TRIAZENES OF THE BENZOTHIAZOLE SERIES CONTAINING ALIPHATIC GROUPS

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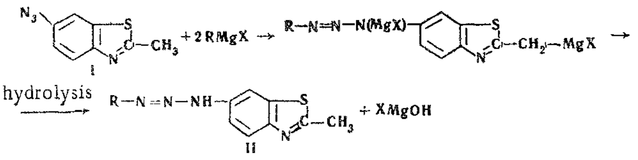
Reaction of 2-methyl-6-azidobenzothiazole with Grignard reagents gives alkyl(aryl)-(2-methylbenzothiazolyl-6)triazenes.

In 1959 a number of authors [1,2] found that triazenes of the general formula R—N═N—NH—Ar, where R is a heterocyclic group, e.g. thiazole, benozthiazole, pyridine, and derivative thereof, Ar is an aromatic group e.g. phenyl or naphthyl containing a carboxyl or sulfonic group, are stabilizers and sensistabilizers of silver chloride photoemulsions. It was of interest to synthesize triazenes of the heterocyclic series with aliphatic groups, and to investigate their photographic activities.

Our aim was to prepare a series of triazenes with the general formula II. Synthesis of these triazenes by coupling diazotized 2-methyl-6-aminobenzothiazole with aliphatic amines [2] proved unsuitable. For synthesis of the above triazenes we chose Dimroth's method [4] involving treating the organic azides with Grignard reagents.

Using 2-methyl-6-azidobenzothiazole (I) in the reaction with Grignard reagents, we synthesized 10 triazenes hitherto undescribed in the literature (table).

The equations are

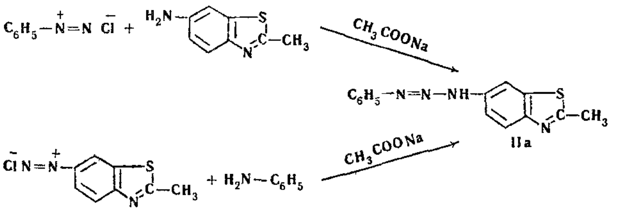


It was previously shown [5] that the methyl group enters into the reaction.

Alkyl(aryl)-(2-methylbenzothiazolyl-6-)triazenes are pale yellow and yellow crystalline compounds or oils, readily soluble in most organic solvents. On heating with acids or water they are decomposed with evolution of nitrogen. Triazenes melt with decomposition. Concentrated sulfuric acid causes a violent detonation with aliphaticaromatic triazenes.

To identify the triazenes we prepared their silver compounds, crystalline pale yellow or yellow compounds, slightly soluble in most organic solvents. They melt with decomposition. When introduced, on a spatula, into the flame of a burner, they burn with detonation.

To demonstrate the structures of the triazenes prepared, we synthesized phenyl(2-methylbenzothiazolyl-6)triazene (IIa), not only by the above method, but also by two others viz. coupling phenyldiazonium chloride with 2-methyl-6-aminobenzothiazole, and (2-methylbenzothiazolyl-6)-diazonium chloride with aniline:



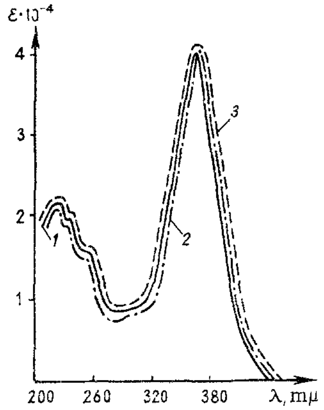
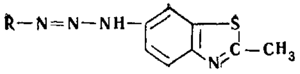


Fig. 1. UV spectra of ethanol solutions of phenyl-(2-methylbenzothiazolyl-6) triazene: 1) Prepared by the Grignard reaction; 2) prepared by coupling (2-methylbenzothiazolyl-6)diazonium chloride with aniline; 3) prepared by coupling phenyldiazonium chloride with 2-methyl-6-aminobenzothiazole.

All the products were identical, and gave undepressed mixed melting points. That they were identical was also confirmed by their UV absorption spectrum plots, shown in Fig. 1.

Since a heterocyclic azide was reacted with a Grignard compound it could be postulated that not only an azido group entered into reaction, but also nitrogen in the heterocyclic ring [5]. To check this we treated 2-methylbenzothiazole (III) with a large excess of phenyl magnesium bromide at elevated temperature. It was shown that under those conditions, part of the phenyl magnesium bromide added

Alkyl(aryl)-(2-methylbenzothiazolyl-6)triazenes



R	Spectrum constants*		Decomp temp, °C		Formula		Found, %		Calculated, %		Triazene yield, %
	λ_{max}, mμ	$\varepsilon_{max} \cdot 10^{-4}$	Triazene	Ag salt of triazene	Triazene	Ag salt of triazene	N	Ag	N	Ag	
CH_3	302	1.766	110—111	190	$C_9H_{10}N_4S$	$C_9H_9AgN_4S$	27.16, 27.44	35.06	27.16	34.45	78.1
C_2H_5	304	1.799	75—76	198	$C_{10}H_{12}N_4S$	$C_{10}H_{11}AgN_4S$	25.36; 25.41	33.00	25.43	32.72	68
n-C_3H_7	305	2.650	60—61	200	$C_{11}H_{14}N_4S$	$C_{11}H_{13}AgN_4S$	23.83; 23.96	32.01	23.91	31.61	22.6
i-C_3H_7	305	1.150	Oil	167—168	$C_{11}H_{14}N_4S$	$C_{11}H_{13}AgN_4S$	23.85; 23.91	32.12	23.91	31.61	57.3
n-C_4H_9	306	1.724	77—78	202—203	$C_{12}H_{16}N_4S$	$C_{12}H_{15}AgN_4S$	22.41; 22.45	30.60	22.56	30.36	28
i-C_4H_9	306	2.456	74—75	178—179	$C_{12}H_{16}N_4S$	$C_{12}H_{15}AgN_4S$	22.70; 22.63	30.51	22.56	30.36	40.5
n-C_5H_{11}	310	1.555	104—105	229	$C_{13}H_{18}N_4S$	$C_{13}H_{17}AgN_4S$	21.71; 21.98	29.54	21.35	29.21	37.8
i-C_5H_{11}	307	1.712	Oil	188	$C_{13}H_{18}N_4S$	$C_{13}H_{17}AgN_4S$	21.77; 21.48	29.62	21.35	29.21	61.7
$C_6H_5CH_2$	307	3.966	116	147—148	$C_{15}H_{14}N_4S$	$C_{15}H_{13}AgN_4S$	19.65; 19.67	27.68	19.85	27.44	43.2
C_6H_5	365	1.900	153—154	174	$C_{14}H_{12}N_4S$	$C_{14}H_{11}AgN_4S$	20.67; 20.96	28.36	20.88	28.73	78.5

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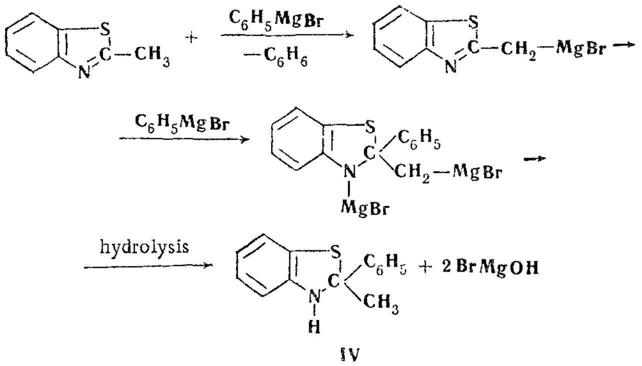
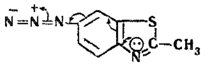
*The data given relate to the main UV absorption maxima of ethanol solutions of the triazenes.

to the nitrogen in the heterocyclic ring, according to the equations



The reaction gave a 10% yield of 2-methyl-2-phenylbenzothiazole IV. This compound had previously been syntheiszed by A. I. Kiprianov and V. A. Portnyagina [6], by condensing o-aminophenylmercaptan with acetophenone. The yield of the IV obtained was determined from the yield of its silver salt.

We did not observe participation of the heterocyclic nitrogen atom in reaction with the Grignard reagents. Obviously this is due to withdrawal of electrons from the nitrogen of the heterocyclic ring by the azido group



We investigated the optical properties of the triazenes synthesized. They all have similar UV absorption curves, characterized by the presence of three maxima. One, the most intense, lies at 302–310 mμ, and the two less intense ones at 224 and 245 mμ. Figure 2 shows the character of the curve for aliphaticaromatic triazenes for the case of ethyl (2-methylbenzthiazolyl-6)triazine. Replacement of the aliphatic group by aryl shifts the main absorption maximum towards the long wave region by 55–63 mμ. The less intense maxima were almost undisplaced, but a third maximum at 233 mμ appeared (see Fig. 1, and table).

EXPERIMENTAL*

2-Methyl-6-azidobenzothiazole (I). Prepared by the reaction of NaN_3 with diazotized 2-methyl-6-aminobenzothiazole. After recrystallizing from aqueous EtOH it formed colorless crystals, which quickly darkened in the light, decomposing at 67–68° [7].

Triazenes (II, table). A 2-fold excess of Grignard reagent of known concentration (~0.2 M) [8] was added to a solution of 2-5 g I in 10 times the amount of ether. Towards the end of the reaction a yellow precipitate formed, in the case of phenyl magnesium bromide the precipitate was bright red. The reaction products were then left for 10–12 hr at room temperature, decomposed, with ice-cooling, with a saturated solution comprising 250 ml 25% NH_4Cl solution and 25 ml 25% ammonia. The triazene was extracted with ether. The ether extract was washed a few times with water until the halogen ion reaction was negative, then dried over Na_2SO_4. After distilling off the ether the residue contained an oil, which usually, on triturating with a glass rod, gave yellow crystals. Yield of crude product almost quantitative.

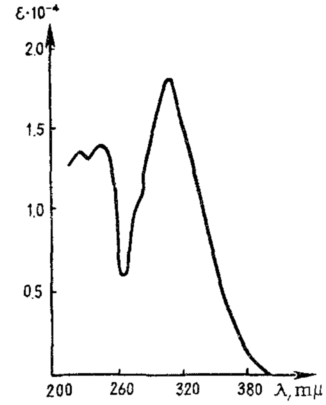


Fig. 2. UV spectrum of ethyl-(2-methylbenzothiazolyl-6)-triazene in EtOH.

Compound I and benzyl (2-methylbenthiazolyl-6) triazene were recrystallized from EtOH, the others from petrol ether or gasoline.

Silver derivatives of the triazenes. A weighed out quantity of carefully purified triazene was dissolved in EtOH, the solution made alkaline with a saturated ethanolic solution of $NaHCO_3$, and an ethanol solution of $AgNO_3$ added until precipitation was complete [9]. The precipitate was filtered off, repeatedly washed on the filter with a saturated ethanol solution of $NaHCO_3$, then with EtOH, and finally with ether, then analyzed without further crystallizing. Yield quantitative. The table gives the decomposition temperatures and analytical data for the silver salts.

Phenyl(2-methylbenzothiazolyl-6)triazene (IIa). a) A solution of 4.1 g (0.025 mole) 2-methyl-6-aminobenzothiazole in 140 ml water plus 30 ml HCl was cooled to 0° and stirred, and a solution of 2.07 g (0.03 mole) $NaNO_2$ in 25 ml water added dropwise. After 30 min 2.8 g (0.03 mole) aniline in 20 ml water was added to the diazotized solution, the mixture made acid with HCl, and a saturated solution of NaOAc (30 g) added. After 20 min the orange precipitate formed was filtered off, and washed with water. Yield of crude material quantitative. After recrystallizing from EtOH the compound formed yellowish-orange crystals, decomp 152–153°. Found: N 20.62; 20.71%. Calculated for $C_{14}H_{12}N_4S$: N 20.88%. The Ag derivative decomp 174°. Found: N 14.45; 14.68; Ag 28.81%. Calculated for $C_{14}H_{11}AgN_4S$: N 14.80; Ag 28.73%.

b) An ethanol solution of 1.7 g (0.01 mole) 2-methyl-6-aminobenzothiazole* was cooled to 0°, and a solution of 1 g (0.001 mole) diazotized aniline added. A

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*With N. P. Strizhak

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saturated solution of NaOAc (15 g) was added to the resultant solution, to neutralize the mineral acid. The precipitate was filtered off, and washed with water. Recrystallization from EtOH gave yellowish-orange crystals decomp 152–153°, yield 1.92 g (76%). Found: N 21.00; 21.20%. Calculated for $C_{14}H_{12}N_4S$: N 20.88%. Ag derivative decomp 173–174°. Found: N 14.32; 14.29; Ag 28.95%. Calculated for $C_{14}H_{11}N_4SAg$: N 14.80; Ag 28.73%.

Undepressed mixed mp with the compound obtained by methods a and b, and by the Grignard synthesis.

Reaction of 2-methylbenzothiazole (III) and phenylmagnesium bromide. 58 ml 1.6 N solution of phenylmagnesium bromide in an equal volume of dry ether was added, with constant stirring, and heating on a water-bath, and over a period of 1 hr, to 7.4 g (0.05 mole) freshly-distilled III in 50 ml dry ether. At first a white precipitate formed, and later, as reaction proceded, this turned lemon-yellow. The reaction mixture was heated on a water-bath for 20 min more, and left for 10–12 hr. Then the contents of the flask were poured into a cooled solution of NH_4Cl containing ammonia. The ether extract, after washing with water, was dried over $CaCl_2$. After distilling off the ether there remained a pale-yellow oil, consisting of 2-methylbenzothiazole (III) and 2-methyl-2-phenylbenzothiazoline (IV), yield 10%. The yield of the latter compound was determined from the yield of its Ag salt. For that purpose 1 g crude product was dissolved in 10 ml EtOH, and ethanolic ammonia solution of $AgNO_3$ added till precipitation was complete. The yellow precipitate was filtered off, repeatedly washed with EtOH, then with ether, and analyzed without further crystallization. Mp 204°, yield 0.12 g (10.6%). Found: Ag 32.61%. Calculated for $C_{14}H_{12}AgN_4S$: Ag 32.33%. Undepressed mixed mp with the Ag compound prepared as described in [6].

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