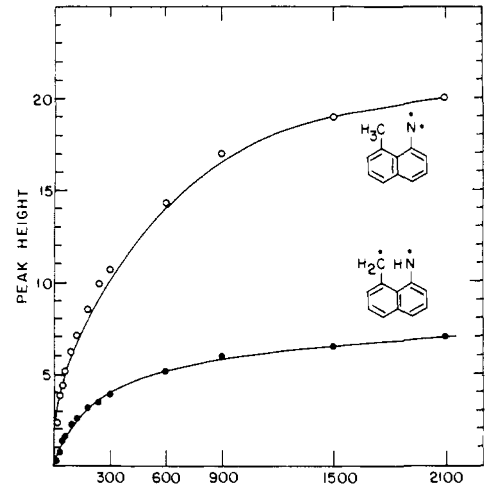


Figure 3. The intensities of **5** and **6** as a function of irradiation time (77 K). The lower curve can be converted into the upper by multiplying by a constant numerical factor of 3.0 ± 0.3. 1-Azido-8-methylnaphthalene does not partition into equal amounts of **5** and **6**.

diyl. Even more striking is a comparison of **2** and **5**. The triplet nitrene is indefinitely stable at 77 K, whereas the triplet carbene could not be detected even at 4 K. If the discrete carbene intermediate is, in fact, on the reaction pathway to **3**, there must be a very large reactivity difference between the triplet states of **2** and **5**.

A complete kinetic analysis of the triplet species described herein is in progress.

Acknowledgments. The authors thank Professor John Swenton for valuable discussions, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

References and Notes

(1) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972,** *11*, 92.

(2) Benson, S. W. "Thermochemical Kinetics"; Wiley: New York, 1968.

(3) Lamola, A. A.; Turro, N. J. "Technique of Organic Chemistry V. XIV, Energy Transfer and Organic Photochemistry", Weissberger, A., Ed.; Interscience: New York, 1969.

(4) (a) Dowd, P. *Acc. Chem. Res.* **1972,** *5*, 242. (b) Closs, G. L.; Kaplan, L. R. *J. Am. Chem. Soc.* **1969,** *91*, 2168. (c) Closs, G. L.; Kaplan, L. R.; Bendall, V. I. *J. Am. Chem. Soc.* **1969,** *89*, 3376. (d) Berson, J. A. *Acc. Chem. Res.* **1978,** *11*, 446. (e) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1975,** *97*, 3857. (f) Platz, M. S., Berson, J. A. *J. Am. Chem. Soc.* **1976,** *98*, 6743. (g) Dowd, P.; Chow, M. *J. Am. Chem. Soc.* **1977,** *99*, 6538.

(5) (a) Watson, C. R., Jr.; Pagni, R. M.; Dodd, J. R.; Bloor, J. E. *J. Am. Chem. Soc.* **1976,** *98*, 2551. (b) Pagni, R. M.; Burnett, M. N.; Dodd, J. R. *J. Am. Chem. Soc.* **1977,** *99*, 1972. (c) Muller, J. F.; Muller, D.; Dewey, H.; Michl, J. *J. Am. Chem. Soc.* **1978,** *100*, 1629. (d) Gisin, M.; Rommel, E.; Wirz, J.; Burnett, M. N.; Pagni, R. M. *J. Am. Chem. Soc.* **1979,** *101*, 2216.

(6) Platz, M. S., *J. Am. Chem. Soc.* **1979,** *101*, 3398.

(7) Smith, *Org. React.* **1946,** *3*, 337.

(8) 1-Azido-8-methylnaphthalene gave satisfactory infrared, NMR, and mass spectra.

(9) (a) Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964,** *41*, 1763. (b) Wasserman, E. *Prog. Phys. Org. Chem.* **1971,** *8*, 319.

(10) Berry, D.; Smith, D. C. C. *J. Chem. Soc., Perkin Trans. 1* **1972,** 699.

(11) Carbene often show dual triplet spectra arising from more than one conformatiȯn. See: Trozzolo, A. M.; Wasserman, E.; Yager, W. A. *J. Am. Chem. Soc.* **1965,** *87*, 129.

(12) McGlynn, S. P.; Azum, T.; Kinoshita, M. "Molecular Spectroscopy of the Triplet State"; Prentice Hall: Englewood Cliffs, N.J., 1969.

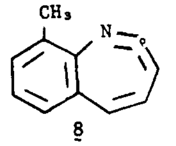
(13) Quast, H.; Bieber, L.; Danen, W. C. *J. Am. Chem. Soc.* **1978,** *100*, 1306.

(14) Breslow, R.; Chang, H. W.; Hill, R.; Wasserman, E. *J. Am. Chem. Soc.* **1967,** *89*, 1112.

(15) A linear Curie–Weiss Law plot will also arise when the singlet and triplet states are exactly degenerate.

(16) Chapman and co-workers have shown that phenylnitrene and pyridylmethylenes photochemically interconvert via aza cycloheptatetraenes. It is conceivable that the hydrogen atom transfer may occur via an intermediate such as **8**. See: Chapman, O. L.; Le Roux, J. P. *J. Am. Chem. Soc.* **1978,** *100*, 282. Chapman, O. L.; Sheridan, R. S.; Le Roux, J. P. *ibid.* **1978,** *100*, 6245.

(17) This treatment assumes that the integrated signal intensity is proportional to peak height, and that the triplet concentration is proportional to the integrated signal intensity.



8

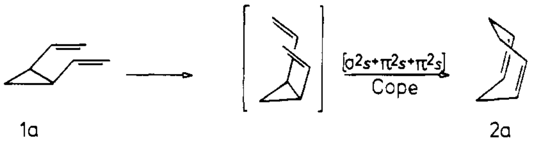
Matthew S. Platz,* John R. Burns
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Received April 9, 1979

Synthesis and Cope Rearrangement of *cis*-1,2-Dialkenylcyclopropanes

Sir:

Attempts to synthesize *cis*-1,2-divinylcyclopropane (**1a**) were largely unsuccessful in the past[1,2] owing to its rapid Cope rearrangement[3] to 1,4-cycloheptadiene (**2a**) (eq 1). They have, however, contributed much to the development and application of fluxional tautomerism which led to studies of several systems with a **1a** skeleton.[2,4] The rearrangement has recently become

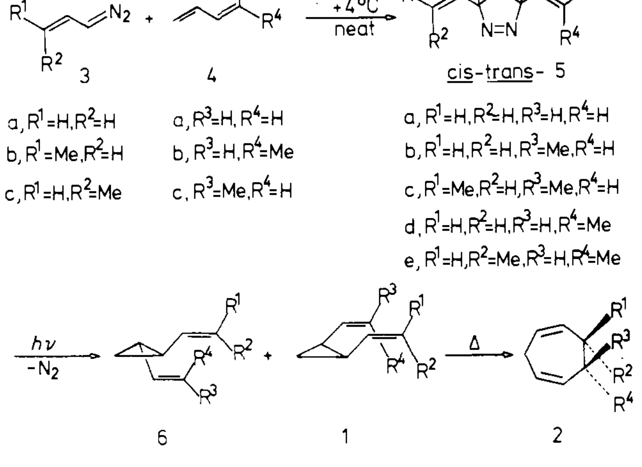


(1)

of additional interest, since derivatives of **1a** were implied as possible precursors in the biosynthesis of natural products (with a **2a** moiety) from marine brown algae (*Dictyopteris* and *Ectocarpus siliculosus*).[5]

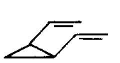
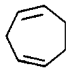
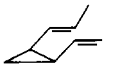
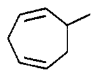
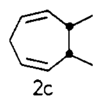
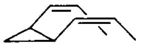
Since **1a** and most of its derivatives were inaccessible until a few years ago,[6] it is not surprising that only few kinetic data for their rearrangements are known so far. We report here a general and convenient synthesis for *cis*-1,2-dialkenylcyclopropanes (and the corresponding trans isomers) and kinetic data for their Cope rearrangements. We had shown before[6b] that low-temperature photolysis of the *cis*- and *trans*-3,5-divinyl-1-pyrazolines (**5a**), obtained via 1,3-dipolar cycloaddition of 3-diazo-1-propene (**3a**) to 1,3-butadiene (**4a**) (Scheme I), provides a simple route to **1a**.[6c] Frontier orbital considerations[7] predict the addition of diazo compounds (**3**) to occur exclusively at the terminal double bonds of conjugated dienes (**4**). This is indeed observed and, since **3** and **4** can be prepared easily in great variety, a large number of derivatives (**1**) becomes accessible this way in a very short synthetic sequence (Scheme I).[8] Moreover, as a further advantage, the stereo-

Scheme I



0002-7863/79/1501-4426$01.00/0

Table I. Kinetic Data and Products in the Cope Rearrangement of *cis*-1,2-Dialkenylcyclopropanes

reactant	product	k_{rel}[a]	$\Delta H^{\ddagger}_{273}$,[b] kcal/mol	$\Delta S^{\ddagger}_{273}$,[b] eu
 1a	 2a	5800[c]	18.8 ± 0.3	−9.4 ± 1
 1b	 2b	1500	19.7 ± 0.3	−8.5 ± 1
 1c	 2c	1100	19.8 ± 0.5	−9.4 ± 1.5
 1d	2d = 2b	1[d]	21.9 ± 0.5	−13.2 ± 1.5
 1e		no Cope rearrangement, only cis–trans isomerization[e]		

[a] At 40 °C by extrapolation of the fast (**1a**, **1b**, **1c**) and slow (**1d**) runs. Rate constants were determined as averages of five runs at six to eight temperatures over a range of at least 40 °C: **1a**, −20 to +20 °C; **1b**, −10 to +30 °C; **1c**, −10 to +30 °C; **1d**, 50 to 98 °C. [b] Errors: standard deviations. [c] k_{1a}(abs. at 5 °C) = $2.44 \times 10^{-4}\ s^{-1}$. [d] k_{1d}(abs. at 80 °C) = $0.84 \times 10^{-4}\ s^{-1}$. [e] Compare ref 11.

chemistry of the double bonds in **3** and **4** is retained throughout this synthesis.[9] Additions of neat **3a**[6c] and (*E*)- and (*Z*)-1-diazo-2-butene (**3b**[10a] and **3c**[10b]) to **4a** and (*E*)- and (*Z*)-1,3-pentadiene (**4b** and **4c**) at +4 °C for 3-4 days yield mixtures (~1:1) of the *cis*- and *trans*-3,5-dialkenyl-1-pyrazolines (**5a–e**). Low-temperature photolysis of **5a–e** (*n*-pentane or $CDCl_3$, −40 °C, Pyrex filter, Hanau TQ 718 lamp) produces in practically quantitative yield mixtures (~1:1) of the corresponding *cis*- and *trans*-1,2-dialkenylcyclopropanes (**1a–e** and **6a–e**).

Both **1a–d** and **6a–d** form the 1,4-cycloheptadienes **2a–d** upon thermolysis (**1e** and **6e** do not undergo a Cope rearrangement, only cis-trans isomerization), but at widely different temperatures. Whereas **6a–d** do not rearrange appreciably below 160 °C,[11] **1a–d** do so readily between −20 and +90 °C depending on the structure (cf. Table I). Irradiations can also be carried out in the probe of an NMR spectrometer,[12] thus allowing direct observations of the reactions in Scheme I. The Cope rearrangements **1** → **2** can be monitored by NMR and a quantitative temperature dependence study leads to the kinetic data of Table I. Since the ^1H NMR chemical shifts of **1**, **2**, and **6** are well separated and the unreactive **6** serves as an internal standard for the integration, the rate constants can be measured with sufficient accuracy. The rearrangement of **1d** is more conveniently monitored by VPC (8% Apiezon L on Chromosorb *W*, *T* = 50 °C).

Rearrangements of type **1** → **2** (eq 1) are generally believed to be concerted $[_{\sigma}2_s + _{\pi}2_s + _{\pi}2_s]$ processes involving cisoid (boat type) conformations in the transition state. Factors influencing the formation of the boat conformation and/or preventing the interaction of the double bonds due to steric hindrance should be destabilizing the transition state, which, in turn, should be reflected in the kinetic data. This has indeed been demonstrated in the thermal rearrangement of *cis*-1,2-dialkenylcyclobutanes[13] and is also observed here (Table I).

The data show that methyl substitution at the terminal carbons of the vinyl groups of **1a** produces a decline in the rate of the rearrangement. In the transition state of **1b** → **2b**, the major steric difference compared with **1a** → **2a**[14] is a methyl-hydrogen interaction (MH). Similarily, **1c** → **2c** has a methyl-methyl interaction (MM) and **1d** → **2d** one MH and one methyl-ring interaction (MR). On the assumption that the interaction free enthalpies remain constant in the series, the relative rate data of Table I can be expressed as follows (kilocalories/mole, calculated at +40 °C, the corresponding values for the *cis*-1,2-dialkenylcyclobutanes[13] in parentheses): $\Delta\Delta G_{MH}^{\ddagger} = 0.84$ (0.22); $\Delta\Delta G_{MM}^{\ddagger} = 1.03$ (0.91); $\Delta\Delta G_{MR}^{\ddagger} = 4.55$ (3.31). By far the largest steric effect is therefore the methyl-ring interaction causing a decrease in the relative rate for the rearrangement **1d** → **2d** by more than three orders of magnitude, whereas the MH and MM interactions in **1b** and **1c**, respectively, are decreasing the rates by only small factors (~4-5). The introduction of two *cis*-methyl groups prevents the Cope rearrangement and in the thermolysis of **1e** only cis-trans isomerization is observed.[11,15] We are presently investigating in detail the influence of differently substituted double bonds and substituents in the 3 position of the cyclopropane ring on the rearrangement.

Acknowledgments. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

References and Notes

(1) Vogel, E.; Ott, K. H.; Gajek, K. *Justus Liebigs Ann. Chem.* **1961**, *644*, 172.

(2) Doering, W. E.; Roth, W. R. *Tetrahedron* **1963**, *19*, 715.

(3) Review: Rhoads, S. J.; Raulins, N. R. *Org. React.* **1975**, *22*, 1. For an early example of the boat-type Cope rearrangement see: Hammond, G. S.; DeBoer, C. D. *J. Am. Chem. Soc.* **1964**, *86*, 899.

(4) Doering, W. v. E.; Roth, W. R. *Angew. Chem.* **1963**, *75*, 27. Schröder, G. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 481; *Chem. Ber.* **1964**, *97*, 3140. Doering, W. v. E.; Ferrier, B. M.; Fossel, E. T.; Hartenstein, J. H.; Jones, M., Jr.; Klumpp, G.; Rubin, R. M.; Saunders, M. *Tetrahedron* **1967**, *23*, 3943. Brown, J. M. *Chem. Commun.* **1965**, 226. Hojo, K.; Seidner, R. T.; Masamune, S. *J. Am. Chem. Soc.* **1970**, *92*, 6641. Katz, T. J.; Cheung, J. J.; Acton, N. *ibid.* **1970**, *92*, 6643. Baird, M. S.; Reese, C. B. *Chem. Commun.* **1970**, 1519.

(5) (a) Moore, R. E.; Pettus, J. A., Jr.; Mistysyn, J. *J. Org. Chem.* **1974**, *39*, 2201. (b) Jaenicke, L.; Müller, D. G. *Fortschr. Chem. Org. Naturst.* **1973**, *30*, 61.

(6) (a) Brown, J. M.; Golding, B. T.; Stofko, J. J., Jr. *J. Chem. Soc., Chem. Commun.* **1973**, 319. *J. Chem. Soc., Perkin Trans. 2* **1978**, 436. (b) Schneider, M.; Rebell, J. *J. Chem. Soc., Chem. Commun.* **1975**, 283. (c) Schneider, M. *Angew. Chem. Intl. Ed. Engl.* **1975**, *14*, 707.

(7) Houk, K. N.; Sims, J.; Duke, R. E.; Strozier, R. W.; Georgie, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 7287. Houk, K. N.; Sims, J.; Watts, C. R.; Luskus, L. J. *ibid.* **1973**, *95*, 7301.

(8) Several of the constituents of marine brown algae[5] are presently synthesized in our laboratory with this method. Compare also: Schneider, M.; Erben, A. *Angew. Chem., Intl. Ed. Engl.* **1977**, *16*, 192.

(9) Another potential method, Wittig reaction with *cis*-1-vinylcyclopropane-2-carbaldehyde,[6a] leads to *Z*/*E* mixtures.

(10) (a) Synthesized via *trans*-crotyl chloride → *N*-*trans*-crotylphthalimide → *trans*-crotylamine → *N*-*trans*-crotylurethane → *N*-nitroso-*N*-*trans*-crotylurethane → **3b**. (b) Synthesized analogously starting from *cis*-crotyl chloride.

(11) Baldwin, J. E.; Ullenius, C. *J. Am. Chem. Soc.* **1974**, *96*, 1542.

(12) Lamp, Philips SP 1000W; irradiation via a quartz light conductor leading directly into the NMR instrument (Bruker HX90R with a modified probe); filter, Schott UG 1; filter solution for the absorption of visible and infrared radiation, a mixture of $NiSO_4 \cdot 7H_2O$ (250 g), $CoSO_4 \cdot 6H_2O$ (50 g), H_2SO_4 (1 g) in H_2O (1 L).

(13) Berson, J. A.; Dervan, P. B. *J. Am. Chem. Soc.* **1972**, *94*, 7597.

(14) The kinetic data for rearrangement **1a** → **2a** are in good agreement with earlier calculations ($\Delta H^{\ddagger}$ = 17.2 kcal/mol, $\Delta S^{\ddagger}$ = −6.6 cal K^{-1} mol^{-1}): Simonetta, M.; Farini, G.; Gramaccioni, P. *J. Am. Chem. Soc.* **1968**, *90*, 1280.

(15) Sasaki, T.; Eguchi, S.; Ohno, M. *J. Org. Chem.* **1972**, *37*, 466.

Manfred P. Schneider,* Angelika Rau
Institut für Chemie, Universität Hohenheim
D-7000 Stuttgart-70, West Germany

Received February 20, 1979