layer was washed with water and dried over magnesium sulfate. Removal of solvent and distillation of the product gave 3.5 g (60%) of geranyl acetate: bp 92–94° (3.5 mm); $n^{20}D$ 1.4645 (lit.[27] bp 242; $n^{20}D$ 1.4628). Vpc and nmr spectra analysis showed that the product was *trans*-geranyl acetate contaminated with a minor amount (below 5%) of the cis isomer (neryl acetate).

(27) "The Merck Index," 8th ed, Merck & Co., Rahway, N. J., 1968, p 487.

Studies on Chrysanthemic Acid. VIII.[1] Syntheses of 1-Vinyl-2-isobutenyl- and 1,2-Diisobutenyl-3,3-dimethylcyclopropanes. Their Thermal Behavior in Comparison with *cis*-2,2-Dimethyl-3-isobutenylcyclopropyl Isocyanate and *cis*-2,2-Dimethyl-3-isobutenylcyclopropanecarboxaldehyde
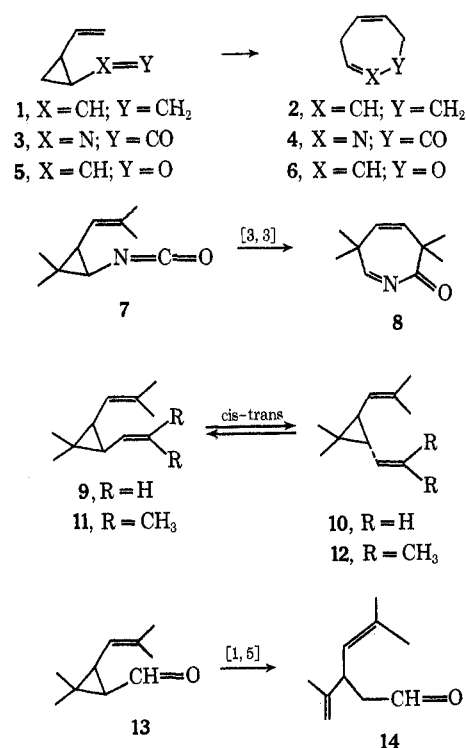
TADASHI SASAKI,* SHOJI EGUCHI, AND MASATOMI OHNO

Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464, Japan

cis- (**9**) and *trans*-1-vinyl-2-isobutenyl- (**10**) and *cis*- (**11**), and *trans*-1,2-diisobutenyl-3,3-dimethylcyclopropanes (**12**) were prepared by the Wittig reaction of *cis*- (**13**) and *trans*-2-isobutenyl-3,3-dimethylcyclopropanecarboxaldehyde (**19**) with methylene- and isopropylidenetriphenylphosphoranes in 52–85% yields, respectively. Cis olefins **9** and **11** were both very stable at room temperature. However, heating the substances neat under nitrogen resulted exclusively in cis-trans isomerization but no Cope rearrangement; the ratio of **9** to **10** was 1:3 after 3 hr at 180° and that of **11** to **12** was 1:2.6 after 3 hr at 170°. From the first-order rate constants for the **11** → **12** isomerization, the kinetic parameters, E_a, log A, and $\Delta S^{\ddagger}$, were calculated as 33 kcal/mol, 12.4 sec^{-1}, and −3.8 eu (443°K), respectively. Similarly, from the rate constants for the Cope rearrangement of 2,2-dimethyl-3-isobutenylcyclopropyl isocyanate (**7**), E_a, log A, and $\Delta S^{\ddagger}$ were calculated as 23 kcal/mol, 7.06 sec^{-1}, and −29 eu (450°K), respectively. Thermal rearrangement of cis aldehyde **13** proceeded rapidly at 173° (the half-life = 14 min) affording exclusively 5-methyl-3-isopropyl-4-hexenal (**14**) by a homo[1,5]sigmatropic rearrangement. The characteristic thermal behavior of **7**, **9**, **11**, and **13** was explained in terms of the steric repulsion between the face to face methyl groups in the cis-like quasiboat transition state required for the Cope rearrangement, in comparison with the simple *cis*-divinylcyclopropane systems, **1**, **3**, and **5**.

It is well known that *cis*-divinylcyclopropane (**1**) cannot be isolated even at −45° because of its extremely facile Cope rearrangement to 1,4-cycloheptadiene (**2**).[2-4] Similar facile concerted bisallylic rearrangements have been recorded for the *cis*-vinylcyclopropyl isocyanate (**3**) → 3,6-dihydro-2*H*-azepin-2-one (**4**) system and the *cis*-vinylcyclopropanecarboxaldehyde (**5**) → 2,5-dihydrooxepin (**6**) system.[5-7] In a previous communication,[8] we reported that *cis*-2,2-dimethyl-3-isobutenylcyclopropyl (chrysanthemyl) isocyanate (**7**) was quite stable and that Cope rearrangement to **8** occurred only under drastic conditions at 144°. We now wish to report syntheses of *cis*- (**9**) and *trans*-1-vinyl-2-isobutenyl- (**10**) and *cis*- (**11**) and *trans*-1,2-diisobutenyl-3,3-dimethylcyclopropanes (**12**) and their thermal behavior in comparison with **7** and

(1) Part VII: T. Sasaki, S. Eguchi, M. Ohno, and T. Umemura, *J. Org. Chem.*, **36**, 1968 (1971).

(2) (a) E. Vogel, K. H. Ott, and K. Gajek, *Justus Liebigs Ann. Chem.*, **644**, 172 (1961); (b) W. v. E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

(3) For a theoretical treatment, see M. Simonetta, G. Favini, C. Mariani, and P. Gramaccioni, *J. Amer. Chem. Soc.*, **90**, 1280 (1968).

(4) For a recent review on the thermal unimolecular reactions of hydrocarbons, see H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969).

(5) E. Vogel, R. Erb, G. Lenz, and A. A. Bothner-By, *Justus Liebigs Ann. Chem.*, **682**, 1 (1965); I. Brown, O. E. Edward, J. M. McIntosh, and D. Vocelle, *Can. J. Chem.*, **47**, 2751 (1969).

(6) S. J. Rhoads and R. D. Cockroft, *J. Amer. Chem. Soc.*, **91**, 2815 (1969).

(7) For the rearrangement of Schiff bases of 1,2-diaminocyclopropane to 2,3-dihydro-1,4-diazepins, see H. A. Staab and F. Vögtle, *Chem. Ber.*, **98**, 2701 (1965).
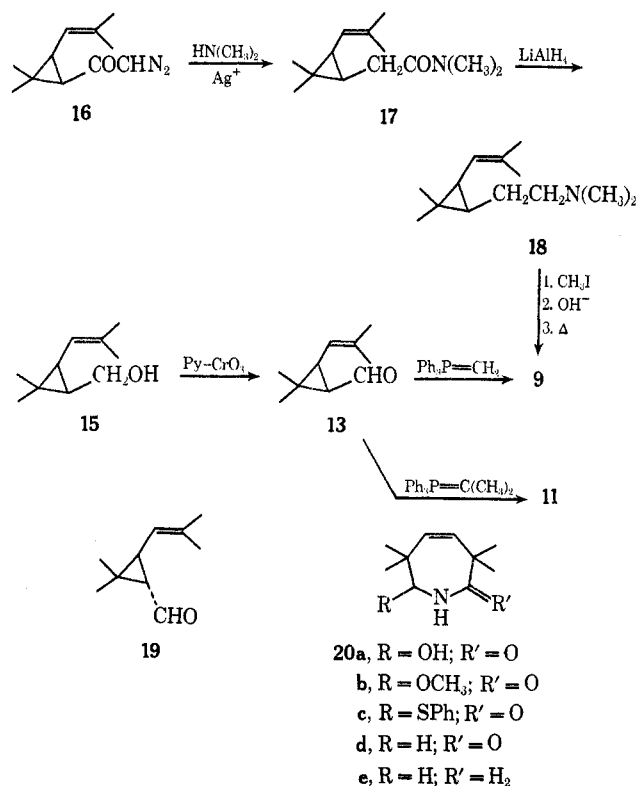
(8) T. Sasaki, S. Eguchi, and M. Ohno, *J. Amer. Chem. Soc.*, **92**, 3192 (1970).

1, X = CH; Y = CH₂ → 2, X = CH; Y = CH₂
3, X = N; Y = CO → 4, X = N; Y = CO
5, X = CH; Y = O → 6, X = CH; Y = O

7 → [3,3] → **8**

9, R = H; **11**, R = CH₃ ⇌ (cis-trans) **10**, R = H; **12**, R = CH₃

13 → [1,5] → **14**

cis-2,2-dimethyl-3-isobutenylcyclopropanecarboxaldehyde (**13**).

Results

cis-Chrysanthemyl alcohol (**15**) was converted to cis aldehyde **13** in 71% yield by oxidation with pyri-

TABLE I

SPECTRAL DATA OF 9–12

Compd	Ir,[a] cm^{-1}		Uv,[b] nm (log ϵ)	Nmr, $\tau^{c,d}$ (J, Hz)				Mass spectrum,[e] m/e (rel intensity, %)
	HC=CH$_2$	HC=C(CH$_3$)$_2$		C=CH	Ring H	CH$_3$		
9	1635	840	198 (4.28)	4.3–5.3	8.5–9.2	8.32	8.89	150 (M$^+$, 22)
	990			(m)	(m)	8.37	9.02	107 (100)
	910					(s)	(s)	
10	1630	850	200 (4.20)	4.1–5.3	8.6–9.1	8.33	8.91	
	990			(m)	(m)	(s)	8.93	
	890						(s)	
11		850	202 (4.18)	5.22	8.67	8.30	8.87	178 (M$^+$, 11)
				(d, 8.0)	(d, 8.0)	8.37	9.10	121 (100)
						(s)	(s)	
12		840	206 (4.23)	5.19	8.84	8.38	8.98	
				(d, 8.0)	(d, 8.0)	(s)	(s)	

[a] Neat. [b] In cyclohexane. [c] In CCl$_4$ at 60 MHz. [d] Area of each signal was compatible with the assigned structures. [e] At 80 eV.

dine–CrO$_3$ complex.[9] The Wittig reaction of **13** with methylenetriphenylphosphorane afforded **9** in 52% yield after purification on a silica gel column and by preparative vpc. The structure of **9** was determined as cis-1-vinyl-2-isobutenyl-3,3-dimethylcyclopropane by the spectral data (Table I) and by an alternative synthesis via the Hofmann degradation of cis-N,N-dimethylhomochrysanthemylamine (**18**); the silver ion catalyzed decomposition of cis-chrysanthemoyldiazomethane (**16**) in aqueous dioxane–dimethylamine afforded cis-N,N-dimethylhomochrysanthemamide (**17**), which was converted to the corresponding amine **18**.

16 $\xrightarrow[\text{Ag}^+]{\text{HN(CH}_3)_2}$ **17** $\xrightarrow{\text{LiAlH}_4}$

18

1. CH$_3$I
2. OH$^-$
3. Δ

15 $\xrightarrow{\text{Py–CrO}_3}$ **13** $\xrightarrow{\text{Ph}_3\text{P=CH}_2}$ **9**

$\xrightarrow{\text{Ph}_3\text{P=C(CH}_3)_2}$ **11**

19

20a, R = OH; R' = O
b, R = OCH$_3$; R' = O
c, R = SPh; R' = O
d, R = H; R' = O
e, R = H; R' = H$_2$

The Hofmann degradation of **18** methiodide yielded an olefin **9**, which was identical with a sample prepared by the Wittig reaction by ir, nmr, and vpc inspections, indicating no cis–trans isomerization during the Wittig

reaction of **13** even under the strongly alkaline conditions employed.

Similarly, trans (**10**), cis (**11**), and trans olefins (**12**) were prepared in 75–85% yields by the Wittig reactions of **13** and trans aldehyde **19** with the corresponding alkylidenetriphenylphosphoranes, respectively. The structures of these olefins were evidenced by the spectral data (Table I).

Both cis olefins **9** and **11** were stable at room temperature; no nmr spectral changes were observed after 1 week. Heating of **9** and/or **11** neat under dry nitrogen resulted exclusively in cis–trans isomerization, but, unexpectedly, no Cope rearrangement: **9** afforded a ca. 1:3 mixture of **9** and **10** after 3 hr at 180° (nmr analysis) and **11**, a 1:2.6 equilibrium mixture of **11** and **12** after 3 hr at 170° (vpc and nmr analyses).

The isomerization of **11** to **12** followed first-order kinetics with the rate constants shown in Table II.

TABLE II

FIRST-ORDER RATE CONSTANTS OF 7 → 8 REARRANGEMENT AND 11 → 12 ISOMERIZATION (VPC)

Temp, °C	k, sec^{-1} (7 → 8)	k, sec^{-1} (11 → 12)
140		1.6 × 10^{-5}
150		4.0 × 10^{-5}
160	3.0 × 10^{-5}	1.0 × 10^{-4}
170	5.3 × 10^{-5}	2.1 × 10^{-4}
180	1.3 × 10^{-4}	
190	1.7 × 10^{-4}	
200	3.5 × 10^{-4}	

The kinetic parameters were calculated as $E_a = 33$ kcal/mol, log $A = 12.4$ sec^{-1}, and $\Delta S^{\ddagger} = -3.8$ eu at 443°K.

cis-Chrysanthemyl isocyanate (**7**) was prepared by thermal decomposition of the corresponding carbonylazide at the refluxing temperature of benzene.[10] The Cope rearrangement of **7** at the refluxing temperature of o-xylene[11] afforded a 1:7 equilibrium mixture of **7** and 3,6-dihydro-3,3,6,6-tetramethyl-2H-azepin-2-one (**8**). From the kinetic study on the **7** → **8** rearrangement, the first-order rate constants were obtained in the temperature range of 160–200° (Table II, vpc analysis). The kinetic parameters were calculated as $E_a = 23$ kcal/mol, log $A = 7.06$ sec^{-1}, and $\Delta S^{\ddagger} = -29$ eu at

(9) T. Sasaki, S. Eguchi, M. Ohno, and T. Umemura, unpublished work. This oxidation method seems superior to those reported using either active manganese dioxide or Jones reagent: L. Crombie and J. Crossley, *J. Chem. Soc.*, 4983 (1963); W. G. Dauben and G. W. Shaffer, *J. Org. Chem.*, **34**, 2301 (1969).

(10) T. Sasaki, S. Eguchi, and M. Ohno, *Tetrahedron*, **25**, 2145 (1969).

(11) At the same temperature, trans-chrysanthemyl isocyanate was thermostable.

CHART I

7, X = N; Y = CO
9, X = CH; Y = CH₂
11, X = CH; Y = C(CH₃)₂
13, X = CH; Y = O
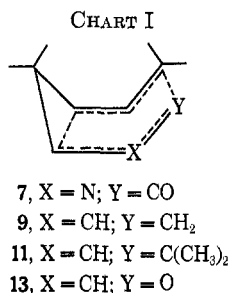
450°K. The E_a value is more or less similar to those reported for the Cope rearrangement of *cis*-1,2-divinylcyclobutane to cycloocta-1,5-diene,[12] of 2-vinylbicyclo-[3.1.0]hex-4-ene to bicyclo[3.2.1]octa-2,6-diene,[13] and of 5 to 6.[6] However, the $\Delta S^{\ddagger}$ shows a much larger negative value compared with −11.7 eu for *cis*-1,2-divinylcyclobutane[12] and those reported for other related systems.[4]

The thermal behavior of cis aldehyde 13 was different from that of isocyanate 7 and olefins 9 and 11: rearrangement of 13 occurred at 173° and afforded a single product 14, which was demonstrated to be known 3-isopropenyl-5-methyl-4-hexenal[14,15] produced by a homo[1,5]sigmatropic rearrangement of 13.

Discussion

The facile Cope rearrangement aptitude of simple *cis*-vinylcyclopropyl systems such as 1, 3, and 5 was in contrast with the present methyl-substituted systems 7, 9, 11, and 13. Considerable steric repulsion between a vinylic methyl group and one of the *gem*-dimethyl groups on a cyclopropane ring might exist in the quasiboat transition state (Chart I, X = N, Y = C=O) for the [3,3]sigmatropic (Cope) rearrangement of 7.[8,16] This was evidenced clearly by the kinetic data of the 7 → 8 rearrangement: the $\Delta S^{\ddagger}$ value was extraordinarily large and negative compared to those reported for other related systems (*vide supra*). This large negative value indicates the presence of a methyl–methyl interaction at the transition state for 7 → 8 conversion; *i.e.*, the interaction leads to prohibition of the free rotation of the face-to-face methyl groups in the transition state with a cis-like quasiboat geometry (Chart I).

The complete prohibition of the Cope rearrangement in 9 and 11 could be explained in terms of greater steric repulsion between the methyl groups on the cyclopropane ring and the two side chains in the transition state with such a geometry [Chart I, X = CH, Y = CH₂; X = CH, Y = C(CH₃)₂].[17] The homolytic ring

cleavage of 9 and 11 can be facilitated by the formation of two allylic radicals and also by the strain relief (*ca.* 27.6 kcal/mol) of a cyclopropane ring,[18,19] resulting in the cis–trans isomerization. In fact, the observed E_a value for 11 → 12 isomerization seems to be one of the lowest for a homolytic cleavage.[4,19]

The preference of 13 for the homo[1,5]sigmatropic rearrangement over the [3,3]sigmatropic rearrangement and the cis–trans isomerization could be explained also by the steric hindrance in the transition state (Chart I, X = CH, Y = O) for the Cope rearrangement; the 1,5-H shift is favored by the ease with which a cyclopropylcarbonyl moiety takes the s-cis-like conformation,[20] and by the large C=O polarity.[21,22]

Experimental Section[23]

cis-1-Vinyl-2-isobutenyl-3,3-dimethylcyclopropane (9). A. By the Wittig Reaction.—*cis*-Chrysanthemylaldehyde (13)[9] (1.3 g, 8.6 mmol) in dry ether (10 ml) was added to a stirred solution of methylenetriphenylphosphorane prepared from triphenylmethyl phosphonium bromide (8.8 g, 28 mmol) and *n*-butyllithium (16 ml of 15% w/w *n*-hexane solution) in dry ether (70 ml) under a dry nitrogen stream, and the mixture was stirred at room temperature for 2 hr. The excess Wittig reagent was decomposed by addition of water and the organic layer was separated. The water layer was extracted once with ether (20 ml). The combined organic layers were dried (Na₂SO₄) and the solvent was removed under reduced pressure to give an oily residue which was purified on a silica gel (Mallinckrodt, 100 mesh) column eluting with petroleum ether (bp 47–52°) to obtain 9 (0.74 g, 52%) as a volatile, colorless oil. An analytical sample was obtained by preparative vpc (silicone SE-30, 130°). Mass spectral analysis of the molecular ion gave *m/e* 150.1398 (calcd for C₁₁H₁₈: 150.1409).

Anal. Calcd for C₁₁H₁₈: C, 87.92; H, 12.08. Found: C, 88.05; H, 12.17.

B. By the Hofmann Degradation of the 18 Methiodide.—To a solution of *cis*-chrysanthemoyl diazomethane prepared from *cis*-chrysanthemoyl chloride (10 g, 53.6 mmol)[24] in dioxane (60 ml) was added aqueous dimethylamine (40%, 100 ml) and aqueous silver nitrate (10%, 30 ml). The mixture was heated at 60° overnight and was concentrated to *ca.* 100 ml. After cooling, the mixture was extracted with ether (five 30-ml por-

(12) G. S. Hammond and C. D. DeBoer, *J. Amer. Chem. Soc.*, **86**, 899 (1964).

(13) J. M. Brown, *Chem. Commun.*, 226 (1965).

(14) The same rearrangemnet has been reported on a mixture of 13 and 19 at 300°: G. Ohloff, *Tetrahedron Lett.*, 3795 (1965).

(15) The half-life of 13 at 173° was calculated as 14 min and that of 19 at 172° as 15 min (vpc analysis). During the rearrangement of 13, the formation of 19 was negligibly small, indicating that the 13 → 14 rearrangement has occurred prior to the cis–trans isomerization.

(16) Recently, the Cope rearrangement of tetramethylhomotropilidene has been shown to proceed *via* a bishomobenzene type (cis-like) transition state: L. Birladeanu, D. L. Harris, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 6387 (1970); see also ref 2b.

(17) It is reported that *cis,cis*-1-hexenyl-2-vinylcyclopropane (Dictyopterene) is stable at room temperature, but its Cope rearrangement to 1-*n*-butyl-1,4-cycloheptadiene occurs smoothly even at 75°: G. Ohloff and W. Pickenhagen, *Helv. Chim. Acta*, **52**, 880 (1969). See also K. C. Das and B. Weinstein, *Tetrahedron Lett.*, 3459 (1969).

(18) For a cyclopropane ring cleavage *via* the trimethylene diradical mechanism, see R. J. Crawford and T. R. Lynch, *Can. J. Chem.*, **46**, 1457 (1968), and ref 4, p 120. For the ring cleavage of ethyl chrysanthemate, see T. Hanafusa, M. Ohnishi, M. Mishima, and Y. Yukawa, *Chem. Ind. (London)*, 1050 (1970).

(19) For a recent review on ring strain, see L. N. Ferguson, *J. Chem. Educ.*, **47**, 46 (1970).

(20) For the conformational study of cyclopropylaldehyde, see G. J. Karabatsos and N. Hsi, *J. Amer. Chem. Soc.*, **87**, 2864 (1965); L. S. Bartell, B. L. Carroll, and J. P. Guillory, *Tetrahedron Lett.*, 705 (1964). For the conformation of ethyl chrysanthemate, see J.-L. Pierre, R. Perraud, and P. Arnaud, *Bull. Soc. Chim. Fr.*, 1539 (1970).

(21) It should be mentioned that a higher temperature is required for 5 → 6 rearrangement compared to those for 1 → 2 and 3 → 4, and that a N=C=O group possesses a linear geometry different from nonlinear ones for C=O and C=C groups.

(22) The activation energy for the 2,2-dimethyl-1-acetylcyclopropane → 5-methyl-5-hexen-2-one rearrangement is known to be smaller than that for the 1-vinyl-2,2-dimethylcyclopropane → 2-methyl-1,4-hexadiene rearrangement: R. M. Roberts, R. G. Landolt, R. N. Greene, and E. W. Heyer, *J. Amer. Chem. Soc.*, **89**, 1404 (1967); H. M. Frey and R. K. Solly, ref 4.

(23) All melting points were obtained on a hot-stage type micro melting point apparatus and are uncorrected. Nmr spectra were recorded on a JEOL JNM-C-60HL spectrometer at 60 MHz, and ir spectra on a JASCO IR-S ir spectrophotometer, and uv spectra on a JASCO ORD/UV-5 spectrophotometer. High-resolution mass spectra were obtained with a JEOL JMS-O1SG mass spectrometer at 75 eV and others with a Hitachi RMS-4 mass spectrometer at 80 eV. Vpc analyses were performed on a K-23 Hitachi gas chromatograph and a Varian gas chromatograph Model 1400, and preparative vpc on a Varian Aerograph Model 700 (silicone SE-30). Microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer.

(24) L. Crombie, J. Crossley, and D. A. Mitchard, *J. Chem. Soc.*, 4957 (1963).

tions) and the combined extracts were washed with water (50 ml), dried (Na₂SO₄), and evaporated to give an oil which was distilled to afford *N*,*N*-dimethylhomochrysanthemamide (**17**) (6.9 g, 63%): bp 107–114° (1 mm); ir (neat) 1655 cm⁻¹ (C=O).

A solution of **17** (6.5 g, 31.1 mmole) in dry ether (20 ml) was added under ice cooling to a stirred suspension of LiAlH₄ (1.5 g, 40 mmol) in ether (50 ml). After stirring was continued for 15 hr at room temperature, the excess LiAlH₄ was decomposed by adding water (50 ml) and the organic layer was separated and dried. Removal of the solvent afforded an oily residue which was distilled to give *cis*-*N*,*N*-dimethylhomochrysanthemylamine (**18**) (4.5 g, 75%): bp 72–75° (1 mm); $n^{22}D$ 1.4656; ir (neat) 845 cm⁻¹ (CH=C); nmr (CCl₄) τ 5.22 (broad d, 1, J = 8.5 Hz, CH=C), 7.78 (t, 2, J = 4.0 Hz, CH₂N), 7.90 (s, 3, NCH₃), 8.32 and 8.35 [each s, 6, C=C(CH₃)₂], 8.63 (d, d, 1, J = 8.0 and 7.0 Hz, C₃-H), 8.98 (d, d, 2, J = 8.0 and 4.0 Hz, C₁-CH₂), 8.94 and 9.08 [each s, 6, C(CH₃)₂], and 9.40 (t, d, 1, J = 8.0 and 7.0 Hz, C₁-H). Amine **18** afforded a crystalline methiodide quantitatively, mp 198–201°.

Anal. Calcd for C₁₄N₂₈NI: C, 49.84; H, 8.37; N, 4.16. Found: C, 49.56; H, 8.16; N, 4.15.

To an ice-cooled solution of the methiodide (3.4 g, 10 mmol) in water (25 ml) was added silver oxide freshly prepared from silver nitrate (8.5 g) and sodium hydroxide (2.2 g). After the mixture was stirred at room temperature for 15 hr, water was removed under reduced pressure to give a brownish residue, which was heated gradually in a flask fitted with a cold trap (−73°). The decomposition occurred rapidly at 77° to give an olefin **9** (0.68 g, 45%) as a volatile oil which was identical with a sample prepared by the Wittig reaction.

cis-1,2-Diisobutenyl-3,3-dimethylcyclopropane (**11**).—*cis*-Chrysanthemyl aldehyde **13** (1.0 g, 6.6 mmol) was added to a stirred solution of isopropylidenetriphenylphosphorane prepared from triphenylisopropylphosphonium bromide (5.0 g, 13 mmol) and *n*-butyllithium (9 ml of 15% w/w in *n*-hexane) in ether (50 ml) under a nitrogen stream. After stirring was continued for 2 hr at room temperature, water (50 ml) was added and the organic layer was separated. Work-up as above afforded **11** (0.88 g, 75%) as a colorless oil. An analytical sample was obtained by preparative vpc. Mass spectral analysis of the molecular ion gave *m/e* 178.1716 (calcd for C₁₃H₂₂: 178.1722).

Anal. Calcd for C₁₃H₂₂: C, 87.56; H, 12.44. Found: C, 87.49; H, 12.54.

trans-1-Vinyl-2-isobutenyl-3,3-dimethylcyclopropane (**10**).—This was prepared similarly from trans aldehyde **19** (1.0 g, 6.6 mmol) in 84% yield (0.84 g) as a colorless oil. Mass spectral analysis of the molecular ion gave *m/e* 150.1398 (calcd for C₁₁H₁₈: 150.1409).

trans-1,2-Diisobutenyl-3,3-dimethylcyclopropane (**12**).—This was obtained similarly in 85% yield (1.0 g) from the trans aldehyde **19** (1.0 g, 6.6 mmol). Mass spectral analysis of the molecular ion gave *m/e* 178.1707 (calcd for C₁₃H₂₂: 178.1722).

3,6-Dihydro-3,3,6-tetramethyl-2*H*-azepin-2-one (**8**) **and Its Derivatives 20a–e.**—A solution of *cis*-chrysanthemyl isocyanate[10] (3.5 g, 21.2 mmol) in dry *o*-xylene (30 ml) was refluxed under a dry nitrogen atmosphere for 60 hr. After evaporation of *o*-xylene, the residue was distilled under a nitrogen stream to give **8** (2.1 g, 60%) as a colorless oil, bp 79° (2 mm), and recovered **7** (0.3 g, 8.6%), bp 50–55° (2 mm). Since **8** was very hygroscopic, it was characterized by the spectral data[8] and by the chemical conversion to **20a**, **20b**, and **20c** with water, methanol, and thiophenol, respectively, in *n*-hexane *or* without solvent; **20a** was obtained as colorless crystals from *n*-hexane, mp 144–145°.

Anal. Calcd for C₁₀H₁₇O₂N: C, 65.54; H, 9.35; N, 7.64. Found: C, 65.79; H, 9.12; N, 7.94.

20b was an oil.

Anal. Calcd for C₁₁H₁₉O₂N: C, 66.97; H, 9.71; N, 7.10. Found: C, 6.71; H, 9.51; N, 6.81.

20c was obtained as colorless crystals from *n*-hexane, mp 102–103°.

Anal. Calcd for C₁₆H₂₁ONS: C, 69.79; H, 7.69; N, 5.09. Found: C, 69.80; H, 7.69; N, 5.12.

Catalytic hydrogenation of **8** (0.45 g, 2.7 mmol) in *n*-hexane (50 ml) over Adams catalyst (0.1 g) under atmospheric pressure gave **20d** (0.46 g, 100%) as colorless crystals, mp 113–114°.

Anal. Calcd for C₁₀H₁₇ON: C, 71.81; H, 10.25; N, 8.38. Found: C, 71.60; H, 10.29; N, 8.29.

LiAlH₄ (0.12 g) reduction of **8** (0.45 g, 2.7 mmol) in dry ether (30 ml) and work-up as usual gave an oily product which was dissolved in *n*-hexane and left standing overnight in a refrigerator to precipitate **20d** as colorless crystals (0.20 g, 40%). From the mother liquor, 2,3,6,7-tetrahydro-3,3,6,6-tetramethyl-1*H*-azepine (**20e**) was obtained as an oil (0.25 g, 60%), which gave crystalline picrate, mp 142–143°.

Anal. Calcd for C₁₆H₂₂O₇N₄: C, 50.26; H, 5.80; N, 14.65. Found: C, 50.22; H, 5.80; N, 14.39.

Kinetic Measurements.—All kinetic measurements were carried out using vpc analyses on a column packed with silicone SE-30 (5%) on Chromosorb G NAW at 140° for **7** → **8**, and on a column packed with silicone SE-30 (3%) on Varaport 30 at 80° for **11** → **12** and **13** → **14**. The samples (1–10 mg) were introduced in a Pyrex glass tube (0.6 cm diameter and 5.0 cm length) under a dry nitrogen atmosphere and the tube was sealed under evacuating by aspirator. The rate constants were calculated each from the peak area ratio of the starting material and the products. The kinetic parameters were calculated from the rate constants over a 30° temperature range (413–443°K) for **11** → **12**, and over a 40° temperature range (443–473°K) for **7** → **8**.