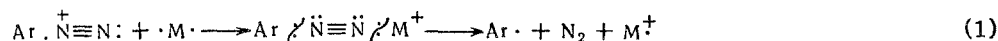


THE DECOMPOSITION OF ARYL DIAZONIUM BOROFUORIDES  
IN NITROBENZENE AND ETHYL BENZOATE  
IN THE PRESENCE OF THE FREE METAL, COPPER POWDER

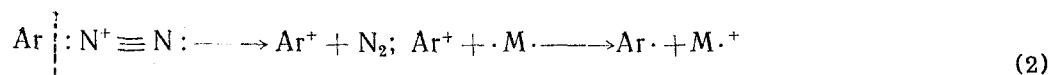
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In previous work [1] it was shown that aryl diazonium borofluorides in the absence of other diazonium salts, di-aryl peroxides, and other sources of aryl radicals, decomposed in solvents with small dielectric constants heterolytically, with transfer of aryl cations in the reaction. We considered it unlikely that the synthesis of metalloorganic compounds (aromatic compounds of mercury, lead, tin, thallium, bismuth, germanium, magnesium) by the action of aryl diazonium borofluorides on free metals also took place by a heterolytic mechanism. It seemed probable that the synthesis of metalloorganic compounds through the aryl diazonium borofluorides took place by one of two possible paths: 1) under the influence of the metal the diazonium cation was converted to the diazo form and this split homolytically:



or 2) the metal reduced the product of heterolytic splitting of the diazonium salt, the aryl cation, converting it to the aryl radical:



In both cases the active agents in the formation of metalloorganic compounds are the aryl radicals.

In order to confirm the formation of aryl radicals in the synthesis of metalloorganic compounds from aryl diazonium borofluorides, we decomposed the aryl diazonium borofluorides in nitrobenzene, and phenyl diazonium borofluoride in ethyl benzoate in the presence of a free metal, copper powder. It was assumed that in the presence of free metal (copper powder) we would observe the products of homolytic action of aryl radicals on nitrobenzene and ethyl benzoate. In the first case there would be entrance of the aryl radical in all three positions of the nitrobenzene, chiefly in the ortho- and para-positions, but not excluding the meta-position, which occurs in decomposition of aryl diazonium borofluorides in nitrobenzene in the absence of copper. In the second case, neither phenyl benzoate nor, as the sole product of entrance of phenyl in the ring of ethyl benzoate, an ester of meta-diphenylcarboxylic acid would be formed, as takes place in the decomposition of phenyldiazonium borofluoride in ethyl benzoate in the absence of copper, but there would be entrance of phenyl into all three positions of the ethyl benzoate, chiefly into the para- or ortho-positions. This would confirm our suggestion as to the mechanism of action of the metals on aryl diazonium borofluorides in the synthesis of metalloorganic compounds.

As expected, in the decomposition of aryl diazonium borofluorides (with the aryl being phenyl, para-tolyl, para-methoxyphenyl, para-chlorophenyl, ortho-carbomethoxyphenyl, and para-carboethoxyphenyl) in nitrobenzene in the presence of a large amount of copper powder, there were formed the products of the homolytic reaction; the aryls entered all three positions of the nitrobenzene, but chiefly the ortho- and para-positions. The reaction products were isolated by distillation and crystallization, and also were analyzed qualitatively by the method of ultraviolet spectroscopy. The decomposition of phenyl diazonium borofluoride in ethyl benzoate in the presence of excess copper powder was also completed by the homolytic mechanism, with formation of the products of the action of the phenyl radical on ethyl benzoate: in the reaction product we did not find phenyl benzoate even as a trace, and the chief product of entry of phenyl in the nucleus of ethyl benzoate was para-diphenylcarboxylic acid ethyl ester, with formation of the meta-isomer in slight amount.

In the decomposition in the presence of copper in nitrobenzene the aryl diazonium borofluorides, with the aryl being phenyl, para-tolyl, and ortho-carbomethoxyphenyl, we observed formation of products of entry of the aryl only in the para- and ortho-positions to the nitro group of nitrobenzene, namely: 4-nitrodiphenyl, isolated by distillation and crystallization; 2-nitrodiphenyl (shown by spectrophotometry in the ultraviolet), 4-methyl-4'-nitrodiphenyl and 4-methyl-2'-nitrodiphenyl; 2-carbomethoxy-4'-nitrodiphenyl, isolated by distillation and crystallization, and 2-carbomethoxy-2'-nitrodiphenyl (shown spectrophotometrically). Formation of the meta-isomer was not observed in these cases. The decomposition of 4-methoxyphenyl- and 4-chlorophenyl diazonium borofluoride gave products of entrance of the aryls into all three positions of the nitrobenzene, ortho-, meta-, and para-, and of these the ortho-isomer was formed in the greatest amount. We isolated by distillation and crystallization 4-methoxy-4'-nitrodiphenyl and 4-methoxy-3'-nitrodiphenyl. The presence of 4-methoxy-2'-nitrodiphenyl, 2'-nitro-, 4'-nitro-, and 3'-nitro-4-chlorodiphenyl was shown spectrophotometrically. In the decomposition of 4-carbomethoxyphenyl diazonium borofluoride we isolated as the chief product of entry into the nucleus 2-nitro-4'-carbomethoxydiphenyl, and the meta-isomer, 3-nitro-4'-carbomethoxydiphenyl was formed in less amount. In this case and in the decomposition of para-methoxy and para-chlorophenyl diazonium borofluoride we isolated from the reaction products the symmetrical azo compounds, the diethyl ester of azobenzene-4, 4'-dicarboxylic-acid, 4,4'-dihydroxyazobenzene, and 4,4'-dichloroazobenzene, respectively. Also, in two cases we isolated the ordinary products of thermal decomposition of aryl diazonium borofluorides: the diaryl (dimethyl ester of diphenic acid in the decomposition of ortho-carbomethoxyphenyl diazonium borofluoride) and a fluoroorganic compound (para-fluorobenzoic acid from the product of decomposition of para-carbomethoxyphenyl diazonium borofluoride).

Hence, the formation of the products of homolytic reaction in decomposition of aryl diazonium borofluorides in nitrobenzene, and ethyl benzoate in the presence of copper, confirms that the presence of the metal converts the heterolytic mechanism of splitting the aryl diazonium borofluorides into the homolytic. This forces us to assume the same action of metals on the mechanism of splitting of diazonium salts in the synthesis of metalloorganic compounds from aryl diazonium borofluorides, and perhaps also from other diazonium salts. The formation along with the diphenyl derivatives of symmetrical azo compounds also, suggests evidently, the use of the first of the possible paths of splitting the diazonium salts (equation 1).

## EXPERIMENTAL

Decomposition of phenyl diazonium borofluoride in nitrobenzene in the presence of copper. In 160 g (1.36 M) of nitrobenzene at 28° we added over the course of half an hour in small portions, alternately, 90 g (1 M) of phenyl diazonium borofluoride and 50 g of copper powder prepared according to Gatterman. No marked rise in temperature occurred, but from the first portions the reaction mixture darkened. It was stirred for 72 hours, after which the reaction for diazonium compound was negative. It was dissolved in benzene, filtered from the copper (there were no lumps of tar), the benzene solution was washed with water, the benzene was distilled off, and the residue was fractionated in a vacuum. After distillation of the first quantity of nitrobenzene, we obtained: fraction I with b.p. 110-170° (3 mm), 4.8 g; fraction II with b.p. 170-200° (3 mm), 0.8 g. Fraction II gradually crystallized and after recrystallization from heptane the m.p. and mixed m.p. with known para-nitrodiphenyl was 113°. From fraction I, after repeated distillations we separated 2.3 g of nitrobenzene and at 2-3 mm and 125-270° we distilled 2.2 g of oil, which was submitted to qualitative spectrographic analysis in the ultraviolet in isooctane solution (SF-4 spectrophotometer of the Dianov-Klovov system). Optical analysis (qualitatively  $\nu_{\max}=43,000\text{ cm}^{-1}$ ,  $\epsilon \cdot 10^{-4}=0.5$ ) showed that this oil absorbed like the ortho-isomer ( $\nu_{\max}=43,000\text{ cm}^{-1}$ ,  $\epsilon \cdot 10^{-4}=1.6$ ), only less intensely. As a result of running a similar decomposition under analogous conditions (ratios of components, temperature, length of reaction) of phenyl diazonium borofluoride in nitrobenzene in the absence of copper, we obtained only meta-nitrodiphenyl.

Decomposition of para-tolyl diazonium borofluoride in nitrobenzene in the presence of copper. In 250 g (2 M) of nitrobenzene at 28° in the course of an hour with stirring we added, alternately, 104 g (0.5 M) of para-tolyl diazonium borofluoride and 50 g of copper powder. Almost no rise in temperature occurred. In the following five days the reaction mixture was heated to 50-55°, and the reaction then went on at room temperature. All the diazonium compound was decomposed (test with  $\beta$ -naphthol) after a month. The mixture was dissolved in benzene and filtered from tar and copper powder. The precipitate of tar and copper powder was made alkaline and submitted to distillation with superheated steam (bath temperature 220°). We distilled over 0.8 g of crystals. After crystallization from acetone the m.p. and mixed m.p. with known 4-methyl-4'-nitrodiphenyl was 140°. The filtrate from the precipitate of tar and the powder was washed with 10% NaOH, with water, and was dried with  $\text{CaCl}_2$ . After distillation of the benzene and (in a vacuum) of most of the nitrobenzene, the residue was distilled with superheated steam (bath tempera-

ture 220-240°). The distillate was extracted with ether, the ether was distilled off, and the residue was fractionated in a vacuum. We obtained the fractions: fraction I with b.p. 75-110° (4 mm), 2.9 g; fraction II with b.p. 150-175° (4 mm), 3.76 g; fraction III, b.p. 175-182° (4 mm), 3.0 g.

Fraction I after repeated distillations (b.p. 45-46° at 3 mm) was shown to be nitrobenzene. Fraction III crystallized; after crystallization from methyl alcohol the weight was 2.3 g, the m.p. and mixed m.p. with known 4-methyl-4'-nitrodiphenyl was 140°. Fraction II did not crystallize when cooled with snow and salt. It was combined with the mother liquors from crystallization of the precipitate of Fraction III and the products of distillation of the tar. After distillation of the solvent it was distilled in a vacuum and gave 3.6 g of oil with b.p. 140-150° (2 mm). Part of the oil was diluted with heptane; on slow cooling there precipitated crystals with m.p. 34°; a mixed m.p. with known 4-methyl-2'-nitrodiphenyl was 34-36°. The oil (b.p. 140-150° at 2 mm) from qualitative spectroscopic analysis in the ultraviolet (solvent isooctane,  $\nu_{\max} = 41,000 \text{ cm}^{-1}$ ) was also 4-methyl-2'-nitrodiphenyl ( $\nu_{\max} = 41,000 \text{ cm}^{-1}$ ) and did not contain meta- and para-isomers.

Decomposition of para-methoxyphenyl diazonium borofluoride in nitrobenzene in the presence of copper. In 250 g (2 M) of nitrobenzene at 28° during two hours, with mixing by a stirrer, was placed, alternately, 111 g (0.5 M) of para-methoxyphenyl diazonium borofluoride and 50 g of copper powder. Stirring was continued for 20 days at 60° and for 10 days at 90°, after which, reaction for diazonium compounds with  $\beta$ -naphthol was negative. The precipitate of tar and copper was filtered off. This precipitate after treatment with 10% sodium hydroxide solution and distillation with superheated steam (bath temperature 220°) gave 0.03 g of yellow crystals; after two crystallizations from methanol, m.p. 64-75°. According to optical analysis (solvent isooctane,  $\nu_{\max} = 38,500 \text{ cm}^{-1}$ ,  $\nu_{\min} = 33,000 \text{ cm}^{-1}$ ) the product was chiefly 4-methoxy-3'-nitrodiphenyl ( $\nu_{\max} = 38,500 \text{ cm}^{-1}$ ;  $\nu_{\min} = 33,000 \text{ cm}^{-1}$ ).

The filtrate from the precipitate of copper and tar was washed with 10% sodium hydroxide solution and distilled with superheated steam (bath temperature 240°). The last drops of the distillate crystallized; after two crystallizations from methanol, red crystals with decomposition point 218-219°, containing nitrogen, were obtained. They were evidently 4,4'-dihydroxyazobenzene. According to the literature data [2], m.p. 216-218°.

The main quantity of the distillate was extracted with ether, dried with sodium sulfate, and after distillation of the ether and nitrobenzene, distilled in a vacuum: fraction I with b.p. 150-175° (2 mm), 3.71 g; fraction II with b.p. 175-180° (2 mm), 5.4 g; fraction III with b.p. 185-190° (2 mm), 0.12 g. From fractions I and II we isolated crystals, after separation by crystallization from methanol, which melted at 82° and gave no melting point depression with 4-methoxy-3'-nitrodiphenyl. Combined together the total weight was 2.6 g. The filtrate from the crystals from fractions I and II from optical analysis ( $\nu_{\max} = 42,000 \text{ cm}^{-1}$ ) was the ortho-isomer (2-nitro-4'-methoxydiphenyl has  $\nu_{\max} = 42,000 \text{ cm}^{-1}$ ), weight 6.5 g. Fraction III crystallized and after crystallization from methanol, the melting point and mixed melting point with 4-methoxy-4'-nitrodiphenyl was 107-108°, weight 0.12 g.

Decomposition of para-chlorophenyl diazonium borofluoride in nitrobenzene in the presence of copper. In 150 g of nitrobenzene we placed at 50°, 65 g of para-chlorophenyl diazonium borofluoride and 50 g of copper. Stirring of the reaction mixture was continued for 16 days at 50° and 5 days at 70°, after which the reaction mixture gave a negative test for diazonium compounds ( $\beta$ -naphthol). The precipitate of tar and copper was filtered off and washed with benzene, 10% sodium hydroxide solution, and was distilled with superheated steam (bath temperature 220°). The first part of the distillate (liquid) was added to the filtrate from the tar and copper. Then the orange crystals which distilled over (4.3 g) were crystallized from methanol and acetone and melted at 180-182°. Found: C 57.65; 57.44; H 3.50; 3.50%.  $\text{C}_6\text{H}_4\text{NCl}$ . Calculated: C 57.30; H 3.21%. According to the literature data [3,4], 4,4'-dichloroazobenzene melts at 183-184°.

The filtrate from the tar and copper, after the usual washing with alkali solution and water and distillation of the benzene and nitrobenzene, was distilled with superheated steam (bath temperature 240°). At first a liquid distilled over, then light crystals and then somewhat darker ones collected separately. To the liquid portion was added the ether extract of the watery distillate, dried with calcium chloride, and after distillation of the solvent it was vacuum distilled; we obtained 2.2 g of a semiliquid mass, b.p. 110-115° (2 mm). The absorption curve in the ultraviolet (solvent, isooctane,  $\nu_{\max} = 42,500 \text{ cm}^{-1}$ ) resembled the absorption curve of 4-chloro-2'-nitrodiphenyl ( $\nu_{\max} = 42,500 \text{ cm}^{-1}$ ). The light crystals which distilled with steam, after recrystallization from heptane, melted at 100-127°, weight 0.2 g, and without further crystallization they were submitted to optical analysis (in isooctane:  $\nu_{\max} = 33,800 \text{ cm}^{-1}$  and  $\nu_{\min} = 40,000 \text{ cm}^{-1}$ ), that is, these crystals contained 4-chloro-4'-nitrodiphenyl ( $\nu_{\max} = 33,800 \text{ cm}^{-1}$ ) and 4-chloro-3'-nitrodiphenyl ( $\nu_{\max} = 40,000 \text{ cm}^{-1}$ ). The fraction of darker crystals, 0.38 g, had  $\nu_{\max} = 33,800 \text{ cm}^{-1}$  and  $\nu_{\min} = 42,500 \text{ cm}^{-1}$ , that is, they had a spectrum like that of 4-chloro-4'-nitrodiphenyl and 4-chloro-2'-nitrodiphenyl. In the crystallization of both fractions a further 4.2 g of crystals of 4,4'-dichloroazobenzene, m.p. 180-182°, separated.

Decomposition of ortho-carbomethoxyphenyl diazonium borofluoride in nitrobenzene in the presence of copper. The experiments were carried out under conditions analogous to the preceding: nitrobenzene 200 g, diazonium borofluoride 100 g, copper 57 g. The temperature for adding the diazonium salt and copper was 24°, duration of addition, about one hour. The mixture was kept for 30 days at room temperature; the precipitate of tar and copper was filtered off. From the precipitate after the usual treatment with alkali solution and distillation with superheated steam and fractionation in a vacuum we obtained the fractions: fraction I with b.p. 147-170° (4 mm), several drops; fraction II with b.p. 170-186° (4 mm), several drops. On cooling, fraction I gave a small quantity of crystals with m.p. 74-78° which gave no melting point depression with 2-carbomethoxy-4'-nitrodiphenyl. All of fraction I had  $\nu_{\max} = 36,000 \text{ cm}^{-1}$  (2-carbomethoxy-4'-nitrodiphenyl,  $\nu_{\max} = 36,000 \text{ cm}^{-1}$ ), from  $\nu_{\max} = 40,000 \text{ cm}^{-1}$  the form of the curve was analogous to the form for 2-carbomethoxy-2'-nitrodiphenyl (has no maximum or minimum). Fraction II on cooling and dilution with ethyl alcohol by spectroscopy in the ultraviolet had a curve analogous to that for 2-carbomethoxy-2'-nitrodiphenyl.

From the filtrate of the precipitate of tar and copper after the usual treatment with aqueous alkali, distillation with superheated steam, and distillation of the nitrobenzene, after two vacuum distillations (b.p. 175-180° at 2 mm) we obtained 3.8 g of a crystalline substance. After crystallization from heptane and alcohol, m.p. 72°,  $\nu_{\max} = 35,500 \text{ cm}^{-1}$ . Found: C 70.54; H 5.17; 5.24%.  $\text{C}_8\text{H}_7\text{O}_2$ . Calculated: C 71.10; H 5.22%.

From the literature [4] for the dimethyl ester of diphenic acid, m.p. 73.5°.

After saponification with 10% aqueous alcoholic solution of KOH, the ester gave diphenic acid, crystallized from water, m.p. 222°. According to the literature [4], the melting point of diphenic acid is 228°. Found: C 69.80; 69.62; H 4.20; 4.31%.  $\text{C}_7\text{H}_5\text{O}_2$ . Calculated: C 69.42; H 4.16%.

Decomposition of para-carbomethoxyphenyl diazonium borofluoride in nitrobenzene in the presence of copper. The experiment was carried out like the previous ones: nitrobenzene 210 g, para-carbomethoxyphenyl diazonium borofluoride 111 g, copper powder 56 g, initial temperature 40-50°. We stirred for two weeks at 70-80°. The precipitate of tar and copper was filtered and washed with benzene. The combined filtrates were washed with 10% NaOH solution, the benzene and nitrobenzene were distilled off, the residue was distilled with superheated steam (bath temperature 240°) and then in a vacuum: b.p. 230-235° (10 mm), 2.6 g. The residue partly crystallized. After crystallization from heptane the m.p. and mixed m.p. with 2-nitro-4'-carbomethoxydiphenyl was 71-72°. Distillation with superheated steam (bath temperature 240°) of the precipitate of tar and copper gave two types of crystals: orange and colorless. The latter were separated from the orange crystals by sublimation. The sublimed colorless crystals melted at 179-180° and dissolved in alkali; acid to litmus. Found: C 59.75, 59.77; H 3.70, 3.79%.  $\text{C}_7\text{H}_5\text{O}_2$ . Calculated: C 60.00; H 3.60%. According to the literature [5] parafluorobenzoic acid melts at 181-182°.

The residue after separation of the sublimate of para-fluorobenzoic acid was red and after crystallization from heptane melted at 143°. Found: C 66.25; 66.31; H 5.59; 5.44%.  $\text{C}_9\text{H}_5\text{O}_2\text{N}$ . Calculated: C 66.24; H 5.52%. According to the literature [6] the diethyl ester of azobenzene-4,4'-dicarboxylic acid melts at 145.5°.

The distillate from distillation of the precipitate of tar and copper, separated from the crystals of para-fluorobenzoic acid and azo compound, was extracted with ether and dried over calcium chloride. After distillation of the ether and nitrobenzene there remained 6.9 g of a yellow semicrystalline precipitate. The crystals were filtered with suction and by crystallization and sublimation were separated from some remaining para-fluorobenzoic acid and azo compound. The crude filtrate had an absorption spectrum curve with  $\nu_{\max} = 40,500 \text{ cm}^{-1}$  similar to that for 2-nitro-4'-carbomethoxydiphenyl ( $\nu_{\max} = 41,000 \text{ cm}^{-1}$ ), but the  $\nu_{\max}$  shifted toward the  $\nu_{\max}$  for 3-nitro-4'-carbomethoxydiphenyl ( $\nu_{\max} = 39,000 \text{ cm}^{-1}$ ). After distillation in a vacuum, b.p. 160-170° (3 mm). We obtained 1 g of crystalline precipitate. The m.p. and mixed m.p. with 3-nitro-4'-carbomethoxydiphenyl was 103-106°.

Decomposition of phenyl diazonium borofluoride in ethyl benzoate in the presence of copper. To a well stirred sample of 14 g of copper powder in 180 g of ethyl benzoate we added in small portions at room temperature in the course of two hours 76 g of phenyl diazonium borofluoride. The temperature after each addition rose to 32°, but decomposition took place slowly. We added 14 g more of copper and continued to stir for two days (stopping at night) at 60° and one day at 80°. After this the reaction for diazonium compounds in the reaction mixture was negative. The reaction mixture was dissolved in ether, filtered from the copper, washed with 10% sodium hydroxide, with water, and dried over calcium chloride. After distilling off the ether and most of the ethyl benzoate we fractionated in a vacuum: fraction I with b.p. 130-152° (2 mm), 3.6 g; fraction II with b.p. 152-210° (2 mm), 3.1 g.

Each fraction was separately saponified by boiling for three hours with 20 ml of 20% potassium hydroxide solution in methyl alcohol. After distillation of the alcohol and acidification with hydrochloric acid we added soda to an alkaline reaction and distilled with steam. In both experiments reaction for phenol in the distillate with ferric chloride or with bromine water was negative. To the residue from the steam distillation we added 3 ml of 10% sodium hydroxide solution, diluted with water. From fraction II in the experiment the precipitate insoluble in alkali was filtered off, heated for 15 minutes with concentrated hydrochloric acid, and the resulting needles, 0.36 g, were recrystallized from ethyl alcohol. The m.p. and mixed m.p. with para-diphenyl carboxylic acid was 222°. Acidification of the alkaline filtrate gave a precipitate which melted after sublimation at 121°; a mixed m.p. with benzoic acid was 121°.

From fraction III in the experiment the alkali insoluble precipitate after similar treatment gave 0.43 g of para-diphenyl carboxylic acid with m.p. 220°. The semisolid precipitate formed by acidifying the alkaline filtrate with hydrochloric acid was extracted with ether, the ether solution was dried with sodium sulfate, the ether was distilled off, and the residue was fractionally crystallized from heptane. We obtained 0.2 g of substance with a m.p. and mixed m.p. with known metadiphenyl carboxylic acid of 159-160°, and 0.35 g of benzoic acid with m.p. and mixed m.p. of 121°. For carrying out theoretical measurements the authors express thanks to I. Ya. Kachkurova.

#### SUMMARY

In the presence of copper powder the decomposition of aryl diazonium borofluorides in nitrobenzene and ethyl benzoate gives products of homolytic splitting of the diazonium salts. The synthesis of metalloorganic compounds from diazonium salts in the presence of metals occurs by a homolytic mechanism.

#### LITERATURE CITED

1. A. N. Nesmeyanov and L. G. Makarova, *Izvest. Akad. Nauk SSSR, Otdel Khim. Nauk*, 213 (1947). *MGU* 132, 109 (1950); L. G. Makrova et al., *Izvest. Akad. Nauk SSSR, Otdel Khim. Nauk*, 565, 693, 1452 (1958).
2. A. Hantzsch, *Ber.* 43, 2512 (1910)
3. D. Vorlander, F. Meyer, *Liebigs Ann. Chem.* 320, 130 (1902).
4. G. Schulz, *Liebigs Ann. Chem.* 203, 97 (1880).
5. O. Wallach, *Liebigs Ann. Chem.* 235, 263 (1886).
6. F. Meyer, K. Dahlem, *Liebigs Ann. Chem.* 326, 332 (1903).

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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