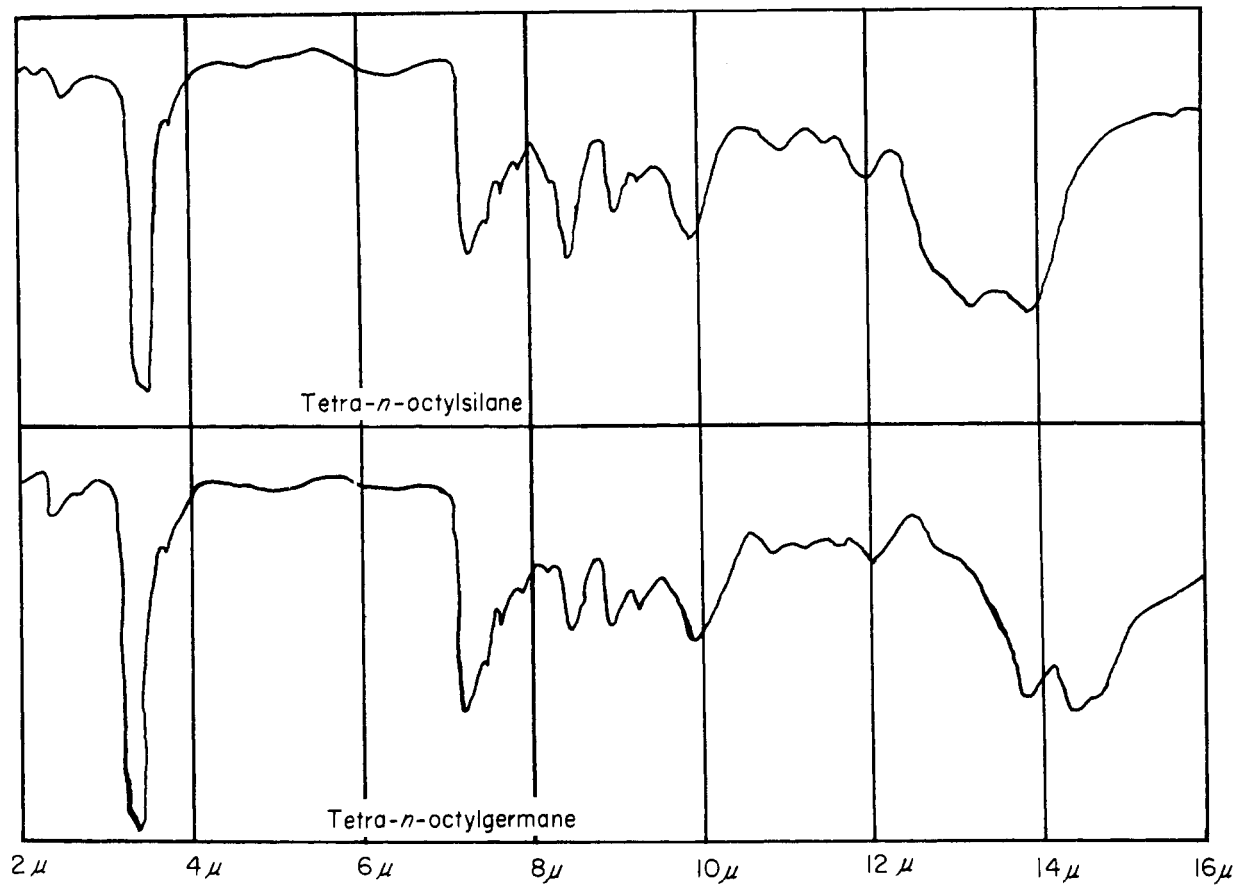


FIGURE 1.

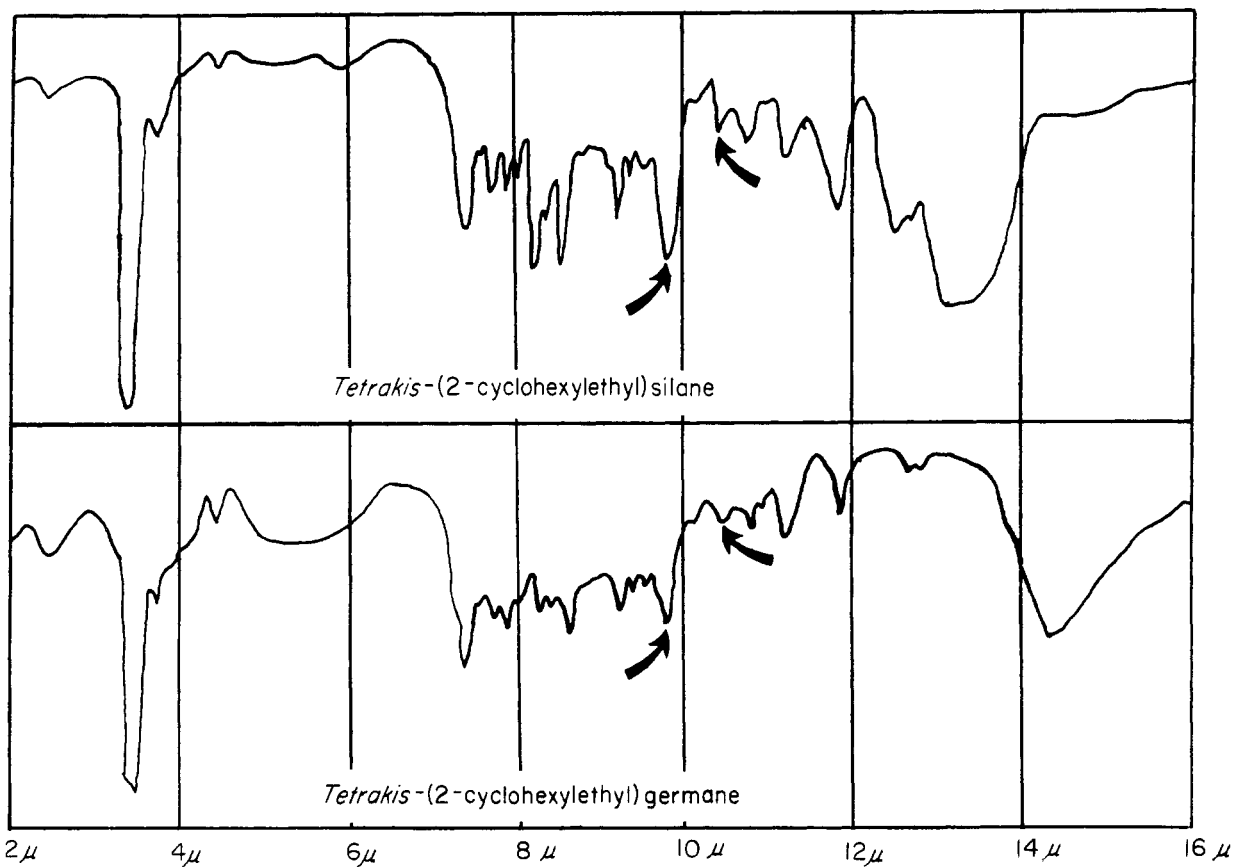


FIGURE 2.

at  $14.5 \mu$  for the germane. Morrison<sup>15</sup> has assigned bands at  $9.92$  and  $10.21 \mu$  to the cyclohexane system. These bands appear to be present (arrows in Figure 2) in both of the spectra.

In general the infrared absorption spectra contained bands in the positions that would be expected.

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(15) Morrison, *J. Chem. Soc.*, 1614 (1951).

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