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Fragmentation-Cyclization Reactions by Photoinduced Electron Transfer

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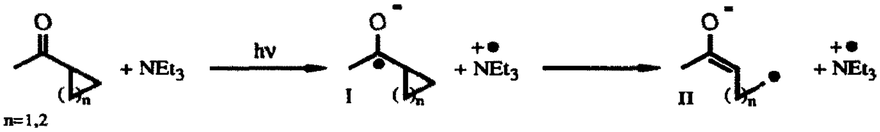
***Key words:** photoinduced electron transfer (PET), ketyl radical anion, bond cleavage, cyclization.*

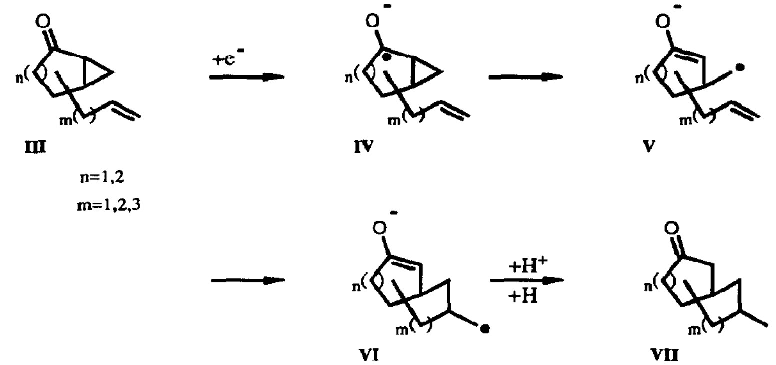
Abstract: Irradiation of unsaturated bicyclo[4.1.0]heptanones and bicyclo[3.1.0]hexanones under reductive PET conditions leads to a regioselective cleavage of the cyclopropane moiety followed by cyclization. By this method various types of ring anellated and spirocyclic compounds are accessible.

Photoinduced electron transfer (PET) reactions have received considerable interest in the past decade [1-4]. Many synthetic applications as well as theoretical rationalizations have been reported and therefore the understanding of PET reactions has increased. Most of this work focused on the formation of C-C bonds whereas their cleavage has gained interest only recently. For example, one of the first examples of a PET induced cleavage of a cyclobutane ring was reported by us [5] in 1990 (scheme 1, n=2). Later this fragmentation method was extented to cyclopropanes and a new ring expansion procedure was developed [6,7]. Further applications were reported by Cossy [8] and most recently by Pandey [9]. A comprehensive study of the mechanism has been published by Maslak [10].



Scheme 1.

We now report on a further extension of the reaction of a PET induced fragmentation-cyclization. For this purpose bicyclo[4.1.0]heptanones and bicyclo[3.1.0]hexanones bearing a suitable unsaturated side chain III were synthesized. Upon photolysis in presence of triethylamine as donor III should cleave according to the process shown in scheme 1. Then the new radical anion V should cyclize to VI followed by H and H^+- transfer to form the rearranged product VII (scheme 2). A similar procedure with samarium(II) diiodide in at least stoichometric amounts has been reported by Motherwell [11].



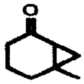
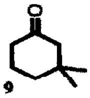
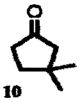
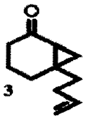
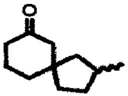
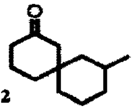
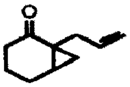
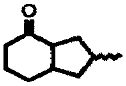
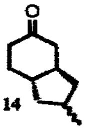
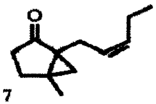
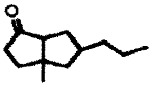
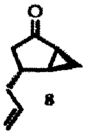
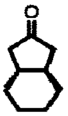
Scheme 2.

The results of our investigations are summarized in the table. In general the starting materials were synthesized from the corresponding cycloalkenones first by introducing the unsaturated chain and then by cyclopropanization according to Corey's method using the $Me_2S(O)CH_2$ ylide [12,13]. Under reductive PET conditions [14] **1-8** form the corresponding products **9-17**. In all cases the cyclopropane ring is cleaved regioselectively at the *exo*-side forming either the 3,3-disubstituted cycloalkanones **9** and **10** or the cyclized products **11-17**.

The results are rationalized in the following way. Due to the better alignment of the involved molecular orbitals the *exo*-cyclic cyclopropyl bond is cleaved selectively. The 3,3-dimethylcycloalkanes (entry 1/2) are formed after transfer of a proton probably from the triethylamine radical cation due to its high acidity. The mechanism of the hydrogen tranfer is still unknown. The two spirocyclic products (entry 3/4) clearly show the radical character of the reaction. Product **11** is formed in good yields as a mixture of two diastereoisomers whereas product **12** was only isolated in poor yields from a complex reaction mixture. A corresponding second isomer was not found. Much attention was paid to the reactions shown in entry 6, 7, and 8. Due to their formation starting from the enone the cyclopropyl moiety and the unsaturated side chain of **6** and **8** are in a *trans* position (Corey's method [12] was used). Since this configuration is not affected during the course of reaction **14** and **17** are also *trans* fixed [13]. This steric requirement even rationalizes the unexpected formation of a six-membered ring as cyclization product (**17**). Entry 7 shows the products formed from the cyclopropyl derivative of *cis*-jasmone. Apart from the two expected bicyclic systems **16** an interesting oxetane **15** is formed by intramolecular Paterno-Büchi reaction. The yields of this reaction are determined for consumed starting material. The reaction was stopped at a conversion of 61%.

In this latter case some solvent effects were investigated as well. With respect to the standard PET conditions [14] no changes in product distribution are found in presence of 1 equivalent of $LiClO_4$. Irradiation in the absence of triethylamine leads to a predominant formation of the oxetane either in benzene or acetonitrile. Using 3 M etheral $LiClO_4$ solution in presence of 4 equivalents of triethylamine affords almost no change of the starting material at all.

Table: Fragmentation-cyclization reactions of unsaturated bicycloalkanones under reductive PET conditions (cf. ref. 13 and 14).

Entry	Starting Material	Yield (%)	Products
1	 **1**	48	 **9**
2	 **2**	39	 **10**
3	 **3**	41 mix. diastereoisomers	 **11**
4	 **4**	8	 **12**
5	 **5**	30 mix. diastereoisomers	 **13**
6	 **6**	23 mix. diastereoisomers	 **14**
7	 **7**	**15**: 37, **16**: 14 mix. diastereoisomers 61% convers.	 **15**  **16**
8	 **8**	20	 **17**

Further investigations of other cyclopropane- and cyclobutane anellated systems are in progress in order to elucidate this new type of PET induced fragmentation-cyclization method.

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12. E. J. Corey, M. Chaykovsky, *J. Am. Chem. Soc.* **1965**, *87*, 1353-1364.
13. A complete description including all experimental details will be published in a full paper in the near future.
14. Typical experimental procedure: Irradiation of a degassed 10^{-1}- 10^{-2} M solution of **1-8** in acetonitrile in presence of 4 equivalents of triethylamine with a Rayonet photoreactor at a wavelength of 300 nm.
15. ^{13}C-NMR (δ ppm); **9**: 18.5 (CH_2), 28.8 (CH_3), 36.2 (C_q), 38.2 (CH_2), 41.0 (CH_2), 55.1 (CH_2), 212.2 (C_q). **10**: 28.2 (CH_3), 36.4 (C_q), 37.2 (CH_2), 37.6 (CH_2), 53.7 (CH_2), 219.9 (C_q). **11** (main isomer): 20.7 (CH_3), 23.8 (CH_2), 33.4 (CH), 33.7 (CH_2), 38.3 (CH_2), 41.2 (CH_2), 47.2 (CH_2), 47.7 (C_q), 53.8 (CH_2), 54.9 (CH_2), 211.9 (C_q). **12**: 19.7 (CH_2), 20.6 (CH_2), 29.4 (CH_2), 31.6 (CH_2), 34.0 (CH), 35.2 (CH_2), 40.4 (CH_2), 41.1 (CH_2), 43.1 (CH_2), 46.6 (C_q), 54.3 (CH_3), 214.2 (C_q). **13** (main isomer): 22.2 (CH_3), 23.9 (CH_2), 27.9 (CH_2), 31.5 (CH), 36.0 (CH_2), 40.0 (CH_2), 40.9 (CH_2), 42.5 (CH), 53.1 (CH), 214.7 (C_q). **14** (main isomer): 23.1 (CH_3), 29.7 (CH_2), 32.5 (CH), 39.7 (CH_2), 40.1 (CH_2), 41.0 (CH_2), 45.8 (CH), 46.3 (CH), 47.4 (CH_2), 212.0 (C_q). **15**: 8.4 (CH_3), 19.5 (CH_2), 20.4 (CH_3), 28.0 (CH_2), 28.3 (C_q), 30.3 (CH_2), 32.6 (CH_2), 33.1 (CH_2), 44.1 (CH), 44.6 (C_q), 87.5 (CH), 102.3 (C_q). **16** (main isomer): 14.6 (CH_3), 22.0 (CH_2), 28.9 (CH_3), 35.4 (CH_2), 37.0 (CH_2), 38.3 (CH_2), 39.2 (CH_2), 40.3 (CH), 47.2 (C_q), 48.9 (CH_2), 59.4 (CH), 223.4 (C_q). **17**: 26.3 (CH_2), 31.4 (CH_2), 43.9 (CH), 45.7 (CH_2), 218.3 (C_q).

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