1106 *J. Org. Chem.* **1985**, *50*, 1106-1107

Notes

Stability of Cycloadducts Obtained by High-Pressure Diels–Alder Reaction between 3,4-Dimethoxyfuran and 1,4-Benzoquinones: Kinetic Studies of Retro-Diels–Alder Reaction

Janusz Jurczak,* Andrzej L. Kawczyński, and
Tomasz Koźluk

Institute of Organic Chemistry and Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warszawa, Poland

Received May 29, 1984

We have recently shown that application of high-pressure conditions (22 kbar, 25 °C, ethyl ether as solvent) enabled the first successful realization of the [4 + 2] cycloaddition reaction between furan and 1,4-benzoquinone.[1] It is stressed that the earlier failure of this reaction, when performed under thermal conditions, is evident in the light of our findings;[1] it is in agreement with the assumption that the equilibrium is strongly shifted toward the substrates and that the cleavage reaction is very fast. In fact, the endo and exo adducts (Scheme I), obtained by high-pressure [4 + 2] cycloaddition of 1,4-benzoquinone to furan, have been found to be extremely unstable under normal pressure,[1] this preventing measurements of the retro-Diels–Alder kinetics.

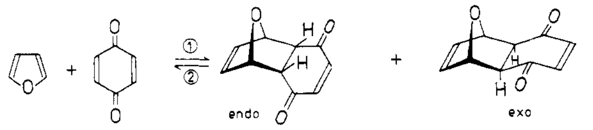
However, it is well-known that 3,4-dimethoxyfuran (1) reacts easily with various 1,4-benzoquinones 2 to give the much more stable cycloadducts 3.[2,3] Therefore, the cycloadducts of this type seem to be proper models for testing the influence of substituents on the rates of the retro-Diels–Alder reaction. The goal of our present kinetic measurements was to verify the hypothesis that the stability of the cycloadducts in solution under atmospheric pressure mainly depends on the substituents in the furan ring.

Results and Discussion

In order to examine the above hypothesis, we synthesized under high pressure three pure crystalline endo adducts (**3a**, **3b** and **3c**)[4,5] and observed the changes in their ^1H NMR spectra measured in a chloroform-*d* solution at various temperatures (Scheme II).

The initial spectra of the cycloadducts 3 as well as the final spectra originating from 3,4-dimethoxyfuran (1) and 1,4-benzoquinones 2 are relatively simple and convenient for quantitative treatment. For example, the initial spectrum of **3a** is as follows: δ 6.71 (s, 2 vinyl H), 5.22 (bs, 2 H_A) 3.68 (s, 6 H, OCH_3), 3.50 (bs, 2 H_B); the final spectrum shows the signals derived form 1,4-benzoquinone (**2a**) [δ 6.88 (s, 4 H_C)] and 3,4-dimethoxyfuran (1) [δ 7.02 (s, 2 H_D), 3.83 (s, 6 H, OCH_3)]. Integration—at suitable time intervals—of the decreasing H_A and H_B signals[6] as well as of the increasing H_C (for the reaction **3a** → 1 + **2a**) and H_C and H_D signals (for the cleavage of **3b** and **3c**) afforded the rate constants *k* and activation energies E_a, recorded in Table I.

Scheme I[a]



[a] (1) 20 kbar, room temperature, (2) 1 atm, room temperature or higher.

Scheme II

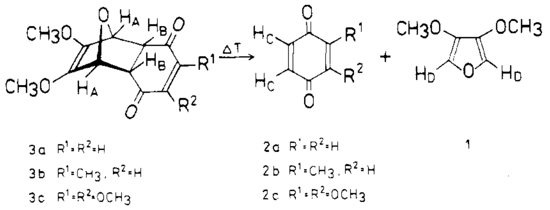


Table I. Rate Constants and Activation Energies for the Retro-Diels–Alder Reaction 3 → 2 + 1

	$10^{-3}(k \pm \Delta k)$, s^{-1}			
compd	T = 299 K	T = 315 K	T = 325 K	E_a, kJ/mol
3a	0.534 ± 0.005	5.81 ± 0.34	15.5 ± 1.1	102.5 ± 1.7
3b	0.435 ± 0.003	5.41 ± 0.22	13.3 ± 0.7	108.4 ± 0.8
3c	0.145 ± 0.009	2.14 ± 0.07	5.35 ± 0.25	114.2 ± 1.2

Comparison of the reaction rates at different temperatures points to an increase in stability in the sequence: **3a** < **3b** < **3c**, this finding expression in the activation energy values. It is assumed that the stability of cycloadduct 3 greatly exceeds that of the cycloadducts obtained by the reactions of furan with substituted 1,4-benzoquinones,[1] as fully confirmed experimentally; in this light it is evident that the substituents in the furan moiety are mainly responsible for the stabilizing effect. Comparison of the stabilities of **3a**, **3b**, and **3c**, at the same time, suggests that the stabilizing effect of the substituents in the quinone moiety is much smaller.

Jenner et al. have recently reported[7] on the thermal instability of the cycloadduct from the Diels–Alder reaction of 2-methylfuran with acrylonitrile. The kinetic and thermodynamic data obtained by these authors are in good agreement with the present findings. In consequence of Jenner's interpretation, we can conclude that the retro-Diels–Alder reaction of cycloadducts 3 would be characterized by an early transition state. This reasoning agrees with our findings that changing of the substituents in the quinone moiety only slightly influences the rate constants.

The present kinetic results and their thermodynamic consequences enabled formulation of conclusions impor-

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(4) According to the ^1H NMR spectra, the bridgehead coupling constants $J_{H_AH_B}$ for endo adducts 3 were evaluated to be about 3 Hz, and those for the corresponding exo adducts to be <1 Hz. Moreover, the signals of H_A and H_B derived from endo adducts as compared to the exo adducts were strongly up-field shifted ($\Delta\delta$ = 0.2–0.3).[2,3] Endo configuration was attributed to adduct **3a** on the basis of X-ray structure determination of its stable hydrogenated derivative.[5]

(5) Suwińska, K.; Andreetti, G. D.; Lipkowski, J.; Jurczak, J.; Koźluk, T. *Acta Crystallogr., Sect. C*, accepted for publication.

(6) Under conditions of the experiment, in all cases, the reactant concentration goes to zero after a period of time varying in dependence on temperature and nature of substituents.

(7) Jenner, G.; Papadopoulos, M.; Rimmelin, J. *J. Org. Chem.* **1983**, *48*, 748.

tant for organic synthesis. Namely, [4 + 2] cycloaddition between furan and substituted 1,4-benzoquinones of type **2** cannot be expected to effectively proceed under thermal conditions. However, cycloadducts of furan and 1,4-benzoquinones can be synthesized by the high-pressure method according to our recently proposed procedure.[1]

Experimental Section

Melting points (uncorrected) were determined on a Kofler block. ^{1}H NMR spectra were recorded with a JEOL JNM-4H-100 spectrometer (δ scale, Me$_4$Si used as an internal standard). High-pressure experiments were performed in an apparatus of the piston-cylinder type, described in our earlier paper.[8]

***endo*-9,10-Dimethoxy-11-oxatricyclo[6.2.1.0^{2,7}]undeca-4,9-diene-3,6-dione (3a).** A sample (540 mg, 5 mmol) of **2a** and 640 mg (5 mmol) of **1** was dissolved in 5 mL of toluene. The mixture was placed in a Teflon brand ampule[9] which was inserted into a high-pressure vessel filled with ligroin as transmission medium, and it was closed with a mobile piston.[8] Then the high-pressure unit was placed between the pistons of a hydraulic press and the pressure was raised to 9.0 kbar at room temperature. The mixture was kept under these conditions for 20 h and decompressed. Subsequently crystalline **3a** which has precipitated under high pressure was immediately removed by filtration; 10 mL of ether were added to the filtrate, and this mixture was cooled to −10 °C to give the second crop of crystalline **3a**. The overall yield of analytically pure endo adduct **3a** was 1.02 g (86.5%): mp 89–90 °C; ^{1}H NMR spectrum cf. text.

Endo adduct 3b: obtained in the same manner, 89% yield; mp 86–87 °C; ^{1}H NMR δ 6.60 (q, $J_{\mathrm{H-CH_3}}$ = 2 Hz, 1 H), 5.18 (bs, 2 H$_A$), 3.68 (s, 6 H, OCH$_3$), 3.50 (bs, 2 H$_B$), 2.00 (d, $J_{\mathrm{H-CH_3}}$ = 2 Hz, 3 H, CH$_3$).

Endo adduct 3c: obtained in the same manner, 88.5% yield; dec over 50 °C; ^{1}H NMR δ 5.18 (bs, 2 H$_A$), 4.02 (s, 6 H, OCH$_3$), 3.72 (s, 6 H, OCH$_3$), 3.48 (bs, 2 H$_B$).

Kinetic Measurements. The experiments were carried out in a NMR tube (ϕ = 4 mm) in a chloroform-*d* solution (initial concentration 0.4 mmol/mL) at three temperatures: 26, 42, and 52 °C. Integration of the decreasing and increasing signals was measured at suitable time intervals between 0.5 and 2 min. The proton derived from CHCl$_3$ served as internal standard. The rate constants and activation energies were calculated by the least-squares method.

Acknowledgment. This work was supported by Polish Academy of Sciences Grant 03.10.

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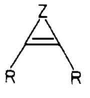
Diphenylthiirene 1-Oxide. The Sulfoxide Functionality and Reactivity

Uri Zoller

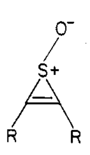
Division of Chemical Studies, University of Haifa-Oranim,
P.O. Kiryat Tivon 36 910, Israel

Received March 21, 1984

Systems of type **1** are unique: In cases of Z = O, S, NR, and PR they may be considered as “classically”antiaromatic as they have a cyclic array of 4nπ electrons predicted by theory to have little delocalization energy.[1]



1



2

On the other hand, on the basis of a naive analogy with cyclopropenones, the ground-state aromatic stabilization of which has been recently reconfirmed,[2] some kind of “aromaticity” can, in principle, be assigned to these systems when Z = SO or SO$_2$, assuming a possibility for transmission of electronic effects via π-conjugation.[3]

The thiirene oxide system **2** is of particular interest due to its being simultaneously both a potentially nonbenzenoid aromatic $(4n + 2)\pi$ and antiaromatic $4n\pi$ Hückel system.

The isolation and the characterization of the first diaryl-substituted members of this class of compounds (i.e., **2**, R = Ph)[4] enables one to carry out “bench scale” chemistry on this class of compounds under ordinary laboratory conditions.

To date, only the chemistry of 2,3-diphenylthiirene 1-oxide has been explored by Carpino et al.[4], whereas the first synthesis of alkyl-substituted thiirene sulfoxide was only very recently reported.[5] The possible preparation of the parent thiirene 1-oxide (i.e., **2**, R = H) is still under examination.[6]

On the basis of the available experimental data as well as extensive theoretical studies of the thiirene 1-oxide system,[7] the following conclusions concerning its structure, properties, and reactivity emerge: 1. Conjugative interactions and/or cyclic π-delocalizations are small compared with closely related systems.[7,8] 2. No significant antiaromatic destabilizing effects can be ascribed to the sulfur unshared pair of electrons. 3. The oxygen moiety in the sulfoxide function is not and probably should not be expected to be highly reactive. Thus, theoretical calculations predict[8] possible spiroconjugative-type[9] interaction between the $\pi^*_{\mathrm{C=C}}$ orbital of the ring and the π orbitals of the SO (which leads to aromatic stabilization and a π charge transfer backwards from the SO to C=C). There exists, however, a rather strong destabilization of the $\pi^*_{\mathrm{SO}}(d_{xz})$ orbital.[8] Experimentally, the ring carbon–carbon double bond rather than the sulfoxide function of thiirene 1-oxides was shown to be the primary active site of chemical attack.[4]

In order to study both the bonding in this Hückel molecule especially at sulfur—via an empirical carbon-13 NMR approach—and the chemical reactivity of the sulfoxide function as a result, we have gathered data on **1** (Z = SO and SO$_2$) and have investigated the reaction of the sulfoxide function of **2** with a variety of reagents.

We report here our results in this attempt to understand the relationship between bonding and chemical reactivity in molecules having this or similar structure.

Results and Discussion

The chemical shift of the vinylic carbon of 2,3-diphenylthiirene 1-oxide (**2a**) was found to be 137.3 ppm (downfield from Me$_4$Si) and those of the corresponding

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