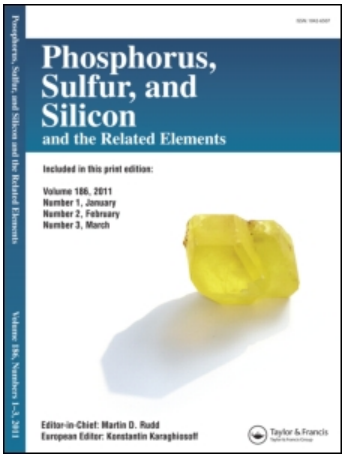

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REACTION OF 5,5-DIPHENYL-2-THIOHYDANTOIN WITH 1,4-DIBROMOBUTANE. THE CRYSTAL AND MOLECULAR STRUCTURE OF 2,3,4,5-TETRAHYDRO-7,7-DIPHENYLIMIDAZO-[2,1-b]-THIAZEPINE-8(7H)-ONE

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REACTION OF 5,5-DIPHENYL-2-THIOHYDANTOIN WITH 1,4-DIBROMOBUTANE. THE CRYSTAL AND MOLECULAR STRUCTURE OF 2,3,4,5-TETRAHYDRO-7,7-DIPHENYLIMIDAZO-[2,1-b]-THIAZEPINE-8(7H)-ONE

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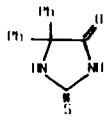
The reaction of 5,5-diphenyl-2-thiohydantoin (**1**) (DPTH) or its potassium salt (DPTH-K) with 1,4-dibromobutane gave two isomeric bicyclic products: 2,3,4,5-tetrahydro-7,7-diphenylimidazo-[2,1-b]-thiazepine-8(7H)-one (6) and 2,3,4,5-tetrahydro-8,8-diphenylimidazo-[2,1-b]-thiazepine-7(8)-one (7) in different ratios depending on the reaction conditions: [DPTH-K, EtOH, *N*-ethylpiperdine; phase transfer catalytical conditions: DPTH-K, Et_3N, benzene/water or DPTH acetone/K_2CO_3]. Compound (**6**) crystallizes in the space group $P2_1/c$ with $a = 10.4624(2)$, $b = 8.3643(1)$, $c = 18.4371(3)$ Å, $\beta = 96.3(1)°$. The 7-membered thiazepine ring in (**6**) adopts a disordered chain conformation. The discussion of some physico-chemical properties and some factors showing the influence on the yield and ratios of isomeric compounds [(**2**), (**3**)], [(**4**), (**5**)] and [(**6**), (**7**)], obtained in the alkylation of DTPH (**1**) with dibromoalkanes, has been carried out.

INTRODUCTION

In continuation of our studies[1-3] on the reactivity and structures of cyclic dialkylation products of 5,5-diphenyl-2-thiohydantoin (**1**) (DPTH) we recently reported the reaction of DPTH with 1,4-dibromobutane. It was found to give two isomeric diphenylimidazothiazepines (**6**) and (**7**), the yield and ratio of which are strongly dependent on the reaction conditions.

RESULTS AND DISCUSSION

A mixture of isomeric diphenylimidazothiazepines (**6**) and (**7**) was obtained with 43.5% yield by treatement at room temperature of the potassium salt of



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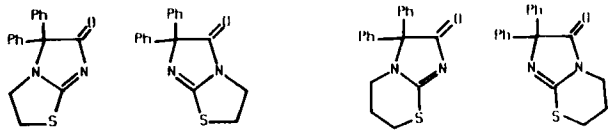

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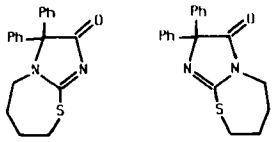


6 7

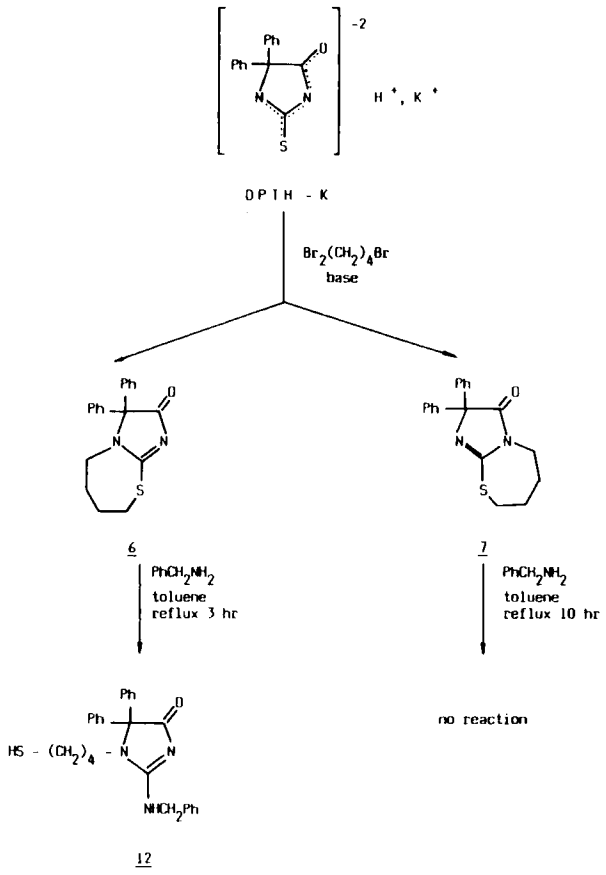
thiohydantoin (DPTH-K) with 1,4-dibromobutane in anhydrous ethanol in the presence of equimolar amount of N-ethylpiperidine. Each pure isomer (**6**) and (**7**), originally present in 1:2 ratio, was obtained after column chromatography and recrystalization from ethanol (m.p. 185–186.5° and 166–168° respectively). (Scheme 1).

A mixture of (**6**) and (**7**) was also obtained by alkylation of DPTH-K with 1,4-dibromobutane under phase transfer catalytical conditions applied by us earlier in the synthesis of isomeric dipthenylimidazothiazolones [(**2**) and (**3**)][3] and diphenylimidazothiazines [(**4**) and (**5**)][2]. Under such conditions the ratio of (**6**) and (**7**) was 1:12.1 and the total yield of both compounds was 56.3%.

Pure isomer (**7**) was obtained by alkylation of DPTH with 1,4-dibromobutane under modified phase transfer catalytical conditions[4] (acetone as the solvent and solid K_2CO_2 as the base). Under these conditions, in the crude product there were observed only traces of isomer (**6**), and pure isomer (**7**) was isolated after recrystallization from ethanol in 74% yield.

The structures of diphenylimidazothiazepines (**6**) and (**7**) were established on the basis of spectroscopic data (MS, ^{1}H NMR, ^{13}C NMR and IR) and chemical correlation (Scheme 2). The structure of (**6**) was also determined by X-ray diffraction.

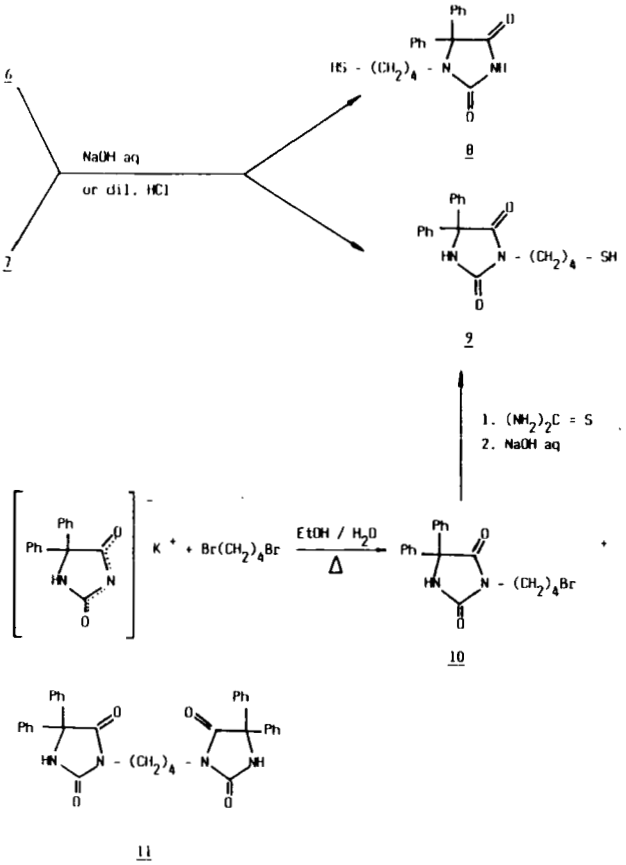
The chemical behaviour of isomeric compounds (**6**) and (**7**) toward nucleophilic reagents is analogous to that of related diphenylimidazothiazines [(**4**) and (**5**)]. Thus, isomer (**6**) is more reactive and shows a typical reactivity for the isothiourea grouping. For example, (**6**) reacts with benzylamine in refluxing toluene (3 hr) to give the corresponding 1-(4-mercaptobutyl)-2-benzylamino-5,5-diphenylhydantoin (**12**). Under the same reaction conditions, isomer (**7**) does not react even after refluxing for 10 hr. Alkaline or acid hydrolysis of isomers (**6**) and



SCHEME 1

(**7**) gave icomeric 4-mercaptobutyl-5,5-diphenyl derivatives of hydantoin [compounds (**8**) and (**9**)]. In order to get conclusive evidence for the proposed structure, compound (**9**) was prepared by a different procedure (Scheme 2). Thus, 5,5-diphenylhydantoin was reacted with 1,4-dibromobutane to give 3-(4-bromobutyl)-5,5-diphenyl-hydantoin (**10**) and a byproduct [compound (**11**)]. The bromo-derivative (**10**) was reacted with thiourea and the isothiouronium salt (**10a**) formed was hydrolyzed under alkaline conditions to give the desired compound (**9**). It should be noted that spectroscopic properties of (**9**) obtained in the way described above were identical with the respective product formed by hydrolysis of (7).

The influence of reaction conditions on the total yield and ratios of isomeric products obtained in the alkylation of DPTH with dibromoalkanes is shown in Table I. In all three cases, the highest total yields were observed for reactions performed under phase transfer catalytical conditions. The ratios of isomeric products of 1,2-dialkylation [compounds (**2**), (**4**) and (**6**)] and 2,3-dialkylation [compounds (**3**), (**5**) and (**7**)] are also determined by the reaction conditions. Thus, aprotic solvent (PTC-conditions) and low concentration of a base (NEt_3,



SCHEME 2

TABLE I

The influence of reaction conditions on the total yield and ratios of isomeric products [(**2**) and (**3**), (**4**) and (**5**), (**6**) and (**7**)] obtained in the alkylation reaction of 5,5-diphenyl-2-thiohydantoin with dibromoalkanes

	Protic solvent			Aprotic solvent PTC: liquid–liquid			Aprotic solvent PTC: liquid–solid			DME		
No.	Yield %	Total yield %	Ratio	Yield %	Total yield %	Ratio	Yield %	Total yield %	Ratio	Yield %	Total yield %	Ratio
2	65	74.5	6.8:1	62	81.3	3.2:1	43	91.5	1:1.1			
3	9.5			19.3			48.5					
4	30.2	61.5	1:1	34.2	98	1:1.9	16	91	1:4.7	45.8	71.8	1.8:1
5	31.3			63.8			75			26		
6	14.3	43.7	1:2.1	4.3	56.3	1:12	—	74	1:74			
7	29.4			52			74					

TABLE II

The comparison of physico-chemical properties of compounds (**2**)–(**7**).

	Products of 1,2-alkylation			Products of 2,3-alkylation		
	2	4	6	3	5	7
IR [cm^{-1}]						
$\rangle C{=}O$	1710	1685	1685	1715	1720	1720
$\rangle C{=}N-$	1480	1490	1475	1590	1560	1555
^{13}C NMR [ppm]						
$\Delta\delta\ \rangle C{=}O$ and $\rangle C{=}N-$	0.13	6.6	2.47	9.04	23.64	17.62
MS [70 eV, m/e]						
M—HCO·(rel. int.)	44	0	8	100	51	13
R_f						
$CHCl_3$: AcOEt = 1 : 1	0.45	0.18	0.31	0.77	0.64	0.76

K_2CO_3) favour the 2,3-dialkylation reaction. Generally, the mutual ratio of isomeric bicyclic products is a result of steric hindrance connected with the size of hydrogenerated ring in such order: thiazole, thiazine and thiazepine derivatives. Due to conjugation of the $\rangle C{=}N-$ and $\rangle C{=}O$ bonds,[3] and 1,2-dialkylation products are thermodynamically more stable. For instance, for derivatives with small thiazole ring isomer (**2**) is predominant. The increasing of steric hidrance, connected with introduction of greater rings (thiazine and especially thiazepine derivatives) leads to rapid growthing of the participation of 2,3-dialkylation products. The comparison of some X-ray data of compounds (**2**), (**4**) and (**6**) confirms the increase of steric crowd in derivatives with thiazine and thiazepine rings. Thus, the angle C(4)–N(2)–C(3) is the biggest one in (**2**) and equal to 131.6(3)°. The value of this angle is decreasing in (4) and (6) to 123.8(2)° and 123.6(1)°, respectively. Also the dihedral angle between both phenyl rings is decreasing from 79.4(4)° in (2) to 69.0(4)° in (4) and 67.5(4)° in (**6**).

The physico-chemical data collected in Table II enable to distinguish easily which isomer is taken into consideration. Thus, the products of 1,2-dialkylation and 2,3-dialkylation show certain general differences in IR, ^{13}C NMR and mass spectra. It was observed that in IR spectra the absorption of the conjugated $\rangle C{=}N-$ and $\rangle C{=}O$ bonds in compounds (**2**), (**4**) and (**6**) occurs at lower frequency (1475–1490 cm^{-1} and 1685–1710 cm^{-1}) than that for separated bonds in compounds (**3**), (**5**) and (**7**) (1555–1590 cm^{-1} and 1715–1720 cm^{-1}). The conjugation of $\rangle C{=}N-$ and $\rangle C{=}O$ bonds shows also an influence on the value of the chemical shift of carbon atoms from these groups in ^{13}C NMR. Generally, for compounds (**2**), (**4**) and (**6**) there were observed smaller differences betwen the values of chemical shift ($\Delta\delta$) of these carbon atoms ($\Delta\delta$ = 0.13–6.60 ppm), than for compounds (**3**), (**5**) and (**7**) ($\Delta\delta$ = 9.04–23.64 ppm). In mass spectra and peaks formed by loss of HCO· (M-29) possess a dignostic value and they are generally more intensive in compounds (**3**), (**5**) and (**7**).

A thin layer chromatography offers also a simple method for distinguishing these isomers, since in the chloroform: ethyl acetate (1 : 1) developing system for

TABLE III

Bond lengths (Å) with E.S.D.'s in parentheses

S	C1	1.740(2)	C6	C7	1.502(4)
S	C7	1.822(3)	C11	C12	1.385(3)
O1	C2	1.219(3)	C11	C16	1.388(3)
N2	C1	1.337(3)	C12	C13	1.381(3)
N2	C3	1.477(3)	C13	C14	1.380(3)
N2	C4	1.464(3)	C14	C15	1.373(3)
N1	C1	1.328(3)	C15	C16	1.385(3)
N1	C2	1.378(3)	C21	C22	1.396(3)
C2	C3	1.554(3)	C21	C26	1.396(3)
C3	C11	1.524(3)	C22	C23	1.385(4)
C3	C21	1.524(3)	C23	C24	1.379(4)
C4	C5	1.512(3)	C24	C25	1.384(3)
C5	C6	1.520(3)	C25	C26	1.383(3)

compounds (**3**), (**5**) and (**7**) it shows a significantly greater R_f values (0.64–0.76) than for compounds (**2**), (**4**) and (**6**).

Crystal and Molecular Structure of 2,3,4,5-tetrahydro-7,7-diphenylimidazo-[2,1-b]-thiazepine-8(7H)-one (**6**)

The results of X-ray analysis of (**6**) in the form of bond lengths and angles are given in Tables III and IV. The view of the molecule is presented on Figure 1, together with the atom numbering system.

The analysis of the thermal vibration of the molecule (**6**) was carried out in the TLS approximation of rigid-body motion.[6] Bond lengths corrected for libration do not differ significantly from the uncorrected values (the deviation does not exceed the corresponding e.s.d's). Nevertheless, only uncorrected values will be used in the following discussion.

TABLE IV

Bond angles (deg) with E.S.D.'s in parentheses

C1	S	C7	102.4(1)	C5	C6	C7	114.5(2)
C1	N2	C3	108.3(1)	S	C7	C6	118.0(2)
C1	N2	C4	127.2(2)	C3	C11	C12	120.4(2)
C3	N2	C4	123.6(1)	C3	C11	C16	120.7(2)
C1	N1	C2	105.8(2)	C12	C11	C16	118.8(2)
S	C1	N2	122.6(1)	C11	C12	C13	120.5(2)
S	C1	N1	120.7(2)	C12	C13	C14	120.5(2)
N2	C1	N1	116.7(2)	C13	C14	C15	119.3(2)
O1	C2	N1	126.0(2)	C14	C15	C16	120.6(2)
O1	C2	C3	123.8(2)	C11	C16	C15	120.3(2)
N1	C2	C3	110.1(2)	C3	C21	C22	120.5(2)
N2	C3	C2	99.2(1)	C3	C21	C26	121.1(2)
N2	C3	C11	111.8(2)	C22	C21	C26	118.3(2)
N2	C3	C21	108.4(1)	C21	C22	C23	120.3(2)
C2	C3	C11	108.3(2)	C22	C23	C24	120.8(2)
C2	C3	C21	112.4(2)	C23	C24	C25	119.6(2)
C11	C3	C21	115.6(2)	C24	C25	C26	120.1(2)
N2	C4	C5	115.1(2)	C21	C26	C25	121.0(2)
C4	C5	C6	113.1(2)				

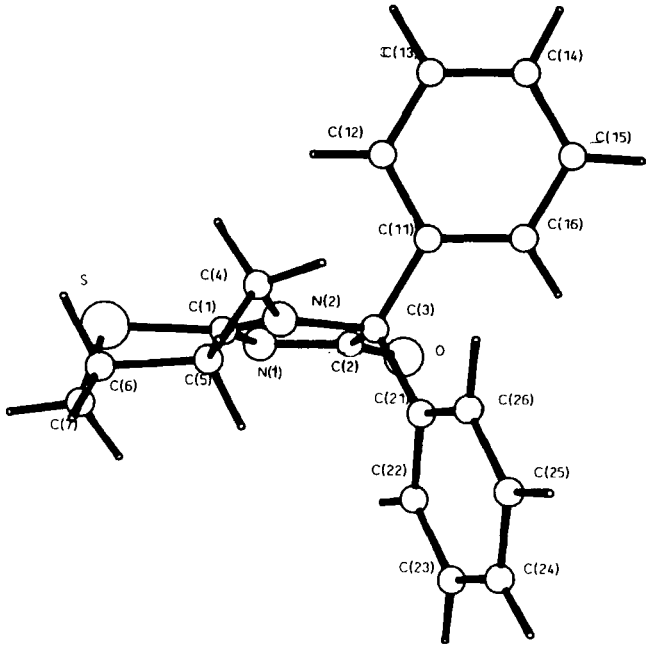


FIGURE 1

The molecule of (**6**) can be described in terms of four rings: two heterocyclic rings and two phenyl rings. The five-membered hydantoin ring is planar with each atom deviating less than 0.006(2) Å from the best plane passing through the atoms N(1), N(2), C(1), C(2) and C(3). The atom C(4) from thiazepine ring, bonded to N(2), is 0.235(3) Å out of this plane. The seven-membered thiazepine ring has a slightly disordered chair conformation[7] with the symmetry plane passing through C(6) atom and bisecting N(2)–C(1) bond. Both benzene rings are inclined to each other at 67.5(4)°. The bond lengths in molecule (**6**) were found to be very close to the corresponding values in other compounds from this series.[1-3] All intramolecular distances are longer than the sum of van der Waals radii.

EXPERIMENTAL

M.ps were determined on Boetius hot stage microscope and were uncorrected. IR-spectra: Specord 71 IR (KBr discs). ^{13}C and ^{1}H NMR: Bruker HX 90 (90 MHz, TMS as int. stand., $CDCl_3$ as solvent). Mass spectra: GCMS 2091 LKB. Tlc: silicagel GF_{254} precoated tlc plates; column chromatography: silica gel (70-230 mesh).

2,3,4,5-tetrahydro-7,7-diphenylimidazo-[2,1-b]-thiazepine-8(7H)-one (**6**) *and 2,3,4,5-tetrahydro-8,8-diphenylimidazo-[2,1-b]-thiazepine-7(8H)-one* (**7**).

A. Reaction of DPTH-K with 1,4-dibromobutane in ethanol. To DPTH-K (3.06 g, 0.01 mol) dissolved on warming in ethanol (40 ml), after cooling, the solutions of 1.13 g (0.01 mol) of N-ethylpiperidine in ethanol (10 ml) and 2.15 g (0.01 mol) of 1,4-dibromobutane in ethanol (10 ml) were added. The mixture was left in a dark place for a week at r. temp. The precipitated solid was filtered off and washed with $CHCl_3$. $CHCl_3$ was evaporated and the residue recrystallized from ethanol

to give 0.95 g (29.1%) of (**7**), m.p. = 166–168°C; R_f – 0.76; IR [cm^{-1}]: 1720, 1555, 1440, 1380, 1310, 1180, 1140, 940, 690. ^{1}H-NMR [ppm]: δ_{CH_2} = 1.78(m) and 2.11(m); δ_{SCH_2} = 2.95(deg. t.); δ_{NCH_2} = 3.79(deg. t.); $\delta_{C_6H_5}$ = 7.18–7.62(m). ^{13}C NMR [ppm]; $\delta_{CH_2CH_2}$ = 28.41 and 30.88; δ_{SCH_2} = 32.05; δ_{NCH_2} = 40.89; δ_{Ph_2C} = 79.82; $\delta_{\text{aromatic carbons}}$ = 126.95, 127.60, 128.32, 139.89; $\delta_{C=O}$ = 162.44; $\delta_{C=N}$ = 180.06. MS (70 eV, m/e): 322(100), 293(13), 224(51), 207(57), 190(23), 180(20), 165(47), 104(22), 84(19), 77(26), 55(22). Anal. calc. for $C_{19}H_{18}N_2OS$: C = 70.78; H = 5.61; N = 8.68. Found: C = 70.55; H = 5.50; N = 8.72.

The ethanol filtrate was evaporated to dryness and compound (**6**) was isolated from the residue by column chromatography using chloroform: ethyl acetate (1 : 1) as an eluent. Recrystallisation of the crude isomer (**6**) from ethanol afforded pure (**6**) –0.46 g (14.3%), m.p. = 185–186.5°C; R_f – 0.31 IR [cm^{-1}]: 1685, 1475, 1410, 1380, 1200, 1150, 945, 750, 695 ^{1}H NMR [ppm]: δ_{CH_2} = 1.62(m) and 2.03(m), δ_{SCH_2} = 3.07(deg. t.), δ_{NCH_2} = 3.51(deg. t.), $\delta_{C_6H_5}$ = 7.29(m) ^{13}C NMR [ppm]: $\delta_{CH_2CH_2}$ = 26.59 and 28.09; δ_{SCH_2} = 30.55, δ_{NCH_2} = 45.37; δ_{Ph_2C} = 81.06; $\delta_{\text{aromatic carbons}}$ = 128.12, 128.64, 128.83, 137.16; $\delta_{C=O \text{ and } C=N}$ = 185.46 and 187.93. MS (70 eV, m/e): 322(100), 293(8), 289(20), 254(19), 234(67), 206(27), 194(19), 165(75), 103(44), 87(22), 77(26), 55(15). Anal. calc. for $C_{19}H_{18}N_2OS$: C = 70.78; H = 5.61; N = 8.68. Found: C = 70.50; H = 5.44; N = 8.52.

B. Reaction of DPTH-K with 1,4-dibromobutane under liquid–liquid PTC. A solution of 1,4-dibromobutane (1.07 g, 0.005 mol), triethyl-amine (0.505 g, 0.005 mol) and hexadecyltributyl-phosphonium bromide (0.126 g, 2.5×10^{-4} mol) in benzene (25 ml) was added to the solution of DPTH-K (1.53 g, 0.005 mol) in water (25 ml). The mixture was stirred in covered flask for 2 days. The precipitate (0.05 g) was filtered off; the benzene layer was evaporated to dryness and the residue was column chromatographed using the mixture of chloroform and ethyl acetate (1 : 1) as an eluent. The collected fraction 2–12 (25 ml) were evaporated, and the residue was washed with chloroform. The crude compound (**7**) obtained after removing chloroform under vaccuo was crystallized from ethanol to give 0.83 g (52%) of analytically pure (**7**). From fractions 24–39, after evaporation of a solvent and recrystallization of the residue from ethanol, 0.07 g (4.4%) of pure compound (**6**) was obtained.

C. Reaction of DPTH with 1,4-dibromobutane under liquid–liquid PTC. To stirred suspension of DPTH (2.68 g, 0.01 mol), K_2CO_3 (4 g) and triethylbenzylammonium chloride (0 3 g, 0.001 mol) in acetone (50 ml), the solution of 1.4-dibromobutane (2.58 g, 0.012 mol) in acetone (10 ml) was added dropwise. The mixture was stirred at r. temp. for two days. Tlc analysis of the reaction mixture showed 3 spots—compound (**7**) as the main product and traces of compound (**6**) and starting DPTH. The precipitate was removed and next washed several times with water. The acetone solution was evaporated to 30–40% of the starting volume and refrigerated. The combined solids: that which was not soluble in water and that obtained from acetone were recrystallized from ethanol to give 2.48 g (74%) of analytically pure (**7**). The previously tlc observed spot of (**6**) disappeared during the work up of the crude reaction mixture.

The same reaction conditions were used for the alkylation of DPTH with dibromoethane and dibromopropane.

In the first case the acetone filtrate obtained after removal of solid was evaporated and from the residue compounds (**2**) and (**3**) were separated by method described by Driscoll *et al.*[5] with 45% and 48.5% yields respectively.

In the second case the precipitate was filtered off, washed several times with water and recrystallized from ethanol to give 1.86 g (61%) of compound (**5**). The filtrate was evaporated to dryness and the residue was column chromatographed using the mixture of chloroform: ethyl acetate (1 : 1) as a eluent. Compound (**5**) was separated as a first fraction (0.45 g, i.e. additional 14%) and as a second fraction 0.52 g (16%) of compounds (**4**) was obtained.

3-(4-bromobutul)-5,5-diphenylhydantoin (**10**). A boiling solution of DPTH-K (2.74 g, 0.01 mol) in 10 ml of water was treated dropwise with solution of 1,4-dibromobutane (3.22 g, 0.015 mol) in 20 ml of ethanol. The mixture was refluxed for the next 4 hrs. The formed precipitate was hot filtered, washed with water, 2% NH_3aq and 2% NaOHaq solutions and recrystallized from DMF to give 0.88 g (15.8%) of (**11**). m.p. = 312–315°C; IR [cm^{-1}]: 3230, 1755, 1685, 1445, 1415, 1380, 1350, 1100, 755, 730, 690. Anal. calc. for $C_{34}H_{30}N_4O_4$: C = 73.11; H = 5.41; N = 10.03. Found: C = 73.25; H = 5.43; N = 9.85.

From the water-ethanolic filtrate crystallized crude compound (**10**). One recrystallization from 80% ethanol afforded analytically pure (**10**)—2.32 g (59.9%). m.p. = 112–115°C R_f – 0.79. IR [cm^{-1}]; 3240, 1760, 1700, 1440, 1415, 1333, 725, 690. Anal. calc. for $C_{19}H_{19}N_2O_2Br$: C = 58.92; H = 4.96; N = 7.23. Found: C = 59.15; H = 5.00; N = 7.05.

3-(4-mercaptobutyl)-5,5-diphenylthydantoin (**9**). *A.* A suspension of (10) (3.87 g, 0.01 mol) and thiourea (0.76 g, 0.01 mol) in ethanol (20 ml) was refluxed for 7 hrs. Removal of the solvent in vaccuo

gave white solid to which the solution of NaOH (1.0 g, 0.025 mol) in 30 ml of water was added. The suspension was refluxed for 2 hrs, next the reaction mixture was filtered and acidified with dil. H_2SO_4. The obtained solid was recrystallized from ethanol to give 2.5 g (73.5%) of pure (**9**). m.p. = 136–138°C; R_f – 0.81. IR [cm^{-1}]: 3100 broad, 1750, 1700, 1440, 1410, 1365, 1325, 1125, 860, 760, 690. MS (70 eV; m/e): 340(37), 307(100), 253(9), 208(28), 180(94), 165(26), 104(54), 77(31). Anal. calc. for $C_{19}H_{20}N_2O_2S$: C = 67.02; H = 5.93; N = 8.22. Found: C = 66.96; H = 6.03; N = 7.98.

B. A suspension of (7) (0.322 g, 0.001 mol) in 5% HClaq (20 ml) was refluxed for 3.5 hrs. The product was crystallized from ethanol to give 0.205 g (60%) of (9). The IR, MS, and tlc properties were identical with those for the material obtained as described in method A.

C. A suspension of (**7**) (0.322 g, 0.001 mol) in 2% NaOHaq (20 ml) was refluxed for 7 hrs (until the solid was dissolved). The reaction mixture was filtered and acidified with dil. H_2SO_4. The resulting solid was filtered, washed with water and recrystallized from ethanol to give 0.22 g (65%) of (9) with the same properties as described above in method A.

1-(4-mercaptobutyl)-5,5-diphenylhydantion (**8**). *A.* A suspension of (7) (0.322 g, 0.001 mol) in 5% HClaq (20 ml) was refluxed for 6 hrs. The product was crystallized from ethanol to give 0.211 g (62)% of (**8**). m.p. = 110–112°C; R_f – 0.76 IR [cm^{-1}]: 3190, 3110, 1750, 1715, 1450, 1410, 1265, 755, 690 MS (70 eV, m/e): 340(6), 307(10), 267(12), 254(100), 222(13), 208(37), 195(13), 194(86), 165(30), 104(21), 91(76), 87(58) Anal. calc. for $C_{19}H_{20}N_2O_2S$: C = 67.02; H = 5.93; N = 8.22. Found: C = 66.72; H = 6.09; N = 7.96.

B. A suspension of (**6**) (0.322 g, 0.001 mol) in 2% NaOHaq (20 ml) was refluxed until the solid was dissolved (ca. 2 hrs). The precipitate obtained after acidification with dil. H_2SO_4, was recrystallized from ethanol to give 0.187 g (55%) of (8). The IR, MS and tlc properties were identical with those for the material obtained as described in method A.

1-(4-mercaptobutyl)-2-benzylamino-5,5-diphenylhydantion (**12**). A suspension of (6) (0.322 g, 0.001 mol) and benzylamine (0.214 g, 0.002 mol) in toluene (15 ml) was refluxed for 3 hrs. The solvent was removed and the residue was recrystallized from ethanol to give 0.241 g (56%) of (12). m.p. = 124–126°C; R_f – 0.41. IR [cm^{-1}]: 3220 broad, 1680, 1595, 1580, 1495, 1265, 1185, 690 MS (70 eV, m/e): 430(100), 397(28), 343(11), 341(43), 262(17), 194(18), 167(8), 91(9) Anal. calc. for $C_{26}H_{27}N_3OS$: C = 72.69; H = 6.33; N = 9.78. Found: C = 72.98; H = 6.25; N = 9.51.

X-Ray analysis of (**6**) *and* (**7**). Colorless crystals of (**6**) and (**7**) were grown by slow evaporation from 1:1 mixture of chloroform and ethyl acetate. The crystals of (**7**) were unsuitable for intensity measurements. The preliminary photographs showed additional reflections due to some randomly distributed crystalline satellites. Therefore, only the X-ray analysis for (**6**) was carried out.

Crystal data for (**6**). $C_{19}H_{18}N_2OS$; $M = 322.42$; F(000) = 680, monoclinic; $a = 10.4624(2)$, $b = 8.3643(10)$, $c = 18.4371(3)$ Å, $\beta = 96.3(1)$; $V = 1603.7$ Å^3; space group $P2_1/c$; $Z = 4$; $d_x = 1.335$ g · cm^{-3}; μ(Cu—Kα) = 17.22 cm^{-1}; $T = 293$ K, $R = 0.0414$ for 2792 reflections.

Crystal of (**6**) used in analysis was cut from long needles dimensions 0.3 × 0.4 × 0.6 mm. The preliminary investigations were carried out with Cu–Kα radiation on the de Jong–Bouman camera. The accurate cell dimensions were derived by least-squares calculation from angular setting of reflections during diffractometric experiment. The intensity data were collected on a CAD-4 diffractometer using Cu–Kα radiation on the $\omega - 2\theta$ scan mode. During the experiment, 3059 reflections ($2\Theta_{max} < 152°$) were measured in the range of indexes h:0–13; k:0–10; l:–23–23 (space group $P2_1/c$). The reflections (–304) and (313) were used as standard reflections and during the experiment no intensity variations for them were observed. A Lorentz-polarization correction but no absorption were applied. From the 3059 reflections measured, according to the criterion $F_0 > 5\sigma(F_0)$, 2792 were assumed to be observed and applied for further calculations.

The structure was solved by direct methods. The initial coordinates for 11 non-H atoms were obtained from the *E*-map calculated on the bases of phases developed by black-box method for centrosymmetric structures (SHEL-X-76). The first difference syntheses gave the position of other non-hydrogen atoms. Then, the structure was refined using *F*'s by standard full-matrix least-squares method and difference electron density syntheses. All H-atoms were located from ΔF-map on the stage of anisotropic refinement for non-H atoms. The temperature factors for H-atoms were kept 1.5 of isotropic temperature factor for parent-carbon atoms, while the position of such atoms were refined. Final $R = 0.0414$ was calculated ($R_w = 0.0443$ with $1/\sigma^2$ weights for observed reflections). The empirical correction for secondary extinction was applied with $g = 0.01479$. Max $\Delta/\sigma = 0.071$ was calculated for H-atom.

Scattering factors were taken from International Tables for X-ray Crystallography (1974). The calculations were performed using programmes written by G. Sheldrick SHEL-X-76 (1976) on ODRA-1350 computer and IBM-PC-AT.

TABLE V

Non-hydrogen fractional atomic coordinates, equivalent temperature factors (A**2) with E.S.D.'s in parentheses, coordinates and thermal factors rounded off to "DCMLS" decimals respectively

Atom	X/A	Y/B	Z/C	Ueq	DCMLS
S	108(1)	5315(1)	3928(0)	55(0)	4.3
O1	1613(2)	449(2)	2754(1)	55(0)	4.3
N2	1993(1)	4536(2)	3097(1)	37(0)	4.3
N1	677(2)	2504(2)	3351(1)	49(0)	4.3
C1	989(2)	4039(2)	3427(1)	42(0)	4.3
C2	1555(2)	1849(2)	2931(1)	43(0)	4.3
C3	2514(2)	3151(2)	2729(1)	37(0)	4.3
C4	2391(2)	6189(2)	2989(1)	42(0)	4.3
C5	3051(2)	7002(3)	3661(1)	51(0)	4.3
C6	2116(2)	7628(3)	4169(1)	56(1)	4.3
C7	1364(3)	6354(3)	4509(1)	58(1)	4.3
V11	2360(2)	3346(2)	1902(1)	37(0)	4.3
C12	1371(2)	4269(2)	1561(1)	45(0)	4.3
C13	1172(2)	4354(3)	809(1)	53(1)	4.3
C14	1943(2)	3503(3)	386(1)	58(1)	4.3
C15	2920(2)	2577(3)	720(1)	55(1)	4.3
C16	3138(2)	2501(2)	1474(1)	45(0)	4.3
C21	3880(2)	2842(2)	3078(1)	40(0)	4.3
C22	4109(2)	1786(3)	3664(1)	52(1)	4.3
C23	5340(2)	1600(3)	4015(1)	66(1)	4.3
C24	6358(2)	2446(3)	3791(1)	63(1)	4.3
C25	6147(2)	3485(3)	3206(1)	54(1)	4.3
C26	4921(2)	3679(2)	2853(1)	46(0)	4.3

Final positional and equivalent isotropic thermal parameters are given in Table V. List of structure factors, anisotropic thermal parameters, H-atom parameters have been deposited.[8]

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