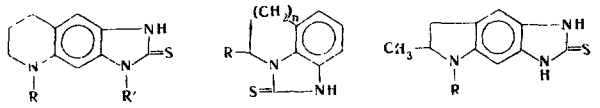
SYNTHESIS OF SOME THIOXOIMIDAZOLE STRUCTURES OF THE QUINOLINE AND INDOLE SERIES

I. G. Il'ina, N. B. Kazennova,
V. G. Bakhmut-skaya, and A. P. Terent'ev*

UDC 547.754'782.9'831.3.07

Some 2-thioxoimidazotetrahydroquinolines and 2-thioxoimidazoindolines have been synthesized by the cyclization with carbon disulfide of the corresponding o-diamines, which were obtained by the reduction of the o-dinitro derivatives with hydrazine hydrate in the presence of Raney nickel.

Continuing our investigations in the thioxoimidazole series [1], we have performed the synthesis of new condensed derivatives with tetrahydroquinoline and indoline.



I, III IV, V VI, VII

I R=H, R′=H; II R=H, R′=C_4H_9; III R=$COCH_3$, R′=H; IV R=H, n=2; V R=CH_3, n=1; VI R=H; VII R=$COCH_3$.

The synthesis of the thioxoimidazole structures (I-VII) was effected on the basis of the diamines obtained by the reduction of the corresponding o-dinitro or o-aminonitro derivatives with hydrazine hydrate in ethanol in the presence of Raney nickel. These diamines are readily oxidized in the air and they were therefore not isolated in the free state but were subjected to cyclization with carbon disulfide immediately.

All the thioxoimidazoles synthesized are crystalline substances of various shades of brown. Their solubility in organic solvents and in water changes in the sequence 2-thioxoimidazoindole > 2-thioxoimidazoquinoline.

The presence of a set of characteristic bands in the IR spectrum once more shows the preferential existence of such structures in the thione form [2, 3].

The UV spectra of all the compounds have a weak absorption band in the 320-360-nm region. The nature of the solvent scarcely affects the nature of the curves.

EXPERIMENTAL

The IR spectra of the compounds were taken on a UR-10 instrument in the form of mulls in paraffin oil, and the UV spectra were taken on a Cary-15 instrument in ethanol.

6,7-Dinitro-, N-acetyl-6,7-dinitro-, and 6,8-dinitrotetrahydroquinolines were obtained as described previously [4]. 5,6-Dinitro-, N-acetyl-5,6-dinitro-, and 5,7-dinitro-2-methylindolines were also obtained as described previously [5].

7-(Butylamino)-6-nitrotetrahydroquinoline. A solution of 0.6 g (2.2 mmoles) of 6,7-dinitrotetrahydroquinoline in 5 ml of butylamine was heated in a sealed tube at 100°C for 10 h. The cooled tube was opened and the pink-red precipitate was filtered off. Yield 0.5 g (71%). mp 148°C (from ethanol). UV spectrum,

*Deceased.

M. V. Lomonosov Moscow State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1112-1114, August, 1973. Original article submitted June 9, 1972.

TABLE 1. Thioxoimidazole Derivatives of Tetrahydroquinoline and Indoline

Comp.	Name	mp, °C	Empirical formula	Found, %			Calc., %			UV spectrum		IR spectrum cm^{-1}	Yield, %
				C	H	N	C	H	N	λ_{max}, nm	log ε		
I	2-Thioxo-1,3,5,6,7,8-hexahydro-imidazo[4,5-g]quinoline	126—128	$C_{10}H_{11}N_3S$	58,6	5,4	20,6	58,5	5,4	20,5	325	3,81	3240—3120; 2490, 1310, 1160	97
II	3-Butyl-2-thioxo-1,3,5,6,7,8-hexa-hydroimidazo[4,5-g]quinoline	150-152	$C_{14}H_{19}N_3S$	64,4	7,3	16,1	64,3	7,4	16,1	260	3,94		100
III	5-Acetyl-2-thioxo-1,3,5,6,7,8-hexa-hydroimidazo[4,5-g]quinoline	>270	$C_{12}H_{13}N_3OS$	58,4	5,3		58,3	5,3		320 415 267 289 322	4,34 2,72 4,18* 4,18 4,17		95
IV	8-Amino-2-thioxo-1,4,5,6-tetra-hydroimidazo[1,4,5-ij]quinoline	>280	$C_{10}H_{11}N_3S$	58,6	5,4	20,5	58,6	5,4	20,5	226 293 322	3,90 3,91 3,86	3240—3120; 2490, 1310, 1160	97
V	7-Amino-4-methyl-2-thioxo-1,4,5,6-tetrahydroimidazo[1,4,5-hi]indole	210—212	$C_{10}H_{11}N_3S$			20,8			20,5	223 262 335			67
VI	6-Methyl-2-thioxo-1,3,6,7-tetra-hydroimidazo[4,5-f]indole	>270	$C_{10}H_{11}N_3S$	58,5	5,4		58,5	5,4		325 341	3,95* 3,98		85
VII	5-Acetyl-6-methyl-2-thioxo-1,3,6,7-tetrahydroimidazo[5,4-f]indole	201—205	$C_{12}H_{13}N_3OS$			17,1			17,0	223 262 335	4,15 3,85 4,28	3240—3120, 2490, 1310	86

*Spectrum taken in dimethyl sulfoxide.

λ_{max}, nm ($\log \varepsilon$): 224 (4.08), 326 (4.25). Found, %: C 66.6; H 7.7; N 16.8. $C_{13}H_{19}N_3O_2$. Calculated, %: C 66.6; H 7.7; N 16.8.

Synthesis of the Thioxoimidazoles. An ethanolic solution of 5.8 mmoles of a dinitro or aminonitro derivative of a tetrahydroquinoline (or indoline) and 3 ml of hydrazine hydrate were placed in a flask with a reflux condenser and a paste of Raney nickel was introduced on the end of a spatula. The mixture was heated in the water bath until the solution was decolorized and then it was filtered from the Raney nickel in a current of nitrogen. The ethanol was distilled off in vacuum. The residual mass was treated with 10 ml of pyridine and 2 ml of dry carbon disulfide and was heated in the boiling water bath for 3 h. The resulting solution was poured into 30 ml of water, the mixture was acidified with acetic acid to pH 4-5, and the precipitate was filtered off, carefully washed free from pyridine with water, and recrystallized from ethanol.

The compounds synthesized are given in Table 1.

LITERATURE CITED

1. A. P. Terent'ev, I. G. Il'ina, E. G. Rukhadze, and I. G. Vorontsova, Zh. Obshch. Khim., 40, 1605 (1970).
2. A. Richardson, J. Org. Chem., 25, 1138 (1960).
3. A. Richardson, J. Org. Chem., 28, 2581 (1963).
4. I. G. Il'ina, N. B. Kazennova, and A. P. Terent'ev, Khim. Geterotsikl. Soedin., 80 (1973).
5. A. P. Terent'ev, I. G. Il'ina, and V. G. Bakhmut-skaya, Khim. Geterotsikl. Soedin., 953 (1971).