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Synthesis of (2S,3S)-3-Amino-2-phenylthietane

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Abstract: Homochiral (2S,3S)-3-amino-2-phenylthietane (**6**) was synthesized by the action of potassium O-ethyldithiocarbonate on 1,3-ditosylate (**3**) or 1,3-diiodide (**7**) derived from (1S,2S)--2-amino-1-phenyl-1,3-propanediol (**1**).

(1S,2S)-2-Amino-1-aryl-1,3-propanediols are waste products of industrial synthesis of chloramphenicol-type antibiotics. They are offered by chemical companies as highly functionalized, optically pure and cheap reagents. Several attempts at making use of these isomers, usually by transforming them into useful reagents, intermediates or building blocks for asymmetric synthesis have been reported from many laboratories. These aminodiols were exploited for the synthesis of several interesting compounds, e.g. important biogenic amines such as (S,S)-pseudoephedrine[1], (R)-phenylalaninol[2], (S)-amphetamine, heterocyclic compounds, e.g. oxazolines[4-6], β-lactams[7] etc. They have found application as chiral auxiliaries in asymmetric synthesis[8], as chelating ligands or catalysts[9-11] and also as resolving agents for optical resolution of organic acids[12,13].

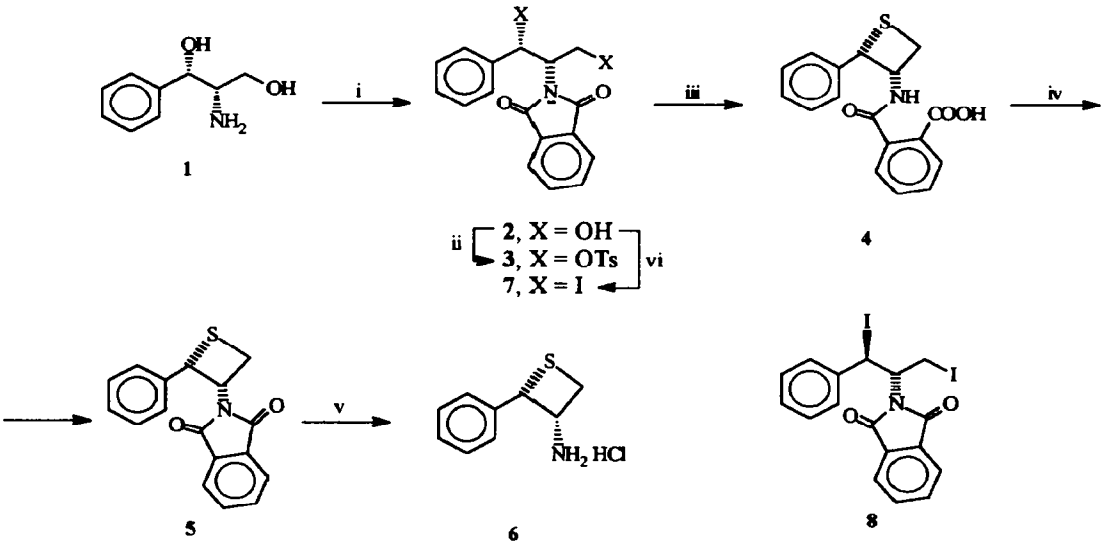
As part of our research program directed towards asymmetric synthesis of isoquinoline alkaloids[14-16] we were in need of optically active 1,3-propanedithiols for the synthesis of optically active 1,3-dithianes. We turned our attention to the possibility of employing (1S,2S)-2-amino-1phenyl-1,3-propanediol (**1**) as a suitable starting material for preparation of the corresponding dithiol.

The most convenient way of a straightforward substitution of a hydroxyl for a thiol functionality is the well known Mitsunobu reaction [17] with the use of thioacetic acid. In the case of 1,3-diols, however, it has been proven[17,18] that substitution of both hydroxyls is a rather low-yielding process. An alternative pathway involves a two-step procedure with the intermediacy of sulfonyl esters or halides. From the usually used sulfur nucleophiles such as hydrosulfide, thiocyanide, thioacetate or xanthogenate ions, the latter ones have been recommended for the synthesis of optically active thiols[19].

Thus, a synthesis starting with ditosylate **3** and diiodide **7** and potassium O-ethyldithiocarbonate was undertaken. To protect the amine function the aminodiol **1** was transformed into N-phthaloyl derivative **2**[3] which was then used as a convenient starting material (Scheme 1).

1,3-Ditosyl ester **3** (m.p. 174-176°C, $[\alpha]_D$ +38.4) was prepared in high yield from diol **2** by stirring with three molar equivalents of tosyl chloride in pyridine at room temperature for six days. ^{1}H-NMR data of diol **2** and its ditosyl ester **3** resembled each other, in particular in the splitting pattern of aliphatic protons (Table 1). The coupling constants between H-1 and H-2 (9.0 and 10.2Hz, respectively) suggested a similar configuration around C-1 and C-2 in both compounds as well as a similar conformation of their molecules.Treatment of tosylate **3** with excess of potassium O-ethyldithiocarbonate in acetone at reflux for 48h[19] provided, surprisingly, thietane **4** (m.p. 182-184°C, $[\alpha]_D$ +215.4), instead of the expected dixanthogenic ester. Thietane **4** was extracted quantitatively from the reaction mixture at pH ca 1. Its structure was elucidated

from spectral data analysis and by converting it into thietane **5** (m.p. 122.5-124°C, $[\alpha]_D$ +213.4) under the action of acetic anhydride in pyridine.



i.  ,160°C; ii. TosCl, PyH; iii. $EtOCSS^- K^+$,acetone; iv. Ac_2O, PyH; v. N_2H_4, n-butanol; vi. PPh_3 / I_2 / imidazole

Scheme 1

Having analysed spectral data of both thietanes **4** and **5** it was possible to confirm not only the presence of four-membered ring system but also to establish the relative configuration around C-2 and C-3. In CI mass spectrum of compound **4** the M+1 ion upon the loss of a water molecule gave rise to a peak at m/z 269, which corresponded to the M+1 ion of compound **5**. The leading fragmentation was common for both thietanes **4** and **5**, except that all fragment ions in spectrum of **4** were protonated. One pathway involved elimination of phthalimide molecule leading to phenylthietenyl ions at m/z 149 and 148, respectively, with the latter ion giving the base peak in spectrum of **5**. The characteristic of thietane retro-2+2 process[20] was evidenced by relatively weak peaks at m/z 123 and 122. The dominating process in spectrum of **4**, not evidenced in spectrum of **5**, was the loss of phthalic anhydride from the M+1 ion to give the base peak at m/z 166, which might correspond to aminophenylthietanyl ion.

A significant difference in ^{1}H-NMR spectra of both thietanes **4** and **5** (Table 2) was the presence of the two one-proton low-field absorptions at 9.00 and 13.0 δ in the spectrum of the former, which disappeared on treatment with D_2O. The presence of carboxylic and amide functionality was also confirmed by IR (1703 and 1650cm^{-1}) and ^{13}C-NMR (167.4 and 167.2δ) spectra. The coupling constants between H-2 and H-3 (J = 8.9 and 9.9Hz) in spectra of both compounds allowed the assumption of a dihedral angle close to 0° suggesting a *cis* relationship between C-2 and C-3. Indeed, the 2S,3S absolute configuration of compound **5** has been confirmed by CD-measurements[21].

Table 1: ^{1}H-NMR data (δ , Hz) of aliphatic protons of compounds **2,3,7,8** (in $CDCl_3$)

Compound	H-1, δ	H-2, δ	H-3, δ	H-3`, δ
2	5.23 d $J_{1,2}$= 9.0 Hz	4.61 td $J_{1,2}$= 9.0 Hz $J_{2,3}$= 10.0 Hz $J_{2,3'}$=4.0 Hz	4.09 t $J_{2,3}$=10.0 Hz $J_{3,3'}$=11.0 Hz	3.41 dd $J_{2,3'}$= 4.0 Hz $J_{3,3'}$= 11.0 Hz
3	5.86 d $J_{1,2}$=10.2Hz	4.78 td $J_{1,2}$=10.2Hz $J_{2,3}$=10.3Hz $J_{2,3'}$=3.6Hz	4.55 t $J_{2,3}$=10.4Hz $J_{3,3'}$=10.8Hz	3.62 dd $J_{2,3'}$=3.7Hz $J_{3,3'}$=10.8Hz
7	5.90 d $J_{1,2}$=11.5Hz	5.10 td $J_{1,2}$=11.5Hz $J_{2,3}$=11.7Hz $J_{2,3'}$=3.7Hz	3.76 dd $J_{2,3}$=11.7Hz $J_{3,3'}$=10.3Hz	3.13 dd $J_{2,3'}$=3.7Hz $J_{3,3'}$=10.3Hz
8	5.61 d $J_{1,2}$=11.2Hz	5.11 td $J_{1,2}$=11.2Hz $J_{2,3}$=11.8Hz $J_{2,3'}$=3.5Hz	4.02 dd $J_{2,3}$=11.8Hz $J_{3,3'}$=10.5Hz	4.43 dd $J_{2,3'}$=3.5Hz $J_{3,3'}$=10.5Hz

Table 2: ^{1}H-NMR data (δ, Hz) of aliphatic protons of compounds **4,5,6**

Compound	H-2, δ	H-3, δ	H-4, δ	H-4`, δ	Solvent
4	5.54 d $J_{2,3}$=8.9Hz	5.83 m J=8.6Hz	3.91 t J=8.7Hz	3.56 t J=8.5Hz	d_5-pyridine
5	5.83 d $J_{2,3}$=9.9Hz	5.58 dt $J_{2,3}$=9.9Hz $J_{3,4}$=9.9Hz $J_{3,4'}$=8.6H	4.17 dd $J_{3,4}$=9.9H	3.19 t $J_{3,4'}$=8.6Hz $J_{4,4'}$=7.9Hz	$CDCl_3$
6·HCl	5.13 d $J_{2,3}$=8.7	4.60 ABq J=8.7Hz	3.49 t J=8.9Hz	3.19 t J=8.7Hz	d_6-DMSO

Taking the above into consideration it seemed obvious that in the reaction of ditosylate **3** with potassium O-ethyldithiocarbonate not only the formation of the thietane ring system but also retention of configuration at C-2 have unexpectedly taken place. Since the reactions of sulfonyl esters with xanthogenate ions are known to proceed with inversion of configuration at a stereogenic carbon[19] it could be understood by assuming that the reaction was a two-step process. In the first step the xanthogenic diester accompanied by inversion of configuration at C-2 could be formed. In the second, the C-2 center could be attacked by sulfur of the primary xanthogenic substituent, or rather a sulfhydryl group, causing the ring closure and second inversion of configuration, as a result of which an overall retention could be observed. It seemed possible that a sulfhydryl ion and not the ester sulfur was the attacking species; it could have been liberated from the ester either by hydrolysis occuring during the prolonged reflux time or by thermal Tschugaeff-type decomposition.

However, attempts undertaken to isolate the intermediate xanthogenic ester were unsuccessful, even in various reaction conditions. Opening of the phthalimide ring was a side reaction. We have noticed that in alkaline solution also in other sulfur analogs of **2** the phthalimide ring tended to open spontaneously. Recyclization could be readily achieved by treatment with acetic anhydride in pyridine.

The title compound, (2S,3S)-3-amino-2-phenylthietane (**6**) was prepared from compound **5** by hydrazinolysis in boiling n-butanol. It was characterized as a hydrochloride salt (m.p. 221-224°C, dec.; $[\alpha]_D$ +121.6). Its mass fragmentation followed that of thietanes **4** and **5** giving rise to fragment ions at m/z 149 (elimination of ammonia) and 120 (retro-2+2 process). The ^{1}H-NMR spectrum (Table 2) was less complex than that of thietane **5** and similar to the spectrum of thietane **4**. The coupling constants between the aliphatic protons were practically identical (8.65 and 8.9Hz) giving rise to two triplets at 3.19 and 3.49 δ for CH_2-group, one ABquartet for H-2 at 5.58 δ and a doublet for H-1 at 5.13 δ.

The same reaction course has been taking place when the corresponding diiodide **7** was treated with potassium O-ethyldithiocarbonate under the same reaction conditions. The diiodide **7** (m.p. 194-197°C,$[\alpha]_D$ +138.1) along with isomer **8** (m.p. 136.5-139.5°C, $[\alpha]_D$ -68.2) were obtained as a 1:1 mixture from the starting diol **2** by the iodine/triphenylphosphine/imidazole method[22,23] in THF at 0°C, while in refluxing toluene compound **7** was the prevailing isomer. Of the two diasteromers the more stable isomer **7** being less soluble in alcohol could be isolated from the reaction mixture simply by crystallization of the crude product from ethanol. Diastereomer **8** turned out to be difficult to obtain in a pure state because of its instability in solution as well as during chromatographic separation. Only small samples of pure **8** were obtainable by fraction crystallization of the crude products after the first crop of compound **7** was collected. The major part of **8** was always contaminated with the isomer **7**.

The relative configuration of isomers **7** and **8** was assigned as 1S,2S and 1R,2S, respectively, on the basis of ^{1}H-NMR data (Table 1). A favorable conformation with *trans*-oriented vicinal hydrogens in both isomers could be deduced from the H-1/H-2 coupling constants[24] which were practically identical in both spectra (J = 11.5 and 11.2Hz), as was the case with compounds **2** and **3** (Table 1). The significant difference in spectrum of the 1R,2S-diiodide **8** as compared with the spectra of the other 1S,2S-isomers (**2**,**3**,**7**) was the chemical shift of the H-3` proton. In spectra of compounds with 1S,2S configuration the presence of this proton was always evidenced at higher field then its geminal H-3 partner, apparently due to a shielding effect caused by a proximate phenyl substituent. In 1R,2S isomer, however, the benzene ring being more distant could not influence the H-3` proton.

Described in this paper is a new series of transformations of the (1S,2S)-2-amino-1-phenyl-1,3-propanediol (**1**) which resulted in the synthesis of new compounds (**3**,**4**,**5**,**6**,**7**,**8**) and is another example of the possibility of practical use of the unwanted, inactive isomers formed during chloramphenicol antibiotics synthesis.

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Experimental Section:

General: Melting points: Koffler block, IR spectra: Perkin-Elmer 180 in KBr pellets, ^{1}H-NMR and ^{13}C-NMR spectra: Varian Gemini 300, TMS as internal standard. Mass spectra, chemical ionization: Finnigan 1015D.

Specific rotation: Perkin-Elmer Polarimeter 243B. Silica gel: Merck 60 70-230 mesh ASTM for column chromatography and Merck DC-Alufolien 60 F_{254} for TLC. (1S,2S)-2-amino-1-phenyl-1,3-propanediol was purchased from Merck-Schuchardt.

(1S,2S)-1-Phenyl-2-phthalimido-1,3-propanediol ditosyl ester (3): A mixture of compound **2**[3](1.48g, 5mmol) and tosyl chloride (2.85g, 15mmol) in pyridine (10ml) was stirred at room temperature for 6 days. Ethyl ether (20ml) was then added, the solid filtered off and washed several times with water, then with ethyl ether to give 2.6g (86%) of ditosyl ester **3**. M.p.174-176°C, $[\alpha]_D$ +38.4 (c=1, $CHCl_3$). IR (KBr), cm^{-1}: 1774 and 1710 (imide C=O). ^{1}H-NMR ($CDCl_3$) δ : 2.18 and 2.32 (2s, 3H each, $ArCH_3$), 3.62 (dd, $J_{2,3'}$= 3.7Hz, $J_{3,3'}$= 10.8Hz, 1H, H-3'), 4.55 (t, $J_{2,3}$= 10.4Hz, $J_{3,3'}$= 10.8Hz, 1H, H-3), 4.78 (ddd, $J_{1,2}$= 10.2Hz, $J_{2,3}$= 10.3Hz, $J_{2,3'}$= 3.6Hz, 1H, H-2), 5.86 (d, $J_{1,2}$= 10.2Hz, 1H, H-1), 8.68 7.47 (m, 13H, Ar-H), 7.73 (s, 4H, Ar-H). CI MS (NH_3) m/z (%): 623 $(M+1+17)^+$ (<1) , 434 (10), 280 (20), 262 (100), 250 (25), 190 (21), 174 (25), 140 (26), 108 (12). Found: C 61.65, H 4.27, N 2.16. $C_{31}H_{27}NO_8S_2$ req.:C 61.47, H 4.49, N 2.31.

Phthalic acid (2S,3S)-N-3(2-phenylthietanyl)monoamid (4): A mixture of tosylate **3** (1.21g, 2mmol) and potassium O-ethyldithiocarbonate (1.08g, 6.7mmol) in acetone (65ml) was heated at reflux for 2 days. The precipitate was filtered off, washed with acetone and the combined filtrates were evaporated. Water (5ml) was added to the residue and extracted with ethyl ether, then rendered acidic with 5% aqueous hydrochloric acid and extracted several times with ethyl acetate. The acetate extracts were evaporated to half of the volume and left for crystallization. In this way pure thietane **4** was obtained in 80% yield. M.p. 182-184°C, $[\alpha]_D$ +215.4 (c=1, acetone). IR (KBr) cm^{-1}: 3315 (NH), 1703 (COOH), 1650 (CONH). ^{1}H-NMR (d_5-pyridine) δ: 3.57 (t, J=8.5Hz, 1H, H-4'), 3.91 (t, J=8.7Hz,1H H-4), 5.83 (m, J=8.6Hz, 1H, H-3), 5.54 (d, $J_{2,3}$=8.9Hz, 1H, H-2), 7.20-7.57 (m, 5H, Ar-H), 7.60-7.80 (m, 4H, Ar-H), 8.17 (m, 1H, disappeares on treatment with D_2O, OH), 10.04 (d, J=8.2Hz, 1H, disappeares on treatment with D_2O, NH).^{13}C-NMR (d_6-DMSO) δ: 30.11 (CH_2), 52.94 (CH), 54.54 (CH), 127.22, 127.39, 127.45, 128.25, 129.19, 130.13, 131.25 (Ar-CH), 137.92, 140.46 (AR-C), 167.18, 167.39 (C=). CI MS (NH_3) m/z (%): 314 $(M+1)^+$ (13), 296 (8), 166 (100), 149 (10), 134 (15). Found: C 65.01, H 4.65, N 4.47. $C_{17}H_{15}NO_3S$ req.: C 65.15, H 4.82, N 4.47.

(2S,3S)-2-Phenyl-3-phthalimidothietane (5): A solution of compound **4** (0.37g, 1.18mmol), acetic anhydride (4ml) and pyridine (4,ml) was kept at room temperature for 18h. It was poured onto ice and extracted with ethyl ether. The organic extracts were washed with 5% aqueous hydrochloric acid, 15% aqueous potassium hydroxide water and dried (Na_2SO_4). The solvent was evaporated to deposit 0.33g (96%) of crude **5**, which was crystallized from 96% ethanol. M.p. 122.5-124°C, $[\alpha]_D$ +213.4 (c=1, acetone). IR (KBr) cm^{-1}: 1770 and 1710 (imide C=O), ^{1}H-NMR ($CDCl_3$) δ: 3.19 (2t, $J_{3,4'}$= 8.6Hz, $J_{4,4'}$= 7.9Hz, 1H, H-4'), 4.17 (dd, $J_{3,4}$= 9.9Hz, $J_{4,4'}$= 7.9Hz, 1H, H-4), 5.58 (2t, $J_{2,3}$= 9.9Hz, $J_{3,4}$= 9.9Hz, $J_{3,4'}$=8.6Hz, 1H, H-3), 5.83 (d, $J_{2,3}$= 9.9Hz, 1H, H-2). 7.25-7.47 (m, 5H, Ar-H), 7.70-7.83 (m, 4H, Ar-H). CI MS (NH_3) m/z (%): 296 $(M+1)^+$ (100), 148 (10), 122 (4). Found: C 69.13, H 4.44, N 4.74. $C_{17}H_{13}NO_2S$ req.: C 69.12, H 4.44, N 4.76.

(2S,3S)-3-Amino-2-phenylthietane hydrochloride (6·HCl): N-Phthaloyl derivative **5** (0.3g, 1mmol) in n-butanol (15ml) and 80% aqueous hydrazine (0.26ml) were heated at reflux for 2h. After cooling to room temperature the precipitate was filtered off and washed with n-butanol. Then 6N hydrochloric acid (0.3ml) was added and the filtrate was concentrated to half of its volume. The precipitate was filtered off and the filtrate concentrated again. It yielded a solid which after crystallization from 96% ethanol gave 0.17g (84%) of hydrochloride salt of **6**. M.p. 221-224°C,dec., $[\alpha]_D$= +121.6 (c=1, methanol). ^{1}H-NMR (d_6-DMSO) δ: 3.19 (t, J= 8.7Hz, 1H, H-4'), 3.49 (t, J= 8.9Hz, 1H, H-4), 4.60 (ABq, J=8.7Hz, 1H, H-3), 5.13 (d, $J_{2,3}$= 8.7Hz, 1H, H-2), 7.31-7.55 (m, 5H, Ar-H), 8.71 (s, broad, disappears on treatment with D_2O, 3H, NH_3^+). CI MS (NH_3) m/z (%): 166 $(M)^+$(100), 149 (20), 120 (2). Found: C 53.24, H 6.09 N 6.91. $C_9H_{11}NS$·HCl req.: C 53.59, H 6.00 N 6.94.

(1S,2S)-1,3-Diiodo-1-phenyl-2-phthalimidopropane (7): To a refluxing solution of aminodiol **2** (1.48g, 5mmol), triphenylphosphine (3.41g, 13mmol) and imidazole (1.2g, 15mmol) in toluene (30ml) iodine (3.3g, 13mmol) was added portionwise. The mixture was kept at reflux for 1h, cooled to room temperature, decanted

and the residue was washed with toluene (2x20ml). The combined organic solution was washed with sat. aqueous $Na_2S_2O_3$, then with water, dried (Na_2SO_4) and the solvent was evaporated. The oily residue was dissolved in ethyl ether (25ml) and the precipitated phosphine oxide was removed by filtration. The filtrate was concentrated and the remainder was dissolved in methanol to deposit pure, crystalline diiodide **7** (0.7g). Additional 1.02g of **7** (total yield 64%) was recovered from mother liquors by column chromatography on silica gel using carbon tetrachloride/ethyl ether (100:1). M.p. 194-197°C, $[\alpha]_D$ +138.1 (c=1, acetone). IR (KBr) cm^{-1}: 1770 and 1710 (imide C=O). ^{1}H-NMR ($CDCl_3$) δ: 3.13 (dd, $J_{2,3`}$= 3.7Hz, $J_{3,3`}$= 10.4Hz, 1H, H-3`), 3.76 (dd, $J_{2,3}$= 11.7Hz, $J_{3,3`}$= 10.4Hz, 1H, H-3), 5.1 (ddd, $J_{1,2}$= 11.5Hz, $J_{2,3}$= 11.7Hz, $J_{2,3`}$= 3.7Hz, 1H, H-2), 5.90 (d, $J_{1,2}$= 11.5Hz, 1H, H-1), 7.31-7.55 (m, 5H, Ar-H), 7.77-7.98 (m, 4H, Ar-H). CI MS (NH_3) m/z (%): 518 $(M+1)^+$(50), 390 (100), 262 (60), 116 (42). Found: C 39.44, H 2.43, N 2.78. $C_{17}H_{13}NI_2O_2$ req.: C 39.49, H 2.32, N 2.71.

(1R,2S)-1,3-Diiodo-1-phenyl-2-phthalimidopropane (8): When the above reaction was run in THF at 0°C, the crude reaction product was a 1:1 mixture of both isomers **7** and **8** as determined by TLC. An analytical sample of diiodide **8** was obtained by fraction crystallization of mother liquors left after the first crop of isomer **7** was collected. M.p. 136.5-139.5°C, $[\alpha]_D$ -68.2 (c=1, acetone). IR (KBr) cm^{-1}: 1775 and 1715 (imide C=O). ^{1}H-NMR ($CDCl_3$) δ: 4.02 (dd, $J_{2,3}$= 11.8Hz, $J_{3,3`}$= 10.5Hz, 1H, H-3), 4.43 (dd, $J_{2,3`}$= 3.5Hz, $J_{3,3`}$= 10.5Hz, 1H, H-3`), 5.11 (ddd, $J_{1,2}$= 11.2Hz, $J_{2,3}$= 11.8Hz, $J_{2,3`}$= 3.5Hz, 1H, H-2), 5.61 (d, $J_{1,2}$= 11.2Hz, 1H, H-1), 7.05-7.32 (m, 5H, Ar-H), 7.62-7.71 (m, 4H, Ar-H). CI MS (NH_3) m/z (%): 390 $(M-I)^+$ (58), 262 (100), 249 (12), 217 (58). Found: C 39.39, H 2.50, N 2.52. $C_{17}H_{13}NO_2I_2$ req.: C 39.49, H 2.32, N 2.71.

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