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Diazo Reactions with Unsaturated Compounds: VI.[1] Reaction of 1-(*p*-Nitrophenylsulfonyl)buta-1,3-diene with Arenediazonium Chlorides

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Abstract—1-(*p*-Nitrophenylsulfonyl)buta-1,3-diene reacts with arenediazonium chlorides in aqueous acetone in the presence of catalytic amounts of $CuCl_2 \cdot 2H_2O$ to form 1-(*p*-nitrophenylsulfonyl)-4-aryl-3-chloro-1-butenes. In the presence of SO_2, 1-(*p*-nitrophenylsulfonyl)buta-1,3-diene does not react with arenediazonium chlorides.

Reactions of 1-arylsulfonylbuta-1,3-dienes with aromatic diazonium salts were not described in the literature [1–7]. 1-Phenyl- and 1-(*p*-tolyl)buta-1,3-dienes react with arenediazonium chlorides to give arylation products, whereas 1-(*p*-nitrophenyl)buta-1,3-diene is not arylated under the same conditions [8].

We found that 1-(*p*-nitrophenylsulfonyl)buta-1,3-diene, in contrast to 1-(*p*-nitrophenyl)buta-1,3-diene, reacts with arenediazonium chlorides at 30°C in aqueous acetone in the presence of catalytic amounts of $CuCl_2 \cdot 2H_2O$ to give 1-(*p*-nitrophenylsulfonyl)-4-aryl-3-chloro-1-butenes **Ia**–**Ie** (Table 1), which are formed by chloroarylation of the double bond remote from the arylsulfonyl group.

$$p\text{-}O_2NC_6H_4SO_2CH{=}CH\text{–}CH{=}CH_2 + p\text{-}RC_6H_4N_2Cl$$

$$\rightarrow p\text{-}O_2NC_6H_4SO_2CH{=}CH\text{–}CHCl\text{–}CH_2C_6H_4\text{–}R\text{-}p + N_2$$

Ia–**Ie**

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

The yields of **Ia**–**Ie** are considerably lower compared to the reactions of arenediazonium chlorides with 1-phenyl- and 1-(*p*-tolyl)buta-1,3-dienes [8].

Along with **Ia**–**Ie**, minor amounts of aryl chlorides are formed. The yields of **Ia**–**Ie** depend on pH of the reaction mixture. In the reactions with diazotized aniline, *p*-toluidine, *p*-bromoaniline, and *p*-chloroaniline, the highest yields are attained at pH 4–5, and with diazotized *p*-nitroaniline, at pH 1.

The catalyst was introduced in the amount of 0.05 mol per mole of diazonium salt. In the presence of SO_2, 1-(*p*-nitrophenylsulfonyl)buta-1,3-diene did not react with arenediazonium chlorides under conditions of chloroarylsulfonylation of unsaturated compounds [9] and was recovered unchanged.

The suggested structure of **Ia** and **Id** is nicely consistent with their ^1H NMR spectra (Table 2), in which the ethylene proton signals are well defined and do not overlap with the signals of other protons. These signals are doublets and doublets of doublets at 6.83–6.86 and 7.08–7.16 ppm for **Ia** and at 6.82–6.87 and 7.07–7.14 ppm for **Id**. The signal of the >CHCl proton is a doublet of triplets at 5.00–5.07 ppm.

We examined the possibility of dehydrochlorination of **Ia**–**Ie**. Experiments showed that the dehydrochlorination did occur on heating with KOH in ethanol or with powdered KOH in dioxane, but it was accompanied by tarring, probably due to increased activity toward nucleophiles of the double bond adjacent to the arylsulfonyl group [10]. Dehydrochlorination of **Ia**–**Ie** by heating with triethylamine was incomplete and yielded a mixture of products which could not be separated by crystallization.

EXPERIMENTAL

The ^1H NMR spectra were taken on a Varian VXR-300 spectrometer (solvent acetone-d_6).

1-(*p*-Nitrophenylsulfonyl)buta-1,3-diene. A 5.51-g portion of 1-(*p*-nitrophenylsulfonyl)-4-chloro-2-butene prepared according to [9] was dissolved in 50 ml of benzene. The solution was cooled with ice-cold water, and 2.8 ml of triethylamine was added dropwise. The mixture was refluxed on a water bath at 70–80°C for 3 h. After cooling, the precipitate of triethylamine hydrochloride was filtered off, the sol-

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[*] For communication V, see [1].

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Table 1. Constants, yields, and elemental analyses of 1-(*p*-nitrophenylsulfonyl)-4-aryl-3-chloro-1-butenes **Ia**–**Ie**

Comp. no.	Yield, %	mp, °C	Found, %		Formula	Calculated, %	
			Cl (Cl + Br)	N		Cl (Cl + Br)	N
Ia	47.4	139.5–140	10.40, 10.21	3.71, 3.89	$C_{16}H_{14}ClNO_4S$	10.08	3.98
Ib	26.8	99.5–100	9.84, 9.91	3.52, 3.74	$C_{17}H_{16}ClNO_4S$	9.69	3.82
Ic	28.6	132–132.5	18.78, 18.54	3.36, 3.71	$C_{16}H_{13}Cl_2NO_4S$	18.36	3.62
Id	28.6	119–119.5	(27.10, 26.91)	2.96, 3.12	$C_{16}H_{13}BrClNO_4S$	(26.78)	3.25
Ie	22.5	152–152.5	9.10, 9.28	6.78, 6.92	$C_{16}H_{13}ClN_2O_6S$	8.93	7.06

Table 2. ^{1}H NMR spectra of 1-(*p*-nitrophenylsulfonyl)-4-aryl-3-chloro-1-butenes **Ia** and **Id**

Comp. no.	δ, ppm
Ia	3.22–3.35 d.d (2H, CH_2, J_1 4.2, J_2 7.2 Hz), 5.00–5.07 d.t (1H, CH, J_1 7.2, J_2 7.5 Hz), 6.83–6.88 d (1H, CH, J 14.5 Hz), 7.08–7.16 d.d (1H, CH, J_1 14.5, J_2 7.5 Hz), 7.22–7.41 m (5H, C_6H_5), 8.07–8.11 d (2H, *p*-$O_2NC_6H_4$), 8.44–8.49 d (2H, *p*-$O_2NC_6H_4$)
Id	3.24–3.36 d.d (2H, CH_2, J_1 2.1, J_2 7.2 Hz), 4.99–5.07 d.t (1H, CH, J_1 7.2, J_2 7.8 Hz), 6.82–6.87 d (1H, CH, J 15 Hz), 7.07–7.14 d.d (1H, CH, J_1 7.8, J_2 15 Hz), 7.25–7.35 m (4H, *p*-ClC_6H_4), 8.07–8.11 d (2H, *p*-$O_2NC_6H_4$), 8.46–8.50 d (2H, *p*-$O_2NC_6H_4$)

vent was distilled off at reduced pressure, and the residue was crystallized from ethanol–water, 2 : 1. Yield 4.5 g (95%); light yellow crystals, mp 102–103°C. Found N, %: 5.88, 5.76. $C_{10}H_9NO_4S$. Calculated N, %: 5.55.

Condensation of 1-(*p*-nitrophenylsulfonyl)buta-1,3-diene with maleic anhydride. A solution of 2.4 g of 1-(*p*-nitrophenylsulfonyl)buta-1,3-diene and 1 g of maleic anhydride in 50 ml of benzene was heated for 2 h on a boiling water bath. Then the reaction mixture was cooled, and the precipitated crystals were separated and recrystallized from benzene–petroleum ether, 1 : 1. Yield 2.1 g (62.3%); white crystals, mp 134–135°C. Found N, %: 4.16, 4.29. $C_{14}H_{11}NO_7S$. Calculated N, %: 4.15.

1-(*p*-Nitrophenylsulfonyl)-4-phenyl-3-chloro-1-butene Ia. A mixture of 60 ml of acetone, 9.6 g of 1-(*p*-nitrophenylsulfonyl)buta-1,3-diene, and 1.6 g of $CuCl_2 \cdot 2H_2O$ was heated to 30°C, and a solution of benzenediazonium chloride, prepared from 3.6 ml of aniline, 13.6 ml of concentrated HCl, and 2.9 g of sodium nitrite and neutralized with sodium hydrogen carbonate to pH 3–4, was added from an externally cooled dropping funnel with vigorous stirring. Gases evolved evenly at 30–32°C. After the gas evolution ceased, the mixture was steam-distilled. The residue after distillation of acetone and by-products was separated and crystallized from ethanol. Yield of **Ia** 6.6 g.

Compounds **Ib**–**Ie** were prepared similarly to **Ia** and crystallized from ethanol. The yields (based on the aromatic amine), constants, and analytical data for **Ia**–**Ie** are listed in Table 1.

REFERENCES

1. Naidan, V.M. and Fesak, A.Yu., *Zh. Obshch. Khim.*, 2000, vol. 70, no. 10, pp. 1702–1704.
2. Dombrovskii, A.V., *Usp. Khim.*, 1957, vol. 26, no. 6, pp. 695–715.
3. Dombrovskii, A.V., in *Reaktsii i metody issledovaniya organicheskikh soedinenii* (Reactions and Methods for Investigation of Organic Compounds), Moscow: Gos. Nauchno-Tekh. Izd. Khimicheskoi Literatury, 1962, vol. 11, pp. 285–373.
4. Rondestvedt, C.S., *Organic Reactions*, Adams, R., Ed., New York: Wiley, 1944. Translated under the title *Organic Reactions*, Moscow: Mir, 1965, coll. 2, pp. 199–266.
5. Rondestvedt, C.S., Jr., *Organic Reactions*, New York, 1976, vol. 24, pp. 225–258.
6. Dombrovskii, A.V., *Usp. Khim.*, 1984, vol. 53, no. 10, pp. 1625–1647.
7. Grishchuk, B.D., Gorbovoi, P.M., Ganushchak, N.I., and Dombrovskii, A.V., *Usp. Khim.*, 1994, vol. 63, no. 3, pp. 269–279.
8. Dombrovskii, A.V. and Ganushchak, N.I., *Zh. Obshch. Khim.*, 1961, vol. 31, no. 6, pp. 1896–1901.
9. Naidan, V.M., Naidan, G.D., Drozdova, S.G., and Musienko, V.M., *Zh. Obshch. Khim.*, 1985, vol. 55, no. 2, pp. 391–395.
10. Sykes, P., *A Guidebook to Mechanism in Organic Chemistry*, New York: Longman, 1986. Translated under the title *Mekhanizmy reaktsii v organicheskoi khimii*, Moscow: Khimiya, 1977, p. 193.