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THE LARGE EFFECT OF A 2-DIMETHYLAMINO SUBSTITUENT ON THERMAL REARRANGEMENTS OF VINYLCYCLOPROPANE

Herman G. Richey, Jr., and David W. Shull
Department of Chemistry, The Pennsylvania State University
University Park, Pennsylvania 16802

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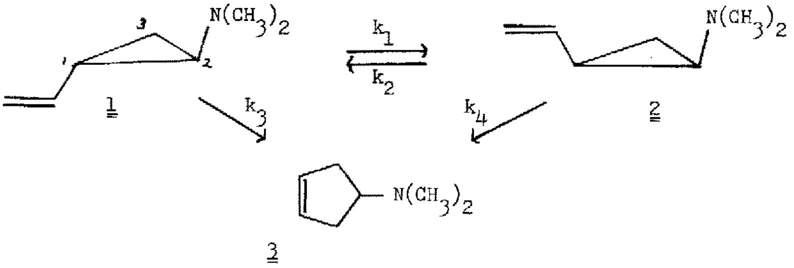
The accelerating effect of a 2-dimethylamino substituent on the thermal 1,3-sigmatropic rearrangement of vinylcyclopropane to cyclopentene exceeds even the large effect of a 2-methoxyl substituent. We reported earlier that a <u>trans</u>-2-methoxyl substituent lowers E_a for the rearrangement of vinylcyclopropane to cyclopentene by 11 kcal/mol.[1] Similarly, for the rearrangement of norbornadiene to cycloheptatriene, a process for which the rate-determining step probably also is a 1,3-sigmatropic rearrangement, a 7-<u>t</u>-butoxy substituent lowers E_a by 15 kcal/mol; the insensitivity of the rate to solvent polarity is consistent with a diradical transition state that has little ionic character.[2]

Gas phase (<u>ca</u>. 10-40 torr) reactions of **1** in the range 178-203° produced **3**.[3,4] However, formation of an equilibrium mixture of **1** and **2** (<u>ca</u>. 2:1)[5] was considerably faster, precluding determination of k_3 and k_4. Rearrangement to **3** of the equilibrating mixture of **1** and **2** followed an Arrhenius expression $k = 2.2 \pm 0.2 \times 10^{10} \exp[(-31.1 \pm 0.7)/RT]$. It is known that <u>trans</u>-2-methoxyvinylcyclopropane rearranges to a cyclopentene at least 20-fold faster than does the <u>cis</u> isomer.[1] If it is assumed for the dimethylamino compounds that k_4 also is negligible compared to k_3, then values of k_3 can be obtained and furnish a slightly different Arrhenius expression, $k_3 = 3.8 \pm 0.3 \times 10^{10} \exp[(-31.2 \pm 1.0)/RT]$.[6]



E_a is reduced even more by the dimethylamino group than by the methoxyl group.[7] For the rearrangement of vinylcyclopropane, $k = 4.09 \times 10^{13} \exp(-49.7/RT)$,[8] and for the rearrangement of <u>trans</u>-2-methoxyvinylcyclopropane, $k_3 = 3.30 \times 10^{12} \exp(-38.7/RT)$.[1] The pre-exponential term also is reduced more by dimethylamino than by methoxyl. For the dimethylamino compounds, k_1 is at least 15-fold faster than the rate (essentially k_3, we assume) for rearrangement to a cyclopentene. However, for the methoxyl compounds, k_1 and k_3 were similar in magnitude. It is puzzling that with respect to the $k_1:k_3$ ratio, the dimethylamino system resembles the much less reactive parent vinylcyclopropane[9] rather than the somewhat less reactive methoxyl system.

It is reasonable to assume that the large effect of the 2-dimethylamino substituent on E_a for rearrangement to a cyclopentene is due to stabilization of a developing radical center at C-2.[10,11] In fact, a value of 28 kcal/mol was suggested in one study for the stabilization of a methyl radical by an α-amino substituent.[12] However, other data indicate that the stabilization of radicals by α-amino substituents may be considerably less,[13] so the possibility remains that in the rearrangement to 3, C-2 of 1 may develop significant cationic character.

REFERENCES AND FOOTNOTES

(1) J. M. Simpson and H. G. Richey, Jr., Tetrahedron Lett., 2545 (1973).

(2) R. K. Lustgarten and H. G. Richey, Jr., J. Am. Chem. Soc., 96, 6393 (1974).

(3) The spectral properties of the new compounds (1, 2, and 3) are in accord with the structural assignments.

(4) Smaller amounts of unidentified compounds also were present.

(5) The apparent equilibrium constant decreased during the course of the reactions, probably due to the presence of an impurity that had the same glpc retention time as 2.

(6) The values of the standard deviations may be misleading. Our subjective estimate of the uncertainties in E_a and in log A are ± 2.0 kcal/mol and ± 0.8.

(7) Significant accelerations of 1,3-sigmatropic rearrangements in other systems by amine [G. R. Krow and J. Reilly, J. Am. Chem. Soc., 97, 3837 (1975)] and by azide [F. Scheidt and W. Kirmse, J. Chem. Soc., Chem. Commun., 716 (1972)] substituents have been noted, but quantitative information is lacking.

(8) C. A. Wellington, J. Phys. Chem., 66, 1671 (1966).

(9) M. R. Willcott and V. H. Cargle, J. Am. Chem. Soc., 89, 723 (1967); 91, 4310 (1969).

(10) It is thought that donor substituents such as alkoxyl or amino may weaken the bonds of cyclopropyl rings [R. Hoffmann, Tetrahedron Lett., 2907 (1970); H. Günther, ibid., 5173 (1970); R. Hoffmann, H. Fujimoto, J. R. Swenson, and C.-C. Wan, J. Am. Chem. Soc., 95, 7644 (1973)]. In fact, in comparison to the C-C bonds of cyclopropane, C_1-C_2 of cyclopropylamine is somewhat longer but C_2-C_3 is essentially the same [M. D. Harmony, R. E. Bostrom, and D. K. Hendrickson, J. Chem. Phys., 62, 1599 (1975)]. We assume that destabilization of 1 and 2 by the dimethylamino substituent is small compared to the rate effects noted in this work [for one of the recent studies of the effects on rates by substituents on cyclopropyl rings, see G. Boche and G. Schneider, Tetrahedron Lett., 2449 (1974)].

(11) Cyclopropylamine rearranges thermally to N-propylidenecyclopropylamine, a reaction in which cleavage to an acylic isomer of cyclopropylamine probably is rate determining, with an E_a about 8 kcal/mol lower than for the isomerization of cyclopropane to propene [K. A. W. Parry and P. J. Robinson, Int. J. Chem. Kinet., 5, 27 (1973)]. However, the rate-determining step, in addition to cleavage of a C-C bond, may involve hydrogen transfer.

(12) R. H. Shapiro and J. Turk, Org. Mass Spectrom., 2, 1067 (1969).

(13) For example, J. E. Collin, M. J. Franskin, and D. Hyatt, Bull. Soc. R. Sci. Liege, 36, 318 (1967) [Chem. Abstr., 69, 6184j (1968)]; D. K. Sen Sharma and J. L. Franklin, J. Am. Chem. Soc., 95, 6562 (1973).

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