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THERMAL AND PHOTOCHEMICAL STUDIES WITH STILBENE OXIDES INTRAMOLECULAR TRAPPING OF CARBONYL YLIDE INTERMEDIATES

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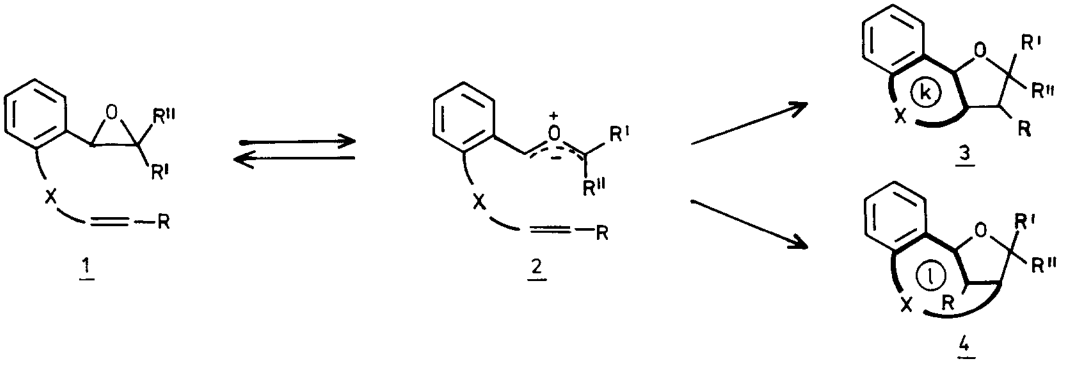
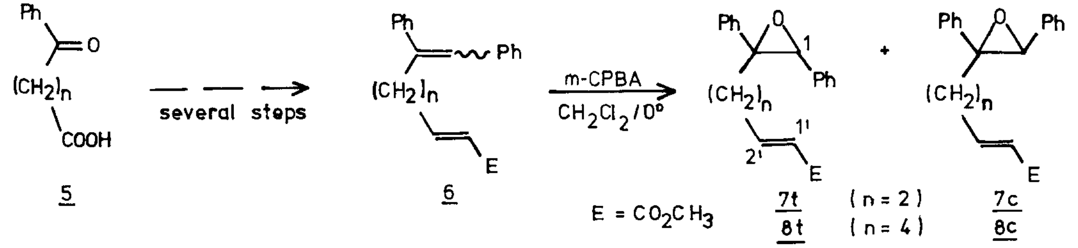
Summary. The annelated tetrahydrofuran derivatives 14 and 15, resp., are formed in moderate yield by intramolecular trapping reaction of the carbonyl ylide intermediates 9, which are generated either by thermal ring opening of the trans-stilbene oxides 7t/8t or by photolysis of the cis-isomers 7c/8c.

The intramolecular cycloaddition of carbonyl ylides to C=C-bonds is now a well documented reaction which has been investigated predominately with dipoles of type 2, the precursors being ene-oxiranes of the general structure 1 [1-3]. Depending on the substituents R/R'/R'' as well as on the nature of the chain X annelated and/or bridged cycloadducts (3/4) were obtained in varying yields. It was of special interest that this method, in contrast to the overwhelming number of reactions with other 1,3-dipoles [4], proved also to be valuable for the preparation of large ring systems containing (till now) up to 34 ring members (see ⓚ and ⓛ in 3/4) [2,5].

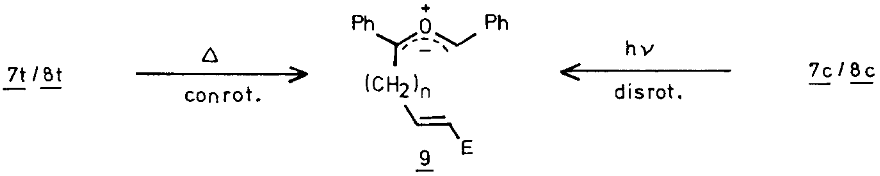


On the other side, the geometry of the o-aryl carbonyl ylide unit in 2 is quite rigid and may disfavor the cycloaddition process in the case of a shorter chain X (leading to 3 with ⓚ ≤ 6). In order to test the reactivity of sterically unrestricted ene-dipoles we undertook investigations with stilbene oxides 7 and 8 which are substituted by a butene and hexene group, respectively, each bearing an activating ester function at the terminal position.



The synthesis of 7 and 8 has been performed with the α,ω-keto acids 5 as starting material. Final regioselective m-CPBA epoxidation of the dienes 6 led to a mixture of the geometrical isomers 7/8, which could be separated by preparative thin layer chromatography [6].

According to theory [7] the same dipolar intermediate 9 (with the favorable exo,exo-arrangement of the phenyl groups) is predicted to be produced either by thermal ring opening of the trans-stilbene oxides 7t/8t or by photoinduced cleavage of the cis-oxiranes 7c/8c. Therefore, depending on the mode of activation, it was reasonable to use the respective isomers for our studies.

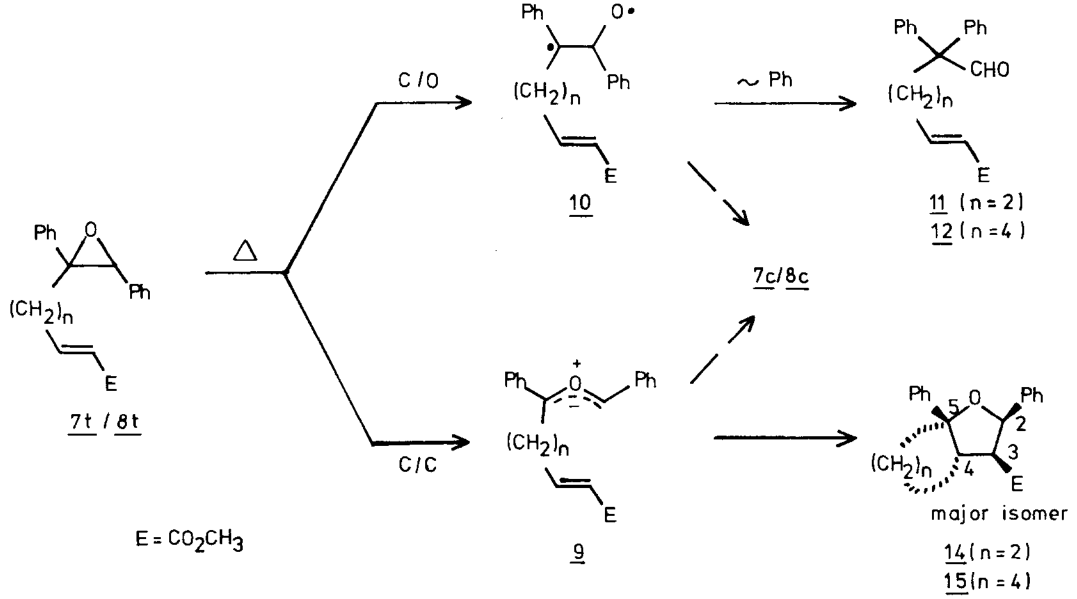


In solution-experiments the ene-oxiranes 7t/8t, not unexpectedly [8], turned out to be thermally stable up to at least 170°C and to give a complex mixture of products with no indication for the formation of cycloadducts at higher temperatures. Apparently catalysed reactions are involved under forced conditions even if inert solvents like isooctane or bromobenzene are employed. However, after short-time-pyrolysis [9] at 450/470°C (10-15 s) a 70% yield of mainly three products was obtained: besides the cis-oxiranes 7c/8c and the aldehydes 11/12 intramolecular cycloadducts of structure 14/15 have been identified, the ratio being approximately 1 : 4 : 4 (for 7t at 450°C) and 1 : 2.5 : 2 (for 8t at 470°C).

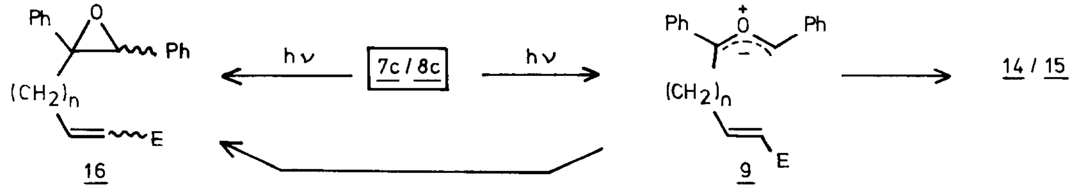
The stereochemical assignment for 14/15 is based upon the following assumptions: (i) The cis-arrangement of the phenyl rings corresponds with the configuration of the dipole 9 (vide supra). (ii) Likewise, the stereochemistry of the double bond of 7/8 should be retained during the cycloaddition step; consequently 4-H and 3-H are in trans-position. (iii) The unusual high field ^{1}H-NMR-absorption of the ester protons at δ= 3.08/3.21 [10] is a safe indication for the cis-geometry of 2-Ph and 2-E [11].

The mechanism of the formation of 7c/8c, 11/12 and 14/15 is outlined in the scheme: competitive C/O- and C/C-cleavage of the epoxides 7t/8t take place to a comparable extent affording the respective diradical 10, which undergoes subsequent phenyl migration to give 11/12, and the dipole 9 as the direct precursor of the annelated tetrahydrofurans 14/15. As can be seen by means of models the predominant formation of a single stereoisomer in each case is the result of a very favorable orientation complex on the route to the cycloadducts. Nevertheless, in spite of the drastic reaction conditions the stereoselectivity remains remarkably high. No conclusion can be drawn whether the cis-isomers of 7/8 are formed through 10 and/or 9 as intermediates.

Scheme



The photochemical results with 7/8 resemble the thermal findings insofar as the same cycloaddition products are formed in comparable yield. Both homologues 7c and 8c undergo photoreactions either by direct or triplet-sensitized excitation. With 7c the best results are obtained using acetone as solvent: after irradiating 100 mg of the epoxide for 5h with a high pressure mercury lamp (pyrex filter) the oxabicyclo[3.2.0]heptane 14 is produced in about 25% yield (conversion 75%). In addition, all stereoisomers of 7 (see structure 16) as well as a number of so far unidentified compounds are formed.



Similar types of products have been detected after the photoreaction of 8c, but in this case direct irradiation with light of 253.7 Å is preferable. After 70% conversion (100 mg of 8c/2 h/CH_3CN) the yield of 15 amounts to about 35%. As mentioned above, again the dipole 9 is supposed to be the central intermediate which may be subsequently transformed into the cycloadducts 14/15.

However, the mechanistic details of the cycloaddition step are still uncertain because the reaction temperature during the photolyses (20 and 0 °C, resp.) seems to be too low for a normal ground state process [8,12].

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[6] 7t: colorless oil; ^{1}H-NMR ($CDCl_3$, 250 MHz): δ= 7.25-7.45 (C_6H_5), 6.81 (2'-H), 5.66 (1'-H), 3.95 (1-H), 1.56/2.0-2.4 (1H/3H,-$(CH_2)_2$-), 3.65 (CO_2CH_3).- 7c: mp 73°C (hexane/ether); UV (CH_3CN): $\lambda_{max}(\epsilon)$= 272 (290,sh), 266 (520,sh), 258 nm (700); ^{1}H-NMR ($CDCl_3$, 250 MHz): δ= 6.95-7.20 (C_6H_5), 6.96 (2'-H), 5.80 (1'-H), 4.16 (1-H), 3.73 (CO_2CH_3), 2.0/2.1-2.5 (1H/3H, -$(CH_2)_2$-).- 8t: colorless oil; ^{1}H-NMR ($CDCl_3$, 250 MHz): δ= 7.2-7.5 (C_6H_5), 6.84 (2'-H), 5.70 (1'-H), 3.92 (1-H), 3.69 (CO_2CH_3), 1.2-1.6/1.8-2.2 (5H/3/,-$(CH_2)_4$-).- 8c: mp 60°C (hexane/ether); UV (CH_3CN): $\lambda_{max}(\epsilon)$= 272 (200,sh), 266 (380,sh), 258 nm (550); ^{1}H-NMR ($CDCl_3$, 250 MHz): δ= 6.95-7.50 (C_6H_5), 6.93 (2'-H), 5.78 (1'-H), 4.14 (1-H), 3.73 (CO_2CH_3), 1.3-1.6/1.8-1.9 (5H/3H,-$(CH_2)_4$-).

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[10] 14: ^{1}H-NMR ($CDCl_3$,250 MHz): δ= 5.75 (2-H), 3.39 (4-H), 3.14 (3-H), 3.08 (CO_2CH_3); $J_{2,3}$= 6.2 Hz, $J_{3,4}$= 0 Hz.- 15: ^{1}H-NMR ($CDCl_3$, 250 MHz): δ= 5.47 (2-H), 3.81 (3-H), 3.29 (4-H), 3.21 (CO_2CH_3); $J_{2,3}$= 9.8, $J_{3,4}$= 8.5 Hz.

[11] See ref. [1)2)5)9)].

[12] For similar results see: J.Brokatzky-Geiger and W.Eberbach, Heterocycles 20, 1519 (1983).

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