43. Dediazoniations of Arene Diazonium Ions in Homogenous Solution. Part IV: Change-over from a Heterolytic to a Homolytic Mechanism in 2,2,2-Trifluoroethanol Pyridine Mixtures[1])

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Summary. There are only two dediazoniation products of benzenediazonium tetrafluoroborate in 2,2,2-trifluoroethanol (TFE), namely phenyl 2,2,2-trifluoroethyl ether (**1**) and fluorobenzene (**2**). The reaction kinetics are strictly first-order with respect to the diazonium salt. The addition of increasing amounts of pyridine to the system results in a gradual decrease in the yields of **1** and **2** and an increase in the yields of the homolytically formed products, benzene (**3**), biphenyl (**4**), isomeric phenylpyridines (**5**) and diazo tar (**6**). The reaction kinetics show that the rate of dediazoniation of the benzene diazonium salt increases with increasing amounts of pyridine. The reaction with added pyridine is no longer first-order with respect to the diazonium ion.

The product analyses and the kinetic data are consistent with the view that in pure TFE this diazonium salt decomposes completely by a heterolytic mechanism. The addition of pyridine brings about a competitive homolytic mechanism which becomes increasingly dominant as the concentration of pyridine increases.

1. Introduction.

– In dediazoniations[2]) of arene diazonium ions, many observations indicate that small changes in the reaction system may change the mechanism and products drastically. Typical examples are the reactions of arene diazonium ions with ethanol where in many cases (heterolytic) ethoxy-dediazoniation competes successfully with (homolytic) proto-dediazoniation [3]. Mention should also be made of the observation of *Bunnett et al.* [4] that in acidic methanol some arene diazonium ions can decompose by a heterolytic or a homolytic mechanism depending on the presence or absence, respectively, of oxygen; the rates of the two pathways differ only by a factor of about 2. Finally, our investigations of arylations in dimethylsulfoxide [5] are worth noting. Arylation of nitrobenzene with (unsubstituted) benzenediazonium ions yields nitrobiphenyl isomers in proportions typical of a heterolytic process, whereas the same reaction with *p*-nitrobenzenediazonium ions is clearly homolytic. Addition of N,N'-diphenylhydroxylamine [5] [6] or sodium nitrite [7] to the reaction with benzenediazonium ion increases the rate dramatically and changes the mechanism to a homolytic one.

The object of the present investigation was to devise a system in which either a pure heterolytic, a pure homolytic or a combination of the two mechanisms could be isolated depending on one particular variable. In a previous paper [1] we described experiments which demonstrate that in pure TFE arene diazonium ions decompose

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[1]) Part III: See [1].

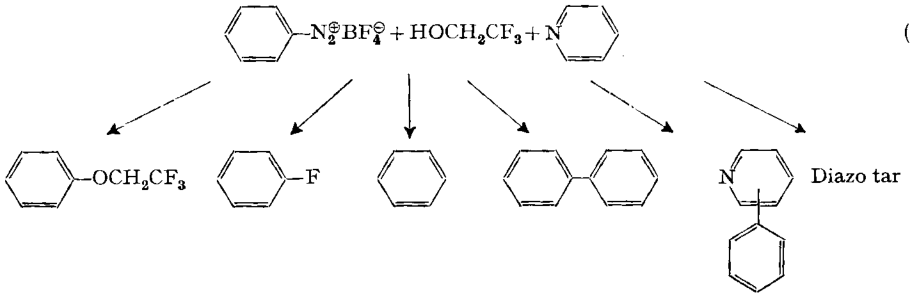
[2]) With respect to the general nomenclature for substitution reactions suggested by *Bunnett* [2] see footnote 2 in [1].

by a heterolytic pathway. On the other hand, *Abramovitch et al.* and *Kobayashi et al.* [8] showed that arylations with diazonium ions in pure pyridine proceed homolytically.

In the present work, therefore, the approach taken was to start with a pure heterolytic process in TFE and, by successive additions of pyridine, gradually to change the system to one in which both the heterolytic and homolytic mechanisms are competing. This change-over was observed from the product distribution and by following the reaction kinetics.

The reactions were carried out without addition of further reaction components, *e.g.* aromatic hydrocarbons as substrates for arylations. Only gegenions (tetrafluoroborate) and solvent molecules were present. This method has two distinct advantages over the classical method of determining arylation product proportions. First, the method chosen allows a better evaluation of the contributions of the heterolytic and homolytic processes to the overall reaction. The second advantage is that one is less hampered by the low yields that are obtained in many of the arylation reactions. For this investigation we chose as substrate benzenediazonium tetrafluoroborate.

2. Product proportions. – We decomposed benzenediazonium tetrafluoroborate in a series of TFE/pyridine mixtures under a nitrogen atmosphere in a closed system at 30.0 ± 0.05°. Six products are formed (eq. 1).



(1)

(1) (2) (3) (4) (5) (6)

heterolytic products homolytic products

Phenyl 2,2,2-trifluoroethyl ether (**1**) is the product of the heterolytic solvolysis and fluorobenzene (**2**) results from a *Schiemann*-type nucleophilic substitution of the diazonium group by fluoride ion[3]; *i.e.* a fluorodediazoniation which is also a heterolytic reaction[4]. By analogy with *Melander*'s interpretation of the respective reaction with ethanol [10], benzene (**3**), the product of proto-dediazoniation, is probably formed from the aryl radical by a hydrogen abstraction from the α-carbon of the solvent; therefore it may be a measure of the homolytic process. Biphenyl (**4**) and phenylpyridines (**5**) are probably also formed by homolytic reactions. We have only identified the 2-substituted isomer of **5**. If the two other isomers are formed at all, they are present in only small quantities. The diazo tars (**6**) are a complex mixture of polymeric compounds which have not been investigated, to our knowledge, in the last twenty years[5]. In this investigation we did not isolate them, but assumed that they account for the difference between the sum of the yields of **1**+**2**+**3**+**4**+**5** and 100%, relative to the amount of diazonium salt introduced into the system. As discussed later in this paper, we have evidence which indicates (but does not prove conclusively) that the diazo tars are the product of a homolytic decomposition.

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[3] It is not known if the nucleophile entering the substitution proper of this reaction is the fluoride ion or the tetrafluoroborate ion of the equilibrium $BF_4^\ominus \rightleftarrows F^\ominus + BF_3$.

[4] The mechanism of the *Schiemann* reaction is not known in detail, see [9].

In Table 1 the product analyses obtained by GLC. for the decomposition of benzenediazonium tetrafluoroborate are shown.

Table 1. *Product analyses for the decomposition of 0.1068* M *benzenediazonium tetrafluoroborate in trifluoroethanol in the presence of increasing amounts of pyridine* (T = 30.0 ± 0.05°, under N_2)

Pyridine M	Mol ratio pyridine/ $ArN_2^{\oplus}$ $BF_4^{\ominus}$	Products[a]) (%)					Total yield of analyzed products (%)	Tar[b]) (%)
		1	**2**	**3**	**4**	**5**		
0.0	0 :1	62.3	34.5	0	0	0	96.8	∼0
0.530	4.96:1	67.3	34.4	0	0	0	101.7	∼0
1.061	9.93:1	57.9	25.5	2.9	0.5	2.1	88.9	11
1.592	14.90:1	43.3	19.7	5.8	0.8	3.9	73.5	26
2.122	19.87:1	41.7	19.2	7.2	1.0	5.1	74.2	26
2.652	24.83:1	39.8	17.8	9.2	1.2	6.7	74.7	25
3.183	29.80:1	33.5	14.3	10.0	1.6	8.7	68.1	32
3 712	34.76:1	18.6	8.1	11.0	1.4	10.6	49.7	50
4.774	44.70:1	15.1	6.6	11.9	1.6	13.2	48.4	52

[a]) Product analyses are averages of 1 to 3 determinations, deviations are ± 4.0%.

[b]) 'Tar' refers to the difference between 'total yield' and 100% (material balance of diazonium ions).

The first entry in Table 1 refers to the dediazoniation in pure TFE. In each of the remaining systems the amount of pyridine is progressively increased.

The first and most obvious feature of Table 1 is that an increase in the pyridine to diazonium ion molar ratio results in a smooth and steady decrease in the percentage of the heterolytic substitution products **1** + **2**. Concurrently, there is a gradual increase in the percentage of reduction product **3** and of the products **4** + **5** which are formed by the homolytic mechanism. The total yield of identifiable products decreases from 100% to 50%. The remaining products do not appear on the gas-chromatograph. They are therefore, very probably, largely or exclusively polymeric tars. The increase in these by-products roughly parallels the increase in the yield of the products **3**, **4** and **5**; this indicates that the tars are probably formed by a homolytic mechanism.

For a particular TFE/pyridine mixture (4.12:1), a variation in the diazonium ion concentration between 0.1068 and 0.0401 M does not change the product distribution significantly (s. Table 2).

The results indicate that in these systems the diazonium salt probably exists as a tight ion pair. The *Schiemann*-type reaction takes place probably within this ion pair, similar to the proper *Schiemann* reaction which is carried out without a solvent. We think that in pure TFE the solvolysis product **1** is not formed in this ion pair, but with either free diazonium ions or in a solvent separated ion pair.

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[5]) Based on *Kobayashi*'s [7] and *Opgenorth*'s [11] recent investigations on the mechanism of interaction of arene diazonium ions with nitrite ions, it seems unlikely that *Pfeil*'s explanation [12] of the rôle of nitrite ions as catalyst for the formation of diazo tars (nitrosation of phenols formed by a primary hydroxy-dediazoniation) is correct: Nitrite ions catalyse the formation of aryl radicals.

Table 2. ***Product analyses for the decomposition of benzenediazonium tetrafluoroborate at various initial concentrations in the same trifluoroethanol/pyridine mixture*** (molar ratio TFE/pyridine 4.12:1) (T = 30.0 ± 0.05°, under N_2)

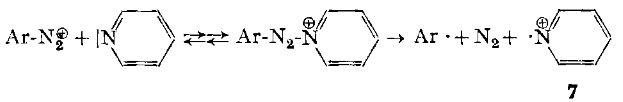
$ArN_2^{\oplus}\,BF_4^{\ominus}$ M	Molar ratio pyridine/ $ArN_2^{\oplus}\,BF_4^{\ominus}$	Products[a]) (%)					Total yield of analyzed products (%)	Tar[a]) (%)
		1	**2**	**3**	**4**	**5**		
0.1068	24.83:1	39.8	17.8	9.2	1.2	6.7	74.7	25
0.0797	33.27:1	34.6	14.7	10.4	1.1	7.7	68.5	32
0.0650	40.80:1	27.4	10.5	11.8	1.3	8.3	59.3	41
0.0534	49.66:1	30.3	12.3	11.5	1.3	8.9	64.3	36
0.0401	66.13:1	34.7	13.3	14.5	1.4	9.8	73.7	26

[a]) See footnotes Table 1.

In the presence of pyridine, however, there are two possibilities of solvent separated ion pairs, namely with TFE or with pyridine. The equilibria between the tight ion pair and the two solvent separated species are not the same. Owing to the large difference in the relative nucleophilicities of TFE and pyridine, the equilibrium with pyridine is much more in favour of the solvent separated species than is the equilibrium with TFE.

Furthermore, the pyridine separated covalent product, the diazopyridinium ion pair $Ar\text{-}N_2\text{-}{}^{\oplus}NC_5H_5\,BF_4{}^{\ominus}$. In other related systems, *e.g.* in water [13] and in pyridine [8] [14], diazopyridinium ions have been detected by various methods. We have begun a detailed study of these equilibria in TFE/pyridine systems.

As discussed elsewhere [5] [15], it is most likely that it is the covalent diazo intermediate which undergoes homolytic fragmentation to form an aryl radical, a molecule of nitrogen and a gegenradical. In the case of the diazopyridinium ion (eq. 2), the pyridine radical cation **7** is the nucleofugal homolytic leaving group [15]. We need a compound which is a good nucleophile in order to form a covalent diazo compound and which, at the same time, is able to form a good homolytic leaving group. Pyridine fulfills the first condition well, but is a mediocre homolytic leaving group as **7** is energetically not a very favourable compound. N,N-diphenylhydroxylamine and nitrite ions (see Introduction) fulfill both conditions for a nucleofugal homolytic leaving group much better.



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(2)[6])

The results shown in Table 3 are for experiments in which products and yields were determined in the same TFE/pyridine mixture but under nitrogen and oxygen. When the reaction is carried out under oxygen instead of nitrogen, the most obvious difference is the considerable decrease in the yield of the products **1**–**5**. In addition to the decrease in the yield of identified products the amount of diazo tar is increased from 25% to 72%. This shows that the presence of oxygen in these systems enhances the formation of polymeric tars.

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[6]) The gegenions and the ion pairs discussed in this paper are not included in this equation.

Table 3. *Product analyses for the decomposition of 0.1068* M *benzenediazonium tetrafluoroborate in a TFE/pyridine mixture* (molar ratio TFE/pyridine 4.12:1) (T = 30.0 ± 0.05°, light excluded)

Conditions	Products (%)					Total yield of analyzed products (%)	Tar[a]) (%)
	1	**2**	**3**	**4**	**5**		
N_2	41.1	18.3	8.8	1.0	5.9	75.1	25
N_2	39.5	17.9	8.9	1.4	7.5	75.2	25
N_2	38.7	17.3	9.8	1.3	6.7	73.8	26
O_2	16.7	8.7	1.6	0	1.2	28.2	72
O_2	16.7	8.1	1.8	0	1.4	28.0	72

a) See footnote Table 1.

3. Kinetics of decomposition of benzenediazonium tetrafluoroborate in TFE/pyridine systems. – Kinetic studies were carried out on the reaction in pure TFE and in various TFE/pyridine mixtures with the same initial diazonium ion concentration. We determined the decrease in the diazonium ion concentration by withdrawing an aliquot portion of the reaction mixture and quenching it in an aqueous solution of excess 2-naphthol-3,6-disulfonic acid. The concentration of the azo compound formed was determined spectrophotometrically.

The reaction in pure TFE was found to be first-order for over 85% of the reaction (Fig. 1). The rate constant is $k = 1.582 \cdot 10^{-4}$ s^{-1}. We would like to emphasize that this result is not only consistent with the S_N1-mechanism for heterolytic dediazoniation, but also with an S_N2-mechanism in which a concerted release of nitrogen molecules occurs with the addition of the nucleophile, a process which was first suggested for aqueous systems by *Lewis et al.* [16] 7). We have discussed this problem in Part III of this series [1].

For the runs in the presence of pyridine, the plots shown in Fig. 1 indicate that these decompositions are no longer first-order in diazonium salt.

In Fig. 2 we have plotted kinetic data carried out under nitrogen and under oxygen with the same initial concentration of diazonium ions (0.1068 M) and the pyridine/TFE ratio shown in run 3 of Fig. 1. In contrast to Fig. 1, concentrations and not logarithms of concentrations are given in Fig. 2. Such a graphical representation demonstrates that the overall kinetics change from exactly first-order in pure TFE (Fig. 1) to an order between one and zero in the presence of pyridine (Fig. 1 and 2).

The product distributions summarized in Tables 1–3 and the kinetic results demonstrate clearly that there is a change-over from a complete heterolytic mechanism in pure TFE to a mixed heterolytic-homolytic mechanism in TFE/pyridine. The contribution of the homolytic reaction is increased with increasing amounts of pyridine or in the presence of pyridine and oxygen.

Preliminary experiments were also made with *p*-chlorobenzenediazonium tetrafluoroborate in analogous TFE/pyridine systems. The results with respect to product ratios and kinetics corresponded in principle to the results described here.

Further investigations on these systems are in progress.

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7) For a critical review see [15].

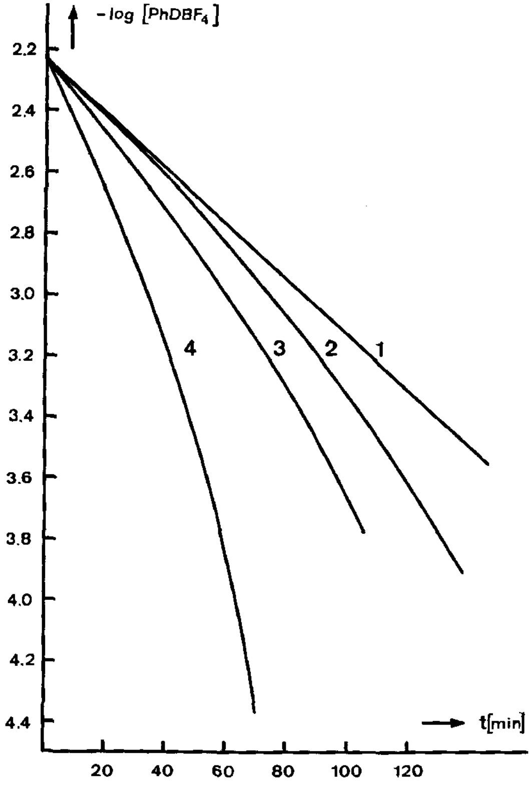

Fig. 1. *Logarithmic plot of the concentration of diazonium ions as a function of time* (30.0 ± 0.05°; [$PhDBF_4$] = 0.1068 M)

① 0.0 ml pyridine/23.4 ml TFE; ② 3.0 ml pyridine/20.4 ml TFE; ③ 5.0 ml pyridine/18.4 ml TFE; ④ 7.0 ml pyridine/16.4 ml TFE

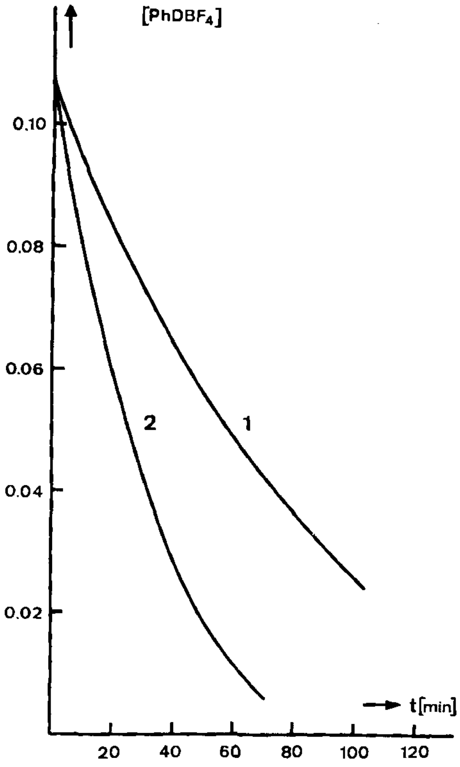

Fig. 2. *Plot of the concentration of diazonium ions as a function of time* (30.0 ± 0.05°; [$PhDBF_4$] = 0.1068 M; 5.0 ml pyridine/18.4 ml TFE)

① under N_2; ② under O_2

4. Experimental part

4.1. *Benzenediazonium tetrafluoroborate.* 0.125 mol aniline (distilled twice) was dissolved in 70 ml aqueous fluoroboric acid solution (40%). The solution was cooled in an ice-salt bath. To the vigorously stirred solution a cold solution of 0.125 mol $NaNO_2$ in 20 ml water was added dropwise. The temperature was always maintained at 0°. Some minutes after the addition was completed, the precipitated benzenediazonium tetrafluoroborate was filtered off, washed once with 30 ml cold fluoroboric acid (10%), twice with cold water and ethanol, and several times with cold ether. A sintered glass filter should be used, and the precipitate stirred well on the filter with each washing before suction is applied. The salt was dried in a vacuum desiccator over P_2O_5 over night. Yield: 80–90%.

4.2. *Solvents.* 2,2,2-Trifluoroethanol (TFE) *Fluka* reagent grade, GLC. showed no by-products. Pyridine: Twice distilled and stored over NaOH.

4.3. *Reference compounds for GLC. analyses.* – *Fluorobenzene* (**2**) (*Fluka*) and *benzene* (**3**) (*Merck*) were shown to be pure by GLC. and were used without further purification.

Phenyl 2,2,2-trifluoroethyl ether (**1**) was synthesized from benzenediazonium tetrafluoroborate in TFE (0.01 mol in 60 ml TFE, at 30.0°). After completion of the reaction, water was added and the solution neutralized with $NaHCO_3$. Then the solution was extracted with ether and dried with Na_2SO_4. Distillation gave **1** (b.p. 130–135°). After redistillation the product was shown to be 99% pure by GLC. Yield: 40%. – NMR. ($CDCl_3$) and MS.: see [1].

Biphenyl (**4**) was recrystallized twice from ethanol/water.

2-Phenylpyridine (**5**) was synthesized from phenyllithium and pyridine [17] (b.p. 139°/12 Torr).

4.4. *Decomposition of the diazonium salt.* The closed system consisted of a three-necked vessel with a built-in thermostated water jacket and fitted with a reflux condenser, glass stopper, and a self-sealing rubber septum. To ensure the system remained closed, a two-way adapter was fitted to the top of the condenser. One arm was attached to a balloon and the other led to the nitrogen inlet valve (pure, dried N_2). The solvents were first degassed (N_2) and put in the vessel under N_2; total volume 23.4 ml. After equilibration at the required temperature the vessel was opened for addition of the diazonium salt and the nitrogen flow was turned on keeping the system under N_2. Usually 0.4797 g diazonium salt were added; $[ArN_2^{\oplus} BF_4^{\ominus}] = 0.1068$ mol/l. After addition the stopper was replaced and the closed system was kept under a slight N_2 pressure (balloon). After completion of the reaction, toluene and dimethylresorcinol were added as internal standards. The mixture was then analyzed directly by GLC. Separation of benzene and fluoro-

Table 4. *Kinetic data for Fig. 1.* Measured concentration of diazonium ions as a function of time, for different solvent compositions, under N_2 (30.0 ± 0.05°)

0 ml pyridine/ 23.4 ml TFE		3.0 ml pyridine/ 20.4 ml TFE		5.0 ml pyridine/ 18.4 ml TFE		7.0 ml pyridine/ 16.4 ml TFE	
t [min]	$[PhDBF_4]$ M	t [min]	$[PhDBF_4]$ M	t [min]	$[PhDBF_4]$ M	t [min]	$[PhDBF_4]$ M
0.0	0.1068	0.0	0.1068	0.0	0.1068	0.0	0.1068
10.50	0.0988	10.0	0.0945	10.0	0.0944	10.0	0.0768
25.10	0.0883	25.0	0.0852	15.0	0.0935	20.0	0.0664
50.10	0.0692	40.0	0.0736	20.0	0.0849	30.0	0.0518
80.05	0.0523	52.0	0.0633	30.0	0.0742	40.0	0.0423
120.0	0.0361	70.0	0.0514	40.0	0.0644	50.0	0.0295
180.0	0.0201	85.0	0.0410	55.0	0.0527	60.0	0.0205
		100.0	0.0344	70.0	0.0425	70.0	0.0126
		125.0	0.0248	85.0	0.0334	80.0	0.0077
				100.0	0.0254		

benzene was accomplished with a column (4.8 m × 2 mm), packed with 20% Carbowax 1500 on Chromosorb W AW 60/80 (internal standard: toluene). Phenyltrifluoroethylether (**1**), biphenyl (**4**) and 2-phenylpyridine (**5**) were analyzed using a column (5.0 m × 2.0 mm) packed with 10% Apiezon L on Chromosorb W 80/100 (internal standard: dimethylresorcinol).

4.5. *Kinetic runs.* An aliquot of the mixture was withdrawn with a syringe. An exact amount of the solution (0.2 ml) was added with a micropipette to 20 ml 0.02 M 2-naphthol-3,6-disulfonic acid in water and $NaHCO_3$ to quench the unreacted diazonium salt. After diazo coupling, 5 ml 10% HCl was added to remove CO_2 and the solution diluted to 250 ml. The optical density was measured at 490 nm ($\varepsilon = 22000\ l \cdot mol^{-1} \cdot cm^{-1}$).

Table 5. *Kinetic data for Fig. 2.* Measured concentration of diazonium ions as a function of time, for 5.0 ml pyridine/18.4 ml TFE solvent composition, under O_2 (30.05 ± 0.05°)

$[PhDBF_4]$ M	0.1068	0.0821	0.0610	0.0414	0.0282	0.0182	0.0108	0.062
t [min]	0.0	10.0	20.0	30.0	40.0	50.0	60.0	70.0

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