Tetrahedron. Vol. 31, pp. 2023 to 2028. Pergamon Press 1975. Printed in Great Britain

REDUCTIVE PHOTOCYCLIZATION OF BENZO[B]FURANS AND THEIR ANALOGS[1]

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(*Received in UK 9 December 1974; Accepted for publication 25 March 1975*)

Abstract—The UV irradiation of substituted 2,3-diphenylbenzo[b]furans and of 2,3-diphenyl-5-t-butylfuran in n-propylamine gives 1,4-dihydro derivatives of the corresponding aromatic cyclized compounds. This reaction does not involve a photoreduction. It can be concluded from deuterium labelling experiments that H atoms of the alkyl chain of n-propylamine are incorporated in the product. When the solvent is not an unhindered primary amine, only totally aromatic photocyclized products are obtained. It is proposed that hydrogens eliminated during formation of the isolated compounds are released in a reductive form and not as radicals. This is supported by the fact that acenaphthylene is reduced when irradiated in n-propylamine together with 2,3-diphenylbenzo[b]furan under conditions which do not promote, photoreduction. This seems to be a general finding in that the irradiation of stilbene in n-propylamine to acenaphthylene is the same as that of 2,3-diphenylbenzo[b]furan.

Photocyclization of stilbene-like compounds to the corresponding phenanthro derivatives is a general process.[3] In most cases, the products are aromatic compounds. Evidence for the formation of 4a,4b-dihydrophenanthrene intermediates has been provided in the case of stilbene[4] and 1,2-diphenylcyclopentene,[5] but such derivatives have never been isolated. The only stable cyclized 4a,4b-dihydrophenanthrene compound reported and caracterized is 1, 3, 4a, 4b, 6, 8-hexamethyldihydrophenanthrene,[6] which exists in equilibrium with its open-chain isomer 1,1',3,3',5,5'-hexamethylstilbene.

When 1,2-diphenylethylene derivatives containing electron-withdrawing substituents at the C-1 or at the C-1 and C-2 are irradiated in degassed solutions, the corresponding 9,10-dihydrophenanthrenes are formed.[7] Srinivasan and Hsu have proved that the formation of 9,10-dihydrophenanthrene derivatives involves two radical abstractions of the solvent hydrogens.[8]

We wish to report the formation of other dihydro derivatives and to analyse the role of primary amines in this reaction.

I. *Structure of the products formed by photocyclization of 2,3-diphenylbenzo[b]furans*

When 2,3-diphenylbenzo[b]furan **1a** is irradiated using solvents such as methanol, ethanol, ether or chloroform it is converted into benzo[b]phenanthro[9,10-d]furan **2a** with a yield of 52%. This photocyclization is to be expected, because it has already been reported that 2,3-diphenyl-6-dodecycloxybenzo[b]furan irradiated in cyclohexane is converted into the corresponding benzo[b]phenanthro[9,10-d]furan.[9]

When **1a** is irradiated under conditions described above, in n-propylamine under nitrogen, a small quantity (12%) of **2a** is formed together with a large amount (65%) of another compound **3a**, which appears to be dihydro derivative of **2a**.

As shown in Table 1, two equivalent vinylic and four equivalent methylene hydrogens appear in the NMR spectrum of **3a** along with eight aromatic protons. The coupling constant between the methylene and vinylic hydrogens, detected by double resonance, is small ($J < 1$ Hz).

Compound **3a** incorporates two Br atoms and the dibromo derivative thus formed is converted into **2a** when refluxed in pyridine. This implies that the two methylene groups are not adjacent. Since **3a** has eight aromatic hydrogens, the two methylene groups must be in the same 6-membered ring. They are, therefore, 1–4 with respect to each other.

To determine the part of the molecule containing the methylene and vinylic protons, we have irradiated 2,3-diphenyl-5-methylbenzo[b]furan (**1b**) and 2,3-diphenyl-5,6-dimethylbenzo[b]furan (**1c**) in n-propylamine. The integration of the NMR spectra of the dihydro derivatives **3b** and **3c** formed from these compounds shows clearly (Table 1), that the presence of one or two Me groups in the benzene part of the molecule has no effect upon the number and upon the chemical shift of the methylene and vinylic hydrogens of the dihydro compounds. It can therefore be concluded that the methylene and vinylic hydrogens are in one of the two side rings of the phenanthrene part of the molecule.

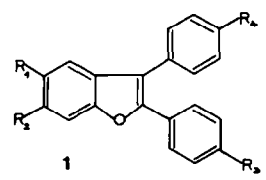
To determine the ring containing these hydrogens we have irradiated 2-phenyl-3(4'-methoxyphenyl)-5-methylbenzo[b]furan (**1d**) and 2-(4'-methoxyphenyl-3-phenylbenzo[b]furan (**1e**) in n-propylamine. Both compounds are thus converted into dihydro derivatives of benzo[b]phenanthro[9,10-d]furan (**3d** and **4** respectively). Integration of the NMR spectrum of these compounds (*cf* Table 1) shows that they contain only one vinylic proton but, like **3a**, four equivalent methylene hydrogens. The coupling constant between the two kinds of hydrogens is small, as in the case of **3a**. ($J < 1$ Hz).

From the NMR spectra (*cf* Table 1) it can be deduced that the OMe group, the vinylic and the methylene hydrogens are in the same 6-membered ring. Comparison of the chemical shifts of the methylene protons of **3a** and of **3d** and **4** (they are very close) suggests that, as in **3a**, also in the two latter compounds the two methylene groups are not adjacent. If it were so, two hydrogens would be allylic and the other two benzylic. Therefore, they would be less deshielded that the corresponding protons of **3a** which are allylic and benzylic at the same time. This argument is supported by the fact that, as **3a** and **3d** incorporate two Br atoms and that the dibromo compounds so formed are transformed into an aromatic

Table 1. NMR spectra of the 1,4-dihydro compounds—Chemical shifts of the various groups of protons (δ in ppm with respect to TMS used as internal reference: solvent: CCl_4).

	Aromatic	Vinylic	Méthylene	Methoxy	Methyl
3a	7.30 - 8.60 (8)	6.12 (2)	3.66 (4)		
3b	6.80 - 9.00 (7)	6.30 (2)	3.90 (4)		2.68 (3)
3c	7.35 - 8.50 (6)	6.21 (2)	3.83 (4)		2.48 (3) 2.54 (3)
3d	7.30 - 8.80 (7)	6.24 (1)	3.78 (4)	4.02 (3)	2.53 (3)
4	7.02 - 8.60 (8)	4.88 (1)	3.80 (4)	3.68 (3)	
10	6.85 (1) 7.30 - 8.60 (4)	6.00 (2)	3.72 (4)		1.45 (9)

The numbers in parentheses are the numbers of protons corresponding to the group.



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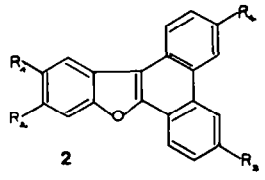

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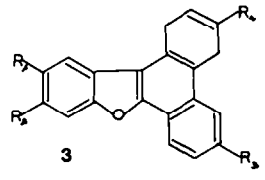
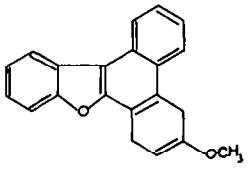


3

a. $R_1=R_2=R_3=R_4=H$
d. $R_1=CH_3, R_2=R_3=H, R_4=OCH_3$

b. $R_1=CH_3, R_2=R_3=R_4=H$
e. $R_1=R_2=R_4=H, R_3=OCH_3$

c. $R_1=R_3=CH_3, R_2=R_4=H$



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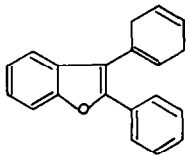

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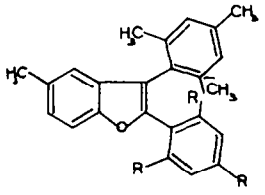


6 R=H

7 R=CH_3

compound, 3-methoxyphenanthro[9,10-d]furan (**2d**), when refluxed in pyridine.

On the basis of the previous arguments it can be deduced that **3d** is 1,4 - dihydro - 3 - methoxy - 12 - methylbenzo[b] - phenanthro[9,10-d]furan and **4** is 5,8 - dihydro - 6 methoxybenzo[b]phenanthro[9,10-d]furan. Because the chemical shifts of the vinylic protons of **3a**, **3b**, **3c** and **3d** are similar and quite different from the chemical shift of the vinylic protons of **4**, it is proposed that the structures of **3a**, **3b** and **3c** are similar to that of **3d**, but different from **4**. This leads to the conclusion that **3a** is 1,4 - dihydrobenzo[b]phenanthro[9,10-d]furan, **3b** its 12-methyl derivative and **3c** its 12,13-dimethyl derivative.

II. *Mechanism of the formation of the dihydro derivatives*

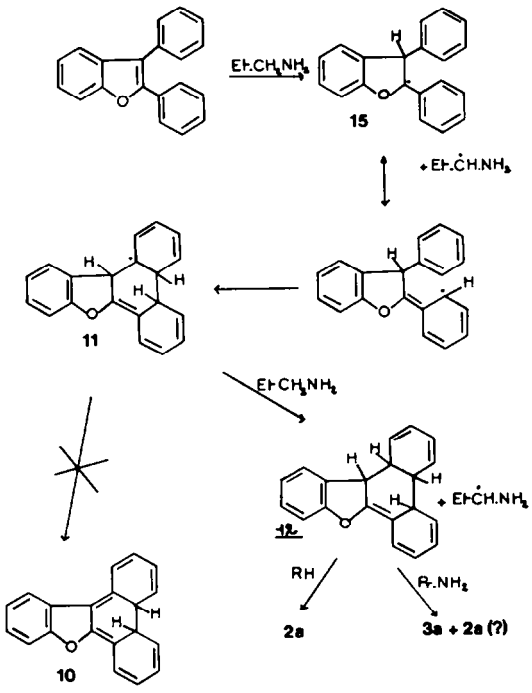
1. *Photoreduction hypothesis.* Since dihydro compounds are formed from 2,3 - diphenylbenzo[b]furans in n-propylamine whereas in methanol, ethanol, ether or chloroform, the photocyclization product is the aromatic derivative, suggests that in n-propylamine the compounds formed in the first step are photoreduced by the amine.[10] The formation of a small amount of **2a** together with **3a** during the photolysis of **1a** in n-propylamine supports this hypothesis.

This is incorrect since **2a** is not photoreduced when irradiated in n-propylamine under conditions used to form **3a** from **1a**. Also it is not reduced when irradiated in n-propylamine containing a small amount of ethanol.[11]

The first step in the formation of **3a** could be the photo reduction of the starting material **1a** prior to cyclization, the primary product being in this case a dihydro compound such as **5**. This assumption, however, is not probable for the following reasons:

5 or an isomer have not been detected. 2 - Phenyl - 3 - (2',4',6' - trimethylphenyl) - 5 - methylbenzo[b]furan (**6**) and 2,3-bis-(2',4',6'-trimethylphenyl)-phenyl)-5-methylbenzo[b]furan (**7**) which, as expected, fail to cyclize upon UV irradiation, are not photoreduced when irradiated in n-propylamine.

When the solvent is triethylamine with or without a small amount of ethanol (protic solvents are known to favor the photoreduction the photreduction of aromatic substrates[11]), di-n-propylamine or t-butylamine, the only photocyclized compound formed from **1a** is **2a**. With diethylamine as the medium, **2a** is the main product (45%), but a small amount of **3a** (10%) is also formed. These facts excluded the hypothesis that the formation of **3a** involves a photoreduction either of the starting compound or a reaction, intermediate. It is well known that the ease of reduction of an aromatic compound or of an olefin decreases when going from a tertiary amine to a primary amine.

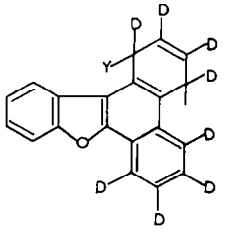


Scheme 1

In n-butylamine, **1a** is converted to **3a** with the same yield as when the solvent is n-propylamine. From these data it can be concluded that dihydro compounds such as **3a** are formed mainly in sterically unhindered primary amines.

2. *Origin of the* C-1 *and* C-4 *hydrogens of* 1,4 - *dihydrobenzo[b]phenanthro*[9,10-*d*]*furan* (**3a**). To determine whether these hydrogens are the ortho dihydrogens of the phenyl substituents of the starting material, eliminated during the photocyclization, we have studied the photocyclization of 2,3-bis(pentadeuterophenyl) benzo[b]furan **8** in n-propylamine. It can be deduced from the integration of the NMR spectrum of the product **9**, that the two hydrogens (2Y) added during the photoreaction to C-1 and C-4 of **9** correspond statistically to 1·25 of protium and 0·75 of deuterium. This means, that not only some deuterium is being released from the ortho positions of the phenyl groups of **8** during the photocyclization but also that hydrogens from n-propylamine are incorporated into the dihydro compound **9** during its formation. Because there is no incorporation of deuterium occurring in **3a** during the irradiation of **1a** in n-propylamine-N,N-d_2, it seems that the hydrogens bonded to C-1 and C-4 of **9** come from the alkyl chain of n-propylamine.

This eliminates the possibility that the photocyclization of 2,3 - diphenylbenzo[b]furan derivatives in n-propylamine proceeds directly, via a dihydro intermediate such as **10** in the case of **3a**. On the other hand, the evidence seems to suggest that, as proposed by Srinivasan and Hsu in the case of some 1,2-diphenylethylenes containing electron-withdrawing substituents, the first step of the photocyclization involves radical abstraction of a hydrogen of the alkyl chain of the amine. The photocyclization could therefore proceed, as shown in Scheme 3, by a double radical abstraction.



9

2 Y = 1,25 H + 0,75 D

The primary reaction product would be a tetrahydro compound such as **12**, which in n-propylamine would give **3a** and **2a** in a smaller amount. It is tempting to speculate that in hydrogenated solvents other than unhindered primary amines, the tetrahydro intermediate is, as in n-propylamine, the primary product, but that in these solvents it is transformed only into the totally aromatic compound **2a**.

3. *Role of unhindered primary amines in the formation of* 1,4 *dihydro compounds.* Dihydro compounds such as **3a** are mainly formed in unhindered primary amines such as n-propylamine or n-butylamine. These solvents, compared with the other solvents used (ether, ethanol, methanol, chloroform, n-dipropylamine, t-butylamine, triethylamine) exhibit no special properties with respect to radical reactions, but it is known that, whereas Birch reduction can be carried out in n-propylamine or n-butylamine, it does not take place in other solvents, in which the photocyclization leads only to totally aromatic compounds.

If we make an assumption that the role of unhindered primary amines is to stabilize the negative charged species released during the formation of the isolated compounds, it means that both the hydrogens coming from the solvent and the hydrogens from the ortho positions of the phenyl goups of the starting material are released in a reductive form and not as radicals.

Therefore, if the photocyclization proceeds by a mechanism as in the Scheme 1, the hydrogen coming from the solvent in the cyclized radical intermediate **11**, is not released as a free radical to any considerable extent. This supports the hypothesis concerning the formation of a tetrahydro derivative such as **12**, by a second radical solvent hydrogen abstraction.

The hypothesis about the release of hydrogens in a reductive form is supported by the following experiment:

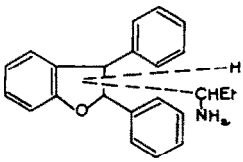
When a solution of a 1:5 mixture of 2,3-diphenylbenzo[b]furan **1a** and acenaphthylene in n-propylamine is irradiated under nitrogen, acenaphthene is formed. This reduction does not occur when the mixture is irradiated in ethanol, or when acenaphthylene itself is irradiated in n-propylamine.

If this hypothesis is correct, such a reduction would occur whenever a non-aromatic intermediate is being transformed into its aromatic derivative.

When a solution of a 1:5 mixture of stilbene and acenaphthylene in n-propylamine is irradiated under the same conditions as above, acenaphthene is formed. No reduction occurs when the mixture is irradiated in ethanol.

The pathway by which the 1,4 dihydrophenanthro[9,10-d]benzo[b]furans are formed cannot be described at this stage of our work. It is probable that compounds which are being reduced are not totally aromatic. Thus, no reduction of **2a** takes place when a 1:5 mixture of **2a** and stilbene is irradiated in such a way that stilbene absorbs most of the light. Phenantherene is the only product in this case. It must be pointed out that a *para*-methoxy group in the 2-phenyl substituted 2,3-diphenylbenzo[b]furan has an effect upon the formation of the 1,4-dihydro compounds.

4. *Minor compounds formed during irradiation of 2,3-diphenylbenzo[b]furan* **1a** *in propylamine.* When **1a** is irradiated in n-propylamine, small amounts of a 1-1 adduct of n-propylamine to **1a** (3%) and of 2 - methyl - 2 - penten - 1 - al **16** (3%) are formed. The adduct is highly insoluble in most of the solvents. It has been characterized only by the high-resolution mass spectrometry of the parent peak. Its formula is either **13** or **14**. **13** can be formed by combination between Et–CH–NH_2 and a radical such as **15**. **14** can be formed by addition of n-propylamine to **1a** via an exciplex (n-propylamine adds to the photoexcited benzo[b]thiophene and gives an adduct of a similar structure).[12] **16** can be formed by aldolisation and crotonisation of propanal. If the adduct formula is **13**, propanal can be formed by hydrolysis n-propylimine itself derived from radical $EtCHNH_2$, if it is **14**, by the mechanism already postulated to explain the formation of **16** during irradiation of benzo[b]thiophene[12] and of 3-methylisothiazole[13] in n-propylamine. In order to support the hypothesis of hydrolysis of an imine, it must be pointed out that n-propylamine was never dried. Being hydroscopic, it always contains some water.



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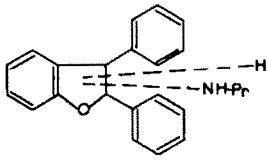

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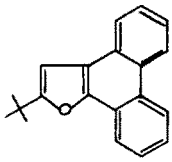

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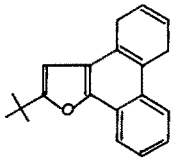

19

III. *Extension of the photoreductive cyclization in n-propylamine to 2,3 - diphenyl - 5 - t - butylfuran*

We have already mentioned that, like **1a**, stilbene is able to reduce acenaphthylene when photocyclized in n-propylamine, but that in the case of stilbene only phenanthrene is formed when it is irradiated in n-propylamine, whereas **1a** is converted into 1-4 dihydro derivative **3a**.

We wanted to know whether the formation of such 1,4-dihydro compounds is characteristic of 2,3-diphenylbenzo[b]furan derivatives or whether it occurs in other cases as well. To try to generalize, we studied the photocyclization of 2,3 - diphenyl - 5 - t - butylfuran **17**. In ethanol, this compound cyclizes upon UV irradiation to 2 - t - butylphenanthro[9,10-b]furan **18** (50%). This was expected, because the photocyclization of 2,3-diphenylfuran to phenanthro[9,10-b]furan has already been reported.[14] When **17** is irradiated in n-propylamine, a dihydrocyclized compound is formed (35%). It adds two Br atoms upon bromination in chloroform, and the adduct so formed is transformed into **18** when refluxed in pyridine. These facts and a comparison of its NMR spectrum with that of **1a** (*cf* Table 1) seem to indicate that the dihydro compound is 2 - t - butyl - 4,7 - dihydrophenanthro[9,10-b]furan **19**. During the photocyclization of **17** in n-propylamine, **18** is also obtained in a small amount (15%). Four or five other compounds are also formed but have not been characterized.

CONCLUSION

Since **19** is obtained from **17** suggests that the formation of 1,4-dihydro compounds upon cyclization of 1,2-diphenylethylene derivatives in n-propylamine is a general process. In such cases where these compounds are not isolated (as, e.g. in the case of stilbene) this may be due to their thermal instability.

It is likely that the role of the unhindered primary amine is to stabilize negatively charged species (hydrogens?) released during oxidation of intermediates, and that in other hydrogenated solvents the photocyclization of 1,2 diphenylethylenes proceeds as in n-propylamine in the first steps of the reaction. This work shows that photocyclization involves radical solvent hydrogen abstraction not only in the cases of one- and/or two electron-withdrawing substituted 1,2-diphenylethylenes.[7,8]

EXPERIMENTAL

The NMR spectra were recorded on a Jeol C 60 HL spectrometer, using TMS as internal reference and CCl_4 as solvent. Elemental analyses were performed at "Service Central de Microanalyse du C.N.R.S." at Thiais (France). The m.ps were determined with a "Reichert-Thermopan" microscope.

Synthesis of the starting compounds. Compounds **1a** (m.p. 120–121°),[15] **1b** (m.p. 114–115°),[16] **1c** (m.p. 145–146°),[16,17] **1d** (m.p. 113–114°)[18] are known and were synthesized according to Arventiev and Ofenberg.[15,18] 2 - (4' - Methoxyphenyl) - 3 - phenylbenzo[b]furan was synthesized by Perrot and Cerutti[19] and was obtained as a gift.

2 - *Phenyl* - 3 - (2',4',6' - *trimethyl*) - 5 - *methylbenzo[b]furan* **6**. This was synthesized according to the method of Japp and Meldrum:[20] a mixture of 2 g of 2,4,6-trimethylbenzoin,[22] 5 g of *p*-cresol, and 10 g of 73% H_2SO_4 was heated at 150–170° during for 20 min with stirring. The cooled mixture was poured into ice-cold water. The product was decanted, filtered and washed with 2N NaOH. It was crystallized from ethanol: m.p. 111–112°.(Found: C, 88·03; H, 6·73; O, 5·00. Calc. for $C_{24}H_{22}O$: C, 88·31; H, 6·79; O, 4·90%); NMR (δ, ppm) CH_3: 2·05 (3H), 2·12 (3H), 2·35 (3H), 2·40 (3H), H(aromatic): 6·65–7·35 (10H).

The position of the 2,4,6-trimethylphenyl substituent was been determined by degradation. **6** (1 g) dissolved in 15 ml AcOH was added to a soln of 1·5 g of CrO_3 in 20 ml AcOH. The soln was heated 1 hr at 100°. Water was added, the ppt was filtered off, dissolved in an alcoholic solution of NaOH and refluxed for 10 min. CO_2 was then bubbled through the soln. The ppt so formed was filtered off and identified as 2-hydroxy-2',4',6'-trimethylbenzophenone by means of its NMR spectrum. The mother liquor was acidified with HCl, the precipitated, benzoic acid was extracted into ether purified by sublimation, and characterized by its m.p. (m.p. 120–121°), mixed m.p., and its IR and NMR spectra.

Formation of unsubstituted benzoic acid proves that the phenyl group bonded to the $C_{(2)}$ of **6** has no Me substituent.

2,3 - *Bis* - (2',4',6',-*trimethylphenyl*) - 5 - *methylbenzo[b]furan* (**7**). This was synthesiszed by the same method as **6**. Using 2,4,6,2',4',6'-hexamethylbenzoin.[22] The product **7** has m.p. 134–135°. (Found: C, 87·68; H, 7·75; O, 4·47. Calc. for $C_{27}H_{28}O$: C, 88·00; H, 7·66; O, 4·34%); NMR (δ, ppm) CH_3: 1·94 (6H); 2·02 (6H); 2·25 (6H); 2·38 (3H); H (aromatic) 6·64–7·30 (6H).

2,3 - *Bis* - (*pentadeuterophenyl*)*benzo[b]furan* (**8**). This was synthesized by reaction of deuterated benzoin with phenol in the presence of boric acid.[15] The deuterated benzoin was prepared by the condensation of pentadeuterated benzaldehyde in the presence of KCN.[21] Pentadeuterated benzaldehyde was synthesized according to the Blomquist and Cedergren method.[23]

2,3 - *Diphenyl* - 5 - *t* - *butylfuran* (**17**). This was synthesized according to Boon's method[24] (m.p. 68–69°).

1. *Photocyclization*

All the irradiations of the 2,3-diphenylbenzo[b]furan derivatives and of 2,3-diphenyl-5-t-butylfuran were carried out in quartz vessels with a Hanau NN 15W low-pressure mercury lamp. N_2 was bubbled through the soln.

1,4 - *Dihydrobenzo[b]phenanthro*[9,10-d]*furan* (**3a**). Compound **1a** (4·2 g; 0·015 mole) dissolved in 300 ml n-propylamine was irradiated for 12 hr. n-Propylamine was then distilled off and the residue washed with 30 ml acetone. The product was filtered off and recrystallized twice from acetone. 2·6 g (65%) of crystalline needles of **3a** were obtained, m.p. 172–173° (sublimation at 132°). (Found: C, 88·80; H, 5·00; O, 6·02. Calc. for $C_{20}H_{14}O$: C, 88·86; H, 5·22; O, 5·92%).

The mother liquor from the photoreaction performed in n-propylamine was concentrated by evaporation of this amine. The residue was separated by TLC on silica gel with benzene-acetone (1·2:3) solvent mixture. The products moving closely to the front consisted of a mixture of unreacted **1a** and of **2a**. **2a** was separated from this mixture by VPC (see below) (0·50 g, 12%) and characterized by its m.p., its mixed m.p. with a sample of **2a** prepared in a different manner (see below), and by its picrate m.p. A more polar compounds (0·125 g, 3%) **13** remained at the bottom of the plate. It was highly insoluble. Its mass spectrum showed that it is an 1:1 adduct of **3a** and n-propylamine.

Mass spectrum of **13** (M^+: 329·177 89, (25) ($C_{23}H_{23}NO$); 300 (4) ($M^+ - Et$); 271·11105, (8) ($C_{20}H_{15}O$); 270·10394, (15) ($C_{20}H_{14}O$); 244,09013 (100) ($C_{18}H_{12}O$).

The NMR spectrum of n-propylamine distilled after the photocyclization showed a singlet at $\delta = 8·75$ ppm. By VPC a compound (3% with respect to the starting **1a**) with the same retention time as that of 2 - methyl - 2 - penten - 1 - al, previously synthesized,[13] was detected.

When the photocyclization of **1a** was performed in n-butylamine **3a** precipitated as it did when the solvent was n-propylamine and in almost the same quantity. It was isolated, crystallized from acetone, and characterized by its m.p. and its mixed m.p. with a sample of **3a**, prepared in n-propylamine, and its NMR spectrum.

1,4-*Dihydro* 2,3-*dibromobenzo[b]phenanthro*[9,10-d]*furan*. To 40 ml of a chloroform solution of **3a** (2·6 g; 0·01M) Br_2 (1·6 g; 0·5 ml) dissolved in 5 ml chloroform was added with stirring. As soon as the color had disappeared, crystalline needles precipitated. After filtration, they were washed with chloroform giving 3·5 g (0·08M) of crude 1,4 - dihydro - 2,3 - dibromobenzo[b]phenanthro[9, 10-d]furan. It was purified by three recrystallizations from benzene; m.p. 241–242°. (Found: C, 56·02; H, 3·32; O, 3·51; Br, 37·25. Calc. for $C_{20}H_{14}Br_2$: C, 55·81; H, 3·25; O, 3·72; Br, 37·20%).

Benzo[b]phenanthro[9,10-d]*furan* (**2a**)

(a) *From* 1,4 *dihydro* - 2,3 - *dibromobenzo*[b]*phenanthro*[9, 10-d]*furan*. This obtained previously (3·5 g, 0·08 mole) was dissolved in 50 ml pyridine and the soln was refluxed for 3 hr. During this reaction pyridine hydrobromide precipitated. After cooling, the soln was diluted by 100 ml water and stirred. After 1 hr, the ppt was filtered off and washed with water giving 1·9 g of **2a**. The crude **2a** was purified by two recrystallizations from EtOH (charcoal) (1·7 g, 40% with respect to **1a**); m.p. 155–156°.

This compound has already been synthesized by a tedious method.[25] The m.p. of the picrate of **2a** synthesized by us was the same as described in the literature (m.p. 161–162°).[25]

(b) *By photocyclization of* 2,3 *diphenylbenzo*[b]*furan* **1a**. Solutions of **1a** (2 g), in ether, methanol, ethanol, chloroform, t-butylamine, di-n-propylamine, or triethylamine were irradiated for 12 hr. After solvent evaporation, the crude material was filtered through a silica gel column with acetone-benzene (3:1) solvent mixture, and then isolated by preparative VPC (Autoprep A 700, 20′ × 3/8″, 30% SE 30 on Chromosorb W column, temp.: 260°).

This procedure gave 1·04 g (52%) of pure **2a** which was characterized by its m.p. and the m.p. of its picrate.

When the solvent was diethylamine **3a** (0·2 g; 10%) precipitated during the irradiation. It was recrystallized from acetone and characterized by its m.p. and mixed m.p. with a sample of **3a** previously prepared. **2a** was also obtained as in the case of other solvents (0·86 g, 43%).

1,4 - *Dihydro* - 1,2 - *methylbenzo*[b]*phenanthro*[9,10-d]*furan* **3b**. This was obtained by photolysis of **1b** in n-propylamine, m.p. 172–173°. (Found: C, 88·72; H, 5·60; O, 5·72. Calc. for $C_{21}H_{16}O$: C, 88·70; H, 5·67; O, 5·63%).

1,4 - *Dihydro* - 11,12 - *dimethylbenzo*[b]*phenanthro*[9, 10-d]*furan* **3c**. This was obtained by photocyclization of **1c** in propylamine, m.p. 210–211°. (Found: C, 88·34; H, 5·98; O, 5·67. Calc. for $C_{22}H_{18}O$: C, 88·56; H, 6·08; O, 5·36%).

1,4 - *Dihydro* - 3 - *methoxy* - 12 - *methylbenzo*[b]*phenanthro* 9,10-d (**3d**). This was obtained by photocyclization of **1d** in n-propylamine, m.p. 186–187°. It sublimes at 165°. (Found: C, 84·28; H, 5·81; O, 9·95. Calc. for $C_{22}H_{18}O_2$: C, 84·05; H, 5·77; O, 10·18%).

1,4 - *Dihydro* - 2,3 - *dibromo* - 3 - *methoxy* - 12 - *methylbenzo[b]phenanthro*[9,10-d]*furan*. To 25 ml of a chloroform soln of **3d** (1 g) Br_2 (0·48 g; 0·15 ml) dissolved in chloroform was added with stirring. After **3d** had partially separated, the soln was concentrated, the product crystallized from EtOH (1·3 g), m.p. 240–241°. It sublimes at 210°. (Found: C, 55·80; H, 3·91; O, 6·71; Br, 33·65. Calc. for $C_{22}H_{18}Br_2O_2$: C, 55·69; H, 3·83; O, 6·76; Br, 33·71%).

3 - *Methoxy* - 12 - *methylbenzo[b]phenanthro*[9,10-d]*furan* (**2d**)

(a) *From* 1,4 - *dihydro* - 2,3 - *dibromo* - 3 - *methoxy* - 12 - *methylbenzo[b]phenanthro*[9,10-d]*furan*. The above compound (**1g**) was dissolved in 25 ml pyridine and refluxed for 3 hr. After cooling, 25 ml water was added. The ppt so formed was filtered off and crystallized from EtOH: 0·60 g. m.p. 172–173°. (Found: C, 84·65; H, 5·10; 0, 10·18. Calc. for $C_{22}H_{16}O_2$: 84·59; H, 5·16; O, 10·24%); NMR (δ, ppm) CH_3, 2·55; $-OCH_3$, 3·95; H (aromatic), 6·95–8·60.

(b) *By photocyclization of* 2 - *phenyl* - 3(4 - *methoxyphenyl* - 5 - *methylbenzo[b]furan* (**1d**). The procedure was the same as that used to photocyclize **1a** to **2a**. The solvent was ethanol. **3d** so formed (45%) was characterized by its m.p. and mixed m.p. with a sample previously prepared.

6 - *Methoxy* - 5,8 - *dihydrobenzo[b]phenanthro*[9,10-d]*furan* (**4**). This was obtained by photocyclization of **1c** in n-propylamine, m.p. 193–194. (Found: C, 83·93; H, 5·38; O, 10·85. Calc. for $C_{21}H_{16}O_2$: C, 83·98; H, 5·37; O, 10·65%).

1,4 - *Dihydro* - (*Y*) - 2,3,5,6,7,8 - *hexadeutero* - *benzo*[b]*phenanthro*[9,10-d]*furan* (**9**). This was obtained by photocyclization of **8** in n-propylamine.

2 - t - *Butyl* - 4,7 - *dihydrophenanthro*[9,10-b]*furan* (**19**). Compound **17** (**2g**) was irradiated in 300 ml n-propylamine for 12 hr. After solvent evaporation, the mixture was chromatographied on a silica gel SiO_2 column. Elution with petroleum ether gave 0·30 g (15%) of **18** and then 0·75 g (35%) of **19**.

18 was characterized by its m.p. and mixed m.p. with some of the same compound obtained when **17** was photocyclized in ethanol. **19** was purified by vacuum sublimation, m.p. 89–90°. (Found: C, 87·02; H, 7·35; O, 5·68 Calc. for $C_{20}H_{20}O$: C, 86·91; H, 7·29; O, 5·79%).

2 - t - *Butyl* - 4,7 - *dihydro* - 5,6 - *dibromophenanthro*[9–10b]*furan* (**20**). To **19** (0·500 g) dissolved in chloroform, Br_2 (0·350 g) dissolved in 5 ml chloroform was added with stirring. After 10 min, chloroform was evaporated under N_2. A crystalline product appeared. It was filtered off and recrystallized from a mixture of benzene and petroleum ether giving 0·600 mg of **19**, m.p. 244–245°. (Found: C, 54·90; H, 4·80; Br, 36·40; O, 4·19. Calc. for $C_{20}H_{20}Br_2O$: C, 55·08; H, 4·62; Br, 36·64; O, 3·66%).

2 - *t* - *Butylphenanthro*[9,10b]*furan* (**18**). (a) Compound **20** (500 mg) was dissolved in 30 ml pyridine. The soln was refluxed for 3 hr. After cooling, the soln was diluted with 80 ml water and stirred. After 1 hr, the ppt (200 mg) was filtered off and washed with water. The crude **18** was recrystallized from MeOH and characterized by its m.p. and its mixed m.p. with a sample of the same compound obtained by photocyclization of **18** in EtOH.

(b) Compound **17** (2 g) was irradiated for 12 hr in EtOH. After solvent evaporation, the mixture was chromatographied on a silica gel column. Elution with petroleum ether gave 1 g (50%) of **18**, m.p. 74–75°. (Found: C, 87·45; H, 6·67; O, 5·92. Calc. for $C_{20}H_{10}O$: C, 87·55; H, 6·61; O, 5·83%).

2. *Competitive photoreduction*

The analytical VPC was performed using a F and M 810 apparatus with a 2m SE 30.

2,3 - *Diphenylbenzo[b]furan* **1a** *and acenaphthylene.* A mixture of **1a** (2·5 g) and acenaphthylene (0·5 g) was irradiated for 24 hr in n-propylamine. **3a** precipitated and after filtration and crystallization from acetone, it was characterized by its m.p. and mixed m.p.

The mother liquor was evaporated and the mixture was analysed by VPC. Unreacted **1a** and **2a** were detected as well as acenaphthylene and acenaphthene (it was characterized by comparison of its retention time with that of an authentic sample). 70% of the acenaphthylene were reduced in acenaphthene.

When the previous mixture was irradiated in EtOH under the same conditions, acenaphthylene was not transformed into acenaphthene. Instead 50% of **1a** were photocyclized to **3a**.

When acenaphthylene (0·5 g) was irradiated alone in n-propylamine under the same conditions, it did not undergo the reaction.

Stilbene and benzo[b]phenanthro[9-10-d]*furan* (**2a**). When a mixture of stilbene (2·5 g) **2a** (0·5 g) was irradiated in 300 ml n-propylamine in a quartz vessel with a RUL-3000 Å 85W lamp of a Rayonet-type RS reactor, for 24 hr phenanthrene, detected by VPC (comparison of the reaction time with that of an authentic sample) was formed. No reduction product of **2a** were detected.

When a mixture of stilbene (2·5 g) acenaphthylene (0·5 g) was irradiated in n-propylamine as above, phenanthrene and acenaphthene (50% of acenaphthylene were reduced) were formed. They were detected by VPC (comparison of their retention times with these of the authentic samples).

When the preceding mixture was irradiated under the same conditions, in EtOH, phenanthrene was formed, but acenaphthylene was not transformed into acenaphthene (the acenaphthene peak did not appear on the chromatogram).

Acknowledgements—The authors wish to express their sincere thanks to Prof. E. Cerutti and Dr. C. Perrot for the gift of **1e**, to Mr. Bourgois for the mass spectrum of **13**, and to Prof. C. Párkányi for his help in translating this paper.

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