Studies on Chrysanthemic Acid. VII.[1] Thermal Decomposition of Chrysanthemyl Oxalate and Deamination of Chrysanthemylamine

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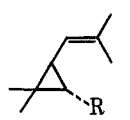
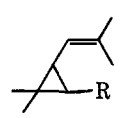
The liquid-phase thermal decomposition of *trans*-chrysanthemyl oxalate (**4**) afforded artemisia triene (**9**) in moderate yields, together with small amounts of oxalic acid under milder conditions (at 160°) compared with those reported for oxalates of general primary and secondary alcohols. The decomposition in the presence of hydroquinone gave similar yields of **9**, but in quinoline the yield was much lower. These results suggested an ion-pair mechanism for the decompositions. Deamination of *trans*-chrysanthemylamine (**7**) with isoamyl nitrite–acetic acid in benzene yielded **9** (38%), chrysanthemyl acetate (**8**) (29.8%), and artemisia acetate (**16**) (27.3%). No appreciable difference between *trans*- (**7**) and *cis*-amine **18** was observed in the product distributions.

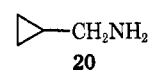
Much attention has been paid recently to cyclopropane ring opening reactions induced by a variety of intermediates involving cation, anion, radical, and carbene, etc.[2] Particularly, carbonium ion promoted reactions have been extensively studied[3] with respect to the classical or nonclassical character[4] and the bisected, bicyclobutonium or homoallylic structure[5] of the intermediates. Related examples are found in acid-catalyzed dehydration of cyclopropyl carbinols, solvolysis of cyclopropylcarbinyl esters and halides, deamination of cyclopropylcarbinylamines, and acid-catalyzed rearrangement of cyclopropylcarbinyl ketones. Substituent effects have been investigated by using a number of alkyl- and arylsubstituted cyclopropylcarbinyl systems.[6] Nevertheless, the 2-vinylcyclopropylcarbinyl system has not been reported yet. This paper deals with the results of thermal decomposition of *trans*-chrysanthemyl (2,2-dimethyl-3-isobutenylcyclopropyl-carbinyl) oxalate (**4**) and deamination of *trans*- (**7**) and *cis*-chrysanthemylamine (**18**). The chrysanthemyl system can be regarded as a model to test the isobutenyl substituent effect on cyclopropane ring opening reactions.[7]



1, R = COOH
2, R = COOEt
3, R = CH_2OH
5, R = COCl
6, R = $CONH_2$
7, R = CH_2NH_2
8, R = CH_2OAc
17, R = CH_2OTs



18, R = CH_2NH_2
19, R = CH_2OAc



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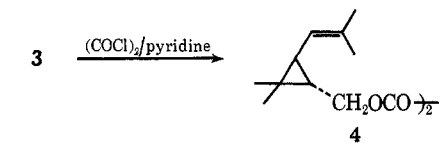


3 $\xrightarrow{(COCl)_2/pyridine}$ **4**

Results and Discussion

Thermal Decomposition of 4.—Treatment of *trans*-chrysanthemol (**3**) with oxalyl chloride in pyridine gave **4** as a colorless oil after chromatography on alumina. The structure was confirmed by analysis and spectral data. This might provide the first example of the successful preparation of a cyclopropylcarbinyl oxalate, since dimethylcyclopropylcarbinol has been reported to give only a rearranged oxalate, and dicylopropylmethyl- and tricyclopropylcarbinols do not react with oxalyl chloride.[8]

Thermolysis of **4** was carried out by heating neat under nitrogen and the resulting products were distilled off directly into a cold trap at *ca.* 0°. Decomposition occurred instantly at 160° under atmospheric pressure affording a volatile colorless oil which contained a small amount of oxalic acid. This oil was shown to be largely artemisia triene (**9**) (2,5,5-trimethyl-1,3,6-heptatriene) by spectroscopic and glpc comparison with an authentic specimen.[9] **9** gave a known maleic anhydride adduct[10] and a nitrosobenzene adduct **10**, confirming the above assignment (Scheme I). The results under several conditions are summarized in Table I.

For the thermal decomposition of oxalates, three distinct reaction paths, *i.e.*, an ion-pair,[11] a free-radical,[12] and a concerted mechanism[13] have been suggested. In the present case, the sole hydrocarbon product **9** is different from the Hofmann degradation of chrysanthemyltrimethylammonium hydroxide (**13**) which has

(1) Part VI: T. Sasaki, S. Eguchi, M. Ohno, and T. Umemura, *Tetrahedron Lett.*, 3895 (1970).

(2) For a recent review, see L. N. Ferguson, *J. Chem. Educ.*, **47**, 46 (1970).

(3) For reviews, see (a) R. Breslow, "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, Chapter 4; (b) M. Hanack and H. J. Schneider, *Angew. Chem.*, **79**, 709 (1967); *Fortschr. Chem. Forsch.*, **8**, 554 (1967); (c) S. Sarel, J. Yovell, and M. Sarel-Imber, *Angew. Chem.*, **80**, 592 (1968).

(4) G. A. Olah, D. P. Kelly, C. L. Jenell, and R. D. Porter, *J. Amer. Chem. Soc.*, **92**, 2544 (1970), and references cited therein.

(5) (a) R. H. Mazur, W. N. White, D. A. Semenov, C. C. Lee, M. S. Silver, and J. D. Roberts, *ibid.*, **81**, 4390 (1959); (b) P. v. R. Schleyer and G. W. Van Dine, *ibid.*, **88**, 2321 (1966).

(6) (a) M. Hanack and H. Meyer, *Justus Liebigs Ann. Chem.*, **720**, 81 (1968); (b) T. Shono, I. Nishiguchi, and R. Oda, *J. Org. Chem.*, **35**, 42 (1970); (c) A. Nishimura, M. Ohta, and H. Kato, *Bull. Chem. Soc. Jap.*, **43**, 1530 (1970).

(7) For photochemical cyclopropane ring opening, see T. Sasaki, S. Eguchi, and M. Ohno, *J. Org. Chem.*, **35**, 790 (1970), and for the [3,3] sigmatropic rearrangement of chrysanthemyl isocyanate, see *J. Amer. Chem. Soc.*, **92**, 3192 (1970).

(8) G. J. Karabatsos, J. M. Corbett, and K. L. Krumel, *J. Org. Chem.*, **30**, 689 (1965).

(9) L. Crombie, R. P. Houghton, and D. K. Woods, *Tetrahedron Lett.*, 4553 (1967).

(10) T. Takemoto and T. Nakajima, *Yakugaku Zasshi*, **77**, 1310 (1957); *Chem. Abstr.*, **52**, 4478*f* (1958).

(11) G. J. Karabatsos and K. L. Krumel, *J. Amer. Chem. Soc.*, **91**, 3324 (1969).

(12) (a) J. Warkentin and D. M. Singleton, *Can. J. Chem.*, **45**, 3035, 3045 (1967); (b) W. S. Trahanovsky, J. A. Lawson, and E. Zabel, *J. Org. Chem.*, **32**, 2287 (1967).

(13) C. H. Depuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960).

SCHEME I

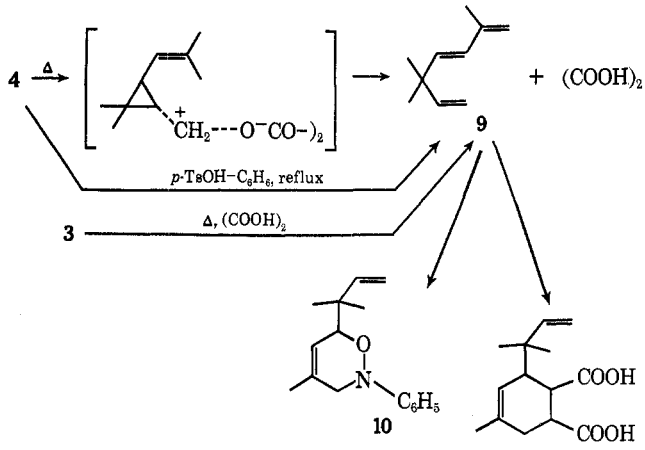


TABLE I

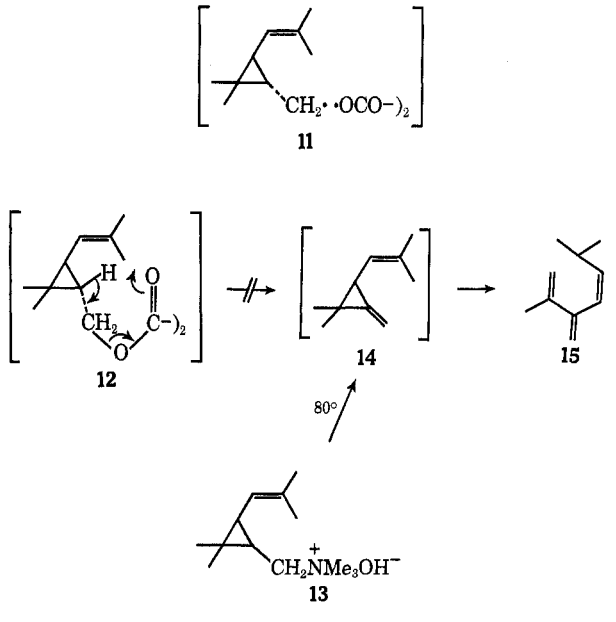
THERMAL DECOMPOSITION OF *trans*-CHRYSANTHEMYL OXALATE (4)

State	Addenda	Dec temp, °C	Yield of 9,[a] %
Neat	None	160	44
Neat	None	134 (100 mm)	51
Neat	Hydroquinone[b]	160	48
Solution	Quinoline	185	18

[a] Oxalic acid is also produced (see Experimental Section). [b] An equimolar amount was used.

been reported to give 2,6-dimethyl-3-methyleneheptа-1,4-diene (**15**) as a major product *via* a methylene cyclopropane derivative (**14**).[14] From this fact, the possibility of a concerted mechanism for the thermolysis of **4** could be excluded (Scheme II).[15] The presence of

SCHEME II



hydroquinone did not affect the decomposition (Table I). From this fact, the radical mechanism involving an intermediate such as **11** is disfavored and the ion-pair mechanism (Scheme I) is suggested. Furthermore, **9** was also produced by *p*-toluenesulfonic acid catalyzed decomposition of **4** in benzene and dehydration of **3** in the presence of oxalic acid, both of which can be assumed to proceed *via* an ion-pair or carbonium ion mechanism. The ion-pair mechanism, therefore, is the most plausible for the decomposition of **4**. The catalytic action of the primarily produced oxalic acid may be involved since the decomposition in quinoline lowered the yield of **9**. The decomposition under reduced pressure gave a somewhat better yield of **9**, which is explained by the lesser loss of **9** due to polymerization. In fact, considerable amounts of polymeric materials were produced in every run.

The decomposition temperature of **4** was considerably lower than those reported for oxalates of other primary and secondary alcohols; for example, cyclopentylcarbinyl and cyclohexyl oxalates have been reported to decompose at 360–370 and 250°, respectively.[16] This demonstrates clearly that the chrysanthemyl moiety has a stabilizing effect on the carbinyl cation involved at the ion-pair transition state by electronic and steric factors such as a strain relief *via* the cyclopropane ring opening, though the facility of thermal decomposition of a simple cyclopropylcarbinyl oxalate is not known yet.

Deamination Reaction of 7 and 18.—Chrysanthemylamines **7** and **18** were prepared by $LiAlH_4$ reduction of the corresponding amides obtained from *trans*- (**1**) and *cis*-chrysanthemic acids *via* the acid chlorides. The deamination was achieved *via* the diazotization of **7** and **18** with isoamyl nitrite–acetic acid in benzene.[17] The product from **7** was purified by chromatography on alumina to give a hydrocarbon (13%) and a mixture of acetates (44%). The hydrocarbon was characterized as **9**. The glpc of the acetate mixture exhibited three peaks in a 48:44:8 ratio. The two major components were isolated as colorless oils by preparative glpc and were characterized as artemisia acetate (**16**) (3,3,6-trimethyl-4-acetoxyhepta-1,5-diene) and *trans*-chrysanthemyl acetate (**8**), respectively. The spectral data of **16** were compatible with the assigned structure and, furthermore, the ir spectrum was practically superimposable on that reported for artemisia acetate from a natural source (*Artemisia annua L.*).[18] The characterization of **8** was based on spectral and glpc comparison with an authentic specimen.[19] The deamination of *cis*-amine **18** under the same conditions yielded also **9**, **16**, and *cis*-chrysanthemyl acetate (**19**) (Scheme III). The product distribution is summarized in comparison with those reported for deamination of cyclopropylcarbinylamine (**20**)[20] and for acetolysis of *trans*-chrysanthemyl tosylate (**17**)[19] (Table II).

The fact that only **16** and **9** were produced as the ring-opened products indicates selective ring cleavage at C_1–C_3 and demonstrates that an isobutenyl group possesses a larger stabilizing effect on the positive car-

(14) H. D. Roth, Abstracts of Papers, 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970, PETR 2.

(15) Pyrolysis of trans acetate **8** resulted in polymerization accompanied with formation of small amounts of acetic acid.

(16) G. J. Karabatsos and K. L. Krumel, *J. Amer. Chem. Soc.*, **91**, 3324 (1969).

(17) *Cf.* L. Friedman and J. H. Bayless, *ibid.*, **91**, 1790 (1969).

(18) T. Takemoto and T. Nakajima, *Yakugaku Zasshi*, **77**, 1307 (1957); *Chem. Abstr.*, **52**, 4478e (1958).

(19) R. B. Bates and D. Feld, *Tetrahedron Lett.*, 4875 (1967).

(20) J. Bayless, L. Friedman, J. A. Smith, F. B. Cook, and H. Shechter, *J. Amer. Chem. Soc.*, **87**, 661 (1965).

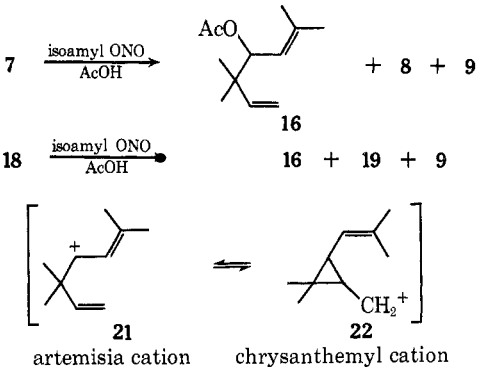
TABLE II

PRODUCT DISTRIBUTION OF DEAMINATION OF CHRYSANTHEMYLAMINE (7 AND 18)

Compd	Solvent	Products (yield, %)[a]		
7[b,c]	C_6H_6	16 (27.3)	8 (29.8)	9 (38)
18[c]	C_6H_6	16 (23.4)	19 (25.0)	9 (48)
20[d,e]	$CHCl_3$	Allyl acetate (13)	Cyclopropyl carbinyl acetate (67)	Cyclobutyl acetate (20)
17[f]	KOAc–HOAc[g] (at 40–60°)		8 (major product)	
	(at 85–90°)			9 (quantitative)[h]

[a] Estimated from relative peak areas on glpc. [b] For isolation, see Experimental Section. [c] An unidentified acetate was also produced both from 7 and 18 in 5 and 4.5%, respectively. [d] Taken from ref 20. [e] The principal product is bicyclo[1.1.0]butane (47%) which is not involved in the per cent composition in this table. [f] Taken from ref 19. [g] Acetolysis. [h] Isolated as the corresponding dimer.

SCHEME III



binyl carbon than a *gem*-dimethyl group.[19,21] However, the properties of the cationic species should be quite different from that involved in the acetolysis of **17** as demonstrated by the data in Table II.[22] The cationic species generated in the deamination is considered to be reactive[22] enough to be trapped by acetate anion rapidly before complete proton loss, affording **16** and **8** as the products corresponding to artemisia cation **21** and chrysanthemyl cation **22**. In the acetolysis at 85–90°, the intermediate cationic species is not highly reactive and consequently liberates a proton to afford the triene **9** as the major product. The formation of the acetate **8** at 40–60° could also be explained by an SN2 type reaction.[23] Comparison of the present data with those reported for **20** under similar conditions discloses that a larger ratio of ring-opened acetates to ring-retained ones is observed for **7** and **18** than for **20**, and, also, no insertion product is formed for **7** and **18** in contrast with the formation of bicyclobutane as one of the principal products for **20**. These differences may originate from the stabilizing effect of the isobutenyl group on the cationic species with a high energy. The fact that **7** and **18** gave the similar results could be explained reasonably by postulating a common intermediate such as a classical carbinyl and a homoallylic type cation but not by a bisected type one.[6]

Finally, it might be mentioned that the formation of **16** from **7** and **18** is useful for the synthesis of artemisia terpenes.

(21) H. M. Walborsky and L. Plonsker, *J. Amer. Chem. Soc.*, **83**, 2138 (1961); A. F. Thomas, *Chem. Commun.*, 1054 (1970).

(22) For other systems, see (a) A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957); (b) W. G. Dauben and J. L. Chitwood, *J. Amer. Chem. Soc.*, **92**, 1624 (1970); (c) D. E. Applequist, M. R. Johnston, and F. Fisher, *ibid.*, **92**, 4614 (1970); (d) W. Cocker, D. P. Hanna, and P. V. R. Shannon, *J. Chem. Soc. C*, 1302 (1969).

(23) *Cf.* P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *J. Amer. Chem. Soc.*, **92**, 2542 (1970), and preceding papers.

Experimental Section[24]

Preparation of *trans*-Chrysanthemyl Oxalate (4).—To an ice-cooled solution of 10.3 g (0.067 mol) of *trans*-chrysanthemol (**3**) which was obtained as an oil, $n^{19.5}$D 1.4758 (lit.[25] $n^{23.5}$D 1.4670), from ethyl chrysanthemate (**2**) by $LiAlH_4$ reduction and 5.3 g (0.067 mol) of dry pyridine in 100 ml of dry ether was added a solution of 4.9 g (0.038 mol) of oxalyl chloride in 25 ml of dry ether with stirring during 1 hr. After the addition, the stirring was continued for a further 1 hr and the mixture was allowed to stand overnight at room temperature. The mixture was poured onto ice–water and extracted with ether (three 150-ml portions). The combined ether extracts were washed with water and dried (Na_2SO_4). Removal of the solvent gave an oily residue which was purified on an alumina (Wako, neutral, grade III) column eluting with benzene to afford 3.8 g (51%) of the oxalate **4** as a colorless oil: n^{17}D 1.4833; ir (neat) 1765, 1740 (C=O), 1670 and 850 cm^{-1} (C=C); nmr (CCl_4) τ 5.05 (broad d, 1, J = 7.0 Hz, CH=C), 5.68 and 5.78 (AB portion of an ABX pattern m, each 1, J_{gem} = 12 Hz, J_{vic} = 7.0 and 8.0 Hz, $CHCH_2OCO$), 8.31 (s, 6, $C=C(CH_3)_2$), 8.66 (d, d, 1, J = 5.5 and 7.0 Hz, C_3 H, partly overlapped with the signal at τ 8.82), 8.82 and 8.91 (s, each 3, C_2 *gem*-dimethyl), 9.00–9.30 (m, 1, C_1 H); mass spectrum *m/e* (rel intensity) 362 (M^+, 5), 226 (30), 136 (90), 121 (100).

Anal. Calcd for $C_{22}H_{34}O_4$: C, 72.89; H, 9.45. Found: C, 72.98; H, 9.35.

Thermal Decomposition of 4.—In a 10-ml, round-bottom flask fitted with a distillation head which is connected to a trap cooled with an ice–salt bath, 0.18 g (0.50 mmol) of **4** was heated under nitrogen in an oil bath. The oxalate decomposed at 160° to afford an oily product (0.060 g, 44%) collected at the trap. Its ir, nmr, and mass spectra were all superimposable on those of an authentic specimen of artemisia triene (**9**).[9] Oxalic acid was also obtained in 30–90° yield as a colorless solid which sublimed onto the wall of the flask and the distillation head.

The decomposition of **4** in the presence of an equimolar amount of hydroquinone was carried out similarly and that in quinoline was carried out by heating a solution of 0.30 g of **4** in 1 ml of dry quinoline at 185° (Table I).

Thermolysis of *trans*-Chrysanthemol (3) in the Presence of Oxalic Acid.—A mixture of 0.77 g (5.0 mmol) of **3** and 1.0 g (7.7 mmol) of oxalic acid dihydrate was heated as described above at 180° to afford 0.63 g (91%) of **9**.

Diels–Alder Reaction of 9. A. With Maleic Anhydride.—A mixture of 0.56 g (4.1 mmol) of **9** and 0.39 g (4.0 mmol) of maleic anhydride in 5 ml of dry benzene was heated under reflux for 1 hr. The cooled reaction mixture was stirred with 30 ml of 10% aqueous sodium hydroxide for 1 day at room temperature and the aqueous layer was separated which on neutralization with 10% hydrochloric acid gave 0.90 g of solids. Recrystallization from acetone afforded 0.66 g (64%) of colorless needles, mp 196–199° dec (lit.[10] mp 201–202°).

B. With Nitrosobenzene.—A mixture of 1.0 g (7.4 mmol) of **9** and 0.80 g (7.5 mmol) of nitrosobenzene in 50 ml of benzene

(24) All melting points and boiling points are uncorrected. Nmr spectra were recorded on a JEOL JNM-C-60HL spectrometer at 60 MHz with TMS an internal standard and mass spectra on a JEOL JMS-01SG mass spectrometer at 75 eV. Ir spectra are obtained with a JASCO IR-S infrared spectrophotometer. Glpc analyses were performed on a K-23 Hitachi gas chromatograph and preparative glpc on a Perkin-Elmer F-21 preparative gas chromatograph. Microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer.

(25) M. Matsui, K. Yamashita, M. Miyano, S. Kitamura, Y. Suzuki, and M. Hamuro, *Bull. Agr. Chem. Soc. Jap.*, **20**, 89 (1956).

was stirred at room temperature for 1 day. Removal of the solvent gave a brownish oily residue which was purified on a silica gel column eluting with *n*-hexane–benzene (1:1 v/v). The main fraction (1.3 g) was further purified on an alumina column eluting with *n*-hexane to give 0.75 g (42%) of the adduct **10** as a colorless oil: ir (neat) 1600, 1500 and 760 (phenyl), 1640, 995 and 915 cm^{-1} (vinyl); nmr (CCl_4) τ 2.93 (m, 5, C_6H_5), 3.85–4.35 and 4.80–5.20 (a typical ABC pattern m, each 1 and 2, $CH{=}CH_2$), 4.46 (broad s, 1, C_5 H), 5.75 (broad s, 1, CHO), 6.44 (broad s, 2, CH_2N),[26] 8.22 (s, 3, $C{=}CCH_3$), 8.86 and 8.93 (s, each 3, $C(CH_3)_2$); mass spectrum *m/e* (rel intensity) 243 (M^+, 15), 131 (90), 105 (95), 94 (90), 92 (85), 80 (90), 78 (100).

Anal. Calcd for $C_{16}H_{21}NO$: C, 78.97; H, 8.70; N, 5.76. Found: C, 78.78; H, 8.60; N, 5.78.

Preparation of *trans*- (7) and *cis*-Chrysanthemylamines (18).—A solution of 9.0 g (0.054 mol) of *trans*-chrysanthemamide (**6**)[27] in 50 ml of dry ether was added to a suspension of 4.5 g (0.12 mol) of $LiAlH_4$ in 50 ml of dry ether under ice–water cooling and the resulting mixture was refluxed for 12 hr. Work-up in the usual way gave crude amine as an oil which was distilled to afford 6.0 g (81%) of the *trans*-amine **7** as a colorless oil: bp 87–90° (20 mm); $n^{17}D$ 1.4814; ir (neat) 3380, 3300, and 1595 (NH_2), and 845 cm^{-1} ($CH{=}C$); nmr (CCl_4) τ 5.18 (broad d, 1, J = 8.0 Hz, CH=C), 7.31 and 7.34 (each d, J = 7.0 Hz, CH_2N), 8.31 (s, 6, $C{=}C(CH_3)_2$), 8.88 (s, 2, NH_2, disappeared on deuteration), 8.88 and 8.97 (s, each 3, C_2 *gem*-dimethyl), 8.97 (d, d, 1, J = 5.0 and *ca.* 8.0 Hz, C_3 H, overlapped with the signal at 8.97), 9.45 (d, t, 1, J = 5.5 and 7.0 Hz, C_1 H).

Treatment of **7** with perchloric acid gave a crystalline perchlorate: mp 76–79°; ir (KBr) 3000 (NH_3^+), 1145, 1115, and 1090 (ClO_4^-), 845 cm^{-1} (CH=C).

Anal. Calcd for $C_{10}H_{20}O_4NCl$: C, 47.37; H, 7.98; N, 5.52. Found: C, 47.37; H, 7.75; N, 5.80.

Similarly *cis*-chrysanthemylamine (**18**) was obtained from *cis*-chrysanthemamide[27] in 54% yield as a colorless oil: bp 81–82° (15 mm); $n^{22}D$ 1.4767; ir (neat) 3335, 3280, and 1595 (NH_2), 845 cm^{-1} (CH=C); nmr ($CDCl_3$) τ 5.06 (broad d, 1, J = 8.0 Hz, CH=C), 7.00–7.60 (m, 2, CH_2N), 8.30 (s, 6, $C{=}C(CH_3)_2$), 8.45 (s, 2, NH_2, disappeared on deuteration), 8.70 (d, d, 1, J = 9.0 and 8.0 Hz, C_3 H), 8.87 and 8.99 (s, each 3, C_2 *gem*-dimethyl), 9.00–9.60 (m, 1, C_1 H). **18** gave a crystalline phenyl urea derivative: mp 96–98°; ir (KBr) 3320, 1645, and 1560 (NHCONH), 1595, 1500, and 765 (phenyl), 840 cm^{-1} (CH=C).

Anal. Calcd for $C_{17}H_{24}ON_2$: C, 74.96; H, 8.88; N, 10.29. Found: C, 75.15; H, 9.12; N, 10.56.

Deamination of Chrysanthemylamines (7 and 18).—A solution of 1.53 g (10 mmol) of **7**, 1.29 g (11 mmol) of isoamyl nitrite, and 0.60 g (10 mmol) of acetic acid in 20 ml of benzene was heated under reflux for 5 hr. Removal of the solvent gave an oily residue which was analyzed on glpc (Table II) and then purified by chromatography on an alumina (Wako, neutral, grade II) column. The first fraction eluted with *n*-hexane afforded 0.175 g (13%) of **9** as an oil identified by comparison with an authentic sample. The second fraction eluted with benzene gave 0.86 g (44%) of the acetate mixture which was analyzed on glpc to give three peaks in a 48:44:8 ratio. Separation by preparative glpc by using a 1.8 m × 8 mm U-shaped column packed with 10% silicone SE-30 on 60–80 mesh Chromosorb W, at 150° gave two pure acetates, **16** and **8**. One of the acetates was artemisia acetate: ir (neat) 1730 (OAc), 1645, 980 and 920 (vinyl), 1675 and 845 cm^{-1} (isobutenyl);[18] nmr (CCl_4) τ 3.94–4.40 and 4.70–5.28 (a typical ABC pattern m, 3, $CH{=}CH_2$), 4.77 (d, 1, J = 10 Hz, C=CH), 5.01 (d, 1, J = 10 Hz, CHOAc), 8.08 (s, 3, OAc), 8.28 (s, 6, $C{=}C(CH_3)_2$), 9.04 (s, 6, $C(CH_3)_2$); mass spectrum *m/e* (rel intensity) 196 (M^+, 15), 124 (70), 110 (100), 108 (95).

Another acetate was identified as *trans*-chrysanthemyl acetate (**8**) by comparison (ir and glpc) with an authentic sample.

The third fraction eluted with benzene gave 0.17 g (12% recovery) of the recovered amine **7**.

Deamination of the *cis*-amine **18** was carried out similarly and the products were analyzed on glpc (Table II).

Preparation of *trans*- (8) and *cis*-Chrysanthemyl Acetates (19).—Since the details about chrysanthemyl acetates (**8** and **19**) have not been described in literature,[19] **8** and **19** were prepared from the corresponding *trans*- (**3**) and *cis*-chrysanthemols, respectively, by acetylation with acetic anhydride in pyridine.

8 was obtained as a colorless oil in 81% yield: bp 113–114° (21 mm); $n^{17}D$ 1.4612; ir (neat) 1740 (C=O), 1665 and 845 cm^{-1} (CH=C); nmr (CCl_4) τ 5.15 (broad d, 1, J = 7.5 Hz, CH=C), 5.81 and 6.11 (AB portion of an ABX pattern m, each 1, J_{gem} = 13.0 Hz and J_{vic} = 7.0 and 9.0 Hz, a diastereotopic CH_2OAc), 8.03 (s, 3, $OCOCH_3$), 8.33 (s, 6, $C{=}C(CH_3)_2$), 8.63 (d, d, 1, C_3 H), 8.88 and 8.96 (s, each 3, C_2 *gem*-dimethyl), 9.10–9.60 (m, 1, C_1 H).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.43; H, 10.26.

19 was obtained as a colorless oil in 56% yield: bp 105.5–106.5° (21 mm); $n^{18}D$ 1.4633; ir (neat) 1735 (C=O), 1655 and 840 cm^{-1} (CH=C); nmr (CCl_4) τ 5.15 (broad d, 1, J = 8.0 Hz, CH=C), 6.05 (d, 2, J = 7.5 Hz, CH_2OAc), 8.05 (s, 3, $OCOCH_3$), 8.31 (s, 6, $C{=}C(CH_3)_2$), 8.67 (t, 1, J = 8.0 Hz, C_3 H), 8.86 and 9.00 (s, each 3, C_2 *gem*-dimethyl), 8.90–9.20 (m, 1, C_1 H).

Registry No.—**4**, 29172-38-1; **7**, 29172-39-2; **7** perchlorate, 29172-40-5; **8**, 29172-41-6; **10**, 29182-49-8; **16**, 29182-50-1; **18**, 29172-42-7; **18** phenylurea derivative, 29172-43-8; **19**, 29172-44-9.

(26) *Cf.* T. Sasaki, S. Eguchi, T. Ishii, and H. Yamada, *J. Org. Chem.*, **35**, 4273 (1970), and references cited therein.

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