Russian Journal of General Chemistry, Vol. 75, No. 4, 2005, pp. 580–582. Translated from Zhurnal Obshchei Khimii, Vol. 75, No. 4, 2005, pp. 619–621.
Original Russian Text Copyright © 2005 by Naidan, Smalius.

Diazo Reactions with Unsaturated Compounds: IX.[1] *ortho*-, *meta*-, and *para*-Nitrophenylsulfonyl-1,3-butadienes in Reaction with 1-Aryl-3,3-dimethyl-1-triazenes

V. M. Naidan and V. V. Smalius

Khmel'nitskii National University, Cherkassy, Ukraine

Received October 15, 2003

Abstract—1-(*m*-Nitrophenylsulfonyl)- and 1-(*p*-nitrophenylsulfonyl)-1,3-butadienes in aqueous acetone in the presence of HCl and copper(I) or copper(II) chloride react with 1-aryl-3,3-dimethyl-1-triaenes to form 1-(*m*-nitrophenylsulfonyl)- and 1-(*p*-nitrophenylsulfonyl)-4-aryl-3-chloro-1-butenes, respectively. 1-(*o*-Nitrophenylsulfonyl)-1,3-butadiene fails to react in similar conditions.

We previously showed [1–4] that butadiene and isoprene in a water–acetic acid–acetone medium saturated with sulfur(IV) oxide in the presence of sodium chloride or HCl and copper(I) chloride react with diazoaminobenzene and 1-aryl-3,3-dimethyl-1-triazenes to give chloroarylsulfonylation products. Proceeding with these studies we established that 1-(*m*-nitrophenylsulfonyl)- and 1-(*p*-nitrophenylsulfonyl)-1,3-butadienes react with 1-aryl-3,3-dimethyl-1-triazenes in the absence of sulfur(IV) oxide if the reaction mixture contains HCl and copper(I) or copper(II) chloride. The reaction involves expulsion of the triazene nitrogen and gives rise to 1-(*m*-nitrophenylsulfonyl)- and 1-(*p*-nitrophenylsulfonyl)-4-aryl-3-chloro-1-butenes **Ia**–**Il** formed by chloroarylation of the dienes by the double bond most distal from the arylsulfonyl group (see table).

$$\begin{gathered}R^1C_6H_4SO_2CH{=}CHCH{=}CH_2 + p\text{-}R^2C_6H_4N{=}NN(CH_3)_2\\ + 2HCl \xrightarrow{CuCl} R^1C_6H_4SO_2CH{=}CHCHClCH_2C_6H_4R^2\text{-}p\\ + (CH_3)_2NH\cdot HCl + N_2,\end{gathered}$$

R^1 = *m*-, *p*-O_2N, R^2 = H (**a**), CH_3 (**b**), Br (**c**), Cl (**d**), O_2N (**e**).

The reaction occurs in aqueous acetone at 28–30°C.

1-(*o*-Nitrophenylsulfonyl)-1,3-butadies fail to react with 1-aryl-3,3-dimethyl-1-triazenes in these conditions, which is probably associated with the fact that the *o*-nitrophenylsulfonyl substituent much decreases the electron density on and, consequently, chemical activity of the diene system, and this effect compares with that of the *p*-nitrophenyl radical [5].

Along with **Ia**–**Il**, a little aryl chlorides and dimethylamine hydrochloride are formed.

Most probably, 1-aryl-3,3-dimethyl-1-triazenes first react with HCl and decompose to give arenediazonium chlorides that then react with unsaturated compounds. Evidence for this suggestion comes from the fact that for successful reaction of triazenes whose basicity is decreased the reaction mixture should be acidified. Thus 1-(*p*-bromophenyl)- and 1-(*p*-chlorophenyl)-3,3-dimethyl-1-triazenes react in the presence of conc. HCl only, and 1-(*p*-nitrophenyl)-3,3-dimethyl-1-triazene, in the presence of a mixture of conc. HCl and H_2SO_4. At the same time, 1-phenyl- and 1-(*p*-tolyl)-3,3-dimethyl-1-triazenes readily react in the presence of 10–15% HCl.

We have studied reactions of 1-(*p*-nitrophenylsulfonyl)-1,3-butadiene [4], 1-(*o*-nitrophenylsulfonyl)-, and 1-(*m*-nitrophenylsulfonyl)-1,3-butadienes with arenediazolnium chlorides to find that here, too, 1-(*o*-nitrophenylsulfonyl)-1,3-butadiene fails to react, and its *meta* and *para* isomers are chloroarylated to form the same 1-(*m*-nitrophenylsulfonyl)-4-aryl-3-chloro-1-butenes **Ia**–**Ie** and 1-(*p*-nitrophenylsulfonyl)-4-aryl-3-chloro-1-butenes **Ig**–**Il**.

It should be noted that with 1-aryl-3,3-dimethyl-1-triazenes as reagents alternative to arenediazonum chlorides, the yields of chloroarylation products increase, and the yields of tarry compounds and Sandmeyer reaction products decrease.

The proposed structure of compound **Ic** is nicely consistent with its ^{1}H NMR spectrum that contains

---

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

Constants, yields, and elemental analyses of chloroarylation products $R^1C_6H_4SO_2CH{=}CHCHClCH_2C_6H_4R^2$-*p*

Comp. no.	R^1	R^2	Yield, %,[a] in reaction with		mp, °C	Found, %		Formula	Calculated, %	
			1-aryl-3,3-dimethyl-1-triazenes	arenediazonium chlorides		N	Cl (Cl+Br)		N	Cl (Cl+Br)
Ia	*m*-O_2N	H	17	15	73–73.5	3.91, 4.05	10.02, 10.12	$C_{16}H_{14}ClNO_4S$	3.98	10.08
Ib	*m*-O_2N	CH_3	36	42	111–112	3.88, 3.96	9.72, 9.78	$C_{17}H_{16}ClNO_4S$	3.82	9.69
Ic[b]	*m*-O_2N	Br	30	24	124–125	3.39, 3.45	(26.85, 26.93)	$C_{16}H_{13}BrClNO_4S$	3.25	(26.78)
Id	*m*-O_2N	Cl	34	32	118–118.5	3.79, 3.85	18.43, 18.50	$C_{16}H_{13}Cl_2NO_4S$	3.62	18.36
Ie	*m*-O_2N	O_2N	24	23	136.5–137	6.67, 6.98	8.59, 8.74	$C_{16}H_{13}ClN_2O_6S$	7.06	8.93
Ig	*p*-O_2N	H	49	24	139.5–140	3.90, 4.11	10.28, 10,32	$C_{16}H_{14}ClNO_4S$	3.98	10.08
Ih	*p*-O_2N	CH_3	47	27	99.5–100	3.94, 4.01	9.74, 9.81	$C_{17}H_{16}ClNO_4S$	3.82	9.69
Ij	*p*-O_2N	Br	34	29	119–199.5	3.36, 3.41	(26.84, 26.93)	$C_{16}H_{13}BrClNO_4S$	3.25	(26.78)
Ik	*p*-O_2N	Cl	35	29	132–132.5	3.68, 3.81	18.40, 18.16	$C_{16}H_{13}Cl_2NO_4S$	3.62	18.36
Il	*p*-O_2N	O_2N	24	23	152–152.5	7.16, 7.24	9.14, 9.29	$C_{16}H_{13}ClN_2O_6S$	7.06	8.93

[a] Compounds **Ic**–**Il** were purified by crystallization from ethanol and compounds **Ia** and **Ib**, from ethanol–water, 3 : 1.

[b] ^1H NMR spectrum, δ, ppm: 3.11–3.15 d.d (2H, CH_2, J_1 3.3, J_2 6.9 Hz), 4.62–4.69 d.d (1H, CH, J_1 6.9, J_2 13.2 Hz), 6.46–6.51 d (1H, CH, *J* 15 Hz), 7.00–7.07 m (1H, CH), 7.35–7.38 d.d (4H, *p*-BrC_6H_4), 7.75–7.80 t (1H, *m*-$O_2NC_6H_4$), 8.07–8.10 d (1H, *m*-$O_2NC_6H_4$), 8.48–8.51 d (1H, *m*-$O_2NC_6H_4$), 8.65 s (1H, *m*-$O_2NC_6H_4$).

ethylene proton signals as a well-defined doublet at δ 6.46–6.51 ppm and a multiplet at δ 7.00–7.07 ppm. The >CHCl proton signal is a doublet of doublets at δ 4.63–4.69 ppm.

EXPERIMENTAL

The ^1H NMR spectra were obtained on a Varian VXR-300 spectrometer, solvent $CDCl_3$.

1-Aryl-3,3-dimethyl-1-triazenes were prepared by azo coupling of the corresponding arenediazonium chlorides with dimethylamine [6]. 1-(*p*-Nitrophenylsulfonyl)-1,3-butadiene was prepared by our previously described procedure [4].

1-Chloro-4-(*m*-nitrophenylsulfonyl)-2-butene was prepared similarly to 1-chloro-4-(*p*-nitrophenylsulfonyl)-2-butene [7] by the reaction of 0.1 mol of butadiene with the solution of arenediazonium salt, prepared from 0.05 mol of *m*-nitroaniline, 17 ml of conc. HCl, 15 ml of glacial acetic acid, and 3.6 g of sodium nitrite. Yield 6 g (44%), yellow crystals, mp 91–92°C (acetic acid–water, 1 : 1). Found N, %: 5.38, 5.12. $C_{10}H_{10}ClNO_4S$. Calculated N, %: 5.08.

1-Chloro-4-(*o*-nitrophenylsulfonyl)-2-butene was prepared as described above by the reaction of the solution of arenediazonium salt, prepared from 0.05 mol of *o*-nitroaniline, 17 ml of HCl, 15 ml of glacial acetic acid, and 3.6 g of sodium nitrite, with 2.3 l of butaene. Yield 6.2 g (45%), light yellow crystals, mp 52–53°C (acetic acid–water, 1 : 1). Found N, %: 5.30, 5.17. $C_{10}H_{10}ClNO_4S$. Calculated N, %: 5.08.

1-(*m*-Nitrophenylsulfonyl)-1,3-butadiene. A solution of 2.8 ml of triethylamine in 5 ml of acetone was added dropwise to a solution of 5.51 g of 1-chloro-4-(*m*-nitrophenylsulfonyl)-2-butene in 30 ml of acetone, cooled with ice water. The mixture was left to stand at room temperature for 1 h. Triethylamine hydrochloride precipitated and was separated, the solvent was removed at reduced pressure, and the solid residue was recrystallized from ethanol–water, 2 : 1. Yield 3.2 g (76%), light yellow crystals, mp 61–62°C. Found N, %: 5.76, 5.90. $C_{10}H_9NO_4S$. Calculated N, %: 5.55.

Refluxing of 2.4 g of the product with 1 g of maleic anhydride in 50 ml of benzene for 5 h gave no adduct.

1-(*o*-Nitrophenylsulfonyl)-1,3-butadiene was obtained similarly to 1-(*m*-nitrophenylsulfonyl)-1,3-butadiene by the reaction of 5.51 g of 4-chloro-1-(*o*-nitrophenylsulfonyl)-2-butene with 2.8 ml of triethylamine. Yield 2.96 g (62%), light yellow crystals, mp 79–80°C (ethanol–water, 2 : 1). Found N, %: 5.70, 5.85. $C_{10}H_9NO_4S$. Calculated N, %: 5.55. ^1H NMR spectrum, δ, ppm: 5.67–5.70 d (1H, CH2, *J* 9 Hz), 5.76–5.82 d (1H, CH_2, *J* 17.1 Hz), 5.41–6.54 m (1H, CH), 6.86–6.91 d (1H, CH, *J* 15 Hz), 7.29–7.31 m (1H, CH), 7.76–7.83 m (3H, *o*-$O_2NC_6H_4$), 8.15–8.18 d.d (1H, *o*-$O_2NC_6H_4$).

Refluxing of 2.4 g of the product with 1 g of maleic anhydride in 50 ml of benzene for 5 h gave no adduct.

3-Chloro-1-(*m*-nitrophenylsulfonyl)-4-phenyl-1-butene (Ia) and 3-chloro-1-(*p*-nitrophenylsulfonyl)-4-phenyl-1-butene (Ig). Acetone, 60 ml, was mixed with 9.6 g of 1-(*m*-nitrophenylsulfonyl)-1,3-butadiene or 1-(*p*-nitrophenylsulfonyl)-1,3- butadiene, 0.68 g of copper(II) chloride, and 7.6 g of 3,3-dimethyl-1-phenyl-1-triazene. The temperature of the reaction mixture was raised to 30°C, and 20 ml of 15% HCl was added to it with vigorous stirring. Uniform gas evolution was observed at 28–30°C. After gas no longer evolved, the reaction mixture was subjected to steam distillation to remove acetone and by-products. The residue was separated and purified by crystallization to obtain 2.3 g of compound **Ia** and 6.9 g of compound **Ig**.

Compound **Ib** was prepared similarly to compound **Ia** and compound **Ih**, similarly to compound **Ig**.

Compounds **Ic**, **Id**, **Ij**, and **Ik** were prepared similarly to compounds **Ia**, **Ib**, **Ig**, and **Ih**, using 10–12 ml of conc. HCl instead of 15% HCl, as well as 9.2 g of 1-(*p*-chlorophenyl)-3,3-dimethyl-1-triazene and 11.4 g 1-(*p*-bromophenyl)-3,3-dimethyl-1-triazene, respectively.

Sulfones **Ie** and **Il** were prepared similarly to compounds **Ic**, **Id**, **Ij**, and **Im**, using, instead of HCl, a mixture of 51.2 ml of conc. HCl with 11.2 ml of conc. H_2SO_4, and 9.72 g of 3,3-dimethyl-1-(*m*-nitrophenyl)- or 3,3-dimethyl-1-(*p*-nitrophenyl)-1-triazene.

The reactions of 1-(*o*-nitrophenylsulfonyl)- and 1-(*m*-nitrophenylsulfonyl)-1,3-butadienes with arenediazonium chlorides were performed by a procedure similar to that described previously for the reactions of the same chlorides with 1-(*p*-nitrophenylsulfonyl)-1,3-butadiene [4] to obtain compounds **Ia**–**Id**.

REFERENCES

1. Naidan, V.M. and Smalius, V.V., *Zh. Obshch. Khim.*, 2004, vol. 74, no. 9, p. 1495.
2. Naidan, V.M., Naidan, G.D., Fesak, O.Yu., Smalius, V.V., Yukhimuk, S.G., Vodop'yan, V.V., and Goncharenko, D.O., *Visn. Cherkas. Univ., Ser. Khim. Navuk*, 2002, no. 30, p. 54.
3. Naidan, V.M. and Smalius, V.V., Abstracts of Papers, *Ukrans'kaya konferents'ya "Dombrovs'ki khimihni chitannya 2003"* (Ukrainian Conf. "Dombrovskii Chemical Readings 2003"), Cherkassy, 2003, p. 18.
4. Naidan, V.M. and Smalius, V.V., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 11, p. 1899.
5. Dombrovskii, A.V. and Ganushchak, N.I., *Zh. Obshch. Khim.*, 1961, vol. 31, no. 6, p. 1896.
6. Pochinok, V.Ya., *Triazeny* (Triazenes), Kiev: Kiev. Gos. Univ., 1968, pp. 16, 62, 155.
7. Naidan, V.M., Naidan, G.D., Drozdova, S.G., and Musienko, V.M., *Zh. Obshch. Khim.*, 1985, vol. 55, no. 2, p. 391.