THE EFFECTS OF METHOXYL AND PHENYL SUBSTITUENTS ON THE THERMAL REARRANGEMENTS OF VINYLCYCLOPROPANE

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Large effects exerted by methoxyl and aryl substituents on the thermal rearrangements of vinylcyclopropane are related to problems concerning the mechanisms of these reactions [1] Kinetic and product studies of the 1,3-sigmatropic[3] rearrangements of vinylcyclopropanes to cyclopentenes have led to proposals of pathways[4] in which the bond changes are concerted and, alternatively, of pathways[8] in which diradicals are intermediates   In a recent study[10] of the stereochemistry of the rearrangements of a set of stereoisomeric, substituted vinylcyclopropanes, it was shown that the cyclopentene products could not have formed solely by the stereochemical pathway predicted[3] for concerted 1,3-sigmatropic rearrangements   Accompanying the isomerization of vinylcyclopropane to cyclopentene is a cis-trans isomerization, revealed by deuterium subsitution at C-2 [9,11] Whether the pathways for cis-trans and sigmatropic isomerizations are related or independent is not settled [9]

Isomers $\underline{1}$, $\underline{2}$, and $\underline{3}$ were the only compounds[12] detected in significant amounts in gas phase (ca 30-150 torr) reactions of $\underline{1}$ and $\underline{2}$ in the range ca 220-250°   Values of k_1, k_2, and k_3 that
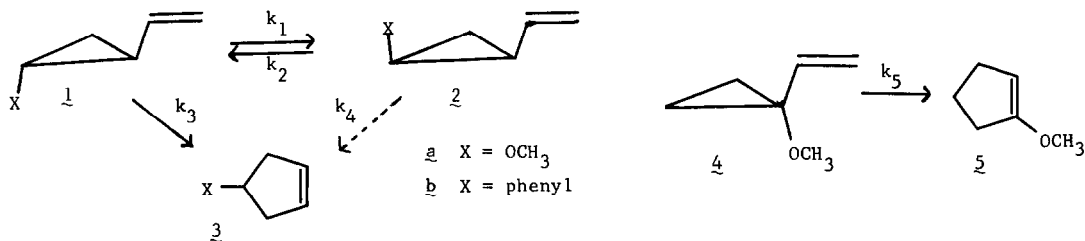
would best fit the changes with time of the concentrations of methoxyl isomers $\underline{1a}$, $\underline{2a}$, and $\underline{3a}$ were determined, k_4 was shown to be negligible ($k_4 < 0.05\ k_3$) and therefore was assumed to be zero in this analysis   An Arrhenius expression $k_3 = 3.30 \pm 0.02 \times 10^{12} \exp[(-38.7 \pm 0.2)/RT]$[13] was

obtained   Formation of an equilibrium mixture of $\underline{1b}$ and $\underline{2b}$ from either of these phenyl isomers

was much faster than formation of $\underline{3b}$, precluding determination of k_3 and k_4 However, if k_4 is

assumed to be zero, then values of k_3 can be obtained and furnish an Arrhenius expression $k_3 =$

$2\,41 \pm 0\,05 \times 10^{13}$ $\exp[(-41\,0 \pm 0\,6)/RT]$ [14]   Isomer $\underline{5}$ and small amounts ($<5\%$) of more volatile

materials were obtained from gas phase (ca 20-100 torr) reactions of $\underline{4}$ in the range 263-287°   An

Arrhenius expression $k_5 = 2\,71 \pm 0\,16 \times 10^{13}$ $\exp[(-44\,7 \pm 1\,2)/RT]$ was obtained [15]   The expression

for rearrangement of vinylcyclopropane to cyclopentene is $4\,09 \times 10^{13}$ $\exp(-49.7/RT)$ [6]   Therefore,

E_a for rearrangement to a cyclopentene is lowered ca 11 and 9 kcal/mole, respectively, by trans

2-methoxyl and 2-phenyl substituents, but only ca 5 kcal/mole by a 1-methoxyl substituent   For

the parent hydrocarbon, the ratio of the rate of cis-trans isomerization[11] to that of cyclopentene

formation[6] is ca 100 at 325°   For the phenyl system, the comparable ratios (k_1 k_3 and k_2 k_3)

exceed 100 at 238°   By contrast, in the methoxyl system, k_1 and k_2 ($2\,4 \times 10^{-5}$ and $9\,1 \times 10^{-5}$

$\sec^{-1}$, respectively, at 237°), although accelerated by the substituent are comparable in magnitude

to k_3 ($8\,5 \times 10^{-5}$ $\sec^{-1}$ at 237°)

The much slower isomerization to $\underline{3a}$ of $\underline{1a}$ than of $\underline{2a}$ can be attributed to steric effects in

the transition state   For example, if it is assumed[16] that planar[17] diradicals are intermediates,

then formation of a cyclopentene requires a cis configuration around the interior allylic bond

(C$\equiv$C) as in $\underline{7}$, rather than a trans configuration as in $\underline{9}$ or $\underline{10}$ Interconversions of diradicals
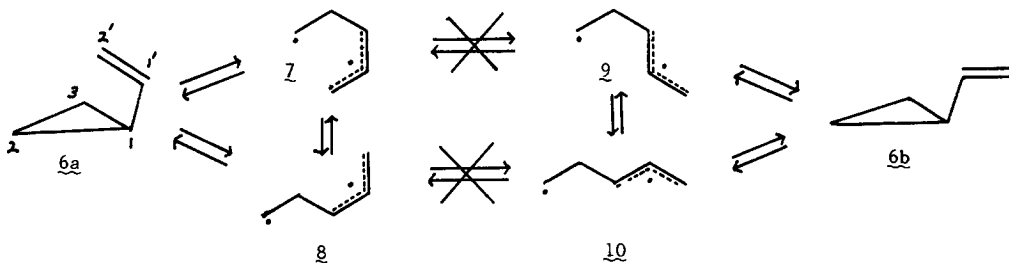
($\underline{7}$ and $\underline{9}$, for example) that require rotation around partial double bonds (C$\equiv$C) should be too

slow to compete with ring closure to regenerate $\underline{6}$ Therefore, the rate of cyclopentene formation

will parallel the ease of forming $\underline{7}$ and $\underline{8}$ from $\underline{6}$ The cisoid transition states (intermediate

between $\underline{6a}$ and $\underline{7}$ or $\underline{6a}$ and $\underline{8}$) leading to $\underline{7}$ and $\underline{8}$ should be increased significantly in energy by

a cis substituent at C-2 [18]

The marked effect of trans-2-substituents on the rate of rearrangement to a cyclopentene

suggests much less bonding between C-1 and C-2 in the transition state than in the reactants [19]

Such a transition state would occur along a concerted pathway only if the development of C-2—C-2'

bonding lagged so far behind the loss of C-1—C-2 bonding that the transition state closely resem-

bled that for cleavage to an acyclic intermediate [20] Therefore, it is attractive to assume that

an acyclic diradical intermediate is formed   The stabilization of the transition state by phenyl

is a substantial fraction of the stabilization that an α-phenyl affords to (fully formed) alkyl

radicals (<u>ca</u> 22 and 15 kcal/mole to the methyl and ethyl radicals, respectively) [21] Stabiliza-

tion of the transition state by methoxyl is a comparable fraction of its stabilization of an

alkyl radical if the largest reported values (<u>ca</u> 22 kcal/mole stabilization of the methyl radi-

cal)[22] are used [23] The extent to which an alkoxyl substituent placed at the "migrating carbon" of

a system undergoing a 1,3-sigmatropic rearrangement lowers E_a (or $H^{\ddagger}$) has varied widely, values

observed for <u>4</u>, <u>1a</u>, <u>anti</u>-5-methoxybicyclo[2 1 1]hex-2-ene,[24] and 7-<u>t</u>-butoxybicyclo[2 2 1]heptadi-

ene[25] (<u>11</u>) are 5, 11, 11, and 15 kcal/mole, respectively   It is unlikely that the rate-accelera-

ting effects of alkoxyl and phenyl are to be attributed to heterolytic[26] rather than to homolytic

cleavages, since the rate of the system (<u>11</u>) exhibiting the largest substituent effect does not

depend significantly upon solvent polarity   Perhaps the relatively small effect in <u>4</u>, a system in

which both the vinyl and methoxyl substituents are located on the same carbon, resides in such

factors as (a) a large steric inhibition to simultaneous conjugation of both substituents and (b)

a larger fraction of chemically unproductive reversion of an intermediate to the reactant [27]

<div align="center">REFERENCES</div>

(1) The rearrangements have been reviewed Ref. 2, H M Frey and R. Walsh, <u>Chem Rev</u> , <u>69</u>, 103
     (1969), C D Gutsche and D Redmore, <u>Advan Alicyclic Chem.</u>, Suppl 1, 1968, Chapter 9

(2) H. M Frey, <u>Advan Phys Org. Chem</u> , <u>4</u>, 147 (1966)

(3) R B. Woodward and R Hoffmann, <u>Angew Chem Int Ed Engl</u> , <u>8</u>, 781 (1969)

(4) For example, references 5-7 and R. Breslow in "Molecular Rearrangements," Vol 1, P de Mayo,
     Ed , Interscience Publishers, New York, 1963, Chapter 4

(5) C S Elliott and H M Frey, <u>J Chem Soc</u> , 345 (1965)

(6) C A Wellington, <u>J Phys Chem</u> , <u>66</u>, 1671 (1966)

(7) A D Ketley, A J Berlin, and L P Fisher, <u>J Org Chem</u> , <u>31</u>, 2648 (1966)

(8) For example, references 2 and 9, and H E O'Neal and S W Benson, <u>J Phys Chem</u> , <u>72</u>, 1866
     (1968)

(9) M R Willcott and V H Cargle, <u>J Amer Chem Soc</u> , <u>89</u>, 723 (1967)

(10) P H Mazzocchi and H J Tamburin, *J Amer Chem Soc* , _92_, 7220 (1970)

(11) M R Willcott, III, and V H Cargle, *J Amer Chem Soc* , _91_, 4310 (1969)

(12) Spectral properties of new compounds (_3a_ and _5_) are in accord with the structural assignment·

(13) The small value of the standard deviation is misleading   Consideration of the range of values of k_3 that gave fairly satisfactory fits to the isomer composition data leads us to a subjective estimate of $\pm$ 1 0 kcal/mole for the uncertainty in E_a

(14) A similar expression, $k = 1\ 68 \pm 0\ 02 \times 10^{13}\ \exp[(-40\ 8 \pm 0\ 6)/RT]$, resulted if it was assumed that $k_3 = k_4$ Our subjective estimate of the uncertainty in E_a is $\pm$ 1 0 kcal/mole.

(15) Our subjective estimate of the uncertainty in E_a is $\pm$ 2 0 kcal/mole

(16) A similar argument could be applied to pathways in which some allylic resonance develops although intermediates are non-planar or never fully formed

(17) Diradicals may be more stable in non-planar arrangements [R Hoffmann, *J Amer Chem Soc* , _90_, 1475 (1968), J A Berson and J M Balquist, _ibid_ , _90_, 7343 (1968), R G Bergman and W L Carter, _ibid_ , _91_, 7411 (1969)]

(18) The retarding effect references 5 and 7, and A D Ketley, A J Berlin, E Gorman, and L P Fisher, *J Org Chem* , _31_, 305 (1966)] of a _cis_ substituent at C-2' (_6a_) on isomerization to a cyclopentene must have a similar origin

(19) We assume that the substituents do not greatly alter the stabilities of the reactants   Conjition of phenyl (and vinyl) with a cyclopropane ring leads only to negligible stabilization [S W Staley, *J Amer Chem Soc* , _89_, 1532 (1967), and references cited therein]   A cyclopropyl ring is predicted to be somewhat destabilized by an alkoxyl substituent [R offmann, *Tetrahedron Lett*   2907 (1970), H Gunther _ibid_ , 5173 (1970)]

(20) We assume that substituent effects would be small if the sum of C-1—C-2 and C-2—C-2' bonding remained constant throughout the reaction

(21) J A Kerr *Chem Rev* , _66_, 465 (1966)

(22) R H Martin, F W Lampe, and R W Taft, *J Amer Chem Soc* , _88_, 1353 (1966), R H Shapiro and J Turk, *Org Mass Spectrom* , _2_, 1067 (1969)

(23) Considerably lower values have been reported for example, L F Loucks and K J Laidler, *Can J Chem* , _45_, 2785 (1969), F R Cruickshank and S W Benson, *Int J Chem Kinet* _1_, 381 (1969), F R Cruickshank and S W Benson, *J Amer Chem Soc* , _91_, 1289 (1969)]

(24) Rearrangement of the substituted system in carbon tetrachloride [F Scheidt and W Kirmse, *Chem Commun* , 716 (1972)] compared with rearrangement of the parent hydrocarbon in the gas phase [H M Frey and R G Hopkins, *J Chem Soc , B*, 1410 (1970)]

(25) Rearrangement in decane to _t_-butoxycycloheptatrienes a reaction presumably involving a 1,3-sigmatropic rearrangement as the initial step [R K Lustgarten and H G Richey Jr , *Tetrahedron Lett* , 4655 (1966)], compared with rearrangement of the parent hydrocarbon in the gas phase [W C Herndon and L L Lowry, *J Amer Chem Soc* , _86_, 1922 (1964)]

(26) Since the orbitals involved could be sufficiently close for some overlap to occur, an intermediate might be a hybrid of "diradical" and "zwitterionic" resonance forms rather than one of these extremes [E W Yankee and T Cram, *J Amer Chem Soc* , _92_ 6328, 6329 6331 (1970), L Salem and C Rowland, *Angew Chem Int Ed Engl* , _11_, 92 (1972)]

(27) E_a for a 3,3-sigmatropic rearrangement, thought to proceed via a diradical, of 2-_endo_-vinylbicyclo[2 2 2]oct-5-ene is lowered only 2 4 $\pm$ 1 6 kcal/mole by a 2-_exo_-hydroxy group [J A Berson and E J Walsh Ir *J Amer Chem Soc* _90_, 4730 (1968)]   In this system the α-oxygen and vinyl substituents also are on the same carbon