

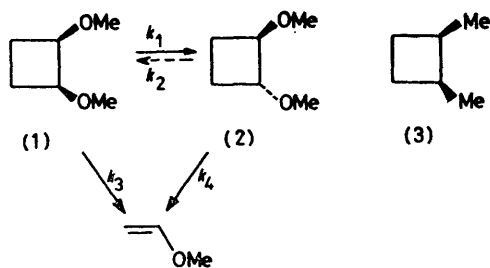
Thermal Rearrangement of Alkoxy-cyclobutanes

By WOLFGANG KIRMSE* and HANS RÜDIGER MURAWSKI
(Abteilung für Chemie der Ruhr-Universität, 4630 Bochum, Germany)

Summary The geometrical isomerization of *cis*-1,2-dimethoxycyclobutane (**1**) to the *trans*-isomer (**2**) and the rearrangement of 1-alkoxy-3-methylenecyclobutanes (**4**) and (**8**) to (**6**) and (**10**), respectively, are modestly accelerated by the presence of alkoxy groups compared to those of the related hydrocarbons; the effect of the alkoxy group in these reactions is, however, much smaller than that in the analogous cyclopropane rearrangements.

THE rates of the vinylcyclopropane rearrangement,¹ the methylenecyclopropane rearrangement,² and the geometrical isomerization of cyclopropane³ are strongly accelerated by substitution of an alkoxy group. These effects have been attributed to the stabilization of intermediate diradicals by alkoxy groups. We report here that the rate enhancements are much smaller in the analogous thermal reorganizations of alkoxy-cyclobutanes.

Geometrical isomerization of *cis*-1,2-dimethoxycyclobutane (**1**)⁴ competes with decomposition to methoxyethene in the temperature range 330–370 °C (Scheme 1). The



SCHEME 1. $10^6 \times k$ (s^{-1}) at 351.8 °C: $k_1 = 1.85$, $k_3 = 4.93$, $k_4 = 0.48$.

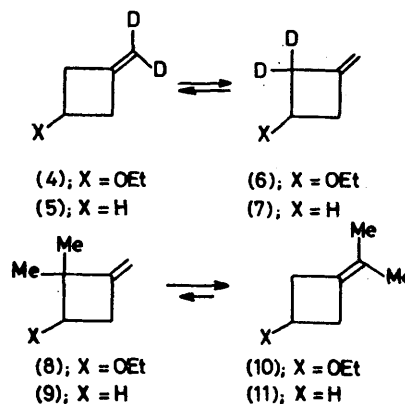
decomposition of *trans*-1,2-dimethoxycyclobutane (**2**)⁴ proceeds more slowly, little (<1%) isomerization to (**1**) being detected. The Arrhenius parameters of (**1**), estimated from

TABLE. Activation parameters of cyclobutane isomerization.

	$E_a/kJ\ mol^{-1}$	$\log A$	Ref.
(1) <i>cis</i> → <i>trans</i>	231.4 ± 1.0^a	14.61 ± 0.08	
Overall	231.6 ± 2.4	15.19 ± 0.20	
(3) <i>cis</i> → <i>trans</i>	251.5	14.81	5
Overall	254.4	15.68	
(4) → (6)	181.6 ± 1.6	13.73 ± 0.16	
(5) → (7)	207.1	14.77	10
(8) → (10)	190.2 ± 0.9	13.78 ± 0.09	
(9) → (11)	204.6	13.68	11

^a Standard deviations from a least-squares treatment.

rates at five different temperatures, may be compared with those of *cis*-1,2-dimethylcyclobutane (**3**)⁵ (Table). The difference in activation energy is *ca.* 20 $kJ\ mol^{-1}$. The activation energies for the geometrical isomerization of *cis*-1,2-dimethoxycyclopropanes (208–209 $kJ\ mol^{-1}$)³ and of *cis*-1,2-dialkylcyclopropanes (246–248 $kJ\ mol^{-1}$)⁶ differ by *ca.* 40 $kJ\ mol^{-1}$.



SCHEME 2

Equilibration of 1-ethoxy-3- $^{2}\text{H}_2$ methylenecyclobutane (**4**)⁷ (Scheme 2) was monitored by n.m.r. and i.r. spectroscopy. The equilibrium constant at 260 °C, $K = (\mathbf{6})/(\mathbf{4}) = 2.11 \pm 0.07$, shows the expected isotope effect.⁸ Deuterium is positioned preferentially at the sp^3 hybridized carbon. With the related pair, 1-ethoxy-2,2-dimethyl-3-methylenecyclobutane (**8**)⁹ and 1-ethoxy-3-isopropylidenecyclobutane (**10**), the equilibrium constant at 280 °C is $K = (\mathbf{10})/(\mathbf{8}) = 3.47 \pm 0.05$. Both (**4**) and (**8**) obey reversible first order kinetics from which the activation parameters (Table) were evaluated. The activation energy for the automerization of (**4**) is smaller by *ca.* 25 kJ mol⁻¹ than that of the parent compound (**5**).¹⁰ The activation energies for the rearrangements of (**8**) and (**9**)¹¹ differ by *ca.* 15 kJ mol⁻¹. A similar trend was found for substitution of alkoxy group in methylenecyclopropane ($\Delta E_a = 55$ kJ mol⁻¹) and in 2,2-dimethyl-1-methylenecyclopropane ($\Delta E_a = 40$ kJ mol⁻¹).² In terms

of activation energies, the effect of the alkoxy group in the methylenecyclobutane rearrangement is less than half of that observed in the analogous methylenecyclopropane rearrangement.

If the dramatically enhanced rates of alkoxy cyclopropane reorganizations were due solely to the stabilization of intermediate diradicals, a similar effect on alkoxy cyclobutane rearrangements should be expected. Our results in the two series suggest an additional destabilizing interaction of alkoxy groups with cyclopropane. Donation of electrons into the lowest antibonding Walsh orbital provides a suitable description.¹² It remains to be seen whether such interaction raises the ground state of alkoxy cyclopropanes or whether it weakens specific carbon-carbon bonds of the cyclopropane ring.

(Received, 23rd February 1978; Com. 195.)

¹ J. M. Simpson and H. G. Richey, Jr., *Tetrahedron Letters*, 1973, 2545.

² W. Kirmse and H.-R. Murawski, *J.C.S. Chem. Comm.*, 1977, 122.

³ W. Kirmse and M. Zeppenfeld, *J.C.S. Chem. Comm.*, 1977, 124.

⁴ Obtained by $\text{CH}_2\text{N}_2\text{-BF}_3\text{-OEt}$, methylation of the corresponding diol: J. M. Conia and J. P. Barnier, *Tetrahedron Letters*, 1971, 4981.

⁵ H. R. Gerberich and W. D. Walters, *J. Amer. Chem. Soc.*, 1961, **83**, 3935, 4884.

⁶ M. C. Flowers and H. M. Frey, *Proc. Roy. Soc.*, 1960, **A257**, 122; C. S. Elliot and H. M. Frey, *J. Chem. Soc.*, 1964, 900.

⁷ Prepared by methylenation of 3-ethoxycyclobutanone (J. B. Sieja, *J. Amer. Chem. Soc.*, 1971, **93**, 130) with $\text{CD}_2\text{I}_2\text{-Mg(Hg)}$, following the procedure of D. Hasselmann, *Chem. Ber.*, 1974, **107**, 3486.

⁸ K. Humski, R. Malojčić, S. Borčić, and D. E. Sunko, *J. Amer. Chem. Soc.*, 1970, **92**, 6534; J. C. Barborak, S. Chari, and P. v. R. Schleyer, *ibid.*, 1971, **93**, 5275; J. J. Gajewski, L. K. Hoffmann, and C. N. Shih, *ibid.*, 1974, **96**, 3705. D. Hasselmann, *Tetrahedron Letters*, 1972, 3465.

⁹ The synthesis of (**8**) involved addition of dimethylketen to ethoxyethene (R. H. Hasek, P. G. Gott, and J. C. Martin, *J. Org. Chem.*, 1964, **29**, 1239), followed by methylenation with $\text{CH}_2\text{I}_2\text{-Mg(Hg)}$.

¹⁰ W. v. E. Doering and J. C. Gilbert, *Tetrahedron Supplement*, 1966, **7**, 397.

¹¹ M. C. Flowers and A. R. Gibbons, *J. Chem. Soc. (B)*, 1971, 362.

¹² R. Hoffmann, *Tetrahedron Letters*, 1970, 2907; H. Günther, *ibid.*, p. 5173.