carbon dimension were processed by a $\pi/6$-shifted sine bell window apodization and Fourier transformation. The proton dimension was then processed by $\pi/3$-shifted sine bell window apodization, Fourier transformation, and power spectra multiplication to yield the final matrix. After scaling for plotting, seven level contour plots of the entire matrix and several submatrices were printed on a Watanabe digital plotter. The total processing time was under 5 min. The plotting time was about 1 h.

Acknowledgment. We are grateful to Dr. I. Holden for introducing us to FUCOUP. This work was supported by NIH GM-22479. R.L.H. was and N.H.N. is a recipient of a Univesity of California Regents' Fellowship (1982-1984 and 1984-1985, respectively).

Registry No. 1, 94621-19-9; **2**, 94621-20-2; **3**, 94621-21-3; **4**, 94621-22-4; **5**, 94621-23-5; **6**, 94621-24-6; **7**, 94621-25-7; btmse, 14630-40-1; *i*-PrOAc, 108-21-4; $CH_2{=}C(CH_3)CH(OH)CH_2C(O)OPr\text{-}i$, 94621-15-5; $CH_2{=}C(CH_3)CH(OMe)(CH_2)_2OH$, 94621-16-6; $CH_2{=}C(CH_3)CH(OMe)CH_2C(O)OPr\text{-}i$, 94621-17-7; $CH_2{=}C(CH_3)CH(OMe)(CH_2)_2OTs$, 94621-18-8; $CpCo(CO)_2$, 12078-25-0; $HC{\equiv}C(CH_2)_2C{\equiv}CSiMe_3$, 1578-34-3; methacrolein, 78-85-3; 1-[1,2-dihydro-4,6-bis(trimethylsilyl)benzocyclobuten-1-yl]-3-methoxy-4-methyl-4-pentene, 94621-26-8.

Base-Induced Proton Tautomerism in the Primary Photocyclization Product of Stilbenes

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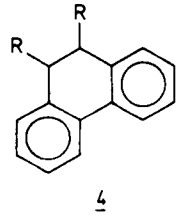
Abstract: The mechanism of the photoformation of 1,4-dihydrophenanthrenes (1,4-DHP) and 9,10-dihydrophenanthrenes from 1,2-diarylethylenes in amine solution is clarified by demonstrating that the amine reacts as a base with the initially formed 4a,4b-dihydrophenanthrene. The predominant formation of 1,4-DHP from stilbene is ascribed to an easy proton transfer from C(4b) to C(4) in 4a,4b-DHP via a deprotonation/protonation step, in which the amine operates as the transferring agent. The product formation in basic *methanolic* solutions proceeds with another mechanism or with less selectivity. When propyl thiolate, having a weak hydrogen-bonding capability, is used as the base, the *solvent*-mediated protonation in the deprotonation/protonation step occurs exclusively at C(9) and leads eventually to 9,10-DHP. When the stronger base sodium methoxide is used, solvent-mediated protonation proceeds rather unselectively at C(2), C(4), and C(9) and causes the ultimate formation of a mixture of 1,2-, 1,4-, and 9,10-DHP. Deuteration experiments indicate that 1,2- and 3,4-DHP are intermediates in the formation of 1,4-DHP (Scheme VII). The former compounds isomerize *photochemically* in the presence of a base. Larger diarylethylenes give only compounds analogous to 9,10-DHP.

In the last decades the photodehydrocyclization of stilbene (**1**) and stilbene-like compounds to phenanthrenes (**3**) has become a well-known photochemical reaction (Scheme I). The 4a,4b-dihydrophenanthrenes (4a,4b-DHP's, **2**) have been accepted as the initially formed photoproducts;[1] their dehydrogenation occurs mostly under oxidative conditions in the presence of O_2, I_2, TCNE, and other oxidants.[1,2] Besides the oxidative reaction, the 4a,4b-DHP's undergo, thermally as well as photochemically, a ring-opening reaction to the parent stilbene.[1a]

Another class of reactions which is exhibited by a number of 4a,4b-DHP's concerns the rearrangement to more stable isomers. Thus, 9,10-DHP's (**4**) have been isolated upon irradiation of several stilbenes with enolizable substituents at the olefinic double bond.[1b,3] Their formation was ascribed to prototropic shifts,[3a,b]



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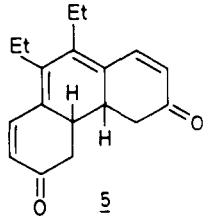

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sometimes in combination with hydrogen radical abstraction recombination steps[3c,d] or thermal as well as photochemical hydrogen shifts[3e,f] in the primary formed 4a,4b-DHP's. According to Doyle and co-workers,[4] 4,4'-dihydroxy-α,α'-diethylstilbene undergoes upon irradiation in a protic medium, even in the presence of oxygen, quantitative conversion into a diketo compound **5**, derived by tautomerism from the corresponding 4a,4b-dihydrophenanthrenediol.

Isomerizations of unsubstituted 4a,4b-DHP's, derived from stilbene or other diarylethylenes, seem to be very rare. Very recently some of us[5] reported on *trans*-6a,16d-dihydrohexahelicene (**8**) formed under argon (Ar) by a [1,5]-suprafacial hydrogen shift from the primary formed photocyclization product (**7**) of 2-styrylbenzo[*c*]phenanthrene (**6**) (Scheme II). Curiously the

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[‡] Université des Sciences et Techniques de Lille.

(1) For recent reviews, see: (a) Muszkat, K. A. *Top. Curr. Chem.* **88**, **1980**, 89. (b) Laarhoven, W. H. *Recl. Trav. Chim. Pays-Bas* **1983**, **102**, 185, 241. (c) Mallory, F. B.; Mallory, C. W. *Org. React. (N.Y.)* **1984**, *30*, 1.
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(3) (a) Rio, G.; Hardy, J. C. *Bull. Soc. Chim. Fr.* **1970**, 3578. (b) Ichimura, K.; Watanabe, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2224. (c) op het Veld, P. H. G.; Laarhoven, W. H. *J. Am. Chem. Soc.* **1977**, *99*, 7221. (d) Srinivasan, R.; Merritt, V. Y.; Hsu, J. N. C.; op het Veld, P. H. G.; Laarhoven, W. H. *J. Org. Chem.* **1978**, *43*, 980. (e) Sargent, M. V.; Timmons, C. J. *J. Chem. Soc.* **1964**, 5544. (f) Wismontski-Knittel, T.; Muszkat, K. A.; Fischer, E. *Mol. Photochem.* **1979**, *9*, 217.
(4) (a) Doyle, T. D.; Filipescu, N.; Benson, W. R.; Banes, D. *J. Am. Chem. Soc.* **1970**, *92*, 6371. (b) Cuppen, Th. J. H. M.; Laarhoven, W. H. *J. Am. Chem. Soc.* **1972**, *94*, 5914. (c) Doyle, T. D.; Benson, W. R.; Filipescu, N. *J. Am. Chem. Soc.* **1976**, *98*, 3262.
(5) Laarhoven, W. H.; Cuppen, Th. J. H. M.; Brinkhof, H. H. K. *Tetrahedron* **1982**, *38*, 3179.

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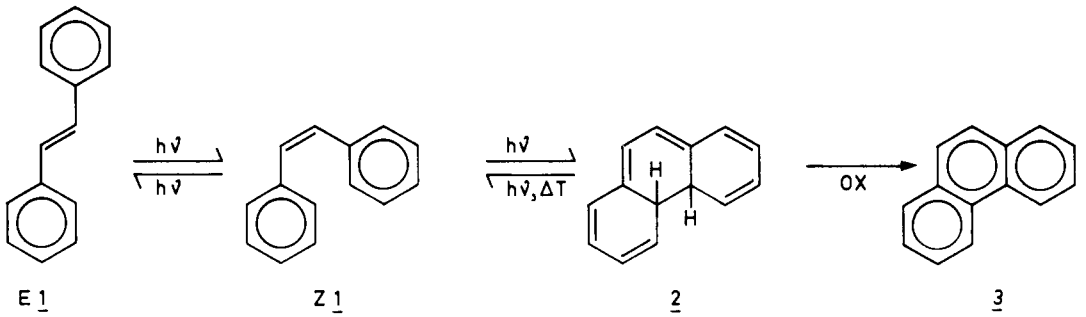
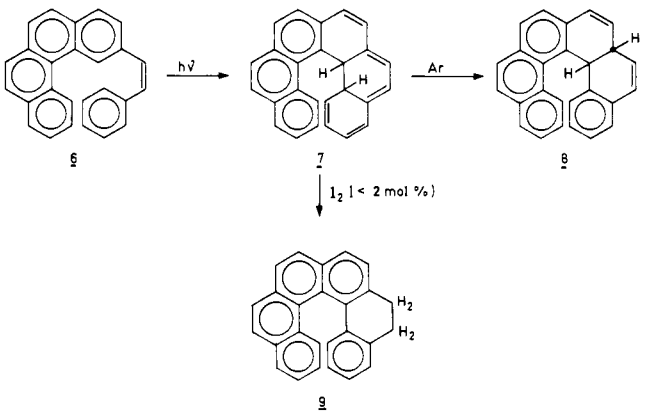
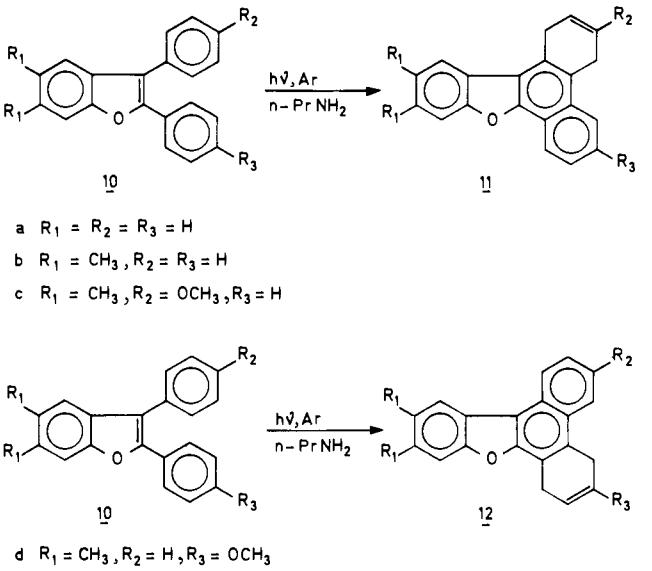
Scheme I



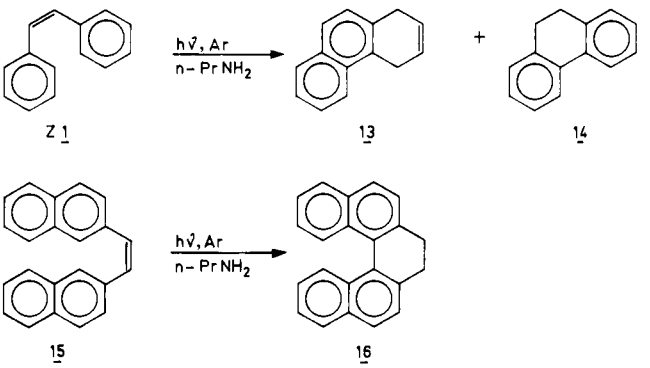
Scheme II



Scheme III



Scheme IV



presence of only a small amount of an oxidant, viz. I_2, altered the reaction pathway, resulting in the formation of 5,6-dihydrohexahelicene (**9**).[6] Isomerizations of 4a,4b-DHP's taking place in the presence of a small amount of an oxidant have been observed earlier.[7]

Several years ago some of us[8] obtained 1,4-dihydrophenanthrene derivatives **11** and **12** upon irradiation of 2,3-diphenylbenzo[*b*]-furans (**10**) in deaerated *n*-propylamine as the solvent (Scheme III). Later, the synthetic application of this reaction was demonstrated by photolyses of other 1,2-diarylethylenes, affording 1,4-DHP's and 9,10-DHP's as the main products.[9,10] They[10] suggested that the amine forces the reaction into an ionic pathway rather than the radical pathway usually invoked in the oxidative process. No conclusive evidence could, however, be given of the mechanism of the reaction, and it seemed worthwhile to engage a detailed investigation into the formation of these DHP's.

Results

Because the formation of 1,4- and 9,10-DHP's is not observed upon irradiation of **1** and **15** in solvents such as methanol, benzene, or (cyclo)hexane, it is clear that the amine enables their formation. At this point we wish to reemphasize that the formation via photoreduction of stilbene or phenanthrene has not been observed.[9,11] Presumably it is the absence of a reaction between stilbene and the primary aliphatic amine, in contrast to that observed between stilbene and secondary or tertiary aliphatic amines,[11] that allows their formation. Therefore, it seems reasonable to suppose that the primary formed photoproduct, viz. the 4a,4b-dihydrophenanthrene, is the precursor of the 1,4- and 9,10-DHP's, especially since the C(4a)–H and C(4b)–H bonds are known to be sensitive to radical and ionic processes.[1,3] Most likely the amine exerts its role on the 4a,4b-DHP.

Experiments in Amine Medium. In order to test the correctness of this hypothesis, we studied the influence of *n*-propylamine on the 4a,4b-DHP **17**, derived from 1,2-di(2-naphthyl)ethylene (**15**) (Scheme IV). This dihydrophenanthrene is especially suited for this purpose because it is oxidized only slowly[12] and has a long thermal half-life time ($\tau_{1/2}$ (25 °C) = 36.8 days[1]).

The photoproduct resulting from irradiation of **15** in deaerated *n*-propylamine solution has been identified as 11,12-dihydrodi-

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(7) (a) Fischer, E., unpublished results. (b) Laarhoven, W. H., unpublished results. Attempts to isolate the DHP's as well as treatment with DDQ resulted in their oxidation, thus affording phenanthrenes.

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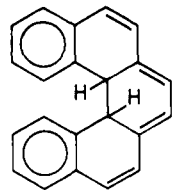
benzo[*c*,*g*]phenanthrene (**16**).[10] Irradiation at 360 nm of 25 mL



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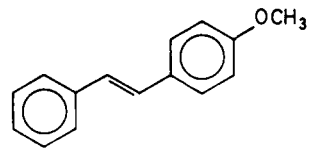


18

of a ca. 10^{-3} M argon-purged cyclohexane solution of **15** for 1 h afforded a certain concentration of the orange-yellow colored **17**. Addition of 25 mL of thoroughly deaerated *n*-propylamine in an argon atmosphere caused an immediate disappearance of the color. After evaporation in vacuo of the solvent, the NMR spectrum of the sample revealed a small signal at δ 2.83 characteristic for the methylene protons of **16**.[10]

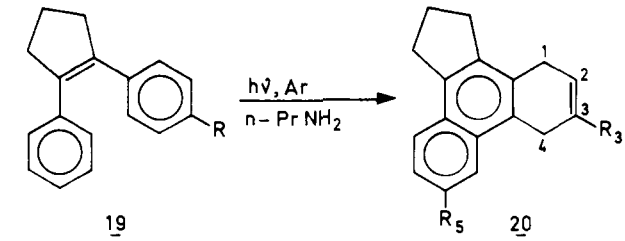
The same result was obtained after addition of the amine in the dark, while after addition of cyclohexane as a blank instead of the amine, only starting material was recovered. When the absorbance change of **17** after addition of the amine was followed at the maximum of the visible absorption band (448 nm[1]) against time, the decay proved to be first order in **17** and second order in the amine, with a rate constant $k = 1.1 \pm 0.1$ L^2/mol^2 min at 30 °C. Comparison with the rate constant of oxidation of **17** in 2,2,4-isooctane ($k = 0.006$ L/mol min at 30 °C[1a]) shows that both reactions have a comparable rate when the amine concentration is roughly equal to the oxygen concentration (usually 10^{-2} M or less[1,13]). At a higher amine concentration, the oxidation will no longer be competitive. These results clearly confirm the intermediacy of the 4a,4b-dihydrophenanthrene in the photoconversion of the diarylethylene in amine medium and the direct participation of the amine in the formation of **16**.

A qualitatively similar result was obtained for stilbene. Irradiation of solutions of stilbene in cyclohexylamine or 1.2 M *n*-propylamine in cyclohexane afforded **13** and **14**. The ratio **13**/**14** was approximately the same as when pure *n*-propylamine is used as the solvent[9] (Table II).

To investigate the influence of substituents on the base-induced formation of 1,4-dihydrophenanthrenes, 0.3×10^{-2} M argon-purged *n*-propylamine solutions of *trans*-stilbene ((*E*)-**1**), *trans*-*p*-methoxystilbene (**18**), 1,2-diphenylcyclopentene (**19a**), 1-(4-(trifluoromethyl)phenyl)-2-phenylcyclopentene (**19b**), and 1-(4-methoxyphenyl)-2-phenylcyclopentene (**19c**) were irradiated through Pyrex at 300 nm for 4 h in a "merry-go-round" apparatus. The product composition of the resulting mixtures was determined by NMR spectroscopy.

trans-Stilbene ((*E*)-**1**) was converted into *cis*-stilbene (50%); the main dihydro, products were **13** (35%) and **14** (5%). *p*-Methoxystilbene (**18**) failed to produce any 1,4- or 9,10-dihydro derivative. (Irradiation for 72 h gave one photoproduct in 20% yield. It was identified from its NMR spectrum (δ 4.7, br s, 1 H; δ 3.5, m, 7 H) as 3-methoxy-1,4-DHP by comparison with the NMR spectrum of 3,6-dimethoxy-1,4-DHP.[9] The rest of the material was a mixture of *cis*- and *trans*-**18**.) The other stilbenes, having a much higher quantum yield of photodehydrocyclization,[1,14,15] were all converted to at least 95%. The cis-fused stilbene **19a** (Scheme V) was converted into only one photoproduct. Its NMR spectrum showed a very narrow AB pattern at δ 6.03 ($J_{AB} = 12.0$ Hz, $J_{allyl} = 1$–2 Hz), corresponding to two cis olefinic protons. Furthermore, besides the signals belonging to the protons of the cyclopentene ring, two two-proton multiplets were present at δ 3.73 and at about δ 3.4, superimposed on a triplet of two methylene protons of the cyclopentene ring. They must correspond to methylene protons. By comparison with the known spectra of 1,4-DHP (**13**), 1,2-DHP (**21**), and 3,4-DHP (**22**) (see Experimental Section), it was concluded that the photoproduct is the 1,4-dihydro derivative **20a** (Scheme V), with the methylene signal at the lower field (δ 3.73) belonging to the protons at C(4). The

Scheme V

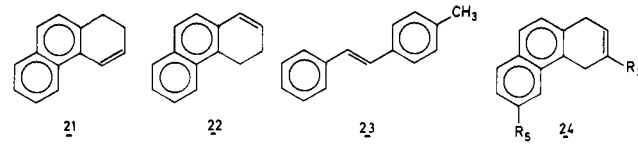


19

a R = H
b R = CF_3
c R = OCH_3

20

a $R_3 = R_5 = H$
b $R_3 = H, R_5 = CF_3$
c $R_3 = OCH_3, R_5 = H$
d $R_3 = H, R_5 = OCH_3$



21 **22** **23** **24**

a $R_5 = H, R_3 = CH_3$
b $R_5 = CH_3, R_3 = H$

photoproducts of **19b** and **19c** were identified by comparison of their NMR spectra with those of other substituted 1,4-DHP's.[9] The NMR spectrum of the *p*-CF_3 derivative exhibited only an AB pattern at δ 6.04 in the region δ 4.0–7.0 and was, therefore, identified as **20b**. The product mixture of the *p*-OCH_3 derivative **19c** showed an AB pattern at 6.0 of very low intensity and a multiplet at δ 4.91, corresponding to one proton. The main product was, therefore, identified as **20c** and the side product as **20d**. All products could readily be converted into the corresponding phenanthrenes by treatment with I_2 in boiling hexane or DDQ in benzene.

The observed difference in chemical yields for the stilbenes parallel the reported difference in quantum yield of photodehydrocyclization.[1,14,16,17] This supports the proposed role of the 4a,4b-DHP in these photoconversions. Furthermore, a strongly directing influence of the substituents is observed. This substituent effect has already been reported[8] for **10c** and **10d** (see Scheme III), and it is also present in *p*-methylstilbene (**23**): upon irradiation in *n*-propylamine, **23** afforded, besides a small amount of the 9,10-dihydro derivative, two other products which were identified as 3-methyl-1,4-DHP (**24a**) and 6-methyl-1,4-DHP (**24b**) by comparison of their NMR spectra with that of 3,6-dimethyl-1,4-DHP.[9] The ratio **24a**/**24b** was 1.9. These substituent effects may point to an ionic mechanism (see further).

In order to make sure that it is merely the amino group that is responsible for the isomerization, it was determined that photolysis of a *tert*-butylamine solution of stilbene yields the same products. Since this amine does not possess α hydrogens, the possibility of a photoreduction[11,18] of the 4a,4b-DHP involving α C–H homolysis could be ruled out, because indeed no other products than **13** and **14** could be detected.

It was concluded that the amine acts as a base by abstraction of a hydrogen atom at C(4a) or C(4b). Therefore, the incorporation of deuterium upon irradiation of N-deuterated amine and the possibility of induction of the conversion under other basic conditions were investigated.

Irradiation in N-Deuterated Amine. Solutions of **10a**, **10b**, and **19a** in N-deuterated *n*-butylamine were irradiated through quartz at 250 nm and through Pyrex at 300 nm. Evaluation of deuterium

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(16) Jungman, H.; Güsten, H.; Schulte-Frohlinde, D. *Chem. Ber.* **1968**, *101*, 2690. Güsten, H.; Klasinc, L. *Tetrahedron* **1968**, *24*, 5499.
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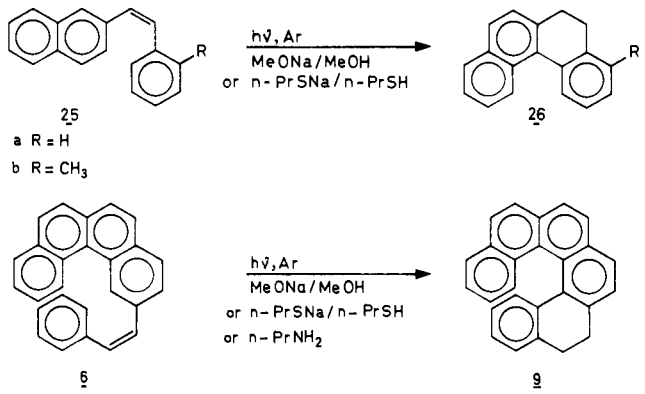
Table I. Percentage of D at the Various Positions in **20a**, **11a**, and **11b** after Irradiation in N-Deuterated *n*-Butylamine[a]

product	position	% D	ratio of D/H
	1	20 ± 5	0.25
	2	10 ± 5	0.11
20a	3	10 ± 5	0.11
	4	40 ± 5	0.67
	1 + 4	37 ± 5	0.59
11a	2 + 3	37 ± 5	0.59
	1 + 4	40 ± 5	0.67
11b	2 + 3	40 ± 5	0.67

[a] For numbering of the positions, see Scheme V.

Scheme VI



incorporation in the resulting 1,4-dihydro derivatives **11a**, **11b**, and **20a** was realized by NMR spectroscopy at 90 and 500 MHz and revealed that deuterium is exclusively incorporated on the 1-, 2-, 3-, and 4-positions. The 500-MHz spectrum of **20a** showed separated signals of all the methylene groups and of the olefinic protons. Unfortunately, the 90- and 500-MHz spectra of **11a** and **11b** gave singlet signals for both olefinic and methylene protons, so that D incorporation could not be determined separately. For all individual positions for compounds **20a** and **11b**, the amount of D incorporated was evaluated by comparison of the signals with those of other aliphatic protons and for compound **11a** by comparison with the aromatic protons. The results (Table I) are independent of the irradiation wavelength.

Irradiations in Basic Alcoholic Solution. Irradiation for 8 h at 300 nm of 5×10^{-3} M deaerated solutions of 2-styrylnaphthalene (**25a**), 2-(2-methylstyryl)naphthalene (**25b**), 1,2-di(2-naphthyl)ethylene (**15**), and 2-styrylbenzo[*c*]phenanthrene (**6**) in 0.2 M $NaOCH_3$ in methanol afforded in high yield (80%) the same 9,10-dihydro derivatives that were previously[9] isolated after irradiations in *n*-propylamine (Schemes IV and VI). This demonstrates that the above described conversions are not limited to amine solutions and affirms the ionic nature of the reaction.

Similar irradiations, employing 6.5×10^{-2} M solutions of *n*-PrSNa in *n*-PrSH, afforded the same products but in much lower yield (8–10%).

A striking change in the product ratio **13**/**14**, compared to that resulting from irradiation in the amine, was observed, however, when stilbene was irradiated in these media.

Table II presents a survey of the composition of the product mixtures obtained from irradiation of stilbene in a variety of basic solutions in a Rayonet photochemical reactor, equipped with a merry-go-round apparatus, through Pyrex at 300 nm. The amounts of the various DHP's in the reaction mixtures after workup were evaluated by NMR and GLC analyses.

From the data in Table II, it can be concluded that the total yield of products decreases at low base concentration. At low base concentrations, the formation of phenanthrene, presumably caused by residual oxygen, became an important side reaction. When *n*-PrSNa was used as the base, only **14** was formed. The use of H_3CONa as the base afforded both **13** and **14**. At lower base concentrations, a third product having multiplets at δ 6.2–6.3 and

Table II. Dihydrophenanthrene Composition of the Reaction Mixtures of Photolysis of Stilbene in Several Deaerated Basic Solvents at 300 nm

base (concn, M) solvent	irradiation time, h	product yield 13	14	21
n-propylamine[a]	16	70	8	
n-propylamine[a]	4	35	5	
cyclohexylamine[a]	16	70	7	
t-butylamine[a]	16	50	12	
n-$PrNH_2$ (1.2 M) cyclohexane[a]	16	30	~4	
n-$PrNH_2$ (1.2 M) MeOH[a]	16	15	30	
$NaOCH_3$ (1.2 M) MeOH[a]	16	40	45	
$NaOCH_3$ (0.6 M) MeOH[a]	16	40	45	
$NaOCH_3$ (0.3 M) MeOH[a]	16	25	35	5–10
$NaOCH_3$ (0.15 M) MeOH[a]	16	5–10	15	5–10
t-BuOK (0.3 M) *t*-BuOH[c]	20	<5	12	12
t-BuOK (0.2 M) *t*-BuOH[c]	20	<5	10	10
n-PrSNa (0.03 M) MeOH[b,d]	8		5	
n-PrSNa (0.3 M) MeOH[b,d]	8		50	
n-PrSNa (0.45 M) MeOH[b,d]	8		70	

[a,b,c] Concentration of stilbene: 3×10^{-3} M (a), 1.5×10^{-2} M (b), 1.9×10^{-2} M (c). [d] 15 vol% benzene because of solubility problems.

Table III. Percentage of D at the Various Positions in **13**, **14**, and **21** after Irradiation of 7×10^{-3} M Solutions of Stilbene in CD_3OD and CD_3OD with 0.6 M $NaOCH_3$

product	position	% D
14	9 + 10	50 ± 5
13[a]	1 + 4	40–50
	2 + 3	40–50[a]
	1	? (0)
	2	50
21	3	0
	4[b]	

[a] The deuterium distribution over C(2) and C(3) was not symmetrical (see text). [b] The signal of H(4) is superimposed by the aromatic signals.

δ 2.3–2.4 became just visible in the NMR spectra of the reaction mixtures. This product could be identified as **21** by comparison with the NMR spectrum and the retention time in GLC analysis of an authentic sample. Enlargement of the stilbene concentration led to product mixtures in which **21** was even present in excess to **13**. The conversion was rather low in such cases. Longer irradiation periods always resulted in the disappearance of **21**.

Because deuterium incorporation might yield further information, 7×10^{-3} M solutions of stilbene in CH_3OD and CD_3OD being 0.6 M in NaOMe were irradiated. After workup the reaction mixture was chromatographed over alumina activated with $AgNO_3$.[19] The fractions were analyzed by NMR spectroscopy. The data of D incorporation are collected in Table III. The incorporation of deuterium at the methylene and olefinic positions in **13** was immediately visible in the NMR spectra by a less extensively split signal of the methylene protons and a partly collapsed signal of one of the olefinic protons.

D incorporation has also taken place in **21** since the signal of H(3) at δ 6.27 showed less splitting than the signal observed upon irradiation in CH_3OH. Assuming no **D** incorporation at C(3) (vide infra), integration indicated 50% D at C(2), which means that the introduced atom has come completely from the solvent. Integrations indicated two protons at C(1). In view of the presence of a persistent impurity with absorption in this region, it can, however, be concluded that at least some D is present at C(1).

No difference in D incorporation after irradiation in CH_3OD and CD_3OD was observed, indicating that a radical abstraction–recombination step as mentioned in ref 3c and d need not be invoked.

In our opinion the presence of D at the olefinic double bond in **13** is only comprehensible when **13** originates from **21** (or **22**)

(18) Cohen, S. G.; Parola, A.; Parsons, G. H. *Chem. Rev.* **1973**, *73*, 141. Barltrop, J. A. *Pure Appl. Chem.* **1973**, *33*, 179.
(19) Murray, E. C.; Keller, R. N. *J. Org. Chem.* **1969**, *34*, 2234.

via H or D transfer. The observation that **21** disappears on prolonged irradiation is another indication for such a process. It would also furnish a satisfactory explanation for the D incorporation at the olefinic double bond in the experiments in amine solutions (see Table I).

Therefore, both **21** and **22** were synthesized,[20-24] and their chemistry was studied under various reaction conditions. (Actually the third reaction product resulting from irradiations in methanolic solution was identified as **21** after the synthesis of **21** and **22**. The NMR data of **21** and **22** given in ref 20 were too incomplete to allow a definite assignment. **21** and **22** could not be distinguished by GLC even under various conditions (column, temperature, N_2 pressure), but their retention times were different from that of **13**.)

Isomerization of 1,2-DHP and 3,4-DHP. Irradiation of deaerated solutions of **13** **21**, and **22** in cyclohexane or methanol did not alter the compounds, so that photochemical isomerizations can be excluded.

The conversion of **21** or **22** into **13** was also not observed when solutions of **21** or **22** in *n*-propylamine or MeOH/*t*-BuOK were left in the dark for 24 h at room temperature. Thermal, base-catalyzed equilibrated between the isomeric DHP's **13**, **21**, and **22** could completely be ruled out by the additional observation that a solution of **13** in CH_3OD/*t*-BuOK did not show any D incorporation on standing for several days at room temperature (compare ref 21).

Irradiation of **21** or **22** in the presence of an amine or a fairly strong base, however, readily gave **13**. In *n*-propylamine, these conversions are very effective and quantitative, having quantum yields which are nearly equal to that of the photoconversion **19a** → **20a** (Φ_{rel} **21** → **13**, 0.86; **22** → **13**, 1.0; **19a** → **20a**, 1.0). In MeOH/*t*-BuOK, the percentage of conversion increased with increasing base concentration. In MeOH/*n*-PrSNA, at comparable concentrations, no conversion into **13** was observed.

The base-induced and light-dependent isomerizations are not parts of an equilibration, in which **13** arises as the major compound, because the occurrence of the reverse reactions (**13** → **21** and **13** → **22**) was never observed: **13** remained unchanged under all conditions, applied to **21** and **22**—separate irradiations of **21** and **22** in MeOH/*t*-BuOK until 50% conversion to **13** afford no trace of **22** and **21**, respectively. Upon irradiation of **21** and **22** in CH_3OD/*t*-BuOK until complete conversion into **13**, the percentage of D at C(1) + C(4) in **13** was 20 ± 5% (i.e., ~0.8D), but no D incorporation at the olefinic double bond in **1o** was observed: this would inevitably be expected if **13** also isomerized into **21** or **22**.

Discussion

From the experiments performed in the amine and alcoholic solution, it is clear that the presence of a base is a prerequisite for the formation of the photoproducts which essentially are isomerized 4a,4b-DHP's and that the isomerization of the primary formed DHP's is an ionic process. The formation of the various products can be rationalized as indicated in Scheme VII.

Interaction of a base with **2** will result in the abstraction of H(4a) or H(4b), as the developing anion will be strongly stabilized by the formation of an aromatic unit. Simultaneous or subequent protonation may lead to several intermediates (**27a-c**) which can be converted into isomers **14**, **21**, **13**, and **22**, containing two aromatic units via a second deprotonation/protonation step. It has been demonstrated that the isomerization of **21** and **22** into **13** are base-induced photochemical reactions.

We assume that all steps depicted in Scheme VII are irreversible. Furthermore, we assume that interconversion of the isomers **27a-c** will be negligible because the methine hydrogen is much more acidic than the methylene hydrogens. A justification of this assumption is found in the relative stability of the various dihydrophenanthrenes (see Table IV).

Bearing in mind that the conversion of **21** and **22** into **13** has been demonstrated, but the isomerizations of **13**, **21**, and **22** into **14** were not observed, it can be concluded that the first deprotonation/protonation step determines the structure of the ultimate product(s). In the isomerizations performed in methanolic solution, this first step is a solvent-mediated reaction, in which the abstraction can be facilitated by simultaneous proton transfer from a solvent molecule. The product ratio of this step is kinetically determined. It does not depend necessarily on the energy differences between **27a**, **b**, and **c** but on the electron densities at various positions in the developing carbanion of **2**.

Scheme VII

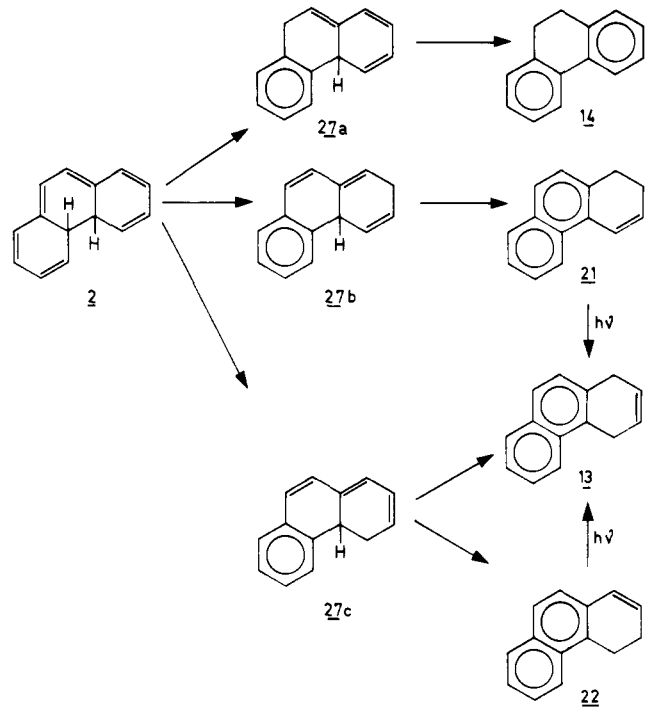
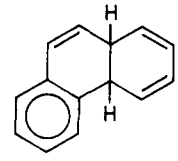


Table IV. Energies (in kJ/mol) of Various Dihydrophenanthrenes Relative to 9,10-DHP (**14**)



28

a cis

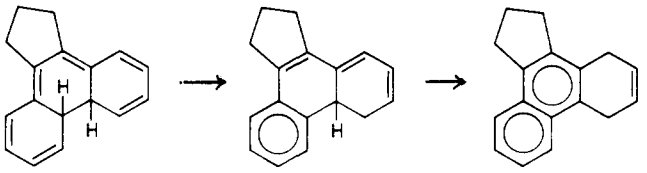
b trans

DHP	ΔE(calcd)[a]	ΔE[b]
2	262	
27a	151	123 ± 17
27b	155	131 ± 17
27c	150	118 ± 17
28a	180	139 ± 17
28b	195	139 ± 17
21	54	58 ± 17
22	58	58 ± 17
13	47	52 ± 17
14	0	0

[a] Calculated by the QCCF/PI method.[23] [b] Data derived from ref 22.

(20) Yagi, H.; Jerina, D. M. *J. Am. Chem. Soc.* **1975**, *97*, 3185. Lehr, R. E.; Schaefer-Ridder, M.; Jerina, D. M. *J. Org. Chem.* **1977**, *42*, 736.
(21) Harvey, R. G.; Sukumaran, K. B. *Tetrahedron Lett.* **1977**, 2387.
(22) Shaw, R.; Golden, D. M.; Benson, S. W. *J. Phys. Chem.* **1977**, *81*, 1716. The value for the heat of formation of 9,10-DHP was taken from their ref 25.
(23) (a) Warshel, A.; Karplus, M. *J. Am. Chem. Soc.* **1972**, *94*, 5612. (b) Warshel, A.; Levitt, M. *QCPE* **1974**, 247. (c) The methine C-H stretching force constant was not optimized. The values of the methylene C-H bond[23a,b] were adopted; for the bending potential describing the ACA angle, the parameters for the ACC angle were used, similar to ref 23d. (d) Paulick, W.; Jung, Ch.; Kempka, U.; Sühnel, J.; Gustav, K. *J. Mol. Struct.* **1981**, *85*, 235.
(24) Hofmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

Scheme VIII

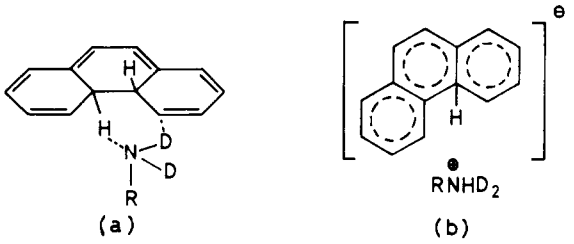


29 30 20a

Table V. Net Electron Density[a] at Various Positions in 4a,4b-Dihydrophenanthrene (2)

position	net electron density	position	net electron density
1	-0.10	4	-0.05
2	-0.08	10a	+0.06
3	-0.13	9	-0.20

[a] Calculated by the extended Hückel method[24] by using the optimized geometry according to the Warshel/Karplus procedure.[23]



(a) (b)

Figure 1.

In the experiments with a thiolate as the base, product yields are low as a consequence of the low hydrogen abstracting capability of the base. Consequently the selectivity is high; only **14** is obtained apparently via **27a** (see Table II).

With a strong base (CH_3O^-), the selectivity is lower. **14** remains the main product, but **21** (via **27b**) and **13** (via **27b** or **c**) arise as side products, and the amounts of these side-products increase when the concentration of CH_3O^- is increased.

Products obtained in CH_3OD contain deuterium at various positions (C(9) and C(10) in **14**, C(1) and C(2) in **21**, C(1), C(2), C(3) and C(4) in **13**, Table I)), indicating that the secondary isomerizations (conversions of the intermediates **27a–c**) are again solvent-mediated, and the same is true for the final steps **21** → **13**, **22** → **13**, because D incorporation in **13** amounts to 2.4–3.0D (0.81–1D at the olefinic positions (see Table III); the data suggest that **13** originates more from **21** or **22** than from **27c**). DHP **21** seems to be the main precursor of **13**. The presence of **22** is never established by NMR in reaction mixtures; with GLC it cannot be detected because its retention time is equal to that of **21**. On the other hand, the ratio **21**/**13** increases at higher stilbene concentrations, where filtering by stilbene becomes more extensive. Another indication for the predominant intermediacy of **21** in the formation of **13** is found in the unequal distribution of D at the positions C(2) and C(3).

The experiments in amine solutions show a different selectivity, giving a 1,4-DHP (**13**) as the main product. This suggests that the isomerization of 4a,4b-DHP proceeds according to another mechanism. The isomerization of **29a** in an N-deuterated amine (Table I) causes a very high D incorporation at C(4) and low D incorporation at the olefinic positions (C(2) and C(3)) of the main product **20a**, suggesting that the main route is as given in Scheme VIII. The formation of **13** from stilbene (**1**) under these conditions should then be ascribed to a route **1** → **2** → **27c** → **13**. The preferential protonation in the first isomerization (**2** → **27c**) at C(4) which has a relatively low electron density (Table V) can be explained when only one amine molecule is involved in this deprotonation/protonation step, as is indicated in Figure 1. This pathway also explains the observed substituent effect. The electron density at C(4) is largely influenced by a substituent at C(3). Other pathways in which two amine molecules are involved in the isomerization (**2** → **27a** → **14** or **2** → **27b** → **21** → **13**) are only side reactions and explain the formation of a slight amount of **14** and D incorporation at the olefinic positions of **13**. In the experiment with *tert*-butylamine (Table II), the pathway via **27a** becomes slightly more important, probably because a transition state as given in Figure 1 is less favorable for steric reasons.

Isomerizations in MeOH/amine give **14** as the main product, because the primary isomerization of **2** becomes again a solvent-mediated step. It deserves attention that the deviating selectivity in isomerizations of 4a,4b-DHP's in amine solutions apparently does not occur with the compounds **10a** and **b**. The resulting products (**11a** and **b**) obtained in a deuterated amine (Table I) show considerable D incorporation at the olefinic carbons. An explanation might be that the acidity of H(4a) and H(4b) of the intermediate 4a,4b-DHP is higher than in **2** or **29**. Their abstraction becomes less dependent on simultaneous protonation at some other position, and the transition state has more carbanion character, because the carbanion is better stabilized by aromatization. This lowers the selectivity of the first isomerization step.

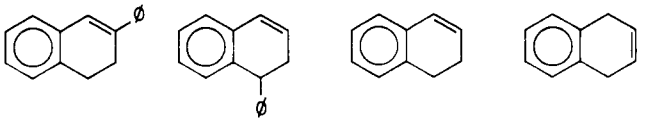
Finally it should be noted that larger diarylethylenes (**6**, **15**, and **25**) yield only 9,10-DHP's, even when irradiated in amine solutions. A transition state as indicated in Figure 1 is apparently unfavorable in isomerizations of 4a,4b-DHP's formed from these compounds, and protonation in the isomerization step occurs only at the position that has the highest electron density.

Conclusion

In summary it can be stated that 4a,4b-DHP's undergo proton tautomerism under basic conditions. The course of the reaction is determined by a delicate interplay of several factors.

In methanolic solutions the selectivity depends on the strength of the base used. PrSNa gives only 9,10-DHP's, because solvent-mediated protonation in the isomerization occurs only at the position of highest electron density (C(9) or C(10)). Using an amine as the base the selectivity is less complete; a 1,4-DHP is a second product. When CH_3O^- is applied as the base, the amounts of 1,4-DHP become considerable, and at lower concentration of the base, even more intermediate side products (1,2-DHP) are found. The solvent-mediated protonation is rather unselective under these considerations and occurs at C(9) or C(10, C(2), and C(4). The absence of 3,4-DHP's and of 1,2-DHP's at higher base concentrations is due to a base-induced and light-dependent conversion of 1,2- and 3,4-DHP's into 1,4-DHP's.

In pure amine solutions, 1,4-DHP's become the main products, because only one amine molecule is involved in the proton transfer. Only a few more examples of amines acting as a proton carrier in a photochemical reaction have been reported.[25,26] In these reactions the amine abstracts a proton from a photochemically formed intermediate in its ground state in analogy to the reactions described in this paper, though the mechanisms of proton transfer are different. D incorporation points to the formation of 1,2- and/or 3,4-dihydro derivatives in those cases, where a 1,4-dihydro derivative is formed. Under the experimental conditions, these dihydrophenanthrenes photoisomerize into the 1,4-DHP. It does,



31 32 33 34

however, not seem to be a general conversion. Irradiation of 3-phenyl-1,2-dihydronaphthalene (**31**) and 1-phenyl-1,2-dihydronaphthalene (**32**), two compounds whose photochemistry has extensively been studied,[27] in *n*-propylamine did not result in the formation of 1-phenyl-1,4-dihydronaphthalene.[27] 1,2-Di-

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(26) van Arendonk, R. J. F. M.; Fornier de Violet, Ph.; Laarhoven, W. H. *Recl. Trav. Chim. Pays-Bas* **1981**, *100*, 256.

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hydronaphthalene (**33**) is converted into 1,4-dihydronaphthalene (**34**), but a large amount of naphthalene is also formed, despite careful degassing procedures. The mechanism of this photoisomerization is at present under investigation.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded on a Bruker WP-60, a Bruker WH-90, or a Bruker WM-500 spectrometer in $CDCl_3$ or CD_2Cl_2 solution and with tetramethylsilane (δ 0) as an internal standard. UV spectra were measured with a Perkin-Elmer 555 spectrometer. GLC analyses were performed with a Girdel instrument equipped with a 2.1-m column filled with Chromosorb W-HP (100–120 mesh) coated with 3% SE-30. Mass spectra were recorded on a Varian MAT SM2B or Finnigan 2200 spectrometer. Melting points were determined by using a Leitz melting point microscope and are uncorrected.

For column chromatography, silica (Merck, 0.063–0.200 mm) or alumina (Baker, aluminum oxide, neutral) was used. HPLC separations (Merck, Kiesel-gel 60H) were carried out on a Jobin-Yvon S.A. Miniprep LC fitted with a Waters Assoc. R404 differential refractometer and a Pye Unicam LC-UV detector.

The amines were dried over molecular sieves (4 Å) or refluxed over potassium hydroxide and distilled immediately before use.

Irradiations. All irradiations were carried out in a Rayonet RPR-100 photoreactor, fitted with RPR 300-nm lamps, through Pyrex, or, where indicated, fitted with Rul 253.7-nm lamps, through quartz.

The solutions were deaerated either by several freeze–pump–thaw cycles to a residual pressure of 2.5×10^{-5} torr or by flushing with argon for 30 min. The argon was purified from oxygen through a BTS catalyst and dried over phosphorus pentoxide, silica, and potassium hydroxide.

The solvents were removed under vacuum or by a stream of nitrogen. The reaction mixtures resulting from irradiation of alcoholic solutions were dissolved in benzene or diethyl ether and washed several times with water. The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure to dryness.

Yields were determined from the crude reaction mixtures by NMR and GLC analyses. In the case of the GLC analyses, the crude reaction mixture resulting from irradiations of amine solutions was initially purified by column chromatography on a neutral alumina column to remove tarry materials.

Isolation of the photoproducts was achieved by column chromatography over silica or alumina by using hexane as the eluent. The decay of **17** in the presence of amine was measured spectrophotometrically at 448 nm at 30 °C. The procedure was as follows: a 10^{-3} M solution of **15** in cyclohexane was flushed with argon for 30 min. Under argon 2 mL of the solution was pipetted into a quartz cuvet and irradiated with a Philips HPK-125 lamp for 1 h. Deaerated *n*-propylamine and cyclohexane were mixed under argon, and 1 mL of the solution was pipetted and added to the irradiated solution of **15** to afford resulting amine concentrations ranging from 0.3 to 0.6 mol/L. The solutions were well shaken, and the absorbance of **17** followed against time.

The relative quantum yields of the photoconversion of **21**, **22** and **19a** in deaerated *n*-propylamine were determined by several irradiations of 4 mL of 2.4×10^{-4} M solutions in a quartz cuvet with a Bausch & Lomb HP-100 light source through a Bausch & Lomb 33-86-79 high intensity monochromator at 313 nm (bandwidth 10 nm). The percentages of conversion were calculated from the UV spectra and were always less than 30%. Tests to control constant light intensity gave percentages of conversion that were equal within 5%.

Starting Materials and Products. The synthesis of most of the starting materials and identification of the products have previously been described.[6,8-10]

***N,N*-Dideuterio-*n*-butylamine.** *n*-Butylamine was deuterated by decomposition of the tetraarsenic-hexa(*n*-butylimide) complex by D_2O according to Vetter[28] and Kahntlehner.[29] The NMR spectrum revealed, besides full N deuteration, the presence of 25% D at the α C atom ($CH_3CH_2CH_2CHDND_2$).

1,4-Dihydrophenanthrene (13) was synthesized and isolated as previously described:[9] UV (methanol) λ_{max} (log ϵ) 321 nm (3.25), 313 (sh, 3.29), 307 (3.40), 291 (3.74), 280 (3.80), 272 (3.77), 260 (3.68), 251 (3.77), 226 (4.66).

Cyclobutyl Phenyl Ketone. This compound was synthesized from cyclobutanecarboxylic acid by refluxing in thionyl chloride and a subsequent Friedel–Crafts acylation following usual procedures: bp 62–64 °C/0.15 mmHg (lit.[30] 78–82 °C/0.7 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.92–3.60 (m, cyclobutyl, H, 6 H), 4.00 (m, α H, 1 H), 7.35–7.55 (m, aromatic H, 3 H), 7.80 –7.96 (m, aromatic H, 2 H).

Cyclobutyldiphenylcarbinol was synthesized by a Grignard reaction, following usual procedures from cyclobutyl phenyl ketone in 70% yield: mp 37.0–37.5 °C (lit.[31] 54 °C); ^{1}H NMR ($CDCl_3$) δ 1.55–2.10 (m, cyclob. H, 6 H), 2.19 (s, OH, 1 H), 3.41 (m, α H, 1 H), 7.16–7.37 (m, aromatic H, 10 H); UV (methanol) λ_{max} (log ϵ) 260 nm (2.63), 217 (3.86); mass spectrum, *m/e* (relative intensity) 238 (M^+, 12), 220 (4), 210 (2), 191 (5), 183 (100), 165 (10), 152 (7), 143 (3), 133 (8), 105 (56); exact mass 238.137 ± 0.003, theory 238.136.

1,2-Diphenylcyclopentene (19a) was prepared in 75% yield by dehydration of cyclobutyldiphenylcarbinol in refluxing 98–100% formic acid for 8 h according to Rio;[32] **19a** was separated from its isomers by HPLC by using hexane as the eluent and recrystallized from ethanol; mp 60–61 °C (lit.[32] 61–62 °C); ^{1}H NMR ($CDCl_3$) δ 2.05 (m, methylene H, 2 H, J = 7.0 Hz), 2.86 (t, methylene H, 4 H, J = 7.0 Hz), 7.13 (s, aromatic H, 10 H); UV (methanol) λ_{max} (log ϵ) 270 nm (4.03), 224 (4.19); mass spectrum, *m/e* (relative intensity) 220 (M^+, 45), 129 (70), 115 (58), 91 (100), 77 (39). Anal. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.82; H, 7.24.

Cyclobutyl(4-(trifluoromethyl)phenyl)phenylcarbinol was synthesized by a Grignard reaction from cyclobutyl phenyl ketone in 70% yield: mp 69.0–70.0 °C; ^{1}H NMR ($CDCl_3$) δ 1.60–2.15 (m, cyclob. H, 6 H), 2.25 (s, OH, 1 H), 3.42 (m, α H, 1 H), 7.2–7.6 (m, aromatic H, 9 H); UV (methanol) λ_{max} (log ϵ) 257 nm (3.22), 219 (4.11); mass spectrum, *m/e* (rel intensity) 306 (M^+, 7), 287 (2), 262 (2), 251 (100), 207 (2), 183 (5), 173 (28), 145 (6), 105 (4); exact mass 306.291 ± 0.003, theory 306.292.

1-(4-(Trifluoromethyl)phenyl)-2-phenylcyclopentene (19b) was prepared in a similar procedure as given for **19a** in 60% yield and obtained as an oil: ^{1}H NMR ($CDCl_3$) δ 2.07 (q, methylene H, 2 H, J = 7.5 Hz), 2.92 (t, methylene H, 4 H, J = 7.5 Hz), 7.0–7.5 (m, aromatic H, 9 H); UV (methanol) λ_{max} (log ϵ) 282 nm (4.02), 228 (4.18); mass spectrum, *m/e* (rel intensity) 288 (M^+, 100), 273 (34), 219 (44), 91 (73); exact mass 288.114 ± 0.003, theory 288.112.

Cyclobutyl(4-methoxyphenyl)phenylcarbinol was synthesized by a Grignard reaction from cyclobutyl phenyl ketone in 80% yield and obtained as an oil: ^{1}H NMR ($CDCl_3$) δ 1.7–2.1 (m, cyclob. H, 6 H), 2.14 (s, OH, 1 H), 3.38 (m, α H, 1 H), 3.76 (s, OCH_3, 3 H), 6.7–6.8 (m, aromatic H, 2 H), 7.2–7.4 (m, aromatic H, 7 H); UV (methanol) λ_{max} (log ϵ) 281 nm (3.13), 275 (3.21), 226 (4.09), 204 (4.32); mass spectrum, *m/e* (rel intensity) 268 (M^+, 18), 250 (6), 236 (5), 227 (41), 220 (22), 213 (100), 201 (19), 160 (74), 135 (54), 105 (60); exact mass 268.146 ± 0.003, theory 268.146.

1-(4-Methoxyphenyl)-2-phenylcyclopentene (19c) was prepared in a similar procedure as given for **19a** in 40% yield and obtained as an oil: ^{1}H NMR ($CDCl_3$) δ 2.02 (q, methylene H, 2 H, J = 7.0 Hz), 2.87 (t, methylene H, 4 H, J = 7.0 Hz), 3.75 (s, OCH_3, 3 H), 6.90 (d, aromatic H, 2 H, J = 8.5 Hz), 7.06 (d, aromatic H, 2 H, J = 8.5 Hz), 7.18 (s, aromatic H, 5 H); UV (methanol) λ_{max} (log ϵ) 276 nm (4.05), 232 (4.21); mass spectrum, *m/e* (rel intensity) 250 (M^+, 97), 235 (23), 219 (35), 91 (100).

9,10-Cyclopenteno-1,4-dihydrophenanthrene (20a). A stream of argon was led through a solution of **19a** (10^{-3} mol/L) in *n*-propylamine during 0.5 h. Then the solution was irradiated in a Pyrex tube at 300 nm for 5 h. After evaporation of the solvent, the product was purified by column chromatography on silica with hexane as the eluent: mp 146.5–147.5 °C; ^{1}H NMR ($CDCl_3$) δ 2.24 (q, methylene H, 2 H, J = 7.0 Hz), 3.01 (t, methylene H, 2 H, J = 7.0 Hz), 3.29 (t, methylene H, 2 H, J = 7.0 Hz), 3.4 (m, methylene H at C(1), 2 H), 3.73 (m, methylene H at C(4), 2 H), J_{allyl} (d, H(2) or H(3), 1 H, $J_{2,3}$ = 12.0, J_{allyl} = 1–2 Hz), 6.05 (d, H(3) or H(2), 1 H, $J_{2,3}$ = 12.0, J_{allyl} = 1–2 Hz), 7.3–8.0 (m, aromatic H, 4 H); UV (methanol) λ_{max} (log ϵ) 327 nm (2.95), 294 (3.77), 2.85 (sh, 3.73), 272 (3.63), 255 (3.69), 240 (4.71), 234 (sh, 4.68), 216 (4.55); mass spectrum, *m/e* (rel intensity) 220 (M^+, 100), 205 (41), 191 (83), 178 (35), 165 (37), 152 (15), 101 (28), 94 (28). Anal. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.77; H, 7.27.

9,10-Cyclopenteno-6-trifluoromethyl-1,4-dihydrophenanthrene (20b) was prepared from **19b** in a similar procedure as given for **20a** and identified from its NMR spectrum: ^{1}H NMR ($CDCl_3$) δ 2.27 (q, methylene H, 2 H, J = 7.0 Hz), 3.04 (t, methylene H, 2 H, J = 7.0 Hz), 3.29 (t, methylene H, 2 H, J = 7.0 Hz), 3.4 (m, methylene H at C(4), 2 H), 3.80 (m, methylene H at C(1), 2 H), 6.04 (AB, H(2) and H(3), 2 H, J = 12.0 Hz), 7.1–8.2 (m, aromatic H, 3 H).

9,10-Cyclopenteno-3-methoxy-1,4-dihydrophenanthrene (20c) and 9,10-cyclopenteno-6-methoxy-1,4-dihydrophenanthrene (20d) were prepared from **19c** in a similar procedure as given for **20a**. They were not separated and identified from the NMR spectrum.

20c: ^{1}H NMR ($CDCl_3$) δ 2.27 (q, methylene H, 2 H, J = 7.0 Hz), 3.0 (t, methylene H, 2 H, J = 7.0 Hz), 3.3 (t, methylene H, 2 H, J =

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7.0 Hz), 3.4 (m, methylene H at C(4), 2 H), 3.6 (m, methylene H at C(1), 2 H), 3.68 (s, OCH_3, 3 H), 4.91 (m, olefinic H, 1 H), 7.0–8.0 (m, aromatic H, 4 H).

20d: ^1H NMR ($CDCl_3$) δ 6.0 (dd, olefinic H, 2 H).

1,2-Dihydrophenanthrene (21). This compound was synthesized by known methods:[20] ^1H NMR ($CDCl_3$) δ 2.2–2.5 (m, methylene H at C(2), 2H), 2.8–3.0 (m, methylene H at C(1), 2 H), 6.1–6.4 (m, olefinic H at C(3), 1 H), 7.2–7.3 (m, olefinic H at C(4), 1H), 7.2–8.2 (7, aromatic H, 6 H); UV (methanol) λ_{max} (log ϵ) 336 nm (3.59), 329 (3.69), 314 (3.88), 301 (3.79), 293 (3.79), 282 (3.62), 275 (3.60), 236 (4.66).

3,4-Dihydrophenanthrene (22) was synthesized by known methods:[20] ^1H NMR ($CDCl_3$) δ 2.3–2.6 (m, methylene H at C(3), 2 H), 3.1–3.3 (m, methylene H at C(4), 2 H), 6.0–6.2 (m, olefinic H at C(2), 1 H), 6.5–6.7 (m, olefinic H at C(1), 1H), 7.2–8.2 (m, aromatic H, 6 H); UV (methanol) λ_{max} (log ϵ) 345 nm (sh, 2.53), 323 (3.68), 311 (3.82), 299 (3.74), 259 (4.71), 249 (4.65), 241 (4.42), 233 (4.27), 212 (4.40).

3-Methyl-1,4-dihydrophenanthrene (24a) and 6-Methyl-1,4-dihydrophenanthrene (24b). An argon-flushed 10^{-3} M solution of *trans-p*-methylstilbene in *n*-propylamine was irradiated at 300 nm for 18 h. After evaporation of the solvent, the NMR spectrum of the crude reaction mixture revealed the presence of two isomers which were identified by comparison with the NMR spectrum of 3,5-dimethyl-1,4-dihydrophenanthrene[9] as **24a** and **24b**.

24a: ^1H NMR ($CDCl_3$) δ 1.92 (s, CH_3, 3 H), 3.3–3.7 (m, methylene H, 4 H), 5.73 (br s, olefinic H, 1 H), 7.1–8.0 (m, aromatic H, 6 H).

24b: ^1H NMR ($CDCl_3$) δ 2.54 (s, CH_3, 3 H), 3.3–3.7 (m, methylene H, 4 H), 6.06 (br s, olefinic H, 2 H), 7.1–8.0 (m, aromatic H, 5 H).

1,2-Dihydronaphthalene (33) was synthesized from α-tetralone following the procedure by which **31** and **32** were synthesized.[27] It was purified by bulb-to-bulb distillation.

1,4-Dihydronaphthalene (34). This compound was synthesized according to the procedure of Nieuwstad and van Bekkum.[33] Protonation of the anion to generate **34** was made by the addition of ethanol.

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Registry No. (*E*)-**1**, 103-30-0; (*Z*)-**1**, 645-49-8; **6**, 20508-11-6; **9**, 69103-81-7; **10a**, 13054-95-0; **10b**, 14770-93-5; **11a**-d_2 (isomer 1), 94484-29-4; **11a**-d_2 (isomer 2), 94484-30-7; **11b**-d_2 (isomer 1), 94484-31-8; **11b**-d_2 (isomer 2), 94484-32-9; **13**, 20244-28-4; **13**-d_2 (isomer 1), 94484-38-5; **13**-d_2 (isomer 2), 94484-39-6; **14**, 776-35-2; **14**-d_2 (isomer 1), 94498-88-1; **15**, 2633-08-1; **16**, 7427-84-1; **17**, 28124-10-9; (*Z*)-**18**, 1657-53-0; (*E*)-**18**, 1694-19-5; **19a**, 1485-98-9; **19b**, 93370-99-1; **19c**, 93371-00-7; **20a**, 94484-21-6; **20a**-*d* (isomer 1), 94484-33-0; **20a**-*d* (isomer 2), 94484-34-1; **20a**-*d* (isomer 3), 94484-35-2; **20a**-*d* (isomer 4), 94484-36-3; **20b**, 94484-22-7; **20c**, 94484-23-8; **20d**, 94484-24-9; **21**, 56179-83-0; **21**-*d* (isomer 1), 94484-40-9; **21**-*d* (isomer 2), 94484-41-0; **21**-*d* (isomer 3), 94484-42-1; **21**-*d* (isomer 4), 94484-43-2; **22**, 38399-10-9; **23**, 4714-21-0; **24a**, 94484-25-0; **24b**, 94484-26-1; **25a**, 2039-70-5; **25b**, 94484-37-4; **26a**, 80663-26-9; **26b**, 80663-27-0; **33**, 447-53-0; **34**, 612-17-9; CD_3OD, 811-98-3; D_2O, 7789-20-0; $CH_3CH_2CH_2CHDND_2$, 94484-18-1; $NaOCH_3$, 124-41-4; *n*-PrSNa, 6898-84-6; *n*-PrSH, 107-03-9; CH_3OD, 1455-13-6; *t*-BuOK, 865-47-4; *t*-BuOH, 75-65-0; *N,N*-dideuterio-*n*-butylamine, 17529-81-6; tetraarsenichexabutylimide, 3690-32-2; cyclobutyldiphenylcarbinol, 4404-60-8; cyclobutyl(4-(trifluoromethyl)phenyl)phenylcarbinol, 94484-19-2; cyclobutyl(4-methoxyphenyl)phenylcarbinol, 94484-20-5; *n*-propylamine, 107-10-8; *trans-p*-methylstilbene, 1860-17-9; α-tetralone, 529-34-0; 3-methoxy-1,4-DHP, 94484-27-2; 3-methyl-9,10-DHP, 94484-28-3; cyclobutyl phenyl ketone, 5407-98-7; cyclobutanecarboxylic acid, 3721-95-7; cyclobutanecarbonyl chloride, 5006-22-4; benzene, 71-43-2; cyclohexane, 110-82-7; stilbene, 588-59-0; *tert*-butylamine, 75-64-9; methanol, 67-56-1; cyclohexaneamine, 108-91-8; naphthalene, 91-20-3.

Structural Studies of a New Antitumor and Antiviral Agent: Selenazofurin and Its α Anomer

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Abstract: The crystal and molecular structures of the new antitumor and antiviral agent selenazofurin (2-β-D-ribofuranosylselenazole-4-carboxamide, $C_9H_{12}N_2O_5Se$ (I)) and its α anomer (2-α-D-ribofuranosylselenazole-4-carboxamide, $C_9H_{12}N_2O_5Se$ (II)) have been determined by using single-crystal X-ray diffraction techniques employing Cu Kα radiation. I crystallizes in space group $P2_12_12_1$ with cell dimensions a = 5.1284 (4) Å, b = 13.083 (1) Å, c = 16.536 (1) Å, and Z = 4. The structure was refined to a conventional R value of 0.049 for all data based on 2359 reflections. The α anomer crystallizes in space group $P2_12_12_1$ with cell dimensions a = 5.4545 (2) Å, b = 9.3964 (4) Å, c = 21.656 (1) Å, Z = 4 and was refined to R = 0.031 for all 1263 independent reflections. The absolute configuration of each structure was confirmed by refinement of the corresponding enantiomorph and application of Hamilton's significance test. The selenazole ring in each structure is close to planar and shows some conjugation. The sugar moiety in selenazofurin shows a C2′ endo pucker, and a C2′ exo pucker is seen in the α-anomer. In each structure the conformation about the C-glycosyl bond is such that the selenazole Se forms a close intramolecular contact with the furanose ring oxygen O1′. These results are compared to those obtained for the thiazole analogue tiazofurin, and a model for drug activity is discussed.

Selenazofurin (2-β-D-ribofuranosylselenazole-4-carboxamide,[1] NSC 340847 (I)) is the selenium analogue of the antitumor agent tiazofurin (2-β-D-ribofuranosylthiazole-4-carboxamide, NSC 286193[5]). In this analogue the sulfur atom in the heterocyclic base is replaced by a selenium atom yielding a C-glycosyl selenazole. Selenazofurin is five times more cytotoxic than tiazofurin against P388 and L1210 cells in vitro and is about equally effective against Lewis lung carcinoma at slightly lower doses.[1,2,3] It is

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