FISSION REACTIONS OF THE AZIRIDINE RING

IV. REACTION OF N-ARYLETHYLENIMINES WITH CARBON DIOXIDE, ITS SULFUR ANALOGS, AND PHENYL ISOTHIOCYANATE*

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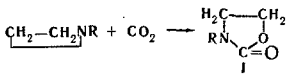
UDC 547.717'787'861 3'789.1

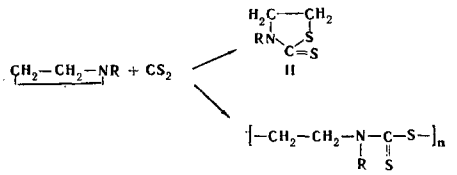
Reaction of N-arylethylenimines with carbon dioxide in the presence of tetraethylammonium bromide gives N-aryl-2-oxazolidones, with N,N'-diarylpiperazines as by-products. Carbon disulfide reacts with N-arylethylenimines under similar conditions to give 1:1 copolymers, together with small amounts of N-arylthiazolidine-2-thiones. Carbon oxysulfide gives copolymers only. The copolymers are converted at 250° C into N-arylthiazolidine-2-thiones and N-arylthiazolidones, respectively. N-Arylethylenimines react with phenyl isothiocyanates to give 2-phenylimino-3-arylthiazolidines.

We have shown previously that N-phenylethylenimine reacts with carbon dioxide and its sulfur analogs [2], and with isothiocyanates [3], in the presence of tetraethylammonium bromide (TEAB), to give five-membered heterocyclic compounds. This paper deals with the reaction of other N-arylethylenimines with the same reagents. Thus, on heating equimolar amounts of N-arylethylenimines with carbon dioxide at 95° C in the presence of TEAB, N-aryl-2-oxazolidones (I) are formed.



The corresponding N,N'-diarylpiperazines are formed in 40% yield as by-products in the reactions with o- and p-methoxyphenylethylenimines. In the reaction of o-tolylethylenimine with carbon dioxide, no oxazolidone is formed, but the ethylenimine dimerizes. The structure of the oxazolidones is confirmed by their synthesis from β-hydroxyethylamines and diethyl carbonate [4].

Reaction of carbon disulfide with N-arylethylenimines under similar conditions results in fission of the ethylenimine ring to give thiazolidine-2-thiones (II) (8-15%). The main reaction products (60-80%) are copolymers of the N-arylethylenimines with carbon disulfide in the molar proportions 1:1. The copolymers break down on heating at 200-250° C to form the corresponding N-arylthiazolidine-2-thiones in 40-50% yield. The yields are increased substantially (80%) when the pyrolysis is carried out in toluene solution in sealed ampuls.

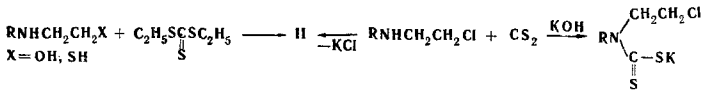


The high yield of the cyclization product indicates the correctness of the assumption that the ethylenimine and carbon dioxide units alternate in the copolymer molecule. The structure of the N-arylthiazolidine-2-

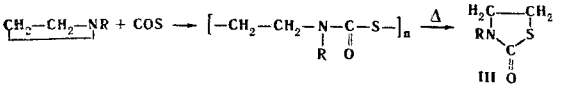
*For part III, see [1].

Translated from Khimiya Geterotsiklicheskikh Soedinenii, Vol. 6, No. 5, pp. 611-615, May, 1970. Original article submitted December 24, 1968.

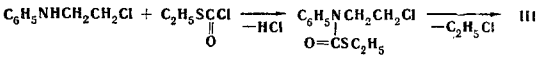
thiones was confirmed by their synthesis by other methods, i.e., the reaction of diethyl thiocarbonate with β-hydroxyethyl- and β-mercaptoethylamines, thiophosgenation of the corresponding β-mercaptoethylamines, and reaction of N-(β-chloroethyl)-N-arylamines with carbon disulfide.



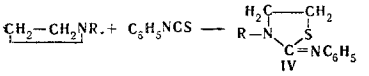
Reaction of carbon oxysulfide with N-arylethylenimines gave only copolymers, which were insoluble in most organic solvents, with the exception of o-cresol.



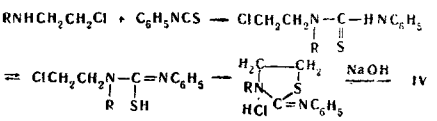
The structure of the copolymers was confirmed by the presence in their IR spectra of strong absorption bands due to the carbonyl group (1670-1675 cm^{-1}), and by the formation of N-arylthiazolidones (III) by thermal degradation. The thiazolidones III have been synthesized previously by the phosgenation of β-mercaptoethylamines [5]. N-Phenyl-2-thiazolidone was obtained by the pyrolysis of ethyl-N-phenyl-N-(β-chloroethyl)thiocarbamate at 250° C.



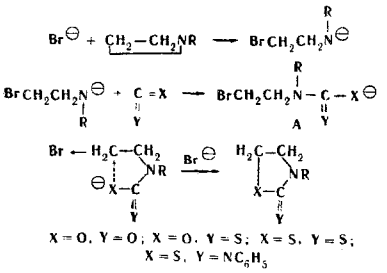
Isothiocyanates react with N-arylethylenimines with opening of the C = S bond to form the corresponding 2-phenylimino-3-arylthiazolidones (IV).



The IR spectra of the compounds obtained show absorption bands $\nu_{N=C}$ at 1632 cm^{-1}. Compound IV was also obtained from N-(β-mercaptoethyl)-N-arylamines and phenyliminophosgene [3], and by alkaline treatment of the corresponding N-(β-chloroethyl)-N-arylthioureas.



The mechanism of the reaction of N-arylethylenimines with some compounds containing double bonds may probably be represented as follows.



The anion A can react with another molecule of the N-arylethylenimine resulting in growth of the chain of alternating ethylenimine and reagent (CS_2 or COS) units, or by elimination of a Br anion to give the five-membered heterocycle.

EXPERIMENTAL

The N-arylethylenimines were synthesized by dehydrochlorination of N-(β-chloroethyl)-N-arylamine hydrochlorides, as in [6].

Reaction of N-Arylethylenimines with Carbon Dioxide. The N-arylethylenimine (0.017 mole), 0.75 g (0.017 mole) of carbon dioxide, and 0.01 g of TEAB were heated in an ampul at 95° C for 10-30 hr. The reaction product was recrystallized from a methanol–heptane mixture. The resulting N-aryloxazolidones gave no depression of the mp on admixture with samples obtained from the corresponding β-hydroxyethylamines and diethyl carbonate [4]: mp, °C, and yield, %, for the following aryl groups: C_6H_5) 120, 80; p-CH_3-C_6H_4) 90, 80; o-$CH_3OC_6H_4$) 75, 50; and p-$CH_3OC_6H_4$) 110, 56. The mp's agreed with the literature values [8]. The reaction of N-o-methoxyphenyl- and N-p-methoxyphenylethylenimines with carbon dioxide also gave 30% yields of N,N'-di-o-methoxyphenylpiperazine, mp 173-174° C (from acetone) [1] and N,N'-di-p-methoxyphenylpiperazine, mp 242° C (from toluene) [7]. With N-o-tolylethylenimine, only N,N'-di-o-tolylpiperazine was formed, in 70% yield, mp 170-171° C (from acetone) [1].

Reaction of N-arylethylenimines with carbon disulfide. The N-arylethylenimine (0.012 mole), 0.91 g (0.012 mole) of carbon disulfide, and 0.01 g of TEAB were kept in an ampul (for conditions, see Table 1). Unreacted ethylenimine and CS_2 were washed out with ether, and the residue treated with hot alcohol, from which II separated in 8-15% yields. The residue contained the copolymers, which were insoluble in most organic solvents (Table 1).

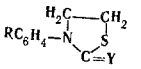
Pyrolysis of Copolymers of N-Arylethylenimines and Carbon Disulfides. The copolymer (0.3 g) was heated for 30 min in an evacuated ampul at 200-250°C. The dark, tarry mass was dissolved in alcohol and treated with decolorizing charcoal to give II in 40-50% yields (Table 2). They gave no depression of the mp with the thiazolidinethiones obtained from carbon disulfide and N-arylethylenimines, or by alternative syntheses, and had almost identical IR spectra.

3-Arylthiazolidine-2-thiones (II). A) These were synthesized in the manner of N-phenylthiazolidine-2-thione [3], from N-(β-hydroxyethyl)-N-tolylamines and diethyl thiocarbonate. We obtained 3-o-tolyl-

TABLE 1. Conditions for the Reaction of N-Arylethylenimines with Carbon Disulfide and Carbon Oxysulfide, and Properties of the Copolymers $[-CH_2CH_2-\underset{\displaystyle R}{N}-\overset{\displaystyle J}{C}-S-]_n$

R	J	Reaction conditions: Duration, hr	Reaction conditions: Temp., °C	Decomp. temp., °C	Solubility	$[\eta]^{40}$	Molecular formula	N, %: Found	N, %: Calculated	Yield, %
C_6H_5	O	40	95	195	o-Cresol, dimethylformamide	0.03	C_9H_9NOS	7.65 7.71	7.81	33
o-$CH_3C_6H_4$	O	20	95	190—191	o-Cresol	0.04	$C_{10}H_{11}NOS$	7.21 7.30	7.24	60
p-$CH_3C_6H_4$	O	5	20	235—240	o-Cresol	0.03	$C_{10}H_{11}NOS$	7.20 7.19	7.24	85
p-$CH_3OC_6H_4$	O	0.5	20	218—220	o-Cresol	0.06	$C_{10}H_{11}NO_2S$	6.92 6.80	6.69	70
C_6H_5	S	10	95	200	o-Cresol	0.02	$C_9H_9NS_2$	7.19 7.20	7.23	73
o-$CH_3C_6H_4$	S	30	95	180—185	Dimethylformamide	0.05 ($[\eta]^{20}$)	$C_{10}H_{11}NS_2$	6.22 6.28	6.69	70
p-$CH_3C_6H_4$	S	5	95	210—215	—	—	$C_{10}H_{11}NS_2$	6.93 6.80	6.69	76
o-$CH_3OC_6H_4$	S	30	95	175—180	Dimethylformamide	0.03 ($[\eta]^{20}$)	$C_{10}H_{11}NOS_2$	6.60 6.70	6.22	80
p-$CH_3OC_6H_4$	S	5	20	185—190	—	—	$C_{10}H_{11}NOS_2$	6.03 6.10	6.22	80

TABLE 2



R	Y	mp °C	Molecular formula	Found					Calculated				
				C, %	H, %	N, %	S, %	M	C, %	H, %	N, %	S, %	M
H	S	128	$C_9H_9NS_2$	55.12 55.58	4.05 4.60	7.12 7.28	32.68 32.95	194	55.38	4.61	7.23	32.77	195
o-CH_3	S	128—129	$C_{10}H_{11}NS_2$	56.79 57.00	5.48 5.40	6.60 6.65	29.84 30.00	209	57.42	5.26	6.69	30.62	209
p-CH_3	S	126	$C_{10}H_{11}NS_2$	57.09 56.56	5.47 5.30	6.70 6.63	29.26 29.90	209	57.42	5.26	6.69	30.62	209
o-CH_3O	S	136	$C_{10}H_{11}NOS_2$	53.09 53.10	5.05 4.99	6.00 6.12	28.03 28.10	224	53.26	4.89	6.22	28.44	225
p-CH_3O	S	120	$C_{10}H_{11}NOS_2$	53.20 53.15	5.00 5.01	6.10 6.15	28.20 28.31	223	53.26	4.89	6.22	28.44	225
H	NC_6H_5	134	$C_{15}H_{14}N_2S$	70.87 70.85	5.03 5.29	11.34 10.75	12.59 12.49	246	70.86	5.51	11.02	12.59	254
o-CH_3	NC_6H_5	83—84	$C_{16}H_{16}N_2S$	71.42 71.10	5.93 6.00	10.83 10.20	11.91 11.60	269	71.64	5.97	10.43	11.94	268
p-CH_3	NC_6H_5	126	$C_{16}H_{16}N_2S$	71.07 71.20	6.08 5.90	10.23 10.30	11.51 11.70	270	71.64	5.97	10.43	11.94	268
o-CH_3O	NC_6H_5	141—142	$C_{16}H_{16}N_2OS$	67.50 67.55	5.69 5.80	9.78 9.70	11.20 11.22	280	67.60	5.64	9.86	11.28	284
p-CH_3O	NC_6H_5	111—112	$C_{16}H_{16}N_2OS$	67.69 67.60	5.79 5.70	9.57 9.80	11.19 11.20	281	67.60	5.64	9.86	11.28	284

thiazolidine-2-thione, mp 123° C (from alcohol), and 3-p-tolylthiazolidine-2-thione, mp 125-126° C (from alcohol).

B) A 9.3-g (0.05 mole) quantity of N-(β-mercaptoethyl)-o-toluidine [9], 8.7 g (0.05 mole) of diethyl thiocarbonate, and 0.1 g of sodium methoxide were heated in an oil bath at 150° C for 2 hr. The ethanethiol was allowed to distill. The residue gave 2.5 g (24%) of 3-o-tolyl-thiazolidine-2-thione, mp 128° C (from alcohol).

C) To a solution of 10.1 g (0.05 mole) of N-(β-mercaptoethyl)-o-anisidene and 11.1 g (0.1 mole) of triethylamine in 50 ml of dry ether was added dropwise at 0-5° C during 1 hr, 5.7 g (0.05 mole) of thiophosgene in 25 ml of dry ether. The solution was stirred at room temperature for 6 hr, treated with water, and the crystalline 3-o-methoxyphenylthiazolidine-2-thione was filtered off to give 6.7 g (60%), mp 136° C (from alcohol).

Reaction of N-Arylethylenimines with Carbon Oxysulfide. The N-arylethylenimine (0.012 mole), 0.71 g (0.012 mole) of carbon oxysulfide, and 0.01 g of TEAB were kept in an ampul (conditions given in Table 1). Unreacted ethylenimine and COS were removed by washing with ether. The residue consisted of a colorless polymer which was insoluble in most solvents other than o-cresol. Precipitated from o-cresol with ether (see Table 1).

Pyrolysis of Copolymers of N-Arylethylenimines and Carbon Oxysulfide. The copolymer (0.3 g) was heated at 250-300° C for 30 min in an evacuated ampul. The resulting dark tarry mass was dissolved in alcohol and treated with decolorizing charcoal to give the 3-arylthiazolidones in 30-50% yields: mp, °C, for the following aryl groups: C_6H_5) 76, o-$CH_3C_6H_4$) 60, p-$CH_3C_6H_4$) 93, and p-$CH_3OC_6H_4$) 102. The mp's agreed with the literature values and were not depressed on admixture with III obtained by phosgenation of the corresponding β-mercaptoethylamines [9]. The IR spectra showed $\nu_{C=O}$ 1670 cm^{-1}.

3-Phenyl-2-thiazolidone. To a solution of 15.5 g (0.1 mole) of N-(β-chloroethyl)aniline and 7.9 g (0.1 mole) of pyridine in 50 ml of benzene was added during 30 min 12.4 g (0.1 mole) of ethylchlorothioformate in 50 ml of benzene. The mixture was stirred at room temperature for 1 hr, and the pyridine salt removed by washing with water. The benzene solution was dried over $MgSO_4$, the benzene distilled off, and the residue pyrolyzed at 200-250° C for 30 min. Ethyl chloride condensed in the trap. From the residue, we obtained 14.3 g (80%) of 3-phenylthiazolidone, mp 76° C (from alcohol), which gave no depression of mp on admixture with the pyrolysis product of the corresponding copolymer.

2-Phenylimino-3-arylthiazolidines (IV) (Table 2). A) The reaction of N-arylethylenimines with phenyl isothiocyanate. The N-arylethylenimine (0.025 mole), 3.4 g (0.025 mole) of phenyl isothicyanate, and 0.01 g of TEAB were heated for 10-40 hr in an ampul at 80-150° C. The reaction product was recrystallized from alcohol to give IV in 85-95% yields. No depression of the mp occurred on admixture with material synthesized by other routes, and the IR spectra were identical.

B) In a manner to the synthesis of 2-phenylimino-3-phenyl(methyl)thiazolidine [3], from N-(β-mercaptoethyl)-o-toluidine and phenyliminophosgene we obtained 2-phenylimino-3-o-tolylthiazolidine, mp 84° C (from alcohol).

C) To a solution of 9.2 g (0.05 mole) of N-(β-chloroethyl)-o-anisidine in 30 ml of ether was added 6.7 g (0.05 mole) of phenyl isothiocyanate. The mixture was stirred at room temperature for 15 hr, and the viscous material which separated was treated with 0.2 N NaOH solution at the boil. The crystals were filtered off to give 60%, mp 141-142° C (from alcohol). In a similar manner we obtained 2-phenylimino-3-phenylthiazolidine, mp 134° C (from alcohol), and 2-phenylimino-3-o-tolylthiazolidine, mp 84° C (from alcohol).

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