

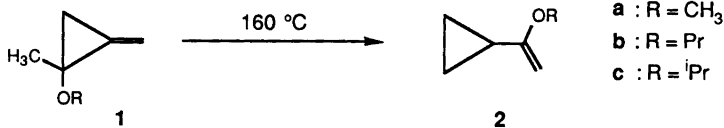
## On the Isomerization of 2-Alkoxy-2-methyl-1-methylenecyclopropanes to 1-Alkoxy-1-cyclopropylethenes

John E. Baldwin,\* Naresh D. Ghatlia and Karin M. O. Lundbäck<sup>§</sup>

Department of Chemistry, Syracuse University, Syracuse, New York 13244, USA

Baldwin, J. E., Ghatlia, N. D. and Lundbäck, K. M. O., 1987. On the Isomerization of 2-Alkoxy-2-methyl-1-methylenecyclopropanes to 1-Alkoxy-1-cyclopropylethenes. – *Acta Chem. Scand.*, Ser. B 41: 698–700.

A 1965 communication reported that 2-isopropoxy-2-methyl-1-methylenecyclopropane (**1c**) at 160 °C afforded 1-isopropoxy-1-cyclopropylethene (**2c**) in 95 % yield<sup>1</sup> (Scheme 1). No rationalization for this abnormal methylenecyclopropane isomerization was offered;<sup>1</sup> the reaction was not mentioned in the subsequent full paper<sup>2</sup> and it has remained unverified and unexplicated.<sup>3</sup>



Scheme 1.

A broad interest in methylenecyclopropane chemistry<sup>4</sup> has led us to a reinvestigation of this reaction. The rearrangement **1c** to **2c** has been confirmed, two additional examples of the reaction have been documented, and a rationale for the overall conversion has been formulated and subjected to an experimental test.

Samples of 2-alkoxy-2-methyl-1-methylenecyclopropanes (**1**) purified by preparative gas chromatography were heated in sealed tubes at 160–170 °C for up to 12 hours. Analysis by capillary GC indicated formation of a single product in each case; isolation of the reaction products by preparative GC followed by mass spectrometric

and <sup>1</sup>H NMR spectroscopic analyses provided convincing evidence to support the assignment of structure **2**. For product **2a**, for instance, the signals for the vinyl methylene protons were seen as an AB pattern at 3.94 and 3.84 ppm; the chemical shifts for vinyl protons predicted for 1-alkoxy-1-alkylethenes are 3.90 and 3.82 ppm.<sup>5</sup> The CH<sub>3</sub>O-singlet appeared at 3.5 ppm, and the

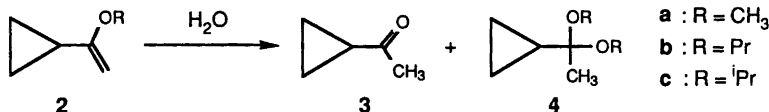
cyclopropyl proton signals at 1.47 (m, 1H) and 0.69–0.55 (m, 4H).

When, however, a rearrangement product was collected by preparative GC and placed in an NMR tube with CDCl<sub>3</sub>, and there was an unavoidable delay in recording the NMR spectrum, the observed absorptions indicated a mixture of compounds. Reexamination of such an NMR sample by GC/MS, and isolation of individual components followed by immediate recording of NMR spectra, served to identify the components as the vinyl ether **2**, cyclopropyl methyl ketone (**3**), and the corresponding dialkyl ketal **4**. Traces of water in the CDCl<sub>3</sub>, apparently, hydrolyzed the vinyl ether to give ketone **3** and an alcohol, and another equivalent of the ether reacted with that alcohol to form ketal **4** (Scheme 2).

The ketals **4** showed some of the expected

\*To whom correspondence should be addressed.

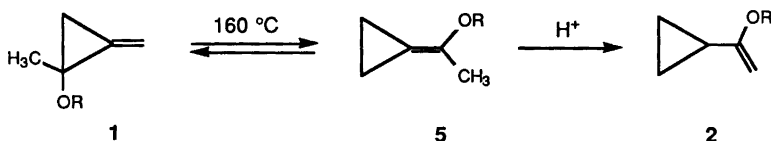
<sup>§</sup>Undergraduate research associate, summer 1986, from the Royal Institute of Technology, Stockholm.



Scheme 2.

complications in NMR spectra from diastereotopic protons; in **4b** the  $-OCH_2-$  proton signals were seen as two 2H multiplets at 3.49 and 3.33 ppm, while the isopropyl methyl groups in **4c** gave doublets at 1.23 and 1.16 ppm.

The rearrangement of **1** to **2** may be most simply formulated as a reversible methylenecyclopropane rearrangement to (1-alkoxyethylidene)cyclopropane (**5**),\* which then may isomerize to the more thermodynamically stable isomer **2** in an acid-catalyzed reaction (Scheme 3). In agreement with this hypothesis it was found that formation of **2a** was suppressed, and a substantial amount (43%) of **5a** accrued, when an octane solution of **1a** was heated in the presence of 1,8-bis(dimethylamino)naphthalene. The intermediate **5a** was characterized by mass spectrometry and NMR (3H singlets at 1.91 and 3.72 ppm).



Scheme 3.

The rearrangement of **1** to **2**, then, which as a purely thermal reaction may not be readily explained, may be viewed as an unexceptional conversion involving two steps, viz. a thermal reaction followed by an acid-catalyzed tautomerization.

## Experimental

Proton NMR spectra were recorded for CDCl<sub>3</sub> solutions with Me<sub>4</sub>Si as internal standard on a "Mohawk 250", an in-house-designed 5.87 Tesla FT spectrometer based on Cryomagnet Systems rf equipment and a Nicolet 1280 computer, or on GE QE-300 or GN-500 spectrometers. Analytical gas-liquid chromatographic analyses were done

\***5c** has been postulated as a possible intermediate in the reaction **1c** → **2c** (Ref. 6).

using 0.2 mm i.d. 25 m cross-linked dimethyl silicone and phenyl methyl silicone fused silica capillary columns, a Hewlett Packard 5790 gas chromatograph with both columns connected to a single injection port, and the two FID detectors connected to HP 3390A and 3392A recording integrators. Preparative gas chromatographic separations were accomplished using a Varian Aerograph A-90P3 and a 0.6 × 366 cm 20% SE-30 on Chromosorb-W HMDS 60/80 column. Mass spectra and GC/MS data were obtained with a Hewlett Packard 5970B mass-selective detector interfaced to a 5890 series gas chromatograph and a 9336 computer.

### 2-Methoxy-2-methyl-1-methylenecyclopropane

(**1a**) was prepared from 1,1-dichloro-2,3-*cis*-dimethylcyclopropane,<sup>7</sup> sodium methoxide, and sodium *tert*-butoxide in dimethyl sulfoxide;<sup>1,2</sup> the

corresponding 2-propyl and 2-isopropyl compounds, **1b** and **1c**, were obtained from the respective potassium alkoxides following the literature precedent.<sup>1,2</sup> NMR spectra for **1a** and **1c** were in accord with the literature reports; **1b** NMR: 5.62 (m, 1H), 5.39 (m, 1H), 3.45 (m, 2H), 1.55 (m, 2H), 1.45 (s, 3H), 1.43–1.36 (m, 1H), 1.17–1.11 (m, 1H), 0.9 (t, 3H); mass spectrum: *m/e* 126 (M<sup>+</sup>, 0.1%), 111 (2), 85 (2), 84 (17.7), 69 (63), 67 (4), 43 (100), 41 (50), 39 (26).

*Rearrangements of 2-alkoxy-2-methyl-1-methylenecyclopropanes (1)* were done in sealed base-washed and distilled water rinsed tubes; neat gas-chromatographically purified samples were heated in a bath of mesitylene at reflux (b.p. 165 °C) for up to 12 h. Reaction mixtures were analyzed by capillary GC, GC/MS, and pro-

ton NMR spectroscopy. **2a**:  $m/e$  98 ( $M^+$ , 63%), 67 (69), 55 (52), 43 (57), 41 (75), 40 (65), 39 (100); NMR: 3.93 (m, 1H), 3.81 (m, 1H), 3.5 (s, 3H), 1.47 (m, 1H), 0.69–0.55 (m, 4H). **2b**:  $m/e$  126 ( $M^+$ , 6.4%), 85 (37), 83 (16), 69 (89), 43 (100), 42 (37), 41 (83), 39 (60); NMR: 3.9 (m, 1H), 3.78 (m, 1H), 3.58 (t, 2H), 1.65 (m, 2H), 1.45 (m, 1H), 0.95 (t, 3H), 0.73–0.55 (m, 4H). **2c**:  $m/e$  126 ( $M^+$ , 10%), 84 (20), 83 (28), 69 (100), 56 (22), 43 (61), 42 (38), 41 (66), 39 (44); NMR: 4.26 (sept., 1H), 3.91 (m, 1H), 3.74 (m, 1H), 1.95–1.88 (m, 1H), 1.18 (d, 6H), 0.67–0.52 (m, 4H).

Partial hydrolysis of a major rearrangement product **2** in  $CDCl_3$  gave two additional compounds, viz. methyl cyclopropyl ketone, identified by its distinctive NMR spectrum<sup>8</sup> and by direct mass spectral and gas chromatographic comparisons with an authentic sample (Aldrich), and a 1,1-dialkoxy-1-cyclopropylethane. The dimethoxy compound **4a** was also synthesized independently from methyl cyclopropyl ketone and methanol,<sup>9</sup> the two samples of the ketal were identical on the basis of GC/MS comparisons.

(1-Methoxyethylidene)cyclopropane (**5a**) was formed by heating a 12% solution of **1a** in octane containing 4.6 mole % of 1,8-bis(dimethylamino) naphthalene for 5.5 h at 153°C. Analysis of the reaction mixture by capillary GC showed **1a** : **2a** : **5a** (retention times 2.96 : 4.38 : 5.05 min on the dimethyl silicone column with the column oven temperature at 40°C for 4 min followed by a temperature gradient of 10°C min<sup>-1</sup>) in the area percentage ratio 45 : 12 : 43. **5a**: NMR: 3H singlets at 1.91 and 3.72 ppm; MS:  $m/e$  98 ( $M^+$ , 7%), 97 (6), 83 (4), 67 (20), 55 (13), 53 (15), 43 (100).

**Acknowledgement.** We thank the National Science Foundation for supporting our studies on molecular rearrangements.

## References

1. Shields, T. C., Shoulders, B. A., Krause, J. F., Osborn, C. L. and Gardner, P. D. *J. Am. Chem. Soc.* **87** (1965) 3026.
2. Shields, T. C. and Gardner, P. D. *J. Am. Chem. Soc.* **89** (1967) 5425.
3. Osborn, C. L., Shields, T. C., Shoulders, B. A., Krause, J. F., Cortez, H. V. and Gardner, P. D. *J. Am. Chem. Soc.* **87** (1965) 3158; Andrews, S. D. and Day, A. C. *J. Chem. Soc., Chem. Commun.* (1966) 667; Deyrup, J. A. and Greenwald, R. B. *Tetrahedron Lett.* (1966) 5091; Shields, T. C., Loving, B. A. and Gardner, P. D. *J. Chem. Soc., Chem. Commun.* (1967) 556; Day, A. C. and Powell, J. T. *J. Chem. Soc., Chem. Commun.* (1968) 1241; Shields, T. C. and Billups, W. E. *Chem. Ind. (London)* (1967) 1999; Welch, J. G. and Magid, R. M. *J. Am. Chem. Soc.* **89** (1967) 5300; Shields, T. C. and Gardner, P. D. *J. Am. Chem. Soc.* **89** (1967) 5425; Lengyel, I. and Sheehan, J. C. *Angew. Chem. Int. Ed. Engl.* **7** (1968) 25; Shields, T. C., Billups, W. E. and Kurtz, A. N. *Angew. Chem. Int. Ed. Engl.* **7** (1968) 209; Andrews, S. D. and Day, A. C. *J. Chem. Soc. B* (1968) 1271; Quast, H. and Schmitt, E. *Angew. Chem. Int. Ed. Engl.* **8** (1969) 449; Barlet, R. and Vo-Quang, Y. *Bull. Soc. Chim. Fr.* (1969) 3729; Weiss, F. *Quart. Rev.* **24** (1970) 278; Doering, W. v. E. and Roth, H. D. *Tetrahedron* **26** (1970) 2825; Gajewski, J. J. *J. Am. Chem. Soc.* **93** (1971) 4450; Ando, T. and Yamanaka, H. *Yuki Gosei Kagaku Kyokaiishi* **29** (1971) 480; Fitjer, L. and Conia, J.-M. *Angew. Chem. Int. Ed. Engl.* **12** (1973) 332; Köbrich, G. *Angew. Chem. Int. Ed. Engl.* **12** (1973) 464; Akiba, K. *Yuki Gosei Kagaku Kyokaiishi* **31** (1973) 635; Binger, B. *Synthesis* (1974) 190; Leandri, G., Monti, H. and Bertrand, M. *Tetrahedron* **30** (1974) 3921; Henseling, K.-O. and Weyerstahl, P. *Chem. Ber.* **108** (1975) 2803; Arct, J., Migaj, B. and Zych, J. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **25** (1977) 695; Berson, J. A. In: de Mayo, P., Ed., *Rearrangements in Ground and Excited States*, Academic Press, New York 1980, Vol. 1, pp. 311–390.
4. Baldwin, J. E. and Chang, G. E. C. *Tetrahedron* **38** (1982) 825; Hudson, B. S., Baldwin, J. E., Chadwick, R. P. and Parker, D. W. *Unpublished results*; Van Derveer, D. G., Baldwin, J. E. and Parker, D. W. *J. Org. Chem.* **52** (1987) 1173; Baldwin, J. E. and Parker, D. W. *Ibid.* **52** (1987) 1475.
5. Pretsch, E., Clerc, T., Seibl, J. and Simon, W. *Tables of Spectral Data for Structure Determination of Organic Compounds*, Springer Verlag, Berlin 1983, p. H215; *Ibid.*, p. H220.
6. Shields, T. C. *Thesis*, University of Texas, Austin, Texas 1966; *Diss. Abstr.* **27** (1967) 4328-B.
7. Weyerstahl, P., Klaumann, D., Finger, C., Nerdel, F. and Buddrus, J. *Chem. Ber.* **100** (1967) 1858; Holbrook, K. A. and Parry, K. A. W. *J. Chem. Soc. B* (1970) 1019; Crossland, I. *Org. Synth.* **60** (1981) 6.
8. Pouchert, C. J. *The Aldrich Library of NMR Spectra*, 2nd ed., Aldrich Chemical Co., Milwaukee, Wisconsin 1983, Vol. 2(1), p. 392B.
9. Roelofsen, D. P. and van Bekkum, H. *Synthesis* (1972) 419.

Received July 31, 1987.