

The Reaction between Carbon Dioxide and Methoxy Substituted Phenylmagnesium and Tolylmagnesium Bromides

GUST.-AD. HOLMBERG

Institute of Organic Chemistry, Abo Akademi, Abo, Finland

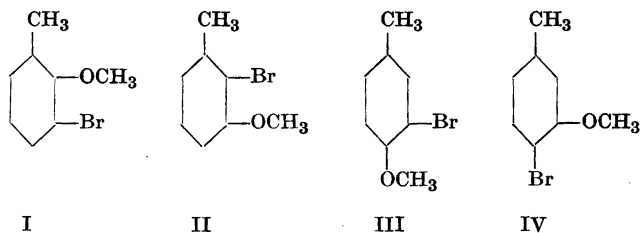
It has recently been shown¹ that besides *o*-methoxy-benzoic acid considerable amounts of 2,2'-dimethoxybenzophenone are formed when gaseous carbon dioxide is allowed to react with *o*-methoxyphenylmagnesium bromide. This ketone formation is not limited to the Grignard reagent mentioned, since Bodroux² isolated 4,4'-dibromobenzophenone and *p*-bromo-benzoic acid from the reaction product of *p*-bromophenylmagnesium bromide and carbon dioxide.

As it was of interest to determine whether ketone formation is a common reaction of methoxyarylmagnesium bromides, the reactions between carbon dioxide on one hand and methoxyphenylmagnesium bromides and methoxy-tolylmagnesium bromides on the other were investigated. Some of these reactions have been studied earlier. Bodroux³ prepared *p*-anisic acid from *p*-methoxyphenylmagnesium bromide and carbon dioxide. Paty and Quelet⁴ obtained *o*-methoxybenzoic acid in the corresponding reaction of *o*-methoxyphenylmagnesium bromide. Darzens and Levy⁵ isolated 2-methyl-4-methoxybenzoic acid, Higginbottom, Hill, and Short⁶ 2-methyl-5-methoxybenzoic acid, and Dubinin⁷ 3-methyl-6-methoxybenzoic acid from the reaction products of the corresponding Grignard reagents and carbon dioxide. However, since in none of these investigations attention has been paid to the formation of ketones, it was considered necessary to repeat the experiments of Bodroux, Darzens and Levy, Higginbottom, Hill, and Short.

The Grignard reagents studied in the present investigation were, thus, prepared from the following bromides:

3-bromo-1-methoxybenzene
 4-bromo-1-methoxybenzene
 3-bromo-2-methoxytoluene
 4-bromo-2-methoxytoluene
 5-bromo-2-methoxytoluene
 6-bromo-2-methoxytoluene
 2-bromo-3-methoxytoluene
 4-bromo-3-methoxytoluene
 5-bromo-3-methoxytoluene
 6-bromo-3-methoxytoluene
 2-bromo-4-methoxytoluene
 3-bromo-4-methoxytoluene

During the course of the work, it was found that Grignard reagents in which the methoxy group and the magnesium atom were in meta and para positions relative to each other give the corresponding acids exclusively. Two of the four compounds in which the methoxy group and the magnesium atom were in ortho position relative to each other, *viz.* those prepared from 3-bromo-2-methoxytoluene (I) and 2-bromo-3-methoxytoluene (II), reacted to give only the acids, whereas the Grignard reagents prepared from 3-bromo-4-methoxytoluene (III) and 4-bromo-3-methoxytoluene (IV) gave both ketone and acid.



If the ketone formation is to be considered a type of ortho effect, this effect is cancelled by a methyl group in the ortho position relative to either the methoxy group or the magnesium atom, *i.e.* the first ortho effect is cancelled by a second ortho effect.

In order to show that the ketone formation is a consequence of an abnormal reactivity of the *o*-methoxy substituted Grignard reagent, *o*-methoxyphenylmagnesium bromide was allowed to react with the reaction product of phenylmagnesium bromide and carbon dioxide. As 2-methoxybenzophenone has a low melting point (39°) and as it is readily soluble in most organic solvents, the ketone itself could not be isolated, but when the reaction product was treated with 2,4-dinitrophenylhydrazine, the corresponding hydrazone was formed. Phenylmagnesium bromide does not form a ketone under these conditions.

In connection with the preparation of the bromides some halogen substituted nitro compounds had to be reduced to the corresponding amines. When stannous chloride is used, a hydrogen atom may be substituted by chlorine or the halogen may be eliminated⁸. Weygand recommended the use of the method of West⁹ in such cases. According to this method the nitro compound is dissolved in methyl alcohol, a small quantity hydrochloric acid is added after which iron powder is added in portions to the vigorously boiling mixture. It was, however, observed that the iron powder formed lumps during the addition and this could not be avoided by boiling nor by effective stirring. A consequence of this was that the reaction did not go to completion. The difficulty was eliminated by mixing the methyl alcohol solution of the nitro compound with iron powder and adding hydrochloric acid to the boiling mixture. In this way excellent yields were obtained.

[EXPERIMENTAL

3-Bromo-1-methoxybenzene was prepared by bromination of nitrobenzene to 3-bromo-1-nitrobenzene¹⁰, followed by reduction to 3-bromoaniline¹⁰, diazotation to 3-bromophenol^{10,11}, and methylation with dimethyl sulphate¹¹.

4-Bromo-1-methoxybenzene was prepared by bromination of anisole¹².

3-Bromo-2-methoxytoluene. 3-Bromo-2-hydroxytoluene was prepared from *o*-cresol according to Brubaker and Adams¹³. The bromocresol (34.0 g) was dissolved in a solution of potassium hydroxide (14.0 g) in water (140 ml) and after addition of dimethyl sulphate (30.0 g) the mixture was shaken for one hour. 3-Bromo-2-methoxytoluene was distilled with steam and isolated by extraction with ether. The ether solution was shaken with dilute potassium hydroxide solution in order to remove any unchanged bromocresol. After drying of the ether phase, evaporation of the solvent left 3-bromo-2-methoxytoluene, which was distilled (b.p. 107–108°/22 mm).

C_8H_9OBr	Calc.	Br	39.74
	Found	»	39.87

The yield of 3-bromo-2-methoxytoluene was 60 per cent of the theoretical amount.

4-Bromo-2-methoxytoluene. *p*-Toluidine was nitrated using a large ratio of sulphuric acid to 2-nitro-4-aminotoluene¹⁴. This was converted into 4-bromo-2-nitrotoluene according to Gibson and Johnson¹⁵. When conducting the latter reaction, it was found advantageous to use a higher ratio of hydrobromic acid (3.5 equivalents) and to dissolve the amine in the acid before adding the sodium nitrite solution.

4-Bromo-2-nitrotoluene (34.0 g) was dissolved in methyl alcohol (110 ml) and iron powder (31.6 g) was added to the solution. The mixture was heated to boiling and concentrated hydrochloric acid (6 ml) was gradually added. After boiling for four hours, more concentrated hydrochloric acid (10 ml) was added and the mixture was filtered while still hot. The methyl alcohol was then distilled from the filtrate. After the residue had been made alkaline, a mixture of 4-bromo-2-aminotoluene and a small amount of unchanged nitro compound was isolated by steam distillation. The amine was converted into its hydrochloride and ether was added to dissolve the nitro compound. The solid hydrochloride was filtered, and the two layers of the filtrate were separated. The aqueous phase was made alkaline and the filtered hydrochloride was added to it. The amine was

dissolved in ether and this ether solution was dried with solid potassium hydroxide. After the ether had been evaporated, 4-bromo-2-aminotoluene, b.p. 138–140/20 mm, distilled. The yield (26.0 g) was 88.5 per cent of the theoretical amount.

A small quantity of the amine was acetylated with acetic anhydride. The acetyl derivative melted at 163–164°.

4-Bromo-2-aminotoluene (25.0 g) was dissolved in a mixture of concentrated hydrochloric acid (45 ml) and water (150 ml). After cooling to 5°, this solution was diazotized with an aqueous solution (30 ml) of sodium nitrite (9.5 g). The filtered solution was then gradually added to a boiling mixture of sulphuric acid (200 ml) and water (400 ml). During this addition, nitrogen was vigorously evolved and an oil distilled with water to the receiver. When the addition was completed, the reaction mixture was allowed to cool and water (600 ml) was added. Both the distillate and the contents of the reaction flask were extracted with ether. After the combined ether solutions had been dried with anhydrous sodium sulphate, the solvent was evaporated. The residue was dissolved in an aqueous solution (65 ml) of sodium hydroxide (6.4 g), and dimethyl sulphate (20 g) was added. After the mixture had been shaken for one hour, 4-bromo-2-methoxytoluene was isolated by steam distillation as in the case of 3-bromo-2-methoxytoluene. It distilled at 102–104°/13 mm.

C_8H_8OBr	Calc.	Br	39.74
	Found	»	39.95

The yield (16.3 g) was 60.4 per cent of the theoretical amount calculated on the quantity of 4-bromo-2-aminotoluene used.

5-Bromo-2-methoxytoluene. *o*-Cresol was methylated according to the method given for the synthesis of anisole in Organic Syntheses¹⁶, the yield being 82 per cent of the theoretical amount. The methoxytoluene was then brominated in chloroform with iron filings as catalyst¹⁷. The yield was 82.5 per cent of the theoretical amount.

6-Bromo-2-methoxytoluene. Technical trinitrotoluene (TNT) was reduced with hydrogen sulphide in dioxane to 4-amino-2,6-dinitrotoluene according to Parkes and Farthing¹⁸. The amine was isolated from the reaction mixture by precipitation with dry hydrogen chloride. Owing to the poor quality of the starting material the yield was only 45–50 per cent of the theoretical amount. The amine was deaminated by diazotation followed by reduction with ethyl alcohol according to Qvist¹⁹, which method gave a yield of 32–37 per cent of the theoretical amount. The 2,6-dinitrotoluene obtained in this way was converted into 2-nitro-6-aminotoluene by partial reduction with ammonium sulphide²⁰. The synthesis was continued over 2-nitro-6-bromotoluene, 6-bromo-2-aminotoluene, and 6-bromo-2-hydroxytoluene to 6-bromo-2-methoxytoluene according to methods which have been previously described for the corresponding substances under the sub-heading “4-Bromo-2-methoxytoluene”. The yields were the following: 2-nitro-6-bromotoluene 72 per cent, 6-bromo-2-aminotoluene 85 per cent, and 6-bromo-2-methoxytoluene 58 per cent of the theoretical amounts. The last mentioned substance, which has not been prepared previously, distilled at 115–116°/20 mm.

C_8H_9OBr	Calc.	Br	39.74
	Found	»	39.69

6-Bromo-2-acetaminotoluene, prepared for identification purposes from 6-bromo-2-aminotoluene, melted at 164–165°.

2-Bromo-3-methoxytoluene. 2-Bromo-3-methoxytoluene was prepared mainly according to Hodgson and Beard²¹. As these authors did not describe the experimental details, the procedure followed is given here.

m-Cresol (63 g) was dissolved in fuming sulphuric acid (250 ml; 18 per cent sulphur trioxide) and the solution was heated to 50° for half an hour. After cooling to 0–5°, the *m*-cresoldisulphonic acid formed was nitrated with a mixture of fuming sulphuric acid (65 ml; 18 per cent sulphur trioxide) and nitric acid (28 ml; *d* 1.52). Next morning the reaction mixture was diluted with water (300 ml). On steam distillation *m*-cresol passed over, but when the temperature of the steam was gradually raised to 180°, 2-nitro-3-hydroxytoluene (51 g; 58 per cent of the theoretical amount) distilled. After filtration the latter compound was dissolved in an aqueous solution (190 ml) of potassium hydroxide (19 g), and dimethyl sulphate (43 g) was added. After the mixture had been shaken for one hour and heated for two hours on the boiling water bath, 2-nitro-3-methoxytoluene (29 g; 52.5 per cent of the theoretical amount) was distilled with steam.

2-Nitro-3-methoxytoluene (35 g) was dissolved in ethyl alcohol (200 ml) and the solution was slowly added to a hot solution of stannous chloride (185 g) in concentrated hydrochloric acid (190 ml) and ethyl alcohol (50 ml). When the reduction was completed, the alcohol was distilled off. After cooling, a complex stannic compound (61 g) separated and was filtered. 2-Amino-3-methoxytoluene was liberated by alkali and removed by steam distillation, after which it was distilled under reduced pressure. The yield (23 g) was 80 per cent of the theoretical amount.

2-Amino-3-methoxytoluene (23 g) was dissolved in 48 per cent hydrobromic acid (50 ml) and diazotized with a solution of sodium nitrite (12 g) in water (20 ml) at a temperature just below 10°. When the addition was completed, the solution was immediately poured through a dropping funnel into a boiling mixture of cuprous bromide (14 g) and 48 per cent hydrobromic acid (15 ml) in a flask provided with steam inlet and a condenser for downward distillation. The 2-bromo-3-methoxytoluene formed was then distilled with steam and the organic layer in the distillate was dissolved in ether. After the ether solution had been freed from phenolic substances by extraction with alkali, it was dried with anhydrous sodium sulphate. After the ether had evaporated, 2-bromo-3-methoxytoluene (b.p. 142–143°/38 mm) distilled. The yield (17 g) was 50.5 per cent of the theoretical amount.

4-Bromo-3-methoxytoluene. *p*-Acetotoluide was converted into 3-nitro-4-aminotoluene according to Gattermann²² and the synthesis was continued over 3-nitro-4-bromotoluene, 4-bromo-3-aminotoluene, and 4-bromo-3-hydroxytoluene to 4-bromo-3-methoxytoluene according to methods described for the corresponding substances under the sub-heading "4-Bromo-2-methoxytoluene". The yields were the following: 3-nitro-4-bromotoluene 82 per cent, 4-bromo-3-aminotoluene 82 per cent, and 4-bromo-3-methoxytoluene (b.p. 131–132°/30 mm) 68 per cent of the theoretical amounts.

4-Bromo-3-acetaminotoluene was prepared for identification purposes by acetylation of 4-bromo-aminotoluene with acetic anhydride. After crystallization from 40 per cent ethyl alcohol, its melting point was 121–122°.

$C_9H_{10}ONBr$	Calc.	N	6.14
	Found	»	6.24

The melting point of the compound has been reported to be 113.7–114.6°²³ and 164°²⁴.

5-Bromo-3-methoxytoluene. *p*-Acetotoluide was nitrated and the nitro compound hydrolyzed to 3-nitro-4-aminotoluene according to Gattermann²². By bromination the last-mentioned substance was converted into 3-nitro-5-bromo-4-aminotoluene²⁵, which was deaminated as follows:

Table 1.

Nr	Bromide, used	Carboxylic acid		Ketone	
		g	m.p.	g	m.p.
1	3-Bromo-1-methoxybenzene	1.30	106—107 ^a	—	
2	4-Bromo-1-methoxybenzene	0.76	183—184 ^a	—	
3	3-Bromo-2-methoxytoluene	0.94	82—83.5 ^a	—	
4	4-Bromo-2-methoxytoluene	0.54	144—145 ^a	—	
5	5-Bromo-2-methoxytoluene	1.30	193—194 ^a	—	
6	6-Bromo-2-methoxytoluene	1.77	150—151 ^a	—	
7	2-Bromo-3-methoxytoluene	1.84	137—138 ^a	—	
8	4-Bromo-3-methoxytoluene	0.56	104—105 ^b	1.05	116—117 ^e
9	5-Bromo-3-methoxytoluene	0.93	131—132 ^c	—	
10	6-Bromo-3-methoxytoluene	1.25	176—177 ^a	—	
11	2-Bromo-4-methoxytoluene	0.98	144—145.5 ^a	—	
12	3-Bromo-4-methoxytoluene	1.02	68—69 ^d	1.41	82—83 ^e

^a After crystallization from water.

^b After crystallization from a small quantity of ether.

^c After crystallization from a mixture of acetic acid and water.

^d After crystallization from a mixture of benzene and ligroin.

^e After crystallization from ligroin.

3-Nitro-5-bromo-4-aminotoluene (46.2 g) was dissolved in a mixture of ethyl alcohol (500 ml) and concentrated sulphuric acid (80 ml). This solution was diazotized with an aqueous solution (90 ml) of sodium nitrite (15 g), the temperature being kept just below 0°. When the nitrite solution had been added, the reaction mixture was carefully warmed until the evolution of nitrogen ceased. The 3-nitro-5-bromotoluene was removed from the dark-coloured solution by steam distillation. After crystallization from alcohol, the substance melted at 82°. The yield (33.4 g) was 77 per cent of the theoretical amount.

The synthesis was continued over 5-bromo-3-aminotoluene and 5-bromo-3-hydroxytoluene to 5-bromo-3-methoxytoluene according to methods described above for the corresponding substances under the sub-heading "4-Bromo-2-methoxytoluene". The yields were the following: 5-bromo-3-aminotoluene 92 per cent and 5-bromo-3-methoxytoluene (b.p. 120—120.5°/22 mm) 55.4 per cent of the theoretical amounts.

5-Bromo-3-acetaminotoluene was prepared for identification purposes by acetylation of 5-bromo-3-aminotoluene with acetic anhydride. After crystallization it melted at 169°.

6-Bromo-3-methoxytoluene. *m*-Methoxytoluene (70 g), prepared from *m*-cresol and dimethyl sulphate according to the method given for anisole in Organic Syntheses¹⁶, was reacted with bromine (92 g) in chloroform (70 ml), iron filings (1 g) being used as catalyst. During the addition of bromine, the temperature was kept at about 30°. When all the bromine had been added, the temperature was raised to 60° for two hours. After the solution had been shaken with an aqueous solution of sodium carbonate and dried with calcium chloride, the solvent was evaporated and the residue distilled under reduced

Table 2.

Nr	Benzoic acid	<i>p</i> -Nitrobenzyl ester		
		m.p.	N	
			Calc.	Found
—	2-Methoxy-	86—87	4.88	4.98
1	3-Methoxy-	79—80	4.88	4.95
2	4-Methoxy-	131—132		*
6	3-Methoxy-2-methyl-	96—97	4.65	4.73
10	4-Methoxy-2-methyl-	126.5—127.5	4.65	4.75
11	5-Methoxy-2-methyl-	110—111	4.65	4.74
7	6-Methoxy-2-methyl-	80—81	4.65	4.66
3	2-Methoxy-3-methyl-	75—76.5	4.65	4.71
5	4-Methoxy-3-methyl-	114—115	4.65	4.81
9	5-Methoxy-3-methyl-	113.5—114	4.65	4.65
12	6-Methoxy-3-methyl-	119—120	4.65	4.70
8	2-Methoxy-4-methyl-	112—113	4.65	4.74
4	3-Methoxy-4-methyl-	109—110	4.65	4.78

* Previously known.

pressure. The yield of 6-bromo-3-methoxytoluene (50 g), b.p. 115—116°/14 mm, was 43.5 per cent of the theoretical amount.

2-Bromo-4-methoxytoluene. *p*-Toluidine was converted over 2-nitro-4-aminotoluene and 2-nitro-4-hydroxytoluene into 2-nitro-4-methoxytoluene according to Ullmann and Dootson²⁶. This nitromethoxy compound was reduced to 2-amino-4-methoxytoluene as follows:

2-Nitro-4-methoxytoluene (100 g) dissolved in ethyl alcohol (315 ml) was gradually added to a warm mixture of stannous chloride (405 g), concentrated hydrochloric acid (510 ml) and ethyl alcohol (175 ml). After this addition the mixture was heated for a quarter of an hour on the boiling water bath, after which it was made alkaline. On steam distillation, 2-amino-4-methoxytoluene, m.p. 44—45.5°, passed over and was collected by filtration. The yield (40.3 g) was 50.4 per cent of the theoretical amount.

2-Amino-4-methoxytoluene (40.3 g), dissolved in 48 per cent hydrobromic acid (110 ml), was diazotized with an aqueous solution (35 ml) of sodium nitrite (20.4 g), the temperature being kept between 0 and 5°. When the addition of the nitrite was completed, the solution was immediately poured through a dropping funnel into a boiling mixture of cuprous bromide (29 g) and 48 per cent hydrobromic acid (30 ml) contained in a flask provided with a steam inlet and a condenser for downward distillation. The 2-bromo-4-methoxytoluene formed was then distilled with steam and the organic layer in the distillate was dissolved in ether. After the solution had been freed from phenolic matter by extraction with alkali, it was dried with anhydrous sodium sulphate. After evaporation of the solvent, 2-bromo-4-methoxytoluene (b.p. 134—137°/38 mm) distilled. The yield (17.4 g) was 29.3 per cent of the theoretical amount.

3-Bromo-4-methoxytoluene. *p*-Cresol was methylated according to the method given for anisole in *Organic Syntheses* ¹⁶, the yield being 84 per cent of the theoretical amount. This methoxytoluene was then brominated in chloroform with iron filings as catalyst ¹⁷. The yield was 54.5 per cent of the theoretical amount.

The reactions between Grignard reagents and carbon dioxide. The Grignard reagent was prepared from each bromide (5 g), an equivalent quantity of magnesium (0.70 g for bromomethoxybenzenes, 0.60 g for bromomethoxytoluenes), and dry ether (25 ml) by heating on the water bath for two hours. Carbon dioxide was then conducted into the solution for one hour. The reaction mixture was poured into dilute hydrochloric acid. After adding more ether, the mixture was shaken and the layers were allowed to separate. The organic phase was extracted successively with aqueous solutions of 1) sodium bicarbonate, 2) sodium carbonate, and 3) sodium hydroxide. The ether was evaporated from the organic phase and unchanged bromide and anisole or methoxytoluene were distilled off with steam. If ketone had formed during the reaction, it was isolated from the residue.

The sodium bicarbonate solution was acidified and the carboxylic acid was collected by filtration.

A very small amount of the carboxylic acid was isolated on acidifying the sodium carbonate solution.

In each case the sodium hydroxide solution contained only a very small amount of oily material which was not examined further.

The results are collected in Table 1.

One of the ketones, *viz.* 2,2'-dimethoxy-5,5'-dimethylbenzophenone, has previously been synthesized ²⁷. In order to characterize it, its 2,4-dinitrophenylhydrazone was prepared according to Wild ²⁸. The melting point of the latter substance was 164–165°.

$C_{23}H_{22}O_6N_4$	Calc.	N	12.44
	Found	»	12.45

2,2'-Dimethoxy-4,4'-dimethylbenzophenone, which was obtained by the reaction of the Grignard reagent of 4-bromo-3-methoxytoluene with carbon dioxide, melted at 117°.

$C_{17}H_{18}O_3$	Calc.	C	75.53	H	6.71
	Found	»	75.60	»	6.57

Its 2,4-dinitrophenylhydrazone melted at 194–195°.

$C_{23}H_{22}O_6N_4$	Calc.	N	12.44
	Found	»	12.32

All the carboxylic acids obtained in the present work have been described previously. Their *p*-nitrobenzyl esters were prepared for identification purposes ²⁹. The results are collected in Table 2.

The reaction between o-methoxy phenylmagnesium bromide and the reaction product of phenylmagnesium bromide and carbon dioxide. Carbon dioxide was conducted into a Grignard solution prepared from bromobenzene (4.00 g), magnesium (0.60 g), and dry ether (25 ml). When the reaction was completed, the mixture was gently warmed on the water bath in order to remove the unreacted gas. In the meantime, a Grignard reagent was prepared from *o*-bromoanisole (5 g), magnesium (0.60 g), and dry ether (25 ml). This solution was now rapidly added to the first Grignard solution. The oily layer formed by the reaction product between carbon dioxide and phenylmagnesium bromide grew thicker during the addition and its colour changed from black to brown. After the mixture had been stirred for a quarter of an hour, it was poured into a mixture of dilute hydrochloric acid and ether. When the solutions had cleared, they were separated and the

organic layer was freed from acid and phenolic matter by extraction with a dilute sodium hydroxide solution. The solvent was removed and volatile substances were distilled off by steam. The residue was a light-coloured oil (2.46 g). From this oil the 2,4-dinitrophenylhydrazone of *o*-methoxybenzophenone was isolated.

$C_{20}H_{16}O_5N_4$	Calc.	N	14.28
	Found	»	14.18

The compound melts at 146–147°.

SUMMARY

1. Methoxyphenylmagnesium bromides and methoxytolylmagnesium bromides in which the methoxy group and the magnesium atom are in meta or para position relative to each other react with carbon dioxide to give the corresponding carboxylic acids only.

2. A methoxy group in ortho position relative to the magnesium atom in a Grignard reagent prepared from bromo derivatives of benzene and toluene leads to the formation of ketone in addition to the acid. Ketone formation does not occur when a methyl group is in the ortho position relative to either the methoxy group or the magnesium atom.

3. *o*-Methoxybenzophenone is formed in the reaction between *o*-methoxyphenylmagnesium bromide and the reaction product of carbon dioxide and phenylmagnesium bromide.

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