SYNTHESIS OF 2-DIETHYLAMINOTHIOCARBONYLTHIO-5,5-DIMETHYLCYCLOHEXANE-1,3-DIONE BY CLEAVAGE OF A PHENYLIODONIUM BETAINE AND PREPARATION OF A NEW TYPE OF TETRATHIAFULVALENE FROM IT

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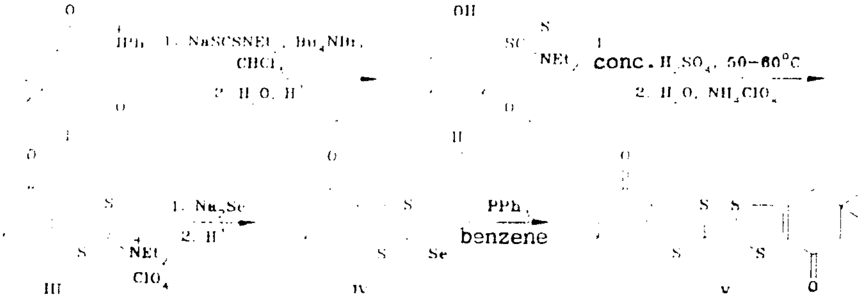
UDC 547.738'442.3

It is known that diaryliodonium salts react with dithiocarbamates to give S-aryldithiocarbamates [1]. To expand the synthetic application of phenyliodonium betaines of β-diketones [2] we studied the reaction of 2-phenyliodonia-5,5-dimethylcyclohexane-1,3-dione betaine (I) [3] with sodium diethyldithiocarbamate. It was shown that the inner iodonium salts undergo this reaction readily. The heretofore unknown derivatives of β-diketones obtained can be used for the synthesis of new 1,3-dithiole systems [4].



Betaine I reacts in chloroform in the presence of tetrabutylammonium bromide with sodium diethyldithiocarbamate at 15-20°C (12 h). Colorless **2-diethylaminothiocarbonylthio-5,5-dimethylcyclohexane-1,3-dione (II)**, with mp 142-144°C (from isopropyl alcohol), was isolated in up to 50% yield after evaporation of the chloroform, dissolving of the residue in water, and acidification. IR spectrum: 1565, 1615 (C=C, C=C); 2570 (O—H···); 2845, 2935 $\mathrm{cm^{-1}}$ (CH_2, CH_3). PMR spectrum ($CDCl_3$): 7.38 (1H, s, OH); 3.95 and 3.89 (4H, 2q, CH_2—N); 2.52 (4H, s, CH_2); 1.40 and 1.25 (6H, 2t, CH_3—C—N); 1.17 ppm (6H, s, CH_3).

Heating a solution of II in concentrated H_2SO_4 at 55-60°C for 1 h with subsequent tenfold dilution with a mixture of dry ethyl acetate and diethyl ether (1:1) and treatment of an aqueous solution of the resulting oil with ammonium perchlorate gave colorless **2-ethylimmonia-4,5,6,7-tetrahydro-6,6-dimethyl-4-oxobenzo-1,2-dithiole perchlorate (III)** with mp 165-168°C (from water). IR spectrum: 1546 (C=C); 1595 ($C=\overset{+}{N}$); 1673 (C=O); 2870, 2930 $\mathrm{cm^{-1}}$ (CH_2, CH_3). PMR spectrum ($CDCl_3$): 3.96 and 3.88 (4H, 2q, CH_2—$\overset{+}{N}$), 2.93 (2H, s, 5-CH_2), 2.52 (2H, s, 7-CH_2), 1.49 (6H, t, CH_3—C—$\overset{+}{N}$), 1.18 ppm (6H, s, CH_3). The yield was 75%.

Acidification (to pH 1-2) of perchlorate III dissolved in an aqueous solution of Na_2Se, obtained from Se and $NaBH_4$ in an argon atmosphere, gave dark-red **4,5,6,7-tetrahydro-6,6-dimethyl-4-oxobenzo-1,3-dithiole-2-selenone (IV)** with mp 116-118°C (from alcohol). IR spectrum: 1550 (C=C); 1674 (C=O); 2865, 2924, 2960 $\mathrm{cm^{-1}}$ (CH_2, CH_3). PMR spectrum ($CDCl_3$): 2.71 (2H, s, 5-CH_2), 2.40 (2H, s, 7-CH_2), 1.18 ppm (6H, s, CH_3). The yield was 65%.

Orange **bis(4,5,6,7-tetrahydro-6,6-dimethyl-4-oxobenzo)tetrathiafulvalene (V)**, with mp 270-278°C (dec., from DMF), crystallized from a solution of selenone IV and triphenylphosphine (1:2) in benzene at 15-20°C (12 h). IR spectrum: 1568 (C=C); 1658 (C=O); 2875, 2960 $\mathrm{cm^{-1}}$ (CH_2, CH_3). UV spectrum (benzene), λ_{max} ($\log\varepsilon$): 305 (4.15), 318 (4.14), 444 nm (3.58). PMR spectrum ($CDCl_3$): 2.46 and 2.33 (4H, two s, CH_2), 1.11 ppm (6H, s, CH_3). Oxidation potentials (CH_3CN): 0.7 and 1.0 V (saturated calomel electrode). The yield was 50%.

Thus we have demonstrated a method for the conversion of cyclic β-diketones to new tetrathiafulvalene derivatives that are capable of forming ion-radical salts.

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FORMATION OF PERHYDROPYRROLO[3,2-c]PYRIDINES IN THE TROFIMOV REACTION

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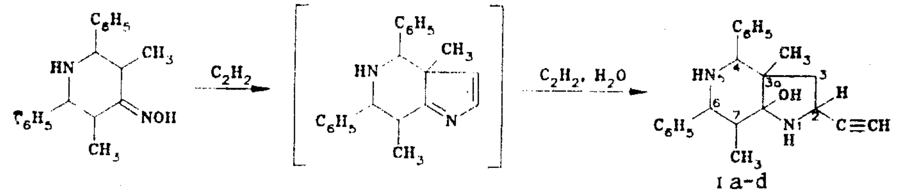
UDC 547.759.828.07.822.3

The condensation of 1,3,5-trimethyl-4-piperidinone oxime with acetylene in a superbase medium gave 2,4,5-trimethyl-1,2,3,4-tetrahydropyrrolo[1,2-c]pyrimidine, which is formed as a result of [1,3]-sigmatropic rearrangement of the primary reaction product 3*a*,5,7-trimethyl-3*a*H-4,5,6,7-tetrahydropyrrolo[3,2-c]pyridine [1].

The heterocyclization of 3,5-dimethyl-2,6-diphenyl-4-piperidinone oxime with acetylene at 80-90°C and an initial pressure of 15 atm in the presence of potassium hydroxide is accompanied by significant resinification. Chromatography of the reaction products gave three individual substances: Ia with mp 112-114°C and R_f 0.15; Ib with mp 155-157°C and R_f 0.31; Ic with mp 143-145°C and R_f 0.53 [all of the R_f values were determined with Silufol and ethyl acetate—hexane (1:3) as the eluent]. A fraction containing a mixture of Ic and Id was also isolated. Compounds Ia-d are a mixture of 3*a*,7-dimethyl-4,6-diphenyl-2-ethynyl-7*a*-hydroxyperhydropyrrolo[3,2-c]pyridine isomers; they were obtained in ~10% overall yield. Their structures were established from their ^{1}H and ^{13}C NMR spectra.



I a-d

Low-intensity molecular-ion peaks with m/z 346 (1-3%), corresponding to their empirical formulas, are observed in the mass spectra of Ia-d. Splitting out of water to give fragment ions with m/z 328 (2-4%) is characteristic for the fragmentation of the M^+ ions. The IR spectra (CCl_4) of Ib, c contain bands of vibrations of, respectively, OH and NH groups at 3610 and 3420 cm^{-1}. In addition, a band of a bonded hydroxy group at 3420 cm^{-1} is present in the spectrum of Ib.

According to the ^{13}C NMR spectra ($CDCl_3$, 100.6 MHz), the Ia and Ib pair is isomeric to the Ic and Id pair with respect to the ring fusion, which is responsible for the difference in the chemical shifts (CS) of the $C_{(7a)}$ atom: 96.83 (Ia), 96.59 (Ib), 107.06 (Ic), and 106.82 ppm (Id). In turn, the Ia and Ic and Ib and Id pairs differ with respect to the configuration of the substituents in the five-membered ring. The cross peaks from the pairs of 2-H and 3*a*-CH_3 protons with coordinates 0.91-4.68 and 0.97-4.76 for isomers Ib and Id, respectively, that are observed in the two-dimensional NOESY spectra ($CDCl_3$, 400 MHz) indicate a trans configuration of the ethynyl group attached to the $C_{(2)}$ atom and the methyl group attached to the $C_{(3a)}$ atom of the radicals. The absence of analogous cross peaks in the NOESY spectra of Ia and Ib attests to a cis configuration of the indicated substituents. The corresponding tetrahydropyrrolo[1,2-c]pyrimidine is not detected in the reaction products. Sigmatropic rearrangement of the intermediate 3H-tetrahydropyrrolopyridine is probably suppressed in the case of a large excess of acetylene. Compounds Ia-d are formed as a result of the addition of water and acetylene to the 3H-pyrrole ring.

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0009-3122/91/2706-0671$12.50 ©1991 Plenum Publishing Corporation