RADICAL ARYLATION OF SUBSTITUTED 3-AMINO-1-INDENTHIONES — CYCLIC VINYLOGS OF THIOAMIDES

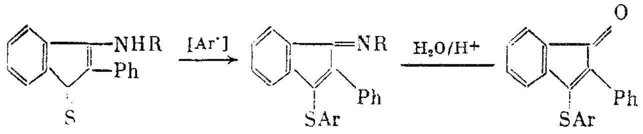
I. I. Kandror, V. A. Usov,
I. O. Bragina, T. L. Usova,
V. K. Bel'skii, and M. G. Voronkov

UDC 541.515:542.91:547.665

Investigation of enaminothioketones (EAT's) — vinylogs of thioamides — revealed both similarities and differences in the chemistry of these two classes of thiocarbonyl compounds [1, 2]. This, however, concerns only nucleophilic and electrophilic reactions, since radical reactions of EAT's were not known. At the same time radical arylations of thioamides described in recent years, which lead to the corresponding S-aryl derivatives [3, 4], suggested the possibility of carrying out these transformations also in a number of EAT's.

In connection with this, in order to compare the behavior of thioamides with their cyclic vinylogs in radical processes we studied the reaction of N-substituted derivatives of 3-amino-2-phenyl-1-indenthione (I) with aryl radicals. Aryldiazonium salts and N-nitrosoacetanilide were used as radical sources. Reactions were carried out in acetone at 20°C.

As seen from Table 1, reactions of N-aryl substituted (Ia, b) with phenyl- and tolyldiazonium fluoroborates readily give 1-arylimino-2-phenyl-3-arylthioindenes (IIa-c) with high yield. The corresponding 1-oxo-2-phenyl-3-arylthioindenes (IIIa, b) are also formed due to partial acidic hydrolysis of arylimines (II) under the reaction conditions.* The hydrolysis degree is significantly lower upon using another source of aryl radicals, N-nitrosoacetanilide, since in this case the acidity of the medium is substantially lower (acetic acid).



(Ia—c) (IIa—c) (IIIa, b)

$R = C_6H_5$ (Ia), $4\text{-}BrC_6H_4$ (Ib), CH_3 (Ic);
$R = Ar = C_6H_5$ (IIa), $R = C_6H_5$, $Ar = 4\text{-}CH_3C_6H_4$ (IIb),
$R = 4\text{-}BrC_6H_4$, $Ar = C_6H_5$ (IIc); $Ar = C_6H_5$ (IIIa), $4\text{-}CH_3C_6H_4$ (IIIb).

It was established earlier that the nature of the N-substituent has a substantial influence on the course of radical arylation of thioamides. In particular, from N-alkyl substituted thioamides S-aryl derivatives are formed with significantly lower yields than from N-arylthioamides [3]. This regularity is observed also in reactions of the corresponding cyclic vinylogs of thioamides. Thus, in case of (Ic) sulfide (IIIa) is the main reaction product. This was caused by the lower resistance of the N-alkylimine group to acidic hydrolysis compared to the N-arylimine group [6]. In both cases water reacts only with the protonated iminium group $=\overset{+}{N}HR$ and does not affect the indenyl aryl sulfide fragment (see [7]).

In radical arylation of thioamides and their analogs with aryldiazonium salts usually the catalysts copper chloride or ferrocene are used, the role of which is reduction of the aryldiazonium cation to an aryl radical as it is generated and oxidation of the intermediate adduct-radical at the step of stabilization of the latter [8].

Arylation of aminoindenthiones (I) with aryldiazonium salts proceeds in the absence of a catalyst, since thioketones (I) themselves initiate a chain oxidation-reduction process

---

*The acetone used contains up to 0.2% of water [5]; hydrolysis is promoted by the HBF_4 formed.

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 901-905, April, 1989. Original article submitted December 14, 1987.

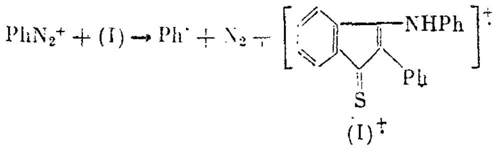
0568-5230/89/3804-0811\$12.50

TABLE 2. Characteristics of Iminosulfides (IIa-c) and Oxosulfides (IIIa, b)

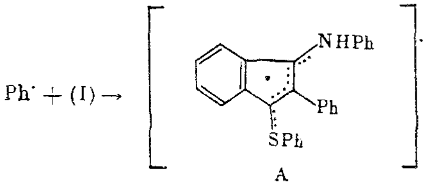
Compound	Mp, °C (solvent)	Molecular formula	Found/Calculated, %				Mass spectrum, m/z (rel. intensity, %)		PMR spectrum, δ, ppm
			C	H	N	S	M+	[M—SAr]+	
(IIa)	125–126 (hexane)	$C_{27}H_{19}NS$	83.11/83,26	4,83/4,92	3,57/3,60	8.12/8,23	389(7,5)	280(100)	6,45–6,55(1H), 6,9–7,1(4H), 7,15–7,50(12H), 7,60–7,75(2H)
(IIb)	164–165 (hexane)	$C_{28}H_{21}NS$	83.35/83.34	5,46/5,25	3,24/3,47	7.89/7.94	403(11)	280(100)	6,45–6,55(1H), 6,9–7,4(15H), 7,6–7,7(2H), 2,31s(3H)
(IIc)	171–173 (alcohol)	$C_{27}H_{18}BrNS$ *	68.61/69.23	3,71/3,87	3,02/2,99	6,70/6,85	469(11)	360(100)	6,6–6,7(1H), 6,9–7,1(4H), 7,2–7,5(9H), 7,6–7,7(4H)
(IIIa)	102–104 (hexane)	$C_{21}H_{14}OS$ **	79,89/80.22	4,51/4,49	–	10.24/10,17	314(73)	205(100)	6,75–7,85(1H), 7,2–7,6(13H)
(IIIb)	85–88 (alcohol)	$C_{22}H_{16}OS$ **	80.20/80,45	4,92/4,91	–	9.47/9,76	328(100)	205(92)	6,75–6,85(1H), 7,05–7,15(2H), 7,2–7,6(10H), 2,29s(3H)

*Br: found 17.09; calculated 17.06.

**νC=O 1695 cm^{-1}.



(1)



(2)

$$(I)^{+\cdot} + A \rightarrow (I) + (II) + H^{+} \quad (3a)$$

$$PhN_2^{+} + A \rightarrow (II) + H^{+} + N_2 + Ph \quad (3b)$$

The role of aminoindenthiones (I) as reducing agents is confirmed by their susceptibility to oxidation ($E_{1/2} \sim 0.291$ V),* which exceeds that of ferrocene ($E_{1/2} = 0.341$ V) [9]. Aryl substituted thioamides are transformed into cation-radicals with significantly more difficulty ($E_{1/2} \sim 0.86$V)† [10]. For thioamides and their analogs such "uncatalyzed" radical arylation was observed only upon using easily reducible salts, for example 4-nitrophenyldiazonium salts [8].

The obtained sulfides (II) and (III) are colorless or yellowish crystalline substances. Their structure was confirmed by elemental analysis and mass and PMR spectra (Table 2). The presence in the mass spectra of these compounds of intense M^{+} and $[M-SAr]^{+}$ ion peaks proves that their radical arylation occurs at the sulfur atom. Since in the PMR spectra the four aromatic rings in (IIa-c) and the three in (IIIa, b) give overlapping complex multiplets in the region of 6.5-7.8 ppm, their complete assignment was not carried out.

The structure of compound (IIa) was unambiguously proved by x-ray structural analysis (Fig. 1).

Thus, the reaction trends for radical arylation of thioamides [3, 4, 8] are observed also for their cyclic vinylogs, aminoindenthiones. Radical arylation of the latter with aryldiazonium salts is a simple and convenient way to synthesize difficultly obtainable S-aryl derivatives.

EXPERIMENTAL

NMR spectra in deuteroacetone (^{1}H) or deuterochloroform (^{13}C) were taken on a Bruker WP-200-SY spectrometer at room temperature with TMS as internal standard. Mass spectra were taken on a DS-60 instrument and IR spectra on a UR-20 instrument with KBr pellets. Aminoindenthiones (Ia-c) were synthesized by a method of [11]†† and N-nitrosoacetanilide by a method of [12].

Radical Arylation of Aminoindenthiones (Ia-c) (general method). Into a flask supplied with magnetic stirrer, condenser, and a nitrogen inlet, were placed 5 mmoles of thione, 5-6

TABLE 1. Radical Arylation of N-Substituted 3-Amino-2-phenyl-1-indenthiones (I) (acetone, 20°C, 1.5-2 h)

Starting compound	Arylating agent	Reaction product, yield, %
(Ia)	$C_6H_5N_2BF_4$	(IIa), 70; (IIIa), 20
(Ia)	$C_6H_5N(NO)COCH_3$	(IIa), 90; (IIIa), traces
(Ia)	$4\text{-}CH_3C_6H_4N_2BF_4$	(IIb), 62; (IIIb), 16*
(Ib)	$C_6H_5N_2BF_4$	(IIb), 50; (IIIa), 44
(Ic)	$C_6H_5N_2BF_4$	(IIIa), 75

*Besides the products shown ditolyl disulfide is also formed in 17% yield.

---

*Determined by L. E. Protasova of the Zelinksy Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk.

†All half wave values $E_{1/2}$ are shown relative to the s.c.e. for a platinum rotating electrode.

††By I. A. Dorofeev of the Zelinksy Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk.

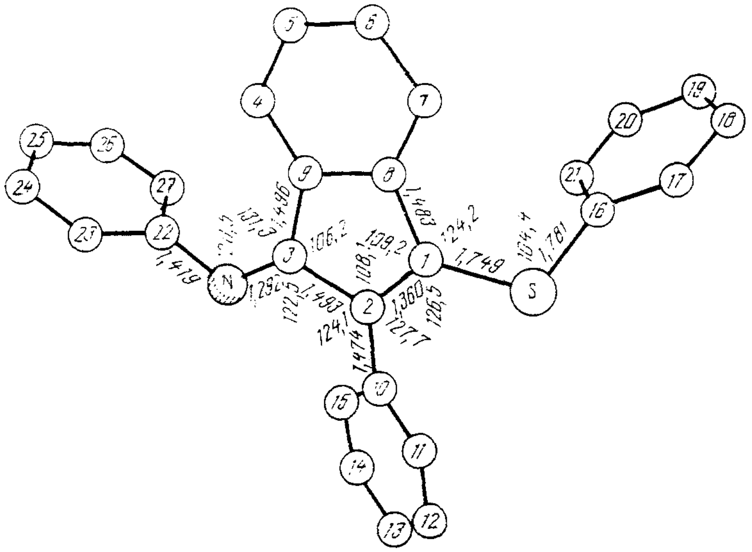


Fig. 1. Structure of 1-phenylimino-2-phenyl-3-phenylthioindene (IIa).

mmoles of diazonium fluoroborate (or N-nitrosoacetanilide), and 30 ml of acetone (previously dried and distilled from $CaCl_2$). The mixture was stirred at ~20°C for 1.5-2 h until complete disappearance of the starting thioketone (as shown by TLC on plates of Silufol UV-254, eluent: benzene): then the acetone was evaporated under vacuum. The residue was dissolved in $CHCl_3$, washed with saturated soda solution, water, and dried above $MgSO_4$. After distillation of the solvent the residue was chromatographed on a column of silica L 40/100 μ with benzene or benzene/alcohol (20:1) as eluent. Yields, melting points, and other characteristics of the obtained compounds are shown in Tables 1 and 2.

X-ray structural analysis of 3-phenylamino-2-phenyl-1-phenylthioindene (IIa) was carried out on a Nicolet diffractometer at ~20°C by the method of $\theta/2\theta$-scanning with MoK_α irradiation. Compound (IIa) crystals are monoclinic, a = 6.066(1), b = 9.806(2), c = 18.166(3) Å, γ = 106.17(2)°, Z = 2, space group $P2_1$, ρ_{calc} = 1.24 g/cm^3; 1034 independent reflections ($I > 3\sigma(I)$, $2\theta \leqslant 46°$). The structure was interpreted by the direct method and refined by least squares in the complete-matrix anisotropic (isotropic for hydrogen atoms) approximation to R = 0.040 (coordinates of atoms and complete tables of interatomic distances and angles can be obtained from the authors).

^{13}C NMR spectrum (δ, ppm): 117.8 (2C): $\underline{121.5}$; $\underline{124.0}$; $\underline{125.2}$; $\underline{126.7}$; $\underline{127.1}$; $\underline{127.6(2C)}$; $\underline{128.0}$; 128.1; $\underline{129.0(4C)}$; $\underline{129.5(2C)}$; $\underline{130.9(3C)}$; 131.9; 133.3; 141.3; 143.0; 1143.5; 151.8; 164.5 (underlined numbers belong to signals of C atoms bound to H).

CONCLUSIONS

1. Radical arylation of 3-arylamino-2-phenyl-1-indenthiones with aryldiazonium fluoroborates or N-nitrosoacetanilide leads to the corresponding 1-arylamino-2-phenyl-3-arylthioindenes with high yield. Partial hydrolysis of the latter under the reaction conditions form 1-oxo-2-phenyl-3-arylthioindenes as by-products.

2. The similarity of thioamides and their vinylogs (the aminoindenthiones) in radical arylation reactions was established.

LITERATURE CITED

1. V. A. Usov and M. G. Voronkov, Sulfur Rep., 2, No. 2, 39 (1982).
2. V. A. Usov, Izv. Akad. Nauk Latv. SSR, Ser. Khim., No. 1, 94 (1986).
3. I. I. Kandor, B. V. Kopylova, and R. Kh. Freidlina, Sulfur Rep., 3, No. 3, 289 (1984).
4. R. Kh. Freidlina, I. I. Kandror, and B. V. Kopylova, Izv. Akad. Nauk SSSR, Ser. Khim., No. 8, 1799 (1983).
5. A. Weissberger, E. Proskauer, J. Riddick, and E. Toops, Jr., Organic Solvents — Physical Properties and Methods of Purification, Interscience, New York (1955).
6. V. A. Usov, L. V. Timokhina, and M. G. Voronkov, Usp. Khim., 55, No. 11, 1761 (1986).

7. V. A. Usov, N. A. Korchevin, Ya. S. Tseplin, and M. G. Voronkov, Zh. Org. Khim., 9, No. 10, 2149 (1973).
8. R. Kh. Freidlina, I. I. Kandror, R. G. Gasanov, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 4, 823 (1984).
9. C. K. Mann and K. K. Barnes, Electrochemical Reactions in Nonaqueous Systems, Dekker, New York (1970).
10. S. J. Reddy and V. R. Krishnan, Indian J. Chem., 17A, 558 (1979).
11. V. A. Usov, Ya. S. Tseplin, N. A. Korchevin, and M. G. Voronkov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 5, 99 (1974).
12. H. France, J. M. Heilbron, and D. H. Hey, J. Chem. Soc., 368 (1940).

REACTIONS OF ORGANYLTHIOCHLOROACETYLENES WITH ALIPHATIC DIAMINES

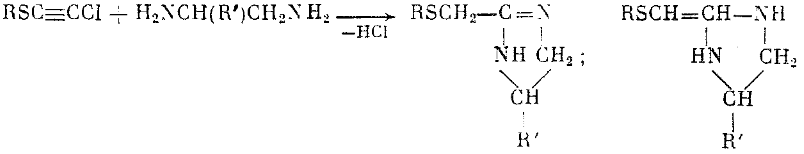
A. N. Mirskova, S. G. Seredkina,
I. D. Kalikhman, O. B. Bannikova,
and M. G. Voronkov

UDC 542.91:547.379'131:
547.415.1:547.781

The presence of several reaction centers in the molecule of organylthiochloroacetylenes and their high reactivity make these compounds promising for organic synthesis [1]. It is known [2-5] that the reactions of organylthiochloroacetylenes with bifunctional sulfur-containing nucelophiles occur with the participation of C—Cl and C≡C bonds and afford various sulfur-substituted heterocycles. Continuing these studies, we studied the reaction of organylthiochloroacetylenes with aliphatic diamines.

The literature describes the reaction of 1-halo-3,3,3-trifluoropropynes with 1,2-diaminoethane [6]. However, it was found that the diamine does not enter into nucleophilic substitution with subsequent intramolecular cyclization, but reacts as a dehalogenating agent.

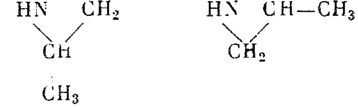
In contrast to this, organylthiochloroacetylenes react facilely with aliphatic 1,2-diamines in ether or benzene at 20-22°C with the formation of 2-(organylthiomethyl)-2-imidazolines (I)-(VI)



(Ia)—(VIa) (Ib)-(VIb)

The reaction of organylthiochloroacetylenes and diamine occurred when their molar ratio was 1:2 in ether or benzene. Compounds (I)-(III) were colorless, crystalline substances, and (IV)-(VI) were viscous liquids, freely soluble in water and alcohols. Their structure and composition were proven by data from IR and Proton-NMR spectroscopy and elemental analysis (Table 1). The IR spectra of imidazolines (I)-(VI) contained intense absorption bands of the C=N bond at 1600 cm^{-1} and NH at 3400 cm^{-1}. The alternative structure (b) was precluded on the basis of the data of proton NMR spectra of compounds (I)-(VI), in which signals of vinyl protons were absent and signals of SCH_2, NCH_2, and NH groups were observed.

Unlike those of (I)-(III), the proton NMR spectra of compounds (IV)-(VI) contained not one, but two groups of signals (Table 1). This doubling of the signals was due to the tautomeric equilibrium (a) ⇄ (b)



(a) (b)

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 906-909, April, 1989. Original article submitted November 17, 1987.

0568-5230/89/3804-0815$12.50