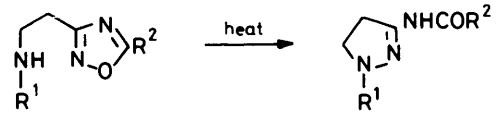
Ring Transformation of 1-[(1,2,4-Oxadiazol-3-yl)methyl]isoquinolines into 2-Acylaminopyrazolo[5,1-*a*]isoquinolines

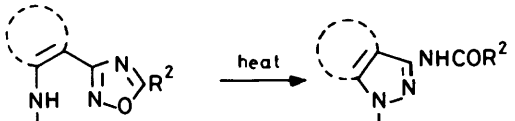
Imre Bata, Gergely Héja, Pál Kiss, and Dezsö Korbonits *
Chinoin Research Centre, H-1325, P.O.B. 110, Budapest, Hungary

Selective reduction of 1-[(1,2,4-oxadiazol-3-yl)methyl]-3,4-dihydroisoquinolines (**8**) gives the tetrahydro derivatives (**12**) which readily isomerize to 2-acylaminopyrazolo[5,1-*a*]isoquinolines (**13**). Compounds (**13**) were also obtained by reaction of the isoquinolinylacetamide oxime (**11**) with esters (**6**). A comparision of ring transformations in the series of compounds (**8**) and (**12**) indicated that both followed the same mechanism. This provided further support to the proposed[1a] extension of the Type-2 Boulton–Katritzky scheme.

Earlier we reported[1] the spontaneous or thermally induced ring rearrangement of 1,2,4-oxadiazoles of type (**1**) and (**3**) to the pyrazolines (**2**) and to the condensed pyrazoles (**4**).

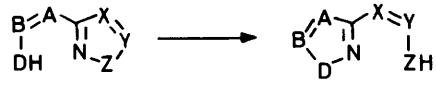


(**1**) (**2**)



(**3**) (**4**)

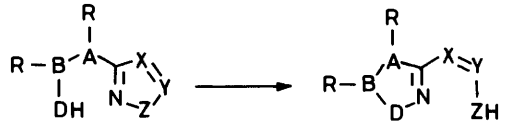
In contrast to the azole–azole isomerizations (**3**) ⟶ (**4**), because of the saturated side-chain the azole–azoline ring transformations (**1**) ⟶ (**2**) do not comply with the second scheme suggested by Katritzky and his co-workers[2a] (Scheme A).



Scheme A. Type-2 Boulton–Katritzky scheme

In the literature,[1a,3] Scheme A is referred to as the Boulton–Katritzky scheme. This may lead to confusion since the same term is used[4] to denote transformations of related bicyclic systems following an earlier suggestion of Boulton, Ghosh, and Katritzky.[5] Although the two types are essentially different,[6] they are often mentioned[7] or discussed[2c] together. Scheme A was also called a 'mononuclear heterocyclic rearrangement' (m.h.r),[7,8] but recently this term was criticized too.[3] In order to avoid misunderstandings we suggested[6,9] that the two kinds of Boulton–Katritzky rearrangement should be denoted as being of Type 1[5] and of Type 2[2a] respectively.

Comparing the uncatalysed ring transformations of the oxadiazoles (**1**) and (**3**) we established[1] that both rearrangements followed the same mechanism. Therefore we suggested the extension of Scheme A for azoles having a saturated side-chain (Scheme B).[1a]



R = H, alkyl, *etc.*, or R + R = a single (π bond between A and B) bond

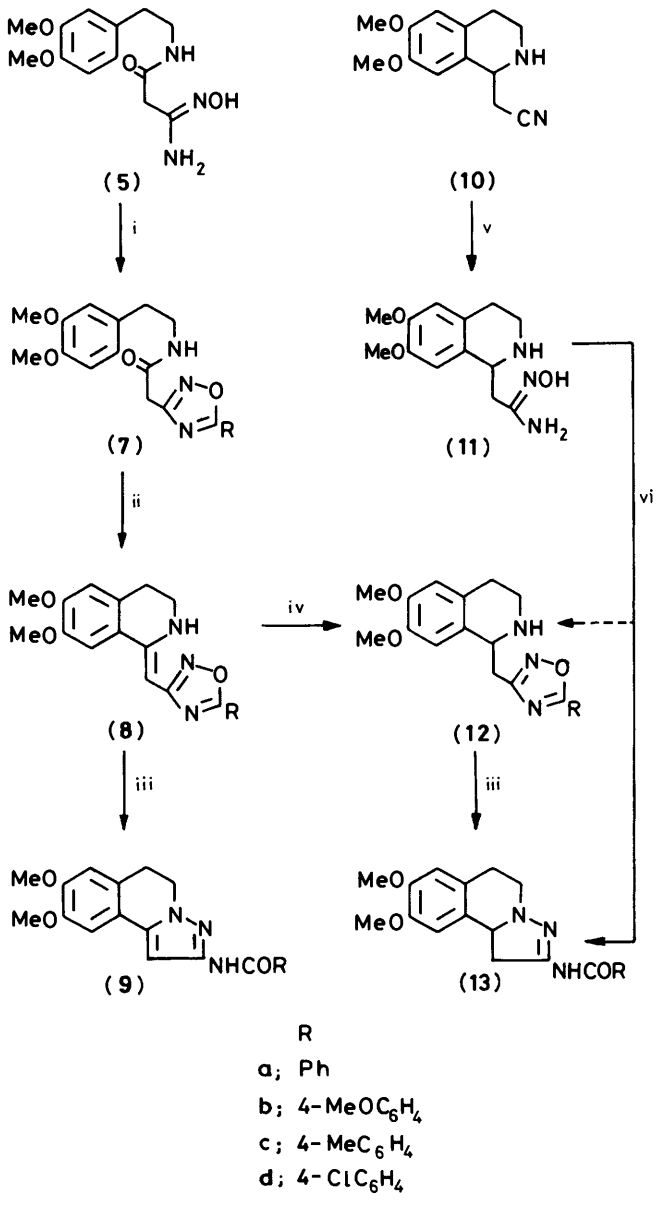
Scheme B. Extended Type-2 Boulton–Katritzky scheme.

Although experiments[1] and theoretical considerations and calculations[6] all indicated the close relationship of isomerizations corresponding to Schemes A and B, so far no example of pairs of compounds differing only in the saturation of the side-chain and which were both amenable to isomerization has been found.

In this paper we describe the synthesis of a series of such pairs, *i.e.* the oxadiazolylmethylisoquinolines (**8**) and (**12**), and their transformation to the pyrazoloisoquinolines (**9**) and (**13**), as outlined in Scheme 1.

The synthesis of the oxadiazole (**8a**) *via* the amides (**5**) and (**7**), as well as the ring transformation of (**8a**) to the pyrazole (**9a**) in boiling xylene by the method of Takács and co-workers has been reported earlier.[10] The 4-substituted phenyl analogues (**8b—d**) and (**9b—d**) were prepared from amide (**5**) in a similar way *via* the amides (**7b—d**). Preparation of the tetrahydroisoquinolines (**12**) was first attempted by ring closure of the amidoxime (**11**) with esters by our established method.[1b,11] Compound (**11**) could be prepared from the nitrile (**10**) with hydroxylamine. Nitrile (**10**) had previously been prepared by reaction of 6,7-dimethoxy-3,4-dihydroisoquinoline with potassium cyanoacetate.[12] For our synthesis we obtained it by reduction of the readily available (3,4-dihydro-6,7-dimethoxyisoquinolin-1-yl)acetonitrile.[13] Compound (**11**) was cyclized in good yield to the tricyclic compounds (**13**) with esters (**6**) in the presence of sodium alcoholates in refluxing ethanol or methanol. However, the postulated intermediate oxadiazole (**12**) could be detected neither during the reaction nor in the end product, probably because it isomerized much faster than it was formed.

The tetrahydro compounds (**12a—d**) could, after some experimentation, be obtained by reduction of the hydrochlorides of the compounds (**8**) at −10 °C in methanol with sodium borohydride. Reduction at higher temperature[14] gave mixtures, which is not surprising in view of the fast isomerization of compounds (**12**) and the known tendency of 1,2,4-oxadiazoles to undergo reductive ring-cleavage.[15] Now the behaviour of model compounds belonging to both series, (**8**) and (**12**), could be studied.



Scheme 1. *Reagents and conditions:* i, RCO_2Et (**6**), NaOEt, EtOH; ii, $POCl_3$; iii, heat; iv, $NaBH_4$, −10 °C; v, H_2NOH; vi, RCO_2Et (**6**), NaOMe, MeOH

In complete analogy with their open-chain aminoethyl congeners[1b] the tetrahydroisoquinolines (**12**) isomerized readily and in excellent yield to the tricyclic pyrazolines (**13**) corresponding to the acylaminopyrazoles (**2**). The rate of transformation depended on solvent polarity [dimethyl sulphoxide (DMSO) > butan-1-ol > dioxane > cyclohexane], and the reaction went to completion in polar solvents (DMSO, dimethylformamide, alcohols) at room temperature within one or two days. In accord with our earlier results[1] the solvent did not play an essential role in the reaction since it could be accomplished also by heating the compounds above their m.p.s for a few minutes.

In the series of compounds (**8**) isomerisation was also solvent dependent but slower.

In the transformation of azoles with unsaturated side-chains the configuration of the latter (*Z* or *E*) may be relevant.[16]

Table 1. Rate constants (k) and half-lives ($t_{\frac{1}{2}}$) for the isomerization of oxadiazoles (**8**) and (**12**) at 110 °C in butan-1-ol

Compound	Aryl 4-substituent	$10^4\ k/s^{-1}$	$t_{\frac{1}{2}}$/min
(**8a**)	H	1.36	85.0
(**8b**)	OMe	1.05	110.0
(**8c**)	Me	1.16	100.0
(**8d**)	Cl	1.65	70.0
(**12a**)	H	30.1	3.83
(**12b**)	OMe	22.4	5.16
(**12c**)	Me	26.7	4.33
(**12d**)	Cl	38.5	3.00

Apparently, owing to fast imine–enamine tautomerism, no such effect was observed in the case of the isoquinolines (**8**).

For a quantitative comparison, rate constants and half-lives of ring transformations for compounds (**8a—d**) and (**12a—d**) were determined in butan-1-ol at 110 °C (Table 1). It can be seen that transformation of the 'saturated side-chain' models (**12**) was about 20 times faster than that of the dehydro analogues (**8**).

The reason for the substantial difference in rates of reaction of compounds (**8**) and (**12**) is that in the enamines (**8**) the nucleophilic activity of the isoquinoline nitrogen is diminished by interaction with the π-electron system, as compared with the secondary amines (**12**).

The effect of *para*-substitution at the C(5) phenyl group of the oxadiazole ring is in accord with our earlier observation[1] that electron-donating substituents decrease, whereas electron-attracting ones increase, the rate of ring isomerization. Recent results of Frenna *et al.* with related oxadiazoles[8] confirmed our earlier results.

Linearity of the Hammett correlation in both series indicates the dominance of electronic effects. It has to be noted that despite the difference in rates there is no significant deviation in the values of the Hammett ρ constants in the two series [0.391 with type (**8**) and 0.447 with type (**12**)]. This result suggests that the delocalized π-electron system of the 1,2,4-oxadiazole ring plays an important role in both cases. Note that no ring isomerization analogous to the one described here takes place when the azole ring is partially saturated.[17] As proposed earlier[1,6] the reaction proceeds in these and similar azole rearrangements by a special S_Ni-type mechanism.

Conclusion.—Results presented here show unequivocally that saturation of the side-chain of the azole ring has practically no influence either on the feasibility of ring isomerization or on its mechanism, whereby the extension[1a] of the Type-2 Boulton–Katritzky scheme is further vindicated.

Experimental

U.v. spectra were recorded in ethanol on a Unicam SP8-100 spectrophotometer, i.r. spectra as KBr discs on Unicam SP 1000 and Spectromom 2000 instruments, and ^1H n.m.r. spectra were taken in $CDCl_3$ on a JEOL FX-100 spectrometer at 100 MHz (only the characteristic signals were given). T.l.c. was carried out on Macherey-Nagel Polygram Sil G/u.v. 254 plates. Evaporations were carried out under reduced pressure. M.p.s, yields, and analytical and spectral data for compounds (**7**)—(**9**), (**12**), and (**13**) are shown in Table 2.

General Method for the Preparation of 3-[2-(3,4-*Dimethoxyphenyl*)*ethyl*]*carbamoylmethyl*-5-(4-*substituted phenyl*)-1,2,4-*oxadiazoles* (**7a—d**).—To a solution of α-[2-(3,4-dimethoxy-

Table 2. Yields, m.p.s, and spectral and analytical data of compounds (**7**)—(**9**), (**12**), and (**13**)

Compound	Yield (%)	M.p. (°C)	λ/nm	$\nu_{max.}$/cm^{-1} (NH, CO)	δ_H	Formula	Found (%) (Required) C	H	N	Cl
(**7a**)	65	153[a]		3 280, 1 645						
(**7b**)	36	144		3 280, 1 650	3.91 (s, 3 H), 6.70 (br, 1 H)	$C_{21}H_{23}N_3O_5$	63.2 (63.5)	5.8 (5.8)	10.5 (10.6)	
(**7c**)	70	146		3 310, 1 660	2.46 (s, 3 H), 6.70 (br, 1 H)	$C_{21}H_{23}N_3O_4$	66.1 (66.1)	6.2 (6.1)	11.0 (11.0)	
(**7d**)	60	171		3 290, 1 655	6.60 (br, 1 H)	$C_{20}H_{20}ClN_3O_4$	59.6 (59.8)	5.0 (5.0)	10.6 (10.5)	8.8 (8.8)
(**8a**)	75	165[b]	340, 259	3 320						
(**8a**)·HCl		170		3 000—2 600		$C_{20}H_{20}ClN_3O_3$	62.4 (62.3)	5.2 (5.2)	10.8 (10.9)	9.5 (9.2)
(**8b**)	45	151	342, 277	3 340	3.88 (s, 3 H), 5.59 (s, 1 H) 7.43 (br, 1 H)	$C_{21}H_{21}N_3O_4$	66.4 (66.5)	5.5 (5.6)	10.9 (11.1)	
(**8b**)·HCl		190		2 900, 2 600		$C_{21}H_{22}ClN_3O_4$	60.4 (60.7)	5.3 (5.3)	10.0 (10.1)	8.7 (8.5)
(**8c**)	70	174	340, 266	3 340	2.43 (s, 3 H), 5.60 (s, 1 H), 7.43 (br, 1 H)	$C_{21}H_{21}N_3O_3$	69.8 (69.4)	6.0 (5.8)	11.7 (11.6)	
(**8c**)·HCl		189		3 000, 2 600		$C_{21}H_{22}ClN_3O_3$	62.8 (63.1)	5.2 (5.6)	10.3 (10.5)	9.0 (8.9)
(**8d**)	65	180	336, 265	3 340	5.56 (s, 1 H), 7.39 (br s, 1 H)	$C_{20}H_{18}ClN_3O_3$	62.3 (62.6)	4.7 (4.7)	11.0 (11.0)	9.4 (9.2)
(**8d**)·HCl		189		2 800, 2 350		$C_{20}H_{19}Cl_2N_3O_3$	56.9 (57.2)	4.4 (4.6)	9.8 (10.0)	17.1 (16.9)
(**9a**)	76	181[c]		3 200, 1 675						
(**9b**)	60	171	277	3 290, 1 680	3.80 (s, 3 H), 9.84 (s, 1 H)	$C_{21}H_{21}N_3O_4$	66.2 (66.5)	5.5 (5.6)	10.9 (11.0)	
(**9c**)	50	176	273	3 280, 1 680	2.38 (s, 3 H), 9.79 (s, 1 H)	$C_{21}H_{21}N_3O_3$	69.3 (69.4)	5.9 (5.8)	11.5 (11.6)	
(**9d**)	45	216	273	3 250, 1 685	10.2 (s, 1 H)	$C_{20}H_{18}ClN_3O_3$	62.8 (62.6)	4.4 (4.7)	10.7 (10.9)	9.0 (9.2)
(**12a**)	83	109	252	3 360	2.29 (s, 1 H), 4.49 (t, 1 H)	$C_{20}H_{21}N_3O_3$	68.4 (68.4)	6.0 (6.0)	12.1 (12.0)	
(**12a**)·HCl		111		3 200, 2 400		$C_{20}H_{22}ClN_3O_3$	61.5 (61.9)	5.7 (5.7)	10.6 (10.8)	8.8 (9.1)
(**12b**)	80	126	281	3 350	2.60—3.40 (m, 7 H), 3.89 (s, 3 H), 4.50 (t, 1 H)	$C_{21}H_{23}N_3O_4$	66.2 (66.1)	6.1 (6.1)	10.9 (11.0)	
(**12b**)·HCl		200		3 100, 2 350		$C_{21}H_{24}ClN_3O_4$	60.1 (60.4)	5.7 (5.8)	10.0 (10.1)	8.6 (8.5)
(**12c**)	83	134	259	3 360	2.60—3.40 (m, 7 H) 2.44 (s, 3 H), 4.51 (t, 1 H)	$C_{21}H_{23}N_3O_3$	68.8 (69.0)	6.3 (6.3)	11.3 (11.5)	
(**12c**)·HCl		186		3 200, 2 400		$C_{21}H_{24}ClN_3O_3$	62.5 (62.8)	6.0 (6.0)	10.2 (10.5)	8.6 (8.8)
(**12d**)	78	117	261	3 320	2.50—3.40 (m, 7 H), 4.50 (t, 1 H)	$C_{20}H_{20}ClN_3O_3$	62.3 (62.3)	5.3 (5.2)	10.7 (10.9)	9.0 (9.2)
(**12d**)·HCl		203		3 200, 2 500		$C_{20}H_{21}Cl_2N_3O_3$	56.5 (56.9)	4.8 (5.0)	9.7 (10.0)	17.0 (16.8)
(**13a**)	90	196	282, 227	3 380, 1 690	4.89 (dd, 1 H), 8.53 (br s, 1 H)	$C_{20}H_{21}N_3O_3$	68.6 (68.4)	6.1 (6.0)	12.2 (12.0)	
(**13b**)	85	198	282	3 320, 1 675	3.84 (s, 3 H), 4.89 (dd, 1 H), 8.69 (s, 1 H)	$C_{21}H_{23}N_3O_4$	65.9 (66.1)	6.0 (6.1)	11.0 (11.0)	
(**13c**)	80	218	282, 232	3 320, 1 680	2.39 (s, 3 H), 4.89 (dd, 1 H), 8.71 (s, 1 H)	$C_{21}H_{23}N_3O_3$	68.8 (69.0)	6.4 (6.3)	11.2 (11.5)	
(**13d**)	95	202	284, 233	3 320, 1 680	4.91 (dd, 1 H), 9.01 (br s, 1 H)	$C_{20}H_{20}ClN_3O_3$	62.2 (62.2)	5.6 (5.2)	10.8 (10.9)	9.0 (9.2)

[a] Lit.,[10] 152 °C. [b] Lit.,[10] 166 °C. [c] Lit.,[10] 185 °C.

phenyl)ethyl]carbamoylacetamide oxime (**5**)[10] (21.5 g, 75 mmol) in dry ethanol (300 ml) the appropriate ester (**6**) (150 mmol) and a freshly prepared solution of sodium (0.075 g-atom) in ethanol (75 ml) was added. After having been refluxed for 4 h, the mixture was cooled, and the precipitated product was separated, washed with water (300 ml), dried, and recrystallized from ethanol (see Table 2).

General Method for the Preparation of 3,4-*Dihydro*-6,7-*dimethoxy*-1-{[5-(4-*Substituted phenyl*)-1,2,4-*oxadiazol*-3-*yl*]-*methyl*}*isoquinolines* (**8a—d**).—To a boiling solution of an oxadiazole (**7**) (60 mmol) in chloroform (200 ml) was added dropwise phosphoryl trichloride (33 ml, 55.2 g, 360 mmol). After an additional 3 h reflux, the solvent and the excess of reagent was evaporated off and the residue was worked up as follows:

In the case of compound (**8b**) the residue was triturated with water (100 ml) and then cooled and carefully neutralized with conc. ammonia. The solid product was filtered off, dried, and crystallized from acetonitrile.

(ii) In the case of compounds (**8a**), (**8c**), and (**8d**) the residue was dissolved in chloroform, the solution was cooled and made alkaline with conc. ammonia, extracted thoroughly with water, dried over magnesium sulphate, and evaporated to dryness, and the residue was crystallized from acetonitrile.

Hydrochlorides of compounds (**8a**—**d**) were prepared by addition of hydrochloric acid in ethyl acetate to their solutions in chloroform. The solutions were evaporated to dryness and the residues were crystallized from ethyl acetate (see Table 2).

General Method for the Preparation of 2-(4-*Substituted benzamido*)-5,6-*dihydro*-8,9-*dimethoxypyrazolo*[5,1-a]*isoquinolines* (**9a**—**d**).—A solution of a dihydroisoquinoline base (**8**) (2.6 mmol) in xylene (10 ml) was refluxed for 8 h. After the mixture had cooled, the product was filtered off, dried, and recrystallized from ethanol (see Table 2).

(1,2,3,4-*Tetrahydro*-6,7-*dimethoxyisoquinolin*-1-*yl*)*acetonitrile* (**10**).—To a solution of (3,4-dihydro-6,7-dimethoxyisoquinolin-1-yl)acetonitrile[13] (46.0 g, 200 mmol) in 2M-sulphuric acid (1 000 ml) at 80 °C was added zinc powder (104.6 g, 1.6 g-atom) in portions during 45 min. The hot solution was decolorized with carbon, filtered, and cooled to 0 °C. The precipitated product was filtered off and suspended in water (200 ml), and the mixture was made alkaline with conc. ammonia. The precipitate was filtered off, washed with water, and recrystallized from water to give compound (**10**) (31.7 g, 68%), m.p. 120—121 °C (lit.,[12] 120 °C). Its i.r. spectrum was identical with that of a sample prepared according to the literature method.

α-(1,2,3,4-*Tetrahydro*-6,7-*dimethoxyisoquinolin*-1-*yl*)*acetamide Oxime* (**11**).—To a suspension of the nitrile (**10**) (17.4 g, 75 mmol) in 95% ethanol (350 ml) was added a solution of hydroxylamine hydrochloride (10.42 g, 150 mmol) and sodium hydrogen carbonate (12.6 g, 150 mmol) in water (50 ml) and the mixture was refluxed for 4 h. The solution was filtered hot, the filtrate was evaporated to dryness, and the residue was extracted with hot ethanol (80 ml). The extract was decolorized with carbon, filtered hot, and cooled to give the *title amidoxime* (**11**) (14.5 g, 73%), m.p. 168—170 °C (170—172 °C after recrystallization from ethanol) (Found: C 58.9, H 7.1, N 15.6. $C_{13}H_{19}N_3O_3$ requires C 58.9, H 7.2, N 15.8%); $\nu_{max.}$ (cm^{-1}) 3 480 (NH), 3 300 (OH), and 1 675 (C=N).

General Method for the Preparation of 1,2,3,4-*Tetrahydro*-6,7-*dimethoxy*-1-{[5-(4-*substituted phenyl*)-1,2,4-*oxadiazol*-3-*yl*]-*methyl*}*isoquinolines* (**12a**—**d**).—To a stirred solution of an imino enamine, (**8**)·HCl (7.0 mmol) in methanol, cooled to −10 °C, was added sodium borohydride (1.3 g, 35 mmol) in portions during 20 min. The mixture was stirred for 1 h without cooling, triturated with water, and extracted with chloroform; the organic layer was evaporated below 20 °C and the residue was crystallized from diethyl ether (see Table 2).

General Method for the Preparation of 2-(4-*Substituted benzamido*)-1,5,6,10b-*tetrahydro*-8,9-*dimethoxypyrazolo*[5,1-a]-*isoquinolines* (**13a**—**d**).—(*a*) A solution of an oxadiazole (**12**) (2.6 mmol) in methanol (20 ml) was refluxed for 3 h and then evaporated, and the residue was crystallized from diethyl ether (see Table 2).

(*b*) To a solution of an amidoxime (**11**) (2.65 g, 10 mmol) and an ester (**6**) (20 mmol) in methanol (30 ml) was added a freshly prepared solution of sodium (0.23 g, 0.01 g-atom) in methanol (10 ml). The mixture was refluxed for 4 h and then evaporated, the residue was triturated with water and extracted with chloroform, and the extract was dried (sodium sulphate) and evaporated to give a residue which was crystallized from diethyl ether to afford a compound (**13a**—**d**) in 70—82% yield. The products were identical with those prepared according to method (*a*).

Transformations (**8**) ⟶ (**9**) and (**12**) ⟶ (**13**) were followed kinetically by u.v. spectrophotometry, as described earlier.[1b]

Acknowledgements

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