Thermal Rearrangement of 1-Alkoxy-2-methylenecyclopropanes

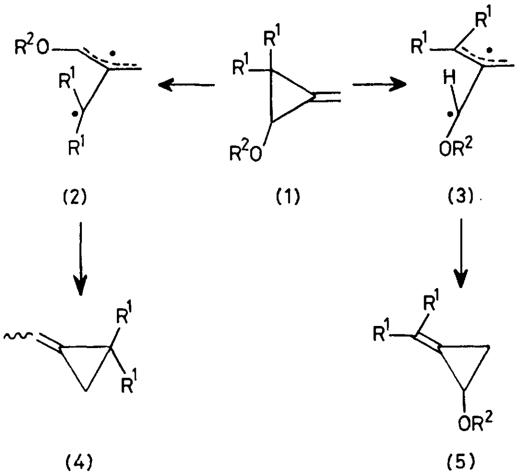
By WOLFGANG KIRMSE* and HANS-RÜDIGER MURAWSKI
(*Abteilung für Chemie der Ruhr-Universität,* 4630 *Bochum, Germany*)

Summary Substitution of alkoxy groups at the migrating carbon atom stabilizes the transition state of the methylenecyclopropane rearrangement by 40—50 kJ mol^{-1}.

WE report the methylenecyclopropane rearrangement which is a further example of 1,3-carbon shifts strongly accelerated by an alkoxy substituent at the migrating carbon atom.[1–3] Methylenecyclopropane, first as Feist's acid,[4] then as a variety of other derivatives,[5,6] has been shown to undergo a 1,3-shift with predominant inversion. Fully concerted birotational mechanisms have been excluded with the aid of appropriate stereochemical labels.[6] Experiment and theory[7] suggest that the methylenecyclopropane rearrangement proceeds by way of an orthogonal methylene–allylic diradical [*e.g.*, (**2**) or (**3**)]. On the basis of this mechanism, stabilization of the transition state by an alkoxy substituent was anticipated.

1-Ethoxy-2-methylenecyclopropane (**1a**) was prepared from 3-ethoxycyclobutanone[8] by carbenoid ring contraction of the tosylhydrazone sodium salt. The rearrangement of (**1a**) to give ethoxymethylenecyclopropane (**4a**) (1,3-shift of the unsubstituted carbon) was of first order and virtually irreversible,[9] $E_a = 156{\cdot}4 \pm 1{\cdot}7$ kJ mol^{-1}, log $A = 14{\cdot}66 \pm 0{\cdot}18$. Optically active (**1a**) was obtained by hydroboration of the racemic mixture with a deficient quantity of dipinan-3-ylborane.[10] Rates of racemization of neat (**1a**) were measured at 60—90 °C to give $E_a = 116{\cdot}1 \pm 1{\cdot}1$ kJ mol^{-1}, log $A = 12{\cdot}79 \pm 0{\cdot}16$. The rate of racemization is not necessarily identical with the rate of 1,3 shift (epimerization has been observed with some substituted methylenecyclopropanes[5,6]), but E_a(rac.) nevertheless refers to the formation of the achiral ethoxymethylene–allylic intermediate (**3a**). Comparison of our results with previous kinetic data (Table) reveals that alkoxy substitution at the allylic framework lowers E_a only by 13—18 kJ mol^{-1} whereas substitution at the migrating carbon stabilizes the transition state by 53—58 kJ mol^{-1}. These quantities are similar to those obtained in the vinylcyclopropane rearrangement[2] (21 and 46 kJ mol^{-1}, respectively).

Enhancement of reaction rate by alkoxy substituents has often been used to detect semi-ionic transition states. A polar analogue of (**3**), bearing a (partial) positive charge on the migrating carbon and a (partial) negative charge on the allylic framework should be stabilized if R is electron-withdrawing, and destabilized if R is electron-donating.



a; R^1 = H, R^2 = Et
b; R^1 = Me, R^2 = Me
c; R^1 = Ph, R^2 = Me

1-Methoxy-2-methylene-3,3-dimethylcyclopropane (**1b**) was obtained by addition of methoxycarbene ($MeOCHCl_2$+MeLi,LiI)[11] to 1,1-dimethylallene. At 120—150 °C (gas phase), 1,3 shifts of the methoxy-substituted carbon (k_1) and of the dimethyl-substituted carbon (k_2) were observed in a ratio ranging from *ca.* 15 to *ca.* 12. The activation energy of the latter reaction, $E_a = 142{\cdot}0 \pm 2{\cdot}8$ kJ mol^{-1}, is in accord with the stabilization of the transition state by substituting methyl groups at the migrating carbon (17—22 kJ mol^{-1}),[12] and a methoxy group at the allylic framework [13—18 kJ mol^{-1}; *cf.* (**1a**) → (**4a**)]. The activation energy associated with the transformation of (**1b**) into (**5b**), $E_a = 130{\cdot}8 \pm 1{\cdot}9$ kJ mol^{-1}, is *ca.* 14 kJ mol^{-1} higher than that observed for the racemization of (**1a**). Part of the discrepancy may be due to the difference in reaction conditions. When (**1b**) was heated in decane at 80—105 °C, only traces of (**4b**) were observed, and $E_a = 124{\cdot}8 \pm 0{\cdot}4$ kJ mol^{-1} was estimated. A modest solvent effect was indicated by a comparison of rates at 90 °C; $k_1 = 2{\cdot}88 \times 10^{-6}$ s^{-1} (gas, extrapolated), $6{\cdot}98 \times 10^{-6}$ s^{-1} (n-decane), and $1{\cdot}00 \times 10^{-5}$ s^{-1} (dimethylformamide).

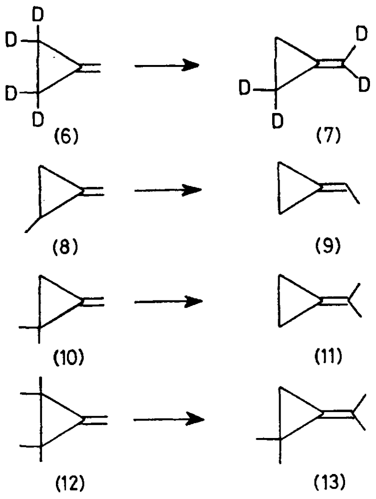


TABLE. Activation parameters and rates of methylenecyclopropane rearrangements

Rearrangement	E_a/kJ mol^{-1}	log A	k at 150 °C/s^{-1}	Ref.
(**6**) → (**7**)	$174{\cdot}0^a$		$6{\cdot}1 \times 10^{-8}$	13
(**8**) → (**9**)	$169{\cdot}0$	$14{\cdot}26$	$2{\cdot}5 \times 10^{-7}$	14
(**10**) → (**11**)	$171{\cdot}5^a$		$1{\cdot}2 \times 10^{-7}$	12
(**12**) → (**13**)	$152{\cdot}3$	$14{\cdot}27$	$3{\cdot}0 \times 10^{-5}$	12
(**1a**) → (**4a**)	$156{\cdot}4$ $\pm 1{\cdot}7^b$	$14{\cdot}66$ $\pm 0{\cdot}18$	$2{\cdot}3 \times 10^{-5}$	
(**1a**) → (**5a**)^c	$116{\cdot}1$ $\pm 1{\cdot}1$	$12{\cdot}79$ $\pm 0{\cdot}16$	$2{\cdot}9 \times 10^{-2}$	
(**1b**) → (**4b**)	$130{\cdot}8$ $\pm 1{\cdot}9$	$13{\cdot}27$ $\pm 0{\cdot}24$	$1{\cdot}3 \times 10^{-3}$	
(**1b**) → (**5b**)	$142{\cdot}0$ $\pm 2{\cdot}8$	$13{\cdot}56$ $\pm 0{\cdot}35$	$1{\cdot}1 \times 10^{-4}$	

[a] Estimated from a single rate constant, assuming log $A = 14{\cdot}26$. [b] Standard deviations from a least-squares treatment. [c] Rate of racemization of the neat liquid.

Photolysis of diphenyldiazomethane in methoxyallene afforded 1-methoxymethylene-2,2-diphenylcyclopropane (**4c**) as the minor product, and 1-methoxy-2-diphenylmethylenecyclopropane (**5c**) as the major product. As (**5c**) cannot form directly from diphenylcarbene and methoxyallene, we assume that the initial adduct (**1c**) has rearranged although it was never heated above room temperature [(**4c**) and (**5c**) were isolated by t.l.c.]. The relative rates of the transformations (**1**) → (**5**) (R = Ph>H>Me) may be interpreted in terms of polar contributions to the transition state. Investigations involving strongly electron-withdrawing groups would serve to substantiate these ideas, but attempted syntheses of (**1**, R = CO_2Et or CF_3) have so far been unsuccessful.

We thank Professor A. de Meijere and Dr. L. U. Meyer for kinetic studies in a flow system.[9]

(*Received*, 24*th November* 1976; *Com.* 1302.)

---

[1] F. Scheidt and W. Kirmse, *J.C.S. Chem. Comm.*, 1972, 716.

[2] J. M. Simpson and H. G. Richey, Jr., *Tetrahedron Letters*, 1973, 2545.

[3] R. K. Lustgarten and H. G. Richey, Jr., *J. Amer. Chem. Soc.*, 1974, **96**, 6393.

[4] E. F. Ullmann, *J. Amer. Chem. Soc.*, 1960, **82**, 505; W. v. E. Doering and H. D. Roth, *Tetrahedron*, 1970, **26**, 2825.

[5] J. J. Gajewski, *J. Amer. Chem. Soc.*, 1971, **93**, 4450.

[6] W. v. E. Doering and L. Birladeanu, *Tetrahedron*, 1973, **29**, 499.

[7] W. J. Hehre, L. Salem, and M. R. Willcott, *J. Amer. Chem. Soc.*, 1974, **96**, 4328.

[8] J. B. Sieja, *J. Amer. Chem. Soc.*, 1971, **93**, 130.

[9] Because of the instability of (**4a**) in static systems at elevated temperatures, rates were measured in a flow reactor at 210—240 °C: *cf.* L. U. Meyer and A. de Meijere, *Chem. Ber.*, in the press.

[10] H. C. Brown, N. R. Ayyangar, and G. Zweifel, *J. Amer. Chem. Soc.*, 1964, **86**, 397.

[11] U. Schöllkopf and J. Paust, *Chem. Ber.*, 1965, **98**, 2221.

[12] R. J. Crawford and H. Tokunaga, *Canad. J. Chem.*, 1974, **52**, 4033.

[13] W. D. Slafer, A. D. English, D. O. Harris, D. F. Shellhamer, M. J. Meshishnek, and D. H. Aue, *J. Amer. Chem. Soc.*, 1975, **97**, 6638.

[14] J. P. Chesick, *J. Amer. Chem. Soc.*, 1963, **85**, 2720.