the excess reagent was removed, and a precipitate (in 50-90% yield) with mp 85-90°C, which was identified as alcohol VI ($\nu_{C=C}$ 1620 cm^{-1}) was isolated.

In conclusion, we sincerely thank A. A. Musina for her assistance in the interpretation of the PMR spectra.

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FORMATION OF SPIRO-SUBSTITUTED 1,3-DITHIOLANES AND THIIRANES IN THE REACTION OF 3-AMINOINDENE-1-THIONES WITH ALIPHATIC DIAZO COMPOUNDS*

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3-Aminoindene-1-thiones react readily with diazomethane to give the corresponding 4,4;5,5-dispiro-substituted 1,3-dithiolanes. The production of both 2,2-spiro-substituted thiiranes and products of desulfuration of the latter is possible in the reaction of 3-aminoindene-1-thiones with substituted diazomethanes. The thermolysis, hydrolysis, and salt-forming reactions of the compounds obtained were investigated.

The reactions of thiocarbonyl compounds with diazoalkanes have been investigated in greatest detail in the case of thioketones [2-9]: thiadiazoles [2, 3], dithiolanes [4-6], thiiranes [4, 7], and other sulfur compounds [8, 9] were obtained. It is assumed that the direction of the reaction does not depend on the reagent ratio but is determined by the specific structures of the thioketone and the diazo compound and the reaction conditions [4]. No data on the cycloaddition of diazoalkanes to the C=S bond of thioamides are available, but individual representatives of thioamides are capable of methylation by diazomethane at the sulfur atom [10]. The reactions of vinylogs of thioamides with diazoalkanes have not been studied.

3-Aminoindene-1-thiones (I) react with diazomethane in ether, benzene, or acetone at −60 to 20°C to give 4,4;5,5-dispiroindene-substituted 1,3-dithiolanes (II) in high yields. The PMR (Table 1) and IR spectra (see the experimental section) confirm the structure of dithiolanes II. The protons of the $-S-CH_2-S-$ group resonate in the form of a singlet, which indicates their equivalence and, consequently, the trans orientation of the indene rings. The described reactions of unsymmetrically substituted thiocarbonyl compounds with diazomethane lead to a mixture of dithiolanes with cis and trans orientations of the substituents [5, 8]. The stereoselectivity of the I→II transformation is evidently due to steric hindrance that develops in the case of cis orientation of the indene rings in the transition state. A complex multiplet is observed instead of the usual triplet signal for the protons of the $-CH_2NCH_2-$ fragment of the piperidine ring in the PMR spectra of IIe,h. This is due to restrained

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*Communication VIII from the series "α, β-Unsubstituted Thio Compounds." See [1] for communication VII.

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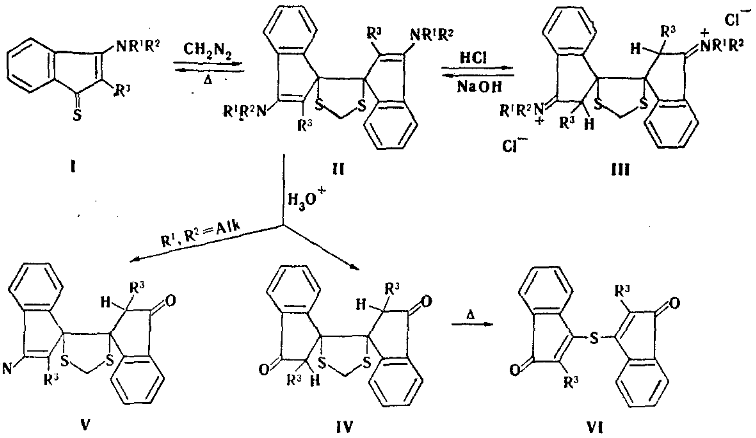
TABLE 1. Parameters of the PMR Spectra of Dithiolanes II

Compound	Solvent	τ, ppm		
		$-S-CH_2-S-$	R^1R^2	Ar
IIa	$CDCl_3$	5,59 (c)	6,51 (c)	2,23—3,70 (m)
IIc	$CDCl_3$	5,65 (c)	7,59 (c)	2,18—3,93 (m)
IId	CCl_4	5,68 (c)	7,31 (q), 9,13 (t)	2,33—3,82 (m)
IIe	CCl_4	5,70 (c)	7,44 (m), 8,59 (m)	2,20—3,95 (m)
IIh	$CDCl_3$	5,67 (c)	7,38 (m), 8,60 (m)	2,25—4,08 (m), 6,31 (s)

rotation about the $=\underset{|}{C}-N\langle$ bond. The above-noted manifestations of the steric factors are confirmed by modeling of the II molecules and will be the subject of a separate communication.

Under the influence of light, solutions of dithiolanes II in aprotic solvents rapidly turn dark green but do not give ESR signals. When methanol or hexane is added, the green solutions are decolorized, and dithiolanes II crystallize without any changes. Under the prolonged action of light, solutions of dithiolanes II turn red because of the formation of a complex mixture of photolysis products.



$I-III$ a $R^1=R^2=H$, $R^3=C_6H_5$; b $R^1=H$, $R^2=R^3=C_6H_5$; c $R^1=R^2=CH_3$, $R^3=C_6H_5$; d $R^1=R^2=C_2H_5$, $R^3=C_6H_5$; e $R^1-R^2=-(CH_2)_5-$, $R^3=C_6H_5$; f $R^1-R^2=-(CH_2)_2O(CH_2)_2-$, $R^3=C_6H_5$; g $R^1=H$, $R^2=C_6H_5$, $R^3=C_2H_5$; h $R^1-R^2=-(CH_2)_5-$, $R^3=4\text{-}CH_3OC_6H_4$; i $R^1=R^2=-(CH_2)_5-$, $R^3=1\text{-}C_{10}H_7$; IV a $R^3=C_6H_5$; b $R^3=C_2H_5$; V $R^1-R^2=-(CH_2)_5-$, $R^3=C_6H_5$; VI $R^3=C_6H_5$

When II are heated in solvents (at 80-110°C) or melted, the dithiolane ring is cleaved to give a mixture of substances from which starting enaminothiones I were isolated. Other probable thermolysis products [11] could not be identified.

In the reaction of hydrogen chloride with dithiolanes II the aminoindene fragments of the molecules are converted to indanimmonium fragments (see [12]) and unconjugated dihydrochlorides III, the neutralization of which leads to starting bases II, are formed. The IR spectra of salts III contain an intense $\nu_{C=N}$ band (1645-1652 cm^{-1}) and $\nu_{C=C}$ bands of aromatic rings (1595 and 1497 cm^{-1}). The $\nu_{C=C}$ band of the five-membered indene ring (1530-1580 cm^{-1}) is absent.

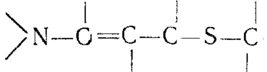
The action of aqueous mineral acids on dithiolanes II causes hydrolysis of the amino groups and leads to dispiro[bis(indane)-1',4;1',5-(1,3-dithiolanes)] IV. The N-substituted (IIa) and N-phenyl-substituted (IIb, g) compounds undergo hydrolysis most readily; hydrolysis of N,N-disubstituted aminoindenedithiolane IIe gives primarily a mixture of dioxo compounds IV and aminooxo derivative V in a molar ratio of 1:4. This result has not as yet been explained unambiguously. The reaction of hydrogen chloride with V gives a hydrochloride salt, which, like salts III, has an indanimmonium structure ($\nu_{C=N}$ 1653 cm^{-1}, $\nu_{C=O}$ 1725 cm^{-1}). In contrast to dithiolanes II, dithiolanes IV and V are stable when they are heated up to their melting points (220-240°C). Bis(1-oxo-2-phenyl-3-indenyl) sulfide VI (see [13]) is present in the products of pyrolysis of dithiolane IVa.

The reaction of many thioketones with diazomethane differs from their reaction with substituted diazomethanes [4]. Aromatic thioketones react with diazomethane to give 1,3-dithiolanes but react with diphenyldiazomethane to give thiiranes. The reaction with monophenyldiazomethane often leads to a mixture of dithiolanes and thiiranes [4].

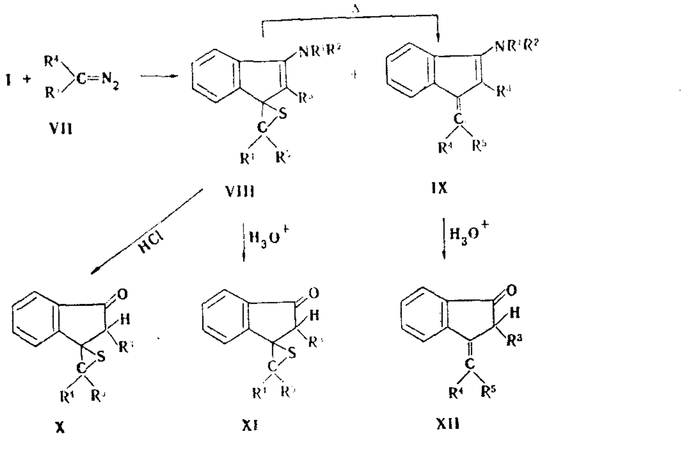
TABLE 2. Chemical Shifts (τ, ppm) of the Olefinic and Aromatic Protons of Dienamines IX (in CCl_4)

Compound	IXa	IXb	IXe	IXh	IXi	IXj	IXk	IX*l*
R^4	CH_3	H	C_6H_5	H	H	H	H	C_6H_5
R^5	CH_3	C_6H_5	C_6H_5	$COCH_3$	COC_6H_5	$COOCH_3$	$COOC_2H_5$	COC_6H_5
$\tau_{=CH}$	—	3,48 s	—	4,14 s	3,44 s	4,44 s	4,43 s	—
τ_{ArH}	2,32– –3,34	2,45– –3,25	2,48– –3,83	1,20– –3,09	1,44– –3,15	1,17– –2,97	1,09– –2,93	2,62– –3,92

3-Aminoindene-1-thiones (I) react with mono- and disubstituted diazomethanes VII to give thiiranes VIII or their desulfuration products IX. Thiiranes VIIIe-g, which are obtained in the reaction of diphenyldiazomethane VIIc with enaminothiones I, can be isolated in the individual state.

Colorless hydrochlorides X ($\nu_{C=N}$ 1635 cm^{-1}) are readily formed in the reaction of HCl with thiiranes VIIIe-g. Thiiranes VIII are hydrolyzed by mineral acids with splitting out of an amino group to give oxo derivatives XI ($\nu_{C=O}$ 1722 cm^{-1}). In contrast to thiiranes VIII, XI are not capable of splitting out sulfur even when they are heated. The increased thermal instability of thiiranes VIII and 1,3-dithiolanes II as compared with thiiranes XI and dithiolanes IV, as well as the corresponding heterocycles described in [11, 14], is evidently due to the presence in their molecules of the  $>N-\overset{|}{C}=\underset{|}{C}-\overset{|}{C}-S-\underset{|}{\overset{|}{C}}$ aminoallylthio grouping. The ease of spontaneous cleavage of the C–S bonds in these heterocycles is explained by the known reasons for the activation of allyl and benzyl C–Z bonds (stabilization of the intermediate ionic or radical states of the molecule) [15]. In the case of dithiolanes II the easy cleavage of the bond between the spiro atoms ($C^1-C^{1'}$) is additionally due to the effect of the bulky substituents at these atoms.

The products of desulfuration of the thiiranes – dienamines IX – are orange, dark red, or red-violet crystalline substances. Bands of medium intensity at 1635 (exocyclic) and 1570-1575 cm^{-1} (endocyclic) in their IR spectra correspond to vibrations of the C=C bond; in the case of IXh, i, *l* the band at 1675 cm^{-1} corresponds to the vibrations of the C=O bond, and the band at 1705 cm^{-1} in the spectra of IXj, k, i corresponds to the vibrations of the C=O bond. The chemical shifts of the vinylene (R^4=H) and aromatic protons in the PMR spectra of IX are presented in Table 2. The narrow singlet signal corresponds to the =CH protons in the PMR spectra; this indicates the formation of only one geometrical isomer of IX. The aromatic protons give a complex multiplet in all cases. In the spectra of IXh-k the signal of one of the aromatic protons is observed at weak field in the form of a separate multiplet (1.09-1.44 ppm). Since IX differ only with respect to substituents R^4 and R^5 attached to the double bond, it may be assumed that resonance for the 7-H proton is observed at weak field.



VII a $R^4=R^5=CH_3$; b $R^4=H$, $R^5=C_6H_5$; c $R^4=R^5=C_6H_5$; d $R^4=H$, $R^5=COCH_3$; e $R^4=H$, $R^5=COC_6H_5$; f $R^4=H$, $R^5=COOCH_3$; g $R^4=H$, $R^5=COOC_2H_5$; h $R^4=C_6H_5$, $R^5=COC_6H_5$; VIII, IX a $R^1-R^2=-(CH_2)_5-$, $R^3=C_6H_5$, $R^4=R^5=CH_3$; b $R^1-R^2=-(CH_2)_5-$, $R^3=R^5=C_6H_5$, $R^4=H$; c $R^1=R^2=-(CH_2)_2O(CH_2)_2-$, $R^3=R^5=C_6H_5$, $R^4=H$; d $R^1=R^2=CH_3$, $R^3=R^5=C_6H_5$, $R^4=H$; e $R^1-R^2=-(CH_2)_5-$, $R^3=R^4=R^5=C_6H_5$; f $R^1-R^2=-(CH_2)_2O(CH_2)_2-$, $R^3=R^4=R^5=C_6H_5$; g $R^1=R^2=CH_3$, $R^3=R^4=R^5=C_6H_5$; h $R^1-R^2=-(CH_2)_5-$, $R^3=C_6H_5$, $R^4=H$, $R^5=COCH_3$; i $R^1-R^2=-(CH_2)_5-$, $R^3=C_6H_5$, $R^4=H$, $R^5=COC_6H_5$; j $R^1-R^2=-(CH_2)_5-$, $R^3=C_6H_5$, $R^4=H$, $R^5=COOCH_3$; k $R^1-R^2=-(CH_2)_5-$, $R^3=C_6H_5$, $R^4=H$, $R^5=COOC_2H_5$; *l* $R^1-R^2=-(CH_2)_5-$, $R^3=R^4=C_6H_5$, $R^5=COC_6H_5$; m $R^1-R^2=-(CH_2)_5-$, $R^3=4\text{-}CH_3OC_6H_4$, $R^4=H$, $R^5=COOC_2H_5$; X $R^1-R^2=-(CH_2)_5-$, $R^3=R^4=R^5=C_6H_5$; XI $R^3=R^4=R^5=C_6H_5$; XII a $R^3=R^4=R^5=C_6H_5$; b $R^3=C_6H_5$, $R^4=H$, $R^5=COCH_3$.

TABLE 3. Dispiro[bis(3'-aminoindene)-1',4;1',5-(1,3-dithiolanes)]

Compound	Dec. temp., °C	Found, %				Empirical formula	Calc., %				Yield, %
		C	H	N	S		C	H	N	S	
IIa	145	75,8	5,1	—	13,1	$C_{31}H_{24}N_2S_2$	76,2	4,9	—	13,1	98
IIb	163	80,5	4,8	—	9,8	$C_{43}H_{32}N_2S_2$	80,6	5,0	—	10,0	92
IIc	120	77,1	6,1	—	11,8	$C_{35}H_{32}N_2S_2$	77,2	5,9	—	11,8	65
IId	137	77,9	6,8	4,6	10,5	$C_{39}H_{40}N_2S_2$	78,0	6,7	4,7	10,7	74
IIe*	160	78,9	6,4	4,6	10,3	$C_{41}H_{40}N_2S_2$	78,8	6,4	4,5	10,3	90
IIf	170	74.6	5,8	4.5	9,9	$C_{39}H_{36}N_2O_2S_2$	74.5	5,7	4,4	10,2	78
IIg	138	76.8	5,7	—	11.6	$C_{35}H_{32}N_2S_2$	77,2	5,9	—	11,8	52
IIh	165	75.6	6,3	3.9	9,4	$C_{43}H_{44}N_2O_2S_2$	75,4	6,4	4,1	9,4	80
IIi	140	82,4	6,6	—	8,1	$C_{49}H_{44}N_2S_2 \cdot C_6H_6$	82,3	6,2	—	8,0	70

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*See [18]. Crystal solvates were isolated with diethyl ether (decomposition temperature 145°C. Found: C 77.4; H 7.1; N 4.2; S 9.4%. $C_{41}H_{40}N_2S_2 \cdot C_4H_{10}O$. Calculated: C 77.4; H 7.2; N 4.0; S 9.2%) and with dioxane (decomposition temperature 148°C. Found: C 77.5; H 6.4; S 10.0%. $2C_{41}H_{40}N_2S_2 \cdot C_4H_8O_2$. Calculated: C 77.3; H 6.6; S 9.6%).

The strong deshielding of this proton is evidently due to the powerful anisotropic effect of the closely located carbonyl group. This indicates a cis-s-cis orientation of the C=O and C=C bonds in IXh-k.

The character of the splitting of the signal of the protons of the condensed benzene ring in the PMR spectra of IXe, *l* is practically identical, and the proton in the 7 position resonates at relatively stronger field (3.80-3.90 ppm). The chemical shift of this proton in the spectra of these compounds is determined by the anisotropic effect of the R^4 phenyl ring, which indicates a trans orientation of the benzoyl group in IX*l* relative to the condensed benzene ring.

The high stereoselectivity of the reactions of enaminothiones I with diazo carbonyl compounds VIId-h is evidently due to spatial shielding of the thiocarbonyl group of I and the corresponding conformational orientation of the functional groups in diazoalkanes VII [16].

Dienes IX are hydrolyzed by aqueous mineral acids more slowly than the corresponding thiiranes VIII; this is due to the decrease in the basicity of the amino group because of lengthening of the conjugation chain.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of 5-10% solutions of the compounds in $CDCl_3$ or CCl_4 were obtained with a Tesla BS 487C spectrometer (80 MHz) with hexamethyldisiloxane or cyclohexane as the standard.

Dispiro {bis [3'-amino-2'-aryl(alkyl)indene]-1',4;1',5-(1,3-dithiolanes)} (II) (Table 3). A mixture of 1 g of enaminothione I [17], 50 ml of absolute ether, and 20 ml of a 0.18 M solution of diazomethane was stirred at 20°C until the violet color vanished. The precipitated dithiolane II was removed by filtration, dried in vacuo, and recrystallized from benzene–methanol (1 : 3). An additional amount of dithiolane II was precipitated from the ether mother liquor by the addition of methanol. The reaction of enaminothione If with diazomethane was carried out in acetone. The IR spectra of dithiolanes II contain intense $\nu_{C=C}$ bands from the five-membered indene ring (1570-1575 cm^{-1}) and aromatic ring $\nu_{C=C}$ bands (1590-1600 and 1490-1500 cm^{-1}).

Thermal Cleavage of Dithiolanes II. A mixture of 2 g of dithiolane IIe and 15 ml of dimethylformamide (DMF) was refluxed for 15 min, after which it was poured into 400 ml of water. The resulting precipitate was removed by filtration, dried, and chromatographed with a column filled with activity II aluminum oxide (elution with chloroform). The substance in the second (from the bottom) dark-violet zone was eluted, and the solvent was evaporated to give 0.93 g (94%) (see [11]) of starting thione Ie. In the case of dithiolane IIb the reaction mixture was poured into 50 ml of a 5% solution of NaOH, the mixture was filtered, and the filtrate was acidified with hydrochloric acid. The precipitated aminothione Ib (0.97 g) was removed by filtration.

Hydrochloride Salts (III) of the Dithiolanes. Dry hydrogen chloride was passed over a solution of 0.5 g of the corresponding dithiolane II in 250 ml of ether until salt III precipitated. The precipitate was removed by filtration, washed with ether, and recrystallized from a mixture of alcohol and ether to give 0.47 g (95%) of salt IIIa (decomposition temperature 202-204°C. Found: Cl 12.6; S 11.0%. $C_{31}H_{24}N_2S_2 \cdot 2HCl$. Calculated: Cl 12.6; S 11.4%); 0.5 g (98%) of salt IIId (decomposition temperature 195-197°C. Found: Cl 9.5; N 3.6; S 8.3%.

TABLE 4. Substituted 1-Methylene-3-aminoindenes IX

Compound	mp, °C	Found, %			Empirical formula	Calc., %			Yield,* %
		C	H	N		C	H	N	
IXa	127—129	87,2	7,8	4,1	$C_{23}H_{25}N$	87,6	7,9	4,4	88
IXb†	150—152	89.5	7,1	3,4	$C_{27}H_{25}N$	89,3	6,9	3,8	64
IXc	165—167	85,3	6.7	—	$C_{26}H_{23}NO$	85,5	6,3	—	49
IXd	128—130	89,3	6,8	4,1	$C_{24}H_{21}N$	89,2	6,5	4,3	73
IXe†	166—167	89,9	6,6	3.0	$C_{33}H_{29}N$	90,2	6,6	3,2	98
IXf	157—159	87,1	6,2	3,1	$C_{32}H_{27}NO$	87,0	6,1	3,2	73
IXg	148—150	90.0	6.3	3,5	$C_{30}H_{25}N$	90,2	6,3	3,5	75
IXh	130—133	83,7	7,1	4,1	$C_{23}H_{23}NO$	83,9	7.0	4,2	41
IXi	153—156	85.7	6.5	3.6	$C_{28}H_{25}NO$	85,9	6,4	3,6	93
IXj	156—159	80,0	6,6	4,1	$C_{23}H_{23}NO_2$	80,0	6,7	4,1	57
IXk	163—164	80.5	7,0	3,8	$C_{24}H_{25}NO_2$	80,2	7,0	3,9	79
IX*l*	172—174	87,2	6,3	3,1	$C_{34}H_{29}NO$	87,4	6,2	3,0	87
IXm	158—160	77,2	7,0	3,6	$C_{25}H_{27}NO_3$	77,1	7,0	3,6	65

*By method A.

†See [19].

$2C_{39}H_{40}N_2S_2 \cdot 4HCl \cdot 3C_2H_5OH$. Calculated: Cl 9.6; N 3.8; S 8.6%); and 0.43 g (84%) of salt IIIe (decomposition temperature 199-200°C. Found: Cl 9.6; N 3.7; S 8.5%. $C_{41}H_{40}N_2S_2 \cdot 2HCl \cdot C_2H_5OH$. Calculated: Cl 9.7; N 3.9; S 8.6%).

Hydrolysis of Dithiolanes II. A mixture of 1 g of the corresponding dithiolane IIa, b, g, 1 ml of concentrated HCl, and 10 ml of methanol was refluxed for 2 h, and the resulting precipitate was removed by filtration, dried, and recrystallized from benzene–methanol to give 0.76 g (98%) of dithiolane IVa (decomposition temperature 240-244°C. Found: C 75.7; H 4.5; S 12.9%. $C_{31}H_{22}O_2S_2$. Calculated: C 75.9; H 4.5; S 13.0%); 0.7 g (90%) of dithiolane IVb (decomposition temperature 216-218°C. Found: C 67.8; H 5.9; S 15.5%. $C_{23}H_{22}O_2S_2 \cdot CH_3OH$. Calculated: C 67.8; H 6.1; S 15.0%). Dithiolanes IV were colorless crystalline substances that were readily soluble in benzene and chloroform but only slightly soluble in hexane and methanol. IR spectrum: $\nu_{C=O}$ 1725 cm^{-1}. Signals at τ 6.01 (s, 2-H) and 6.18 ppm (s, $S-CH_2-S$) are observed in the PMR spectrum of IVb (in $CDCl_3$). In the case of dithiolane IIe the reaction mixture was diluted with 30 ml of water and filtered. The filtrate was made alkaline with 10 ml of 5% NaOH solution and filtered to give 0.79 g of a mixture of oxoenamino- (V) and dioxo-1,3-dithiolane IVa. The mixture of IVa and V was chromatographed with a column filled with activity II aluminum oxide (elution with chloroform) to give 0.62 g (78%) of dispiro[(3'-oxo-2'-phenylindan)-1',4-(1,3-dithiolane)-5,1''-(3''-piperidino-2''-phenylindene)] V (decomposition temperature 195-197°C. Found: C 77.7; H 5.5; N 2.5; S 11.5%. $C_{36}H_{31}NOS_2$. Calculated: C 77.5; H 5.6; N 2.5; S 11.5%) and 0.13 g (19%) of dispiro-[bis(3'-oxo-2'-phenylindan)-1',4;1',5-(1,3-dithiolane)] IVa. IR spectrum of V: $\nu_{C=O}$ 1712 cm^{-1} and five-membered indene ring $\nu_{C=C}$ 1570 cm^{-1}. PMR spectrum ($CDCl_3$): 6.59 (s, 2-H), 5.81 (s, $S-CH_2-S$), 8.59 (m, $CH_2CH_2CH_2$), and 7.38 ppm (broad multiplet, CH_2NCH_2).

The corresponding salt, which decomposes at 175-179°C, was obtained in 96% yield when hydrogen chloride was passed above an ether solution of dithiolane V. Found: Cl 5.9; N 2.4; S 10.8%. $C_{36}H_{31}NOS_2 \cdot HCl$. Calculated: Cl 6.8; N 2.4; S 10.3%.

Spiro[(3'-amino-2'-phenylindene)-1',2-(3,3-diphenylthiiranes)] VIIIe-g. A mixture of 1 g of enaminothione Ic-e, 0.9 g of diphenyldiazomethane, and 80 ml of ether was stirred at 20°C in the dark for 2.5 h, after which the corresponding precipitated VIIIe-g was removed by filtration and reprecipitated from a solution in 3 ml of benzene containing two drops of acetic acid by the addition of methanol. This procedure yielded 1.23 g (80%) of piperidino derivative VIIIe (decomposition temperature 155-158°C. Found: C 84.3; H 6.2; N 3.1; S 6.8%. $C_{33}H_{29}NS$. Calculated: C 84.1; H 6.2; N 3.0; S 6.8%); 1.12 g (72%) of morpholino derivative VIIIf (decomposition temperature 158-161°C. Found: C 81.4; H 5.7; S 6.8%. $C_{32}H_{27}NOS$. Calculated: C 81.2; H 5.7; S 6.8%); and 0.37 g (23%) of dimethylamino derivative VIIIg (decomposition temperature 146-149°C. Found: C 85.8; H 6.1; S 7.4%. $C_{30}H_{25}NS$. Calculated: C 85.5; H 5.9; S 7.6%).

Hydrogen chloride was passed above a solution of 0.5 g of thiirane VIIIe in 100 ml of ether, and the resulting colorless precipitate of salt X [0.5 g (98%)], which decomposed at 180-185°C (from methanol–ether), was removed by filtration. Found: Cl 7.1; N 2.6; S 6.2%. $C_{33}H_{29}NS \cdot HCl$. Calculated: Cl 7.0; N 2.7; S 6.3%.

Spiro[(3'-oxo-2'-phenylindan)-1',2-(3,3-diphenylthiirane)] XI. A mixture of 0.5 g of thiirane VIIIe, 10 ml of acetic acid, and 1 ml of concentrated HCl was refluxed for 1 h, after which it was cooled and diluted with 10 ml of H_2O. The mixture was then filtered to give 0.37 g (85%) of colorless crystals of oxo derivative XI, which decomposes at 200-202°C. Found: C 83.2; H 5.0; S 8.0%. $C_{28}H_{20}OS$. Calculated: C 83.2; H 5.0; S 7.9%.

1-Methylene-2-aryl-3-aminoindenes IX. A) A mixture of 1 g of the corresponding enaminothione I, 1 g of diazo compound VIIa, b, and 50 ml of ether was stirred in the dark at 20°. The precipitated olefins IXa-d were removed by filtration and recrystallized from benzene–hexane (1 : 4) (see Table 4). The reaction of enaminothiones I with diazo carbonyl compounds VIId-h was carried out in refluxing dioxane in the presence of 1 g of copper powder. The reaction mixture was filtered, 50% aqueous methanol was added to the filtrate, and the precipitated IX was removed by filtration.

B) A solution of 1 g of thiirane VIIIe-g in 10 ml of benzene was refluxed for 3 h, after which half the benzene was evaporated, and 30 ml of hexane was added to the concentrated solution. The precipitated IX (85-87% yields) were removed by filtration.

Compound IXe was also obtained by reaction of thiobenzophenone with 3-piperidino-2-phenyl-1-diazoindene [1].

Hydrolysis of Enaminoindene Olefins IXe, h. A mixture of 0.5 g of IXe, h, 5 ml of CH_3COOH, and 1 ml of concentrated HCl was refluxed for 4 h, after which it was diluted with water, and the precipitate was removed by filtration and recrystallized from ethanol to give 0.18 g (47%) of 1-oxo-2-phenyl-3-(diphenylmethylene)indan (XIIa) (colorless crystals with mp 202-203°C. Found: C 89.8; H 5.7%. $C_{28}H_{20}O$. Calculated C 90.0; H 5.4%) and 0.3 g (67%) of light-yellow crystals of 1-oxo-2-phenyl-3-(2-oxopropylidene)indan (XIIb). IR spectrum: indan $\nu_{C=O}$ 1710, acetyl group $\nu_{C=O}$ 1690, and $\nu_{C=C}$ 1625 cm^{-1}. Found: C 82.4; H 5.3%. $C_{18}H_{14}O_2$. Calculated: C 82.4; H 5.3%.

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