EXPERIMENTAL

IR spectra were measured on a Specord IR-75 (KBr tablets), electronic absorption spectra on a Specord UV-vis (in methanol and toluene), and fluorescence spectra in the same solvents using an SF-4A spectrometer monochromator, an FEU-38 detector, and a DRS-500 mercury lamp source. The fluorescence spectra were corrected. Absorbance at long-wave excitation did not exceed 0.2. PMR spectra for IIIa were measured on a Varian XL-100 instrument using TMS as internal standard.

2-Bromo-1,3,3-triarylpropanones have been described in [3]. Dihydrochalcone was obtaine by method [4].

2-Bromo-1,3-diphenylpropanone (IIa). A solution of 1,3-diphenylpropanone (2 g, 9.5 mmol in glacial acetic acid (15 ml) was heated to 50°C and bromine (5 ml) was added cautiously wit stirring. When the solution had become light yellow, it was poured into iced water (100 g). The precipitated solid was filtered off and crystallized from methanol to give 2.4 g (87%) with mp 58°C.

Compounds IIb-g were obtained similarly (Table 2).

3-Aryl-2-benzyl-1,2-dihydroquinoxaline (IIIa). A mixture of 1,2-phenylenediamine (1.1 g 10 mmole), 2-bromo-1,3-diphenylpropanone (2.9 g, 10 mmole), and sodium acetate (0.83 g, 10 mmole) in methanol (50 ml) was refluxed with continuous passage of a stream of methane or car bon gas for 6 h. The salt was filtered off and the filtrate cooled to 5°C. Filtration then gave a crystalline product (1.0 g, 34%) with mp 139-140°C (from methanol).

IIIb-g were prepared in the same way.

LITERATURE CITED

1. N. N. Kolos, B. Insuasti, Kh. Kiroga, and V. D. Orlov, Khim. Geterotskil. Soedin., No. 8, 1127 (1986).
2. V. D. Orlov, F. G. Yaremenko, N. N. Kolos, N. S. Pivnenko, and V. F. Lavrushin, Khim. Geterotsikl. Soedin., No. 4, 544 (1980).
3. V. D. Orlov, B. Insuasti, and Kh. Kiroga, Ukr. Khim. Zh., 52, 316 (1986).
4. H. A. Weidlich and M. M. Delius, Chem. Ber., 74, 1195 (1941).

SYNTHESIS OF AZOTRIAZINES

L. M. Mironovich, V. K. Promonenkov,
and S. E. Bogushevich

UDC 547.873:542.943

Condensation of 4-nitroso-3-thio-6-phenyl-1,2,4-triazin-5-one with aromatic amines led to azotriazines.

Substituted 1,2,4-triazin-5-ones have found wide usage as herbicides. The majority of these herbicides have a substituent (alkyl, amino) in the 4-position of the triazine ring [1] but others (e.g., azo groups) have been little studied.

This study was aimed at the preparation of azotriazines by condensation of 4-nitroso-1,2,4-triazin-5-ones with aromatic amines. The usual method for such compounds involving azo coupling of an aromatic amine of phenol with a diazonium salt was unacceptable because of the instability of triazine diazonium salts. Reaction of nitrous acid with 4-amino-1,2,4-triazin-5-one leads to cleavage of the amino group [2]. In view of the weak electrophilicity of $Ph\text{-}N_2^+$, together with the rather poor activity of 1,2,4-triazin-5-ones in electrophilic substitutions, the reaction of phenyldiazonium salts with 1,2,4-triazin-5-ones showed little

---

Chernigov Branch, Kiev Polytechnic Institute, Chernigov 150027. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 833-835, June, 1987. Original article submitted December 30, 1985.

0009-3122/87/2306-0687$12.50 ©1987 Plenum Publishing Corporation

TABLE 1. Parameters for IIa-f

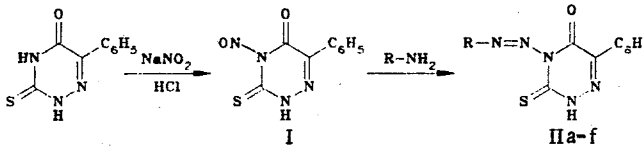
Compound	mp, °C	Found, %				Empirical formula	Calculated, %				Yield, %
		C	H	N	S		C	H	N	S	
IIa	256—257	57,9	3,7	22,2	10,6	$C_{15}H_{11}N_5OS$	58,1	3,6	22,7	10,4	78
IIb	239—240	59,3	4,1	21,4	9,8	$C_{16}H_{13}N_5OS$	59,4	4,04	21,7	9,9	76
IIc	245—252*	46,4	2,86	18,3	16,2	$C_{15}H_{11}N_5O_4S_2$	46,3	2,84	18,0	16,4	63
IId	245—246*	50,6	2,87	23,3	9,2	$C_{15}H_{10}N_6O_3S$	50,8	2,84	23,7	9,0	68
IIe	258—259*	48,9	2,48	22,3	8,8	$C_{15}H_9N_6O_4S$	48,7	2,45	22,8	8,7	72
IIf	246—247*	52,3	2,8	22,7	7,1	$C_{19}H_{12}ClN_7O_2S$	52,1	2,76	22,4	7,3	76

---

*With decomposition.

promise. Hence the method of choice was the condensation of 4-nitroso-1,2,4-triazin-5-one with aromatic amines. An advantage of this method was the potential for preparation of azo compounds without an activating group in the aromatic residue.

4-Nitroso-3-thio-6-phenyl-1,2,4-triazin-5-one (I) was obtained by nitrosation of 3-thio-6-phenyl-1,2,4-triazin-5-one with sodium nitrite in acid and its structure was proved by elemental analysis, UV, IR, and PMR spectroscopy. Refluxing I with aromatic amines (aniline, m-toluidine, sulfanilic acid, o-nitroaniline, 2-amino-5-nitrophenol, or 1-phenyl-4-amino-5-chloropyridazin-6-one) in glacial acetic acid gave the arylazo-4-(3-thio-6-phenyl-1,2,4-triazin-5-ones) (IIa-f). The yields (63-78%) depended little on the structure of the aromatic amine and the products were light colored crystalline substances melting, with decomposition, at high temperatures. They were insoluble in water but soluble in organic solvents containing acid.



II a $R=C_6H_5$; b $R=3\text{-}CH_3—C_6H_4$; c $R=4\text{-}HO_3S—C_6H_4$; d $R=2\text{-}NO_2—C_6H_4$;
e $R=2\text{-}OH—4\text{-}NO_2—C_6H_3$; f $R=HC=N—N(C_6H_5)—C(O)—C(Cl)=C—$

The structures of IIa-f were confirmed by elemental analysis, UV, IR, and PMR spectroscopy.

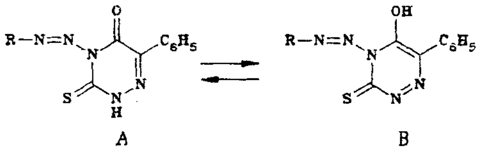
The IR spectra of IIa-f showed absorption at 1420-1410 cm^{-1} assigned to the N=N vibration and the absence of a band at 1500 cm^{-1} (for $\nu_{N-N=O}$) seen in I. The bands at 1420-1410 cm^{-1} can be compared with those of nonsymmetrical azobenzenes [3, p. 46], and a trans configuration assigned to IIa-f. The C=O absorption was shifted 60-70 cm^{-1} to high frequency and the C=S absorption 20-25 cm^{-1} to low frequency of their position in I.

The PMR spectroscopic signals for IIa-f showed two groups of signals at 7.05-7.40 and 7.84-8.37 ppm. The group at 7.05-7.40 ppm was assigned to the phenyl ring at the 6-position of the triazine ring being shifted to higher field of the position in I (m, 7.27-7.78 ppm). The other group (m, 7.84-8.37) was assigned to protons in the substituted benzene rings attached to the azo link and was in satisfactory agreement with chemical shifts calculated by an additive method [4]. Singlet proton signals were also seen for ring substituents. Thus the tolylazo compound IIb showed a 2.36 ppm singlet for the CH_3 group and IIf a 6.5 ppm singlet for the pyridazine ring 3-H.

The electronic spectra of I, IIa-f showed four absorption bands (240-258 nm) analogous to those found in azoheterocycles (pyrimidine, pyridazine, pyridine, pyrazine) [5]. The intense band (log ε 4.2-4.3) at 293 nm must be assigned to the π → π* transition of the triazine conjugated system $S=\overset{|}{C}—N=N—\overset{|}{C}=\overset{|}{C}—O—$ because of its insensitivity to pH (from 3 to 11) [6] and the presence of similar bands (λ 280-300 nm, log ε 4.3-4.5) [3, p. 72] in thiosemicarbazones. The indicated chromophore may arise as a result of tautomeric change:

TABLE 2. Spectral Parameters for IIa-f

Compound	UV spectrum, λ_{max}, nm (log ε)	IR spectrum, cm^{-1}	PMR spectrum, δ, ppm
IIa	362,5 (4,59), 293,3 (4,26), 258,3 (2,89), 252,5 (2,61), 246,7 (2,66), 240,8 (2,64)	3445 ($N_{(2)}$—H), 1680 (C=O), 1410 (—N=N—), 1160 (C=S)	7,1—7,32 (m C_6H_5); 7,9—8,31 (m C_6H_5—N=N)
IIb	362,5 (4,62), 293,3 (4.26), 258,3 (2,92), 252,5 (2,63), 246,7 (2,66), 240,8 (2,66)	3475 ($N_{(2)}$—H), 1690 (C=O), 1415 (—N=N—), 1165 (C=S)	2,36 (s CH_3); 7,05—7,3 (m, C_6H_5); 7,84—8,04 (m C_6H_4—N=N—)
IIc	385,0 (3,28), 362,5 (4,59), 293,3 (4,26), 258,3 (2,89), 252,5 (2,61), 246,7 (2,66), 240,8 (2,64)	3427 ($N_{(2)}$—H), 1690 (C=O), 1420 (—N=N—), 1160 (C=S)	7,05—7,4 (m, C_6H_5); 8,05—8,37 (m, C_6H_4—N=N—); 12,0 (s, 1H)
IId	362,5 (4,64), 293,3 (4,30), 258,3 (2,93), 252,5 (2,65), 246,7 (2,70), 240,8 (2,67)	3458 ($N_{(2)}$—H), 1690 (C=O), 1415 (—N=N—), 1165 (C=S)	7,08—7,37 (m C_6H_5); 7,96—8,28 (m, C_6H_4—N=N—)
IIe	362,5 (4,59), 293,3 (4,26), 258,3 (2,89), 252,5 (2,61), 246,7 (2,66), 240,8 (2,63)	3423 ($N_{(2)}$—H), 1690 (C=O), 1410 (—N=N—), 1160 (C=S)	7,08—7,34 (m C_6H_5); 7,95—8,3 (m C_6H_3—N=N—); 9,4 (s, 1H)
IIf	383,3 (3,23), 362,5 (4,62), 293,3 (4,28), 258,3 (2,92), 252,5 (2,63), 246,7 (2,69), 240,8 (2,16)	3410 ($N_{(2)}$—H), 1680 (C=O), 1420 (—N=N—), 1165 (C=S)	6,5 (s, 1H); 7,05—7,39 (m, C_6H_5); 8,0—8,34 (m, C_6H_5—N)



Substituted 3-thio-1,2,4-triazin-5-ones (e.g., the 4-amino-6-tert butyl analog) exist principally in form B according to [6]. For all of the compounds described, a characteristic absorption at 362.5 nm was observed which can be assigned to a π → π* in the $C_6H_5\overset{|}{C}{=}N{-}N$ system (replacement of the 6-phenyl substituent with tert-butyl caused this band to disappear). As a result of the absence of intense bands between 380 and 720 nm in their electronic spectra IIa-f were only weakly colored.

EXPERIMENTAL

IR spectra were recorded on a UR-10 instrument (KBr tablets), PMR spectra on a BS-467 (60 MHz) in $(CD_3)_2CO$ (HMDS internal standard), and electronic absorption spectra on a Beckman instrument in dioxan (c = 10^{-3} mole/liter). Product purity was monitored by TLC on silufol UV-254 plates with chloroform:acetone (3:1) eluant. The physical parameters for the compounds prepared are given in Tables 1 and 2.

Arylazo-4-(3-thio-6-phenyl-1,2,4-triazin-5-ones) (IIa-f). To a suspension of 3-thio-4-nitroso-6-phenyl-1,2,4-triazin-5-one (0.05 mole) in glacial acetic acid (50 ml) was added with stirring the corresponding amine (0.05 mole). The mixture was refluxed for 12-15 h, cooled, the solid filtered off, washed with glacial acetic acid (25 ml), and dried in vacuo. The product was purified by crystallization from alcohol.

LITERATURE CITED

1. H. Neunhoeffer and P. Willey (eds.), The Chemistry of Heterocyclic Compounds, Vol. 33, Interscience, New York (1978), p. 1070.
2. A. Dornow, H. Pietsch, and P. Marx, Chem. Ber., 97, 2647 (1964).
3. L. A. Kazitsyna and N. B. Kupletskaya, Applications of UV, IR, and NMR Spectroscopy in Organic Chemistry [in Russian], Vyssh. Skhola, Moscow (1971), p. 263.
4. B. I. Ionin, B. A. Ershov, and A. I. Kol'tsov, NMR Spectroscopy in Organic Chemistry [in Russian], Khimiya, Leningrad (1983), p. 268.
5. A. Gordon and R. Ford, Chemist's Companion, Wiley (1973).
6. P. W. Albro, C. E. Parker, G. D. Marbury, O. Hermander, and E. T. Corbin, Appl. Spectrosc., 4, 556 (1984).