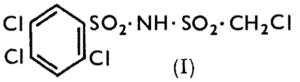
611. *Arylamides of Halogenated Methane- and Ethane-sulphonic Acids.*

By W. V. Farrar.

A number of arylamides is described, of general formula $ArNH{\cdot}SO_2R$, where $R = CH_2Cl$, $CHCl_2$, CCl_3, CH_2Br, CH_2I, CH_2F, CHF_2, $CHClF$, $CH_2{\cdot}CH_2Cl$, and $CHCl{\cdot}CH_3$. All except those containing fluorine are decomposed by hot dilute alkali, the various routes having been investigated.

Chloromethanesulphonanilide is decomposed in a rather unexpected way by dilute alkalis, giving aniline, formaldehyde, chloride, and sulphite ion.[1,2] In connection with other work, several related compounds have been made and their behaviour with alkali is here recorded.

Chloromethanesulphonyl chloride is best prepared from sodium chloromethanesulphonate and phosphorus pentachloride; the alternative preparation, by aqueous chlorination of *s*-trithian,[3,4] is difficult to standardise, and the product, despite careful fractionation, always contains troublesome impurities. When pure chloromethanesulphonyl chloride is used, the only by-product of reaction with *p*-chloroaniline is *p*-chloro-*NN*-di(chloromethanesulphonyl)aniline. A recent modification of the "trithian" method[5] gave no chloromethanesulphonyl chloride in our hands. Rough measurements of the rate of alkaline decomposition of some *N*-arylchloromethanesulphonamides showed some variation with the nature of the aryl group, though no definite trend could be discerned. The disulphonylamine (I) was quite stable to boiling 2N-sodium hydroxide.

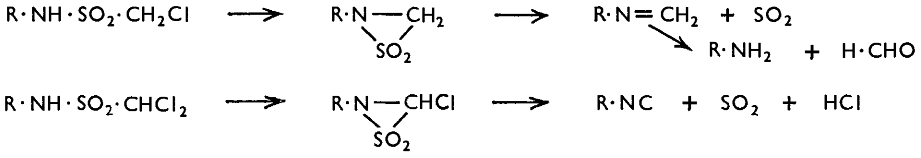


(I)

Arylamides of bromomethanesulphonic acid and of iodomethanesulphonic acid were decomposed by alkali in the same way as the chloro-analogues.

Sodium dichloromethanesulphonate was prepared from chloroform and aqueous sodium sulphite; although the yield is low the method is more convenient than that of Backer.[6] Reaction with phosphorus pentachloride gave dichloromethanesulphonyl chloride.[7] This substance shows, in moderate form, the abnormal behaviour that is so marked in trichloromethanesulphonyl chloride (see below); the aryl amides are formed only in moderate yield, accompanied by much coloured tar. With *p*-chloroaniline, small amounts of di-*p*-chlorophenylformamidine hydrochloride and *p*-chloro-*NN*-bis(dichloromethanesulphonyl)aniline were isolated. The mechanism by which the former compound is produced is not known.

p-Chlorodichloromethanesulphonanilide was rapidly decomposed at 100° by N-sodium carbonate; the product was mainly *p*-chlorophenyl isocyanide. This is compatible with the mechanism suggested by Bordwell and Cooper[2] for the hydrolysis of chloromethanesulphonanilide, involving a three-membered cyclic intermediate:



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[1] Johnson and Douglass, *J. Amer. Chem. Soc.*, 1941, **63**, 1571.

[2] Bordwell and Cooper, *J. Amer. Chem. Soc.*, 1951, **73**, 5187.

[3] Kostsova, *Acta Univ. Voronegiensis*, 1935, **8**, No. 4, 92; *Chem. Abs.*, 1938, **32**, 6618.

[4] Douglass, Simpson, and Sawyer, *J. Org. Chem.*, 1949, **14**, 272.

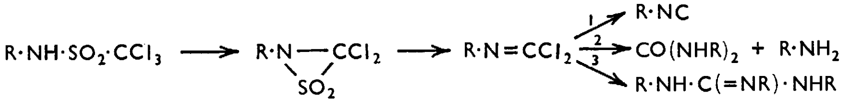
[5] Brintzinger, Koddebusch, Kling, and Jung, *Chem. Ber.*, 1952, **85**, 455.

[6] Backer, *Rec. Trav. chim.*, 1926, **45**, 830.

[7] McGowan, *J. prakt. Chem.*, 1884, **30**, 299.

Trichloromethanesulphonyl chloride oxidises arylamines to coloured products, being reduced to trichloromethanesulphinic acid; [8] it has been confirmed in the present work that no trace of arylamide is formed. It proved possible, however, to oxidise *p*-chlorotrichloromethanesulphenanilide [9] to the sulphonanilide by permanganate. Hydrogen peroxide gave the rather unstable sulphinanilide.

The alkaline decomposition of *p*-chlorotrichloromethanesulphonanilide was complex, giving *p*-chloroaniline, di-*p*-chlorophenylurea, tri-*p*-chlorophenylguanidine, and *p*-chlorophenyl isocyanide. These compounds can be fitted into a scheme similar to the above, in which the primary decomposition product is *p*-chlorophenyl isocyanide dichloride:



1. SO_2; 2. H_2O; 3. R·NH$_2$

Sodium difluoromethanesulphonate was readily formed by the reaction of chlorodifluoromethane with aqueous sulphite at 120°; it was converted, *via* the sulphonyl chloride, into the anilide. Chlorofluoromethane was not available for similar preparation of derivatives of fluoromethanesulphonic acid, but these were obtained by a different method. Dichlorofluoromethane reacted with aqueous sulphite at 180° to give an inseparable mixture of sodium fluoromethanesulphonate and sodium chlorofluoromethanesulphonate. This mixture was converted into the mixed anilides, which were readily separated by crystallisation. All these arylamides containing fluorine were completely stable to N-sodium hydroxide at 100°. Trifluoromethanesulphonanilide has recently been described,[10] and would also appear to be stable to alkali, though this is not specifically stated.

2-Chloroethanesulphonyl chloride reacts with aniline [11] to give ethylenesulphonanilide and 2-anilinoethanesulphonanilide; 2-chloroethanesulphonanilide could not be isolated. With *p*-chloroaniline, all three corresponding products were formed, and could be separated by fractional extraction with aqueous sodium carbonate. *p*-Chloro-2-chloroethanesulphonanilide is instantly decomposed by cold dilute sodium hydroxide, giving a precipitate of the sparingly soluble sodium salt of *p*-chloroethylenesulphonanilide.

1-Chloroethanesulphonyl chloride [12] reacted readily with arylamines, but of the amides only the *p*-chloroanilide was eventually obtained in satisfactory form. This compound, dissolved in cold dilute sodium hydroxide, deposited crystals of *p*-chloroaniline after a few hours.

EXPERIMENTAL

Chloromethanesulphonyl Chloride.—(i) *From* s-*trithian*. *s*-Trithian (200 g.) suspended in water (1 l.) was chlorinated to saturation at 0—10° with good agitation (15—20 hr.). The lower layer of crude chloride (250—300 g.) was distilled, the material of b. p. 160—170° (200—230 g.) being chloromethanesulphonyl chloride of approx. 90% purity. The higher yields claimed in the literature [4] could not be consistently obtained, though occasionally experiments gave yields much higher or much lower than the above. The yield evidently depends on factors not under complete control; there were " good " and " bad " batches of *s*-trithian, the more coarsely crystalline material giving the best results. Even carefully fractionated samples of sulphonyl chloride made by this method, however, had no definite crystallising point.

(ii) *From sodium chloromethanesulphonate*. Sodium chloromethanesulphonate (258 g.) and

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[8] Battegay and Kern, *Bull. Soc. chim. France*, 1927, **51**, 46.

[9] Connolly and Dyson, *J.*, 1934, 822.

[10] Gramstad and Haszeldine, *J.*, 1957, 4069.

[11] Goldberg, *J.*, 1945, 634.

[12] Müller, *J. prakt. Chem.*, 1927, **116**, 191.

phosphorus pentachloride (340 g.) were heated at 100° for 2 hr. Volatile material (<100°/20 mm.) was distilled off and the distillate fractionated. Chloromethanesulphonyl chloride distilled at 165—166°/750 mm. (198 g.); it had *d* 1·65, f. p. −40·5°.

Preparation of Arylamides.—Method A. The sulphonyl chloride and the amine (2 mol.) were set aside overnight in benzene; amine hydrochloride was filtered off, and the filtrate extracted with 2N-sodium hydroxide. Acidification of the alkaline extract gave the arylamide, usually as an oil which crystallised when scratched.

Method B. The amine, sulphonyl chloride (1 mol.), and pyridine (1·2 mol.) were stirred in benzene at 45—50° overnight, and the product was extracted with aqueous alkali as before.

Chloro-chloromethanesulphonanilides.—Made by method A from sulphonyl chloride of method (ii) (79% yield) the p-*chloro-anilide* formed needles (from ethanol), m. p. 106° (Found: C, 35·3; H, 3·4. $C_7H_7O_2NCl_2S$ requires C, 35·0; H, 2·9%). The benzene layer after extraction contained p-*chloro*-NN-*di*(*chloromethanesulphonyl*)*aniline*, m. p. 124° (7%; from ethanol) (Found: C, 27·7; H, 2·4; Cl, 30·3. $C_8H_8O_4NCl_3S_2$ requires C, 27·25; H, 2·3; Cl, 30·2%). When the sulphonyl chloride, prepared by method (i), was used the yield of the *p*-chloroanilide was much lower (30—60%), and the following by-products could be isolated in varying amount by fractional crystallisation: di-*p*-chlorophenylformamidine hydrochloride[13] (free base, m. p. 179°); *sym*-tris-*p*-chlorophenylguanidine hydrochloride[14] (free base, m. p. 132°); and 6-chloro-3-*p*-chlorophenyl-3,4-dihydroquinazoline,[15] m. p. 187°. All were identified by mixed m. p. with authentic specimens.

2,4-*Dichloro*-, m. p. 108° (Found: C, 30·6; H, 2·45. $C_7H_6O_2NCl_3S$ requires C, 30·6; H, 2·2%), and 2,4,5-*trichloro-chloromethanesulphonanilide*, m. p. 114° (Found: C, 27·4; H, 1·7. $C_7H_5O_2NCl_4S$ requires C, 27·2; H, 1·65%), were prepared by method B, and were crystallised from ethanol.

Hydrolysis of N-*Arylchloromethanesulphonamides.*—The arylamide (5·00 g.), in N-sodium carbonate (100 c.c.), was heated for 2 hr. at 100°. The solution was then cooled, filtered, and acidified, and the recovered arylamide dried. The following results were obtained:

Arylamide:	Anilide	*p*-chloroanilide	2,4-dichloroanilide	2,4,5-trichloro-anilide
Recovery, %	nil	20	32	trace

All were completely decomposed after 1 hr. in N-sodium hydroxide at 100°.

2,4,5-*Trichloro*-N-*chloromethanesulphonylbenzenesulphonamide* (I).—Sodium 2,4,5-trichlorobenzenesulphonamide (from 25 g. of sulphonamide), benzene (200 c.c.), and chloromethanesulphonyl chloride (15 g.) were refluxed for 16 hr. The solid was freed from benzene, taken up in warm dilute sodium carbonate solution, and extracted with ether. The extracts contained unchanged sulphonamide (11·5 g.). The aqueous portion when salted out gave the *sodium salt* (15 g.) of the sulphonamide (I), recrystallised from a little hot water as platelets, m. p. 280—282° (Found: C, 21·1; H, 1·3; Cl, 35·8. $C_7H_4O_4NCl_4S_2Na$ requires C, 21·2; H, 1·0; Cl, 35·9%). The free *imide* was made by recrystallising the sodium salt (1 g.) from 3N-hydrochloric acid (20 c.c.); it formed water-soluble needles, m. p. 155—156° (Found: C, 23·0; H, 1·3. $C_7H_5O_4NCl_4S_2$ requires C, 22·5; H, 1·35%). It was not altered by refluxing for 2 hr. with N-sodium hydroxide.

Bromomethanesulphonanilide.—This *bromo-compound* was made from bromomethanesulphonyl bromide[3] and aniline by method A; it formed prisms, m. p. 77°, from light petroleum (Found: C, 33·8; H, 3·45. $C_7H_8O_2NBrS$ requires C, 33·6; H, 3·25%).

Iodomethanesulphonanilide.—Iodomethanesulphonyl chloride was prepared from sodium iodomethanesulphonate[16] and phosphorus pentachloride. The *anilide*, prepared from it by method A, formed prisms, m. p. 70°, from light petroleum (Found: C, 28·4; H, 2·75. $C_7H_8O_2NIS$ requires C, 28·3; H, 2·75%). Both the bromo- and the iodo-anilide were rapidly decomposed by boiling N-sodium hydroxide; aniline, formaldehyde, sulphite, and halide ions were detected in the product.

Dichloromethanesulphonyl Chloride.—Chloroform (120 g.), sodium sulphite heptahydrate (250 g.), and water (800 g.) were heated for 5 hr. at 125° in an autoclave (100 lb./sq. in.). The

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[13] Backer and Wanmaker, *Rec. Trav. chim.*, 1949, **69**, 247.

[14] Bly, Perkins, and Lewis, *J. Amer. Chem. Soc.*, 1922, **44**, 2896; Beilstein and Kurbatow, *Annalen*, 1875, **176**, 49.

[15] Wagner and Eisner, *J. Amer. Chem. Soc.*, 1937, **59**, 879.

[16] Lauer and Langkammerer, *J. Amer. Chem. Soc.*, 1935, **57**, 2361.

aqueous layer was separated from unchanged chloroform (*ca.* 60 g.), evaporated to dryness, and crystallised from hot ethanol, giving sodium dichloromethanesulphonate as transparent plates, which became opaque on being dried (20—25 g.) (Found: Na, 12·15. Calc. for CHO_3Cl_2SNa: Na, 12·3%). Longer reaction times or higher temperatures gave larger yields of a product deficient in chlorine (cf. ref. 17).

Sodium dichloromethanesulphonate (57 g.) and phosphorus pentachloride (63 g.) were heated for 2 hr. at 100°, and volatile material was distilled off [$<$100°(bath temp.)/20 mm.]. Fractionation of this distillate gave dichloromethanesulphonyl chloride as an irritating liquid (31 g.), b. p. 176—177°, 64°/14 mm.: f. p. $-35°$ (cf. ref. 7).

Dichloromethanesulphonyl Compounds.—Dichloromethanesulphonanilide, m. p. 78° (Found: C, 35·4; H, 3·0; N, 5·6. $C_7H_7O_2NCl_2S$ requires C, 35·0; H, 2·95; N, 5·8%), and the p-*chloroanilide*, m. p. 103° (Found: C, 31·1; H, 2·2. $C_7H_6O_2NCl_3S$ requires C, 30·6; H, 2·2%), were prepared by method A in 60—65% yield, and were recrystallised from light petroleum. In the preparation of the latter, the benzene solution after extraction deposited a small amount of di-*p*-chlorophenylformamidine hydrochloride; the mother liquors on evaporation yielded p-*chloro*-NN-*bisdichloromethanesulphonylaniline* (2%), m. p. 230° (decomp.), as compact prisms from acetic acid (Found: C, 23·2; H, 1·9; N, 3·0. $C_8H_6O_4NCl_3S_2$ requires C, 22·8; H, 1·45; N, 3·3%).

2,4,5-*Trichlorodichloromethanesulphonanilide*, m. p. 168° (Found: C, 24·9; H, 1·3. $C_7H_4O_2NCl_5S$ requires C, 24·45; H, 1·2%), was formed in only 8% yield by method B. The remainder was a highly coloured tar.

Hydrolysis of p-*Chlorodichloromethanesulphonanilide*.—The *p*-chloro-compound (5 g.) and aqueous sodium carbonate (5%; 100 c.c.) were refluxed for 1 hr. The flask then contained a dark gum (*ca.* 1 g.) and an aqueous solution containing sulphite but not formaldehyde. The condenser contained *p*-chlorophenyl isocyanide (1·2 g.), m. p. 56—64°, raised to 62—66° by recrystallisation (lit.,[18] m. p. 71°).

p-*Chlorotrichloromethanesulphenanilide*.—Trichloromethanesulphenyl chloride (40 g.), ether (200 c.c.), water (200 c.c.), and sodium carbonate (24 g.) were stirred at 10—20°, and *p*-chloroaniline (26 g.) was added during 15 min. After 2 hr., the ether layer was removed and the solvent allowed to evaporate. The gummy residue was extracted with cold petroleum, the extract filtered from amorphous material, and the solvent again allowed to evaporate, leaving the p-*chlorosulphenanilide* as brownish crystals (44 g.). Recrystallisation from a small volume of petroleum gave almost colourless prisms, m. p. 49° (Found: C, 30·8; H, 2·1. $C_7H_5NCl_4S$ requires C, 30·3; H, 1·8%). Connolly and Dyson [9] report this compound as an unstable oil; in a sealed container it is stable indefinitely at 0°.

p-*Chlorotrichloromethanesulphinanilide*.—The sulphenanilide (3 g.) dissolved in acetic acid (11 c.c.) was treated with 100-vol. hydrogen peroxide (4 c.c.) and set aside for 1 hr. at 20—30°. The crystalline product (1·95 g.) formed needles, m. p. 157—158° (decomp.) from acetone (Found: C, 28·6; H, 1·6. $C_7H_5ONCl_4S$ requires C, 28·65; H, 1·7%). It was extensively decomposed after a few weeks' storage. The mother liquors from this preparation slowly deposited a small amount of a sulphur-free product which appeared to be a mixture of polychloronitrosobenzenes.

p-*Chlorotrichloromethanesulphonanilide*.—The *p*-chloro-sulphenanilide (15 g.), in acetone (750 c.c.) and acetic acid (75 c.c.), was treated with 0·1N-potassium permanganate (750 c.c.) and set aside until the pink colour disappeared (2—3 hr.). The whole was evaporated almost to dryness, and the residue extracted several times with aqueous sodium carbonate. Acidification of the extracts and recrystallisation of the precipitate from ethanol gave the *sulphonanilide* (6 g.) as heavy needles, m. p. 147° (Found: C, 27·2; H, 2·1. $C_7H_5O_2NCl_4S$ requires C, 27·2; H, 1·65%).

Alkaline hydrolysis. *p*-Chlorotrichloromethanesulphonanilide (2·0 g.) and sodium carbonate solution (10%; 50 c.c.) were heated at 100° for 2 hr. A small amount of *p*-chloroaniline sublimed; *p*-chlorophenyl isocyanide was recognised by its odour. The flask contained a clear liquid (containing sulphite) and a dark solid (*ca.* 0·8 g.) from which was isolated (1) *NN'*-di-*p*-chlorophenylurea, m. p. *ca.* 300—310° (decomp.) (Found: C, 55·9; H, 3·6; N, 9·7. Calc. for $C_{13}H_{10}ON_2Cl_2$: C, 55·5; H, 3·6; N, 9·95%), and (2) *NN'N''*-tri-*p*-chlorophenylguanidine, best isolated as its hydrochloride which formed fine needles, m. p. 288—289° (decomp.),

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[17] Strecker, *Annalen*, 1868, **148**, 92.

[18] Ingold, *J.*, 1924, 87.

from aqueous ethanol. The free base had m. p. 132° (lit.[14] 135°) (Found: C, 58·7; H, 3·6; N, 10·9. Calc. for $C_{19}H_{14}N_3Cl_3$: C, 58·4; H, 3·6; N, 10·75%), and did not depress the m. p. of an authentic sample.[14]

N-*Aryldifluoromethanesulphonamides.*—Chlorodifluoromethane (86 g.) was added to sodium sulphite heptahydrate (250 g.) and water (500 g.) in an autoclave. The mixture was heated for 20 hr. at 120° (230 lb./sq. in.) and then cooled, excess of chlorodifluoromethane was allowed to escape, and the product was evaporated to dryness. Recrystallisation from ethanol gave *sodium difluoromethanesulphonate* as plates containing solvent, which was lost at 100° (34·5 g.) (Found: Na, 15·7. CHO_3F_2SNa requires Na, 15·0%). This was then heated with phosphorus pentachloride, and the product shaken (in benzene) with ice–water to decompose phosphorus oxychloride. The benzene solution was then allowed to react with amines without isolation of the sulphonyl chloride. The following arylamides were thus prepared: *Difluoromethanesulphonanilide*, m. p. 59° (method A) (Found: C, 40·5; H, 3·55. $C_7H_7O_2NF_2S$ requires C, 40·6; H, 3·4%); p-*chlorodifluoromethanesulphonanilide*, m. p. 92° (method A) (Found: C, 34·75; H, 2·65. $C_7H_6O_2NClF_2S$ requires C, 34·8; H, 2·5%); 2,4-*dichlorodifluoromethanesulphonanilide* (method B), m. p. 94° (Found: C, 30·4; H, 1·8. $C_7H_5O_2NCl_2F_2S$ requires C, 30·3; H, 1·8%). All recrystallisations were from petroleum.

Derivatives of Fluoromethanesulphonic and Chlorofluoromethanesulphonic Acid.—Sodium sulphite (anhydrous, 200 g.), dichlorofluoromethane (52 g.), and water (460 g.) were heated in an autoclave at 180° for 20 hr. (240 lb./sq. in.), the solvent evaporated, and the residue recrystallised from ethanol, giving a mixture (20·5 g.) of sodium fluoromethanesulphonate and sodium chlorofluoromethanesulphonate (Found: Cl, 15·6%). This was converted into mixed sulphonyl chlorides by reaction with phosphorus pentachloride, and then into mixed arylamides by method A. The mixed anilides were separated by crystallisation from benzene–light petroleum into *fluoromethanesulphonanilide* (less soluble), needles, m. p. 86·5° (Found: C, 44·45; H, 4·3. $C_7H_8O_2NFS$ requires C, 44·45; H, 4·3%), and *chlorofluoromethanesulphonanilide*, diamond-shaped prisms, m. p. 63° (Found: C, 37·5; H, 3·35. $C_7H_7O_2NClFS$ requires C, 37·6; H, 3·15%). The *p*-chloroanilides were not so readily separated: however, chlorination in chloroform solution gave a mixture of p-*chloro-chlorofluoromethanesulphonanilide*, needles, m. p. 78°, from petroleum (Found: C, 32·9; H, 2·6. $C_7H_6O_2NCl_2FS$ requires C, 32·55; H, 2·35%), and 2,4-*dichlorofluoromethanesulphonanilide*, laths, m. p. 139°, from petroleum (Found: C, 32·55; H, 2·65. $C_7H_6O_2NCl_2FS$ requires C, 32·55; H, 2·35%), which could be separated because of the low solubility of the latter in cold ethanol.

1,p-*Dichloroethanesulphonanilide.*—This was obtained from 1-chloroethanesulphonyl chloride [12] by method A as a gum which crystallised very slowly, but was eventually obtained as large prisms, m. p. 70°, from benzene–petroleum (Found: C, 37·6; H, 3·6. $C_8H_9O_2NCl_2S$ requires C, 37·8; H, 3·55%). The monochloro-anilide could not be obtained crystalline.

Reaction of 2-*Chloroethanesulphonyl Chloride with* p-*Chloroaniline.*—A mixture of 2-chloroethanesulphonyl chloride (20 g.), *p*-chloroaniline (45 g.), and benzene (300 c.c.) was kept for 20 hr. at 15—20°. Amine hydrochloride (25 g.) was filtered off, and the filtrate extracted with 2N-sodium carbonate (30 × 100 c.c.). Extracts 1—10 on acidification gave gums which crystallised only slowly; recrystallisation from petroleum gave needles, m. p. 50°, of p-*chloroethylenesulphonanilide* (Found: C, 43·75; H, 3·25. $C_8H_8O_2NClS$ requires C, 44·15; H, 3·7%) which formed a sparingly soluble sodium salt. Extracts 11—29 crystallised readily on acidification to give crude 2,p-*dichloroethanesulphonanilide* (6·6 g.). Four crystallisations from benzene–petroleum gave slender needles, m. p. 78° (Found: C, 37·95; H, 3·35. $C_8H_9O_2NCl_2S$ requires C, 37·8; H, 3·55%). From the benzene solution, after the carbonate extractions, was isolated 2-p-*chloroanilino*-N-p-*chlorophenylethanesulphonamide*, m. p. 86° (from benzene–petroleum) (Found: C, 49·05; H, 4·2. $C_{14}H_{14}O_3N_2Cl_2S$ requires C, 48·7; H, 4·1%).

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