3,7,10-Trimethyl-4,13-dioxo-8-aza-4,5,6,6a-tetrahydro-5,6a-propanofluoranthene (XVIII). A mixture of 3 g (8.5 mmole) of dibasic acid XVII and 140 g of PPA was heated with stirring at 150-160° for 2.5 h, after which 300 ml of water was added, and the mixture was neutralized with sodium carbonate. The reaction products were extracted with chloroform, and the extract was worked up to give 0.3 g (11%) of light-yellow crystals of XVIII with mp 144-146° [from benzene–hexane (2:1.5)]. IR spectrum: 1683 and 1727 cm^{-1} (arylalkyl and dialkyl C=O, respectively). PMR spectrum, δ: 8.00 (1H, 1-H), 7.36 (1H, J = 8.0 Hz, 2-H), 8.3 (1H, s, 10-H), 3.7 (1H, m, 4a-H), 2.73 (3H, s, CH_3), and 2.63 (3H, s, CH_3). Found: C 78.1; H 7.7; N 4.2%; M 317. $C_{21}H_{19}NO_2$. Calculated: C 79.5; H 6.0; N 4.4%; M 317. The picrate had mp 178-180° (from alcohol). Found: N 10.0%. $C_{21}H_{19}NO_2 \cdot C_6H_3N_3O_7$. Calculated: N 10.2%.

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PREPARATION OF 3-ARYL-2-QUINOXALONES

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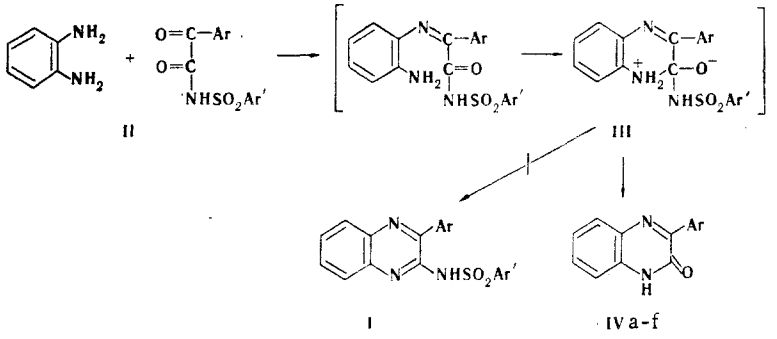
Arenesulfonamides are split out in the reaction of N-(arylsulfonyl)arylglyoxylamides with o-phenylenediamine to give 3-aryl-2-quinoxalones.

Quinoxaline derivatives that have bacteriostatic action are known [1]. We made an attempt to obtain arenesulfamido derivatives (I) of quinoxaline by condensation of o-phenylenediamine with N-(arylsulfonyl)arylglyoxylamides (II). Amides II were synthesized by arenesulfonamidation of arylglyoxals [2]. However, regradless of the nature of the arylsulfonyl group, 3-aryl-2-quinoxalones (IVa-f) rather than I are formed, and arenesulfonamides are split out.



II III I IV a-f

Ar′ = C_6H_5, 4-ClC_6H_4, 4-BrC_6H_4, 3-$NO_2C_6H_4$, 4-$CH_3C_6H_4$; Ar see Table 1

The first act in the reaction is probably formation of a C=N bond between the nitrogen atom of one amino group of o-phenylenediamine and the carbonyl carbon atom of the aroyl residue of II. Nucleophilic attack on the free amino group by the carbon atom of a second carbonyl group evidently leads to the formation of dipolar ion III. Its stabilization may occur via two pathways: either by splitting out of water to give an arenesulfonamidoquinoxaline

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TABLE 1. 3-Aryl-2-quinoxalones (IVb-f)

Compound	Ar	mp, °C (from dioxane)	Found, %			Empirical formula	Calc., %			M		Yield, %
			C	H	N		C	H	N	found	calc. (for the monomer)	
IVb	4-BrC_6H_4	265—267	55,5	3,4	9,2	$C_{14}H_9BrN_2O$	55,7	3,0	9,4	610	301,1	41
IVc	4-ClC_6H_4	253—254	65,5	4,1	10,7	$C_{14}H_9ClN_2O$	65,5	3,5	10,9	520	256,7	47
IVd	4-$NO_2C_6H_4$	349—350[6]	62,5	3,9	15,6	$C_{14}H_9N_3O_3$	62,9	3,4	15,7	538	267,2	40
IVe	4-$CH_3OC_6H_4$	258—259	71,8	5,0	11,0	$C_{15}H_{12}N_2O_2$	71,6	4,7	11,1	501	252,2	51
IVf	2-Thienyl	261—262	61,1	3,4	12,0	$C_{12}H_8N_2OS$	60,5	3,4	11,7	—	238,1	54

(I) or by splitting out of an arenesulfonamide to give 2 3-aryl-2-quinoxalone (IV). The second pathway is actually realized. It is energically more favorable, since it specifies cleavage of only the C-N and N-H bonds (1110 kJ/mole), whereas cleavage of the C=O bond and two N-H bonds (1440 kJ/mole) [3] is necessary in the case of splitting out of water. In addition, splitting out of the bulky arenesulfonamido group should be preferred from the point of view of steric hindrance. The unusual course of the reaction is apparently due to the strong electron-acceptor effect of the sulfo group, which weakens the C-N bond.

The structures of IVa-f were confirmed by their IR spectra and determination of their molecular masses; IVa was also identified by comparison with an authentic sample obtained from o-phenylenediamine and benzoylformic acid [4]. Compounds IVa-f are yellow crystalline solids that are only slightly soluble in most organic solvents and have high melting points (Table 1). The absorption band of the N-H group in the IR spectra of IVa-f is diffuse and shifted to 2860-3020 cm^{-1}; this constitutes evidence for strong association of the amide hydrogen atom, which participates in the formation of hydrogen bonds of the N-H···O type [5]. The molecular weights found in this research indicate a dimeric structure for IV (Table 1).

EXPERIMENTAL

The IR spectra of the KBr pellets were taken on a UR-20 spectrophotometer. The molecular weight was determined by a cryoscopic method in phenol. The melting-point depression comprised 1.65 (IVa), 1.20 (IVb), 1.40 (IVc), 1.35 (IVd), and 1.45° (IVe), in a quinoxalone—phenol weight ratio approximately equal to 1 : 10.

3-Phenyl-2-quinoxalone (IVa). A) A solution of 1.08 g (0.01 mole) of o-phenylenediamine in 10 ml of methanol was added to a solution of 2.89 g (0.01 mole) of N-(phenylsulfonyl)-phenylglyoxylamide in 20 ml of methanol, and the mixture was refluxed for 15 min. The precipitated IVa was removed by filtration of the hot solution and recrystallized from dioxane to give 1.23 g (57%) of yellow needles with mp 246-247° (mp 247° [4]). IR spectrum: 1668 (C=O) and 2850 cm^{-1} (N-H).

B) A solution of 2.84 g (0.01 mole) of o-phenylenediamine sulfate in 10 ml of water was added to an alcohol solution of 2.89 g (0.01 mole) of N-(phenylsulfonyl)phenylglyoxylamide, and the mixture was refluxed for 1 h. It was then allowed to stand for 24 h, and the precipitate was removed by filtration and recrystallized from dioxane to give 1.02 g (46%) of yellow needles of IVa with mp 245-247°.

C) A thoroughly ground mixture of 2.89 g (0.01 mole) of N-(phenylsulfonyl)phenylglyoxylamide and 1.08 g (0.01 mole) of o-phenylenediamine was heated in a test tube to the melting point (80-90°) for 5 min, after which it was cooled and washed with hot methanol. The residue was recrystallized from dioxane to give 0.91 g (41%) of IVa with mp 246-247°.

Compounds IVb-f (Table 1) were similarly obtained by method A.

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