ISSN 1070-4280, Russian Journal of Organic Chemistry, 2014, Vol. 50, No. 2, pp. 296–297. © Pleiades Publishing, Ltd., 2014.
Original English Text © R.D. Savka, N.T. Pohodylo, M.D. Obushak, 2014, published in Zhurnal Organicheskoi Khimii, 2014, Vol. 50, No. 2, pp. 303–304.

SHORT COMMUNICATIONS

Effective Method of β-Keto Sulfones Synthesis

R. D. Savka, N. T. Pohodylo, and M. D. Obushak

Ivan Franko Lviv National University, Lviv, 79005 Ukraine
e-mail: obushak@in.lviv.ua

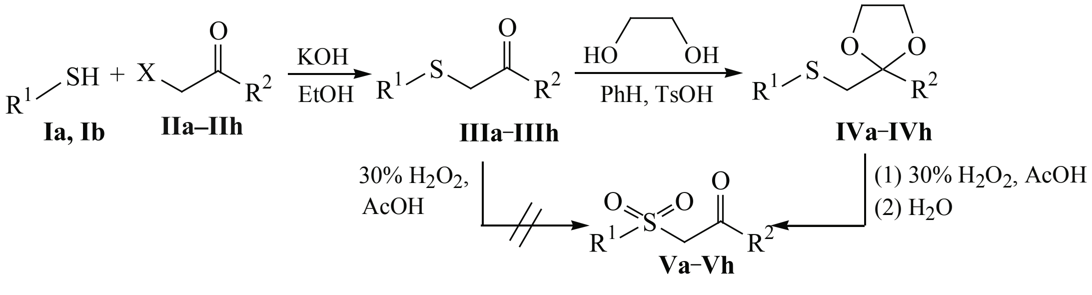
Received September 20, 2013

DOI: 10.1134/S1070428014020274

β-Keto sulfones are widely used in organic synthesis as reagents in Michael and Knoevenagel reactions [1–3], for preparation of vinyl sulfones [4], polyfunctional 4*H*-pyrans [3], chalcones, alkynes, allenes, and compounds of other classes [1,5–9]. In this connection various approaches are developed to the synthesis of β-keto sulfones [10–18], but many among them require severe conditions, preparation of initial compounds, and the yields of products in these reactions are often low.

Looking for an efficient and cheap method of β-keto sulfones synthesis aiming at their application as methylene-active reagents in the preparation of 1,2,3-triazoles [19] we developed a procedure for the synthesis of β-keto sulfones with the use of available thiols **I** and β-haloketones **II**. The reaction of thiophenol (**Ia**) and 4-methylthiophenol (**Ib**) with β-haloketones **IIa–IIh** afforded β-keto sulfides **IIIa–IIIh**. The oxidation of these compounds with hydrogen peroxide in acetic acid [20] did not result in selective formation of sulfones **V**, but gave a mixture of reaction products. This result may be ascribed to the concurrent reaction of the keto group oxidation analogously to Baeyer-Villiger reaction. For instance, the oxidation of compound **IIIa** with hydrogen peroxide in acetic acid at room temperature led to the formation of a mixture of β-keto sulfone **Va** and methylsulfonylbenzene in a ratio 2 : 1 [21]. Keto sulfides may be oxidized with potassium permanganate [22], but at the oxidation β-keto sulfides **III** in this way sulfones **V** formed in low yields. Considering these results we protected the keto group in compounds **IIIa–IIIh** by converting them in 1,3-dioxolanes **IVa–IVh**. At the oxidation of compounds **IVa–IVh** with hydrogen peroxide in acetic acid followed by treating the reaction mixture with water the target β-keto sulfones **Va–Vh** formed in high yields (see the table).

General procedure of preparation of β-keto sulfones Va–Vh [1-(arylsulfonyl)alkan-2-ones Va, Vb and 1-aryl-2-(arylsulfonyl)ethan-1-ones Vc–Vh]. To a solution of 2.8 g (50 mmol) of KOH and 50 mmol of thiophenol (**Ia**) or 4-methylthiophenol (**Ib**) in 25 mL of ethanol was added 50 mmol of β-haloketone **IIa–IIh**. The mixture was left standing for 1 h at room temperature and then it was diluted with water. The obtained (arylsulfanyl)alkan-2-one (β-keto sulfide) **III** was separated from water phase and used in the next stage without additional purification. The solution of 40 mmol of β-keto sulfide **IIIa–IIIh**, 8.2 mL (144 mmol) of ethylene glycol, and 8.8 mg (0.08 mmol) of *p*-toluenesulfonic acid in 45 mL



β-Keto sulfones **Va–Vh**

Compound no.	X (**IIa–IIh**)	R^1	R^2	Yield, %[a]	References[b]
Va	Cl	Ph	Me	69	[21]
Vb	Cl	Ph	$CH_2CH(CH_3)_2$	67	[15]
Vc	Br	4-MeC_6H_4	Ph	70	[14]
Vd	Br	4-MeC_6H_4	4-MeC_6H_4	68	[14]
Ve	Br	4-MeC_6H_4	4-$MeOC_6H_4$	67	[14]
Vf	Br	4-MeC_6H_4	4-FC_6H_4	70	[14]
Vg	Br	4-MeC_6H_4	4-ClC_6H_4	71	[14]
Vh	Br	4-MeC_6H_4	4-$NO_2C_6H_4$	65	[14]

[a] Yields are reported with respect to initial compounds **I, II**.

[b] Constants and spectral characteristics of sulfones **Va–Vh** are in agreement with published data.

of benzene was boiled collecting the distilled water in the Dean–Stark trap. On the completion of the reaction the mixture was cooled to room temperature and twice washed with water. The organic layer was separated, dried with $MgSO_4$, and evaporated. The residue, 1,3-dioxolane **IVa–IVh**, was further used without additional purification. To a solution of 25 mmol of 1,3-dioxolane **IVa–IVh** in 15 mL of acetic acid was added in small portions 7.4 mL of 30% H_2O_2 solution, the reaction mixture was heated to the temperature no higher than 75°C, then for 3 h at 80–85°C. The mixture was cooled to room temperature, diluted with water, and left overnight. The precipitated white crystals of compounds **Va–Vh** were filtered off and washed with water.

REFERENCES

1. Simpkins, N.S., *Sulfones in Organic Synthesis*, Baldwin, J.E., Ed., Oxford: Pergamon, Press, 1993.
2. Marco, J.-L., Fernandez, I., Khiar, N., Fernandez, P., and Romero, A., *J. Org. Chem.,* 1995, vol. 60, p. 6678.
3. Marco, J.L., *J. Org. Chem.,* 1997, vol. 62, p. 6575.
4. Sengupta, S., Sarma, D.S., and Mondal, S., *Tetrahedron Asymm*., 1998, vol. 9, p. 2311.
5. Ihara, M., Suzuki, S., Taniguchi, T., Tokunaga, Y., and Fukumoto, K., *Tetrahedron,* 1995, vol. 51, p. 9873.
6. Baldwin, J.E., Adlington, R.M., Crouch, N.P., Hill, R.L., and Laffey, T.G., *Tetrahedron Lett.,* 1995, vol. 36, 7925.
7. Looker, J.J., *J. Org. Chem.,* 1966, vol. 31, p. 2714.
8. Gotor, V., Rebolledo, F., and Liz, R., *Tetrahedron Asymm*., 2001, vol. 12, p. 513.
9. Sengupta, S., Sarma, D.S., and Mondal, S., *Tetrahedron,* 1998, vol. 54, p. 9791.
10. Julia, M. and Paris, J.-M., *Tetrahedron Lett.,* 1973, vol. 14, p. 4833.
11. Durst, T., In *Comprehensive Organic Chemistry*, Barton, D.H.R. and Ollis, W.D., Eds., Oxford: Pergamon, Press, 1979, vol. 4, p. 174.
12. Trost, B.M., *Chem. Rev.,* 1978, vol. 78, p. 363.
13. Holmquist, C.R. and Roskamp, E.J., *Tetrahedron Lett.,* 1992, vol. 33, p. 1131.
14. Kamigata, N., Udodaira, K., and Shimizu, T., *J. Chem. Soc., Perkin, Trans. I,* 1997, p. 783.
15. Kartrizky, A.R., Abdel-Fattah, A.A.A., and Wang, M., *J. Org. Chem.,* 2003, vol. 68, p. 1443.
16. Grossert, J.S., Dubey, P.K., Gill, G.H., Stancey, T., Cameron, T.S., and Gardner, P.A., *Can. J. Chem.,* 1984, 62, p. 798.
17. Mitin, A.V., Kashin, A.N., and Beletskaya, I.P., *Russ. J. Org. Chem*., 2004, vol. 40, p. 841.
18. Suryakiran, N., Srikanth, Reddy, T., Asha, Latha, K., Lakshman, M., and Venkateswarlu, Y., *Tetrahedron Lett.,* 2006, vol. 47, p. 3853.
19. Pokhodylo, N.T., Matiychuk, V.S., and Obushak, M.D., *Synthesis,* 2009, p. 2321.
20. Serushkina, O.V., Dutov, M.D., Sapozhnikov, O.Yu., Ugrak, B.I., and Shevelev, S.A., *Russ. J. Org. Chem.*, 2002, vol. 38, p. 1819.
21. Prakash, G.K.S., Zhao, X., Chacko, S., Wang, F., Vaghoo, H., and Olah, G.A., *Beilst. J. Org. Chem.,* 2008, vol. 4, no. 17, p. 1860.
22. Looker, J.J., *J. Org. Chem.,* 1966, vol. 31, p. 2973.