Letters to the Editor

First examples of arenediazonium 4-dodecylbenzenesulfonates: synthesis and characterization*

O. A. Gusel´nikova, K. V. Kutonova, M. E. Trusova, P. S. Postnikov, and V. D. Filimonov*

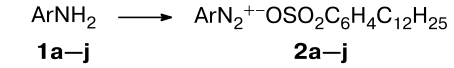
National Research Tomsk Polytechnic University,
30 prosp. Lenina, 634050 Tomsk, Russian Federation.
Fax: +7 (382 2) 56 3637. E-mail: guselnikovaoa@tpu.ru

Arenediazonium salts are among the most commonly used building blocks in organic synthesis.[1—3] The chemistry of diazonium salts in highly polar solutions is well understood,[4] while their behavior in nonpolar media is not enough investigated. Earlier, we have demonstrated that diazotization of anilines with sodium nitrite in CCl_4 in the presence of 4-dodecylbenzenesulfonic acid (DBS) produces arenediazonium dodecylbenzenesulfonates (ADBS) as intermediates. They are soluble in CCl_4 and react with this solvent to give aryl chlorides without using copper catalysts.[5] Even this single example provides evidence for very unusual properties of ADBS, which calls for further investigations of these compounds. However, in our previous study,[5] we have used commercial DBS (≥90% purity, Aldrich, CAS No. 121-65-3) and ADBS not as an individual isolated substance. The present work was aimed at preparative synthesis and study of individual ADBS, for which high-purity DBS samples must be employed.

TLC analysis using benzene—ethanol (9 : 1) as an eluent revealed that commercial DBS contains, apart from DBS itself (R_f 0.1), an impurity with R_f 0.9. According to ^1H and ^{13}C NMR data, this impurity consists of alkylbenzenes. They were removed by flash chromatography on Silicagel L (40/100μ) with hexane as an eluent. Subsequent elution with ethyl acetate gave pure DBS in 92% yield as a non-crystallizable thick oil.

For the synthesis of individual ADBS, we optimized the diazotization conditions (Scheme 1, Table 1). An appropriate aromatic amine **1a—j** (1.0 mmol) was added in the dark in four portions within a minute to a stirred solution of DBS (1.2 mmol) and Bu^tONO (1.2 mmol) in Et_2O (10 mL). The resulting precipitates of ADBS **2a—j** were filtered off, washed with diethyl ether, and dried in air at room temperature.

Scheme 1



1a—j **2a—j**

Reagents and conditions: DBS, Bu^tONO, Et_2O, ~20 °C, 5—20 min.

Compounds **2a—j** are surprisingly stable, which is uncommon with diazonium salts, and can be stored in the

*According to the materials presented at the Conference Cluster on Organic Chemistry "OrgChem-2013" (June 17—21, 2013, St.-Petersburg—Repino, Russia).

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 0289—0290, January, 2014.

Table 1. Yields and selected properties of the ADBS obtained by diazotization of aromatic amines in the presence of DBS

Ar	τ/min[a] (%)	Yield /°C	T.decomp. /J g^{-1}	$E_{decomp.}$ $\delta_{C(1)}$	^{13}C NMR ν(N≡N)/cm^{-1}		IR	
					ADBS	ADT[b]	ADBS	ADT
2-$NO_2C_6H_4$ (**2a**)	5	85	112	440	125.52	123.14	2316	2301
3-$NO_2C_6H_4$ (**2b**)	14	80	112	313	125.14	124.56	2314	2307
4-$NO_2C_6H_4$ (**2c**)	8	90	114	352	125.42	121.96	2320	2304
4-$OMeC_6H_4$ (**2d**)	12	73	131.8	118	114.90	110.24	2289	2275
2-Br-4-$NO_2C_6H_3$ (**2e**)	8	42	106.8	458	125.52	—	2309	—
C_6H_5 (**2f**)	11	56	112	410	118.63	115.60	2301	2299
4-$COOMeC_6H_4$ (**2g**)	6	47	77.8	306	126.78	124.78	2325	2303
2-ClC_6H_4 (**2h**)	3	90	96	561	125.53	—	2319	—
2-MeC_6H_4 (**2i**)	12	58	124	205	125.42	123.5	2284	2280
4-BrC_6H_4 (**2j**)	14	67	97	319	125.36	—	2302	—

[a] The reaction time.
[b] Arenediazonium tosylates.

dark at room temperature for several weeks, showing no signs of decomposition. In this respect, they are similar to related arenediazonium tosylates (ADT).[6] However, unlike ADT, ADBS **2a**—**j** are excellently soluble in nonpolar solvents (benzene, CCl_4, and $CHCl_3$) as well as in water, acetone, acetic acid, alcohols, and DMSO.

Structures **2a**—**j** were confirmed by IR and NMR spectroscopy. The IR spectra contain characteristic absorption bands at 2300—2320 cm^{-1} (—N$^+$≡N). The ^{13}C NMR spectra show relatively high-field signals at δ 114.9—125.5 for the $C(1)_{arom}$ atom directly bound to the diazonium group, which is typical of diazonium salts. The other signals in the ^{1}H and ^{13}C NMR spectra also correspond to structures **2a**—**j**.

Compounds **2a**—**j** were examined for thermal stability and explosion hazard by DSC/DTA/DTG under nitrogen. As expected, these diazonium salts decompose with elimination of N_2 upon heating. Their exothermic decomposition energies are substantially lower than 800 J g^{-1} (see Table 1), so these ADBS can be classified as nonexplosives according to the UNECE international standard.[7] On the whole, the decomposition energies of salts **2a**—**j** are close to or lower than those of ADT.[8]

The unique property of ADBS to be soluble in many nonpolar solvents opens up new scope in the chemistry of diazonium salts.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 12-03-31594/12mol_a).

References

1. F. Mo, G. Dong, Y. Zhong, *Org. Biomol. Chem.*, 2013, **11**, 1582.
2. H. Zollinger, *Diazo Chemistry*, Weinheim—New York—Basel—Cambridge—Tokyo, 1994.
3. K. H. Saunders, *Aromatic Diazocompounds and Their Technical Applications*, London, 1949, p. 83.
4. D. Sutton, *Chem. Rev.*, 1993, **93**, 995.
5. K. V. Kutonova, M. E. Trusova, P. S. Postnikov, V. D. Filimonov, *Russ. Chem. Bull.* (*Int. Ed.*), 2012, **61**, 206 [*Izv. Akad. Nauk, Ser. Khim.*, 2012, 203].
6. V. Filimonov, M. Trusova, P. Postnikov, E. Krasnokutskaya, Y. M. Lee, H. Y. Hwang, H. Kim, K.-W. Chi, *Org. Lett.*, 2008, **18**, 3961.
7. http://www.unece.org/trans/danger/danger.htm.
8. K. V. Kutonova, M. E. Trusova, P. S. Postnikov, V. D. Filimonov, J. Parello, *Synthesis*, 2013, **45**, 2706.

Received October 18, 2013;
in revised form November 27, 2013