SYNTHESIS AND REGIOSELECTIVITY OF THE [3,3]-SIGMATROPIC REARRANGEMENT OF SUBSTITUTED 2-ALLYLTHIO- AND 2-ALLYLSELENO-1,4-DIHYDROPYRIDINES

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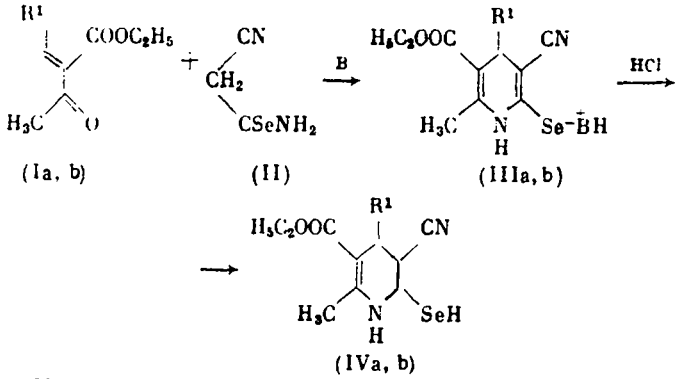
The reaction of 3-cyano-1,4-dihydropyridine-2-thiolates and the corresponding selenolates with allyl bromide gave 2-allylthio- and 2-allylseleno-3-cyano-1,4-dihydropyridines, which, upon heating in various solvents or in the solid state, undergo [3,3]-sigmatropic rearrangement to give 3-cyano-3-allyl-1,2,3,4-tetrahydropyridine-2-thiones and the corresponding selenones. The resultant pyridinethiones are alkylated by alkyl halides at the sulfur atom and are oxidized by iodine to give disulfides.

[3,3]-Sigmatropic rearrangements for allylthiopyridines have been studied in considerable detail [1, 2]. These reactions usually proceed at high temperature over a prolonged period using a catalyst and are not regioselective [1-4]. In contrast, there is no information available on sigmatropic rearrangements for hydrogenated allylthio- and allylselenopyridines as a consequence of the relative inavailability of hydrogenated sulfur- and selenium-containing pyridines. While methods have recently been developed for preparing pyridine-2-thiolates [5-8], the methods for synthesizing their selenium analogs have not been studied extensively [8]. In order to study the sigmatropic rearrangement and establish its regioselectivity, we developed a method for preparing hydrogenated pyridine-2-selenolates and pyridyl-2-selenols. The reaction of ethyl arylmethyleneacetoacetates (I) and cyanoacetamide (II) in the presence of excess 4-methylmorpholine gave 1,4-dihydropyridine-2-selenolates (IIIa) and (IIIb). This reaction proceeds regioselectively in absolute ethanol under argon under mild conditions at 25°C in 68-79% yield.



(I), (III), (IV): $R^1 = C_6H_5$ (a); 2-C_4H_3O (b); B = 4-methylmorpholine.

Acidification of salts (III) by the addition of dilute hydrochloric acid in ethanol gave the corresponding selenols (IV). The formation of (IV) as a selenol was indicated by IR and PMR spectroscopy. Thus, the PMR spectra of (IV) show singlets for NH (9.5 ppm) and C^4–H protons (4.4 ppm) of 1,4-dihydropyridine in addition to the characteristic signals of the substituent protons. The IR spectra of these compounds contain the stretching band for a conjugated nitrile group at 2205 cm^{-1}. If a substituted 3,4-dihydropyridine-2(1H)-selenone were formed, the IR and PMR spectra would be different. The existence of the hydro-

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TABLE 1. Physicochemical and Elemental Analysis Data of 2-Allylthio- and 2-Allylseleno-4-aryl-3-cyano-1,4-dihydropyridines (VIa)-(VIf) and 3-Allyl-4-aryl-3-cyano-1,2,3,4-tetrahydropyridine-2-thiones and 2-selenones (VIIa)-(VIIf)

Compound	Yield, %	Mp, °C	Found / Calculated, % C	H	N	Y	Chemical formula
(VIa)	61	249–250	72,16 / 71,97	6,48 / 6,33	8,25 / 7,99	9,00 / 9,15	$C_{21}H_{22}N_2OS$
(VIb)	70	243–245	58,71 / 58,74	4,72 / 4,93	6,02 / 6,52	6,99 / 7,47	$C_{21}H_{21}BrN_2OS$
(VIc)	93	127–128 (benzene–hexane)	62,48 / 62,69	4,69 / 4,97	7,90 / 8,12	9,02 / 9,30	$C_{18}H_{17}ClN_2OS$
(VId)	24	86–87 (chloroform–hexane)	66,81 / 67,03	6,37 / 5,92	8,01 / 8,23	9,57 / 9,42	$C_{19}H_{20}N_2O_2S$
(VIe)	85	78–80	58,90 / 58,92	5,25 / 5,20	7,25 / 7,23	20,33 / 20,38	$C_{19}H_{20}N_2O_2Se$
(VIf)	80	74–76	54,08 / 54,12	4,79 / 4,81	7,44 / 7,42	20,97 / 20,93	$C_{17}H_{18}N_2O_3Se$
(VIIa)	98 *(a)	248 (methanol)	72,10 / 71,97	6,20 / 6,33	7,15 / 7,99	8,90 / 9,15	$C_{21}H_{22}N_2OS$
(VIIb)	98 *(a) 96 *(b)	241–243 (methanol)	58,62 / 58,74	4,87 / 4,93	6,35 / 6,52	7,81 / 7,47	$C_{21}H_{21}BrN_2OS$
(VIIc)	67	132–134 (benzene–hexane)	62,81 / 62,69	5,18 / 4,97	7,92 / 8,12	9,75 / 9,30	$C_{18}H_{17}ClN_2OS$
(VIId)	10 *(a) 98 *(b)	177–178 (benzene–hexane)	66,71 / 67,03	6,35 / 5,92	8,25 / 8,23	8,94 / 9,42	$C_{19}H_{20}N_2O_2S$
(VIIe)	90	158–160 (benzene)	58,88 / 58,92	5,22 / 5,20	7,21 / 7,23	20,42 / 20,38	$C_{19}H_{20}N_2O_2Se$
(VIIf)	92	203–205 (methanol)	54,16 / 54,12	4,83 / 4,81	7,40 / 7,42	20,89 / 20,93	$C_{17}H_{18}N_2O_3Se$

*The method of preparation is indicated in parentheses (see Experimental Sec.).

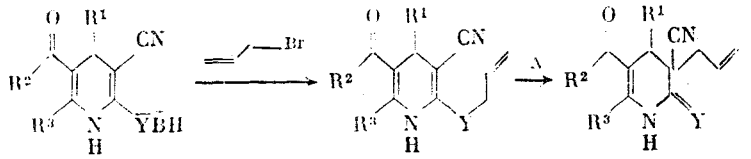
genated selenium-containing pyridines in a single tautomeric form (1,4-dihydropyridine-2-selenol) distinguishes these compounds from their sulfur analogs, which exist predominantly as 3,4-dihydropyridine-2(1H)-thiones or a mixture of these thiones with the corresponding pyridine-2-thiones [8].

2-Allylthio- and 2-allylseleno-1,4-dihydropyridines (VIa)-(VIf) were obtained in high yield by the reaction of 1,4-dihydropyridine-2-selenolate (IIIa) and (IIIb) or 1,4-dihydropyridine-2-thiolate salts (Va)-(Vd) and allyl bromide in ethanol at 25°C (Table 1). The reaction proceeds with high regioselectivity relative to the sulfur or selenium atom with a 61-93% yield of (VI). This regioselectivity is probably related to the redistribution of electron density in starting reagents (III) and (V), localization of negative charge on the sulfur or selenium atom, and realization of an S_N2 mechanism. The localization of excess electron density on the sulfur atom in morpholinium 5-acetyl-6-methyl-4-(2-nitrophenyl)-3-cyano-1,4-dihydropyridine-2-thiolate has been observed, which is in good accord with the physicochemical and x-ray diffraction structural analysis data and the reactivity of this thiolate [9]. (See scheme on following page.)

Upon heating, 1,4-dihydropyridines (VIa)-(VIf) in various solvents or in the solid state are all converted with high regioselectivity into 3-allyl-4-aryl-3-cyano-1,2,3,4-tetrahydropyridine-2-thiones or their corresponding selenones (VIIa)-(VIIf). Selenium derivatives (VIe) and (VIf) undergo the rearrangement with especial readiness. Upon recrystal-

TABLE 2. IR and PMR Spectral Data for 2-Allylthio- and 2-Allylseleno-4-aryl-3-cyano-1,4-dihydropyridines (VIa)-(VIf) and 3-Allyl-4-aryl-3-cyano-1,2,3,4-tetrahydropyridine-2-thiones and 2-selenones (VIIa)-(VIIf)

Compound	ν, cm^{-1}		δ, ppm			
	CN	CO	NH (s)	CH (s)	CH_2 (m)	other signals
(VIa)	2205	1610	9,49	4,49	3,67	0,94 s (3H, CH_3), 1,02 s (3H, CH_3), 2,11 m (2H, CH_2), 2,47 m (2H, CH_2), 5,08–5,17 m (2H, CH_2=), 5,78 m (1H, CH=), 7,21 m (5H, C_6H_5)
(VIb)	2203	1621	9,74	4,48	3,69	0,91 s (3H, CH_3), 1,01 s (3H, CH_3), 2,12 m (2H, CH_2), 2,44 m (2H, CH_2), 5,11 m (2H, CH_2=), 5,76 m (1H, CH=), 7,11 d, 7,51 d
(VIc)	2200	1608	9,49	4,66	3,66	(4H, 4-BrC_6H_4), 2,06 s (3H, CH_3CO), 2,31 s (3H, CH_3), 4,95 m (1H, CH_2=), 5,02 m (1H, CH_2=), 5,69 m (1H, CH=), 7,16 d, 7,40 d (4H, 4-ClC_6H_4)
(VId)	2204	1676	9,45	4,48	3,76	1,05 t (3H, CH_3CH_2), 2,32 s (3H, CH_3), 3,96 q (2H, CH_3CH_2), 4,97 m (1H, CH_2=), 5,15 m (1H, CH_2=), 5,73 m (1H, CH=), 7,27 m (5H, C_6H_5)
(IVe)	2202	1675	9,43	4,50	3,72	1,08 t (3H, CH_3CH_2), 2,33 s (3H, CH_3), 3,96 q (2H, CH_3CH_2), 4,95 m (2H, CH_2=), 5,84 (1H, CH=), 7,26 m (5H, C_6H_5)
(VIf)	2205	1669	8,80	5,17	3,96	1,20 t (3H, CH_3CH_2), 2,10 s (3H, CH_3), 5,00 m (2H, CH_2=), 5,85 m (1H, CH=), 6,25 m, 6,90 m, 7,35 m (3H, C_4H_3O)
(VIIa)	2205	1638	12,36	4,12		0,93 s (3H, CH_3), 1,06 s (3H, CH_3), 2,22 m (2H, CH_2), 2,60 m (4H, CH_2, CH_2–CH=), 5,13 m (1H, CH_2=), 5,30 m (1H, CH_2=), 7,25 m (5H, C_6H_5)
(VIIb)	2206	1645	12,42	4,13		0,93 s (3H, CH_3), 1,06 s (3H, CH_3), 2,24 m (2H, CH_2), 2,59 m (4H, CH_2, CH_2–CH=), 5,25 m (2H, CH_2=), 5,85 m (1H, CH=), 7,07 d, 7,53 d (4H, 4-BrC_6H_4)
(VIIc)	2248	1676	12,14	4,24		2,11 s (3H, CH_3CO), 2,38 s (3H, CH_3), 2,69 d (2H, CH_2–CH=), 5,23 m (2H, CH_2=), 5,86 m (1H, CH=), 7,18 d, 7,41 d (4H, 4-ClC_6H_4)
(VIId)	2264	1728	12,17	4,05		1,12 t (3H, CH_3CH_2); 2,45 s (3H, CH_3), 2,67 d (2H, CH_2–CH=), 4,04 q (2H, CH_3CH_2), 5,27 m (2H, CH_2=), 5,90 m (1H, CH=), 7,20 m (5H, C_6H_5)
(VIIe)	2255	1720	12,90	4,02		1,11 t (3H, CH_3CH_2), 2,45 s (3H, CH_3), 4,00 m (4H, CH_3CH_2, CH_2–CH=), 5,33 m (2H, CH_2=), 5,92 m (1H, CH=), 7,28 (5H, C_6H_5)
(VIIf)	2252	1720	12,85	4,20		1,20 t (3H, CH_3), 2,10 s (3H, CH_3), 4,00 m (4H, CH_3CH_2, CH_2–CH=), 5,30 m (2H, CH_2=), 5,85 m (1H, CH=), 6,20 m, 6,35 m, 7,50 m (3H, C_4H_3O)



(IIIa, b), (Va–d) (VIa–f) (VIIa–f)

(V), (VI), (VII): $R^1 = C_6H_5$, $R^2 - R^3 = CH_2C(CH_3)_2CH_2$, Y = S (a); $R^1 = 4\text{-}BrC_6H_4$, $R^2 - R^3 = CH_2C(CH_3)_2CH_2$, Y = S (b); $R^1 = 4\text{-}ClC_6H_4$, $R^2 = R^3 = CH_3$, Y = S (c); $R^1 = C_6H_5$, $R^2 = C_2H_5O$, $R^3 = CH_3$, Y = S (d); $R^1 = C_6H_5$, $R^2 = C_2H_5O$, $R^3 = CH_3$, Y = Se (e); $R^1 = 2\text{-}C_4H_3O$, $R^2 = C_2H_5O$, $R^3 = CH_3$, Y = Se (f).

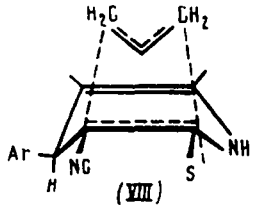
lization from benzene, these compounds are almost completely converted into selenones (VIIe) and (VIIf) in 90-92% yields. The regioselectivity of this reaction is determined by comparing the physicochemical indices of starting (VI) and reaction products (VII).

Derivatives (VIa)-(VIf) and (VIIa)-(VIIf) were clearly identified by the nitrile group band in their IR spectra (Table 2). 1,4-Dihydropyridines (VIa)-(VIf) have a strong band for a conjugated nitrile group at 2200-2205 cm^{-1}. This band is diminished and shifted

to 2248-2266 cm^{-1}, characteristic for nonconjugated nitrile groups, upon migration of the allyl group to C^3 in the pyridine ring.

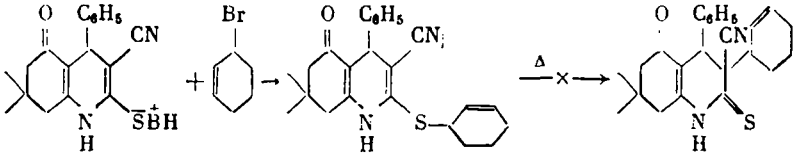
The PMR signals for the C^4H, NH, and YCH_2 protons are diagnostic (see Table 2). Thus, the signal for C^4H in allylthio- and allylselenopyridines (VIa)-(VIf) is found at δ 4.48-5.17 ppm, which is characteristic for 1,4-dihydropyridines [10], is shifted to 4.02-4.20 ppm after the rearrangement. The NH group protons in (VIa)-(VIf) have signals at 8.8-9.49 ppm, characteristic for the analogous protons of 1,4-dihydropyridines [10]. After the rearrangement, the NH group proton signals are shifted to δ 12.14-12.90 ppm, which is characteristic for 3,4-dihydropyridine-2(1H)-thiones [11]. The CH_2S and CH_2Se group protons are seen as multiplets at 3.66-3.76 and 3.72-3.96 ppm, respectively, which is characteristic for the signals of the α-protons of the allylthio and allylseleno substituents [12, 13].

In order to study the allyl rearrangement in the case of (VIb), we carried out this reaction in DMSO-d_6 in an NMR tube at 100°C. Upon heating this solution of (VIb), NMR signals arise for the protons of the rearrangement (VIIb), whose intensity increases with the concurrent decrease in the signals of the starting reagent. After 5 min of heating, only the signals for rearrangement product (VIIb) are observed. NMR signals for compounds other than (VIb) and (VIIb) were not detected during the experiment. This indicates the lack of long-lived intermediates. The available data on the Claisen arrangement [1, 2] and our present results suggest that this reaction proceeds synchronously with the formation of intramolecular six-membered transition state (VIII).



(VIII)

In order to support this hypothesis, we synthesized a cyclic analog of allyl derivatives (Va) and (Vb), namely, 3-cyano-2-(2-cyclohexen-1-ylthio)-1,4,5,6,7,8-hexahydroquinoline (IX).

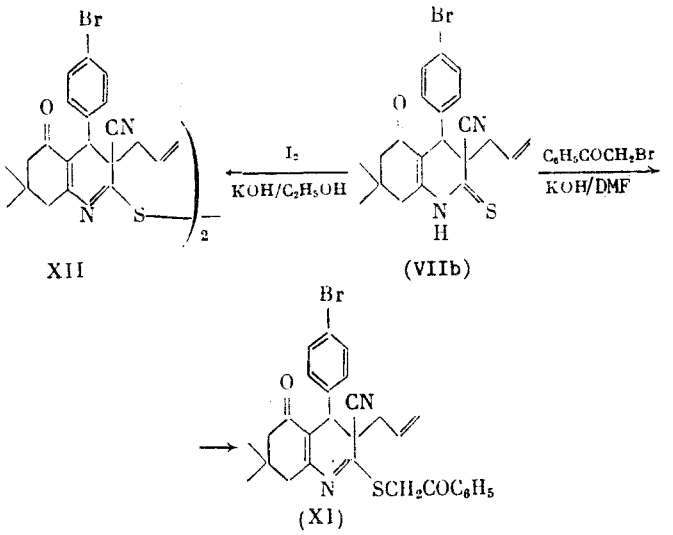


(Va) (IX) (X)

Rearrangement of the cyclohexyl fragment was not observed upon heating (IX) in ethanol and DMSO or without solvent. The formation of (X) was also not detected in a derivatographic study. This failure may serve to support the hypothesis of an intramolecular rearrangement.

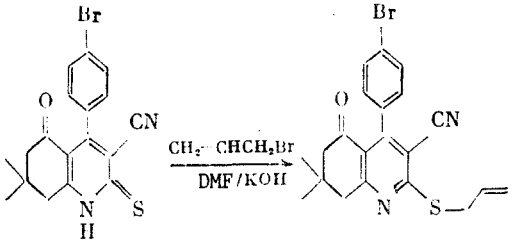
The rearrangement proceeds upon heating 2-allylthioquinolines (VIa) and (VIb) in the absence of solvent without melting. The melting points of products (VIIa) and (VIIb) are detected instead of the melting points of starting (IVa) and (IVb) (see Table 1). A derivatographic study of the solid phase reaction was carried out. The rearrangement of (VIa) to (VIIa) proceeds with energy evolution at 98-136°C, while the rearrangement from (VIb) to (VIIb) proceeds with energy evolution at 133-163°C. Both compounds subsequently melt at temperatures characteristic for rearrangement products (VIIa) and (VIIb) and decompose with the evolution of energy and gaseous products. It is interesting that the rearrangement does not take place upon heating (VIc)-(VIf) up to the melting point; these compounds melt with decomposition and the evolution of gaseous products. The solid phase rearrangement of (VId) was carried out by the prolonged heating of a sample at constant 65°C.

The chemical properties of the rearrangement products were studied for (VIIb). Similar to pyridinethiones [8, 12], (VIIb) reacts with phenacyl bromide in KOH/DMF with the formation of 2-phenacyl derivative (XI) and is oxidized by iodine in alkaline ethanol to give disulfide (XII).



The structures of (XI) and (XII) were supported by physicochemical and elemental analysis data (see Experimental Sec.).

We carried out the reaction of 5,6,7,8-tetrahydroquinoline-2(1H)-thione (XIII) with allyl bromide in KOH/DMF in order to compare the properties of 1-allylthio-1,4-dihydropyridines with the properties of the dehydrogenated analogs.



We have already shown that pyridine-2(1H)-thiones are alkylated only at the sulfur atom [12], although quinoline-2(1H)-thiones react with the analogous reagents to form N-allylquinoline-2-thiones [14]. We have established that (XIII) forms only 2-allylthio derivatives (XIV) in 70% yield. This compound does not undergo a thermal rearrangement analogous to that studied by Litvinova [4].

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer in vaseline mull. The PMR spectra were taken on the Bruker WP-100 spectrometer at 100 MHz in DMSO-d_6 with TMS as the internal standard. The purity of the products was carried out by thin-layer chromatography on Silufol UV-254 plates using 3:5 2-butanone–hexane as the eluent. The spots were developed with iodine vapor.

4-Methylmorpholinium 6-Methyl-4-phenyl-3-cyano-5-ethoxycarbonyl-1,4-dihydropyridine-2-selenolate (IIIa). A mixture of 0.01 mole ethyl benzylideneacetoacetate (Ia), 0.01 mole cyanoselenoacetamide (II), and 0.8 ml 4-methylmorpholine was stirred under argon in 15 ml ethanol at 25°C until selenamide (II) was dissolved and then rapidly filtered. The filtrate was maintained for 24 h. The precipitate was separated and washed with ethanol and hexane to give (IIIa) in 79% yield, mp 124-126°C (dec.). IR spectrum (ν, cm^{-1}): 2180 (CN), 1665 (CO). PMR spectrum (δ, ppm): 8.39 s (1H, NH), 7.22-7.40 m (5H, C_6H_5), 4.28 s (1H, C^4H), 3.92 q (2H, $C\underline{H}_2CH_3$), 3.76 m (4H, CH_2OCH_2), 3.14 m (4H, CH_2NCH_2), 2.75 s (3H, CH_3N), 2.33 s (3H, CH_3), 1.05 t (3H, $C\underline{H}_3CH_2$). Found: C, 56.19; H, 6.19; N, 9.40; Se, 17.47%. Calculated for $C_{21}H_{27}N_3O_3Se$: C, 56.25; H, 6.07; N, 9.37; Se, 17.61%.

4-Methylmorpholinium 6-methyl-4-(2-furyl)-3-cyano-5-ethoxycarbonyl-1,4-dihydropyridine-2-selenolate (IIIb) was obtained in 68% yield analogously to (IIIa), mp 120-122°C (dec.). IR spectrum (ν, cm^{-1}): 2185 (CN), 1680 (CO). PMR spectrum (δ, ppm): 8.64 s (1H,

NH), 7.45 m, 6.29 m, 5.87 m (3H, C_6H_3O), 4.45 s (1H, C^4H), 3.97 q (2H, $C\underline{H}_2CH_3$), 3.74 m (4H, CH_2OCH_2), 3.00 (4H, CH_2NCH_2), 2.67 s (3H, NCH_3), 2.22 s (3H, CH_3), 1.10 t (3H, $C\underline{H}_3CH_2$). Found: C, 52.12; H, 5.82; N, 9.44; Se, 17.87%. Calculated for $C_{19}H_{25}N_3O_4Se$: C, 52.05; H, 5.74; N, 9.58; Se, 18.01%.

6-Methyl-4-phenyl-3-cyano-5-ethoxycarbonyl-1,4-dihydropyridine-2-selenol (IVa). A suspension of 5.6 mmoles selenolate (IIIa) in 15 ml ethanol was diluted by the addition of 5 ml 10% hydrochloric acid with stirring under argon. The mixture was filtered. The precipitate which separated after 0.5 h was filtered and washed with ethanol and hexane to give (IVa) in 89% yield, mp 113-115°C (dec.). IR spectrum (ν, cm^{-1}): 2205 (CN), 1695 (CO). PMR spectrum (δ, ppm): 9.53 s (1H, NH), 7.4-7.9 m (5H, C_6H_5), 4.47 s (1H, C^4H), 3.93 q (2H, $C\underline{H}_2CH_3$), 2.27 s (3H, CH_3), 1.06 t (3H, $C\underline{H}_3CH_2$). Found: C, 55.21; H, 4.50; N, 8.01; Se, 22.33%. Calculated for $C_{16}H_{16}N_2O_2Se$: C, 55.34; H, 4.64; N, 8.07; Se, 22.74%.

6-Methyl-4-(2-furyl)-3-cyano-5-ethoxycarbonyl-1,4-dihydropyridine-2-selenol (IVb) was obtained in 60% yield analogously to (IVa), mp 97-98°C. IR spectrum (ν, cm^{-1}): 2205 (CN), 1700 (CO). PMR spectrum (δ, ppm): 9.81 s (1H, NH), 7.51 m, 6.34 m, 6.04 m (3H, C_4H_3O), 4.46 q (1H, C^4H), 4.03 q (2H, $C\underline{H}_2CH_3$), 2.29 s (3H, CH_3), 1.14 t (3H, $C\underline{H}_3CH_2$). Found: C, 49.76; H, 4.28; N, 8.38; Se, 23.49%. Calculated for $C_{14}H_{14}N_2O_3Se$: C, 49.86; H, 4.18; N, 8.31; Se, 23.41%.

2-Allylthio-4-aryl-3-cyano-1,4-dihydropyridines (VIa)-(VId) (see Tables 1 and 2). A sample of 24 mmoles allyl bromide was added to a suspension of 20 mmoles pyridylthiolate (Va)-(Vd) in 40 ml ethanol and stirred for 3-5 h. The precipitate was filtered off and washed with ethanol and hexane. The filtrate with the wash ethanol was diluted with 100 ml water. The precipitate was again filtered off to give (VIa)-(VIc). Product (VId) was isolated by diluting the reaction mixture with 100 ml water and adding 10% hydrochloric acid to pH 2 and was maintained for 3 h. The solution was decanted from the tarry residue. The precipitate was washed with water, dried in the air, and heated at reflux in 1:5 chloroform–hexane. The hot mixture was filtered. A precipitate of (VId) separated from the filtrate upon cooling.

2-Allylseleno-4-aryl-3-cyano-1,4-dihydropyridine (VIe, f) (see Tables 1 and 2). To a suspension of 0.9 mmole selenolate (IIIa, b) in 10 ml ethanol, cooled to −10°C and stirred in an argon atmosphere, was added 0.9 mmole allylbromide. Stirring was continued for 20 min. Then the reaction mixture was diluted with 10 ml water and a precipitate was isolated which was washed with water and cooled to −10°C with ethanol and hexane.

3-Allyl-4-aryl-7,7-dimethyl-5-oxo-3-cyano-1,2,3,4,5,6,7,8-octahydroquinoline-2-thiones (VIIa) and (VIIb) (see Tables 1 and 2). a) A sample of 0.5 g 1,4,5,6,7,8-hexahydroquinoline (VIa) or (VIb) was maintained for 3 h at constant 140°C. b) A suspension of 5 mmoles hexahydroquinoline (VIb) in 20 ml ethanol was heated at reflux for 3 h. The precipitate was filtered off and washed with ethanol and hexane.

3-Allyl-6-acetyl-6-methyl-4-(4-chlorophenyl)-3-cyano-1,2,3,4-tetrahydropyridine-2-thione (VIIc) (see Tables 1 and 2). A solution of 1 mmole (VIc) in 7 ml DMSO was heated for 1 h at 80-100°C. The reaction mixture was cooled to 25°C and diluted with 100 ml water. The precipitate was filtered off and washed with water.

3-Allyl-5-methyl-4-phenyl-3-cyano-5-ethoxycarbonyl-1,2,3,4-tetrahydropyridine-2-thione (VIId) (see Tables 1 and 2) was obtained as a side-product in the synthesis of allylthiopyridine (VId). The tarry precipitate was heated at reflux in chloroform–hexane and the insoluble precipitate was recrystallized from benzene–hexane to give (VIId).

A sample of 0.5 g (VId) was maintained at constant 65°C for 20 h.

3-Allyl-4-aryl-6-methyl-3-cyano-5-ethoxycarbonyl-1,2,3,4-tetrahydropyridine-2-selenones (VIIe) and (VIIf) (see Tables 1 and 2). A suspension of 10 mmoles (VIe) or (VIf) in 15 ml benzene was heated to reflux and filtered. Cooling of the reaction mixture gave (VIIe) and (VIIf).

7,7-Dimethyl-5-oxo-4-phenyl-3-cyano-2-(2-cyclohexen-1-ylthio)-1,4,5,6,7,8-hexahydroquinoline (IX). A mixture of 10 mmoles quinolinethiolate (Va) and 12 mmoles 3-bromocyclohexene in 20 ml ethanol was stirred for 7 h at 20°C. The precipitate was filtered off, washed with ethanol and hexane, and recrystallized from ethyl acetate to give (IX) in 28% yield, mp 177-179°C (dec.). IR spectrum (ν, cm^{-1}): 2216 (CN), 1622 (CO). PMR spectrum (δ, ppm): 0.92 s (3H, CH_3), 1.03 s (3H, CH_3), 1.65-2.43 m [10H, $(CH_2)_3$, C^6H_2, C^8H_2], 4.15 m (1H, CHS), 4.49 s (1H, C^4H), 5.77 m (2H, CH=CH), 7.22 m (5H, C_6H_5), 8.84 s (1H, NH). Found: C, 73.75; H, 6.84; N, 7.24; S, 8.12%. Calculated for $C_{24}H_{26}N_2OS$: C, 73.81; H, 6.71; N, 7.17; S, 8.21%.

3-Allyl-4-(4-bromophenyl)-7,7-dimethyl-5-oxo-2-phenacylthio-3-cyano-3,4,5,6,7,8-hexahydroquinoline (XI). A sample of 0.8 ml 10% KOH and 1.55 mmoles phenacyl bromide were added to a suspension of 1.5 mmole (VIIb) in 3 ml DMF. The reaction mixture was diluted with water and maintained for 3 h. The precipitate was filtered off, dried in air, and recrystallized from 1:2 benzene–hexane to give (XI) in 67% yield, mp 148-150°C. IR spectrum (ν, cm^{-1}): 2256 (CN), 1717, 1665 (CO). PMR spectrum (δ, ppm): 0.88 s (3H, CH_3), 0.93 s (3H, CH_3), 2.19-2.60 m (6H, C^8H, C^6H_2, CH_2CH=), 4.07 s (1H, C^4H), 4.81 s (2H, CH_2S), 5.16-5.33 m (1H, CH_2=), 5.90 m (1H, CH=), 6.98 and 7.47 d (4H, 4-BrC_6H_4), 7.66 and 8.09 (5H, C_6H_5). Found: C, 63.57; H, 5.06; N, 5.21; S, 5.72%. Calculated for $C_{29}H_{27}BrN_2O_5S$: C, 63.62; H, 4.97; N, 5.12; S, 5.86%.

Bis[3-allyl-4-(4-bromophenyl)-7,7-dimethyl-5-oxo-3-cyano-3,4,5,6,7,8-hexahydro-2-quinolyl]disulfide (XII). A sample of 2.1 ml 10% KOH was added to a suspension of 2 mmoles quinolylthione (VIIb) in 10 ml ethanol, and after 30 min, a solution of 2 mmoles I_2 in 15 ml ethanol was added. The reaction mixture was stirred for an additional 2 h. The precipitate formed was filtered off, washed with ethanol and hexane, and recrystallized from ethyl acetate–benzene to give (XII) in 70% yield, mp 221-223°C. IR spectrum (ν, cm^{-1}): 2262 (CN), 1682 (CO). PMR spectrum (δ, ppm): 1.04 s (3H, CH_3), 1.08 s (3H, CH_3), 2.32-2.66 m (6H, C^6H_2, C^8H_2, CH_2CH=), 4.27 s (1H, C^4H), 5.29-5.41 m (2H, CH_2=), 6.02 m (1H, CH=), 7.06 and 7.54 d (4H, 4-BrC_6H_4). Found: C, 58.72; H, 4.90; N, 6.47; S, 7.37%. Calculated for $C_{42}H_{40}Br_2N_4O_2S_2$: C, 58.88; N, 4.71; N, 6.54; S, 7.48%.

2-Allylthio-4-(4-bromophenyl)-7,7-dimethyl-5-oxo-3-cyano-5,6,7,8-tetrahydroquinoline (XIV). A mixture of 3 mmoles quinolylthione (XIII), 1.9 ml 10% KOH, and 3.6 mmoles allyl bromide in 10 ml DMF was stirred for 3 h at 25°C. The reaction mixture was diluted with 50 ml water and maintained for 3 h. The precipitate was filtered off, washed with water, and recrystallized from heptane to give (XIV) in 70% yield, mp 141-142°C. IR spectrum (ν, cm^{-1}): 2226 (CN), 1692 (CO). PMR spectrum (δ, ppm): 1.05 s [6H, $(CH_3)_2C$], 2.49 and 3.13 s (4H, C^6H_2, C^8H_2), 4.04 d (2H, CH_2S), 5.17-5.38 m (2H, CH_2=), 5.95 m (1H, CH=), 7.24 and 7.65 d (4-BrC_6H_4). Found: C, 58.89; H, 4.54; N, 6.51; S, 7.42%. Calculated for $C_{21}H_{19}BrN_2OS$: C, 59.02; H, 4.48; N, 6.56; S, 7.50%.

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