with chloroform (three 100-ml portions). The extract was dried with sodium sulfate, the solvent was evaporated, and the residue was chromatographed in chloroform. The characteristics of XXV and XXVII-XXIX are presented in Tables 3-5.

8,9;17,18-Dibenzo-1,4,7-trioxa-10,13,16-triazacyclooctadecane (XXVI). A 5.0-g (0.217 mole) sample of sodium was added in the course of 2 h to a heated (to 100°C) solution of 3.82 g (7.47 mmole) of XXI in 100 ml of n-butyl alcohol. After the sodium had dissolved completely, the solution was cooled and washed with water (three 100-ml portions), and 120 ml of 20% HCl solution was added to the butanol layer. After prolonged shaking, the butanol layer was separated and discarded, and the aqueous layer was made alkaline with 30% KOH solution to pH ~ 12 and cooled. The precipitate was separated, washed with 200 ml of water, and dried in vacuo to give 1.78 g (67%) of product. The characteristics are presented in Tables 3-5.

LITERATURE CITED

1. A. A. Formanovskii and A. S. Murakhovskaya, Khim. Geterotsikl. Soedin., No. 2, 267 (1985).
2. K. B. Yatsimirskii and Ya. D. Lampeka, The Physical Chemistry of Metal Complexes with Macrocyclic Ligands [in Russian], Naukova Dumka, Kiev (1985).
3. G. W. Gokel and S. H. Korzeniowski, Macrocyclic Polyether Syntheses, Springer, Berlin–Heidelberg–New York (1982), p. 156.
4. M. Hiraoka, Crown Compounds [Russian translation], Mir, Moscow (1986).
5. I. S. Markovich, N. A. Filyagina, V. M. Dziomko, Yu. S. Ryabokobylko, G. M. Adamova, and S. L. Zelichenok, Khim. Geterotsikl. Soedin., No. 2, 185 (1983).
6. L. P. Poddubnykh, S. G. Dmitrienko, N. M. Kuz'min, A. A. Formanovskii, and Yu. A. Zolotov, Zh. Neorg. Khim., 31, 1812 (1986).
7. J. C. Lockhart and M. E. Tomson, J. Chem. Soc., Perkin 1, No. 2, 202 (1977).
8. S. A. Hogberg and D. J. Cram, J. Org. Chem., 40, 151 (1975).
9. T. Neilson, H. C. S. Wood, and A. G. Wylie, J. Chem. Soc., 371 (1962).
10. J. T. Clerk, E. Pretsch, and S. Sternhell, ^{13}C Kernresonanzspektroskopie, Akad. Verlagsges., Frankfurt am Main (1973), p. 101.
11. J. C. Biernat, E. Jereczek, and A. Bujenski, Pol. J. Chem., 53, 929 (1979).

SYNTHESIS AND PROPERTIES OF SOME DERIVATIVES OF 2-THIONOINDENO[1,2-d]-PYRIMIDINE AND INDENO[1,2-d][3,1]THIAZINE

A. Z. Zandersons, V. K. Lusis,
É. É. Liepin'sh, D. Kh. Mutsenietse,
E. L. Khanina, and G. Ya. Dubur

UDC 547.869.1'859'572.3'496.3.07

Derivatives of 2-thiono-5-oxo-2,3,4,5-tetrahydroindeno[1,2-d]pyrimidine and 5-oxo-1,2,4,5-tetrahydroindeno[1,2-d][3,1]thiazine are formed in the cyclocondensation of 2-arylideneindan-1,3-diones with thiourea and N-monomethylthiourea, while only derivatives of indeno[1,2-d]-pyrimidine are formed in the reaction with N,N-dimethylthiourea. S- and $N_{(3)}$-Alkylation occur in the alkylation of 2-thiono-4-phenyl-5-oxo-2,3,4,5-tetrahydroindeno[1,2-d]pyrimidine, while only the N-methyl derivative is formed in the alkylation of 2,5-dioxo-4-phenyl-1,2,4,5-tetrahydroindeno[1,2-d][3,1]thiazine.

It is known [1, 2] that 2-oxoindeno[1,2-d]pyrimidines are formed in the condensation of urea with derivatives of indan-1-one or indan-1,3-dione. In the opinion of Benera and Nayak [3], the condensation of 2-arylideneindan-1,3-diones with thiourea leads to 2-thiono-4-aryl-5-oxo-2,3,4,5-tetrahydroindeno[1,2-d]-pyrimidines, although only the results of elementary analysis for sulfur are presented for confirmation of the structures of the reaction products. From 2-benzylideneindan-1,3-indole and thiourea we obtained a substance with a

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1136-1141, August, 1988. Original article submitted February 16, 1987.

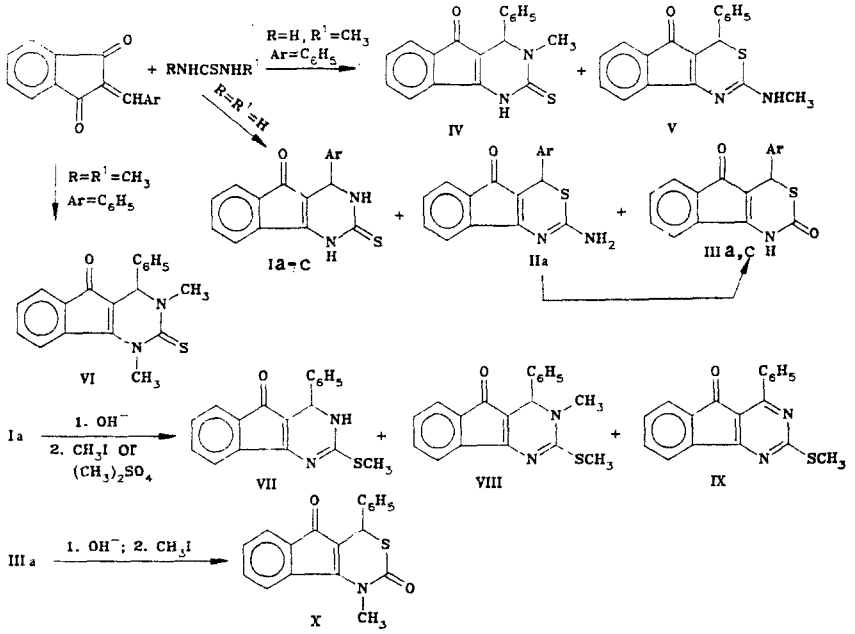
0009-3122/88/2408-0936$12.50

TABLE 1. Characteristics of the Synthesized Compounds

Compound	mp, °C	Found, %				Empirical formula	Calc., %			
		C	H	N	S		C	H	N	S
Ia	275...277	69,3	4,1	9,4	10,5	$C_{17}H_{12}N_2OS$	69,8	4,1	9,6	10,9
Ib	248...251	69,9	4,5	9,1	10,3	$C_{18}H_{14}N_2OS$	70,6	4,6	9,1	10,5
Ic	268...271	60,2	3,2	12,3	9,3	$C_{17}H_{11}N_3O_3S$	60,5	3,3	12,5	9,5
IIa	217...219	69,0	4,1	9,4	10,7	$C_{17}H_{12}N_2OS$	69,8	4,1	9,6	10,9
IIIa	205...207	69,2	3,6	4,7	10,8	$C_{17}H_{11}NO_2S$	69,6	3,8	4,8	10,9
IIIc	214...216	60,1	2,9	8,2	9,4	$C_{17}H_{10}N_2O_4S$	60,4	3,0	8,3	9,5
IV	267...270	70,3	4,5	9,1	10,3	$C_{18}H_{14}N_2OS$	70,6	4,6	9,1	10,5
V	200...202	70,2	4,6	9,2	10,5	$C_{18}H_{14}N_2OS$	70,6	4,6	9,1	10,5
VI	183...185	71,0	4,9	8,7	9,9	$C_{19}H_{16}N_2OS$	71,2	5,0	8,7	10,0
VII	191...193	70,4	4,5	9,0	10,2	$C_{18}H_{14}N_2OS$	70,6	4,6	9,1	10,5
VIII	172...174	70,4	5,0	8,5	9,9	$C_{19}H_{16}N_2OS$	71,2	5,0	8,7	10,0
IX	164...166	70,9	3,9	9,1	10,5	$C_{18}H_{12}N_2OS$	71,0	4,0	9,2	10,5
X	176...178	69,8	4,2	4,4	10,4	$C_{18}H_{13}NO_2S$	70,3	4,3	4,6	10,4

melting point that does not correspond to that presented in [3]; however, the set of data from spectral methods of investigation confirms the 2-thiono-4-phenyl-5-oxoindenopyrimidine structure (Ia).

We also observed that indeno[1,2-d][3,1]thiazine derivatives II are formed along with indenopyrimidines I.



I—IIIa Ar = C_6H_5; Ib Ar = $C_6H_4CH_3$-*p*; Ic IIIc Ar = $C_6H_4NO_2$-*p*

According to the concepts regarding the mechanism of the Biginelli reaction [4], the formation of the pyrimidine ring begins with the addition of urea to the C=C bond of the other reaction component. It is also usually assumed [5] that the first act in the formation of the 1,3-thiazine ring is the addition of the polar sulfur atom of the thiourea molecule to the C=C bond of, for example, the vinyl ketone or arylidenecyclohexanone. However, initial reaction of the NH_2 grouping of the thiourea molecule with the carbonyl function of the α,β-unsaturated ketone is not excluded. For example, both products of addition of the sulfur atom of the thiourea molecule to the C=C bond of the ketone and products of reaction of the NH_2 and CO groups were isolated and subsequently converted to derivatives of 2-thionopyrimidine and 2-amino-1,3-thiazine in an investigation of the reaction of thiourea with β-methoxyethyl vinyl ketones [6]. Replacement of thiourea by N-methylurea in the condensation with benzylideneindandione leads to the formation of 3-methyl-2-thionoindenopyrimidine IV and 2-methylaminoindenothiazine V, while the condensation with sym-dimethythiourea leads to 1,3-dimethylindenopyrimidine VI in low yield. 1-Methyl-2-thionoindenopyrimidine is not formed in the reaction with methylthiourea. These facts indicate that initial reaction of the NH_2 group of thiourea with the C=O function of the diketone with subsequent intramolecular addi-

TABLE 2. Spectral Characteristics of the Synthesized Compounds

Compound	PMR spectrum, δ, ppm					IR spectrum, ν, cm⁻¹		UV spectrum, λ, nm (log ε)
	4-H	1-NH or 1-CH_3	3-NH or 3-CH_3	2-substituent	J, Hz	5-CO	NH	
Ia	5,36 (d, 1H)	11,76 (s, 1H)	9,88 (d, 1H)	—	J_{34}=2,5	1680	3255, 3171	441 (3,37)
IV	5,61 (s, 1H)	11,86 (s, 1H)	3,19 (s 3H)	—	—	1678	3245	442 (3,42)
VI	5,13 (s, 1H)	4,11 (s, 3H)	3,44 (s, 3H)	—	—	1678	—	446 (3,23)
VII	5,52 (d, 1H)	—	9,68 (d 1H)	2,60 (s, 3H)	J_{34}=2,2	1665	3235	482 (3,52)
VIII	5,56 (s, 1H)	—	3,04 (s, 3H)	2,68 (s, 3H)	—	1678	—	485 (3,58)
IIa	5,34 (s, 1H)	—	—	8,67 (s, 2H)	—	1660	3210	470 (3,47)
V	5,38 (s 1H)	—	—	3,09 (d, 3H), 8,91 (q 1H)	J_{NH-CH_3}=4,4	1668	3190	472 (3,54)
IIIa	5,54 (s, 1H)	12,03 (s, 1H)	—	—	—	1704	3160	423 (3,00)
X	5,46 (s, 1H)	4,06 (s, 3H)	—	—	—	1700	—	426 (3,07)

tion of another nucleophilic center of thiourea – either a nitrogen atom or a sulfur atom – to the C=C bond of the resulting intermediate predominates.

Oxoindenothiazines III are products of nucleophilic substitution of the NH_2 group of thiazine II by an OH group; this was proved by a separate experiment. 2-Oxoindenothiazines III are the principal products in the condensation of 2-arylideneindandione with thiourea in ethanol in the presence of HCl, and they can be obtained preparatively under these conditions (Table 1). It must be noted that only part of the indenopyrimidine I is isolated from the reaction mixture in the form of a precipitate in all of the remaining cases and that complete separation of the reaction mixtures is carried out by chromatography.

The 2-thionoindenopyrimidines obtained are readily alkylated in an alkaline medium. 2-Thiono-4-phenyl-5-oxo-1H-2,3,4,5-tetrahydroindeno[1,2-d]pyrimidine (Ia) reacts with methyl iodide or dimethyl sulfate to give a mixture of mono- and dialkylation products – 2-methylthio-4-phenyl-5-oxo-3H-4,5-dihydroindeno[1,2-d]pyrimidine (VII) and 2-methylthio-3-methyl-5-oxo-4,5-dihydroindeno[1,2-d]pyrimidine (VIII). An increase in the reaction temperature promotes the formation of dialkyl derivatives VIII: at 20°C the ratio of alkylation products VIII:VII = 2, whereas at 70°C it is equal to six (with CH_3I as the alkylating agent). 2-Methylthio-4-phenyl-5-oxoindeno[1,2-d]pyrimidine (X), which is the oxidized form of pyrimidine VII, is also formed in insignificant amounts in the alkylation of pyrimidine Ia.

Alkylation at the nitrogen atom with the formation of 1-methyl-4-phenyl-2,5-dioxo-1,2,4,5-tetrahydroindeno[1,2-d][3,1]thiazine (X) occurs in the reaction of 2,5-dioxo-4-phenyl-1,2,4,5-tetrahydroindeno[1,2-d][3,1]thiazine (IIIa) with methyl iodide.

The spin–spin coupling of the 3-H and 4-H protons (^3J = 2.5 Hz) observed in the ^1H NMR spectrum (Table 2) of indenopyrimidine Ia makes it possible to assign the signal at 9.88 ppm to the $N_{(3)}$–H proton and the signal at 11.76 ppm to the $N_{(1)}$–H proton. Consequently, the signal of the N–H proton at 11 ppm and the appearance of the signal of the 4-H proton in the form of a singlet in the spectrum of monomethylpyrimidine IV confirm the structure of the $N_{(3)}$-methyl isomer. Broadening of the signal of the carbon atom of the N–CH_3 group, which corresponds to the small value of the constant of spin–spin coupling ($J \approx 0.8$ Hz) between the 4-H proton and this carbon atom, is observed in the ^{13}C NMR spectrum of IV (Tables 3 and 4).

The formation of $N_{(1)}$-, $N_{(3)}$-, and S-alkyl products is possible in the alkylation of indenopyrimidine Ia. The strong-field shift of the protons of the methyl group observed in the ^1H NMR spectra of VII and VIII as compared with the signals of the N–CH_3 groups of indenopyrimidines IV and VI and the detection of $[M - SCH_3]^+$ ions in the mass spectra indicate the formation of S-alkyl products in the reaction. This is confirmed by the appearance in the ^{13}C NMR spectra of VII and VIII of a signal at ~13 ppm, which is characteristic [7, p. 158] for the carbon atom of the S–CH_3 group. The observance of a constant of spin-spin coupling (^3J = 2.2 Hz) between the 4-H and N–H protons proves the 2-methylthio-3H-4,5-dihydroindenopyrimidine structure (VII) and excludes the alternative 2-methylthio-1H-4,5-dihydroindenopyrimidine structure. The spin-spin coupling between the carbon atom of the N–CH_3

TABLE 3. Chemical Shifts in the ^{13}C NMR Spectra of the Synthesized Indeno[1,2-d]pyrimidines and Indeno[1,2-d]thiazines

Compound	$C_{(2)}$	$C_{(4)}$	$C_{(4a)}$	$C_{(5)}$	$C_{(5a)}$	$C_{(6)}$	$C_{(7)}$	$C_{(8)}$	$C_{(9)}$	$C_{(9a)}$	$C_{(9b)}$	C_{Ph}				$N_{(1)}-CH_3$	2-XCH_3*	$N_{(3)}-CH_3$
												$C_{(i)}$	$C_{(o)}$	$C_{(m)}$	$C_{(p)}$			
Ia	175,24	53,77	105,68	189,13	133,00	121,25	130,68	132,21	120,66	135,52	152,43	142,44	126,81	128,72	127,99	—	—	—
IV	175,50	61,07	105,74	188,78	132,94	121,22	130,77	132,24	120,78	135,26	151,08	140,36	126,61	129,01	128,34	—	—	40,87
VI	178,96	59,75	108,20	188,72	133,12	123,15	130,60	132,68	121,77	136,52	153,99	139,77	126,44	129,17	128,44	38,87	—	43,54
VII	167,91	53,53	107,15	191,18	133,82	120,28	129,92	131,92	118,72	140,59	163,78	143,58	126,58	128,69	127,87	—	12,70	—
VIII	169,17	62,18	107,18	190,72	134,00	120,31	129,92	131,89	118,78	140,36	161,96	141,00	126,73	128,95	128,37	—	14,08	37,68
IIa	164,18	39,64	102,40	191,13	133,32	118,70	129,98	132,18	120,34	142,15	168,09	143,55	126,55	128,81	127,61	—	—	—
V	162,05	—**	103,01	191,37	133,38	118,88	130,09	132,30	120,42	142,21	167,53	143,42	126,63	128,90	127,71	—	29,13	—
IIIa	166,45	42,04	103,83	190,39	131,30	120,25	130,89	132,91	121,54	137,10	155,80	142,64	126,96	128,98	127,90	—	—	—
X	166,61	39,25	108,89	190,07	133,23	123,61	130,37	131,64	121,99	137,73	158,58	141,56	126,71	128,95	127,89	33,72	—	—

*X = S, NH.

**The signal is overlapped with the signal of the solvent — d_6-DMSO.

TABLE 4. Some Long-Range Spin-Spin Coupling Constants (SSCC) in the ^{13}C NMR Spectra of Indeno[1,2-d]pyrimidines and Indeno[1,2-d][3,1]-thiazines

Compound	Coupling	J, Hz	Compound	Coupling	J, Hz
Ia	4H-$C_{(4a)}$	7,3	VII	4H-$C_{(4a)}$	7,4
	3H-$C_{(4a)}$	3,4		3H-$C_{(4a)}$	3,0
	1H-$C_{(4a)}$	5,3	VIII	4H-$C_{(4a)}$	7,4
IV	4H-$C_{(4a)}$	7,3		4H-CH_3	2,0
	1H-$C_{(4a)}$	4,6	IIa	4H-$C_{(4a)}$	8,0
VI	4H-$C_{(4a)}$	6,8	III	4H-$C_{(4a)}$	8,0
	4H-CH_3	2,5	V	4H-$C_{(4a)}$	8,5

group and the 4-H proton (^3J = 2.0 Hz) proves that the CH_3 substituent is attached to the $N_{(3)}$ atom of indenopyrimidine VIII. The significant strong-field shift (up to 23 ppm) of the signal of the $C_{(4)}$ atom in the ^{13}C NMR spectra of indenothiazines IIa, III, and X as compared with the corresponding signals of indenopyrimidines indicates that the $C_{(4)}$ atom is adjacent to sulfur atom, i.e., the formation of indeno[1,2-d][3,1]thiazine. This fact and the close chemical shifts of the signals of the $C_{(9b)}$ atom of indenothiazines IIa and V and indenopyrimidines VII and VIII, which characterize the same $-C_{(9b)}-N_{(1)}=C_{(2)}-$ structural fragment of the indicated molecules, constitute evidence for the indeno[1,2-d][3,1]thiazine structure, since the signal of the $C_{(9b)}$ atom of the alternative indeno[1,2-d][3,1]thiazine should be shifted significantly, and the signal of the $C_{(4)}$ atom should differ little from the signals observed for indenopyrimidines.

A 2-oxo structure is more likely for indenothiazines III than the 2-hydroxy form: the proton resonance signal at 12.03 ppm is close in value to the signal of the $N_{(1)}$–H proton of indenopyrimidine Ia or IV, and the absorption at 3190 cm^{-1} in the IR spectrum corresponds to the stretching vibrations of an NH group; however, spin-spin coupling between the 1-H proton and the $C_{(4a)}$ atom is absent in the ^{13}C NMR spectrum. It should also be noted that the compounds that contain a $C_{(9b)}-N=C_{(2)}$ fragment (derivatives IIa, V, VII, and VIII) are considerably more deeply colored than indenothiazines with structure III.

EXPERIMENTAL

The IR spectra of suspensions of the compounds in mineral oil were recorded with a PE 580 B spectrometer. The UV spectra of solutions of the compounds in ethanol ($c = 1 \cdot 10^{-4}$ M) were recorded with a Specord M 40 spectrophotometer. The ^1H and ^{13}C NMR spectra were recorded with a WM-360 spectrometer (with tetramethylsilane as the internal standard). The mass spectra were obtained with an MS-50 spectrometer (AEI) at an ionizing-electron energy of 70 eV; the samples were introduced through a direct-input system.

The reaction products were separated by chromatography with a column packed with L 40/100 silica gel (400 g) or by means of preparative TLC on a plate with a silica gel layer with a thickness of 2 mm; unless indicated otherwise, the eluent was chloroform–hexane–acetone (9:7:1). The substances were recrystallized from ethanol for elementary analysis.

Characteristics of the synthesized compounds are shown in Tables 1-4.

Reaction of 2-Benzylideneindan-1,3-dione with Thiourea. A 2.34-g (10 mmole) sample of benzylideneindandione and 5.0 g (65 mmole) of thiourea were refluxed for 4 h in 120 ml of acetic acid with the addition of three drops of concentrated HCl, after which the mixture was cooled, and the resulting red precipitate was removed by filtration to give 1.6 g (55%) of indenopyrimidine Ia. The filtrate was evaporated to dryness, the residue was treated with two 50-ml portions of chloroform, and the mixture was filtered. The chloroform solution was evaporated to a volume of 10 ml, and the concentrate was chromatographed with a column. The eluates from the yellow, orange, and red bands were collected. Workup of the eluate from first band gave 0.1 g of 2-oxothiazine IIIa, workup of the eluate from the second band gave another 0.15 g of indenopyrimidine Ia (60% overall yield), and workup of the eluate from the red band gave 0.5 g (17%) of 2-aminothiazine IIa.

Similarly, from the corresponding 2-arylideneindan-1,3-diones we obtained indenopyrimidines Ib, c, for which the yields after direct isolation from the reaction mixtures (without chromatography) were 45% and 40%, respectively.

2,5-Dioxo-4-phenyl-1,2,4,5-tetrahydroindeno[1,2-d][3,1]thiazine (IIIa). A) A 2.34-g (10 mmole) sample of benzylideneindandione and 5.0 g (65 mmole) of thiourea were refluxed for 5 h in 100 ml of ethanol with the addition of 1.5 ml of concentrated HCl, after which the mixture was cooled, and the resulting yellow crystals of oxothiazine IIIa were removed by filtration to give 1.5 g (50%) of product. Compound IIIc was similarly obtained.

B) Two drops of concentrated HCl were added to 0.4 g (1.4 mmole) of 2-aminothiazine IIa in 50 ml of ethanol, and the mixture was refluxed until the red color of the solution disappeared. The solvent was evaporated, and the residue was chromatographed on a plate. Workup of the eluate from the dark-yellow band gave 0.1 g (25%) of oxothiazine IIIa.

2-Thiono-3-methyl-4-phenyl-5-oxoindeno[1,2-d]pyrimidine (IV) and 2-Methylamino-4-phenyl-5-oxoindeno[1,2-d][3,1]thiazine (V). A 2.34-g (10 mmole) sample of benzylideneindandione and 5.0 g (55 mmole) of N-methylthiourea were refluxed for 5 h in 75 ml of acetic acid with three drops of concentrated HCl, after which the mixture was evaporated, the residue was dissolved in 100 ml of chloroform, and the solution was filtered. The filtrate was concentrated to a volume of ~10 ml, and the concentrate was chromatographed with a column. The eluates from the orange and red bands were collected. Workup of the eluate from the orange band gave 0.8 g (26%) of 3-methylindenopyrimidine IV, while workup of the eluate from the red band gave 0.3 g (17%) of 2-methylaminothiazine V.

2-Thiono-1,3-dimethyl-4-phenyl-5-oxoindeno[1,2-d]pyrimidine (VI). A 2.34 g (10 mmole) sample of benzylideneindandione and 4.0 g (40 mmole) of sym-dimethylurea were refluxed for 3 h in 75 ml of acetic acid with three drops of concentrated HCl, after which the mixture was evaporated, and the residue was treated with 50 ml of chloroform. The mixture was filtered, the chloroform was evaporated to a volume of ~10 ml, and the concentrate was chromatographed with a column. The eluate from the red band was collected and worked up to give 0.25 g (8%) of indenopyrimidine VI.

Alkylation of 2-Thiono-4-phenyl-5-oxotetrahydroindeno[1,2-d]pyrimidine (Ia). A 1.16-g (4 mmole) sample of indenopyrimidine Ia was dissolved by heating in 40 ml of DMSO, and 1.12 g (20 mmole) of ground KOH was added. The dark-red reaction mixture was cooled to room temperature, and 1.5 ml (24 mmole) of methyl iodide or 2.24 ml (27 mmole) of dimethyl sulfate was added. After 2 h, the reaction mixture was diluted with 0.5 liter of water, and the aqueous mixture was extracted with chloroform (three 150-ml portions). The chloroform extract was washed with water (three 200-ml portions), dried over Na_2SO_4, and evaporated to a volume of ~10 ml. The concentrate was chromatographed with a column. Successive collection and workup of the eluates from the yellow, bright-red, and dark-red bands gave a small amount (<0.1 g) of indenopyrimidine IX, 0.74 g (58%) of dialkyl derivatives VIII, and 0.35 g (29%) of monoalkyl derivative VII. In the case of alkylation with dimethyl sulfate the yields of VII and VIII were 0.78 g (62%) and 0.27 g (21%), respectively.

1-Methyl-4-phenyl-2,5-dioxoindeno[1,2-d][3,1]thiazine (X). A 1.85-g (6.3 mmole) sample of thiazine IIIa was dissolved by heating in 400 ml of acetone, 10 ml (0.16 mole) of methyl iodide was added, and the mixture was allowed to stand for 1 h. The reaction mixture was filtered, the filtrate was evaporated, and the viscous residue was triturated with 15 ml of ethanol. The resulting yellow precipitate was removed by filtration to give 0.5 g of thiazine X. The filtrate was evaporated, and the residue was chromatographed on a plate (elution with chloroform). Workup of the eluate from the yellow band gave another 0.2 g of product. The overall yield of 1-methyl-2-oxothiazine X was 35%.

LITERATURE CITED

1. F. A. Grunsberg, A. K. Aren, and G. Ya. Vanag, Izv. Akad. Nauk Latv. SSR, Ser. Khim., No. 3, 324 (1968).
2. V. P. Mamaev and E. N. Lyubimova, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim., No. 2, 96 (1969).
3. R. K. Benera and A. Nayak, Indian J. Chem., 14B, 223 (1976).
4. F. Sweet and J. D. Fissekis, J. Am. Chem. Soc., 95, 8741 (1973).
5. T. Lorand and D. Szabo, Acta Chim. Hung., 95, 363 (1977).
6. R. M. Khachatryan and S. A. Vartanyan, Armyansk. Khim. Zh., 25, 338 (1972).
7. J. B. Stothers, Carbon-13 NMR Spectroscopy, New York–London (1972).