CONCLUSIONS

A one-step method was developed for the stereospecific reduction of acetylenic aldehydes to the (Z)-alken-1-ols by hydroboration with 9-borabicyclp[3.3.1]nonane and subsequent acidolysis.

LITERATURE CITED

1. C. A. Henrick, Tetrahedron, 33, 1845 (1977).
2. B. G. Kovalev and R. I. Ishchenko, Zh. Org. Khim., 10, 463 (1974).
3. S. Krishamurthy and H. C. Brown, J. Org. Chem., 40, 1864 (1975).
4. H. C. Brown, C. G. Scouten, and R. Liotta, J. Am. Chem. Soc., 101, 96 (1979).
5. G. A. Tolstikov, V. N. Odinokov, R. I. Galeeva, A. S. Bakeeva, and V. R. Akhunova, Tetrahedron Lett., 4851 (1979).
6. U. M. Dzhemilev, G. G. Balezina, L. A. Volkova, V. P. Krivonogov, and G. A. Tolstikov, Khim. Prir. Soedin., 97 (1980).

RADICAL PHENYLATION OF AMIDES OF THIOCINNAMIC ACID

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Previously we had shown that when thioamides R—C(S)—NHR' are subjected to radical phenylation they form the corresponding S-phenyl isothioamides R—C(SPh)=NR' in those cases where R and R' are aryl groups [1]. The yield of the isothioamides drops when one of these groups is replaced by an alkyl substituent, while they are not formed at all when both groups are replaced in a similar manner, and diphenyl disulfide becomes practically the sole sulfur-containing reaction product [2]. In this connection it was interesting to study the phenylation of the N-alkyl- and N-arylamides of thiocinnamic acid in order to ascertain the effect of a phenyl group, located in the vinylog position to the thioamide grouping, on the studied reaction.

In the present paper we studied the phenylation of the thioamides PhCH=CH—CS—NHR (I) with R = Ph (a) and C_2H_5 (b). N-Nitrosoacetanilide (NAA) was used as the source of phenyl radicals.

In the case of thioamide (Ia) the reaction proceeds the same as with thiobenzanilides, i.e., it leads to the formation of isothioamide (IIa) in high yield. The structure of (IIa) was confirmed by the PMR data. Although the signals of the vinyl protons could not be iso-

$$\underset{\text{(Ia)}}{\text{PhCH=CH—CS—NHPh}} \xrightarrow{\text{HAA}} \underset{\text{(IIa)}}{\text{PhCH=CH—C(SPh)=NPh}} \qquad (1)$$

lated at a frequency of 60 MHz (they are masked by the signals of the protons of the phenyl groups), the upfield half of the AB system of the vinyl group was manifested distinctly at a frequency of 200 MHz. The corresponding downfield lines (located inside the signal of the phenyl groups) were identified employing double resonance. The mass spectra also confirmed the structure of (IIa).

Similar to S-phenylisothiobenzanilide, isothioamide (IIa) is a crystalline solid that is stable at room temperature.

The phenylation of thioamide (Ib) proceeded somewhat differently. Apparently, also in this case the reaction leads to the initial formation of the isothioamide PhCH=CH—C(SPh)=NC_2H_5 (IIb), but this compound could not be characterized adequately due to its instability. It decomposes even at room temperature, and when its purification was attempted by chromatographing on an SiO_2 column we isolated Ph_2S_2 and isothioamide (III), which contained an additional PhS group in the β position. The structure of (III) was proved via the PMR and mass

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$$PhCH(SPh)-CH_2-C(SPh)=NC_2H_5 \quad (III)$$

spectra. Besides the signals of the protons of the ethyl and phenyl groups, the PMR spectrum has the characteristic signals of the $\diagdown CH-CH_2$ fragment. The alternate structure $PhCH_2-CH(SPh)-C(SPh)=NC_2H_5$ was excluded on the basis of the mass spectrum, which, together with the peak of the molecular ion, has an intense peak that corresponds to the Ph—CH—SPh fragment, which unequivocally confirms the structure of (III).

It may be assumed that the unstable isothioamide (IIb) decomposes with the ejection of a PhS radical, which then adds to another (IIb) molecule (in which connection this addition is regioselective); the radical formed is stabilized by the cleavage of hydrogen to give (III).

$$PhS^{\cdot} + PhCH=CH-C(SPh)=NC_2H_5 \rightarrow PhCH-\dot{C}H-C(SPh)=NC_2H_5 \rightarrow (III) \quad (2)$$

(IIb) SPh; SPh; SPh

To verify this assumption we reacted isothioamide (IIa) with thiophenol under radical conditions. Actually, it proved that PhS radicals add regioselectively to the double bond. The structure of bis-sulfide (IV) was proved via the PMR and mass spectra. The PMR spectrum

$$PhCH=CH-C(SPh)=NPh + PhSH \rightarrow PhCH(SPh)-CH_2-C(SPh)=NPh \quad (3)$$

(IIa) (IV)

has signals that are characteristic for the ABX system of the $C(H^X)(H^B)-C(H^A)$ fragment (the nonequivalence of the protons of the CH_2 group is related to the presence of an adjacent asymmetric carbon atom). Besides the peak of the molecular ion, the mass spectrum of (IV) has the peaks of the characteristic fragments, in particular Ph—CH—SPh which uniequivocally confirms the structure of (IV).

It is interesting to mention that when bis-sulfide (IV) is chromatographed on an SiO_2 plate it appears as two spots with close R_f values, which is apparently explained by the fact that it represents a mixture of the E and Z isomers [3].

The results obtained confirm the possible formation of bis-sulfide (III) by reaction (2), which is confirmed by the fact that Ph_2S_2 is formed along with (III), evidently via dimerization of the PhS radicals.

In conclusion it should be mentioned that the phenyl group in cinnamic acid derivatives apparently exerts a smaller stabilizing effect on the isothioamide group than in benzoic acid derivatives: The phenylation of thioamide (Ib) proceeds in the same way as the reaction with purely aliphatic thioamides [2]. However, an important difference of this reaction is the fact that the stable β-phenylthiohydrocinnamic acid derivative (III) is obtained.

EXPERIMENTAL

The PMR spectra were taken on Hitachi—Perkin-Elmer (60 MHz) and Bruker WP-200SY (200 MHz) spectrometers in deuteroacetone solution (δ 2.06 ppm). The mass spectra were obtained on an MS-30 instrument.

The N-phenylamide of thiocinnamic acid (Ia) was obtained as described in [4].

The N-ethylamide of thiocinnamic acid (Ib) was obtained in a similar manner in 70% yield, mp 109°C. Found: C 69.11; H 6.84; N 7.38; S 16.91%. $C_{11}H_{13}NS$. Calculated: C 69.06; H 6.85; N 7.32; S 16.76%.

Phenylation of N-Phenylamide of Thiocinnamic Acid (Ia). A solution of 1.6 g (6.7 mmoles) of thioamide (Ia) and 1.2 g (7.2 mmoles) of NAA in 25 ml of acetone was stirred for 20 h at 20° in an argon stream. After distilling off the acetone the residue was chromatographed on a SiO_2 column, using a 10:1 benzene—alcohol mixture as the eluant. We obtained 0.1 g (6%) of the starting thioamide (Ia) and 1.7 g (80%) of the phenyl ester of N-phenyliminothiocinnamic acid (IIa) as an oil that crystallized when rubbed with alcohol, mp 91-93° (from alcohol). Found: C 79.23; H 5.08; N 4.46; S 10.47%. $C_{21}H_{17}NS$. Calculated: C 79.96;

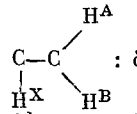
H 5.43; N 4.44; S 10.46%. PMR spectrum (200 MHz; δ, ppm): 6.56 d, 7.54 d, $J_{CH=CH}$ = 16.1 Hz, 6.7-7.7 m. Mass spectrum (m/z): 315 (M^+, 1%); 206 ($M^+ - SPh$, 100%).

Phenylation of N-Ethylamide of Thiocinnamic Acid (Ib). A solution of 2.3 g (12 mmoles) of thioamide (Ib) and 2.2 g (13 mmoles) of NAA in 30 ml of acetone was stirred for 20 h at 20° in an argon stream. After removal of the acetone the residue was chromatographed on an SiO_2 column, using a 10:1 hexane–alcohol mixture as the eluant. We obtained 0.1 g (8%) of Ph_2S_2, 0.7 g (30%) of the starting thioamide (Ib), and 2.1 g of a mixture of Ph_2S_2, (IIb), and (III) as a dark red oil. This mixture was rechromatographed, using a 2:1 $CHCl_3$–hexane mixture as the eluant, to give 0.2 g of Ph_2S_2, 0.4 g of (IIb), and 1 g of (III).

Found for (IIb): S 11.38%. $C_{17}H_{17}NS$. Calculated: S 11.99%.

Compounds (III) is the phenyl ester of β-phenylthio-N-ethyliminothiohydrocinnamic acid. Found: C 72.64; H 5.80; N 3.54; S 16.09%. $C_{23}H_{23}NS_2$. Calculated: C 73.16; H 6.14; N 3.71; S 16.99%. PMR spectrum (60 MHz; δ, ppm): 1.15 t (3H), 2.75 d (2H), 3.45 qu (2H), 4.73 t (1H), 7.08 s (5H), 7.33 s (10 H). Mass spectrum (m/z): 377 (M^+, 3%), 268 ($M^+ - SPh$, 63%), 199 (Ph – CH – SPh, 100%).

Addition of Thiophenol to Isothioamide (IIa). A solution of 0.09 g (0.29 mmoles) of (IIa), 0.063 g (0.57 mmole) of thiophenol, and 0.008 g of azobisisobutyric acid dinitrile in 0.5 ml of acetone was heated in a sealed glass ampul in an argon atmosphere for 5 h at 70°. The acetone was evaporated and the residue was analyzed by PMR (200 MHz). The signals of the vinyl protons of the starting isothioamide (Ia) are completely absent in the spectrum,

and the characteristic signals of the  : $\delta_A = 3.00$, $\delta_B = 3.04$, $\delta_X = 4.85$ ppm, J_{AX} = 10.0, J_{BX} = 5.4 Hz fragment appear. In addition, the spectrum has the signals of the phenyl groups and the SH group of the unreacted thiophenol, and also of the CH_3 groups from the decomposition products of the initiator.

The phenyl ester of β-phenylthio-N-phenyliminothiohydrocinnamic acid (IV) was isolated from the reaction mixture by chromatographing on an SiO_2 column (eluant = 1:1 benzene–hexane mixture). Mass spectrum (m/z): 425 (M^+, 1%); 3,6 ($M^+ - SPh$, 15%); 207 ($M^+ - 2SPh$, 100%); 199 (Ph–CH–SPh, 42%).

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CONCLUSIONS

1. The radical phenylation of the N-phenylamide of thiocinnamic acid using N-nitrosoacetanilide gives the phenyl ester of N-phenyliminothiocinnamic acid in high yield.

2. The N-ethylamide of thiocinnamic acid under analogous conditions gives the phenyl ester of β-phenylthio-N-ethyliminothiohydrocinnamic acid, which is explained by the secondary transformations of the unstable phenyl ester of N-ethyliminothiocinnamic acid formed as an intermediate.

3. The phenyl ester of N-phenyliminothiocinnamic acid adds thiophenol regioselectively under radical conditions to give the phenyl ester of β-phenylthio-N-phenyliminothiohydrocinnamic acid.

LITERATURE CITED

1. I. I. Kandror, I. O. Bragina, and R. Kh. Freidlina, Dokl. Akad. Nauk SSSR, 249, 867 (1979); I. I. Kandror and I. O. Bragina, Izv. Akad. Nauk SSSR, Ser. Khim., 683 (1981).
2. I. I. Kandror and I. O. Bragina, Izv. Akad. Nauk SSSR, Ser. Khim., 2121 (1982).
3. W. Walter, W. Ruback, and C. O. Meese, Chem. Ber., 113, 171 (1980).
4. N. Pravdic and V. Hahn, Croat. Chem. Acta, 34, 85 (1962).