Studies of *N*-Sulfinyl Compounds. I. Reaction of *N*-Sulfinylanilines with Ethylene Carbonate*[1]

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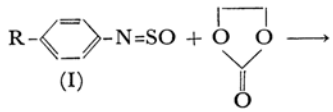
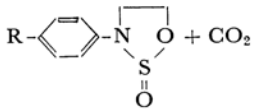
(Received June 10, 1967)

It is well known that *N*-sulfinyl compounds behave as dienophils in the Diels-Alder reaction[1] and undergo 1, 2-addition to certain carbonyl compounds.[2] Also, *N*-sulfinylaniline reacts as a 1, 3-dipolarophil with benzonitrile oxide[3] and with diphenylnitrilimine.[4] These observations indicate that *N*-sulfinyl compounds exhibit reactivities similar to those of isocyanates. Ethylene carbonate, which can behave like the 1, 3-dipolar reagent, reacts with phenyl isocyanate under the influence of lithium halide to give the adduct, 1, 3-oxazolidine-2-one.[5]

Consequently, it may be expected that the reaction of *N*-sulfinylanilines (I) with ethylene carbonate (II) will give the new heterocyclic compound, 1, 2, 5-thiazolidine-1-oxide (III).



(I) (II)



(III)

As part of the investigation of the reactions of *N*-sulfinyl compounds, the reaction of I with II was studied under various conditions.

Results and Discussion

The reaction of *N*-sulfinylaniline (Ia, R=H) with II gave colorless needles (IVa) (mp 162—164°C), with both carbon dioxide and sulfur dioxide evolving in different yields varying with the conditions. The compound IVa was proved, by a mixed-melting-point determination and by a study of the infrared spectrum as well as by elemental analysis, to be identical with *N*, *N'*-diphenylpiperazine, which was prepared from 2-phenylaminoethanol.[6]

In the reaction of Ia with II, the effect of the reaction conditions on the yield of IVa was first examined.

The Effect of the Reaction Temperature. On the basis of the study on the temperature dependence of the decomposition of II with lithium bromide reported by Gulbins *et al.*,[5] it seemed to be desirable for the reaction of I with II to be carried out above 170°C.

As is shown in Table 1, however, when the reaction was carried out at 170°C IVa was obtained in a poor yield and a large amount of a resinous material was formed. Moreover, the yield of IVa decreased with an increase in the reaction time (Runs 1—3). In the reactions at 160 and 150°C, phenomena similar to those mentioned above were also observed. Although the yield of IVa was poor in the reaction at 140°C, it increased with the reaction time (Runs 6—8); at long reaction times no resinous material was found to be formed.

TABLE 1. EFFECT OF THE REACTION TEMPERATURE UNDER THE INFLUENCE OF LITHIUM BROMIDE[a]

Run	II/Ia[b]	Reaction time, hr	Temp. °C	Yield of IVa,[c] %
1	1	1	170	7.2
2	1	2	170	+
3	1	3	170	+
4	1	3	160	+
5	1	3	150	4.2
6	1	2	140	+
7	1	3	140	10.0
8	1	6	140	15.3
9	1.5	3	140	14.0
10	1.5	4	140	31.5
11	1.5	6	140	40.0
12	1.5	11.5	140	50.0

a) The molar ratio of lithium bromide to II was 0.1.
b) Molar ratio.
c) The yields in this and the other tables are based on I, and a plus sign, +, indicates a trace amount.

*1 Presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1967.

1) O. Wichterle and J. Roček, *Chem. Listy*, **47**, 1768 (1953); G. Kresze and W. Wucherpfennig, *Angew. Chem.*, **79**, 109 (1967).
2) G. Kresze and R. Albrecht, *ibid.*, **74**, 781 (1962).
3) P. Rajagopalan and B. G. Advani, *J. Org. Chem.*, **30**, 3369 (1965).
4) R. Huisgen, R. Grashey, M. Seidel, H. Knupfer and R. Schmidt, *Ann.*, **658**, 169 (1962).
5) K. Gulbins, G. Benzing, R. Maysenholder and K. Hamann, *Chem. Ber.*, **93**, 1975 (1960).
6) R. E. Rindfusz and V. L. Harnack, *J. Am. Chem. Soc.*, **42**, 1720 (1920).

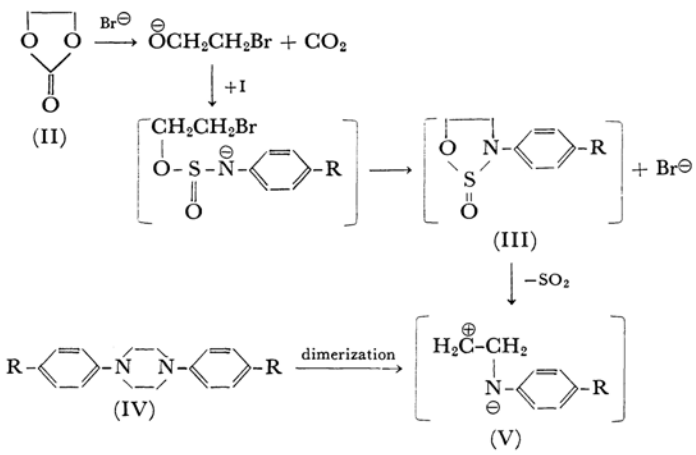


Chart 1.

The time dependence of the decomposition of II with lithium bromide at 140°C was determined according to the Gulbins method;[5] the degrees of the decomposition for 1, 3, and 6 hr were 4.9, 10.2, and 21.6% respectively.

In view of the above data, it was thought advisable to use an excess amount of II in order to raise the yield of IVa. The treatment of I with 1.5 molecular amounts of II afforded IVa in a fair yield (Runs 10—12).

The Effect of the Catalyst. The results are given in Table 2. Under the influence of lithium bromide, the maximum yield of IVa was obtained when the molar ratio of the catalyst to II was 0.1. Its yield rapidly decreased and a large amount of a resinous material came to be formed as the amount of the catalyst increased.

Table 2. Effect of the catalyst[a]

Catalyst	Mol[b] ratio	II/Ia[c]	Reaction time, hr	Yield of IVa, %
LiBr	0.05	1.5	6	25
LiBr	0.1	1.5	6	40
LiBr	0.2	1.5	4	+
TEABr[d]	0.002	1	11	23
TEABr	0.05	1.5	4	32
TEABr	0.05	1.5	5	34

a) The reaction mixture of Ia, II, and the catalyst was heated at 140°C.
b) Molar ratio of the catalyst to II.
c) Molar ratio.
d) The reaction mixture was refluxed in xylene.

It is also known that quaternary ammonium halides are efficient catalysts for the addition of isocyanates to 1, 2-epoxides.[7] Reactions were carried out in the presence of tetraethylammonium bromide (TEABr); these results are also shown in Table 2. Although TEABr was also an effective catalyst, it was found that IVa and TEABr were very difficult to separate when the molar ratio of TEABr to II was over 0.05.

The Effect of the Substituent in *N*-Sulfinylanilines. The reactions of *N*-sulfinyl-*p*-toluidine (Ib, R=CH_3) and *N*-sulfinyl-*p*-chloroaniline (Ic, R=Cl) with II afforded the corresponding *N*, *N'*-diarylpiperazines, IVb and IVc. The results under the influence of lithium bromide and TEABr are summarized in Table 3.

Table 3. Effect of the substituent*

Substituent	Catalyst	Yield of IV, %
H	LiBr	40
H	TEABr	32
CH_3	LiBr	15
CH_3	TEABr	11
Cl	LiBr	47.5
Cl	TEABr	43

* The reaction of I with 1.5 molecular amounts of II was carried out at 140°C for 6 hr. The molar ratios of lithium bromide and of TEABr to II were 0.1 and 0.05 respectively.

Table 3 shows that the order of the reactivity of I in the reaction with II was Ic>Ia>Ib.

On the basis of the above observations and from other considerations,[3,7] the formation of IV may be interpreted as in Chart 1. That is, the expected 1, 2, 5-thiazolidine-1-oxide (III) is formed, and the subsequent elimination of sulfur dioxide from III yields the intermediate V. The dimerization of V then leads to the formation of IV.

Experimental[8]

Materials. The *N*-sulfinylanilines (I) were prepared by the reported method[9] and were purified by

7) G. Speranza and W. J. Peppel, *J. Org. Chem.*, **23**, 1922 (1958).

8) All melting and boiling points are uncorrected.
9) A. Michaelis and R. Herz, *Ber.*, **23**, 3480 (1890).

fractional distillation. *N*-Sulfinylaniline (Ia): bp 80°C/12 mmHg (lit.[9] 80°C/12 mmHg), yield 80%. *N*-Sulfinyl-*p*-toluidine (Ib): bp 91.5—92°C/6 mmHg (lit.[9] 224°C), yield 70%. *N*-Sulfinyl-*p*-chloroaniline (Ic): bp 101—102°C/5 mmHg (lit.[9] 237°C), yield 70%. Ethylene carbonate (II) were purified by distillation. Bp 110°C/18 mmHg.

The Reaction of I with II. A mixture of 0.03 mol of I and specified amounts of II and of the catalyst was stirred under a slow stream of dry nitrogen at a constant temperature. After a specified reaction time, the reaction mixture was cooled and 25 m*l* of ethanol were added, giving crystals. The crystals were collected, washed with 100 m*l* of water, and dried. The recrystallization of the crystals from xylene afforded *N*, *N'*-diarylpiperazine as colorless needles. The results, along with various reaction cinditions, are listed in Tables 1—3.

N, *N'*-Diphenylpiperazine (IVa): mp 162—164°C (lit.[10] 163—164°C).

Found: C, 80.81; H, 7.79; N, 11.66%. Calcd for $C_{16}H_{18}N_2$: C, 80.63; H, 7.61; N, 11.76%.

N, *N'*-Di-*p*-tolylpiperazine (IVb): mp 184.5—186.5°C.

Found: C, 80.88; H, 8.39; N, 10.50%. Calcd for $C_{18}H_{22}N_2$: C, 81.16; H, 8.33; N, 10.52%.

N, *N'*-Di-*p*-chlorophenylpiperazine (IVc): mp 234.5—236°C.

Found: C, 62.87; H, 5.23; N, 9.06%. Calcd for $C_{16}H_{16}N_2Cl_2$: C, 62.54; H, 5.21; N, 9.12%.

The authors are indebted to Mr. E. Shiozaki of this laboratory for his microanalyses.

10) H. W. Heine, B. L. Kapur and C. S. Mitch, *J. Am. Chem. Soc.*, **76**, 1173 (1954).