Russian Journal of Organic Chemistry, Vol. 40, No. 2, 2004, pp. 191–194. Translated from Zhurnal Organicheskoi Khimii, Vol. 40, No. 2, 2004, pp. 218–221.

Reaction of Arendiazonium Salts and SO_2 with α-Nitroolefins

E. E. Bilaya, N. D. Obushak, A. M. Buchinskii, and N. I. Ganushchak

Ivan Franko Lviv National University, L'viv, 79005 Ukraine

e-mail: obushak@in.lviv.ua

Received February 21, 2003

Abstract—In reaction of β-nitrostyrene and 2-(2-nitrovinyl)furan with arenediazonium chlorides and SO_2 in the presence of copper(II) chloride products were obtained resulting from addition of arylsulfonyl group and a hydrogen atom across the C=C bond: 2-nitro-1-phenylethylsulfonylarenes and 2-(1-arylsulfonyl-2-nitroethyl)furans respectively. An anion-radical mechanism of the reaction was suggested.

Unsaturated compounds react with arenediazonium chlorides and sulfur(IV) oxide under catalysis with copper salts [1–11]. The reaction was shown to afford a product of arylsulfonyl group and nucleophile addition across the double bond 1–8] or to involve a replacement by arylsulfonyl group of hydrogen, halogen, or carboxy group [7–11]. The part of nucleophiles play in these reactions chloride [1, 3, 4], bromide [3, 4], thiocyanate- [2, 4], xanthate, and diethyldithiophosphate ions [3, 4], and also a hydroxy group [5–8]. The route taken by the reaction depends on the character of the unsaturated compound. The strong electron-acceptor substituents at the double bond change the character of the reaction [12, 13]. In the present study we investigated in more detail the reaction of α-nitroolefins with arenediazonium chlorides and SO_2.

We established that β-nitrostyrene **I** and 2-(2-nitrovinyl)furan **II** reacted with the diazonium salts and SO_2 in the presence of copper(II) chloride as catalyst in a mixture water–acetone–acetic acid to furnish products of arylsulfonyl group and hydrogen atom addition at the double bond, compounds **IVa–IVf, Va Vb** (Tables 1 and 2).

We failed to detect unsaturated sulfones and products of arylsulfonyl group and chlorine addition to the double bond that should be expected to be present basing on results of [1–11]. The degree of monomer conversion attained 45–60%. Arenesulfonyl chlorides formed beside compounds **IVa–IVf, Va, Vb** in 40–60% yield.

Table 1. Yields, melting points[a], and elemental analyses of (2-nitro-1-phenylethyl)sulfonylarenes **IVa–f** and 2-(1-arylsulfonyl-2-nitroethyl)furans **Va, b**

Compd. no.	Yield, %	mp, °C	Found, %				Formula	Calculated, %			
			C	H	N (Br)	S		C	H	N (Br)	S
IVa	35	186–187	57.69	4.61	4.78	11.04	$C_{14}H_{13}NO_4S$	57.72	4.50	4.81	11.01
IVb	31	110–112	58.78	5.02	4.54	10.55	$C_{15}H_{15}NO_4S$	59.00	4.95	4.59	10.50
IVc	43	148	58.90	4.82	4.62	10.48	$C_{15}H_{15}NO_4S$	59.00	4.95	4.59	10.50
IVd	30	145	55.88	4.59	4.28	10.01	$C_{15}H_{15}NO_5S$	56.06	4.70	4.36	9.98
IVe	24	143	45.37	3.31	3.62 (21.63)	8.47	$C_{14}H_{12}BrNO_4S$	45.42	3.27	3.78 (21.58)	8.66
IVf	45	154	49.88	3.49	8.38	9.44	$C_{14}H_{12}N_2O_6S$	50.00	3.60	8.33	9.53
Va	27	129–130	52.85	4.61	4.60	10.72	$C_{13}H_{13}NO_5S$	52.87	4.44	4.74	10.86
Vb	26	151–152	44.05	3.02	8.60	9.70	$C_{12}H_{10}N_2O_7S$	44.17	3.09	8.59	9.83

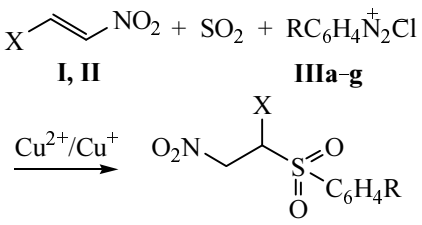
[a] mp, °C**: IVa**, 186–187 [14]; **IVc**, 147.5–148 [14]; **IVf**, 148–150 [15].

1070-4280/04/4002-0191©2004 MAIK "Nauka/Interperiodica"

Table 2. ^{1}H NMR spectra of sulfones **IVa–f** and **Va, b**, δ, ppm (*J*, Hz)

Compd. no.	CH_2	CH	R (s, 3H)	X	$SO_2C_6H_4$
IVb	5.27–5.40 m (2H)	5.51 d.d (1H), ^2J 13.5, ^3J 5.4	2.52	7.30–7.43 m (7H), 7.57–7.68 m (2H)	
IVc	5.23–5.55 m (3H)		2.42	7.27–7.36 m (5H)	7.37 d (2H), 7.53 d (2H)
IVd	5.23–5.35 m (2H)	5.47 d.d (1H), ^2J 12.9, ^3J 4.2	3.90	7.30–7.40 m (5H)	7.06 d (2H), 7.56 d (2H)
IVe	5.40–5.48 m (2H)	5.57 d.d (1H), ^2J 8.1, ^3J 5.7		7.32–7.43 m (5H)	7.59 d (2H), 7.78 d (2H)
IVf	5.34–5.62 m (3H)			7.32–7.43 m (5H)	7.78 d (2H), 7.96 d (2H)
Va	5.27 d.d (1H, ^2J 14.7, ^3J 10.0), 5.35 d.d (1H, ^3J 5.7)	5.63 d.d (1H)	2.37	6.45 m (1H, 4-H), 6.51 d (1H, 3-H), 7.64 br.s (1H, 5-H)	7.41–7.55 m (3H), 7.59 d (1H)
Vb	5.36 d.d (1H, ^2J 15.0, ^3J 9.0), 5.44 d.d (1H, ^3J 5.0)	5.91 d.d (1H)		6.47 m (1H, 4-H), 6.58 d (1H, 3-H), 7.65 br.s (1H, 5-H)	7.98 d (2H), 8.42 d (2H)

Besides copper(II)chloride the reaction is catalyzed by copper(II) acetate. Both catalysts ensure comparable yields of compounds **IVa–g, Va, b**, whereas these sulfones do not form in the absence of catalysts.



I, II **IIIa–g**

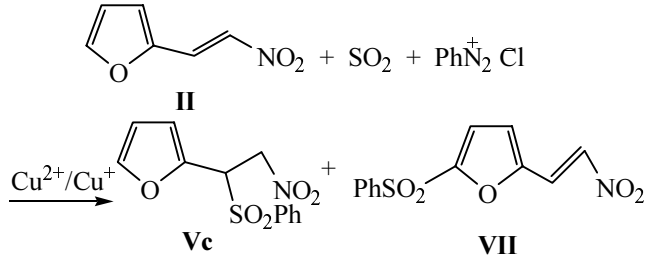
IVa–f, Va, b

X = Ph (**I, IV**), 2-furyl (**II, V**); **III, IV**, R = H (**a**), 2-Me (**b**), 4-Me (**c**), 4-MeO (**d**), 4-Br (**e**), 4-NO_2 (**f**), 3-Me (**g**); **V**, R = 3-Me (**a**), 4-NO_2 (**b**).

$$SO_2 + RC_6H_4\overset{+}{N}_2\,Cl^- \xrightarrow[-Cu^{2+}]{Cu^+} ArSO_2Cl + N_2$$

IIIa–g **VIa–g**

In reaction of benzyldiazonium chloride **IIIa** with 2-(2-nitrovinyl)furan **II** alongside compound **Va** formed also a product of arylsulfonylation in the position *5* of furan ring **VII**.



II **Vc** **VII**

Arylsulfonyl group enters into the α-position with respect to the aromatic group of alkene (in contrast to the cases described in [1–11]) and into the β-position with respect to the acceptor substituents. The

$$ArSO_2Cl + SO_2 + H_2O \longrightarrow ArSO_2H + HCl + H_2SO_4$$

VIa–g

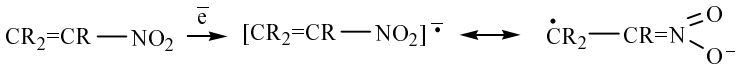
regiodirection of reaction corresponds to that of formation of products at the sulfinic acids nucleophilic addition across a double bond [14–17]. Actually, arenesulfinic acids may arise in the course of the reaction by reduction of arenesulfonyl chlorides by the following scheme [18]:

$$\mathbf{I} + 4\text{-}MeC_6H_4SO_2Cl \xrightarrow[or\ Cu^+]{Cu^{2+}} \mathbf{IVc}$$

VIII

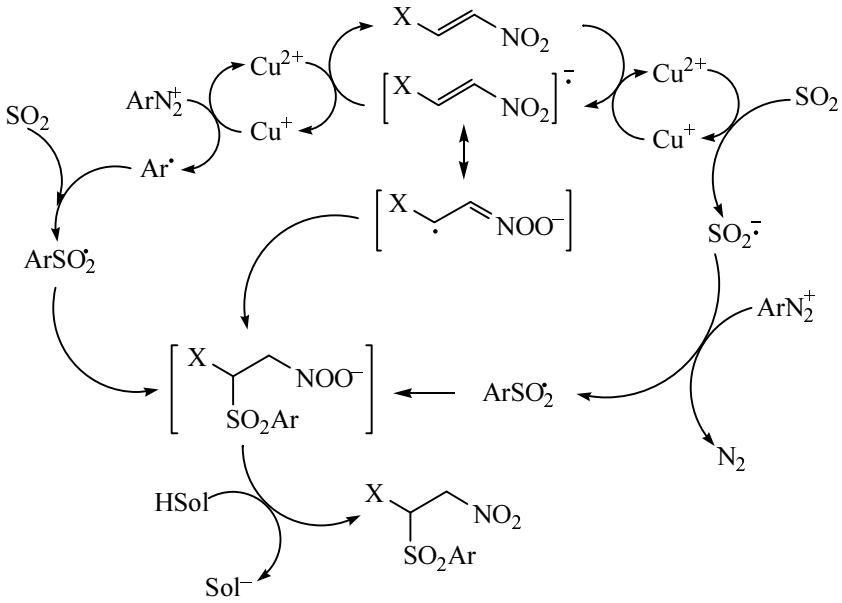
We established however, that compound **IVc** formed also in reaction of olefine **I** with *p*-toluenesulfonyl chloride **VII** in the presence of $CuCl_2$ (or CuCl).

The formation of an anion $ArSO_2^-$ under conditions of this reaction is hardly probable. It is known that alkyl-(or aryl)sufonyl radicals form here [19] and not sulfanate anions. Besides the capability of arenesulfinate anion to be involved in the nucleophilic addition as S- or O-alkylating agent also should be taken in consideration. In this case the less sterically strained compound would be the sulfinic acid ester that we have not detected among the reaction products. In the reactions with sodium benzenesulfinate an ion-radical mechanism is operative [20]. Besides the copper salts are active promoters of ion-radical processes [21–25].



Hence in the reaction under study of alkenes and dienes with arenediazonium salts and SO_2 occurred the addition of an arylsulfonyl group and a hydrogen atom in contrast to the previously described addition of an arylsulfonyl group and a nucleophile [1–8]. This difference is apparently due to the fact that for the electron-deficient nitroolefins the anion-radical state is more stable than cation-radical one [26–28].

The anion-radical mechanism of a reaction between an electron-deficient olefin (b,c,c-trifluorostyrene) and arenediazonium salts was substantiated in [29]. Besides the one-electron transfer to form ion-radicals is also characteristic of the arendiazonium cations [18, 25, 30, 31]. Taking into account these data and our experimental results the following scheme may be suggested:



It is therefore presumable that olefins with strong electron-withdrawing substituents at the double bond react with arenediazonium salts and SO_2 according to the mechanism of anion-radical addition [29].

EXPERIMENTAL

^{1}H NMR spectra of compounds **IV** and **V** were registered on a spectrometer Varian VXR-300 (300 MHz) in CD_3COCD_3 (**IVb–f**)or DMSO-d_6 (**Va–c**), internal reference HMDS.

Reaction of arenediazonium chlorides and SO_2 with compounds I and II. To a mixture of 50 ml of acetone and 50 ml of acetic acid saturated with sulfur(IV) oxide was added 4 g of $CuCl_2 \cdot 2H_2O$ and 0.1 mol of compound **I** or **II**. The mixture was stirred at 15–20°C while a water solution of arenediazonium chloride **IIIa–g** prepared by diazotization of.1 mol of an appropriate amine was gradually added. The reaction was continued till the nitrogen evolution stopped. Then the reaction mixture was diluted with 300–500 ml of water. The separated oily or crystalline (in case of compounds **IVe, f** and **Va, b**) substance was washed with water, hexane, or petroleum ether, and recrystallized from ethanol. Thus were obtained compounds **IVa–f**, **Va, b**. On evaporation of the remaining filtrate arenesufonyl chlorides **VIa–g** were isolated.

In reaction between benzenediazonium chloride **IIIa** with 2-(2-nitrovinyl)furan **II** were obtained compounds **Va** and **VII** in 18 and 12% yield respectively. ^{1}H NMR spectrum, δ, ppm: 5.29 d.d (**Va**; 0.6 H, CH_2, ^2J 14, ^3J 8 Hz), 5.38 d.d (**Va**; 0.6 H, CH_2, ^3J 5.3 Hz), 5.68 d.d (Va; 0.6 H, CH), 6.44 m (**Va**; 0.6 H, H^4 of furan), 6.49 d (**Va**; 0.6 H, H^3 of furan, J 3.0 Hz), 6.77 br.s (**VII**; 0.4 H, H^3 of furan), 7.28 d (**VII**; 0.4 H, H^4 of furan., J 3.4 Hz), 7.55–7.82 m (**Va** + **VII**; 5.6 H, C_6H_5, CH=CH, H^5 of furan.), 7.99–8.06 m (**VII**; 0.8 H, C_6H_5). The integral intensities of signals and elemental analysis indicate that the ratio of compounds **Va** and **VII** is equal to 3:2.

Reaction of *p*-toluenesulfonyl chloride with c-nitrostyrene. To a solution of 19 g (0.1 mol) of *p*-toluenesulfonyl chloride **VIII** and 14.9 g (0.1 mol) of β-nitro-

styrene **I** in 50 ml of acetone was added 4 g of $CuCl_2 \cdot 2H_2O$ (or 3 g of CuCl), and the mixture was vigorously stirred at 20–25°C for 10 h. Isolation and purification of the product obtained was done as described above. Compound **IVc** was obtained in 25% yield.

REFERENCES

1. Naidan, V.M., Naidan, G.D., and Litvin, G.V., *Zh. Org. Khim.*, 1978, vol. 14, p. 2622.
2. Naidan, V.M., Naidan, G.D., and Dombrovskii, A.V., *Zh. Obshch. Khim.,* 1979, vol. 49, p. 1829.
3. Naidan, V.M. and Naidan, G.D., *Zh. Obshch. Khim.,* 1980, vol. 50, p. 2611.
4. Naidan, V.M., Naidan, G.D., Drozdova, S.G., and Musienko, V.M., *Zh. Obshch. Khim.,* 1985, vol. 55, p. 391.
5. Bilaya, E.E., Obushak, N.D., and Ganushchak, N.I., *Zh. Org. Khim.*, 1999, vol. 35, p. 655.
6. Bila, A. and Ganushchak, M., and Obushak, M., *Visnik L'viv. Universitetu, Ser. Khim*., 2001, vol. 40, p. 173.
7. Bilaya, E.E., Obushak, N.D., Ganushchak, N.I., and Buchinskii, A.M., *Zh. Org. Khim.* , 1996, vol. 32, p. 1528.
8. Bila, E.E. and Obushak, M.D., *Visnik L'viv. Universitetu, Ser. Khim*., 1995, vol. 35, p. 74.
9. Obushak, N.D., Bilaya, E.E., and Ganushchak, N.I., *Zh. Org. Khim.* , 1991, vol. 27, p. 2372.
10. Bila, E., Ganushchak, M., and Obushak, M., *Visnik L'viv. Universitetu, Ser. Khim*., 2001, vol. 40, p. 176.
11. Bila, E. and Ganushchak, M. , *Visnik L'viv. Universitetu, Ser. Khim.,* 2000, vol. 39, p. 256.
12. Buchins'kii, A.M., Obushak, N.D., and Bila, E.E., *Visnik L'viv. Universitetu, Ser. Khim.,* 1997, vol. 37, p. 86.
13. Obushak, N.D., Buchinskii, A.M., Bilaya, E.E., and Ganushchak, N.I., *Zh. Obshch. Khim.,* 1997, vol. 67, p. 1405.
14. Cason, L.F. and Wanser, C.C., *J. Am. Chem. Soc*., 1951, vol. 73, p. 142.
15. Messinger, P., *Arch. Pharm.,* 1973, vol. 306, p. 458.
16. Achmatowicz, O. and Michalski, J., *Roczn. Chem.,* 1956, vol. 30, p. 243.
17. Obushak, M., Bila, E., Matiichuk, V., and Ganushchak,. *Visnik L'viv. Universitetu, Ser.Khim*., 2002, vol. 41, p. 167.
18. Saunders, K.H. and Allen, R.L.M., *Aromatic, Diazo, Compounds,* London: Edward, Arnold, 1985, p. 726.
19. Tanaskov, M.M. and Stadnichuk, M.D., *Zh. Obshch. Khim.,* 1978, vol. 48, p. 1140.
20. Todres, Z.V., *Ion-radikaly v organicheskom sinteze* (Ion Radicals in Organic Synthesis), Moscow: Khimiya, 1986, p. 149.
21. Bowman, W.R., Heaney, H., and Smith, P.H.G., *Tetrahedron Lett*., 1984, vol. 25, p. 5821.
22. Liedholm, B., *Acta Chem. Scand. B,* 1984, vol. 38, p. 877.
23. Bilaya, E.E., *Cand. Sci. (Chem.) Dissertation,* L'vov, 1989.
24. Bila, E.E., Obushak, M.D., and Ganushchak, M.I., *Pol. J. Chem*., 2000, vol. 74, p. 1567.
25. Obushak, N.D., Lyakhovich, M.B., and Bilaya, E.E., *Zh. Org. Khim.*, 2002, vol. 38, p. 47.
26. Todres, Z.V., Nekrasova, G.V., Lipina, E.S., and Chernyshova, T.M., *Izv. Akad. Nauk, SSSR, Ser.Khim*., 1979, p. 126.
27. Todres, Z.V., Kuryaeva, T.T., Ryzhova, G.L., and Kursanov, D.N., *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1980, p. 1602.
28. Shvekhgeimer, G.A., Zvolinskii, V.I., Kobrakov, K.I., and Bargamov, G.G., *Dokl. Akad. Nauk SSSR.,* 1984, vol. 278, p. 888.
29. Bilaya, E.E., Obushak, N.D., and Ganushchak, N.I., *Zh. Org. Khim.* , 1997, vol. 33, p. 1068.
30. Singh, P.R. and Kumar, P., *Austr. J. Chem.,* 1972, vol. 25, p. 2133.
31. Singh, P.R. and Kumar, P., *Tetrahedron Lett*., 1972, p. 613.