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RADICAL ANIONIC CYCLIZATION REACTIONS VIA PHOTOCHEMICALLY INDUCED ELECTRON TRANSFER [1]

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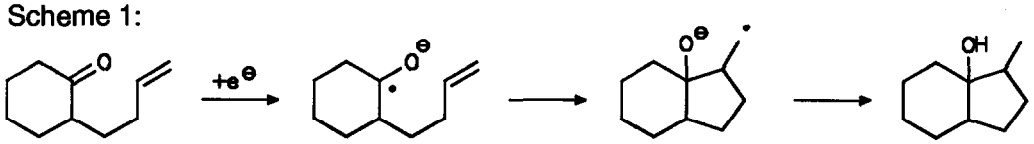
Abstract: Irradiating cyclohexenones containing an olefinic side chain under electron transfer-conditions (PET) leads to new spirocyclic products **3**, as well as [2+2]-cycloaddition products **2**. A new reductive cyclobutane ring opening allows photochemical conversion of cyclobutanes **2** to spirocyclic compounds **3**.

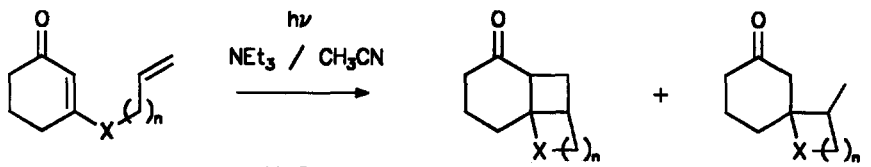
Radical reactions have opened a wide scope of possibilities in organic synthesis [2] and radical cyclizations are well documented [3]. Cyclization of radical anions can be achieved by electrochemically [4] as well as by photochemically [5] induced electron transfer (PET).

Scheme 1:



We now report on the radical anionic cyclization of olefinic enones which can effectively compete with intramolecular [2+2]-cycloaddition to form new spirocyclic products (see scheme 2).

Scheme 2:



1a-e

a: X=O, n=1
b: X=O, n=2
c: X=O, n=3
d: X=O, n=4
e: X=CH_2, n=2

2a-e **3a-e**

3-Alkenyloxy-2-cyclohexenones and 3-alkenyl-2-cyclohexenones (e.g. **1a-d** and **1e**) are easily accessible with variable length of the side chain.[6] The [2+2]-cycloaddition of such compounds has been intensively studied.[7a,b]

Of the two possible modes of [2+2]-cycloaddition, "*crossed*" (head to head) and "*straight*" (head to tail), only the "*straight*" cycloadducts are depicted in order to simplify the schemes presented, though NMR experiments [8] clearly show the structures of **2c** and **2e** to be of the "*straight*" mode, with *cis*-fused rings, and **2a** to be "*crossed*".

Irradiation under electron transfer conditions (i.e. in the presence of a donor such as triethylamine) in some cases results in the formation of new compounds with a spirocyclic structure [8,9] (see scheme 2 and table). These products are not observed in absence of a donor.

Table: Yield[a] of spirocyclic product at 100% conversion:

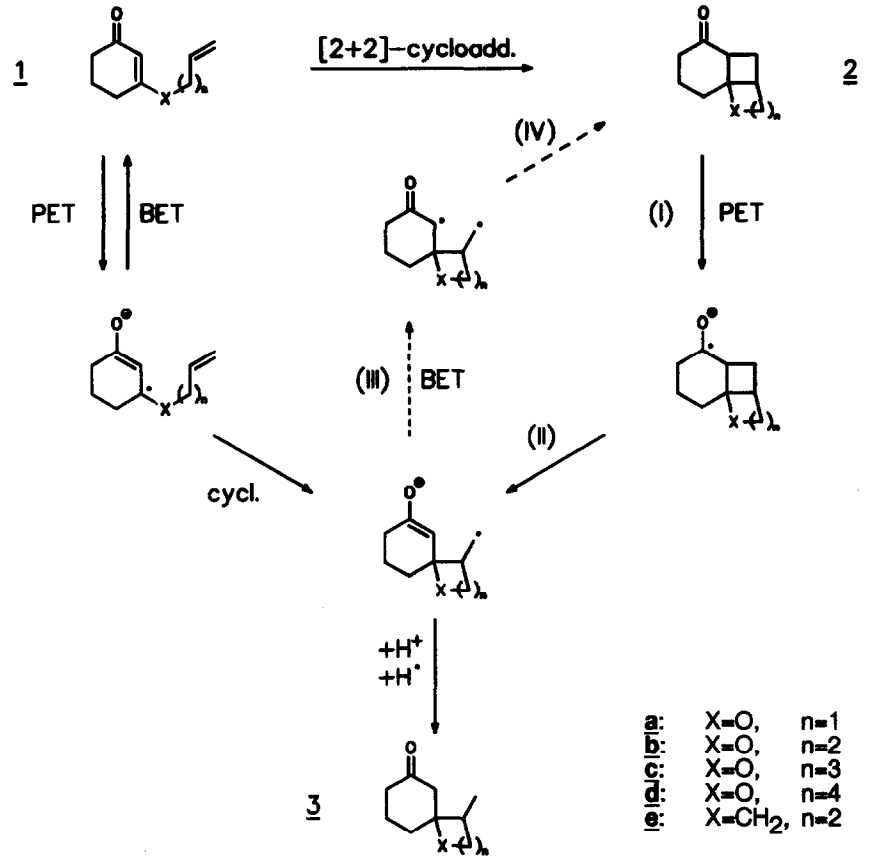
	HPK[b]	254 nm[c]	300 nm[c]	350 nm[c]	100% conv.
1a	*no spirocyclic product observed.*[d]				< 10 h
1b	4%	< 1%	11%	6%	< 10 h[e]
1c	22%	5%	45%	30%	20 h
1d	*no spirocyclic product observed.*[d]				12 - 15 d[f]
1e	13%	13%	19%	29%	2 h

Reaction conditions: An acetonitrile solution containing the resp. starting material (0.5 mM), triethylamine (2.5 mM) and decane (internal standard) was irradiated in a sealed glass tube (pyrex glass for 300 and 350 nm irrad., otherwise quartz glass) under argon atmosphere. -

a) Determined by capillary GLC. - b) Philips 125W high pressure mercury burner in a "Merry-Go-Round" type apparatus. - c) In a RAYONET reactor fitted with a "Merry-Go-Round" inset. - d) Main product is [2+2]-cyclo-adduct. - e) Longer irradiation yields up to 30% spiro product **3b** - f) Estimated after 30% conversion

Irradiation times for full conversion increase dramatically with a rising number of CH_2-groups and spiro product formation is only observed with medium chain lengths. The proposed mechanism presented (scheme 3) can explain these experimental results: If the chain length is too long, back-electron-transfer (BET) takes place before cyclization can occur and [2+2]-cyclization is the only remaining reaction pathway. Short chains, on the other hand, enable fast [2+2]-cyclization, which seems to compete effectively with electron transfer.

Scheme 3: Proposed mechanism when irradiating under electron transfer-conditions



Irradiation of pure isolated [2+2]-cycloaddition products **2b**, **2c** or **2e** in presence of triethylamine results in spiro product formation (**3b**, **3c** or **3e**; 40 - 80%) without any trace of the original starting material (**1b**, **1c** or **1e** resp.) being detectable during irradiation. This reductive cyclobutane ring opening probably takes place via a PET-mechanism (I, II in scheme 3), since it is not observed in absence of triethylamine. Attempts to obtain a spirocyclic product of **1a** by irradiating its [2+2]-product **2a** under the same conditions, failed to yield an identifiable product. This might be due to the structure of **2a** which is "*crossed*".

It cannot be ruled out that in presence of triethylamine [2+2]-product formation via a PET-pathway (III, IV in scheme 3) takes place. Verification of this pathway by trapping the biradicals involved was attempted by irradiating in presence of oxygen, but no new products or selectivities which would confirm this pathway could be observed [10].

Spiro product formation is enhanced by correct choice of the wavelength employed during irradiation. This may be caused by $\pi \rightarrow \pi^*$ excitation (**1c**: λ_{max}=244nm, ε = 16000) being more favourable to [2+2]-product formation, whereas $n \rightarrow \pi^*$ excitation (**1c**: λ_{max}=294nm, ε = 78) allows enhanced spiro-product formation.
Further improvement may be achieved by enabling electron transfer without excitation of the enone, thereby avoiding direct [2+2]-cycloaddition. Investigations concerning photosensitized reactions and use of photochemically excitable donor amines are in progress.

Acknowledgements: This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the Bayer AG, Philips Bildröhrenwerke AG, and Heraeus (Orginal Hanau).

References and Notes:

[1] Radical Ions and Photochemical Charge Transfer Phenomena, Part 29. For part 28 see M.Vondenhof, J Mattay, Chem.Ber. in press.

[2] B.Giese in "Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds", Pergamon Press 1986.

[3] A.L.J. Beckwith, Tetrahedron 37 (1981), 3073.

[4] T.Shono, J.Am.Chem.Soc. 100 (1978), 545.

[5] D.Belotti, J.Cossy, J.P.Pete, C.Portella, J.Org.Chem. 51 (1986), 4195.

[6] Compounds **1a-d** were synthesized by heating a cyclohexane solution of 1,3-cyclohexanedione, the respective alcohol and p-toluenesulfonic acid in a Dean-Stark type apparatus under reflux.
Compound **1e** was prepared by addition of 3-ethoxy-2-cylohexenone to the respective Grignard reagent followed by usual work-up procedure.

[7] a) For reviews on [2+2]-cycloadditon to enones see e.g.: M.Demuth, G.Mikhail, Synthesis 1989, 145 or M.T.Crimmins, Chem.Rev. 88 (1988), 1453.
b) For dependence of regiochemical outcome on substitution of the olefinic moiety see: S.Wolff, W.C.Agosta, J.Am.Chem.Soc. 105 (1983), 1292 or E. Fischer, R.Gleiter, Angew.Chem. 101 (1989), 925; Int.Ed.Engl. 28 (1989), 925.

[8] The structures of all new compounds were assigned by ^{1}H NMR, ^{13}C NMR and decoupling experiments. Characteristic coupling patterns:
2c ("*straight*"): α-CH (m, 2.9 ppm) - CH_2 (m, 2.1 ppm), ^3J = 6/9 Hz
2a ("*crossed*"): α-CH (dd, 3.17 ppm) - CH (dd, 2.55 ppm), ^3J = 2,5 Hz
3c (spirocyclic): CH_3 (d, 0.92 ppm), ^3J = 7 Hz

[9] Isolated spirocyclic product contained only one of two possible diastereomers.

[10] Irradiation under an oxygen atmosphere in presence of triethylamine leads to exclusive [2+2]-cycloaddition at strongly reduced conversion rates, which indicates electron transfer quenching by $^3O_2$ (see e.g. K.A.Zaklika, B.Kaskar, A.P.Schaap, J.Am.Chem.Soc. 102 (1980), 389.).

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