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ГЕТЕРОЦИКЛИЗАЦИЯ 3 ПРОПАРГИЛСУЛЬФАНИЛ-5-ФЕНИЛ-1,2,4-ТРИАЗИНА: ТАНДЕМНЫЕ РЕАКЦИИ С БРОМОМ, ПРИВОДЯЩИЕ К СИНТЕЗУ НОВЫХ ПРОИЗВОДНЫХ 7 ФЕНИЛ[1,3]ТИАЗОЛО[3,2-*B*][1,2,4]ТРИАЗИНИЯ

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Производные 1,2,4-триазин-3-тиона проявляют широкий спектр биологической активности, обладают оптико-электронными свойствами, могут быть использованы в качестве синтонов в синтезе различных пиридинов по реакции Дильса-Альдера. Наибольший интерес, в том числе и для органического синтеза, представляют конденсированные 1,2,4-триазины. В настоящей работе нами установлено, что взаимодействие 3 пропаргилсульфанил-5-фенил 1,2,4-триазина, полученного алкилированием 5-фенил-2,3-дигидро-1,2,4-триазин-3-тиона 3 бромпропином в ацетоне в присутствии триэтиламина, с галогенами приводит к аннелированию тиазольного цикла. [1,3]Тиазоло[3,2-b][1,2,4]триазиниевые системы при этом в зависимости от типа галогена содержат в своей структуре либо эндо-, либо экзоциклическую двойную связь. Так, например, под действием иода на пропаргилсульфид образуется темный осадок трииодида (3Z) 3-иодметилен-7-фенил-2,3-дигидро[1,3]тиазоло[3,2-b][1,2,4]триазиния, строение которого подтверждено методом ^{1}H и ^{13}C ЯМР спектроскопии, включая двумерные эксперименты 2D ^{1}H-^{13}C HSQC, HMBC и ^{1}H-^{1}H NOESY. Обработка полученного трииодида иодидом натрия в ацетоне приводит к синтезу соответствующего моноиодида, который выпадает из реакционной смеси в виде темно-красного осадка. Реакция с бромом, в отличие от гетероциклизации под действием иода, представляет собой необычную каскадную реакцию, включающую стадии электрофильной гетероциклизации, присоединения брома и элиминирования бромоводорода и приводящую к образованию бромида 3 дибромметил-7-фенил[1,3]тиазоло[3,2-b][1,2,4]триазиния. Следует отметить, что отличительным признаком протекания гетероциклизации 3 пропаргилсульфанил-5-фенил 1,2,4-триазина под действием иода и брома можно считать смещение сигнала ароматического протона триазинового кольца в сторону слабого поля в ^{1}H ЯМР спектре продуктов реакции. По-видимому, это связано с образованием положительно заряженного атома азота.

Ключевые слова: 3-пропаргилсульфанил-5-фенил-1,2,4-триазин, гетероциклизация, тандемные реакции, [1,3]тиазоло[3,2-*b*][1,2,4]триазиниевые системы

HETEROCYCLIZATION OF 3-PROPARGYLSULFANYL-5 PHENYL-1,2,4-TRIAZINE: TANDEM REACTIONS WITH BROMINE LEADING TO NEW DERIVATIVES OF 7 PHENYL[1,3]THIAZOLO[3,2-*B*][1,2,4]TRIAZINIUM

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Derivatives of 1,2,4-triazine-3-thione exhibit biological activity in a wide range. They have optoelectronic properties and can be used as synthons in synthesis of various pyridines by the Diels-Alder reaction. 1,2,4-Triazines are of the greatest interest, for organic synthesis in particular. In the present study we have established that the interaction of 3-propargylsulfanyl-5-phenyl-1,2,4-triazine, obtained by alkylation of 5-phenyl-2,3-dihydro-1,2,4-triazine-3-thione with 3-bromopropyne in acetone in the presence of triethylamine, with halogens leads to annelation of thiazole cycle. At that, [1,3]thiazolo[3,2-b][1,2,4]triazinium systems contain either endo- or exocyclic double bond in their structure, depending on the halogen type. By way of example, iodine acting on propargyl sulfide forms a dark precipitate of (3Z)-3-iodomethylene-7-phenyl-2,3-dihydro-[1,3]thiazolo[3,2-b][1,2,4]triazinium triiodide, the structure of which has been confirmed by ^{1}H and ^{13}C NMR spectroscopy, including two-dimensional 2D ^{1}H-^{13}C HSQC, HMBC and ^{1}H-^{1}H NOESY experiments. Treatment of the obtained triiodide by sodium iodide in acetone leads to synthesis of the corresponding monoiodide, which precipitates from the reaction mixture as a dark red precipitate. Reaction with bromine, as distinct from heterocyclization under iodine action, comprises an unusual cascade reaction including the stages of electrophile heterocyclization, bromine addition, and hydrogen bromide elimination, which leads to formation of 3-dibromomethyl-7-phenyl[1,3]thiazolo[3,2-b][1,2,4]triazinium bromide. It should be pointed out that the identifying feature of 3-propargylsulfanyl-5-phenyl-1,2,4-triazine heterocyclization under iodine and bromine action is the signal bias of the aromatic proton in a triazine ring towards weak field in the ^{1}H NMR spectrum of the reaction products. This is presumably associated with formation of the positively charged nitrogen atom.

Key words: 3-propargylsulfanyl-5-phenyl-1,2,4-triazine, heterocyclization, tandem-reactions, [1,3]thiazolo-[3,2-*b*][1,2,4] triazinium system

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INTRODUCTION

It is well known that derivatives of 1,2,4-triazine-3-thione exhibit pesticide activity [1], as well as anticancer [2], psychotropic [3], and antiviral activity [4]. Annelated derivatives of triazines offer promise in the field of drug development [5-9], in particular for neurodegenerative diseases [10]. Besides, 3-methylsulfanyl-1,2,4-triazine has been used as a base for oligomers with optoelectronic properties [11]. Derivatives of 1,2,4-triazine are used as synthons in synthesis

of various pyridines according to the Diels-Alder reaction [12-15].

In the literature [16] there are data for alkylation in tetrahydrofuran of 5-phenyl-2,3-dihydro-1,2,4-triazine-3-thione (**1**) by benzyl, butenyl, and butynyl halides, proceeding at the sulfur atom. Heterocyclization of 3-allylsulfanyl- [17], 3-cinnamylsulfanyl-5-phenyl-1,2,4-triazine [18], as well as 3-alkenylsulfanyl- [19] and 3-propargylsulfanyl-5*H*-[1,2,4]triazino[5,6-*b*]indoles [20] under the action of halogens progresses with participation of the N-2 nitrogen atom of the triazine cycle producing thiazolo(thiazino)[3,2-*b*][1,2,4]-triazine systems. In the present study in an effort to obtain new annulated heterocyclic systems 3-propargylsulfanyl-5-phenyl-1,2,4-triazine (**2**) has been synthesized for the first time, and its interaction with halogens has been investigated.

EXPERIMENTAL PART

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE-500 spectrometer (500 and 126 MHz). The chemical shifts were measured from the internal standard TMS for ^{1}H and the solvent signal for ^{13}C. Complete assignment of the ^{1}H and ^{13}C signals was carried out with the help of combination of two-dimensional NMR experiments 2D ^{1}H-^{13}C HSQC, HMBC, and ^{1}H-^{1}H NOESY.

The mass spectrum of 3-propargylsulfanyl-5-phenyl-1,2,4-triazine **2** was recorded on a GCMS SHIMADZU QP2010 Ultra spectrometer in the electron ionization mode (70 eV).

Elemental analysis was carried out on a Carlo Erba CHNS-O EA 1108 analyzer.

5-Phenyl-2,3-dihydro-1,2,4-triazine-3-thione (1) was obtained by condensation of phenylglyoxal with thiosemicarbazide according to the described method [21].

3-Propargylsulfanyl-5-phenyl-1,2,4-triazine (2). To a solution of 0.189 g (1 mmol) of compound **1** in acetone (10 ml) Et_3N (2 ml) and 0.119 g (1 mmol) of 3-bromopropyne-1 were added. The reaction mixture was stirred for 12 h at room temperature and filtered in 24 h. The solvent was distilled from the filtrate. The residue was treated with water. The formed precipitate was filtered off and dried. Yield was 0.193 g (85%), m.p. 72-73 °C (from *i*PrOH). ^{1}H NMR (500 MHz, DMSO-d_6) δ, ppm /*J*, Hz: 3.21 (1H, t, ^{4}J 2.6, H-3'), 4.17 (2H, d, ^{4}J 2.6, H-1'), 7.63 (2H, t, *J* 7.5, H_m), 7.69 (1H, tt, *J* 7.2, 1.4, H_p), 8.36 (2H, dd, *J* 8.4, 1.4, H_o), 9.88 (1H, s, H-6). ^{13}C NMR (126 MHz, DMSO-d_6), δ, ppm: 18.57 (C-1'), 73.42 (C-3'), 79.75 (C-2'), 127.98 (C_o), 129.34 (C_m), 132.54 (C_i), 133.00 (C_p), 143.22 (C-6), 154.33 (C-5), 170.74 (C-3). MS, *m/z*: 227 $[M]^+$. Found, %: C 63.15, H 3.74, N 18.61. Calculated for $C_{12}H_9N_3S$, %: C 63.41; H 3.99; N 18.49.

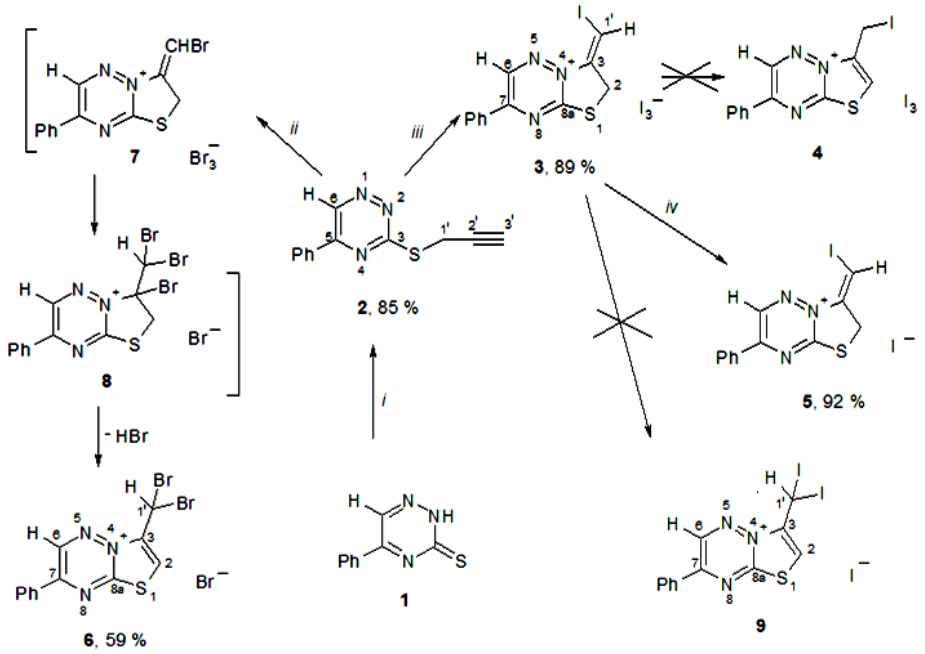
(*Z*)-3-Iodomethylene-7-phenyl-2,3-dihydro-[1,3]thiazolo[3,2-*b*][1,2,4]triazinium triiodide (3). To a solution of 0.203 g (0.8 mmol) I_2 in chloroform (15 ml) a solution of 0.095 g (0.4 mmol) propargyl sulfide **2** in chloroform (10 ml) was added. The reaction mixture was left to stand at room temperature for 72 h. The produced black precipitate was filtered off and dried. Yield was 0.274 g (89%), m.p. (decomp.) 140-141 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ, ppm /*J*, Hz: 4.51 (2H, d, *J* = 3.2, H-2), 7.80 (2H, dd, *J* = 8.6, 7.5, H_m), 7.99 (1H, tt, *J* = 7.5, 1.2, H_p), 8.19 (1H, t, *J* = 3.2, H-1'), 8.66 (2H, d, *J* = 8.6, 1.2, H_o), 10.05 (1H, s, H-6). ^{13}C NMR (126 MHz, acetone-d_6) δ, ppm: 36.88 (C-2), 78.95 (C-1'), 131.32 (C_m), 131.77 (C_i), 132.15 (C_o), 138.62 (C_p), 142.54 (C-3), 143.43 (C-6), 163.18 (C-7), 174.06 (C-8a). Found, %: C 19.36, H 0.99, N 5.58. Calculated for $C_{12}H_9I_4N_3S$, %: C 19.61; H 1.23; N 5.72.

To obtain **(3*Z*)-3-iodomethylene-7-phenyl-2,3-dihydro[1,3]thiazolo[3,2-*b*][1,2,4]triazinium iodide (5)** 0.130 g (0.18 mol) of triiodide **3** were dissolved in acetone (10 ml) and NaI (10 mg) was added. The produced red precipitate was filtered off, washed with acetone and dried. Yield was 0.078 g (95%), m.p. (decomp.) 162-163 °C.

3-Dibromomethyl-7-phenyl[1,3]thiazolo-[3,2-*b*][1,2,4]triazinium bromide (6). To a solution of 0.050 g (0.22 mmol) propargyl sulfide **5** in chloroform (5 ml) under stirring and cooling in ice a solution of 0.023 ml (0.44 mmol) Br_2 in chloroform (2 ml) was added. The reaction mixture was left to stand at room temperature for 24 h. The produced orange precipitate was filtered off, washed with chloroform and dried. Yield was 0.061 g (59%), m.p. 178-179 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ, ppm. / *J*, Hz: 7.78 (2H, t, *J* 7.7, H_m), 7.89 (1H, t, *J* 7.4, H_p), 7.92 (1H, s, H-1'), 8.62 (2H, d, *J* 7.6, H_o), 9.11 (1H, s, H-2), 10.57 (1H, s, H-6). ^{13}C NMR (126 MHz, DMSO-d_6), δ, ppm: 24.53 (C-1'), 125.59 (C-2), 130.09 (C_o), 130.14 (C_m), 131.06 (C_i), 135.80 (C_p), 137.15 (C-3), 143.10 (C-6), 155.57 (C-7), 163.17 (C-8a). Found, %: C 30.68, H 1.59, N 9.22. Calculated for $C_{12}H_8Br_3N_3S$, %: C 30.93; H 1.73; N 9.02.

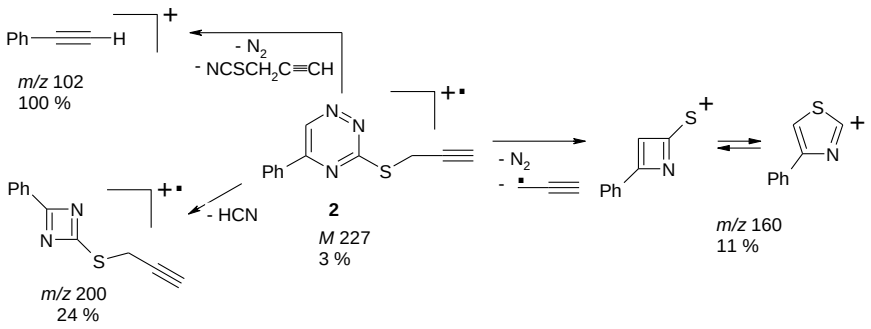
RESULTS AND DISCUSSION

We have carried out alkylation of compound **1** by 3-bromopropyne-1 in acetone in the presence of triethylamine at room temperature. In the process, we have obtained a previously unknown propargyl sulfide **2**, which has been studied in the electrophilic heterocyclization reactions with iodine and bromine (Scheme 1).



i: $BrCH_2C{\equiv}CH$, Et_3N, acetone, 20-22 °C, 24 h; *ii*: Br_2, $CHCl_3$, 0-5 °C, 20min, 20-22 °C, 24 h;
iii: I_2, $CHCl_3$, 20-22 °C, 72 h; *iv*: Me_2CO, NaI, 20-22 °C, 20 min.

Scheme 1. The scheme of synthesis and heterocyclization of 3-propargylsulfanyl-5-phenyl-1,2,4-triazine 2
Схема 1. Схема синтеза и гетероциклизации 3-пропаргилсульфанил-5-фенил-1,2,4-триазина 2

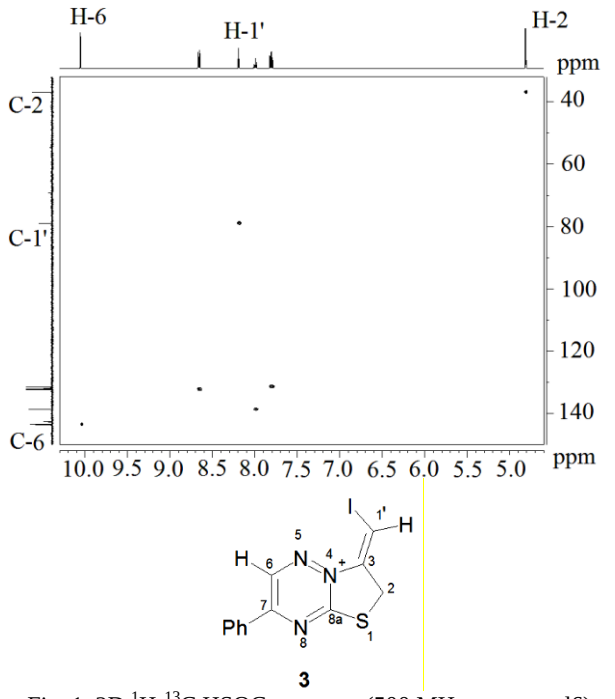


Scheme 2. The fragmentation scheme of 3-propargylsulfanyl-5-phenyl-1,2,4-triazine 2
Схема 2. Схема фрагментации 3-пропаргилсульфанил-5-фенил-1,2,4-триазина 2

The mass spectrum of propargyl sulfide **2** contains the molecular ion peak of small intensity, while the peak with *m/z* 102 is the most intensive. This peak is related to phenylacetylene formed at elimination of the nitrogen molecule and propargyl thiocyanate from the molecular ion (Scheme 2).

The molecular ion is also fragmented through elimination of the N_2 molecule and propargyl radical with formation of thiazolium cation (*m/z* 160). Elimination of hydrocyanic acid from the molecular ion leads to formation of 2-phenyl-4-propargylsulfanyl-1,3-diazet, as demonstrated by the peak with *m/z* 200 in the mass spectrum.

Interaction of propargyl sulfide **2** with iodine in chloroform produces dark precipitate of (3*Z*)-3-iodomethylene-7-phenyl-2,3-dihydro[1,3]thiazolo[3,2-*b*][1,2,4]-triazinium triiodide (**3**) (see Scheme 1). Its structure is confirmed by the ^{1}H NMR and ^{13}C NMR spectroscopy, including two-dimensional ^{1}H-^{13}C HSQC, HMBC, and ^{1}H-^{1}H NOESY experiments. Characteristic chemical shifts of C-2 (δ_C 36.88 ppm), C-3 (δ_C 142.54 ppm) and C-1' (δ_C 78.95 ppm) prove to the structure **3** and eliminate the alternative structure **4**, which is possible if triiodide **3** isomerizes. Spectrum 2D HSQC testifies that the C-1' carbon atom is bonded to the H-1' proton (δ_H 8.19 ppm), the chemical shift of which corresponds to a proton at an sp^2-hybridized carbon atom (Fig. 1). The Z-configuration of the exocyclic double bond is corroborated by the spin-spin coupling between the H-2 and H-1' protons, $^4J_{HH}$ = 3.2 Hz, as well as by the cross peak between these protons in the 2D NOESY spectrum.



3

Fig. 1. 2D ^{1}H-^{13}C HSQC spectrum (500 MHz, acetone-d6) of compound 3

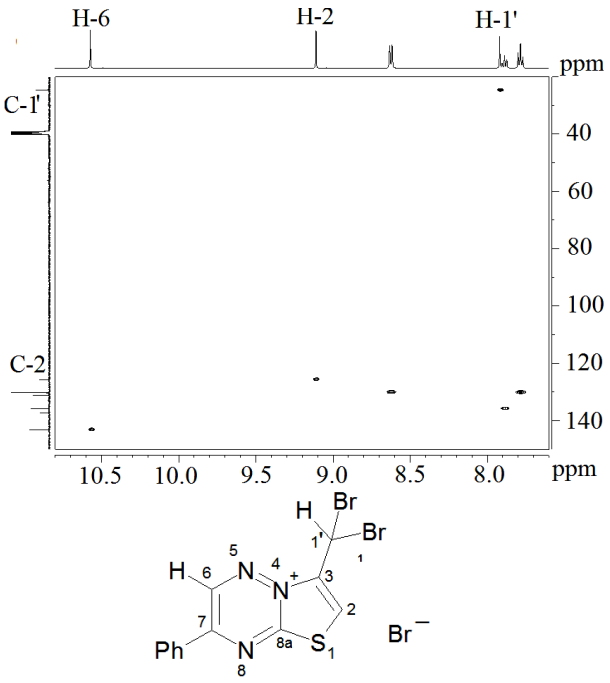
Рис. 1. 2D ^{1}H-^{13}C HSQC спектр (500 МГц, ацетон-d6) соединения 3

When triiodide **3** is treated by sodium iodide in acetone, (3*Z*)-3-iodomethylene-7-phenyl-2,3-dihydro[1,3]thiazolo[3,2-*b*][1,2,4]triazinium iodide (**5**) is formed, which precipitates from the reaction mixture as a dark red sediment.

Studying the interaction of compound **2** with bromine we have unexpectedly obtained 3-dibromomethyl-7-phenyl[1,3]thiazolo[3,2-*b*][1,2,4]triazinium bromide (**6**) (see Scheme 1). The probable explanation is that the initially formed 3-bromomethylene-7-phenyl-2,3-dihydro[1,3]thiazolo[3,2-*b*][1,2,4]triazinium tribromide (**7**) then turns into 3-bromo-3,3-dibromomethyl-2,3-dihydro-7-phenyl[1,3]-thiazolo-[3,2-*b*][1,2,4] triazinium bromide (**8**). The latter undergoes dehydrobromination, which leads to formation of aromatic structure **6**. It is worthy of note that the described chain of transformations is an example of a previously unknown domino (cascade) reaction.

This brings up the question: why are similar transformations not observed at heterocyclization of propargyl sulfide **2** by iodide? It is presumably related to the fact that iodine is a weaker electrophile than bromine and does not add to the endocyclic bond of triiodide **3.**

In the ^{1}H NMR spectrum of bromide **6** the signal of the H-2 aromatic proton is observed at δ_H 9.11 ppm, as well as the signals of dibromomethyl group in the downfield at δ_H 7.92 ppm, while the signal of the SCH_2 group protons in the area 3.5-4.5 ppm is absent, though it should be present in the case of structures **7** or **8**. According to the data of the 2D ^{1}H-^{13}C HSQC experiment the H-1' proton is bonded with the carbon atom at δ_C 24.53 ppm, the upfield shift of which is caused by steric shielding of two bromine atoms (Fig. 2).



6

Fig. 2. 2D ^{1}H-^{13}C HSQC spectrum (500 MHz, DMSO-d6) of compound 6

Рис. 2. 2D ^{1}H-^{13}C HSQC спектр (500 МГц, ДМСО-d6) соединения 6

A characteristic feature of heterocyclization occurring for compound **2** under the action of halogens is probably the shift in the ^{1}H NMR spectrum of the aromatic proton signal of the triazine ring in the direction of downfield for halides **3** and **6** compared to the initial propargyl sulfide **2** to 0.17 and 0.69 ppm, respectively. The signal shift can be related to formation of positive charge at the nitrogen atom.

CONCLUSION

Thus, alkylation of triazinethione **1** by 3-bromoprop-1-yne has produced previously unknown propargyl sulfide **2**. Heterocyclization of compound **2** under the action of iodine has led to annulation of the thiazole cycle. Interaction of compound **2** with bromine in chloroform does not stop at formation of the heterocyclization product with the exocyclic double bond. It then continues with further electrophilic addition of bromine and elimination of hydrogen bromide that leads to formation of 3-dibromomethyl-7-phe-

nyl[1,3]thiazolo[3,2-*b*][1,2,4]triazinium bromide **6** with the endocyclic double bond.

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