

Diazo Reactions with Unsaturated Compounds: VIII.¹ Reaction of 1,3-Butadiene and Isoprene with Aromatic and Aliphatic–Aromatic Triazenes in the Presence of Sulfur(IV) Oxide

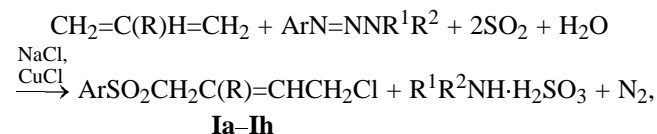
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Abstract—1,3-Butadiene and 2-methyl-1,3-butadiene react with 1,3-diphenyltriazene, 1,3-di-*p*-tolyltriazene, and 1-aryl-3,3-dimethyl-1-triazenes in a sulfur(IV) oxide-saturated water-acetic acid-acetone solution containing NaCl or hydrochloric acid, and catalytic amounts of copper(I) chloride to form 1,4-arylsulfonyl-chlorination products.

It is known [2] that 1,3-butadiene (divinyl) and 2-methyl-1,3-butadiene (isoprene) in a sulfur(IV) oxide acetic acid-acetone solution in the presence of catalytic amounts of copper(I) chloride react with arenediazonium chlorides to form chloroarylsulfonylation products. Proceeding with these investigations, we found that divinyl and isoprene react with 1,3-diphenyl-, 1,3-di-*p*-tolyl-, and 1-aryl-3,3-dimethyl-1-triazenes in similar conditions in the presence of NaCl or hydrochloric acid, yielding the same δ -haloarylsulfonylalkenes. The reactions occur at 5–10°C in a complex catalytic system comprising acetone, water, acetic acid, NaCl or HCl, and copper(I) chloride. The system is saturated with sulfur(IV) oxide. Nitrogen is evolved from the triazene group, and arylsulfonyl radicals and chlorine atoms add to the diene conjugated double bond system.

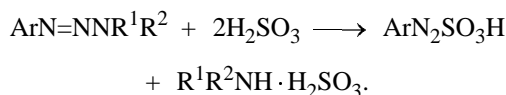


R = H, CH₃; R¹ = H, R² = C₆H₅; R¹ = H, R² = *p*-CH₃C₆H₄;
R¹ = R² = CH₃; Ar = C₆H₅, *p*-CH₃C₆H₄, *p*-ClC₆H₄,
p-BrC₆H₄, *p*-O₂NC₆H₄.

The reactions with 1,3-butadiene gave 1-arylsulfonyl-4-chloro-2-butenes **Ia–Ic** and the reactions with isoprene, 1-arylsulfonyl-4-chloro-2-methyl-2-butenes **Id–Ih** (see table). Along with products **Ia–Ih**, from

the aqueous layer of the reaction mixture with 1,3-diphenyltriazene, preliminarily neutralized with sodium bicarbonate, we isolated aniline, and after the reactions with 1,3-di-*p*-tolyltriazene and 1-aryl-3,3-dimethyl-1-triazenes, *p*-toluidine and dimethylamine, respectively.

Most probably, the reaction involves the following processes. Arenetriazenes react with the sulfurous acid present in the reaction mixture to form arenediazonium and ammonium salts.



Similar decomposition of aromatic and aliphatic–aromatic triazenes under the action of other acids has been described in [3–5].

Arenediazonium hydrosulfites in aqueous medium enter exchange reaction with NaCl and convert into arenediazonium chlorides, and the latter in the presence of copper(I) chloride decompose to form aromatic radicals [6–11]. The aromatic radicals react with sulfur oxide [12–15] to give arylsulfonyl radicals, and the latter react with the diene hydrocarbon.

Our experiments showed that the higher is the basicity of the triazene, the higher is its reactivity to 1,3-butadiene and isoprene. Thus aliphatic–aromatic triazenes proved more reactive than aromatic whose basicity is lower [3]. For this reason, the yields of compounds **Id** and **Ie** are much higher from 3,3-dimethyl-1-phenyl-1-triazene and 3,3-dimethyl-1-*p*-tolyl-1-triazene than from 1,3-diphenyltriazene and

¹ For communication VII, see [1].

Constants, yields, and elemental analyses of 1-arylsulfonyl-4-chloro-2-butenes and 1-arylsulfonyl-4-chloro-2-methyl-2-butenes $\text{ArSO}_2\text{CH}_2\text{C}(\text{R})=\text{CHCH}_2\text{Cl}$ **Ia–Ih**^a

Comp. no.	R	Ar	Yield, %	mp, °C	IR spectrum, ν , cm^{-1}	
					C=C	SO ₂
Ia	H	<i>p</i> -ClC ₆ H ₄	47	67.5–68	970, 1620	1160, 1310
Ib	H	<i>p</i> -BrC ₆ H ₄	50.5	82–82.5	970, 1620	1160, 1310
Ic	H	<i>p</i> -O ₂ NC ₆ H ₄	60	142–143	970, 1620	1160, 1310
Id	CH ₃	C ₆ H ₅	65	72–73	1000, 1660	1160, 1310
Ie	CH ₃	<i>p</i> -CH ₃ C ₆ H ₄	47	84–85	1000, 1660	1160, 1310
If	CH ₃	<i>p</i> -ClC ₆ H ₄	59	78–79	1000, 1620	1160, 1310
Ig	CH ₃	<i>p</i> -BrC ₆ H ₄	52	99–99.5	–	–
Ih	CH ₃	<i>p</i> -O ₂ NC ₆ H ₄	62	137	1000, 1620	1145, 1310

Comp. no.	Found, %		Formula	Calculated, %	
	Cl+(Cl + Br)	N		Cl+(Cl + Br)	N
Ia	26.63, 26.91	5.18, 5.21	C ₁₀ H ₁₀ Cl ₂ O ₂ S	26.74	5.08
Ib	(37.37), (37.44)		C ₁₀ H ₁₀ BrClO ₂ S	(37.26)	
Ic			C ₁₀ H ₁₀ ClNO ₄ S		
Id	14.68, 14.27	5.00, 4.71	C ₁₁ H ₁₃ ClO ₂ S	14.49	4.83
Ie	13.82, 14.01		C ₁₂ H ₁₅ ClO ₂ S	13.70	
If	25.40, 25.57		C ₁₁ H ₁₂ Cl ₂ O ₂ S	25.20	
Ig	(35.28), (35.81)		C ₁₁ H ₁₂ BrClO ₂ S	(35.64)	
Ih			C ₁₁ H ₁₂ ClNO ₄ S		

^a For published data, see [2].

1,3-di-*p*-tolyltriazene, respectively. 3,3-Dimethyl-1-(*p*-nitrophenyl)-1-triazene which is much less basic due to the presence of the nitro group is more reactive than other 1-aryl-3,3-dimethyl-1-triazenes [3] and reacts only if HCl is added to the reaction mixture instead of aqueous NaCl. The copper(II) chloride catalyst that is reduced in the reaction mixture with sulfur(IV) oxide to copper(I) chloride was introduced in reaction in an amount of 0.1 mol per 1 mol of triazene.

The structures of compounds **Ia–Ih** were proved by their IR spectra. The latter contain strong bands of the sulfonyl group at 1160 and 1310 cm^{-1} and weak bands of the unconjugated double bond at 1620–1660 cm^{-1} . The lack in the spectra of bands at 905–908 cm^{-1} suggest 1,4 addition of arylsulfonyl radicals and chlorine atom to the diene hydrocarbon. The strong band near 970 cm^{-1} in the spectra of compounds **Ia–Ic** points to a *trans* structure of the CH=CH fragments.

Compound **Id** was synthesized independently from isoprene and phenylsulfonyl chloride by the procedure in [16] and by isoprene chlorophenylsulfonylation [2].

EXPERIMENTAL

The IR spectra were synthesized on a UR-20 spectrophotometer in KBr.

1,3-Diphenyltriazene was synthesized by azo coupling of benzenediazonium with aniline, and 1,3-di-*p*-tolyltriazene and 1-aryl-3,3-dimethyl-1-triazenes, by azo coupling of *p*-methylbenzenediazonium chloride with *p*-toluidine and of arenediazonium chlorides with dimethylamine [3], respectively.

4-Chloro-1-(*p*-nitrophenylsulfonyl)-2-butene (Ic). Acetone, 24 ml, was mixed with 24 ml of glacial acetic, 8 ml of water, 28 ml of conc. HCl, and 0.68 g of copper(I) chloride. The resulting solution was cooled to -18°C and saturated with sulfur(II) oxide prepared from 52 g of sodium sulfite and conc. HCl, and then with 1.8 l of 1,3-butadiene. After the saturation had been complete, the temperature of the reaction mixture was raised to 15°C , and 7.8 g of 3,3-dimethyl-1-(*p*-nitrophenyl)-1-triazene was added to it in small portions. Uniform gas evolution was observed at 0 – 5°C . When the reaction had been complete, the reaction mixture was poured into 300 ml of water.

The crystals that formed were separated and recrystallized from ethanol–water, 2:1.

1-(*p*-Chlorophenylsulfonyl)- and 1-(*p*-Bromophenylsulfonyl)-4-chloro-2-butenes (Ia, Ib) were prepared similarly to sulfone **Ic** using a solution of 4.8 g of NaCl in 24 ml of water instead of HCl and 7.4 g of 1-(*p*-chlorophenyl)-3,3-dimethyl-1-triazene and 9.2 g of 1-(*p*-bromophenyl)-3,3-dimethyl-1-triazene, respectively, instead of 3,3-dimethyl-1-(*p*-nitrophenyl)-1-triazene. Compound **Ia** was purified by crystallization from ethanol–water, 1:1, and compound **Ib**, from acetic acid–water, 1:1.

4-Chloro-2-methyl-1-(phenylsulfonyl)-2-butene (Id). *a.* Acetone, 24 ml, was mixed with 24 ml of glacial acetic acid, 24 ml of water, and 0.68 g of copper(I) chloride. The resulting solution was saturated with sulfur(IV) oxide as described for sulfone **Ic**. After the saturation had been complete, 4.8 g of powdered NaCl and 8 ml of isoprene. The temperature of the reaction mixture was raised to 10°C, and 6 g of 3,3-dimethyl-1-phenyl-1-triazene was added to it. Uniform gas evolution was observed at 10–15°C. After the reaction had been complete, the reaction mixture was poured into 300 ml of water. The crystals that formed were separated and recrystallized from ethanol–water, 1:1.

b. 1,3-Diphenyltriazene, 7 g, was added in small portions to the same reaction mixture as that described in procedure *a*. Gas evolution was observed at 5–10°C. Compound **Id**, 2.5 g (35%), was obtained and purified as in procedure *a*.

4-Chloro-1-(phenylsulfonyl)-2-methyl-2-butene was also obtained independently by the reaction of 3.6 g of phenylsulfonyl chloride, 2.5 ml of isoprene, 2 g of triethylamine hydrochloride, and 2 g of copper(I) chloride in 10 ml of acetonitrile (yield 1 g), as well as by isoprene chlorophenylsulfonylation [2]. Mixed samples of sulfone **Id** with compounds obtained by independent synthesis showed no melting point depression.

1-(Arylsulfonyl)-4-chloro-2-methyl-2-butenes **Ie–Ig** were prepared similarly to sulfone **Id** using, instead of 3,3-dimethyl-1-phenyl-1-triazene, 6.6 g of 3,3-dimethyl-1-*p*-tolyl-1-triazene, 7.4 g of 1-(*p*-chlorophenyl)-3,3-dimethyl-1-triazene, and 9.2 g of 1-(*p*-bromophenyl)-3,3-dimethyl-1-triazene, respectively. The products were purified by recrystallization from acetic acid–water, 1:1.

4-Chloro-1-(*p*-nitrophenylsulfonyl)-2-methyl-2-butene (Ih) were prepared similarly to sulfone **Ic** using 6.4 ml of isoprene instead of 1,3-butadiene and purified by recrystallization from ethanol–water, 1:1.

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