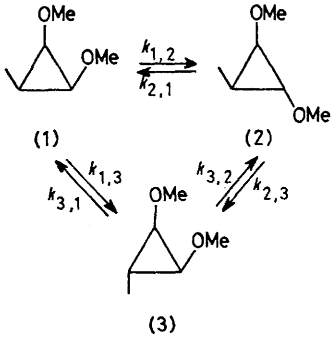
Thermal Rearrangement of Alkoxycyclopropanes

By Wolfgang Kirmse* and Manfred Zeppenfeld
(*Abteilung für Chemie der Ruhr-Universität*, 4630 *Bochum, Germany*)

Summary 1,2-Dimethoxy-3-methylcyclopropanes (**1**)—(**3**) undergo geometrical isomerization with activation energies of *ca.* 210 kJ mol^{-1}; comparison with 1-methoxy-2,3-dimethylcyclopropanes (**4**)—(**6**) indicates preferred single rotation about the C(1)–C(2) bond.

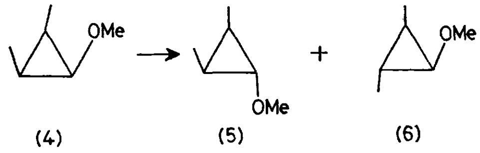
The rates of 1,3-carbon shifts are strongly accelerated by alkoxy substitution at the migrating carbon;[1] activation energies are lowered by 40—63 kJ mol^{-1} compared to the corresponding rearrangements of the parent hydrocarbons. These effects have been explained in terms of the stabilization that alkoxy substituents afford to free radicals, although some of the reactions studied may proceed by concerted paths.



Scheme. $10^5 \times k$ (s^{-1}) at 288·2 °C: $k_{1,2}$ 2·35, $k_{1,3}$ 1·14, $k_{2,1}$ 0·030, $k_{2,3}$ 0·107, $k_{3,1}$ 0·28, and $k_{3,2}$ 1·88.

Diradicals are clearly involved in the geometrical isomerization of 1,2-disubstituted cyclopropanes[2] even if they do not represent distinct minima on the potential surface ('continuous diradicals').[3] On the other hand, a synchronous double rotation mechanism is prominent in the stereomutation of 1,2-dideuteriocyclopropane.[4] We report here that alkoxy substitution promotes the diradical rather than the synchronous reaction mode.

The three stereoisomers of 1,2-dimethoxy-3-methylcyclopropane (**1**)—(**3**) were prepared by addition of methoxycarbene ($MeOCHCl_2$ + MeLi,LiI)[5] to 1-methoxypropene and characterised by their n.m.r. spectra. Geometrical isomerization of (**1**)—(**3**) proceeded without competing structural isomerization.† Rate constants obtained by extrapolation to zero conversion are shown in the Scheme.



Arrhenius parameters were estimated from rates at five different temperatures ranging from 260 to 310 °C. (**1**) ($k_{1,2} + k_{1,3}$): $E_a = 208{\cdot}1 \pm 3{\cdot}5$ kJ mol^{-1}, log $A = 14{\cdot}89 \pm 0{\cdot}32$; (**3**) ($k_{3,1} + k_{3,2}$): $E_a = 209{\cdot}5 \pm 3{\cdot}7$ kJ mol^{-1}, log $A = 14{\cdot}75 \pm 0{\cdot}34$. These activation energies are *ca.* 63 kJ mol^{-1} lower than that of the *cis–trans* isomerization of *cis*-1,2-dideuteriocyclopropane ($E_a = 272{\cdot}4$ kJ mol^{-1}).[6] The dissociation energies of 1,2-dimethoxyethane (298 kJ mol^{-1})[7] and ethane (368 kJ mol^{-1}) differ by a comparable amount. The stabilization of free radicals by alkoxy substituents appears to be fully utilized in the isomerization of (**1**) and (**3**).

The (**1**) → (**2**) transformation may take place by single rotation about the C(1)–C(2) bond, or by double rotation about the C(1)—C(3) and C(2)—C(3) bonds. We subjected 1-methoxy-2,3-dimethylcyclopropane[5] (**4**) to the same reaction conditions and found $k_{4,5} + k_{4,6} = 3{\cdot}6 \times 10^{-7}$ s^{-1} at 288 °C.

The slow rate of isomerization of (**4**) differs from that of (**1**) by a factor of 100, suggesting that the C(1)—C(2) bond of (**1**) breaks in preference to C(1)–C(3) and C(2)–C(3) bonds; the rate constants $k_{1,2}$ and $k_{1,3}$ would thus provide an estimate of single and double rotation. Like other cyclopropanes bearing radical stabilizing groups,[2,3] (**1**) and (**3**) show no preference for synchronous double rotation.‡

(*Received*, 24*th November* 1976; *Com.* 1303.)

---

† The material balance was >95% at temperatures up to 300 °C. At temperatures above 300 °C, substantial loss of material occurred although no products in addition to (**1**)—(**3**) were detected. Vinyl ethers which might be formed by structural isomerization were not isolated despite all attempts at 'seasoning' the reaction vessel.

‡ Extended Hückel calculations support the idea that single rotation becomes competitive with double rotation when radical stabilizing groups are attached to cyclopropane: A. Gavezzotti and M. Simonetta, *Tetrahedron Letters*, 1975, 4155.

[1] F. Scheidt and W. Kirmse, *J.C.S. Chem. Comm.*, 1972, 716; J. M. Simpson and H. G. Richey, Jr., *Tetrahedron Letters*, 1973, 2545; R. K. Lustgarten and H. G. Richey, Jr., *J. Amer. Chem. Soc.*, 1974, **96**, 6393; W. Kirmse and H. R. Murawski, preceding communication.
[2] R. G. Bergman and W. Carter, *J. Amer. Chem. Soc.*, 1968, **90**, 7344; 1969, **91**, 7411; R. J. Crawford and T. R. Lynch, *Canad. J. Chem.*, 1968, **46**, 1457; A. Chmurny and D. J. Cram, *J. Amer. Chem. Soc.*, 1973, **95**, 4237.
[3] W. v. E. Doering and K. Sachdev, *J. Amer. Chem. Soc.*, 1974, **96**, 1168.
[4] J. A. Berson, L. D. Pedersen, and B. K. Carpenter, *J. Amer. Chem. Soc.*, 1976, **98**, 122.
[5] U. Schöllkopf and J. Paust, *Chem. Ber.*, 1965, **98**, 2221.
[6] E. W. Schlag and B. S. Rabinovitch, *J. Amer. Chem. Soc.*, 1960, **82**, 5996.
[7] L. F. Loucks and K. J. Laidler, *Canad. J. Chem.*, 1967, **45**, 2785.