

Reaction Between some 6-Halogeno-2,2-dimethyl-, 2,2,6-Trimethyl- and 2,2-Diaryl-2*H*-naphtho[1,2-*b*]-pyrans and 1,1-Diphenylethene

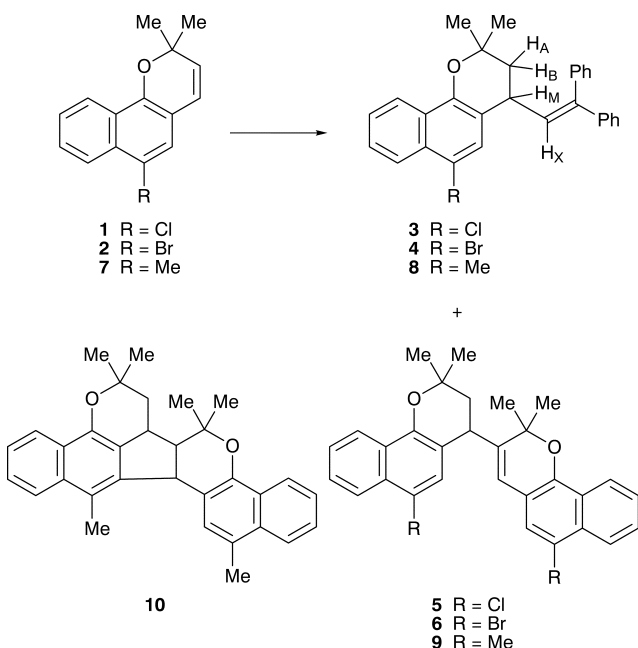
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6-Halogeno-2,2-dimethyl- and 2,2,6-trimethyl-2*H*-naphtho[1,2-*b*]pyran reacted with 1,1-diphenylethene in acid solution to give 6-halogeno-3,4-dihydro-2,2-dimethyl- and 3,4-dihydro-2,2,6-trimethyl-4-(2,2-diphenylvinyl)-2*H*-naphtho[1,2-*b*]pyran, respectively, along with their corresponding dimers, the reaction between 2,2-diaryl-2*H*-naphtho[1,2-*b*]pyrans and 1,1-diphenylethene, under identical conditions, yielded 3,4-dihydro-4-(2,2-diarylvinyl)-2,2-diphenyl-2*H*-naphtho[1,2-*b*]pyrans, by a different mechanism.

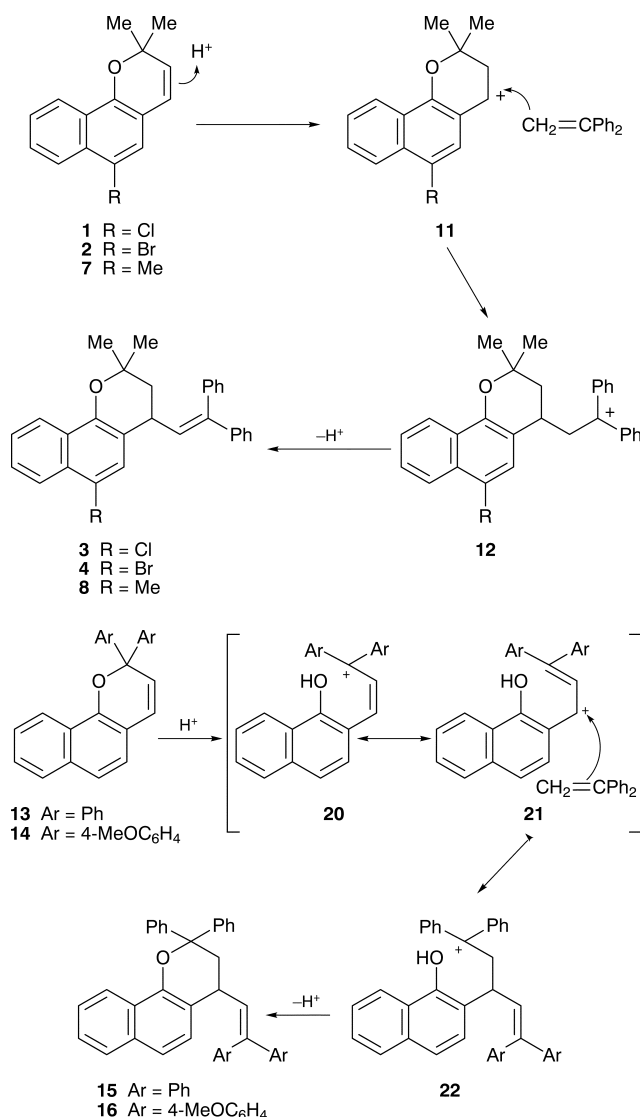
The reaction between 6-chloro- and 6-bromo-2,2-dimethyl-2*H*-naphtho[1,2-*b*]pyrans (**1** and **2**)¹ and 1,1-diphenylethene in acetic acid containing a few drops of sulfuric acid afforded the adducts 6-chloro- and 6-bromo-3,4-dihydro-2,2-dimethyl-4-(2,2-diphenylvinyl)-2*H*-naphtho[1,2-*b*]pyrans (**3** and **4**, respectively) and their corresponding dimers (**5** and **6**).¹ Similar treatment of 2,2,6-trimethyl-2*H*-naphtho[1,2-*b*]pyran (**7**) furnished adduct **8** and dimer **9**, but no dimer **10**¹ was isolated from the reaction mixture. The proposed structures for adducts **3**, **4** and **8** are supported by ¹H NMR and mass spectral data.



A proposed mechanism for the formation of adducts **3**, **4** and **8** involves the initial protonation of the olefinic double bond of the 6-substituted-2,2-dimethyl-2*H*-naphtho[1,2-*b*]pyran to give the carbonium ion **11**, which reacts with 1,1-diphenylethene to yield carbonium ion **12**. The loss of a proton from **12** then furnishes the adduct. Further evidence for the proposed structures was obtained by the ozonolysis of adducts **3**, **4** and **8**.

The setting aside for 2 days of a solution of equimolar proportions of 2,2-diphenyl- or 2,2-bis(4-methoxyphenyl)-2*H*-naphtho[1,2-*b*]pyran (**13** and **14**, respectively) in acetic acid, to which was added a few drops of sulfuric acid, yielded 3,4-dihydro-2,2-diphenyl-4-(2,2-diphenylvinyl)-2*H*-

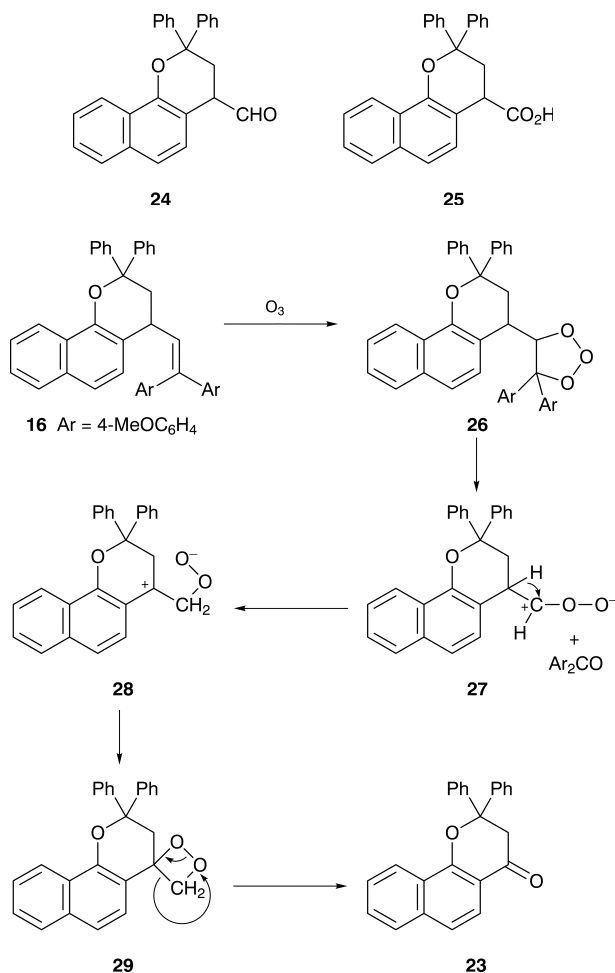
naphtho[1,2-*b*]pyran (**15**) and 3,4-dihydro-2,2-diphenyl-4-[2,2-bis(4-methoxyphenyl)vinyl]-2*H*-naphtho[1,2-*b*]pyran (**16**), respectively. The structures of adducts **15** and **16** are similar to those of the adducts obtained by the same reaction between 3,3-diaryl-1*H*-naphtho[2,1-*b*]pyran and 1,1-diphenylethene.²



The proposed mechanism for the formation of adducts **15** and **16** involves, initially, the protonation of the oxygen on the pyran ring, leading to the opening of the oxygen ring

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and the formation of a resonance stabilized carbonium ion, **20** and **21**, which reacts with 1,1-diphenylethene to give carbonium ion **22**, which cyclizes with the loss of a proton and the reformation of the pyran ring to afford adducts **15** and **16**.



Decomposition of the ozonide **26**, obtained from adduct **16** on boiling with water, resulted in the isolation of 2,3-dihydro-2,2-diphenyl-4-oxo-1,2-naphthopyran (**23**) and not the expected 3,4-dihydro-2,2-diphenyl-2H-naphtho[1,2-b]pyran-4-carbaldehyde (**24**) or -4-carboxylic acid (**25**). It is suggested that boiling the ozonide **26** with water splits off 4,4'-dimethoxybenzophenone and leaves a complex ion (**27**). The ion **27** then rearranges to give a second complex ion, **28**, which ring closes to give intermediate **29**. The final step involves the loss of formaldehyde and formation of 2,3-dihydro-2,2-diphenyl-4-oxo-1,2-naphthopyran (**23**).

2,2-Bis(4-methoxyphenyl)-2H-naphtho[1,2-b]pyran (**14**) was obtained by the pyrolysis at 200 °C of the acetate of 3,4-dihydro-2,2-bis(4-methoxyphenyl)-2H-naphtho[1,2-b]pyran-4-ol, obtained by reduction of the parent ketone prepared from 4,4'-dimethoxybenzophenone and 2-acetyl-1-naphthol.

Techniques used: ¹H NMR and mass spectrometry

References: 8

Schemes: 4

Table 1: ¹H NMR data of 6-halogeno-3,4-dihydro-2,2-dimethyl- and 3,4-dihydro-2,2,6-trimethyl-4-(2,2-diphenylvinyl)-2H-naphtho[1,2-b]pyrans

Table 2: Mass spectra data of adducts in Table 1

Table 3: ¹H NMR data of 3,4-dihydro-2,2-diphenyl-4-(2,2-diphenylvinyl)-2H-naphtho[1,2-b]pyran and 3,4-dihydro-2,2-diphenyl-4-[2,2-bis(4-methoxyphenyl)vinyl]pyran

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