CONCLUSIONS

The oxidative dimerization of a mixture of the trans and cis isomers of 2-methyl-2-ethynylcyclopropanecarboxylic acid in the presence of CuCl and NH_4Cl gives, along with bis(trans-1-methyl-2-carboxyl-1cyclopropyl)diacetylene (53% yield), also the corresponding dilactone, and specifically bi(1-methyl-4-oxo-3oxabicyclo[3.1.0]-2-hexalidene)methyl (14% yield), which is probably formed via the intramolecular cyclization of the intermediately formed bis(cis-1-methyl-2-carboxy-1-cyclopropyl) diacetylene.

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TWO PATHS FOR STABILIZATION OF INTERMEDIATE

RADICAL ARYLATION OF THIOAMIDES

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Recently, we described the radical arylation of thiomides using the phenyl radicals generated by the thermolysis of either phenylazotriphenylmethane (PAT) or N-nitrosoacetanilide (NAA) [1, 2].

The reaction of phenyl radicals with thioamides of the (I) type goes by scheme (1) to give the corresponding S-phenylisothioamides in 80-100% yields. From scheme (1) it follows that the stabilization of the intermediate radicals A leads to the formation of the isothioamide provided a relatively labile hydrogen atom is found β to the radical center on the nitrogen atom. As a result, radical arylation in the given case is localized in the fragment S = C - NH (also see [3]).

$$\begin{array}{ccc} Ar - C - NHAr \xrightarrow{Ph'} Ar' - \dot{C} - NHAr' \xrightarrow{R'} RH + Ar - C = NAr' \\ \vdots & & & \\ S & & SPh & & \\ (I) & & (A) \end{array}$$
(1)

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It is seemed of interest to study the direction of the stabilization of the intermediate radicals in those cases where labile hydrogen atoms are present in both β positions,

$$\begin{array}{c} Ph_{2}CH-C-NHPh \xrightarrow{Ph'} Ph_{2}CH-C-NHPh \xrightarrow{R} \\ \downarrow \\ S \\ (II) \end{array} \xrightarrow{I} SPh \\ (IV) \xrightarrow{Ph_{2}CH-C=NPh} \\ -RH \\ \downarrow \\ -Ph_{2}C=C-NHPh \\ (V) \xrightarrow{I} SPh \end{array}$$
(2)

i.e., where localization of the arylation is also possible in the fragment $\ S=C-CH-$.

On the example of reacting the anilide of diphenylthioacetic acid with NAA it was shown that here only one arylation product is formed in high yield. The elemental analysis and mass spectral data confirmed the empirical formula of this compound and the presence of a phenyl group on the sulfur atom, but did not permit making choice between structures (IV) and (V). This choice was made on the basis of the PMR and IR spectra.

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Besides a broad multiplet of the phenyl protons in the 6.9-7.5 ppm region, the PMR spectrum of the obtained compound had only one singlet at 5.09 ppm, whose position remained constant with change in the temperature (in the range 20-75°C), and which did not disappear after shaking the substance with D_2O , which indicates that this singlet belongs to CH, and not to the NH proton. The IR spectrum of this compound in dilute CCl_4 solution lacks absorption in the 3200-3400 cm⁻¹ region (the IR spectrum of a solution of the starting thioamide (II) has the band $\nu_{\rm NH}$ 3360 cm⁻¹), which unequivocally excludes structure (V). As a result, the arylation of thioamide (II) also leads to the formation of S-phenylisothioamide (IV). However, it is known that S-substituted iso-thioamides can exist in equilibrium with the S,N-acetals of ketenes: (IV) = (V), in which connection in the case of diphenylthioacetic acid derivatives this equilibrium is almost completely shifted toward the isothioamide form [4]. In this connection, either the initial complete or partial formation of product (V), with its subsequent rapid isomerization to (IV), can also not be excluded in the studied example.

This possibility is excluded during the arylation of the N,N-disubstituted thioamide (III). It proved that the reaction of (III) with either NAA or PAT gives diphenylketene S-phenyl N-diethyl acetal (VI) in high yield,

$$\begin{array}{ccc} Ph_2CH-C-NEt_2 \xrightarrow{Ph^{*}} Ph_2CH-C-NEt_2 \xrightarrow{R^{*}} Ph_2C=C-NEt_2 \\ \parallel & & | & \\ (III) & S & SPh & (IV) & SPh \end{array}$$
(3)

i.e., in this case the arylation is localized in the S = C - CH - CH fragment. The structure of the obtained compound was confirmed by the PMR and mass spectra. The PMR spectrum indicates the presence of three phenyl groups, in which connection, based on the mass spectral data, one phenyl group is linked to sulfur.

As a result, during the arylation of thioamides it is possible for the intermediate radicals to be stabilized by both paths, and specifically by the cleavage of a hydrogen atom from them from both the NH and the CH group (see Scheme 2).

EXPERIMENTAL

The PMR spectra were obtained on a Perkin-Elmer R-32 instrument (90 MHz) using CCl_4 as the solvent and TMS as the standard. The mass spectra were obtained on an MS-30 instrument, equipped with a DS-50 system for processing the data at a temperature of 20° for direct insertion of the sample, an ionization chamber temperature of 250°, and an ionizing voltage of 70 eV.

<u>Diphenylthioacetic Acid Diethylamide</u>. A stirred suspension of 4.5 g (17 mmoles) of diphenylacetic acid diethylamide and 1.7 g (7.6 mmoles) of P_2S_5 in 50 ml of benzene was refluxed for 5 h until solution was complete. Evaporation of the benzene gave 2.7 g (58%) of the thioamide as white crystals with mp 123–125° (from alcohol). Found: C 76.51; H 7.45; N 4.91; S 11.39%. C₁₈H₂₁NS. Calculated: C 76.28; H 7.47; N 4.95; S 11.31%.

<u>Phenylation of Diphenylthioacetic Acid Anilide (II).</u> A solution of 1.2 g (4 mmoles) of (II) [5] and 0.75 g (4.5 mmoles) of NAA in 25 ml of acetone was stirred at room temperature in an argon atmosphere for 20 h. The acetone was evaporated and the residue was chromatographed on a column packed with SiO₂ (50 g), using benzene for elution, to give 0.15 g of the starting compound and 1 g (67%) of isothioamide (IV) as light yellow crystals with mp 85-89°. Found: C 82.23; H 5.74; N 3.64; S 8.13%. C₂₆H₂₁NS. Calculated: C 82.28; H 5.58; N 3.69; S 8.45%. Mass spectrum: m/e 379 (M⁺); 270 (M⁺ - SC₆H₅).

<u>Phenylation of Diphenylthioacetic Acid Diethylamide.</u> a) Using NAA. A solution of 0.5 g (1.8 mmoles) of the thioamide and 0.33 g (2 mmoles) of NAA in 15 ml of acetone was stirred at room temperature in an argon atmosphere for 20 h. The acetone was evaporated and the residue was chromatographed on a column packed with SiO₂ (50 g), using a 9:1 heptane-alcohol mixture for elution, to give 0.5 g (79%) of diphenylketone S-phenyl N-diethyl acetal with mp 79-80° (from heptane). Found: C 79.85; H 7.30; N 4.21; S 9.15%. $C_{24}H_{25}NS$. Calculated: C 80.25; H 7.01; N 3.89; S 8.91%. PMR spectrum (δ , ppm): 0.89 t (6H), 2.87 quin (4H); 6.8-7.3 (15H). Mass spectrum: m/e 359 (M⁺, 26%); 250 (M⁺ - SC₆H₅, 100%).

b) Using PAT. A solution of 0.5 g (1.8 mmoles) of the thioamide and 1.25 g (3.6 mmoles) of PAT in 35 ml of acetone was refluxed in an argon atmosphere for 10 h. After evaporation of the acetone the reaction mixture was worked up as indicated above to give 0.47 g (75%) of product with mp 79°.

CONCLUSIONS

On the example of the radical phenylation of the N-phenyl and N,N-diethyldiphenylthioacetates it was shown that the intermediate radicals can be stabilized by the cleavage of a hydrogen atom from them from both NH and the CH group.

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