Diazo Reactions with Unsaturated Compounds: XI.¹ Reactions of Benzene-, p-Methylbenzene-, and p-Methoxybenzenesulfonyl-1,3-butadienes with Arenediazonium Chlorides and 1-Aryl-3,3-dimethyl-1-triazenes

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Received July 19, 2005

Abstract—1-(*p*-Methylbenzene)- and 1-(*p*-methoxybenzenesulfonyl)-1,3-butadienes in aqueous acetone in the presence of copper(I) or copper(II) chlorides react with arenediazonium chlorides and 1-aryl-3,3-dimethyl-1-triazenes to form 1-(*p*-methylbenzene)- and 1-(*p*-methoxybenzenesulfonyl)-4-aryl-3-chloro-1-butenes, respectively. 1-(Benzenesulfonyl)-1,3-butadiene undergoes tarring under the same conditions. **DOI:** 10.1134/S1070363206080238

We previously showed [1-3] that 1-(*p*-nitrobenzene)-1-(*m*-nitrobenzene)-, 1-(*p*-chlorobenzene)-, and 1-(*p*-bromobenzenesulfonyl)-1,3-butadienes react with arenediazonium chlorides and 1-aryl-3,3-dimethyl-1-triazenes to form the corresponding chloroarylation products.

Proceeding with these studies, we found that 1-(benzenesulfonyl)-1,3-butadiene is reactions with

arenediazonium chlorides and 1-aryl-3,3-dimethyl-1triazenes undergoes complete tarring, whereas 1-(*p*methylbenzene)- and 1-(*p*-methoxylbenzenesulfonyl)-1,3-butadienes are chloroarylated by a double bond the most remote from the arenesulfonyl group to form 1-(*p*-methylbenzene)- (**Ia**–**Ie**) and 1-(*p*-methoxybenzenesulfonyl)-4-aryl-3-chloro-1-butenes (**If**–**Ik**) (see table).

$$\begin{split} R^{1}C_{6}H_{4}SO_{2}CH=CH-CH=CH_{2} + p \cdot R^{2}C_{6}H_{4}N_{2}Cl \\ \downarrow \\ R^{1}C_{6}H_{4}SO_{2}CH=CH-CHCl-CH_{2}C_{6}H_{4}R^{2} \cdot p + N_{2} \\ \uparrow_{-(CH_{3})_{2}NH \cdot HCl} \\ R^{1}C_{6}H_{4}SO_{2}CH=CH-CH=CH_{2} + p \cdot R^{2}C_{6}H_{4}N=NN(CH_{3})_{2} + 2HCl \\ R^{1} = p \cdot CH_{3}, \ p \cdot CH_{3}O; \ R^{2} = H \ (\textbf{a, f}), \ CH_{3} \ (\textbf{b, g}), \ Br \ (\textbf{c, h}), \ Cl \ (\textbf{d, j}), \ O_{2}N \ (\textbf{e, k}). \end{split}$$

The reactions with arenediazonium chlorides and 1-aryl-3,3-dimethyl-1-triazenes occur in aqueous acetone in the presence of CuCl or $CuCl_2$ at $30-32^{\circ}C$, yielding aryl chlorides, along with compounds **Ia–Ik**. With 1-aryl-3,3-dimethyl-1-triazenes, dimethylamine hydrochloride is formed together with the two mentioned products. Most probably, 1-aryl-3,3-dimethyl-

1-triazenes first react with HCl and decompose to form arenediazonium chlorides that then react with the unsaturated compounds.

The yields of products **Ia**, **Ib**, **Id**, and **Ie** are higher than those of **If**, **Ig**, **Ii**, and **Ik**, probably because of the stronger tendency of 1-(*p*-methoxybenzenesulfonyl)-1,3-butadiene for tarring compared to 1-(*p*methylbenzenesulfonyl)-1,3-butadiene. With arenediazonium chlorides instead of 1-aryl-3,3-dimethyl-1-

¹ For communication X, see [1].

Comp. no.	Yields, %					
	with triazenes ^b	with diazonium chlorides ^c	mp, °C	Found, %	Formula	Calculated, %
Ia ^d	24	19	68–69	Cl 10.88, 10.96	C ₁₇ H ₁₇ ClO ₂ S	Cl 11.05
Ib	46	37	102-103	Cl 10.30, 10.41	$C_{18}H_{19}ClO_2S$	Cl 10.59
Ic	38	30	80-81	Cl+Br 28.94, 28.96	$C_{17}H_{16}BrClO_2S$	Cl+Br 28.86
Id	47	38	86-87	Cl 19.78, 19.84	$C_{17}H_{16}Cl_2O_2S$	Cl 19.96
Ie	23	18	74–74.5	N 3.64, 3.72	$C_{17}H_{16}CINO_4S$	N 3.83
				Cl 9.45, 9.48	1, 10	Cl 9.69
If	15	11	63–64	Cl 10.28, 10.34	C ₁₇ H ₁₇ ClO ₃ S	Cl 10.52
Ig	20	14	72–72.5	Cl 9.96, 10.00	$C_{18}H_{19}ClO_3S$	Cl 10.10
Ih ^e	38	31	102-102.5	Cl+Br 27.83, 27.86	C ₁₇ H ₁₆ BrClO ₃ S	Cl+Br 27.75
Ij	31	24	89–90	Cl 18.98, 19.01	$C_{17}H_{16}Cl_2O_3S$	Cl 19.09
				N 3.42, 3.50		Cl 9.28
Ik	16	13	80-81	Cl 9.12, 9.26	C ₁₇ H ₁₆ CINO ₅ S	N 3.67

Constants, yields, and elemental analyses of compounds $p-R^1C_6H_4SO_2CH=CH-CHCl-CH_2C_6H_4R^2-p$ formed by chloro-arylation of 1-(*p*-methylbenzenesulfonyl)- and 1-(*p*-methoxylbenzenesulfonyl)-1,3-butadienes^a

^a Compounds **Ia–Ie** were purified by crystallization from ethanol–water, 2:1; compounds **If–Ik** were crystallized from acetic acid–water, 1:1. ^b 1-Aryl-3,3-dimethyl-1-triazenes. ^c Arenediazonium chlorides. ^d ¹H NMR spectrum, δ , ppm: 2.459 s (3H, CH₃C₆H₄), 3.145–3.181 m (2H, CH₂), 4.645–4.664 d.d (1H, CH, J_1 6, J_2 7.2 Hz), 6.458–6.497 d (1H, CH, J 13.6 Hz), 6.919–6.972 d.d (1H, CH, J_1 6.4, J_2 14.8 Hz), 7.145–7.167 d (2H, p-CH₃C₆H₄, J 8.8 Hz), 7.260–7.350 m (5H, C₆H₅), 7.691–7.711 d (2H, p-CH₃C₆H₄, J 8 Hz). ^e ¹H NMR spectrum, δ , ppm: 3.103–3.129 d.d (2H, CH₂, J_1 3.6, J_2 6.8 Hz), 6.419–6.459 d.d (1H, CH, J_1 1.2, J_2 14.8 Hz), 6.846–6.900 d.d (1H, CH, J_1 6.8, J_2 14.8 Hz), 7.006–7.033 m (4H, CH₃OC₆H₄), 7.381–7.42 d.d (2H, p-BrC₆H₄, J_1 1.6, J_2 6.4 Hz), 7.706–7.728 d.d (2H, p-BrC₆H₄, J_1 2, J_2 6.8 Hz).

triazenes, the yields of chloroarylation products are higher, whereas the yields of tarry and Sandmeyer reaction products are lower.

It should be noted that 1-(benzenesulfonyl)-, 1-(p-methylbenzenesulfonyl), and 1-(p-methoxylbenzenesulfonyl)-1,3-butadienes, unlike 1-(p-nitrobenzenesulfonyl)-, 1-(m-nitrobenzenesulfonyl), and 1-(o-nitrobenzenesulfonyl)-1,3-butadienes [2], proved to be highly reactive compounds. They undergo chemical transformations on storage, heating, and on vacuum distillation of the solvents from their benzene, acetone, and ether solutions. Bearing this in mind, we brought 1-(benzenesulfonyl)-, 1-(p-methylbenzenesulfonyl)-, and 1-(p-methoxylbenzenesulfonyl)-1,3-butadienes in reaction without preliminary purification.

1-(Benzenesulfonyl)-, 1-(*p*-methylbenzenesulfonyl)-, and 1-(*p*-methoxylbenzenesulfonyl)-1,3-butadienes undergo complete tarring when heated with maleic anhydride. For this reason, we failed to obtain adducts of these dienes with this anhydride.

The proposed structures of compounds **Ia** and **Ih** are nicely consistent with the ¹H NMR spectra that show ethylene proton signals appearing as a doublet at

6.458–6.497 ppm and a doublet of doublets at 6.919– 6.972 ppm for compound **Ia** or a doublet of doublets at 6.419–6.459 ppm and a doublet of doublets at 6.846–6.900 ppm for compound **Ih**. The >CHCl proton signal is a doublet of doublets 4.645–4.664 ppm for compound **Ia** and a doublet of doublets at 4.607–4.627 ppm for compound **Ih**.

In the presence of sulfur(IV) oxide, 1-(benzenesulfonyl)-, 1-(*p*-methylbenzenesulfonyl)-, and 1-(*p*methoxylbenzenesulfonyl)-1,3-butadienes fail to react both with arenediazonium chlorides and with 1-aryl-3,3-dimethyl-1-triazenes under the conditions of chloroarylsulfonylation of unsaturated compounds [4].

EXPERIMENTAL

The ¹H NMR spectra were obtained on a Varian-Gemini-400 spectrometer in CDCl₃.

1-Aryl-3,3-dimethyl-1-triazenes were prepared by azo coupling of the corresponding arenediazonium chlorides with dimethylamine [5].

4-Chloro-1-(benzenesulfonyl)-2-butene was prepared similarly to 4-chloro-1-(*p*-nitpobenzenesul-

fonyl)-2-butene [4] by the reaction of 2.3 l of butadiene with a solution of diazonium salt, prepared from 4.5 ml of aniline, 17 ml of conc. HCl, and 3.6 g of sodium nitrite and neutralized to pH 3–4 with NaHCO₃. When gaseous products no longer evolved, the reaction mixture was poured into 300 ml of water, and the organic layer was treated with ether. The ethereal extract was washed with water and dried with Na₂SO₄. The ether was then removed, and the residue was distilled in a vacuum to obtain 4.9 g (43%) of a light yellow liquid, bp 140–144°C (10⁻² mm Hg), n_D^{20} 1.5590 [6].

4-Chloro-1-(*p*-methylbenzenesulfonyl)-2-butene was prepared in a similar way by the reaction of a solution of diazonium salt prepared from 5.35 g of *p*-toluidine, 17 ml of conc. HCl, and 3.6 g of sodium nitrite, neutralized to pH 3–4 with NaHCO₃, with 2.3 l of butadiene. When gaseous products no longer evolved, the reaction mixture was poured into 400 ml of water. A precipitate formed and was separated and crystallized from ethanol–water, 1:1, to obtain 3.3 g (27%) of colorless crystals, mp 66–67°C. Found Cl, %: 14.26, 14.30. C₁₁H₁₃ClO₂S. Calculated Cl, %: 14.48.

4-Chloro-1-(*p*-methoxylbenzenesulfonyl)-2butene was prepared similarly to 4-chloro-1-(*p*-methylbenzenesulfonyl)-2-butene by the reaction of a solution of arenediazonium salt prepared from 6.15 g of *p*-anisidine, 17 ml of conc. HCl, and 3.6 g of sodium nitrite with 2.3 l of butadiene. Yield 2.7 g (21%), colorless crystals, mp 61–61.5°C (from acetic acid–water, 1:2). Found Cl, %: 13.42, 13.54. $C_{11}H_{13}ClO_3S$. Calculated Cl, %: 13.59.

1-(Benzenesulfonyl)-1,3-butadiene. A solution of 6.9 ml of triethylamine in 10 ml of acetone was added in small portions to a solution of 11.52 g of 4-chloro-1-(benzenesulfonyl)-2-butene in 50 ml of acetone. A precipitate of triethylamine hydrochloride formed. The reaction mixture was allowed to stand for 30 min at room temperature, the precipitate was filtered off, and the acetone solution was poured into 400 ml of water. The oily material that formed was crystallized from hexane under dry ice cooling. Yield 73% (besed on triethylamine hydrochloride). Melts at room temperature [4]. Found S, %: 16.32, 16.41. C₁₀H₁₀O₂S. Calculated S, %: 16.50.

1-(*p***-Methylbenzenesulfonyl)-1,3-butadiene** was prepared similarly to 1-(benzenesulfonyl)-1,3-butadiene by the reaction of 12.23 g of 4-chloro-1-(*p*-methylbenzenesulfonyl)-2-butene with 6.9 ml of triethylamine and isolated by crystallization from hexane under dry ice cooling. Yield 87% (besed on triethyl-

amine hydrochloride). Melts at room temperature. Found S, %: 15.20, 15.25. $C_{10}H_{12}O_2S$. Calculated S, %: 15.39.

1-(*p***-Methoxylbenzenesulfonyl)-1,3-butadiene** was prepared and isolated in a similar way by the reaction of 13.03 g of 4-chloro-1-(*p*-methoxylbenzene-sulfonyl)-2-butene with 6.9 ml of triethylamine. Yield 83% (based on triethylamine hydrochloride). Melts at room temperature. Found S, %: 14.02, 14.16. $C_{11}H_{12} \cdot O_3S$. Calculated S, %: 14.29.

3-Chloro-1-(*p*-methylbenzenesulfonyl)-4-phenyl-**1-butene (Ia).** *a*. Copper(I) chloride, 0.85 g, and 9.5 g of 3,3-dimethyl-1-phenyl-1-triazene were added to an acetone solution of 1-(p-methylbenzenesulfonyl)-1,3butadiene prepared as described above from 12.23 g of 4-chloro-1-(*p*-methylbenzenesulfonyl)-2-butene. The reaction mixture was heated to 30°C, after which 25 ml of 15% HCl was added with vigorous stirring so that gaseous products evolved evenly. The temperature of the reaction mixture was maintained at $30-32^{\circ}$ C. After the addition of HCl had been complete, the reaction mixture was stirred until gases no longer evolved and then poured into 400 ml of water. The crystals that formed were separated and crystallized from ethanol–water, 2:1.

b. Copper(II) chloride, 2 g, was added to an acetone solution of 1-(*p*-methylbenzenesulfonyl)-1,3butadiene prepared as described in procedure *a*. A solution of benzenediazonium chloride prepared from 4.55 ml of aniline, 17 ml of conc. HCl, and 3.6 g sodium nitrite, neutralized to pH 3–4 with NaHCO₃, was then added with vigorous stirring. The reaction mixture was stirred until gases no longer evolved. The products were isolated as described in procedure *a*.

3-Chloro-1-(*p***-methoxylbenzenesulfonyl)-4phenyl-1-butene (If)** was prepared similarly to compound **Ia** from 1-(*p*-methoxylbenzenesulfonyl)-1,3butadiene obtained by dehydrochlorination of 13.03 g of 4-chloro-1-(*p*-methoxylbenzenesulfonyl)-2-butene with triethylamine, like with 1-(*p*-methylbenzenesulfonyl)-1,3-butadiene.

Compounds **Ib**, **Ic**, **Id**, **Ig**, **Ih**, and **Ij** were prepared similarly to **Ia**, using 15 ml of conc. HCl instead of 15% HCl, and 11.5 g of 1-(*p*-chlorophenyl)-3,3-dimethyl-1-triazene and 14.25 g of 1-(*p*-bromophenyl)-3,3-dimethyl-1-triazene, respectively.

Sulfones **Ie** and **Ik** were prepared similarly to **Ic**, **Id**, **Ih**, and **Ij**, using a mixture of 64 ml of conc. HCl and 14 ml of conc. H_2SO_4 instead of conc. HCl.

RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 76 No. 8 2006

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