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Reaction of Pentafluorophenyl(diphenyl)phosphine with Nitrilimines

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Abstract—Reaction of pentafluorophenyl(diphenyl)phosphine with nitrilimines is a multistep process leading to formation of unstable fused heterocycles with a fluorophosphorane moiety as primary products. Their hydrolysis involves opening of the heteroring and subsequent cleavage of the N–N bond in intermediate phosphorylated hydrazones. The final products are diphenyl(6-arylamino-2,3,4,5-tetrafluorophenyl)phosphine oxides.

We recently [1, 2] reported on the reactions of diethyl pentafluorophenylphosphonite and bis(pentafluorophenyl)phenylphosphine with nitrilimines, which resulted in formation of new fused heterocyclic compounds, substituted 5,6,7,8-tetrafluoro-1,4-dihydro-1,2,4λ^5-benzodiazaphosphinine 4-oxides, which attract interest as potential biologically active substances. The key step in this process is formation of cyclic intermediates having a phosphonium [1] or phosphorane structure [2].

We have found that intermediate cyclic phosphoranes are also formed in reactions of nitrilimines with another tervalent phosphorus derivative, pentafluorophenyl(diphenyl)phosphine. However, unlike the reactions reported in [1, 2], further transformations of these intermediates involve opening of the heteroring. The reaction is a multistep process which is likely to begin with nucleophilic attack by the phosphine phosphorus atom on the positively charged carbon atom in nitrilimine. Dipolar ions **Ia**–**IVa** thus formed undergo intramolecular ring closure via aromatic nucleophilic substitution of the *ortho*-fluorine atom by nitrogen. The released fluoride ion adds to the phosphorus atom to give heterocyclic fluorophosphorane **Ib**–**IVb** (Scheme 1). Products **Ib**–**IVb** are brown oily substances which gradually crystallize on storage. They are fairly stable below 20°C in the absence of atmospheric moisture and are readily soluble in diethyl ether. The ^{31}P NMR spectra of **Ib**–**IVb** contain a typical upfield doublet at δ_P –96.1 to –99.4 ppm, $^1J_{PF}$ = 625–662 Hz. Fluorophosphoranes **Ib**–**IVb** are readily hydrolyzed by the action of water or even of atmospheric moisture to form hydrogen fluoride and hydroxyphosphoranes **Ic**–**IVc** as primary intermediates which are converted into phosphine oxides **Id**–**IVd**. The latter contain a hydrazone moiety, and they loose benzonitrile (R = Ph) or ethyl cyanoformate molecule (R = EtOCO) to give the final products, diphenyl(6-arylamino-2,3,4,5-tetrafluorophenyl)phosphine oxides **V**–**VII**.

The proposed scheme is supported by the formation of the same phosphine oxide (**V**) from two different fluorophosphoranes, **Ib** and **IVb** [R = Ph and EtOC(O), respectively; Ar = Ph]. Products containing a cyano group (benzonitrile and ethyl cyanoformate) were detected by IR spectroscopy. After addition of water to fluorophosphorane **Ib** obtained from *C*,*N*-diphenylnitrilimine (R = Ar = Ph), an absorption band at 2240 cm^{-1} (which is typical of the C≡N bond in benzonitrile) appeared in the IR spectrum of the reaction mixture. Treatment with water of fluorophosphoranes **IIb**–**IVb** derived from *N*-aryl-*C*-ethoxycarbonylnitrilimines [R = EtOC(O), Ar = *p*-BrS$_6$H$_4$, *p*-MeC$_6$H$_4$, Ph] gave rise to IR absorption at 2250 cm^{-1}, which belongs to the C≡N bond in ethyl cyanoformate.

Cleavage of the N–N bond in intermediate products **Id**–**IVd** can be regarded as a new example of the aminonitrile rearrangement which is well known for hydrazones [3]. Analogous decomposition of phosphorylated hydrazones was observed previously [4, 5] in the hydrolysis of 1,4-dihydro- and 1,4,5,6-tetrahydro-1,2,4-diazaphosphininium chlorides (nitrilimine adducts with diphenylalkenyl- and diphenylalkynylphosphines).

6-Arylamino-2,3,4,5-tetrafluorophenyl(diphenyl)phosphine oxides **V**–**VII** are colorless or slightly yellowish crystalline substances, which can be stored for a long time under normal conditions. They are readily soluble in chloroform, acetone, benzene, and tetrahydrofuran, sparingly soluble in diethyl ether, and

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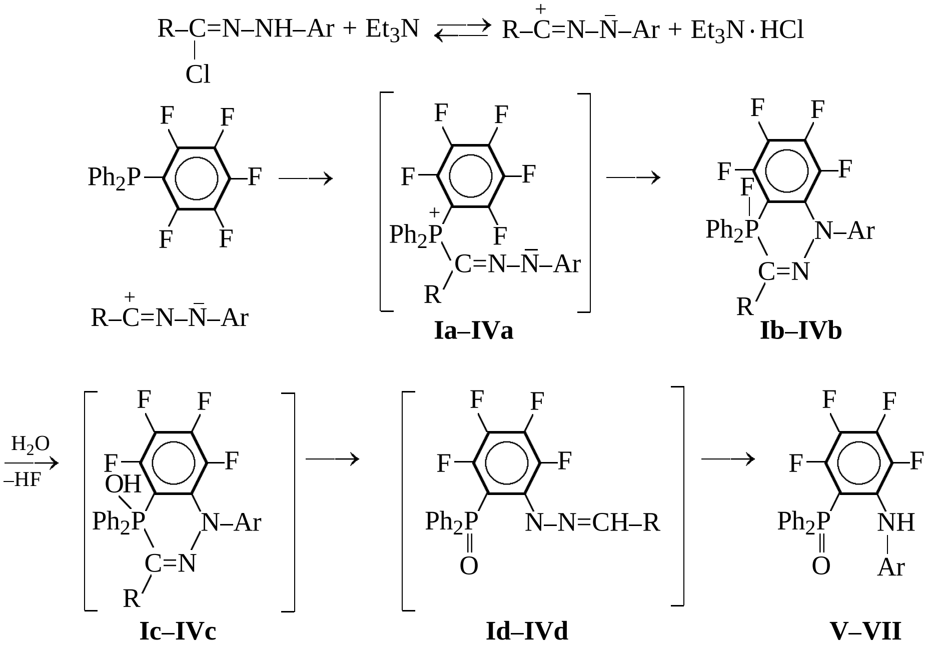
Scheme 1.



I, R = Ph; **II**–**IV**, R = EtOC(O); **I**, **IV**, Ar = Ph; **II**, Ar = *p*-BrC_6H_4; **III**, Ar = *p*-MeC_6H_4; **V**, Ar = Ph; **VI**, Ar = *p*-BrC_6H_4; **VII**, Ar = *p*-MeC_6H_4.

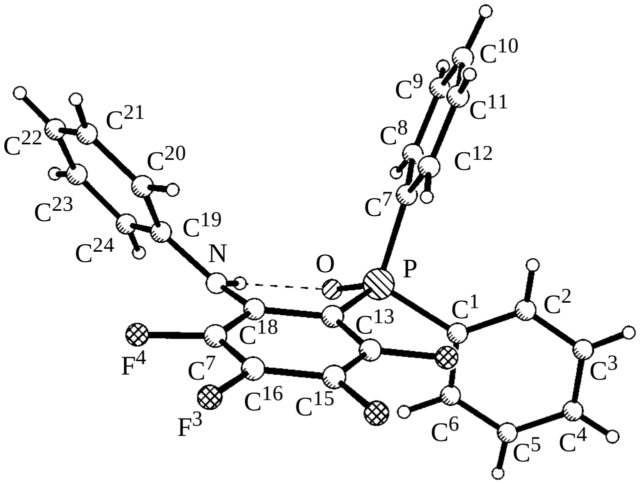


Fig. 1. Structure of the molecule of diphenyl(2,3,4,5-tetrafluoro-6-phenylaminophenyl)phosphine oxide (**V**).

poorly soluble in hexane. The phosphorus nucleus in **V**–**VII** gives a signal at δ_P 29.7–32.1 ppm in the ^{31}P NMR spectrum, which is typical of triarylphosphine oxides [6]. The ^1H NMR spectra of **V**–**VII** contain signals from the NH proton (δ 9.61–9.65 ppm) and aromatic protons (δ 6.64–7.80 ppm). The presence of NH and PO groups is confirmed by the IR spectra which display absorptions at 3150–3185 (ν N–H) and 1240–1245 cm^{-1} (ν P=O).

The structure of phosphine oxide **V** was unambiguously proved by X-ray analysis. The results are presented in Figs. 1 and 2 and Tables 1–3. The principal geometric parameters of molecule **V** are in agreement with the known data for triarylphosphine oxides [7]. The $P–C_{arom}$ bond lengths are 1.79 Å and 1.83 Å for unsubstituted and fluorinated phenyl rings, respectively. The bond angles at the tetrahedral phosphorus atom range from 106.5 to 113.5°. The dihedral angle between the planes of the phenyl rings on the nitrogen is 56.8°.

The P=O and N–H groups in molecule **V** form intramolecular hydrogen bond which gives rise to a six-membered ring having a *sofa* conformation. The phosphorus atom deviates by 0.480 Å from the plane formed by the other atoms, the latter being coplanar within 0.063 Å. The intramolecular hydrogen bond has the following parameters: distances, Å: N–H 0.84, H···O 2.01, N···O 2.750; $\angle$NHO 146°.

EXPERIMENTAL

The IR spectra were recorded on an IKS-29 spectrophotometer in KBr. The ^1H NMR spectra were measured on a Bruker AC-200 instrument (200 MHz; internal stabilization using ^2H resonance line). The ^{31}P NMR spectra were obtained on the same instrument at 81.4 MHz in $CDCl_3$ using 85% H_3PO_4 as reference.

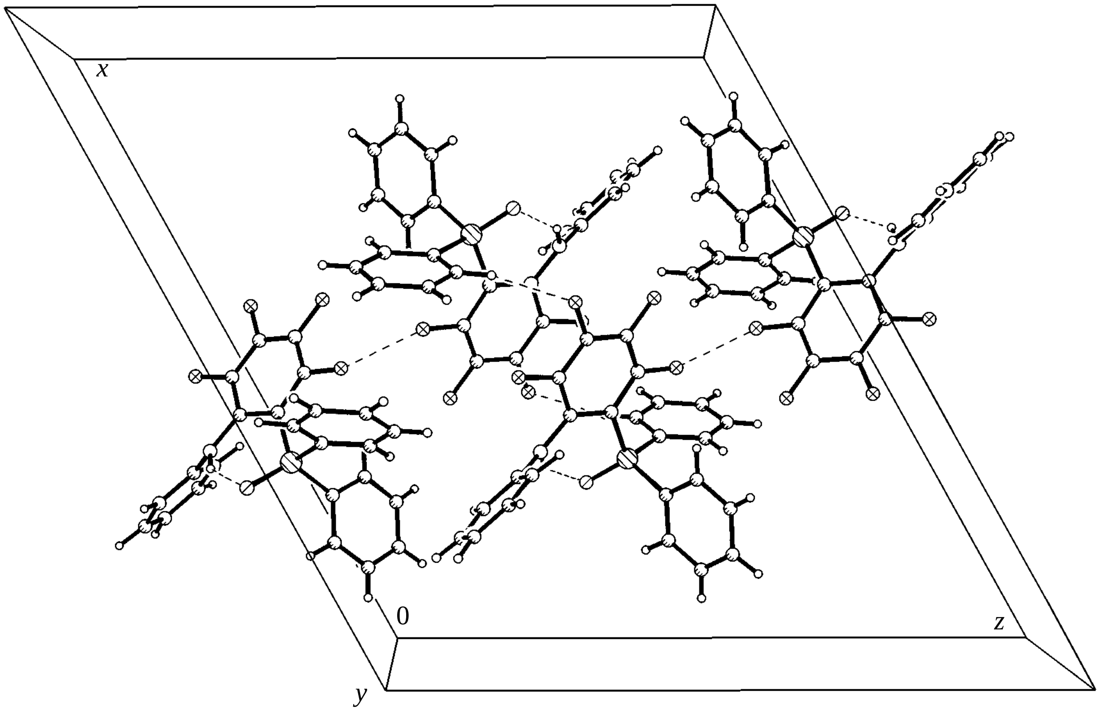


Fig. 2. Structure of a unit cell of diphenyl(2,3,4,5-tetrafluoro-6-phenylaminophenyl)phosphine oxide (**V**) in crystal.

Table 1. Bond lengths in the molecule of diphenyl(2,3,4,5-tetrafluoro-6-phenylaminophenyl)phosphine oxide (**V**)

Bond	*d*, Å	Bond	*d*, Å
P–O	1.4813(18)	C^7–C^8	1.382(4)
P–C^7	1.794(2)	C^8–C^9	1.387(5)
P–C^1	1.796(2)	C^9–C^{10}	1.358(5)
P–C^{13}	1.832(2)	C^{10}–C^{11}	1.362(5)
F^1–C^{14}	1.339(3)	C^{11}–C^{12}	1.372(4)
F^2–C^{15}	1.346(3)	C^{13}–C^{14}	1.384(3)
F^3–C^{16}	1.340(3)	C^{13}–C^{18}	1.420(3)
F^4–C^{17}	1.350(3)	C^{14}–C^{15}	1.366(3)
N–C^{18}	1.377(3)	C^{15}–C^{16}	1.363(4)
N–C^{19}	1.412(3)	C^{16}–C^{17}	1.367(3)
C^1–C^2	1.377(3)	C^{17}–C^{18}	1.387(3)
C^1–C^6	1.378(3)	C^{19}–C^{20}	1.381(4)
C^2–C^3	1.379(4)	C^{19}–C^{24}	1.383(3)
C^3–C^4	1.359(5)	C^{20}–C^{21}	1.387(4)
C^4–C^5	1.369(5)	C^{21}–C^{22}	1.365(5)
C^5–C^6	1.372(4)	C^{22}–C^{23}	1.372(5)
C^7–C^{12}	1.378(4)	C^{23}–C^{24}	1.377(4)

Table 2. Bond angles in the molecule of diphenyl(2,3,4,5-tetrafluoro-6-phenylaminophenyl)phosphine oxide (**V**)

Angle	ω, deg	Angle	ω, deg
OPC^7	113.46(12)	$C^{18}C^{13}P$	119.60(17)
OPC^1	111.62(11)	$F^1C^{14}C^{15}$	116.7(2)
C^7PC^1	106.11(11)	$F^1C^{14}C^{13}$	120.0(2)
OPC^{13}	110.28(10)	$C^{15}C^{14}C^{13}$	123.3(2)
C^7PC^{13}	106.47(11)	$F^2C^{15}C^{14}$	121.0(2)
C^1PC^{13}	108.61(11)	$F^2C^{15}C^{16}$	120.2(2)
$C^{18}NC^{19}$	125.9(2)	$C^{14}C^{15}C^{16}$	118.8(2)
$C^2C^1C^6$	118.8(2)	$F^3C^{16}C^{15}$	119.8(2)
C^2C^1P	123.5(2)	$F^3C^{16}C^{17}$	120.1(2)
C^6C^1P	117.73(19)	$C^{15}C^{16}C^{17}$	120.1(2)
$C^1C^2C^3$	120.9(3)	$F^4C^{17}C^{16}$	117.5(2)
$C^4C^3C^2$	119.5(3)	$F^4C^{17}C^{18}$	120.0(2)
$C^3C^4C^5$	120.3(3)	$C^{16}C^{17}C^{18}$	122.5(2)
$C^6C^5C^4$	120.4(3)	$NC^{18}C^{17}$	120.8(2)
$C^5C^6C^1$	120.1(3)	$NC^{18}C^{13}$	121.4(2)
$C^{12}C^7C^8$	118.6(3)	$C^{17}C^{18}C^{13}$	117.6(2)
$C^{12}C^7P$	123.47(19)	$C^{20}C^{19}C^{24}$	119.5(2)
C^8C^7P	117.7(2)	$C^{20}C^{19}N$	123.1(2)
$C^7C^8C^9$	119.7(3)	$C^{24}C^{19}N$	117.3(2)
$C^{10}C^9C^8$	120.9(3)	$C^{19}C^{20}C^{21}$	119.7(3)
$C^9C^{10}C^{11}$	119.6(3)	$C^{22}C^{21}C^{20}$	120.7(3)
$C^{10}C^{11}C^{12}$	120.4(3)	$C^{21}C^{22}C^{23}$	119.5(3)
$C^{11}C^{12}C^7$	120.9(3)	$C^{22}C^{23}C^{24}$	120.7(3)
$C^{14}C^{13}C^{18}$	117.7(2)	$C^{23}C^{24}C^{19}$	119.9(3)
$C^{14}C^{13}P$	122.71(18)		

X-Ray diffraction data for diphenyl(2,3,4,5-tetrafluoro-6-phenylaminophenyl)phosphine oxide (V) were obtained on a CAD-4 diffractometer (MoK_α irradiation, θ/2θ-scanning). Monoclinic crystals, $C_{24}H_{16}F_4NOP$. Unit cell parameters: a = 28.322(6), b = 8.586(2), c = 19.287(4) Å; β = 118.83(3)°; V = 4108.8(15) Å^3; Z = 8, d_{calc} = 1.427 g/cm^3; space

Table 3. Coordinates of atoms (×10^4, Å) and their equivalent isotropic temperature factors (U×10^3, $Å^2$) in the molecule of diphenyl(2,3,4,5-tetrafluoro-6-phenylaminophenyl)phosphine oxide (**V**)

Atom	x	y	z	U_{eq}
P	6312(1)	6116(1)	4765(1)	43(1)
F^1	5231(1)	5570(2)	3268(1)	79(1)
F^2	4413(1)	3739(2)	3052(1)	78(1)
F^3	4474(1)	2051(2)	4278(1)	77(1)
F^4	5324(1)	2293(2)	5715(1)	69(1)
O	6603(1)	6679(2)	5593(1)	59(1)
N	6203(1)	4136(3)	6007(1)	50(1)
C^1	6064(1)	7702(3)	4073(1)	43(1)
C^2	6092(1)	7735(3)	3380(2)	65(1)
C^3	5912(1)	9010(4)	2884(2)	72(1)
C^4	5704(1)	10251(4)	3084(2)	71(1)
C^5	5672(1)	10235(4)	3769(2)	81(1)
C^6	5851(1)	8970(3)	4264(2)	60(1)
C^7	6722(1)	4957(3)	4488(1)	47(1)
C^8	7265(1)	5303(4)	4835(2)	68(1)
C^9	7588(1)	4532(4)	4587(2)	84(1)
C^{10}	7377(1)	3433(4)	4010(2)	79(1)
C^{11}	6843(1)	3085(4)	3669(2)	79(1)
C^{12}	6517(1)	3836(3)	3905(2)	64(1)
C^{13}	5741(1)	4891(3)	4616(1)	40(1)
C^{14}	5276(1)	4773(3)	3894(1)	48(1)
C^{15}	4853(1)	3835(3)	3770(1)	50(1)
C^{16}	4885(1)	2975(3)	4385(2)	51(1)
C^{17}	5331(1)	3081(3)	5115(1)	47(1)
C^{18}	5771(1)	4002(3)	5256(1)	40(1)
C^{19}	6481(1)	2891(3)	6522(1)	44(1)
C^{20}	6424(1)	1359(3)	6277(2)	55(1)
C^{21}	6731(1)	211(4)	6811(2)	68(1)
C^{22}	7092(1)	581(4)	7575(2)	73(1)
C^{23}	7152(1)	2107(4)	7814(2)	67(1)
C^{24}	6846(1)	3262(4)	7297(1)	53(1)
H^2	6235(11)	6860(3)	3232(15)	68(8)
H^3	5938(12)	8980(4)	2423(18)	88(10)
H^4	5571(12)	11080(4)	2722(17)	77(9)
H^5	5532(14)	11070(4)	3936(18)	94(11)
H^6	5817(12)	8920(3)	4737(17)	81(9)
H^8	7404(12)	6050(4)	5260(18)	78(9)
H^9	7935(14)	4820(4)	4820(2)	103(12)
H^{10}	7591(14)	2930(4)	3810(2)	113(12)
H^{11}	6706(13)	2290(4)	3321(19)	90(11)
H^{12}	6159(12)	3650(3)	3665(16)	70(8)
H^{20}	6192(11)	1150(3)	5722(16)	65(8)
H^{21}	6700(12)	–800(4)	6628(18)	87(11)
H^{22}	7313(13)	–210(4)	7940(19)	91(10)
H^{23}	7383(13)	2410(3)	8350(2)	92(10)
H^{24}	6892(10)	4330(3)	7475(15)	57(8)
H^{1N}	6398(10)	4930(3)	6087(14)	50(8)

group $C2/c$. The structure was solved by the direct method; the final divergence factors were R = 0.0262 and R_W = 0.0728 [from 1978 reflections with $I > 2\sigma(I)$].

Diphenyl(2,3,4,5-tetrafluoro-6-arylaminophenyl)phosphine oxides V–VII. A solution of 0.005 mol of diphenyl(pentafluorophenyl)phosphine, 0.005 mol of the corresponding *N*-arylcarbohydrazonoyl chloride, and 2 ml of triethylamine in 20 ml of anhydrous THF (in reactions with *N*-*p*-bromophenyl-*C*-ethoxycarbonylnitrilimine) or benzene (in reactions with the other nitrilimines) was kept for 24 h at 20°C under argon. The precipitate of triethylamine hydrochloride (90–98%) was filtered off and washed with the corresponding solvent, and the filtrate was evaporated under reduced pressure. According to the ^{31}P NMR data, the brown oily residue was fluorophosphorane **Ib**–**IVb**, δ_P, ppm: –99.4 (**Ib**), –96.5 (**IIb**), –96.2 (**IIIb**), –96.1 (**IVb**); $^1J_{PF}$, Hz: 625.3 (**Ib**), 648.0 (**IIb**), 650.3 (**IIIb**), 662.6 (**IVb**). The residue was treated with 10–15 ml of dry diethyl ether, and the solution was separated from the undissolved oily material by decanting. Water, 0.005 mol, was added to the ether solution, and the mixture was kept for 12 h at 20°C. The solvent was removed under atmospheric pressure, and the semicrystalline residue was washed with 5 ml of cold (–10°C) diethyl ether and recrystallized from the same solvent with cooling to 0 to –10°C.

Diphenyl(2,3,4,5-tetrafluoro-6-phenylaminophenyl)phosphine oxide (V). Yield 75% (from *C*,*N*-diphenylnitrilimine) and 84% (from *N*-phenyl-*C*-ethoxycarbonylnitrilimine). mp 139–141°C. IR spectrum, ν, cm^{-1}: 3180 (N–H), 1245 (P=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.80–7.80 m (15H, H_{arom}), 9.65 s (1H, NH). ^{31}P NMR spectrum ($CHCl_3$): δ_P 30.5 ppm. Found, %: C 65.54; H 3.48; N 3.00; P 6.85. $C_{22}H_{16}F_4NOP$. Calculated, %: C 65.31; H 3.65; N 3.17; P 7.02.

(6-*p*-Bromophenylamino-2,3,4,5-tetrafluorophenyl)diphenylphosphine oxide (VI). Yield 90%. mp 133–135°C. IR spectrum, ν, cm^{-1}: 3150 (N–H), 1240 (P=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.64–7.79 m (14H, H_{arom}), 9.61 s (1H, NH). ^{31}P NMR spectrum ($CHCl_3$): δ_P 29.7 ppm. Found, %: C 55.64; H 3.12; N 2.54; P 5.77. $C_{24}H_{15}BrF_4NOP$. Calculated, %: C 55.41; H 2.90; N 2.69; P 5.95.

Diphenyl(2,3,4,5-tetrafluoro-6-*p*-tolylaminophenyl)phosphine oxide (VII). Yield 86%. mp 126–128°C. IR spectrum, ν, cm^{-1}: 3185 (N–H), 1240 (P=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.27 s (3H, Me), 6.74–7.80 m (14H, H_{arom}), 9.65 s (1H, NH). ^{31}P NMR spectrum ($CHCl_3$): δ_P 32.1 ppm.

Found, %: C 65.80; H 3.78; N 3.27; P 6.90. $C_{25}H_{18}F_4NOP$. Calculated, %: C 65.94; H 3.98; N 3.08; P 6.80.

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