SYNTHESIS OF TRIAZENES OF THE BENZOTHIAZOLE, BENZIMIDAZOLE, AND PYRIDINE SERIES, AND INVESTIGATION OF THE KINETICS OF THEIR PHOTOCHEMICAL DECOMPOSITION

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Disubstituted alkyl(aryl)heteryltriazenes were synthesized by the reaction of the azides of benzothiazole, benzimidazole, and pyridine with Grignard reagents. The kinetics of their cleavage by UV irradiation were investigated.

We have previously described the reactions of 6-azido-2-methylbenzothiazole with organomagnesium halides [1] which lead to the formation of disubstituted triazenes.

The aim of this study was the synthesis of triazenes from organomagnesium compounds and 5-azido-2-methylbenzothiazole, 2-(p-azidophenyl)benzothiazole, 6-azido-1,2-dimethylbenzimidazole, 5-azido-1-phenyl-2-methylbenzimidazole, and β-azidopyridine. It was shown that, as in the case of 6-azido-2-methylbenzothiazole, these azides react with organomagnesium halides only at the azido group to form the disubstituted triazenes presented in Table 1.

To shed some light on the problem of the photostability of triazenes of different structure, the kinetics of their photochemical cleavage were investigated. The photolysis of triazenes has not been studied from a kinetic point of view. The use of the photochemical decomposition of methylphenyltriazene as a source of CH_3 free radicals is described in [2].

We used alkyl(aryl)heteryltriazenes I, IX-XI, XV, XX, XXI, XXVIII, XXX, and XXXIV (see Table 1) as well as diazoaminobenzene and methylphenyltriazene for the kinetic investigations.

The judgment regarding the rate of photochemical decomposition of the triazenes with time was accumulated on the basis of the results of spectrophotometric and gasometric methods of analysis.

The dependence of the change in the concentration of triazene solutions on the irradiation time during measurement of the absorption intensity of the UV spectra is shown in Fig. 1. It is apparent that alkyltriazenes are photolytically decomposed faster than aryltriazenes.

The gasometric determination of the rate of decomposition of the triazines with time was based on measurements of the volume of nitrogen, which is the product of their photolytic cleavage.

Special experiments were set up to establish whether photolysis of the triazenes is accompanied by thermal decomposition. Solutions of triazenes IX, XII, and XXXIV ($c = 1 \cdot 10^{-3}$ M) in alcohol were placed in the cuvette of a thermostat and held in succession at 30 to 70 deg. It turned out that these compounds do not decompose in a period of time sufficient for their photolysis under the given conditions. In [3] it was shown that triazenes do not decompose in anhydrous methanol and dry benzene at 20 and 40 deg. The addition of water to alcohol solutions results in an increase in the rate of thermal decomposition of the triazenes, but a prolonged period is required for their complete decomposition.

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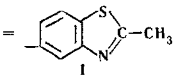
TABLE 1. Alkyl(aryl)heteryltriazenes R−N=N−NH−R [1]

R′ =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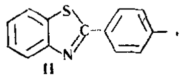
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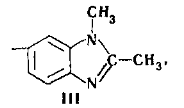
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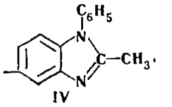
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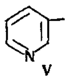
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Compound	R	R′	λ_{max}, nm	$\varepsilon_{max}\times10^{-4}$	Dec. temp.	Empirical formula	N, % found	N, % calculated	Yield, %
I	CH_3	R^1	285	1,73	145—147	$C_9H_{10}N_4S$	27,14	27,15	66
II	C_2H_5	R^1	295	1,64	120	$C_{10}H_{12}N_4S$	24,31	24,41	55
III	n-C_3H_7	R^1	290	1,64	140—142	$C_{11}H_{14}N_4S$	23,81	23,90	64
IV	i-C_3H_7	R^1	290	1,43	134	$C_{11}H_{14}N_4S$	23,39	23,90	63
V	n-C_4H_9	R^1	290	1,56	148—150	$C_{12}H_{16}N_4S$	22,43	22,56	61
VI	i-C_4H_9	R^1	290	1,46	140	$C_{12}H_{16}N_4S$	22,40	22,56	72
VII	n-C_5H_{11}	R^1	270	1,68	162	$C_{13}H_{18}N_4S$	21,51	21,35	55
VIII	i-C_5H_{11}	R^1	270	1,82	158	$C_{13}H_{18}N_4S$	21,56	21,35	54
IX	C_6H_5—CH_2	R^1	290	2,00	124—126	$C_{15}H_{14}N_4S$	19,53	19,83	46
X	C_6H_5	R^1	365	2,34	158—160	$C_{14}H_{12}N_4S$	20,81	20,88	53
XI	CH_3	R^2	350	5,00	130—135	$C_{14}H_{12}N_4S$	20,31	20,08	77
XII	C_2H_5	R^2	340	6,12	110—112	$C_{15}H_{14}N_4S$	19,62	19,83	70
XIII	n-C_3H_7	R^2	345	4,81	120—125	$C_{16}H_{16}N_4S$	18,59	18,90	82
XIV	i-C_3H_7	R^2	350	6,23	Oil*	$C_{16}H_{16}N_4S$	18,70	18,90	76
XV	n-C_4H_9	R^2	350	5,10	94—95	$C_{17}H_{18}N_4S$	17,82	18,04	98
XVI	i-C_4H_9	R^2	345	5,60	100—103	$C_{17}H_{18}N_4S$	18,00	18,04	72
XVII	n-C_5H_{11}	R^2	345	6,60	130—135	$C_{18}H_{20}N_4S$	16,93	17,26	60
XVIII	i-C_5H_{11}	R^2	340	6,80	95—100	$C_{18}H_{20}N_4S$	17,00	17,26	65
XIX	C_6H_{11}	R^2	395	4,31	135—138	$C_{20}H_{20}N_4S$	16,85	16,36	68
XX	C_6H_5—CH_2	R^2	350	4,89	140—145	$C_{20}H_{16}N_4S$	15,81	16,02	98
XXI	C_6H_5	R^2	380	4,81	152—154	$C_{19}H_{14}N_4S$	16,68	16,95	66
XXII	C_2H_5	R^3	295	1,94	95	$C_{11}H_{15}N_5$	32,28	32,32	74
XXIII	C_6H_5	R^3	305	1,42	170—172	$C_{15}H_{15}N_5$	28,51	28,74	50
XXIV	CH_3	R^4	308	1,42	104	$C_{15}H_{15}N_5$	26,28	26,39	48
XXV	.C_2H_5	R^4	310	1,58	113	$C_{16}H_{17}N_5$	24,91	25,07	52
XXVI	n-C_3H_7	R^4	320	1,70	120	$C_{17}H_{19}N_5$	23,65	23,87	49
XXVII	n-C_4H_9	R^4	350	1,82	125	$C_{18}H_{21}N_5$	22,32	22,45	75
XXVIII	C_6H_5	R^4	360	1,69	186—187	$C_{20}H_{17}N_5$	21,30	21,39	95
XXIX	CH_3	R^5	275	1,44	96—98	$C_6H_8N_4$	41,00	41,14	78
XXX	C_2H_5	R^5	275	1,61	98—100	$C_7H_{10}N_4$	37,12	37,29	67
XXXI	n-C_3H_7	R^5	280	1,58	118	$C_8H_{12}N_4$	37,12	37,29	67
XXXII	n-C_4H_9	R^5	275	1,52	115	$C_9H_{14}N_4$	31,12	31,43	69
XXXIII	C_6H_5—CH_2	R^5	290	1,60	132—133	$C_{11}H_{12}N_4$	27,80	27,63	84
XXXIV	C_6H_5	R^5	350	1,71	152—153	$C_{11}H_{10}N_4$	27,82	28,22	59

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* d_4^{20} 1.0498, n_D^{20} 1.5120.

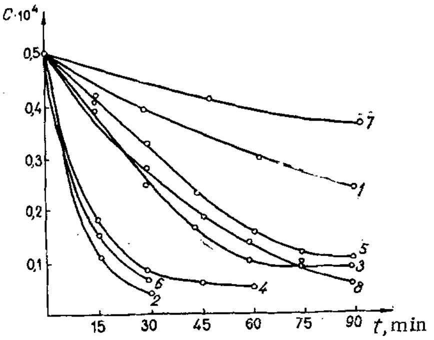


Fig. 1

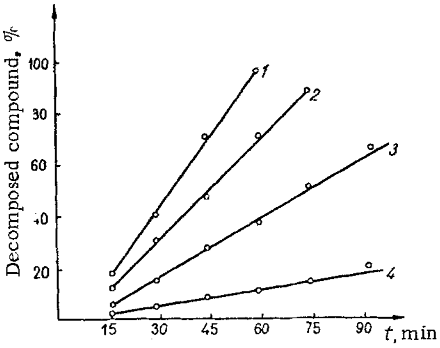


Fig. 2

Fig. 1. Dependence of the change in concentration of triazene solutions on irradiation time: 1) diazoaminobenzene; 2) methylphenyltriazene; 3) phenyl(β-pyridyl)triazene; 4) ethyl(β-pyridyl)triazene; 5) phenyl(2-methyl-5-benzothiazolyl)triazene; 6) methyl(2-methyl-5-benzothiazolyl)triazene; 7) phenyl(1-phenyl-2-methyl-5-benzothiazolyl)triazene; 8) benzyl(2-methyl-5-benzothiazolyl)triazene.

Fig. 2. Rate of photolysis of triazenes (c 1 · 10^{-3} M at 30 deg): 1) R = CH_3; 2) R = C_4H_9; 3) R = $C_6H_5CH_2$; 4) R = C_6H_5.

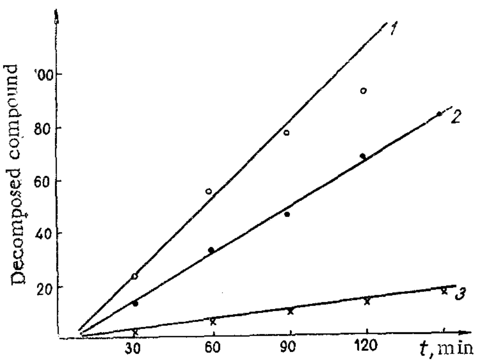
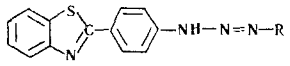


Fig. 3. Dependence of the rate of decomposition of phenyl(β-pyridyl)triazene on irradiation time for various concentrations: 1) $5 \cdot 10^{-3}$; 2) $1 \cdot 10^{-3}$; and 3) $0.5 \cdot 10^{-3}$ M.

Under the conditions of our experiments, the amount of nitrogen evolved during the photolysis of the triazenes is proportional to the exposure time and depends on the structure of the triazene.

Data on the rate of photolytic cleavage of the following triazenes is presented in Fig. 2.



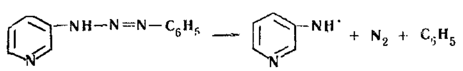
XI $R=CH_3$; XV $R=C_4H_9$; XX $R=C_6H_5-CH_2$; XXI $R=C_6H_5$

As seen from the graphical dependence presented, triazene with a methyl group (Curve 1) decomposes almost completely on exposure for 60 min, while triazene with a phenyl group (Curve 4) undergoes only 10% decomposition. This is apparently due to the different degree of conjugation of the groups attached to the triazene grouping. According to our results on the rate of photochemical decomposition, triazenes of this type can be arranged in the following order:

$$\mathrm{Alk-N_3H-Het > C_6H_5-CH_2-N_3H-Het > C_6H_5-N_3H-Het},$$

where Alk = CH_3, C_2H_5, C_3H_7, C_4H_9, etc., and Het = a heterocyclic residue.

The kinetics of the photolysis of phenyl(β-pyridyl)triazene (XXXIV) at three concentrations ($0.5 \cdot 10^{-3}$, $1 \cdot 10^{-3}$, and $5 \cdot 10^{-3}$ M) in alcohol were investigated in greater detail to determine the reaction order for the photolytic cleavage of triazenes. The process was thermostated at 30 deg. As seen from Fig. 3, the dependence of the rate of decomposition of the compound on the exposure time is linear. The rate constants were calculated from the slopes of these lines, and the reaction order was determined. The kinetic calculations indicated that the photochemical cleavage of phenyl(β-pyridyl)triazene is almost first order. It can be assumed that the initial step of the photolytic cleavage is



It is known from [4] that photochemical processes are usually complex and that the reaction order may change. The effective quantum yield must be determined for the precise characteristics of a photolytic process. We are now engaged in investigations in this direction.

EXPERIMENTAL

We have previously [1] described the method for the synthesis of alkyl(aryl)heteryltriazenes from organomagnesium compounds. The azides required for this purpose were synthesized by the reaction of sodium azide with the appropriate diazo compounds [5, 6]. 2-(p-Azidophenyl)benzothiazole (dec. 147 deg) was prepared for the first time by a similar method.

The triazenes thus synthesized (see Table 1) are crystalline substances (more infrequently oils) of different shades of yellow, and sometimes colorless. They are quite soluble in many organic solvents. They are decomposed with nitrogen evolution by dilute mineral acids. With concentrated sulfuric acids the alkylheteryltriazenes give a characteristic fulmination accompanied by the liberation of dense smoke. They form silver derivatives at the active hydrogen atom of the triazeno group.

The UV spectra of the alkyl(aryl)heteryltriazenes are distinguished by high absorption and have analogous curves which are characterized by the presence of two maxima: the more intense maximum lies at 270-395 nm, while the less intense maximum lies at 224-260 nm. The molar extinction coefficients for the long-wave absorption maxima of alcohol solutions of the triazenes in the UV region are presented in Table 1.

Spectrophotometric and Gasometric Methods for the Determination of the Rate of Photochemical Decomposition of the Triazenes. 1) A 5-ml sample of an alcohol solution of the triazene ($0.5 \cdot 10^{-3}$ M) was irradiated in a quartz cuvette with the integral spectrum of a PRK-4 lamp at a distance of 200 mm from the light source with light intensity $j = 2 \cdot 10^{-2}$ W/ cm^2 in the plane of the sample. The process was thermostated at 30 deg; this was achieved by feeding water to the outer jacket of the cuvette. Each sample was irradiated for 15, 30, 45, 60, 75, and 90 min. The UV absorption spectra were measured with an SF-4A spectrophotometer before irradiation and after each irradiation interval. To take solvent evaporation into account, the irradiated solution of the triazene was transferred quantitatively to a volumetric flask, and a solution ($0.5 \cdot 10^{-4}$ M) was prepared from it and subjected to spectroscopic investigation.

2) A setup consisting of a Kipp generator, a quartz cuvette, a TL-500 thermostat, a micro nitrogen meter, and a PRK-4 lamp light source was assembled for the gasometric measurements; this setup made it possible to determine the amount of nitrogen evolved with time during the photolysis of the triazenes. The irradiation was carried out in an atmosphere that was thoroughly freed of carbon dioxide. A 25-ml sample of an alcohol solution of the triazene ($0.5 \cdot 10^{-3}$, $1 \cdot 10^{-3}$, and $5 \cdot 10^{-3}$ M) was taken and successively exposed for 15, 30, 60, 90, and 120 min at constant temperature and light intensity. Each time the amount of evolved nitrogen was measured and converted to standard conditions.

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