Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 1992, **2**(1), 20–21
Mendeleev Communications

An Efficient Access to α-Tetralones and their Derivatives *via O*-Quinodimethanes Generated by Isochromene Ring Cleavage

Sergei V. Verin,* Dmitrii E. Tosunyan and Evgenii V. Kuznetsov

Institute of Physical and Organic Chemistry, Rostov State University, 344104 Rostov-on-Don, Russia. Fax: +7 863 228 5667

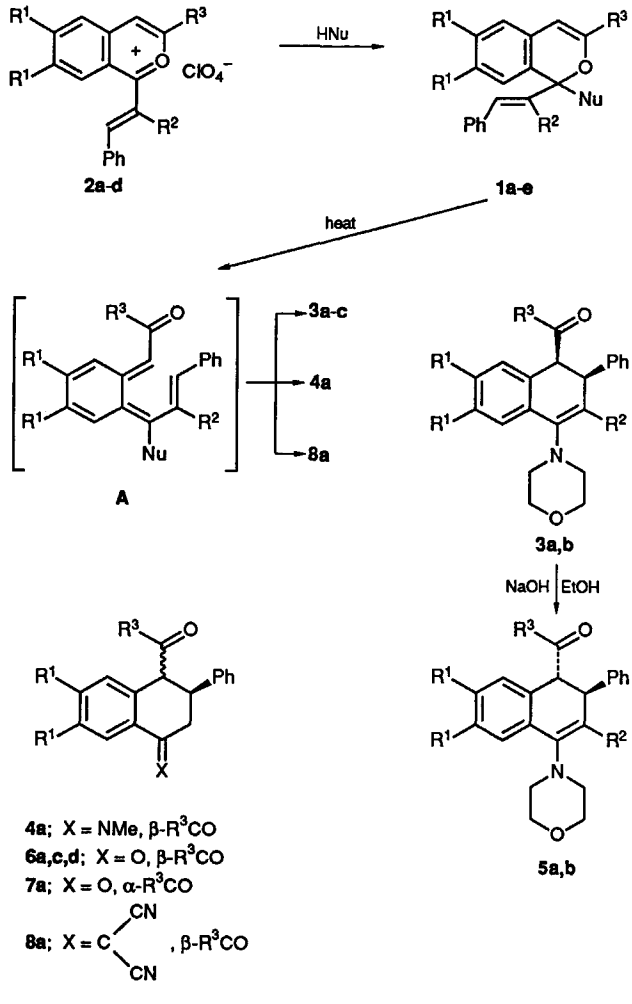
The stereoselectivity of the formation of *cis*-3,4-dihydronaphthalenes from 1-styryl substituted isochromenes proves the intermediacy of *O*-quinodimethanes in this reaction.

There has been considerable interest recently in the application of inter- and intra-molecular reactions involving *O*-quinodimethanes to the construction of hetero- and carbo-cyclic compounds.[1] One possible method for the generation of these highly reactive substances is the ring cleavage of benzoannelated systems, of which the benzocyclobutenes are the best known examples.[2] It is known that suitable isochromenes may be used to generate *O*-quinodimethanes by photolysis.[3] However, in our previous paper[4] the thermal rearrangement of a 1-(1-carboxy-2-hydroxypropenyl) substituted isochromene into a naphthalene derivative was accounted for in terms of the intermediate formation of *O*-quinodimethanes.

In order to prove this proposal, we decided to examine the behaviour of 1-styryl substituted isochromenes of type **1**, in which the double bond in the 1-position was expected to provide an intramolecular trap for any *O*-quinodimethane generated. These compounds **1** must be formed by nucleophilic addition to the corresponding 2-benzopyrylium salts of type **2**, but the conditions required for this interaction and the stability of the adducts proved to be different. Thus, **2a–d** combine with morpholine and methylamine at room temperature. However, the products **1a,c–e** ($R^2 = H$), already at 20 °C, slowly undergo the conversion into the *cis*-dihydronaphthalenes **3a,c** when the nucleophile is morpholine, and into the *cis*-imine **4a** (Nu = NHMe). These rearrangements occur rapidly in boiling ethanol in 75–90% yields from **2**. Meanwhile, isochromene **1b** ($R^2 = Me$, 92% from **2b**) is rather stable and heating up to 200 °C without solvent is necessary to transform it into **3b** in 82% yield, apparently because of the steric effect of the methyl group (Scheme 1).

The stereoselectivity of the reactions under discussion strongly suggests that *cis*-carbocycles **3a–c** and **4a** are formed by an electrocyclic disrotatory cyclization of the *O*-quinodimethanes **A**. The resulting *cis*-configuration is not thermodynamically favourable for the dihydronaphthalene ring since it easily reverts to a *trans*-configuration (**3a,b→5a,b**) *via* an exocyclic carbonyl group enolization in ethanol solution containing alkali.

In order to estimate the possible influence of the methoxy groups on the transformation of the isochromene ring, we studied the reaction of the 6,7-unsubstituted salt **1d** with morpholine and after heating the crude reaction mixture for a short time in AcOH–H_2O solution, we isolated the *cis*-α-tetralone **6d** in 60% overall yield. Evidently, this product was



a; $R^1 = MeO$, $R^2 = H$, $R^3 = 3,4\text{-}(MeO)_2C_6H_3$, $Nu = N(CH_2CH_2)_2O$
b; $R^1 = MeO$, $R^2 = Me$, $R^3 = 3,4\text{-}(MeO)_2C_6H_3$, $Nu = N(CH_2CH_2)_2O$
c; $R^1 = MeO$, $R^2 = H$, $R^3 = Me$, $Nu = N(CH_2CH_2)_2O$
d; $R^1 = R^2 = H$, $R^3 = 4\text{-}MeOC_6H_4$, $Nu = N(CH_2CH_2)_2O$
e; $R^1 = MeO$, $R^2 = H$, $R^3 = 3,4\text{-}(MeO)_2C_6H_3$, $Nu = NMe$

Scheme 1

afforded with retention of configuration by mild hydrolysis of the previously formed enamine of type **3**, which was difficult to purify. The other α-tetralones *cis*-**6a,c** and *trans*-**7a** were also obtained almost quantitatively on hydrolysis of the corresponding enamines **3a,c** and **5a** under the same conditions.

The structures of the products isolated, with the exception of **1a,c–e**, were determined on the basis of analytical data and by means of IR, MS and ^{1}H NMR spectra. The latter were also used for configuration and conformation elucidation.[6] Owing to the lability of **1a,c–e** the structure of these colourless products was demonstrated only by their reverse conversion immediately after formation into the initial salts.**2a,c,d**.†

Thus, taking into account the ready availability of the 2-benzopyrylium salts **2**,[5] the methodology developed here may be efficiently applied to the stereoselective synthesis of α-tetralones and dihydronaphthalene derivatives. Nitrogen-containing nucleophiles are not necessarily required for such transformations since the related compound **8a** was afforded by heating **2a** in *tert*-butyl alcohol with malononitrile in the presence of sodium *tert*-butoxide.

† Products **3–8** are racemic.

Received: Moscow, 26th June 1991
Cambridge, 11th October 1991; Com. 1/03509F

References

1 J. L. Charlton and M. M. Alauddin, *Tetrahedron*, 1987, **43**, 2873, and references cited therein.
2 K. Shishido, A. Yamashita, K. Hiroya, K. Fukumoto and T. Kametani, *Tetrahedron*, 1989, **34**, 5791.
3 A. Padwa and A. Au, *J. Am. Chem. Soc.*, 1976, **98**, 5581.
4 S. V. Verin, D. E. Tosunyan, E. V. Kuznetsov and Yu. A. Zhdanov, *Khim. Geterotsikl. Soedin.*, 1990, 315.
5 E. V. Kuznetsov, I. V. Shcherbakova and A. T. Balaban, *Adv. Heterocycl. Chem.*, 1990, **50**, 157.
6 S. V. Verin, D. E. Tosunyan and E. V. Kuznetsov, *Khim. Geterotsikl. Soedin.*, in the press.