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INVESTIGATION OF THE DECOMPOSITION OF 1,3-DIARYL-5-(3-CHLORO-2-QUINOXALYL)-

FORMAZANS BY PMR AND MASS SPECTROMETRY

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In contrast to triarylformazans, 1,3-diaryl-5-(3-chloro-2-quinoxalyl)formazans are unstable in ordinary organic solvents. When they are heated in chloroform, they undergo acidic cleavage, which leads to the formation of 3-chloro-2-quinoxalylhydrazones of p-substituted benzaldehydes and arenediazonium cations. These compounds, as a result of a redox reaction with the participation of the solvent, are converted to 4-chloro-1-(4-Y-phenyl)-1,2,4-triazolo[4,3-a]quinoxalines, substituted benzenes, nitrogen, and hydrogen chloride. The formation of the latter transforms the entire decomposition process into an autocatalytic process. Effects of chemical polarization of the nuclei (CPN), which unambiguously indicate the intermediate formation of diazoaryl radicals during the process, are observed in the PMR spectra of the final products. Such CPN effects, which were also observed in dimethyl sulfoxide (DMSO) and glacial acetic acid, indicate a process involving the oxidative formation of annelated triazoles from α-azahetarylhydrazones via a radical pathway within a solvent "cage."

We have previously shown [1] that when 1,3-diaryl-5-(3-chloro-2-quinoxalyl)formazans I-XII are heated in chloroform, they undergo cleavage, as a result of which, three ring 4-chloro-1-(4-Y-phenyl)-1,2,4-triazolo[4,3-a]quinoxalines (XVI-XVIII), substituted benzenes (XIX-XXIII), nitrogen, and hydrogen chloride are formed (see Scheme 1).

Sedov and co-workers [2] have demonstrated the instability of quinoxalylformazans in acidic media; this is, on the whole, also characteristic for other unsymmetrical hetaryl-

TABLE 1. Characteristic Ions in the Mass Spectra of XVI-XVIII

Com- pound*	m/z value,† (I, %)					
	$[M]^{+\cdot}$	$[M-H]^+$	$C_8H_4N_3Cl$ $[M-ArCN]^{+\cdot}$	$C_8H_4N_3$ $[M-ArCN,$ $-Cl]^{+\cdot}$	$C_7H_4N_2$ $[M-ArCN,$ $-CNCl]^{+\cdot}$	$[Y-C_6H_4-C\equiv N]^{+\cdot}$
XVI	310 (100)	309 (41)	177 (24)	142 (8)	116 (12)	133 (20)
XVII	280 (100)	279 (45)	177 (49)	142 (13)	116 (17)	103 (20)
XVIII	325 (100)	324 (17)	177 (77)	142 (33)	116 (41)	148 (15)

*The mass spectra of XVII and XVIII were obtained by subtraction.
†The m/z values of the ions that contain the ^{35}Cl isotope are given in italics. An $[M-NO_2]^+$ ion peak with m/z 279 (12%) is observed in the mass spectrum of XVIII.

Scheme 1
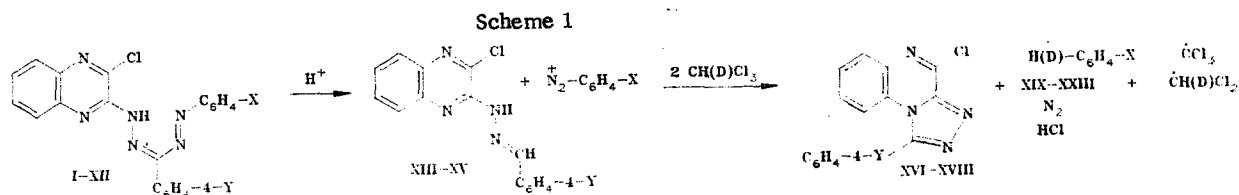
I—VII, XIII, XVI Y=OCH₃; VIII—IX, XIV, XVII Y=H; X—XII, XV, XVIII Y=NO₂;
I, XIX X=p-N(CH₃)₂; II, X, XX X=p-i-C₃H₇; III, IX, XI, XXI X=p-n-C₄H₉; IV, VIII, XII,
XXII X=H; V X=p-NO₂; VI X=m-NO₂; VII X=o-NO₂; XXIII X=NO₂

formazans [3-5]. However, we have observed the decomposition of hetarylformazans in ordinary organic solvents for the first time.

It is apparent that the observed process is complex and involves many steps. We were able to demonstrate this by a detailed investigation of formazans I-XII* in various organic solvents, viz., chloroform, dimethyl sulfoxide (DMSO), glacial acetic acid, and their per-deutero analogs. To ascertain the mechanism of the process we added various reagents, viz., quinone, hydroquinone, 3-chloro-2-quinoxalylhydrazones XIII-XV, trifluoroacetic acid, alcohol, and mixtures of them.

We followed the course of the reaction by means of PMR spectroscopy. The determination of the compositions and the identification of the reaction products were accomplished via the PMR and mass spectra. The mass-spectral analysis of solutions of the products of decomposition of formazans I-XII in chloroform and DMSO was carried out after the reaction.

Peaks of ions with m/z = 36 and 38, the intensities of which corresponded to the natural ratio of chlorine isotopes, were observed in all of the mass spectra of the products of decomposition in chloroform recorded immediately after introduction of the reaction mixtures into the ion source (without heating); these peaks were identified as hydrogen chloride. The intensities of these peaks decrease rapidly with time. Peaks of heavier ions whose compositions would contain chlorine were not observed. The formation of DCl did not occur when the reaction was carried out in CDCl₃; this indicates the direct participation of the proton of the hydrogen atom of the amino group of the formazan in the formation of HCl.

To separate the mixtures we used molecular distillation, realized directly in the source, for which the mass spectra were recorded at various temperatures (0-250°C). To iso-late the ions that belong to a single component we constructed mass chromatograms (the dependences of the change in the intensities of the peaks of ions with definite m/z values on the time and temperature). In addition, we carried out mutual subtraction of the mass spectra, which is allowed by the standard program of processing the mass spectra with a computer.
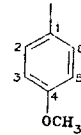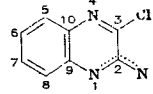
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*The decomposition of formazan upon heating in chloroform was not observed; however, the addition of trifluoroacetic acid led to the formation of XVIII.

TABLE 2. Chemical Shifts of the Signals of the Protons in the PMR Spectra of the Quinoxalyformazans and Annelated Triazoles

Com-pound*	Solvent	3-Aryl			5-Quinoxalyl			
		2,6-H	3,5-H	4-Y	5-H	6-H	7-H	8-H
IV	CDCl₃	8,18	7,02	3,89	7,92	7,56	7,72	8,07
XVI	CDCl₃	7,62	7,14	3,94	8,04	7,59	7,42	7,62
XVI	d₆-DMSO	7,69	7,25	3,92	8,02	7,63	7,49	7,50
VIII	CDCl₃	8,22	7,55—7,66		7,92	7,55	7,72	8,08
XVII	CDCl₃	7,65—7,69			8,04	7,57	7,35	7,60
XVII	d₆-DMSO	7,75—7,77			8,04	7,67	7,54	7,37
XII	CDCl₃	8,46	8,33	—	7,96	7,62	7,79	8,10
XVIII	CDCl₃	8,00	8,53	—	8,11	7,67	7,41	7,47
XVIII	d₆-DMSO	8,09	8,53	—	8,08	7,69	7,49	7,40

*The signals of the protons of the first phenyl ring of formazans IV, VIII, and XII are found at 8.07 (2H, m, 2,6-H) and 7.44-7.70 ppm (3H, m, 3,4,5-H). The signals of the NH proton are found at 14.49 (IV), 14.74 (VIII), and 15.29 ppm (XII).

TABLE 3. ^{13}C NMR Spectra of IV and XVI

	C atom No.	IV (ppm)	XVI (ppm)	Δδ, ppm
3-Aryl	1-C	128,34	125,91	−2,4
	2,6-C	129,30	131,53	+2,2
	3,5-C	113,97	114,83	+0,9
	4-C	160,80	162,01	+1,2
	4-OCH₃	55,37	55,60	+0,2
meso-C		146,66	151,19	+4,5
5-Quinoxalyl	2-C	145,06	142,26	−2,8
	3-C	137,21	142,79	+5,6
	5-C	127,98	130,11	+2,1
	6-C	127,45	128,25	+0,8
	7-C	130,67	129,50	−1,2
	8-C	127,80	116,02	−11,8
	9-C	141,24	135,69	−4,6
	10-C	138,73	119,11	−19,6

The compounds obtained were identified on the basis of a comparison of the reaction products obtained under identical conditions but with variation of the X and Y substituents and also by comparison of the products obtained in deuterated and undeuterated solvents.

To estimate the amounts of each of the components the mass spectra were summed up over the entire time of vaporization of the samples, after which we calculated the fractions of the molecular ions (or the sums of the molecular and intense fragment ions) of each of the components in the total ion current.

According to the mass-spectrometric data, in the products of the deomposition of formazans I-VII the principal product is a compound with a molecular mass of 310 (based on the ^{35}Cl isotope); correspondingly, the principal products of the decomposition of formazans VIII and IX and X-XII are compounds with molecular masses of 280 and 325. Structures XVI-XVIII were assigned to these substances on the basis of an analysis of the PMR and ^{13}C NMR spectra (Tables 2 and 3). The principal pathway of their fragmentation involves cleavage of the N—N and C—N bonds in the triazole ring, in which two fragments, one of which has m/z = 177 in all of the mass spectra and a Cl atom in its composition ([M − ArCn]⁺), are formed. The second fragment ion (ArCn⁺) and m/z = 133 for XVI (Y = OCH₃), m/z = 103 for XVII (Y = H), and m/z = 148 for XVIII (Y = NO₂). Thus the fragmentation of XVI-XVIII (Table 1) is in good agreement with the proposed structures.

All of the experimental data, as well as a study of the properties of the quinoxalyl-formazans in chloroform, made it possible to assume that the decomposition that we observed takes place from the open form of the formazan, the amount of which prior to the reaction ranges from 5% to 25%, according to our estimates. The addition of quinone and, particularly, alcohol, substantially lengthened the induction period of the reaction (Table 4); this is

t, °C	$C \cdot 10^3$ moles/liter		Period, sec		Benzene		K_{obs} for quinone	Yield† (%)	Reagent
	formazan	reagent	induction	half conversion	K_{obs}	yield* (%)			
60	3	—	1200	—	0	—	—		—
60	14	—	700	—	—1,2	80			—
60	30	—	500	—	—2,2	70			—
60	16	50	1650	—	—1,5	—			H₂O
60	16	30	4200	—	—	—		Compound XVI	Ethanol
60	15—20	0	600±100	80±10	—(1,5—2,0)	80		100	—
60	23	10	1200	—	—1,5	57		140	Hydrazone XIII
60	26	20	1740	—	—1,6	56		160	Same
60	25	38	4900±100	—	—1,0	55		220	„ „
60	13	9	500	70	—5,3	60	—6,5	Hydroquinone 20	Quinone
60	13	36	900	100	—7,0	50	—7	40	Quinone
60	16	16	700	—	—3,1	70	—10	Quinone 5	Hydroquinone
60	15	23	500	—	—3,1	70	—10	5	Hydroquinone
40	16	0	2800±200	240±10	—1	65	—	—	—
40	30	0,3	360	220	—	67	—	—	Trifluoroacetate acid
40	17	0,7	240	170	—	—	—	—	Same
40	16	2,3	95	145	—	67	—	—	„ „
40	16	9,0	0	60	0	—	—	—	„ „

*The yield of benzene was determined on the basis of a 100% yield of XVI.

†The yields ov XVI and hydroquinone were determined with respect to the formazan; a small amount of quinone is formed when hydroquinone is added.

probably associated with stabilization of the open form by means of an intramolecular hydrogen bond. The same decomposition reaction includes conversion of the formazan, under the influence of acids, to a hydrazone with splitting out of an arylazo group in the form of an arenediazonium cation, as described in [6-8]. The induction period of the reaction was shortened markedly when trifluoroacetic acid was added (Table 4). In accordance with our assumption, the hydrazones are then oxidized to XVI-XVIII under the influence of the arenediazonium cation within a solvent "cage." It is precisely this that makes possible, from the observed (in the PMR spectra) effects of chemical polarization of the nuclei (CPN), the formation of radical pair RP_1 (Scheme 2), as in the well-known reduction of arenediazonium salts by amines [9] or hydroquinone [10], in which similar CPN effects are observed in the PMR spectra [9, 10]. Subsequent transformations evidently lead to the formation of an arylazohydride and to the development of RP_2 and RP_3 radical pairs with "intracage" radical exchange, as in [11]. The presence in the mass spectra of the products of decomposition of the formazan of low-intensity peaks of molecular ions that correspond to the product of "cage" recombination of $X-C_6H_4N_2-CH(D)Cl_2$ indicates the undoubted participation of RP_3 in the formation of CPN effects.

The integral negative polarization, in conformity with Kaptein's rules [12], that is observed in the PMR spectra may be created both in RP_1 and in RP_3 (the lifetime of RP_2 is absolutely too brief for singlet—triplet evolution), since (RH₂ is the hydrazone) $g_{X-C_6H_4\dot{N}_2} <$ $g_{RH_2}^{+\cdot}$. The $g_{RH}^{+\cdot}$ value is evidently close to $g_{Ph_3N}^{+\cdot} = 2.0036$ [13], whereas on the other hand, $g_{X-C_6H_4-\dot{N}_2} < g_{CHCl_2}^{\cdot}$; $g_{CHCl_2}^{\cdot} = 2.0081$ [14], and $g_{X-C_6H_4-\dot{N}_2} = 2.0005-2.0007$ [15]. The calculated (by Abronin) hyperfine interaction (hfi) constants of the diazophenyl radical are positive [16]. We have previously noted [1] on the basis of a comparison of the data on 1,3-diarylformazans with different substituents in various positions of the phenyl ring that the CPN is formed in the radical pair with the participation of the diazoaryl radical rather than the aryl radical.

Subsequently (Scheme 2), a molecule of hydrogen chloride and two free radicals are also formed in each act of "intracage" oxidation; this creates the prerequisites for excitation of a radical-chain reaction, as a result of which a molecule of the formazan or additional amounts of hydrazones XIII-XV may be oxidized, which indeed is observed when XIII is added to

the reaction solution of formazan IV. The increase in the observed coefficient of intensification of polarization (K_{obs}) in the decomposition of IV and VIII and the manifestation of CPN effects in the thermolysis of formazans II, III, and IX, which contain alkyl substituents, when quinone (a radical acceptor) is added indicate the possibility of the free-radical oxidation of formazans and the resulting hydrazone. Polarization of the protons in the direct acidolysis of IV by trifluoroacetic acid (Table 4) is evidently absent for the same reason. The formation of chloroform in the thermolysis of formazans III and IV in tetrachloromethane also serves as a confirmation of the free-radical destruction. Chain breaking apparently occurs in the recombination of $\overset{\bullet}{C}Cl_3$ or $\overset{\bullet}{C}H(D)Cl_2$ radicals with one another, as noted in [17].

Scheme 2
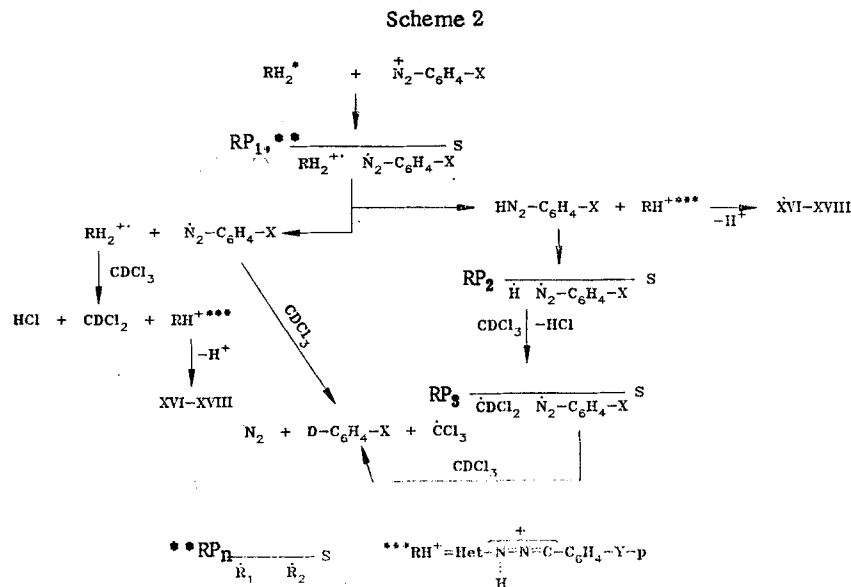
For a detailed study of the process we measured the kinetics of the decomposition of formazans IV and V and the rate of formation of product XVI under various conditions.

Treatment of the concentration dependences in accordance with [18] showed that the kinetic rate equation corresponds to an autocatalytic process in which the rate-determining step is the formation of the acid:

$$W = k[IV] + \alpha k_a[IV][XVI]^*, \tag{1}$$

where W is the rate of formation of XVI, k is the rate constant for monomolecular decomposition, k_a is the rate constant for an autocatalytic process, and α is a coefficient of proportionality between the acid (HCl) and XVI concentrations.

The data were treated by both integral and differential methods; this made it possible to evaluate the ratio between the acid and XVI concentrations. Whereas in the case of treatment of the data by the integral reaction equation:

$$k_a[IV]_0\tau = \ln\frac{[IV]_0[XVI]}{[IV]} + \ln\alpha\frac{k_a}{k}, \tag{2}$$

where $[IV]_0$ is the initial formazan concentration, α does not enter into the expression for the calculated value, in the case of the differential method via the equation:

$$\frac{W}{[IV]} = k + \alpha k_a[XVI] \tag{3}$$

the αk_a value is calculated.

The coincidence of the rate constants (Table 5) determined by these methods indicates approximately equimolar yields of hydrogen chloride with respect to XVI (i.e., $\alpha \simeq 1$) and indirectly confirms the oxidation scheme that we proposed. We evaluated the energies of activation of the decomposition of the formazans from the Arrhenius equation and found values of ~10-12 kcal/mole (42-50 kJ/mole) for IV and ~12-14 kcal/mole (50-58 kJ/mole) for V; these

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*Instead of the acid concentration, we used the XVI concentration, which we assumed was proportional to it.

TABLE 5. Principal Characteristics of the Decomposition of Quinox-alylformazans in Deuterochloroform

Compound	Reaction temp., °C	Formazan concn, moles/liter	Period, sec		Reaction time,* sec	k_a, mole^{-1}·sec^{-1}		E, kcal/mole	Yield of benzene, %
			induc-tion	half conver-sion		integral reaction	differential reaction		
IV	39	15	2800±200	240±10	300±20	1,2±0,2	1,1±0,2	10—12	65±5
	49	15	1100±100	150±10	210±10	2,1±0,5	2,3±0,4		70±5
	60	15	600±100	80±10	120±10	3,7±0,5	3,5±0,7		80±5
V	47	16	7400±300	820±30	1100±30	0,53±0,05	0,51±0,05	12—14	70±5
	53	15	4000±300	700±30	900±30	0,76±0,08	0,77±0,08		75±5
	60	16	1300±100	390±30	510±30	1,07±0,10	1,05±0,11		70±5

*The time required for 90% conversion of the formazan.

values somewhat exceed the energy of stabilization of the hydrogen bond in triphenylformazan [7-8 kcal/mole (30-38 kJ/mole) [19,20]].

The decomposition of formazans I-XII in DMSO and its deutero analog leads to the same principal products; however, the role played by a radical-chain reaction is diminished substantially. Additional amounts of hydrazones XIII-XV are oxidized to a lesser extent, and the CPN have substantially higher values relative to the coefficient of intensification of CPN (K_{obs}) [1]. The rate-determining step in the decomposition is evidently diffusion of the formazans into the solution; this is associated with the extremely low solubilities of quinoxalylformazans in DMSO.

The decomposition of formazans X-XII in d_6-DMSO proceeds via different pathyways, including those that probably proceed without a preliminary acidolysis step, as indicated by the decrease in the yield of benzene to 20-30% (the yield was determined by integration of the signals in the PMR spectra with respect to XVIII) and the formation of substituted anilines.

This is associated with the better purification of d_6-DMSO, since the addition to the solution of an equimolar amount of trifluoroacetic acid increased the yield of benzene up to its normal value, viz., 70-80%, the same yield as in the case of the reaction in undeuterated DMSO.

When the decomposition of formazans IV, VI, and XII was carried out in glacial acetic acid in accordance with the conditions in [6-8], in the PMR spectra we observed CPN effects similar to those that occurred in the decomposition of formazans in chloroform.

Thus by means of a combination of PMR spectroscopy and fragment mass spectroscopy one can obtain quite complete and reliable information regarding all of the principal steps in this complex and multistep reaction. The interpretation of the CPN data made it possible to ascertain that the oxidation of hetarylhydrazones may take place within the solvent "cage" to give radical pairs.

It is interesting to note that in various steps of the process one observed the successive manifestation of specific chemical properties that are due both to the introduction of a heterocyclic substituent into the formazan system (acidic cleavage) and to the presence in it of an α-azaheterocyclic fragment (oxidation to annelated triazoles [21]).

In conclusions, the authors than B. I. Buzykin and S. V. Rykov for their valuable remarks during the discussion of the results of this research.

EXPERIMENTAL

The PMR spectra were obtained with a Varian XL-100-12 spectrometer (100 MHz) under continuous conditions. The concentration of the solutions of the formazans in d_1-chloroform was $(1-3) \cdot 10^{-2}$ mole/liter.

The assignment of the signals in the PMR spectra was made with the aid of homonuclear INDOR [22]; the chemical shifts of the signals of the protons were determined from the centers of the multiplets within a first-order approximation (the maximum error did not exceed ±0.03 ppm).

The ^{13}C NMR spectra were obtained under pulse conditions with Fourier transformation with the same spectrometer at 25.16 MHz.

The accuracy in the determination of the chemical shifts in the PMR spectra was ±0.01 ppm (except for the multiplets, the positions of which were established by the INDOR method), and the accuracy in determining the chemical shifts in the ^{13}C NMR spectra was ±0.05 ppm. The chemical shifts of the signals are given on the δ scale with tetramethylsilane (TMS) as the internal standard.

The mass spectra were obtained with AEI MS-702 and LKB 2091 spectrometers with direct introduction of the samples. The ionizing-electron energy was 70 eV (where necessary, the spectra were recorded at 15-20 eV).

Formazans I-XII were synthesized by the standard method [2, 23] by diazo coupling in an alkaline medium of the corresponding quinozalylhydrazones with diazotized substituted anilines.

4-Chloro-1-(4-methoxyphenyl)-1,2,4-triazolo[4,3-a]quinoxaline (XVI). A 0.42-g (1 mmole) sample of formazan IV was dissolved in 40 ml of chloroform, and the solution was refluxed for 1-2 h (until the solution became colorless). The solvent was removed by distillation to dryness, and the residue was recrystallized from alcohol to give 0.21 g (68%) of colorless crystals in the form of fine needles that were soluble in organic solvents but insoluble in water and had mp 222-223°C. Found: C 62.1; H 3.5; Cl 11.5; N 17.8%; M 310.7. $C_{16}H_{11}ClN_4O$. Calculated: C 61.8; H 3.6; Cl 11.4; N 18.0%.

Monitoring of the purity of the compound obtained was carried out by thin-layer chromatography (TLC) on Silufol UV-254 plates. The structure of XVI was determined from the ^{13}C NMR spectra (Table 3). The shielding of the 8-C and 10-C carbon-13 atoms of the quinoxalyl fragment relative to formazan IV indicates a transition from the electron-acceptor effect of the 1-N nitrogen atom of the heteroring to an electron-donor effect associated with the formation of an annelated triazole and, evidently, with a change in its hybridization. Similar changes in the chemical shifts have been observed in the tautomeric transition from the amino to the imino form [24, 25], which was associated with a transition from sp^2 hybridization of the nitrogen atom of the heteroring to sp^3 hybridization [25].

Compounds XVII and XVII were not isolated in individual form; they were identified from the PMR (Table 2) and mass spectra (Table 1).

Decomposition of Formazan IV. A 15 to 30-mg (0.03-0.06 mmole) sample of formazam IV was dissolved in 2.2 ml of d_1-chloroform, and an ampul containing the prepared solution was placed in the themostatable pickup of the NMR spectrometer. The reaction was carried out at 40-60°C. The completion of the reaction was established from the absence of further changes in the PMR spectra. The yield of benzene was 65-85% relative to XVI from the ratio of the integral intensities of the signals of the benzene protons and the 5-H proton of the quinoxalyl group in the PMR spectra.

The formation of benzene was confirmed by the "fingerprint" method.

4-Methoxybenzaldehyde 3-Chloro-2-quinoxalylhydrazone. A 23.8-mg (0.057 mmole) sample of formazan IV, 3.5 mg (0.034 mmole) of quinone, and 12.1 mg (0.114 mmole) of hydroquinone were dissolved in 2.2 ml of $CDCl_3$, and an ampul containing the prepared solution was placed in the pickup of the NMR spectrometer. The reaction was carried out at 60°C. The yield of hydrazone XIII was estimated to be 15-20%; its formation was confirmed by the fingerprint method. The low yield of the hydrazone indicated the principal role played by "intracage" oxidation of the hydrazone by the benzeneiazonium cation during the formation of XVI, since the addition of a competing reducing agent (hydroquinone) in a large excess amount did not substantially change the course of the process. Quinone was added to suppress the "intracage" radical-chain oxidation of the hydrazone. In the absence of quinone signals of hydrazone XIII were absent in the PMR spectra.

The decomposition of formazans I-XII in dimethyl sulfoxide (DMSO) was carried out at 100°C. Formazans III, IV, VII, IX, XI, and XII also decomposed at 120-150°C.

In order to carry out the reaction commercial undeuterated DMSO was first distilled and dried until its water content was $\sim 10^{-2}$% (monitoring was carried out by comparing the areas of the signals of water and the $^1H-^{13}C$ satellite from DMSO in the PMR spectrum). Commercial d_6-DMSO was used without purification (according to the PMR data, its water content was $\sim 10^{-2}$%).

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