

SHORT COMMUNICATIONS

Singular Transformations of Arenesulfonic Acids *N*-(1-Aryl-2,2-dichloroethyl)amides under the Action of Secondary Amines

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In the course of reactivity investigation of typical members of the series of amidodichloroethyl-substituted arenes **Ia–Ic** whose synthesis we had previously developed starting from dichloroacetic aldehyde imines [1, 2] we discovered their singular reactions in highly polar aprotic solvents in the presence of secondary amines and inorganic bases which led to the formation of 4-chlorobenzenesulfonic acid *N*-(2-oxo-2-arylethyl)amides in fair yields.

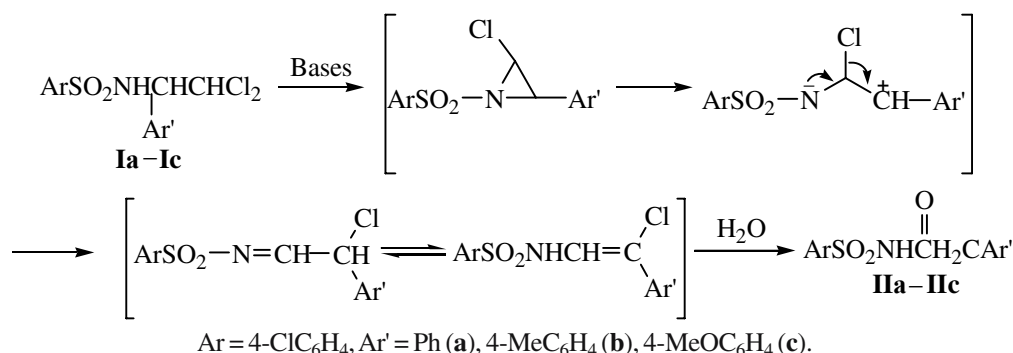
The best yield of aminomethylbenzophenones **Ia–Ic** was attained in reaction carried out in DMF in the presence of five-fold molar excess of sodium or potassium carbonates and diethylamine. At the use of other inorganic bases and amines the reaction mixture suffered tarring thus resulting in lower yields of aminocarbonyl compounds **Ia–Ic**. The reaction did not proceed in the absence of any base.

The structure of compounds **Ia–Ic** was established from their spectra and was consistent with their elemental analysis.

The presumable route to compounds **Ia–Ic** apparently involves a stage of *N*-sulfonyl-2-chloro-3-arylaziridine formation which under the reaction conditions was capable to undergo a ring opening, a chlorine atom migration, tautomeric transformations, and a hydrolysis as shown in the scheme.

The study of the reaction aiming at revealing the process pathways and at development of efficient procedures for preparation of new polyfunctional sulfonamides derivatives is under way.

4-Chlorobenzenesulfonic acid *N*-(2-oxo-2-phenylethyl)amide (IIa). A mixture of 1.83 g (5 mmol) of 4-chlorobenzenesulfonic acid (**Ia**) *N*-(2,2-dichloro-1-phenylethyl)amide, 3.45 g (25 mmol) of K₂CO₃, 2.60 ml (25 mmol) of diethylamine, and 10 ml of DMF was stirred for 1 h. The reaction mixture was diluted with 50 ml of water, neutralized with 10% hydrochloric acid, left standing for 24 h, then the separated precipitate of compound **IIa** was reprecipitated from aqueous ammonia solution and recrystallized from CCl₄. Yield 0.9 g (58%), mp 141–



143°C. IR spectrum, ν , cm^{-1} : 1150, 1345 (SO_2), 1700 ($\text{C}=\text{O}$), 3270 (NH). ^1H NMR spectrum, δ , ppm: 4.46 s (2H, CH_2), 5.68 br.s (1H, NH), 7.46, 7.60, 7.83 m (9H, Ar). Found, %: C 54.38; Cl 11.83; N 4.73; S 10.23. $\text{C}_{14}\text{H}_{12}\text{ClNO}_3\text{S}$. Calculated, %: C 54.28; Cl 11.45; N 4.52; S 10.35.

4-Chlorobenzenesulfonic acid *N*-[2-oxo-2-(4-tolyl)ethyl]amide (IIb) was similarly obtained from 1.90 g (5 mmol) of amide **Ib**. Yield 1.09 g (67%), mp 172–174°C. IR spectrum, ν , cm^{-1} : 1150, 1345 (SO_2), 1695 ($\text{C}=\text{O}$), 3280 (NH). ^1H NMR spectrum, δ , ppm: 2.41 s (3H, CH_3), 4.42 s (2H, CH_2), 5.68 br.s (1H, NH), 7.25, 7.72 *AA'*/*BB'* and 7.48, 7.81 *AA'*/*BB'* (8H, $2\text{C}_6\text{H}_4$). ^{13}C NMR spectrum, δ , ppm: 21.93 (CH_3), 48.51 (CH_2), 128.14, 128.75, 129.52, 129.75, 138.55, 139.41, 141.08, 145.53 ($2\text{C}_6\text{H}_4$), 191.55 ($\text{C}=\text{O}$). Found, %: C 55.41; Cl 11.08; N 4.37; S 9.31. $\text{C}_{15}\text{H}_{14}\text{ClNO}_3\text{S}$. Calculated, %: C 55.64; Cl 10.95; N 4.33; S 9.90.

4-Chlorobenzenesulfonic acid *N*-[2-oxo-2-(4-methoxyphenyl)ethyl]amide (IIc) was similarly obtained from 1.98 g (5 mmol) of amide **Ic**. Yield 0.73 g

(43%), mp 161–163°C. IR spectrum, ν , cm^{-1} : 1150, 1345 (SO_2), 1700 ($\text{C}=\text{O}$), 3270 (NH). ^1H NMR spectrum, δ , ppm: 3.85 s (3H, OCH_3), 4.37 s (2H, CH_2), 5.66 br.s (1H, NH), 6.89, 7.43 *AA'*/*BB'* and 7.79, 7.81 m (8H, $2\text{C}_6\text{H}_4$). ^{13}C NMR spectrum, δ , ppm: 49.01 (OCH_3), 56.38 (CH_2), 115.08, 129.53, 130.32, 130.60, 131.14, 138.98, 140.21, 165.45 ($2\text{C}_6\text{H}_4$), 191.16 ($\text{C}=\text{O}$). Found, %: C 53.32; Cl 10.78; N 4.29; S 9.72. $\text{C}_{15}\text{H}_{14}\text{ClNO}_4\text{S}$. Calculated, %: C 53.02; Cl 10.43; N 4.12; S 9.44.

IR spectra were recorded on Specord IR75 instrument from KBr pellets. ^1H and ^{13}C NMR spectra were registered on a spectrometer Bruker DPX-400 (400.6 and 100.61 MHz respectively) from 5–10% solutions in CDCl_3 , internal reference HMDS. Initial amides **Ia–Ic** were synthesized as in [2].

REFERENCES

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