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Diazo Reactions with Unsaturated Compounds: XIII.¹ Reactions of *p*-(Buta-1,3-dien-1-ylsulfonyl)benzenesulfonamide with Arenediazonium Chlorides, 1-Aryl-3,3-dimethyltriaz-1-enes, and Arenediazonium Tetrachlorocuprates(II)

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Abstract—p-(Buta-1,3-dien-1-ylsulfonyl)benzenesulfonamide reacted with arenediazonium chlorides, 1-aryl-3,3-dimethyltriaz-1-enes, and arenediazonium tetrachlorocuprates(II) in aqueous acetone in the presence of copper(II) chloride to give the corresponding p-(4-aryl-3-chlorobut-1-en-1-ylsulfonyl)benzenesulfonamides.

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We previously showed [1–4] that 1-(*p*-nitrophenylsulfonyl)-, 1-(*m*-nitrophenylsulfonyl)-, 1-(*p*chlorophenylsulfonyl)-, 1-(*p*-bromophenylsulfonyl)-, 1-(*p*-methylphenylsulfonyl)-, 1-(*p*-methoxyphenylsulfonyl)-, and 1-(*p*-carboxyphenylsulfonyl)buta-1,3dienes react with arenediazonium chlorides and 1-aryl-3,3-dimethyltriaz-1-enes to give the corresponding chloroarylation products.

In the present study we found that *p*-(buta-1,3-dien-1-ylsulfonyl)benzenesulfonamide reacted with arenedi-

azonium chlorides, 1-aryl-3,3-dimethyltriaz-1-enes, and arenediazonium tetrachlorocuprates(II) in a similar way to produce p-(4-aryl-3-chlorobut-1-en-1-ylsulfonyl)benzenesulfonamides **Ia–Ie** (Scheme 1, Table 1) as a result of addition of chlorine and aryl group at the double bond most distant from the sulfonyl group. The reactions of p-(buta-1,3-dien-1-ylsulfonyl)benzenesulfonamide with arenediazonium tetrachlorocuprates(II) were carried out in aqueous acetone at 32–34°C, and the reactions with arenediazonium chloride and 1-aryl-3,3-dimethyltriaz-1-enes occurred under analogous



For communication XII, see [1].

 Comp.
 Yield, %
 mp, °C
 Found, %
 Calculated, %

 No
 Yield, %
 The product of p - (buta-1,3-dien-1-ylsulfonyl)

Comp. no.	Yield, %	mp, °C	Found, %		E	Calculated, %	
			N	Hlg	Formula	Ν	Hlg
Ia	47 (<i>a</i>), 64 (<i>b</i>), 70 (<i>c</i>)	185–186	3.72	9.32	$C_{16}H_{16}ClNO_4S_2$	3.63	9.19
Ib	43 (<i>a</i>), 51 (<i>b</i>), 54 (<i>c</i>)	149–150	3.60	8.90	$C_{17}H_{18}ClNO_4S_2$	3.50	8.87
Ic	36 (<i>a</i>), 37 (<i>b</i>), 40 (<i>c</i>)	189.5–190.5	3.06	24.91	$C_{16}H_{15}BrClNO_4S_2$	3.01	24.82
Id	35 (<i>a</i>), 39 (<i>b</i>), 39 (<i>c</i>)	158–159	3.45	16.77	$C_{16}H_{15}Cl_2NO_4S_2$	3.33	16.87
Ie	24 (<i>a</i>), 29 (<i>b</i>), –	195–196	6.45	8.29	$C_{16}H_{15}ClN_2O_6S_2$	6.50	8.23

Table 2. ¹H NMR spectra of *p*-(4-aryl-3-chlorobut-1-en-1-ylsulfonyl)benzenesulfonamides Ia–Ie

Comp. no.	Chemical shifts δ , ppm (<i>J</i> , Hz)				
Ia	3.13-3.26 m (2H, CH ₂), 5.05 d.d (1H, CH), 6.95–7.05 m (2H, CH), 7.17–7.24 m (5H, C ₆ H ₅), 7.67 s (2H, NH ₂), 7.95 d (2H, C ₆ H ₄ , $J = 8.5$), 8.03d (2H, C ₆ H ₄ , $J = 8.5$)				
Ib	2.22 s (2H, CH ₃), 3.08–3.20 m (2H, CH ₂), 5.00 d.d (1H, CH), 6.94 d (1H, CH, $J = 15$), 7.00 t (3H, CH, C ₆ H ₅ , $J = 8.5$, 8.5), 7.06 d (2H, C ₆ H ₄ , $J = 8.0$), 7.65 s (2H, NH ₂), 7.95 d (2H, p -H ₂ NSO ₂ C ₆ H ₄ , $J = 8.5$), 8.03 d (2H, p -H ₂ NSO ₂ C ₆ H ₄ , $J = 8.0$)				
Ic	3.09-3.27 m (2H, CH ₂), $5.05 d.d$ (1H, CH), $6.99-7.07 m$ (2H, CH), $7.18 d$ (2H, <i>p</i> -BrC ₆ H ₄ , <i>J</i> = 8.0), $7.45 d$ (2H, <i>p</i> -BrC ₆ H ₄ , <i>J</i> = 8.0), $7.64 s$ (2H, NH ₂), $8.00 d$ (2H, C ₆ H ₄ , <i>J</i> = 9.0), $8.06 d$ (2H, C ₆ H ₄ , <i>J</i> = 8.0)				
Id	3.11–3.29 m (2H, CH ₂), 5.05 d.d (1H, CH, <i>J</i> = 6.5, 6.0), 6.99–7.07 m (2H, CH), 7.24 d (2H, <i>p</i> -ClC ₆ H ₄ , <i>J</i> = 8.5), 7.31 d (2H, <i>p</i> -ClC ₆ H ₄ , <i>J</i> = 8.5), 7.65 s (2H, NH ₂), 7.99 d (2H, C ₆ H ₄ , <i>J</i> = 8.5), 8.06 d (2H, C ₆ H ₄ , <i>J</i> = 8.5)				
Ie	3.23-3.48 m (2H, CH ₂), $5.16 d.d$ (1H, CH), $7.63 s$ (2H, NH ₂), $7.09 d$ (2H, CH), $7.53 d$ (2H, C ₆ H ₄ , $J = 7.5$), $8.05 d$ (4H, C ₆ H ₄ , p -O ₂ NC ₆ H ₄), $8.15 d$ (2H, p -O ₂ NC ₆ H ₄ , $J = 8.0$)				

conditions in the presence of copper(II) chloride. In the latter case (with 1-aryl-3,3-dimethyltriaz-1-enes) hydrochloric acid was also added to the reaction mixture. Apart from compounds **Ia–Ie**, the corresponding aryl chlorides were also formed, while the reactions with 1-aryl-3,3-dimethyltriaz-1-enes were accompanied by formation of dimethylamine hydrochloride as well. Most probably, 1-aryl-3,3-dimethyltriaz-1-enes react initially with hydrochloric acid to give arenediazonium chlorides which then react with the diene.

The yields of **Ia–Id** in the reactions of p-(buta-1,3dien-1-ylsulfonyl)benzenesulfonamide with arenediazonium tetrachlorocuprates(II) were higher than in the reactions of the same diene with 1-aryl-3,3-dimethyltriaz-1-enes. The lowest yields of compounds **Ia–Ie** were obtained in the reactions of p-(buta-1,3dien-1-ylsulfonyl)benzenesulfonamide with arenediazonium chlorides.

The assumed structure of compounds **Ia–Ie** was well consistent with their ¹H NMR spectra (Table 2) which clearly displayed signals from protons at the double bond as a multiplet at δ 6.95–7.05 (**Ia**), doublet

at 6.94 (**Ib**), multiplet at 6.99–7.07 (**Ic**, **Id**), or doublet at 7.09 ppm (**Ie**). The CHCl proton signal appeared as a doublet of doublets at δ 5.05 (**Ia–Id**) or 5.16 ppm (**Ie**). Large spin–spin coupling constants for protons at the double bond (**Ib**, J = 15 Hz) indicate *trans* orientation of these protons.

EXPERIMENTAL

The ¹H NMR spectra were recorded on a Varian Gemini-400 spectrometer from solutions in DMSO- d_6 . Initial 1-aryl-3,3-dimethyltriaz-1-enes were synthesized by azo coupling of the corresponding arenediazonium chlorides with dimethylamine [5]. Arenediazonium tetrachlorocuprates(II) were prepared according to the procedure described in [6].

4-(4-Chlorobut-2-en-1-ylsulfonyl)benzenesulfonamide was synthesized in a way similar to the synthesis of 4-chloro-1-(*p*-nitrophenylsulfonyl)but-2ene [7] by reaction of 2.3 l of gaseous buta-1,3-diene with a solution of diazonium salt prepared from 8.6 g of 4-aminobenzenesulfonamide. Yield 9.2 g (59.5%), white crystals, mp 200–201°C (from ethanol–water, 1:2). ¹H NMR spectrum, δ , ppm: 4.16 d (2H, CH₂), 4.24 d (2H, CH₂), 5.74–5.79 m (2H, CH), 7.65 s (2H, NH₂), 8.04 s (4H, C₆H₄). Found, %: N 4.69, 4.76. C₁₀H₁₂CINO₄S₂. Calculated: N 4.52%.

4-(Buta-1.3-dien-1-vlsulfonvl)benzenesulfonamide. A solution of 6.9 ml of triethylamine in 20 ml of benzene was added in small portions to a solution of 15.5 g 4-(4-chlorobut-2-en-1-ylsulfonyl)benzenesulfonamide in 130 ml of benzene, and the mixture was heated for 3 h at 70-80°C on a water bath. The precipitate of triethylamine hydrochloride was filtered off, the filtrate was evaporated under reduced pressure, and the precipitate was separated and recrystallized from ethanol-water (1:2). Yield 6.5 g (47.6%), white crystals, mp 184–185°C. ¹H NMR spectrum, δ, ppm: 4.92 s (2H, NH₂), 5.68d (1H, CH, J = 9.0 Hz), 5.80 d (1H, CH, J = 17.0 Hz), 6.37-6.44 m (2H, CH₂),7.32d.d (1H, CH, J = 11.0, 11.5 Hz), 8.05 d (2H, C₆H₄, J = 8.0 Hz), 8.10 d (2H, C₆H₄, J = 7.5 Hz). Found, %: N 4.93, 5.02. C₁₀H₁₁O₄S. Calculated: N 5.12%.

4-(Aryl-3-chlorobut-1-en-1-ylsulfonyl)benzenesulfon-amides Ia-Ie (general procedures). a. A threenecked flask was charged with 60 ml of acetone, 10 ml of water, 1.6 g of copper(II) chloride, and 10.92 g of 4-(buta-1,3-dien-1-ylsulfonyl)benzenesulfonamide, the mixture was heated to 30-32°C, and a solution of arenediazonium chloride prepared from 0.04 mol of the corresponding aromatic amine, 13.6 ml of concentrated hydrochloric acid, and 2.9 g of sodium nitrite was added dropwise under continuous stirring. Solutions of benzene-, 4-methylbenzene-, 4-chlorobenzene-, and 4-bromobenzenediazonium chlorides were preliminarily neutralized to pH 3-4 by adding NaHCO₃. When the addition of arenediazonium salt was complete, the mixture was stirred until gaseous products no longer evolved and poured into 300 ml of water. The precipitate was filtered off and purified by recrystallization from aqueous ethanol (1:1).

b. The corresponding 1-aryl-3,3-dimethyltriz-1-ene, 0.04 mol, was added to the reaction mixture prepared as described in a, and 20 ml of 15% hydrochloric acid (in the synthesis of **Ia** and **Ib**), 12 ml of concentrated hydrochloric acid (**Ic**, **Id**), or a mixture of 51 ml of concentrated hydrochloric acid and 11 ml of concentrated sulfuric acid (**Ie**) was added, maintaining the temperature at 28–30°C. When the reaction was complete, the product was isolated as described above in a.

c. A mixture of 80 ml of acetone, 20 ml of water, 9.6 g of 4-(buta-1,3-dien-1-ylsulfonyl)benzenesulfonamide, and 0.02 mol of the corresponding arenediazonium tetrachlorocuprate(II) was vigorously stirred at 32–34°C until gaseous products no longer evolved. The mixture was then treated as described above.

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