Tetrahedron Letters, Vol.32, No.10, pp 1315-1316, 1991
Printed in Great Britain

0040-4039/91 $3.00 + .00
Pergamon Press plc

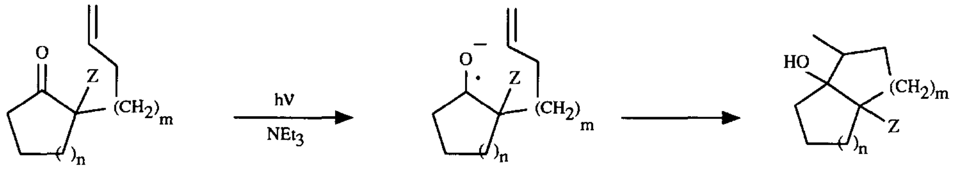
RADICAL ANION RING OPENING REACTIONS VIA PHOTOCHEMICALLY INDUCED ELECTRON TRANSFER

J. Cossy[a], P. Aclinou[b], V. Bellosta[a], N. Furet[a], J. Baranne-Lafont[a], D. Sparfel[a], C. Souchaud[a].

[a] Laboratoire de Chimie Organique, associé au CNRS, E.S.P.C.I. 10 rue Vauquelin, F-75231 Paris Cédex 05.
[b] Laboratoire des réarrangements thermiques et photochimiques, associé au CNRS, U.F.R. Sciences, F-51062 Reims Cédex.

Summary : *Ketyl radical anions can induce the opening of adjacent strained ring such as cyclopropane, cyclobutane, epoxide and 7-oxabicyclo[2.2.1]heptane.*

It is well established that ketones can be reduced under photochemical conditions in the presence of amines [1]. The primary process is thought to involve a very fast electron transfer from the amine to the triplet excited state of the ketone [2,3]. Recently, we have shown that δ,ε-unsaturated ketyl radical anions produced by photoinduced electron transfers from a donor such as hexamethylphosphotriamide or triethylamine can undergo efficient cyclization with the formation of cyclopentanol derivatives [4]. Similar cyclizations can be achieved also under electrochemical conditions [5]

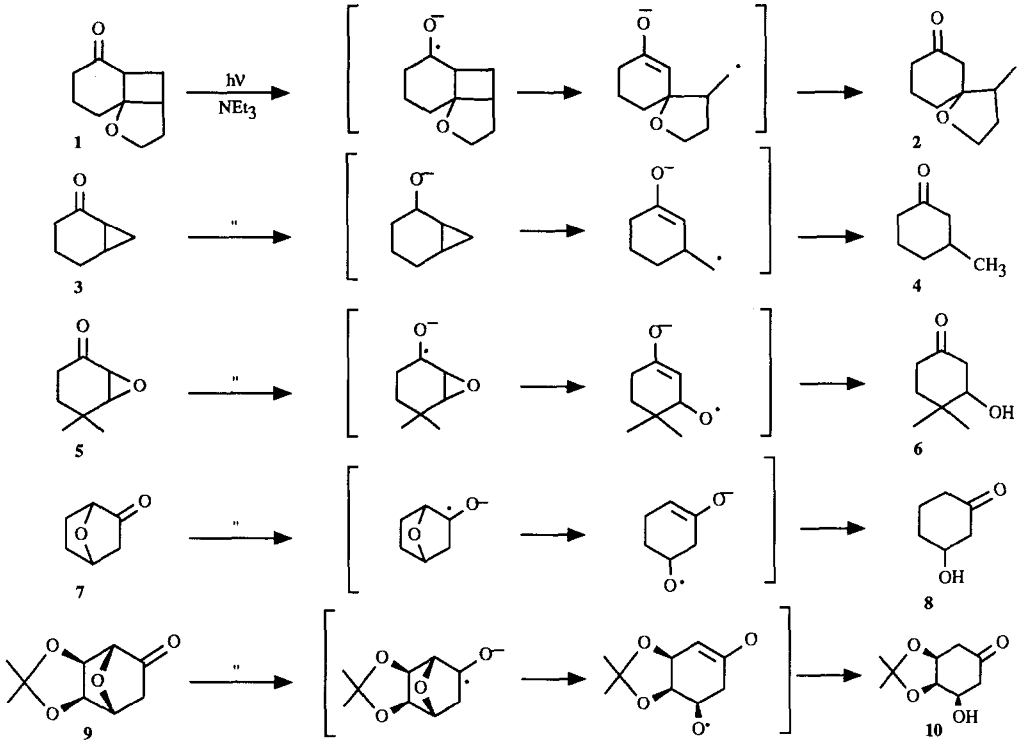


$Z = H, CO_2CH_3$; n = 1, 2 ; m = 1,2

We now show that ketyl radical anions can induce the opening of adjacent strained rings with the formation of the corresponding products of reduction. A recent publication by Bischof and Mattay [6] reporting the photoreduction of the tricyclic ketone **1** into the corresponding spirocyclic ether **2** urges us to publish our results on the same reaction and on related ring opening reactions.

The ketones **3** [7], **5** [8], **7** [9] and **9** [10] are readily obtained according to published procedures. When irradiated[11] (254 nm, quartz vessel) in CH_3CN (0.05 M solutions) in the presence of 5 equivalents of triethylamine, (20 °C), the corresponding ketones **4**, **6**, **8** and **10** were obtained and isolated in moderate to good yields. The time of the irradiation was critical as the ketone **2**, **4**, **6**, **8**, **10** underwent further photochemical processes under the conditions of their formation.

Thus, in our conditions, the irradiation of **1** (0.1 g) led to 100 % conversion after 1 hr and **2** could be isolated in 60 % yield. In the case of bicyclo[4.1.0]heptan-2-one **3** (0.5 g), after 2 hrs of irradiation, 50 % conversion was observed and **4** [12], was isolated in 48 % yield by flash chromatography on silica gel. Similarly, epoxy-ketone **5**, underwent 50 % conversion after one hour of irradiation, and **6** could be isolated in 45 % yield. The β-hydroxycyclohexanone **8** was obtained in 40 % yield on irradiating 7-oxabicyclo[2.2.1]heptan-2-one **7** [9] for 45 min (80 % conversion). Longer irradiation times led to higher conversion rates but the yields of the isolated products of photoreduction were not improved. A very clean photoreduction was observed, on irradiating the tricyclic ketone **9** [10] (0.2 g, 1 hr), which led to the partially protected 2,3,4-trihydroxycyclohexanone **10** [13] (85 % yield).



Plausible mechanisms for the photoreductions reported here are indicated ; further experimental studies are necessary to ascertain them. These preliminary results show, however, that ketyl radical anions generated photochemically can induce the opening of adjacent strained rings such as cyclopropane, cyclobutane, epoxide and the tetrahydrofuran moiety of 7-oxa bicyclo[2.2.1]heptanes. We are exploring the application of these new reactions in the synthesis of natural products and compounds of biological interest.

Acknowlegments : We thank Prof. P. Vogel, Dr. Y. Auberson and Miss D. Fattori, Université of Lausanne, for gifts of samples of compounds **7** and **9** and for helpful discussions.

References and Footnotes

1 Cohen, S.G. *Chem. Rev.*, **1973**, *73*, 141.
2 Simon, J.D. ; Peters, K.S. *J. Am. Chem. Soc.*, **1982**, *104*, 6542.
3 Yip, K.S. ; Loufty R.O. ; Chow, Y.L. ; Magzinski, L.K. *Can. J. Chem.*, **1972**, *50*, 3426.
4 Belotti, D. ; Cossy, J. ; Pète, J.P. ; Portella, C. *Tetrahedron Lett.*, **1985**, *26*, 4591.
5 Shono, T. *J. Am. Chem. Soc.*, **1978**, *100*, 545.
6 Bischof, E.W. ; Mattay, J. *Tetrahedron Lett.*, **1990**, *31*, 7137.
7 Corey, E.J. ; Chaykorsky, M. *J. Am. Chem. Soc.*, **1965**, *87*, 1353.
8 Wasson, R.L. ; House , H.O. "Organic Syntheses", Collect. Vol. IV, p. 552, Wiley, New York, 1963 ; .
9 Warm, A. ; Vogel, P. *Helv. Chim. Acta*, **1988**, *71*, 624.
10 Wagner, J. ; Vieira, E. ; Vogel, P. *Helv. Chim. Acta*, **1988**, *71*, 624.
11 A "merry-go-round" irradiator was used with 12 Philips TUV 15 lamps.
12 Identified by comparison with authentic samples.
13 IR ($CHCl_3$) : ν_{OH} = 3610 cm^{-1}, ν_{CO} = 1720 cm^{-1}. ^{1}H-NMR 250 MHz ($CDCl_3$) : 1.40 (s, 3H) 1.50 (s, 3H) 2.20 (s, 1H) 2.40-2.80 (m, 4H) 3.90-4.10 (m, 1H) 4.50 (m, 1H) 4.60 (m, 1H). ^{13}C NMR ($CDCl_3$) : 23.90, 25.83, 41.16, 42.62, 66.01, 71.52, 74.06, 109.06, 206.63. SM : m/e = 186 ; 168 (100 %).

(Received in France 21 December 1990)