HETEROCYCLIC ANALOGS OF PLEIADIENE. 58.* THIOCYANOGENATION OF PERMIDONES. SYNTHESIS OF PERIMIDONE-6,7-DISULFIDES

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The thiocyanogenation of 1,3-disubstituted perimidones gives good yields of their 6(7)-monothiocyano and 6,7-dithiocyano derivatives. Alkaline hydrolysis of these derivatives leads to the formation of the corresponding disulfides. The reduction of 1,3-dimethylperimidone-6,7-disulfide is accompanied by the destruction of the disulfide bridge and may be used for the synthesis of 6,7-dialkylmercaptoperimidones.

In the search for highly conducting organic materials ("organic metals") which usually consist of radical-ion salts, greatest importance is found for the π -electron and geometrical features of the donor and acceptor, between which the electron transfer occurs. The donor, which has recently been attributed an especially important role [2], should have a low ionization potential, highly developed conjugated bond system (in order to obtain a stable radical-cation) and rather high symmetry (in order to facilitate the packing of the species forming the conducting circuits in the crystal lattice). Among the best present donors are tetrathiofulvalene and tetrathiotetracene (I), the first ionization potential of which is 6.9 eV [3]. We have previously shown that the perimidine molecule is the strongest organic π -donor. It was of interest to find even stronger π -donors which form stable radical-cations among the perimidine derivatives. In the present work, we studied the previously unreported perimidine-6,7-disulfide system (II) which is, to some extent, an analog of tetrathiotetracene (I).



IIIa, b X=O, IV X=CH₂; IIIa, IV R=CH₃, III b R=C₆H₅CH₂

An obvious pathway for the synthesis of II lies in the introduction of two mercapto groups at $C(\mathfrak{s})$ and $C(\mathfrak{r})$ of the perimidine molecule with their subsequent oxidation. It appeared possible to use 6,7-dithiocyanoperimidine as a percursor for 6,7-dimercaptoperimidine and for this purpose, we studied the thiocyanogenation of perimidines.

Unfortunately, we were unable to carry out this synthesis for perimidine itself since the action of dithiocyanogen on this compound forms a complex compound mixture, which is difficult to separate. This is not surprising since electrophilic substitution in the perimidine series occurs at both the 6(7) and 4(9) positions. In order to avoid this difficulty, we used 1,3-dialkyl derivatives of perimidone (III) and 2,3-dihydroperimidine (IV) which undergo electrophilic substitution virtually only at the para position; the chlorination reaction is the only exception [5].

*Communication 57, see ref. [1].

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Donor	λ _{max} , nm	
	long-wave- length band of the donor	charge trans- fer band
1,3-Dimethylperimidone (IIIa) 1,3-Dimethylperimidone-6,7-disulfide (VIIIa)	317 364	520 640

TABLE 1. Position of the Long-Wavelength Absorption Band for Donors IIIa and VIIIa and Their Complexes with 1,3,5-Trinitrobenzene

The action of an equimolar amount of dithiocyanogen (generated by the action of bromine on potassium thiocyanate) on IIIa and IIIb in acetic acid gives their 6(7)-monothiocyano derivatives Va and Vb in close to 90% yield. The use of two molar equivalents of dithiocyanogen gives 6,7-dithiocyano derivatives VIIa and VIIb, which may also be obtained by the thiocyanogenation of Va and Vb. The introduction of the thiocyano groups at C(6) and C(7)is indicated by IR and PMR spectroscopy (see Experimental). The treatment of these monothiocyano derivatives by water-ethanol solutions of alkali rapidly and quantitatively yields disulfides VIa and VIb, while the 6,7-dithiocyano derivatives VIIa and VIIb under the same conditions readily yield the desired 6,7-perimidone disulfides VIIIa and VIIIb.



V-VIIIa R=CH₃; b R=C₆H₅CH₂

The molecular mass of disulfides VIIIa and VIIIb determined by mass spectrometry indicates their intramolecular structure. The PMR spectra of IIIa and IIIb in the aromatic proton region consists of two symmetrical doublets related to 4(9)-H and 5(8)-H and is typical for perimidones with identical substituents at $C_{(6)}$ and $C_{(7)}$.

The thiocyanogenation of dihydroperimidine IV under the same conditions led to the formation of a very complex mixture of compounds, which could not be separated. Thus, we attempted to reduce the C=O group in disulfide VIIIa, which usually permits the facile synthesis of dihydroperimidines from perimidones [6]. However, the action of lithium aluminum hydride in hexamethylphosphorotriamide or sodium in liquid ammonia on disulfide VIIIa initially reduces the S-S bond and gives dianion IX, which does not undergo further reduction. The formation of dianion IX was confirmed by its facile conversion to 1,3-dimethyl-6,7-di-(methylthio)perimidone (X) upon the action of methyl iodide. The carbonyl group in (X) is reduced by lithium aluminum hydride, leading to the formation of 2,3-dihydroperimidine XI in 89% yield.



The electron-donor properties of 1,3-dimethylperimidone-6,7-disulfide were studied in order to compare them with the analogous properties of 1,3-dimethylperimidone [7]. For this purpose, we determined the position of the charge transfer band in the complexes of 1,3dimethylperimidone-6,7-disulfide VIIIa with 1,3,5-trinitrobenzene (Table 1). This table indicates that the introduction of a two-sulfur bridge significantly increases the donor capacity of the system.

Thus, we have synthesized a new sulfur-containing aromatic perimidine system whose physicochemical properties will be the subject of future study.

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer. The PMR spectra were taken on a Tesla spectrometer at 60 MHz with HMDS as the internal standard. The UV spectra were taken on an SF-4A spectrophotometer in chloroform. The mass spectra were taken on a Jeol JMS-01-JC-2 mass spectrometer with direct sample inlet into the ion source.

<u>1,3-Dimethyl-6(7)-thiocyanoperimidone (Va).</u> A sample of 1.25 g (12.5 mmoles) potassium thiocyanate was added to a solution of 0.53 g (2.5 mmoles) 1,3-dimethylperimidone in 40 ml glacial acetic acid at room temperature. After dissolution of the salt, a solution of 0.125 ml (2.5 mmoles) bromine in 10 ml glacial acetic acid was added dropwise. Then, the mixture was stirred for 10 min and poured into 250 ml cold water. The precipitate was filtered off, washed with water and recrystallized from ethanol to yield 0.6 g (90%) (Va) as colorless crystals with mp 178-180°C. IR spectrum (in CHCl₃): 2165 cm⁻¹ (C-SCN). PMR spectrum (in CDCl₃): 3.27 (6H, s), 6.40 (2H, m), 7.17 ppm (4H, m). Found: C, 62.2; H, 4.1; N, 15.5; S, 11.9%. Calculated for $C_{14}H_{11}N_{3}OS: C$, 62.3; H, 4.1; N, 15.6; S, 11.9%.

<u>1,3-Dimethyl-6,7-dithiocyanoperimidone (VIIa).</u> A sample of 2 g (20 mmoles) potassium thiocyanate was added to a solution of 0.53 g (2.5 mmoles) 1,3-dimethylperimidone in 40 ml glacial acetic acid at room temperature. After dissolution of the salt, a solution of 0.3 ml (6 mmoles) bromine in 20 ml glacial acetic acid was added dropwise. The mixture was stirred for 1.5 h at room temperature and poured into 250 ml cold water. The precipitate was filtered off, washed with water and recrystallized from ethanol to give 0.73 g (90%) (VIIa) as colorless crystals with mp 225°C (dec.). IR spectrum (in CHCl₃) 2165 cm⁻¹ (C-SCN). PMR spectrum (in CF₃COOH): 3.17 (6H, s), 6.60 (2H, d, J = 9 Hz), 7.75 (2H, d, J = 9 Hz). Found: C, 55.4; H, 3.4; N, 17.4; S, 19.8%. Calculated for C₁₅H₁₀N₄OS₂: C, 55.2; H, 3.1; N, 17.2; S, 19.6%.

<u>1;3-Dibenzy1-6(7)-thiocyanoperimidone (Vb)</u> was obtained by analogy to 1,3-dimethyl-6(7)-thiocyanoperimidone in 86% yield as colorless crystals with mp 200-202°C (from ethanol). IR spectrum (in CHCl₃): 2165 cm⁻¹ (C-SCN). Found: C, 74.2; H, 4.4; N, 9.6; S, 7.8%. Calculated for $C_{26}H_{19}N_{5}OS$: C, 74.1; H, 4.5; N, 9.9; S, 7.6%.

1,3-Dibenzyl-6,7-dithiocyanoperimidone (VIIb) was obtained by analogy to VIIa. The reaction time was 3 h. The product was obtained in 98% yield as colorless crystals with mp 220°C (dec., from ethanol). IR spectrum (CHCl₃): 2165 cm⁻¹ (C-SCN). Found: C, 67.6; H, 3.7; N, 12.0; S, 13.5%. Calculated for $C_{27}H_{16}N_4OS_2$: C, 67.7; H, 3.8; N, 11.7; S, 13.4%.

Bis(1,3-dimethylperimidone-6) Disulfide (VIa). A sample of 10 ml 10% NaOH in 1:1 water-ethanol was added to 0.54 g (2 mmoles) perimidone Vb and the mixture was heated at reflux for 20 min. The precipitate was filtered off, washed with water and dried to yield 0.48 g (98%) (VIa) as light yellow crystals with mp 250°C (from toluene). M 486 (mass spectroscopy). Found: C, 64.3; H, 4.6; N, 11.6; S, 12.5%. Calculated for $C_{26}H_{22}N_4O_2S_2$: C, 64.2; H, 4.5; N, 11.5; S, 13.1%.

Bis (1,3-dibenzylperimidone-6) Disulfide (VIb) was obtained by analogy to disulfide VIa in 97% yield at yellow crystals with mp 210-212°C (from toluene). Found: C, 75.8; H, 4.8; N, 7.2; S, 8.3%. Calculated for C₅₀H₃₈N₄O₂S₂: C, 75.9; H, 4.8; N, 7.1; S, 8.1%.

<u>1,3-Dimethylperimidone-6,7-disulfide (VIIIa)</u> was obtained by analogy to disulfide VIa in 98% yield as yellow-brown crystals with mp 208-210°C (from benzene). PMR spectrum (in CDCl₃): 3.40 (6H, s), 6.38 (2H, d, J = 8 Hz), 7.00 (2H, d, J = 8 Hz). M 274 (mass spectrometry). Found: C, 56.8; H, 3.7; N, 10.3; S, 23.2%. Calculated for $C_{13}H_{10}N_2OS_2$: C, 56.9; H, 3.6; N, 10.2; S, 23.4%.

1,3-Dibenzylperimidone-6,7-disulfide (VIIIb) was obtained by analogy to disulfide VIIIa in 96% yield as light brown crystals with mp 193-195°C (from benzene). Found: C, 70.3; H, 4.2; N, 6.7; S, 15.2%. Calculated for C25H18N2OS2: C, 70.4; H, 4.2; N, 6.6; S, 15.0%. 1,3-Dimethyl-6,7-di(methylthio)perimidone (X). A sample of 0.23 g (10 mmoles) metallic sodium was added in small portions to a suspension of 1.3 g (5 mmoles) 1,3-dimethylperimidone-6,7-disulfide in 100 ml liquid ammonia. After the addition of all the sodium, 1.2 ml (15 mmoles) methyl iodide was added to the reaction mixture. The mixture was instantaneously decolorized. Stirring was continued for 0.5 h. Liquid ammonia was evaporated and the dry residue in the flask was washed with water, filtered off and dried to give 0.8 g (55%) product) as almost colorless crystals with mp 139-141°C (from ethanol) which oxidize upon standing in the air. PMR spectrum (in CDCl₃): 2.40 (6H, s), 6.55 (2H, d, J = 9 Hz), 7.50 ppm (2H, d, J = 9 Hz). Found: C, 59.4; H, 5.3; N, 9.0; S, 20.9%. Calculated for $C_{15}H_{16}N_2OS_2$: C, 59.2; H, 5.3; N, 9.2; S, 21.0%

<u>1,3-Dimethyl-2,3-dihydro-6,7-di (methylthio)perimidine (XI).</u> A sample of 0.3 g (1 mmole)) perimidone X was added to a suspension of 0.12 g (3 mmoles) lithium aluminum hydride in 20 ml absolute ether heated at reflux. The mixture was stirred at reflux for 0.5 h, filtered and evaporated to yield 0.25 g (89%) product as colorless crystals with mp 105-107°C (from ethanol). PMR spectrum (in CDCl₃): 2.42 (6H, s), 2.92 (6H, s), 4.07 (2H, s), 6.53 (2H, d, J = 9Hz), 7.53 ppm (2H, d, J = 9 Hz). Found: C, 62.2; H, 6.2; N, 9.8; S, 22.0%. Calculated for C₁₅H₁₈N₂S₂: C, 62.1; H, 6.2; N, 9.7; S, 22.1%.

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