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Diazo Reactions with Unsaturated Compounds: XII.[1] Reaction of 1-(*p*-Carboxybenzenesulfonyl)-1,3-butadiene with Aryldiazonium Chlorides, 1-Aryl-3,3-dimethyl-1-triazenes, and Aryldiazonium Tetrachlorocuprates(II)

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Abstract — 1-(*p*-Carboxybenzenesulfonyl)-1,3-butadiene reacts in aqueous acetone with aryldiazonium chlorides and 1-aryl-3,3-dimethyl-1-triazenes in the presence of copper(II) chloride and with tetrachlorocuprates(II) to form 1-(*p*-carboxybenzenesulfonyl)-4-aryl-3-chloro-1-butenes.
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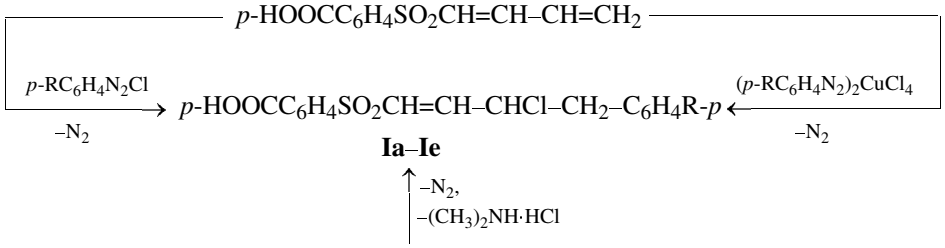
We have shown previously [1–3] that 1-(*p*-nitrobenzenesulfonyl)-, 1-(*m*-nitrobenzenesulfonyl)-, 1-(*p*-chlorobenzenesulfonyl)-, 1-(*p*-bromobenzenesulfonyl)-, 1-(*p*-methylbenzenesulfonyl)-, and 1-(*p*-methoxybenzenesulfonyl)-1,3-butadienes react with aryldiazonium chlorides and 1-aryl-3,3-dimethyl-1-triazenes to give the corresponding chloroarylation products.

In this study we found that 1-(*p*-carboxybenzenesulfonyl)-1,3-butadiene reacts similarly with aryldiazonium chlorides and tetrachlorocuprates(II) and with 1-aryl-3,3-dimethyl-1-triazene to form 1-(*p*-carboxybenzenesulfonyl)-4-aryl-3-chloro-1-butenes **Ia**–**Ie** (see table), the products of chloroarylation of the double bond remote from the arenesulfonyl group.



$$p\text{-HOOCC}_6\text{H}_4\text{SO}_2\text{CH=CH–CH=CH}_2 + p\text{-RC}_6\text{H}_4\text{N=NN(CH}_3)_2 + 2\text{HCl},$$

R = H (**a**), CH_3 (**b**), Br (**c**), Cl (**d**), O_2N (**e**).

The reaction with aryldiazonium tetrachlorocuprates(II) occurs in aqueous acetone at 32–34°C, and with aryldiazonium chlorides and 1-aryl-3,3-dimethyl-1-triazenes it occurs under the similar conditions in the presence of copper(II) chloride. In the reaction with 1-aryl-3,3-dimethyl-1-triazene, hydrochloric acid was added to the reaction mixture.

Along with compounds **Ia**–**Ie**, aryl chlorides are formed, and in the case of 1-aryl-3,3-dimethyl-1-triazene, dimethylamine hydrochloride is additionally obtained. Most probably, 1-aryl-3,3-dimethyl-1-triazenes in the first step react with hydrochloric acid to give aryldiazonium chlorides, which subsequently react with the diene.

Aryldiazonium tetrachlorocuprates(II) react with 1-(*p*-carboxybenzenesulfonyl)-1,3-butadiene to form products **Ia**–**Id** in a higher yield as compared to their yields from 1-aryl-3,3-dimethyl-1-triazenes. The lowest yields of **Ia**–**Ie** are observed in the reaction of 1-(*p*-carboxybenzenesulfonyl)-1,3-butadiene with aryldiazonium chlorides.

[1] For communication XI, see [1].

Constants, yields, and elemental analyses of the products of chloroalkylation of 1-(*p*-carboxybenzenesulfonyl)-1,3-butadiene *p*-HOOC–$C_6H_4SO_2CH$=CH–CHCl–$CH_2C_6H_4R$-*p*

Comp. no.	R	Yield, %			mp, °C	Found, %	Formula	Calculated, %
		reactions with aryldiazonium chlorides	reactions with triazenes[a]	reactions with aryldiazonium tetrachlorocuprates				
Ia	H	52	55	58	159–160	Cl 10.34, 10.02	$C_{17}H_{15}ClO_4S$	Cl 0.10
Ib	CH_3	40	49	60	177–178	Cl 9.91, 9.50	$C_{18}H_{17}ClO_4S$	Cl 9.71
Ic	Br	33	39	47	193–194	(Cl+Br) 27.13, 26.52	$C_{17}H_{14}BrClO_4S$	(Cl+Br) 26.84
Id	Cl[b]	47	52	56	191–192	Cl 18.78, 18.11	$C_{17}H_{14}Cl_2O_4S$	Cl 18.40
Ie	O_2N	28	32	–	197–198	N 3.28, 3.33 Cl 8.90, 8.85	$C_{17}H_{14}ClNO_6S$	N 3.53 Cl 8.95

[a] 1-Aryl-3,3-dimethyl-1-triazenes. [b] ^{1}H NMR spectrum, δ, ppm: 3.117–3.258 m (2H, CH_2), 4.080–5.025 d.d (1H, CH, J_1 7.2, J_2 14.4 Hz), 6.856–6.893 d (1H, CH, J 14.8 Hz), 6.959–7.015 d.d (1H, CH, J_1 7.6, J_2 14.8 Hz), 7.196–7.245 t (4H, *p*-ClC_6H_4), 7.852–7.873 d (2H, *p*-$O_2NC_6H_4$), 8.142–8.163 d (2H, *p*-$O_2NC_6H_4$), 13.40–13.65 s (1H, COOH).

The suggested structure of **Id** well agrees with its ^{1}H NMR spectrum. The ethylene protons give a doublet at δ 6.856–5.893 ppm and a doublet of doublets at 6.959–7.015 ppm. The signal of the >CHCl proton is manifested as a doublet of doublets at 4.949–5.025 ppm. Large coupling constants (J 14.8 Hz) of the ethylene protons are indicative of their *trans* arrangement in **Id**.

EXPERIMENTAL

The ^{1}H NMR spectra were taken on a Varian Gemini-400 spectrometer in DMSO-d_6.

1-Aryl-3,3-dimethyl-1-triazenes were prepared by azo coupling of the corresponding aryldiazonium chlorides with dimethylamine [4].

Aryldiazonium tetrachlorocuprates(II) were prepared according to [5].

1-(*p*-Carboxybenzenesulfonyl)-4-chloro-2-butene was prepared similarly to 1-(*p*-nitrobenzenesulfonyl)-4-chloro-2-butene [6]. Butadiene, 0.1 mol, reacted with a diazonium salt solution prepared from 0.05 mol of *p*-aminobenzoic acid to give 5.8 g (42%) of a white crystalline substance, mp 202–203°C (from 1 : 2 ethanol–water). Found, %: Cl 12.76, 12.84. $C_{11}H_{11}ClO_4S$. Calculated, %: Cl 12.90.

1-(*p*-Carboxybenzenesulfonyl)-1,3-butadiene. To a solution of 0.05 mol of 1-(*p*-carboxybenzenesulfonyl)-4-chloro-2-butene in 130 ml of benzene, a solution of 0.1 mol of triethylamine in 20 ml of benzene was added in small portions. The reaction mixture was heated on a water bath at 80°C for 2 h. The triethylamine hydrochloride precipitate was filtered off, and the benzene solution of the diene was evaporated at reduced pressure. The oily residue was treated with stirring with 16 ml of 10% HCl. The precipitate obtained was separated and crystallized from a 1 : 2 ethanol–water mixture to give 11 g (92.3%) of a white crystalline substance, mp 174–175°C. Found, %: S 13.20, 13.78. $C_{11}H_{10}O_4S$. Calculated, %: S 13.45.

All the attempts to obtain the adduct of this diene with maleic anhydride failed. The reaction mixture underwent tarring in the course of heating of an acetone or dioxane solution of the reactants.

1-(*p*-Carboxybenzenesulfonyl)-4-aryl-3-chloro-1-butenes Ia–Ie. *a*. To a mixture of 75 ml of acetone, 10 ml of water, 2 g of copper(II) chloride, and 11.91 g of 1-(*p*-carboxybenzenesulfonyl)-1,3-butadiene, a solution of aryldiazonium chloride prepared from 0.05 mol of appropriate aromatic amine, 17 ml of concentrated hydrochloric acid, and 3.6 g of sodium nitrite was added dropwise with stirring at 32–34°C. The solutions of phenyl-, *p*-tolyl-, *p*-chlorophenyl-, and *p*-bromophenyldiazonium chlorides were preliminarily neutralized with sodium bicarbonate to pH 3–4. After the addition of the diazonium salt solution was complete, the reaction mixture was stirred until liberation of gaseous products ceased and then was poured into 400 ml of water. The crystalline precipitate was separated and recrystallized from a 1 : 2 acetic acid–water mixture.

b. To the mixture described above (procedure *a*), 0.063 mol of appropriate aryldimethyltriazene was added. After that, in the syntheses of **Ia** and **Ib**, 30 ml of 15% hydrochloric acid was added dropwise with stirring. In the case of **Ic** and **Id**, the reaction mixture was treated with 15 ml of concentrated hydrochloric acid. When preparing **Ie**, a mixture of 64 ml of concentrated hydrochloric acid and 14 ml of concentrated sulfuric acid was used. The temperature of the reaction mixture was maintained in the range 32–34°C. The target products were isolated as in procedure *a*.

c. A mixture of 100 ml of acetone, 25 ml of water, 11.91 g of 1-(*p*-carboxybenzenesulfonyl)-1,3-butadiene, and 0.025 mol of appropriate aryldiazonium tetrachlorocuprate(II) was vigorously stirred at 32–34°C until the liberation of gaseous products ceased. The reaction products were isolated similarly to methods *a* and *b*.

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