Pergamon

Tetrahedron Letters, Vol. 37, No. 30, pp. 5363-5364, 1996

0040-4039/96 $15.00 + 0.00

PII: S0040-4039(96)01107-0

Dimethyldioxirane Oxidations of Some Cyclopropanes

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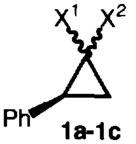
Abstract: Phenylcyclopropanes and halo-phenyl-substituted cyclopropanes do not react with dimethyldioxirane. Bicyclo[4.1.0]heptane (**4**) , however, is oxidized by this reagent to the 2-ketone (**5**). Bicyclo[6.1.0]nonane (**6**) gives all three possible ketones (**7** - **9**). Even exo-9-bromobicyclo[6.1.0]nonane (**10**) can be converted by dimethyldioxirane to a ketone to which structure **11** is assigned. Copyright © 1996 Elsevier Science Ltd

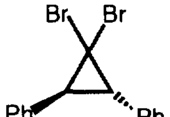
Isolated or *in situ* generated dioxiranes are emerging as novel selective oxidants (for reviews, see [1-3]). Reactions with C-H bonds are highly stereo- and regioselective favoring tertiary over secondary positions. Initially formed secondary alcohols are converted further into ketones in most cases. Dioxirane reactions of cyclopropane derivatives have not found attention yet - except for the rigid systems of Binor S and 2,4-didehydroadamantane. [4] Here, bridgehead insertion (21 % yield of 7-hydroxy-2,4-didehydroadamantane) and oxidation in α position to the three-membered ring (29 % yield of 2,4-didehydroadamantan-10-one) compete.

We wanted to know whether secondary, tertiary, or benzylic cyclopropane C-H bonds would be reactive towards dioxirane at all and how halide substituents on cyclopropanes would influence the reactivity. Preliminary results are related here. Compounds **1a** - **3b** were found to be totally inert when treated with excess dimethyldioxirane in acetone at room temperature for one day to two weeks. An oxidation occurred, however, when bicyclo[4.1.0]heptane (**4**) was the substrate, and bicyclo[4.1.0]heptan-2-one (**5**) was obtained. [5] When extending this reaction to bicyclo[6.1.0]nonane, all three possible ketones in the larger ring, **7** - **9**, were observed. Bicyclo[6.1.0]nonan-2-one (**7**) was the product formed in the highest proportion (~65 rel.%) and the 3-ketone **8** was the least prevailing one (~10 rel. %).[6]

1	X^1	X^2
a	Cl	Cl
b	Cl	H
c	H	H



1a-1c



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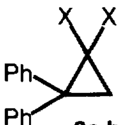
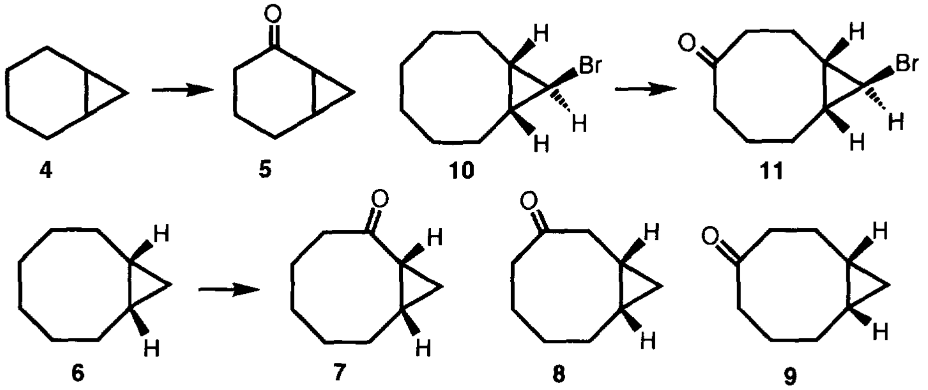


3a,b

3	X
a	Br
b	H

Up to now there were only two methods for the preparative keto functionalization of a methylene group α to a cyclopropane unit: dry ozonization introduced by de Meijere [7] and the $NaIO_4/RuO_2$ oxidation developped by Yamada et al. [8] Interestingly, application of the ozone method to **6** gave 88 % of **7**, 7 % of **9**, and a very small amount of the 2,7-diketone, but apparently no **8**. *The present method is a new alternative for the oxidation of bicyclo[n.1.0]alkanes.*



Finally, *exo*-9-bromobicyclo[6.1.0]nonane (**10**) could be converted, but not the 9,9-dibromo derivative. Here only one, crystalline product was formed. Analysis, IR and ${}^{13}C$ NMR spectral data indicated that compound **11** was present.[9] When the strong deactivation by halide substituents was considered, oxidative attack at the most remote position appeared very reasonable indeed. No products were obtained in all cases if the dioxirane was generated *in situ.*

Acknowledgement: Support was given by the University (Project "Polycyclen", OZ 21940) and the Fonds der Chemischen Industrie.

References and Notes

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2. Adam, W.; Curci, R.; Edwards, J.O., *Acc. Chem. Res.* **1989**, *22* , 205-211.
3. Murray, R.W., *Chem. Rev.*, **1989**, *89* , 1187-1201.
4. Teager, D.S.; Murray, R.K. Jr., *J. Org. Chem.* **1993**, *58*, 5548-5550.
5. Not optimized isolated yield: 23 %, b.p. 73-75°C (0.5 Torr).-**5** was identified by its ${}^{13}C$ NMR data which were identical to the literature values (Ceccherelli; P.Curini, M.; Marcotullio, M.C.; Rosati, O.,*Tetrahedron* **1992**, *48* , 9767 - 9774).
6. Not optimized yield of purified **7**-**9** mixture: 9 %. The compounds were identified by their ${}^{13}C$ NMR data which were identical to the literature values (Meier, H.; Antony-Mayer, C.; Schulz-Popitz, C.; Zerban, G., *Liebigs Ann. Chem.* **1987**, 1087-1094).
7. de Meijere,A.;Proksch,E.,*Angew.Chem.* **1976**, *88*, 802-803;*Angew.Chem.Int.Ed.Engl.* **1976**, *15*, 761-762.
8. Hasegawa, T.; Niwa, H.; Yamada, K. *Chem. Lett.* **1985**, 1385-1386.
9. 4 % yield (not optimized); m.p. 55°C (from pentane); IR: 1700 cm-1; ${}^{13}C$ NMR: δ 22.3 (C-7), 23.7 (C-9), 27.3 (C-8), 27.4 (C-1), 27.6 (C-2, C-6), 40.2 (C-5), 44.7 (C-3), 215.7 (C-4); $C_9H_{13}BrO$ (217.4) calc. C, 49.79, H, 6.04; found C, 49.75, H, 6.18.

(*Received in Germany* 3 *May* 1996; *accepted* 5 *June* 1996)