ACID-CATALYZED ACETYLATION OF N-METHALLYL LACTAM AND IMIDE DERIVATIVES

V. N. Voshchula, S. V. Tolkunov,
M. Yu. Zubritskii, and V. I. Dulenko

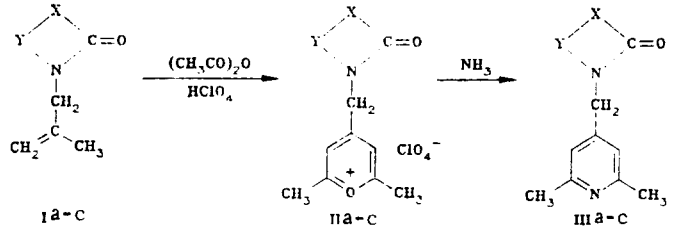
UDC 547.829'813.07:542.951

The reactions of N-methallyl derivatives of cyclic amides and imides with acetic and propionic anhydride have been studied in the presence of perchloric acid. The reaction products have been found to be pyrylium and oxazolinium salts. The relationship between the reaction pathway and the structure of the imide or amide starting material has also been determined. Pyrylium salts have been converted to their corresponding pyridine bases.

We have previously shown [1] that N-methallylphthalimide reacts with acyl perchlorates to give high yields of 2,6-dialkyl-4-phthalimidomethyl-pyrylium salts, which in turn react with ammonia and primary and secondary amines to give phthalimidomethyl-substituted pyridine and benzene derivatives.

In continuation of these studies of the synthesis and properties of functionalized pyrylium salts [1-3], and also in order to prepare potentially biologically active compounds, we have now investigated the acetylation of a series of N-methallyl derivatives of cyclic imides and lactams (IIa-g).

The starting materials, compounds Ia-g, were synthesized via alkylation of the appropriate lactams and imides with methallyl chloride in the presence of a base, according to a method similar to that reported in the literature [4-6]. Acetylation of the five-membered ring imide derivatives Ia-c with acetic anhydride in perchloric acid led to the formation of the corresponding 2,6-dimethyl-4-imidomethylpyrylium perchlorate salts IIa-c. Salts IIa, c could be converted to their respective pyridines IIIa, c by treatment with ammonia or ammonium carbamate in refluxing alcohol. Pyridine IIIb could be obtained from salt IIb via treatment with ammonium acetate in acetic acid, since the thiazolidinedione ring is unstable in basic solution.



I—III a X=CH_2CH_2, Y=CO; b X=SCH_2, Y=CO; c X=o-C_6H_4, Y=SO_2

Thus, in analogy with the behavior of M-methallylphthalimide [1], compounds Ia-c undergo olefin bisacylation reactions [7]. In contrast, reaction of the methallyl derivatives Id-g with acetic anhydride in the presence of perchloric acid resulted in the formation of condensed oxazolinium perchlorate salts IVa, b and Va, b. A similar cyclization reaction of allylamides in sulfuric acid has been described earlier in the literature [8-10], although the oxazolinium salts were not isolated in those cases; their formation was indicated by the PMR spectra of the corresponding acids in sulfuric acid solution.

It is interesting that the glutaramide Id and caprolactam Ie derivatives, with flexible (bent) structures, undergo cyclization after protonation of the methallyl groups to give dimethyloxazolinium salts IVa, b, although in the case of the naphthalimide If and pyrrolidone Ig derivatives, in which approach of the carbonyl oxygen and β-carbocation center is

Institute of Physical Organic Chemistry and Coal Chemistry, Academy of Sciences of the Ukrainian SSR, Donetsk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1414-1419, October, 1988. Original article submitted February 18, 1987; revision submitted November 4, 1987.

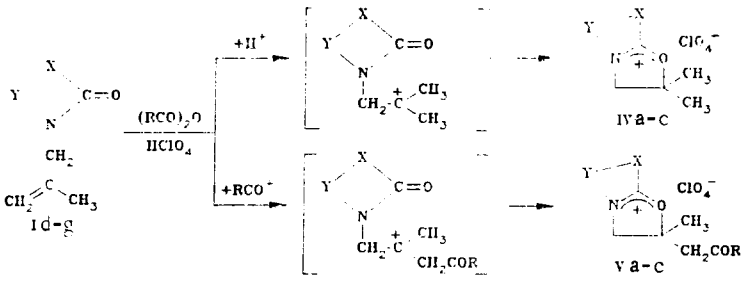
TABLE 1. Physical Characteristics of Compounds I-VI

Compound	mp, °C or bp, °C (mm Hg)	Found, %				Molecular formula	Calculated, %				Yield, %
		C	H	N	Hal (S)		C	H	N	Hal (S)	
Ia	36...37; 105 (5)	62,4	7,2	9,0	—	$C_8H_{11}NO_2$	62,7	7,2	9,1	—	81
Ib	160 (25)	49,6	5,3	8,0	(18,4)	$C_7H_9NSO_2$	49,1	5,3	8,2	(18,7)	67
Ic	79...80	55,9	5,1	5,9	(13,2)	$C_{11}H_{11}NSO_2$	55,7	4,7	5,9	(13,5)	87
Id	110 (5)	64,5	8,1	8,4	—	$C_9H_{13}NO_2$	61,7	7,8	8,1	—	30
Ie	112 (5)	71,6	10,1	8,2	—	$C_{10}H_{17}NO$	71,8	10,2	8,4	—	42
If	100...101	76,3	5,1	5,6	—	$C_{16}H_{13}NO_2$	76,5	5,2	5,6	—	85
Ig	95 (12)	69,5	9,6	10,1	—	$C_8H_{13}NO$	69,0	9,4	10,1	—	71
Ih	91...92	71,3	5,1	7,0	—	$C_{12}H_{11}NO_2$	71,6	5,5	7,0	—	50
Ii	97...98	51,2	3,7	5,0	28,3	$C_{12}H_{10}BrNO_2$	51,5	3,6	5,0	28,5	53
Ij	116...117	59,7	6,4	12,2	—	$C_{11}H_{14}N_2O_3$	59,5	6,4	12,6	—	64
IIa	243...244	45,3	4,5	4,1	11,0	$C_{12}H_{14}ClNO_7$	45,1	4,4	4,4	11,1	64
IIb	205...206	40,0	3,5	4,1	10,5 (9,3)	$C_{11}H_{12}ClNSO_7$	39,1	3,6	4,1	10,5 (9,5)	36
IIc	230...231	44,1	3,2	3,5	8,5 (7,7)	$C_{15}H_{14}ClNSO_8$	44,6	3,5	3,5	8,8 (7,9)	18
IIIa	111...112	66,3	6,1	12,5	—	$C_{12}H_{14}N_2O_2$	66,0	6,5	12,8	—	83
IIIb	119...120	55,5	5,3	11,6	(13,6)	$C_{11}H_{12}N_2SO_2$	55,9	5,1	11,9	(13,6)	60
IIIc	165...166	59,6	5,1	9,3	(10,5)	$C_{15}H_{14}N_2SO_3$	59,6	4,7	9,3	(10,6)	80
IVa	124...125	41,2	5,2	5,3	13,2	$C_9H_{11}ClNO_6$	40,4	5,3	5,2	13,3	37
IVb	175...176	45,3	6,2	5,1	13,1	$C_{10}H_{17}ClNO_5$	45,0	6,4	5,3	13,3	38
IVc	—	55,0	4,0	4,1	10,3	$C_{16}H_{14}ClNO_6$	51,6	4,0	4,0	10,1	97
Va	—	55,3	4,0	3,5	9,2	$C_{18}H_{16}ClNO_7$	54,9	4,1	3,6	9,0	93
Vb	117	42,5	5,8	4,9	12,7	$C_{10}H_{16}ClNO_6$	42,6	5,7	5,0	12,6	12
Vc	91...95	44,5	6,2	4,8	11,9	$C_{11}H_{18}ClNO_6$	44,7	6,1	4,7	12,0	25
VI	206...207	73,7	5,2	4,6	—	$C_{18}H_{15}NO_3$	73,7	5,2	4,8	—	100

TABLE 2. Spectral Characteristics of Compounds I-VI

Compound	PMR spectrum, δ, ppm (J, Hz)	IR spectrum, cm^{-1}
Ia	1.55 (3H, s, CH_3); 2.47 (4H, s, CH_2CH_2); 3.63 (2H, s, CH_2); 4.40 (2H, d, $=CH_2$)	1770, 1725, 1670, 1330, 1290, 1250, 1180, 1080, 1010, 975, 920, 830, 730, 705
Ib	1.6 (2H, s, CH_3); 3.97 (4H, s, $2CH_2$); 4.7 (2H, d, $=CH_2$)	2990, 2935, 1760, 1715, 1690, 1685, 1670, 1425, 1390, 1330, 1235, 1050, 1025, 980, 955, 900, 795, 700
Ic	1.73 (3H, s, CH_3); 4.25 (2H, s, CH_2); 5.00 (2H, s, $=CH_2$); 7.9...8.3 (4H, m, Harom)	
Id	1.57 (3H, s, CH_3); 1.8 (2H, t, $J=7$ Hz, 4-CH_2); 2.53 (4H, t, $J=7$ Hz, 3-and5-CH_2); 4.1 (2H, s, N—CH_2); 4.42 (2H, d, $=CH_2$)	
Ie	1.63 (9H, s, CH_3 and 4,5,6-CH_2); 2.5 (2H, d, $J=8$ Hz, 3-CH_2); 3.33 (2H, d, $J=8$ Hz 7-CH_2); 3.97 (2H, s, N—CH_2); 4.9 (2H, s, $=CH_2$)	2970, 2930, 2855, 1650, 1490, 1450, 1375, 1360, 1290, 1255, 1230, 1200, 1150, 985, 900
If	2.1 (3H, s, CH_3); 4.72 (4H, d, $2CH_2$); 7.67...8.63 (6H, m, Harom)	
Ig	1.5 (3H, s, CH_3); 1.77...2.43 (4H, m, 3-and 4-CH_2); 3.17 (2H, t, $J=7$ Hz, 5-CH_2); 3.67 (2H, s, N—CH_2); 4.73 (2H, s, $=CH_2$)	3075, 2920, 1700, 1500, 1470, 1450, 1430, 1375, 1350, 1310, 1290, 1260, 1245, 1225, 1200, 1190, 1175, 1030, 945, 900
Ih	—	1735, 1615, 1350, 1335, 1185, 920, 770, 765
Ii	—	1755, 1730, 1605, 1350, 1325, 1190, 1180, 1130, 925, 825,
Ij	—	1730, 1445, 1430, 1410, 1160, 920
IIa	3.0 (6H, s, 2-and6-CH_3); 3.1 (4H, s, CH_2CH_2); 5.1 (2H, s, N—CH_2); 7.9 (2H, s H_{arom})	1780, 1720, 1660, 1555, 1490, 1330, 1310, 1180, 1095, 1030, 930, 835
IIb	3.0 (6H, s, 2-and6-CH_3); 4.3 (2H, s, 5-CH_2); 5.1 (2H, s, CH_2); 7.9 (2H, s, Harom)	1760, 1700, 1685, 1660, 1555, 1490, 1415, 1360, 1330, 1170, 1100, 1030, 990
IIc	3.0 (6H, s, 2-and6-CH_3); 5.4 (2H, s, CH_2); 8.0...8.3 (6H, m, Harom)	1780, 1720, 1650, 1545, 1100, 950, 740, 730
IIIa	2.37 (6H, s, 2-and6-CH_3); 2.63 (4H, s, CH_2CH_2); 4.43 (2H, s, N—CH_2); 6.77 (2H, s, H_{arom})	1780, 1710, 1670, 1620, 1570, 1340, 1170, 915
IIIb	2.37 (6H, s, 2-and6-CH_3); 3.93 (2H, s, 5-CH_2); 4.5 (2H, s, N—CH_2); 6.77 (2H, s, H_{arom})	1755, 1680, 1670, 1610, 1575, 1430, 1350, 1340, 1325, 1245, 1235, 1170, 985, 900, 710
IIIc	2.37 (6H, s, 2-and6-CH_3); 6.77 (2H, s, 3-and 5-H pyridine); 7.93...8.15 (4H, m, H_{arom})	1735, 1620, 1575, 1345, 1325, 1265, 1185, 1160, 1130, 1060, 880, 760
IVa	1.7 (6H, s, 2-CH_3); 2.32...2.75 (2H, m, 7-CH_2); 3.0 (2H, t, $J=6$ Hz, 8-CH_2); 3.27 (2H, t, $J=6$ Hz, 6-CH_2); 4.2 (2H, s, 3-CH_2)	1770, 1575, 1520, 1370, 1100
IVb	1.7 (6H, s, $2CH_3$); 1.97 (6H, s, 6,7,8-CH_2); 2.78...3.13 (2H, m, 5-CH_2); 3.72...4.02 (2H, m, 9-CH_2); 4.1 (2H, s, 3-CH_2)	1655, 1345, 1295, 1225, 1205, 1180, 1100
IVc	1.7 (6H, s, $2CH_3$); 3.77 (2H, s, 3-CH_2); 8.43...9.2 (6H, m, Harom)	1720, 1600, 1535, 1520, 1100
Va	2.0 (3H, s, CH_3); 2.4 (3H, s, CH_3-acetonyl); 2.92 (2H, s, CH_2-acetonyl); 3.77 (2H, s, 3-CH_2); 8.6...9.27 (6H, m, Harom)	
Vb	1.78 (3H, s, CH_3); 2.38 (3H, s, CH_2-acetonyl); 2.67...3.2 (4H, m, 6-and7-CH_2); 3.53 (2H, s, CH_2-acetonyl); 3.77...4.27 (4H, m, 3-and 5-CH_2)	1735, 1690, 1510, 1100
Vc	1.12 (3H, t, $J=7$ Hz, CH_2-propionyl); 1.78 (3H, s, CH_3); 2.45...3.05 (6H, m, 6-and7-CH_2 and CH_2-ethyl); 3.43 (2H, s, CH_2-acylmethyl) 3.72...4.17 (4H, m, 3and5-CH_2)	1735, 1690, 1510, 1100
VI	2.1 (3H, s, CH_3); 2.23 (3H, s, 2-CH_3); 4.53 (2H, s, CH_2); 6.1 (1H, s, CH); 7.72...8.97 (6H, m, H_{arom})	1705, 1685, 1660, 1620, 1590, 1240, 1210, 785

hindered due to their rigid structures, cyclization was observed to take place after acetylation to give the methylacetonyloxazolinium salts Va, b. Upon replacement of acetic anhydride by propionic anhydride N-methallylnaphthalimide If gave the dimethyloxazolinium salt IVc, although N-methallylpyrrolidone Ig gave the methylpropionylmethyloxazolinium salt Vc.

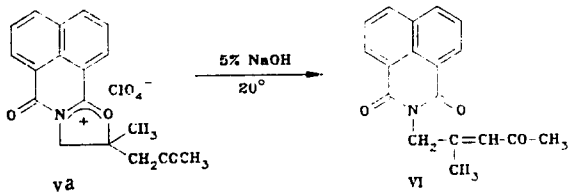


I d, IV a X = $(CH_2)_3$, Y = CO; I e, IV b XY = $(CH_2)_5$; I b, IV c, V a X = 1,8-naphthalene Y = CO; I g V b, c XY = $(CH_2)_3$; V a, b R = CH_3; V c R = C_2H_5

The direction of heterocyclization of compounds Ia-g under these experimental conditions apparently depends on both structural and electronic factors; the question of these two factors will not be considered further in this paper, however.

The structures of all the newly prepared pyrylium and oxazolinium perchlorates were confirmed by their IR and PMR spectra.

The basic cleavage product, ketoimide VI, was prepared from salt Va.



In the case of the reactions of 1-methallylisatin Ih, 1-methallyl-5-bromoisatin Ii, and dimethallyl parabanate Ij, it was not possible to isolate individual (pure) reaction products due to the large amount of resinification which occurred.

EXPERIMENTAL

IR spectra were recorded on a UR-20 spectrophotometer using Vaseline mulls; PMR spectra were obtained on a Tesla BS-467 (60 MHz) spectrometer. The spectra of compounds Ib, d, e, and g were recorded for the pure liquids, while the spectrum of Ia was taken in CCl_4, Ic, f in CD_3CN, II, IV, V in trifluoroacetic acid, and VI in C_5D_5N; TMS was used as the internal standard in all cases.

The (physical and spectral) characteristics of compounds I-VI are summarized in Tables 1 and 2. The starting materials, compounds Ia-d, f, and j were prepared by alkylation of sodium or potassium derivatives of the appropriate imides, or of the imides themselves, in the presence of 1 mmole potassium carbonate by methallyl chloride in dry DMF, according to a procedure analogous to that reported for phthalimide [4]. After dilution of the reaction mixture with water compounds Ia, b, d were extracted into methylene chloride and the extracts dried over calcium chloride; the solvent was evaporated and the product distilled under vacuum. Compounds Ic, f, and j were filtered and crystallized from alcohol.

N-Methallylcaprolactam Ie and 1-methallylpyrrolid-2-one were prepared according to [5]; 1-methallylisatin Ih and 1-methallyl-5-bromoisatin Ii were prepared according to [6].

2,6-Dimethyl-4-succinimidomethylpyrylium, Perchlorate (IIa). To a solution of 3 g (20 mmole) methyallylsuccinimide Ia in 10 ml acetic anhydride was added 2 ml 70% perchloric acid at such a rate that the temperature did not exceed 60°C. The mixture was then stored for 1 h at room temperature. Ether was added and the resulting precipitate was removed by filtration. Yield 4.1 (64%).

2,6-Dimethyl-4-[(2,4-thiazolidindionyl-3)methyl]pyrylium Perchlorate (IIb). The acylating mixture was prepared from 40 ml acetic anhydride and 5 ml 70% $HClO_4$ and cooled to 20°C. This solution was added to a mixture of 8.55 g (7.2 ml, 50 mmole) 3-methallylthiazolidine-2, 4-dione Ib, which resulted in a deep color and an exotherm to 40°C. The mixture was allowed to stand overnight and then diluted with 350 ml ether. The salt was deposited from solution in the form of an oil, which was refluxed in alcohol and then filtered. Yield of salt IIb 6 g (36%) as an orange-yellow solid.

2,6-Dimethyl-4-[(1,1-dihydroxydibenzo[d]isothiazolinon-3-yl-2-)methyl]-pyrylium Perchlorate (IIc). A solution of 4.74 g (20 mmole) Ic in 20 ml acetic anhydride was prepared and 2 ml of 70% $HClO_4$ was added and the mixture allowed to stand overnight. The mixture was diluted with ether and the resulting oil which precipitated was refluxed with alcohol; the crystalline salt which formed was filtered, washed with alcohol, and dried. Yield 1.43 g (18%) of salt IIc as light yellow needles.

N-[(2,6-Dimethylpyridyl-4)methyl]succinimide (IIIa). To a suspension of 6.4 g (20 mmole) perchlorate IIa in 50 ml alcohol was added gaseous ammonia for a period of 30 min. The solution was refluxed for 20 min, the alcohol was removed, and the residue was extracted with benzene and washed with water. After removal of the benzene the residue was crystallized from hexane. Yield 3.6 g (83%).

3-[(2,6-Dimethyl-4-pyridyl)methyl]thiazolidine-2,4-dione (IIIb). A mixture of 10.2 g (30 mmole) IIb and 10 g ammonium acetate was refluxed in 50 ml glacial acetic acid for 1 h. The majority of the acetic acid was distilled at reduced pressure on a water bath and the residue was treated with a solution of 60 g sodium carbonate in 500 ml water and extracted with 2 × 50 ml methylene chloride. The extract was dried over potassium carbonate and passed through a short alumina column to remove the resinous impurity; the methylene chloride was then evaporated on a water bath. Yield 4.25 g (60%). The hydrochloride salt was prepared by dissolving the product in ether and adding an ether solution of HCl. The hydrochloride precipitated out, mp 188-190°C (sealed capillary).

2-[(2,6-Dimethyl-4-pyridyl)methyl]benzo[d]isothiazolin-3-one 1,1-Dioxide (IIIc). A mixture of 1.21 g (3 mmole) IIc and 1 g ammonium carbamate in 20 ml methanol was refluxed for 15 min, then poured into 150 ml water, and the resulting turbid mass was extracted with 15 ml methylene chloride. The extract was evaporated and the residue crystallized from a small amount of methylene chloride. Yield 0.7 g (80%).

5-Keto-2,2-dimethyl-5,6,7,8-tetrahydropyrido[2,1-b]oxazolinium Perchlorate (IVa). To a solution of 3.34 g (20 mmole) N-methallylglutaramide Id in 10 ml acetic anhydride was added 2 ml 70% $HClO_4$. The mixture was allowed to stand 2 h, then diluted with 200 ml ether. The resulting oil which precipitated was dissolved in hot isopropyl alcohol with 1-2 drops 70% $HClO_4$. A colorless precipitate of salt IVa was formed and removed by filtration, then washed with ether and dried. Yield 0.2 g (37%).

2,2-Dimethyltetrahydroazepino[2,1-b]oxazolinium Perchlorate (IVb). To a solution of 8.35 g (50 mmole) N-methallylcaprolactam Ie in 50 ml acetic anhydride was added slowly 12 ml of 70% $HClO_4$. The reaction mixture was stored at 60°C for 30 min, then allowed to stand overnight. The mixture was diluted with 100 ml ether and the resulting crystals were removed by filtration. Yield 5 g (38%).

2,2-Dimethyl-5-oxo-2,3-dihydro-5H-benzo[d,e]isoquinolino[1,2-b]oxazolinium Perchlorate (IVc). A suspension of 2.51 g (10 mmole) If in 20 ml propionic anhydride was treated with stirring with 1 ml 70% $HClO_4$. A light yellow precipitate of salt IVc formed immediately. The mixture was stirred 1 h, then the product IVc was removed by filtration and washed with ether and dried. Yield 3.4 g (97%).

2-Methyl-2-acetonyl-5-oxo-2,3-dihydro-5H-benzo[d,e]isoquinolino[1,2-b]oxazolinium Perchlorate (Va). A suspension of 5.03 g (20 mmole) If in 20 ml acetic anhydride was treated with 2 ml 70% $HClO_4$. Compound If dissolved, and the mixture turned a yellow color as Va began to deposit copiously from solution. The mixture was heated on a boiling water bath for 15 min, cooled, and the precipitate of Va was removed by filtration, washed with isopropyl alcohol, then ether, and dried. Yield 6.75 g. An additional 0.6 g of salt was deposited upon dilution of the mother liquor with 100 ml ether. Total yield 7.35 g (93%). Light yellow crystals, mp 210-211°C (dec).

2-Methyl-2-acetonyl-5,6-dihydro-7H-pyrrolo[2,1-b]oxazolinium Perchlorate (Vb). N-Methallylpyrrolidone Ig (2.8 g, 20 mmole) was added to a cooled (20°C) mixture of 15 ml acetic anhydride and 2 ml 70% $HClO_4$ and the mixture was allowed to stand for 12 h. The mixture was diluted with 200 ml ether and the resulting oil which precipitated was dissolved in 3 ml isopropyl alcohol and cooled to 0°C. The resulting colorless salt which formed was filtered and washed with a small amount of isopropyl alcohol and ether and dried. Yield 0.7 g (12%).

2-Methyl-2-propionylmethyl-5,6-dihydro-7H-pyrrolo[2,1-b]oxazolinium Perchlorate (Vc). N-Methallylpyrrolidone Ig (2.8 g, 20 mmole) was dissolved in 25 ml propionic anhydride and 2 ml 70% $HClO_4$ was added. The mixture was allowed to stand overnight, then treated with 200 ml ether, and the resulting oil was dissolved in 3 ml isopropyl alcohol and cooled to 0°C. The salt precipitated out and was filtered and washed with a small amount of isopropyl alcohol and then ether, and dried. Yield 1.5 g (25%).

N-(4-Oxo-2-methylpenten-2-yl-1)naphthalimide (VI). Salt Va was treated with a 5% NaOH solution in aqueous methanol. The resulting white precipitate was filtered, washed with water, and dried, then recrystallized from benzene. Quantitative yield.

LITERATURE CITED

1. V. I. Dulenko, V. M. Golyak, and V. I. Gubar', InFOU Akad. Nauk UkrSSR, VINITI 17.04.86, No. 2798-B86.
2. V. I. Dulenko, V. M. Golyak, N. N. Alekseev, and V. I. Gubar', Khim. Geterotsikl. Soedin., No. 7, 904 (1983).
3. V. I. Dulenko, V. M. Golyak, N. N. Alekseev, and N. F. Gorenko, ibid., No. 10, 1318 (1984).
4. J. C. Sheeman and W. A. Bolhofer, J. Am. Chem. Soc., 72, 2786 (1950).
5. E. Thielepape, Chem. Ber., 68, 751 (1935).
6. G. Tacconi, P. P. Righetti, and G. Desimoni, J. Prakt. Chem., 315, 339 (1973).
7. A. T. Balaban and C. D. Nenitzescu, Annalen, 625, 74 (1959).
8. S. P. McManus, J. T. Caroll, and C. V. Pittman, J. Org. Chem., 35, 3768 (1970).
9. S. P. McManus, C. V. Pittman, and P. E. Fanta, ibid., 37, 2353 (1972).
10. C. V. Pittman, S. P. McManus, and J. W. Larsen, Chem. Rev., 72, 357 (1972).

CONDENSED THIOLANE 1,1-DIOXIDE SYSTEMS.

3.* TWO MODES OF CYCLIZATION OF N-SUBSTITUTED trans-3-CHLORO-4-THIOUREIDOTHIOLANE 1,1-DIOXIDES

G. I. Khaskin, A. B. Rozhenko, E. G. Khil'chevskaya, and T. É. Bezmenova†

UDC 547.789.61'785.5'732.07:541.124

Reaction of trans-3-chloro-4-aminothiolane 1,1-dioxide hydrochloride with aryl isothiocyanates gives, according to the base involved, cis-perhydrothieno[3,4-d]imidazole-2-thione 5,5-dioxides or the hitherto undescribed cis-2-arylimino-perhydrothieno[3,4-d]thiazole 5,5-dioxides.

Two principal methods are known for the synthesis of cis-fused bicylic systems containing the thiolane 1,1-dioxide ring, namely from cis-bifunctionally substituted thiolane 1,1-dioxides [2, 3], or by intramolecular cyclization of 4-substituted 2-thiolene 1,1-dioxides [4-6]. The latter can be obtained, for example, by elimination, a reaction which has been well studied in the thiolane 1,1-dioxide series [7, 8]. A third possible route for the cyclization to give cis-fused systems, nucleophilic substitution by the S_N2 mechanism, has not hitherto been realized in the thiolane 1,1-dioxide series.

We have found that trans-3-chloro-4-aminothiolane 1,1-dioxide hydrochloride (I) reacts with aryl isothiocyanates in the presence of strong bases (triethylamine, aqueous sodium carbonate) to give the known cis-perhydrothieno[3,4-d]imidazole-2-thione 5,5-dioxides (IIIa-c) [5, 9]. The use of less basic tertiary amines (pyridine or N,N-dimethylaniline) facili-

*For Part 2, see [1].
†Deceased.

Department of Petroleum Chemistry, Institute of Physical Organic Chemistry and Carbon Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev 252160.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1420-1423, October, 1988. Original article submitted March 26, 1987; revision submitted February 26, 1988.

0009-3122/88/2410-1180$12.50