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STUDIES ON CHRYSANTHEMIC ACID—III

SYNTHESES AND REACTIONS OF ISOCYANATES FROM CHRYSANTHEMIC ACID[1]

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Abstract—Chrysanthemyl isocyanate (**4**, *cis*:*trans* = 5/5) was prepared from chrysanthemic acid (**1**, *cis*:*trans* = 4/6) *via* the corresponding acid chloride (**2**) and acid azide (**3**). In these successive reactions, any appreciable change of the isomer ratio was not observed, indicating that the Curtius rearrangement proceeds through a concerted process. Chrysanthemoyl-isocyanate (**6**) and -isothiocyanate (**7**) were prepared from **2** and some reactions of these isocyanates, (**4**, **6**, and **7**) were carried out to obtain chrysanthemyl and chrysanthemoyl urea and urethane derivatives (**8a–j**, **9a**, **b**, and **10a**, **b**), imidazotrione derivatives (**11a**, **b**) and a thiadiazole derivative (**12**). The reaction of chrysanthemamide (**5a**, **b**) with oxalyl chloride to give a spiro oxazolidine-4,5-dione (**17a**, **b**) was investigated and its mechanism proposed.

SUBSEQUENT to our paper on the reactivity of the isobutenyl group in chrysanthemic acid,[2] the isocyanates readily derived from chrysanthemic acid (**1**) have been prepared in order to study other functional groups of the acid and a new rearrangement of chrysanthemamide with oxalyl chloride (**5**) to a spiro derivative of oxazolidine-4,5-dione (**17**). Generally this reaction is expected to afford an acylisocyanate.

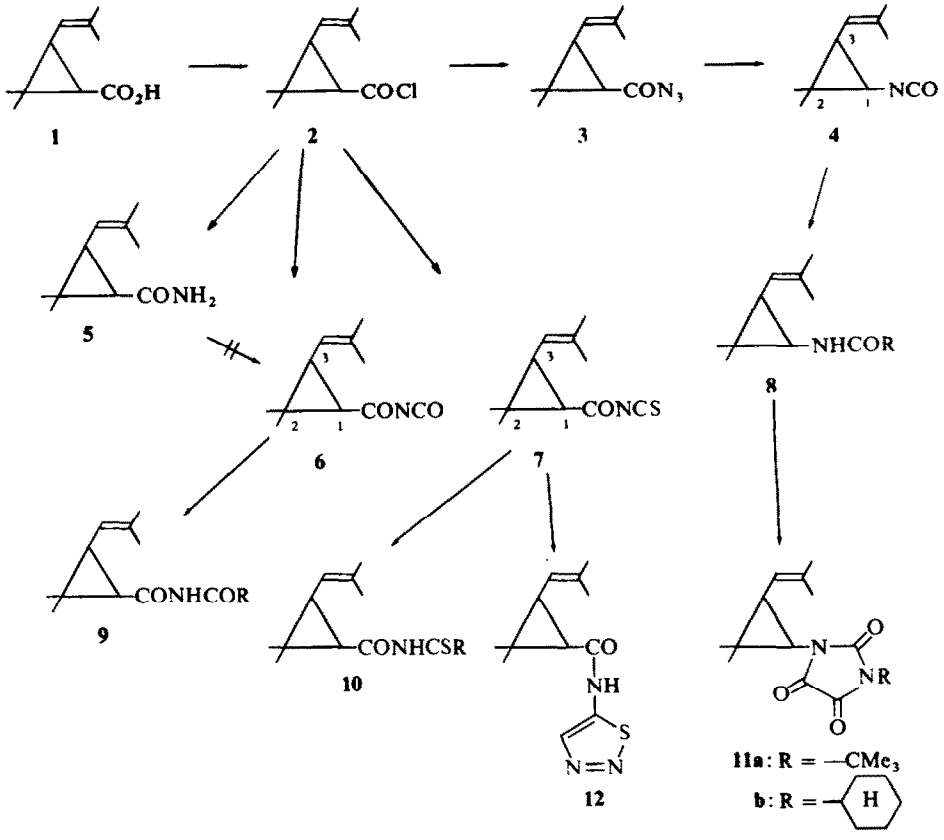
Syntheses of the isocyanates

Chrysanthemyl isocyanate (**4**). The procedure employed for the preparation of **4** was the Curtius rearrangement of the corresponding acid azide (**3**) rather than the Hofmann reaction of chrysanthemamide (**5**), because the presence of bromine-labile groups like a cyclopropane ring and an ethylenic linkage in **5** do not favour the Hofmann reaction. Chrysanthemoyl chloride (**2**) prepared from **1** was treated in acetone with excess aqueous sodium azide to give crude **3** (ν_{N_3} 2150 and ν_{CO} 1700 cm^{-1}), which was, without isolation, immediately converted to the isocyanate **4** (ν_{NCO} 2270 cm^{-1}) Pure **4** was obtained as a liquid, b.p. 49–51°/2 mm, in an overall yield of 51%.* In the above experiment, a mixture of *cis*- and *trans*-chrysanthemic acid (*cis*:*trans* = 4/6) was chosen as the starting material and in the final product **4**, after the successive reactions (**1** → **2** → **3** → **4**), the *cis*-*trans* isomer ratio (5/5) was more or less similar to that of **1**, which was determined by measuring the relative integral ratio of the NMR signals at τ 7·44 for the *cis*-isomer and 7·69 for the *trans*-isomer due to C—1-H of **4**. This result implies that any appreciable reactivity-difference in the Curtius rearrangement did not involve the *cis*- and *trans*-isomers. Therefore, it could be concluded that: (a) There seems no participation of the azide group or the carbonyl nitrene (which is

* The yield was calculated from **2**.

assumed to be produced in the decomposition of **3**) with the double bond of **3**.* Hence, the rearrangement of **3** in an extrusion of nitrogen to **4** may proceed not *via* the carbonyl nitrene (a very reactive intermediate) but rather through a concerted mechanism as proposed recently in the pivaloyl system.[3a] (b) As the Cope rearrangement[4] of **4** does not take place at the temperature of benzene boiling even for the *cis*-isomer, **4** must be more stable than *cis*-2-vinyl cyclopropyl isocyanate[5] and benzonorcaradienyl isocyanate[6] which readily undergo Cope rearrangements under similar conditions. This stability of **4** must be due to the presence of *gem*-dimethyl groups in the molecule.†

Chrysanthemoyl isocyanate (**6**) *and isothiocyanate* (**7**). Two methods were investigated for the preparation of the more reactive **6**: As briefly described,[1] treatment of **2** with silver cyanate affords chrysanthemoyl isocyanate as a very hygroscopic liquid, while



SCHEME I

* Even if any participation might be involved, there must be no difference in its extent between the *cis*- and *trans*-isomers, that will be unlikely.

† Very recently, a concerted mechanism of the Curtius, Hofmann, and Lossen rearrangements has also been reported.[3b]

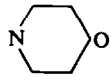
‡ However, distillation after heating **4** in *o*-xylene under reflux for 8 hr yielded mostly the *trans*-isomer (92% *trans* and 8% *cis*) in 53%, indicating that the *cis*-isomer can rearrange under these conditions.

the reaction of **5** with oxalyl chloride is not applicable for this purpose because of an abnormal rearrangement, which will be described in detail later. Chrysanthemoyl isothiocyanate (**7**) was obtained in good yield as a liquid by treatment of **2** with potassium thiocyanate (ν_{NCS} 1970 and ν_{CO} 1710 cm^{-1}; b.p. 95–96°/3 mm).

Reactions of isocyanates. Each isocyanate was converted to the corresponding urea (**8a–i** from **4**, **9a** from **6** and **10a** from **7**) and urethane (**8j** from **4**, **9b** from **6**, and **10b** from **7**). The m.ps, yields, and analyses of all these derivatives are summarized in Table 1. The urea derivatives, **8c** and **8f** were further converted to imidazotrione derivatives **11a** and **11b**, which are the first examples of chrysanthemyl heterocycles.

The reactivity of isocyanates, **4**, **6**, and **7** towards diazomethane[7] as a 1,3-dipole, and their cycloaddition to dicyclohexyl carbodiimide,[8] was examined. It was found that only **7** reacts with diazomethane at the C=S double bond to give a thiadiazole derivative **12** in low yield.

TABLE 1. UREA AND URETHANE DERIVATIVES (**8**, **9**, AND **10**) OF CHRYSANTHEMYL-, CHRYSANTHEMOYL-ISOCYANATE, AND CHRYSANTHEMOYL ISOTHIOCYANATE

Compound R	M.p. °C[a]	Yield (%)	Formula		Analysis C	H	N
8a NH_2	171–173	63	$C_{10}H_{18}ON_2$	Req.	65·89	9·96	15·37
				Found	66·00	9·50	15·50
8b NHC_6H_5	155–158	63	$C_{16}H_{22}ON_2$	Req.	74·38	8·58	10·84
				Found	74·62	8·65	11·10
8c $NHC(CH_3)_2$	120–123	89	$C_{14}H_{26}ON_2$	Req.	70·54	10·99	11·75
				Found	70·04	11·08	11·44
8d 	148–150	39	$C_{14}H_{24}O_2N_2$	Req.	66·63	9·59	11·10
				Found	66·45	9·90	11·05
8e 	120–122	93	$C_{15}H_{26}ON_2$	Req.	71·95	10·47	11·19
				Found	71·45	10·46	11·19
8f NH-cyclohexyl	111–116	76	$C_{16}H_{28}ON_2$	Req.	72·68	10·67	10·60
				Found	72·17	10·76	10·48
8g $NHCH(CH_3)CH_2NHCONH—Y$[b]	189–194	61	$C_{23}H_{40}O_2N_4$	Req.	68·28	9·97	13·85
				Found	68·08	10·38	14·08
8h $NH—C_6H_4—CO_2H$(*para*)	150 dec	24	$C_{17}H_{22}O_3N_2$	Req.	67·52	7·33	9·27
				Found	67·12	7·30	9·35
8i $NH—C_6H_4—NH$(*ortho*)$CONH—Y$[b]	177–180	6	$C_{26}H_{38}O_2N_4$	Req.	71·19	8·73	12·78
				Found	71·29	8·78	12·22
8j $OCH_2CH=CH_2$	41–44	48	$C_{13}H_{21}O_2N$	Req.	69·92	9·48	6·27
				Found	69·77	9·55	6·20
9a NHC_6H_5[c]	150–154	70	$C_{17}H_{22}O_2N_2$	Req.	71·30	7·74	9·78
				Found	71·20	7·61	9·63
9b $OCH_2CH=CH_2$[c]	Liquid	21	$C_{14}H_{21}O_3N$	Req.	66·90	8·42	5·57
				Found	66·71	8·27	5·63
10a NHC_6H_5[c]	122–125	70	$C_{17}H_{22}ON_2S$	Req.	67·54	7·34	9·27
				Found	67·41	7·08	9·23
10b $OCH_2CH=CH_2$[c]	Liquid	41	$C_{14}H_{23}O_2NS$	Req.	62·51	8·62	5·21
				Found	62·56	8·46	4·98

[a] All samples were recrystallized from acetone or aqueous acetone.
[b] Y = Chrysanthemyl.
[c] The *trans*-isomer.

Reaction of chrysanthemamide with oxalyl chloride. In the reaction of **5** (ca. 1:1-mixture of **5a** and **5b**) with oxalyl chloride no trace of acyl isocyanate was produced at temperatures of about 30°. Instead, a rearranged product **17** was obtained.[1] The use of both pure *cis*- and *trans*-amides, **5a** and **b** as starting material, yielded the same product in similar yields of about 25% which was, however, lowered to 10% in reactions of longer time (24 hr). The NMR spectrum of this product in DMSO-d_6, shown in Fig. 1, suggests a mixture of two possible isomers with the spiro structure, **17a** and **17b**. Thus, the signals at τ 5·75 (0·7 H, d, J = 12·6 Hz) and 6·97 (0·7 H, d, J = 12·6 Hz) are assignable to C—3′-H and C—2′-H, respectively, of the main isomer, while the weak signals at τ 5·93 (0·3 H, d, J = 12·6 Hz) and 6·75 (0·3 H, d, J = 12·6 Hz) are due to C—3′-H and C—2′-H of the minor isomer.* The relative integral ratio of these signals indicates a selective formation of one isomer in ca. 7:3. A *trans* relationship between a chloro and an isopropenyl group in both **17a** and **17b** is indicated from $J_{C—3'\text{-}H,\,C—2'\text{-}H}$ = 12·6 Hz and also by the fact that these configurations are compatible with the mechanism of formation as described below. †

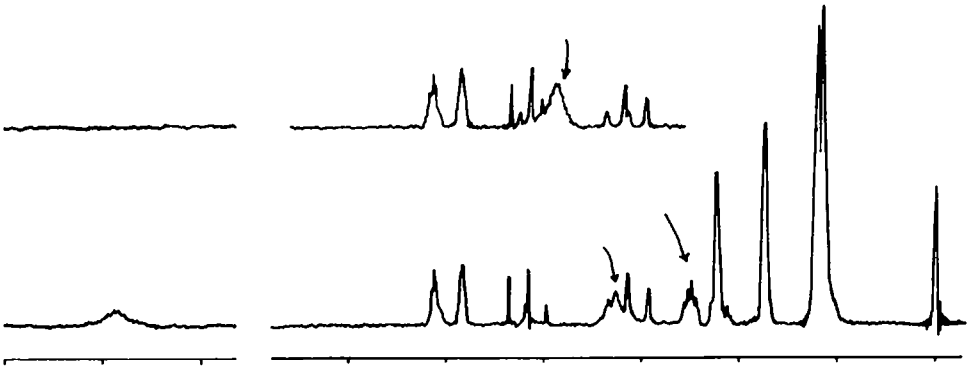
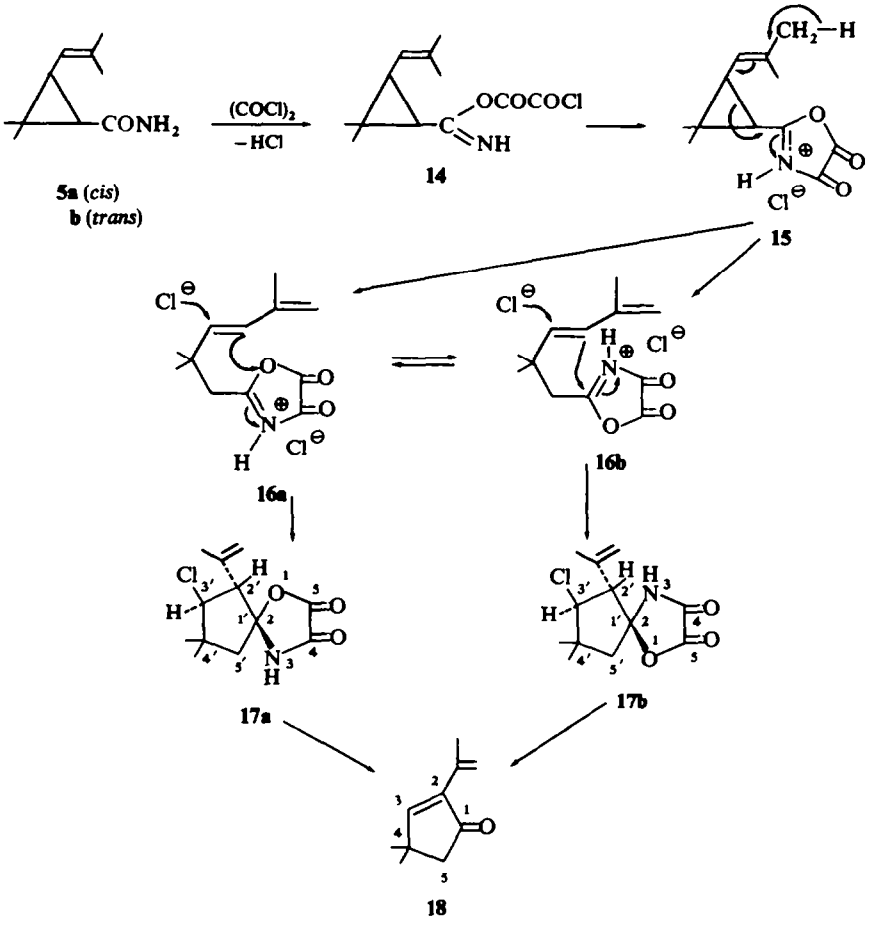


FIG. 1 NMR spectrum of **17** (a mixture of **17a** and **b**): the lower in DMSO-d_6 and the upper in DMSO-d_6 + D_2O.

In order to confirm the structure, **17a, b** was treated with ammonia-acetone affording oxamide and 3,3-dimethyl-2-isopropenyl cyclopentenone **18** as an oily material which exhibits a strong IR absorption band at 1700 (cyclopentenone) and weak bands at 1630 and 1590 (double bonds) cm^{-1}. The NMR spectrum of its 2,4-dinitrophenyl hydrazone has the signals at τ −0·88 (1 H, broad s, NH), 0·86, 1·66, and 2·14 (3 H, in an ABX pattern, phenyl protons), 3·41 (1 H, s, C—3-H), 3·89 and 4·69 (each 1 H, broad s, methylene protons at C-2-isopropenyl), 7·34 (2 H, s, C—5-H), 7·93 (3 H, s, methyl protons of C-2-isopropenyl), and 8·71 (6 H, s, *gem*-methyls protons at C-4), supporting the structure **18**. The same compound **18** was also produced from **17a, b** on alkaline hydrolysis with ethanolic potassium hydroxide, or methanolysis in the

* The weak signal at τ 7·86 in Fig. 1 was also assignable to a half of signals due to C-5′-methylene protons of the minor isomer.

† In our preliminary communication (Ref. 1), a *cis* stereochemistry of C—2′H to C—3′-H was predicted, however, recent reports on larger coupling constants of 11 Hz between vicinal *trans*-protons in certain cyclopentane rings encouraged us to assign a *trans*-relationship of C—2′-H to C—3′-H from the observed larger coupling constants.



SCHEME II

presence of a trace of sulfuric acid, or treatment with acidic 2,4-dinitrophenyl hydrazine reagent. Thus, the isolation of oxamide and **18** and facile formation of the latter both in acidic and alkaline media support the structure **17**.

Mechanism of the formation of **17a** *and* **b**. The formation of **17a, b** from **5a** and **b** with oxalyl chloride is illustrated in Scheme II. In the first step, **5a, b** is O-acylated with oxalyl chloride to give **14** which then cyclizes to an oxazoline-4,5-dione.[9] Precipitation of ammonium chloride was observed at an early stage on treatment of the reaction mixture with methanol, supporting the presence of an imino group. The formation of an oxazoline-4,5-dione intermediate is supported by its isolation recently from the reaction of adamantane-1-carboxamide with oxalyl chloride.* An oxazolinium cation **15**, could be a key intermediate for a cyclopropane ring cleavage to give a diene derivative **16**, in which the diene assumes a stable *trans* configuration with two possible orientations of the oxazoline-4,5-dione ring against the diene as shown

* Recently we have reported that adamantane-1-carboxamide with oxalyl chloride affords adamanthyl-oxazoline-4,5-dione which was isolated and further rearranged to a spirohomoadamantane oxazolidine-4,5-dione on treatment with ethanol.[11]

in **16a** and **b***. A cyclopropane ring opening caused by a neighbouring cation has been shown to give an open-chain triene system in which the stable *trans*-diene is involved.[13] The possibility of a cyclopropane ring cleavage by hydrogen chloride liberated from oxalyl chloride was excluded by the fact that **2** was prepared with thionyl chloride in good yields and a successful application of the Ritter reaction on **1**.[2] Recyclization of **16** to **17** may be initiated by the attack of an imminium cation to the diene just like an addition reaction of electrophilic reagents to alkenes (*trans*-additions) as shown in **16a** and **b**, affording **17a** and **b**, in which a chloro and an isopropenyl group take a *trans*-configuration. Of the two intermediates, **16a** and **b**, the former was assumed to be more favorable because of a better orientation of pi-orbitals, thus, leading to the selective formation of one of the isomers, probably **17a**.

As Speziale *et al.* reported acyl isocyanate formation from primary amides and oxalyl chloride,[9] the reaction of **5** with oxalyl chloride was followed spectroscopically (IR) at the temperature of boiling 1,2-dichloroethane. Only a small amount of an acyl isocyanate was detected and no pure acyl isocyanate derivative could be isolated from the intractable tar formed.[1] This temperature-dependence of the reaction of carboxamides with oxalyl chloride also occurs in other systems.* In the reactions of chrysanthemanilide (**19**) and N-methylchrysanthemanilide (**20**) with oxalyl chloride only O-acylation occurs with **19** and no reaction with **20** as summarized in Table 2.

TABLE 2. REACTIONS OF CHRYSANTHEMYL AMIDES WITH OXALYL CHLORIDE[a]

Amide		Room temp[c]	Refluxing temp[d]
5a, b	$RCONH_2$[b]	Rearrangement to **17**	Acyl isocyanate
19	$RCONHC_6H_5$[b]	O-Acylation	O-Acylation
20	$RCON(CH_3)C_6H_5$[b]	No reaction	No reaction

[a] An excess amount of oxalyl chloride was used (Experimental).
[b] R = Chrysanthemyl.
[c] Solvent was methylene dichloride and 1,2-dichloroethane.
[d] Solvent was 1,2-dichloroethane.

EXPERIMENTAL

All m.ps were determined on a Yanagimoto micromelting point apparatus (hot stage-type) and are uncorrected. Microanalyses were carried out on a Yanagimoto C.H.N. Corder, Model MT-1. Infrared spectra were recorded on a JASCO Model IR-S infrared spectrophotometer and UV spectra, on a JASCO Model ORD/UV-5 spectrophotometer. NMR spectra were obtained with a Varian A-60 or a Hitachi H-6013 spectrometers and are reported in τ values relative to TMS as an internal standard. NMR signals in singlet are designated as s, doublet as d, triplet as t, quartet as q, and multiplet as m. Mass spectra were determined using JEOLCO's JMS-01SG working at 70 ev. of electron energy.

Chrysanthemyl isocyanate **4**. Treatment of chrysanthemic acid (a mixture of *cis*- and *trans*-isomers in 4:6) with $SOCl_2$ by the known method[14] gave **2**; b.p. 105–110°/21·5 mm, n_D^{20} 1·4880 (lit.[14] b.p.$_{cis}$ 113–118/20 mm, n_D^{22} 1·4900, and b.p.$_{trans}$ 113–114°/20 mm, n_D^{23} 1·4856). To a stirred soln of 12 g (0·064 mole) of **2** in 100 ml acetone was added a soln of sodium azide (8·0 g) in 15 ml water under ice-cooling. After 3 hr stirring, water (200 ml) was added and the reaction mixture was extracted with ether (50 ml × 4). The ethereal extract was dried (Na_2SO_4), and concentrated to ca. 10 ml which was then added dropwise to refluxing dry benzene (200 ml). The mixture was heated under reflux for a further 3 hr, during which the IR band at 2150 (ν_{CON_3}) cm^{-1} disappeared. The benzene soln was concentrated and distilled to give 5·4 g (51%)† of **4**: b.p. 49–50°/

* At this stage of the reaction, any difference between the *cis*- and *trans* isomers may disappear.
† See footnote * p. 2149).

2·5 mm; n_D^{20} 1·4720; IR (neat) 2270 (NCO) and 845 (C═CH) cm^{-1}; NMR (CCl_4) τ 5·15 and 5·27 (1 H, two overlapped d, J = ca. 8 Hz, —CH═C in *cis*- and *trans*-**4**, respectively), 7·44 (0·5 H, d, J = 6·2 Hz, C—1-H of *cis*-**4**), 7·69 (0·5 H, d, J = 4·0 Hz, C—1-H of *trans*-**4**), 8·24 and 8·30 (6 H, each s, C═CMe_2), 8·78, 8·92, 8·98 and 9·01 (6 H, C—2-Me). (Found: C, 72·78; H, 9·02; N, 8·48. $C_{10}H_{15}ON$ requires: C, 72·69; H, 9·15; N, 8·61%).

Refluxing 2·4 g of **4** in 5 ml dry *o*-xylene for 8 hr and distillation recovered 1·28 g (53% recovery) of an isocyanate which was ca. 92% pure *trans*-**4**: b.p. 40–41°/1·0 mm; IR (neat) 2270 (NCO); NMR ($CDCl_3$) τ 5·21 (1 H, broad d, J = ca. 8·0 Hz, —CH═C), 7·39 (ca. 0·08 H, d, J = 6·0 Hz, C—1-H of *cis*-**4**), 7·63 (0·92 H, d, J = 4·1 Hz, C—1-H of *trans*-**4**), 8·29 (6 H, s, C═CMe_2, 8·66 (ca. 1, q, J = ca. 4·0 and 8·0 Hz, C—3-H of *trans*-**4**), 8·78 (3 H, s, C— 2-Me), 8·91 (ca. 0·3 H, s, C—2-Me of *cis*-**4**), and 9·00 (3·2 H, s, C—2-Me of *trans*-**4**, superimposed with the signal of the C—2-Me of *cis*- **4**).

Chrysanthemoyl isocyanate (**6**). Compound **6** was prepared from **2** (*trans*-isomer) and silver cyanate in 51% yield: b.p. 61–62°/1·0 mm; n_D^{22} 1·4740 (lit.[1] b.p. 60·5–61·5°/1·0 mm).

Chrysanthemoyl isothiocyanate (**7**). A mixture of 5·6 g (0·030 mole) of **2** (*trans*-isomer) and 5·0 g (0·051 mole) potassium thiocyanate in 25 ml dry ether was refluxed for 5 hr. Insoluble materials were filtered off and the filtrate was concentrated, and distilled yielding 4·2 g (68%) of **7**: b.p. 95–96°/3 mm; n_D^{22} 1·4526; IR (neat) 1970 (NCS) and 1710 (CO) cm^{-1}. It was characterized as its phenylthiourea derivative **10a**, yield, m.p. and analysis are shown in Table 1 and other physical data are as follows: IR (KBr) 3220 (NH), 1675 (CO), 1600, 720 and 680 (phenyl), and 1160 (C═S) cm^{-1}; NMR ($CDCl_3$) τ 0·44 (1 H, broad s, NH), 2·10–2·70 (5 H, complex m, phenyl protons), 5·03 (1 H, d, J = 8·5 Hz, CH—C<u>H</u>═C), 7·70 (1 H, q, J = 8·5 and 6·0 Hz, C—3-H), 8·20 (6 H, s, C═$C(CH_3)_2$), 8·56 (ca. 1 H, d, J = ca. 6·0 Hz, C—1-H, superimposed partly with the signal at τ 8·64), 8·64 and 8·77 (6 H, each s, *gem*-dimethyl protons at C-2).

General procedure for urea and urethane derivatives from **4**, **6**, *and* **7**. An equimolar amount of an amine or an alcohol was added to a benzene soln of **4**, or **6**, and or **7** and the resulting mixture was stirred at room temp until the reaction was complete (TLC control). After removal of the solvent, the solid residue was recrystallized from acetone or aqueous acetone and the liquid residue was purified on a silica-gel column. All these results are summarized in Table 1.

Prepararation of N-*chrysanthemyl imidazotrione derivatives*, **11a** *and* **b**. A mixture of 240 mg (1·00 mmole) of **8c** and 330 mg (2·41 mmoles) oxalyl chloride in 5 ml 1,2-dichloroethane was refluxed for 1 hr and removal of the solvent gave a white solid which was recrystallized as colorless needles from aqueous acetone to afford 150 mg (54%) of **11a**: m.p. 116–118°; IR (KBr) 1760 (shoulder) and 1735 (CO) cm^{-1}; NMR ($CDCl_3$) τ 5·08 (1 H, broad d, J = 8·0 Hz, CH—C<u>H</u>═C), 7·73 (1 H, d, J = 4·5 Hz, C—1-H), 7·98 (1 H, q, J = ca. 8·0 and 4·5 Hz, C—3-H), 8·23 (6 H, s, C═CMe_2), 8·36 (9 H, s, N—CMe_3), and 8·84 and 8·95 (each 3 H, s, *gem*-dimethyl at C—2). From this NMR data, **11a** was indicated as a *trans*-isomer over 95%. (Found: C, 65·38; H, 8·21; N, 9·58. $C_{16}H_{24}O_3N_2$ requires: C, 65·72; H, 8·27; N, 9·58%).

Similarly, derivative **11b** was prepared from **8f** in 18% yield: m.p. 154–156°; IR (KBr) 1760 (sh) and 1725 (CO) cm^{-1}. (Found: C, 67·61; H, 7·85; N, 8·61. $C_{18}H_{26}O_3N_2$ requires: C, 67·90; H, 8·23; N, 8·80%).

Reaction of chrysanthemoyl isothiocyanate (**7**) *with diazomethane*. Diazomethane (prepared from 2 g of nitrosomethyl urea and dried over KOH pellets) in ether was distilled into an ethereal soln of **7** (540 mg in 25 ml) and the mixture was kept for a week. After removal of excess diazomethane and the solvent, the residue was washed with n-hexane and recrystallized from acetone-n-hexane to give 120 mg (19%) of **12** as colorless needles: m.p. 167–169°; IR (KBr) 3150 (NH), 1680 and 1550 (CONH), 1650 and 1630 (both weak and shoulder, C═C and N═N) cm^{-1}; NMR ($CDCl_3$) only signals due to chrysanthemoyl moiety were observed between 1·5–10·0 τ at τ 5·03 (1 H, d, J = ca. 8·0 Hz, CHC<u>H</u>═C), 7·67 (1 H, q, J = ca. 8·0 and 5·0 Hz, C—3-H), 8·28 (6 H, s, C═CMe_2), ca. 8·35 (ca. 1 H, d, J = ca. 5·0 Hz, C—1-H), 8·70 and 8·80 (6 H, each s, *gem*-dimethyl at C—2). (Found: C, 57·63; H, 6·59; N, 16·40. $C_{12}H_{17}ON_3S$ requires: C, 57·38; H, 6·83; N, 16·7%).

Reaction of chrysanthemamide (**5**) *with oxalyl chloride*. Compound **5** (a mixture of ca. 1:1 *cis*- and *trans*-isomers, prepared from **2** and ammonia, m.p. 120–126° from ether) was suspended in dry dichloromethane (1·67 g in 15 ml) in an ice-cooled 3-necked flask fitted with a drying tube ($CaCl_2$), a separating funnel and a magnetic stirrer. By means of the funnel, 1·55 g oxalyl chloride in 5 ml dichloromethane was added dropwise with stirring resulting in a yellowish soln. After 0·5 hr, the cooling bath was removed and the mixture was kept at room temp (ca. 20°) for 3–5 hr, during which evolution of HCl gas was observed (by formation of NH_4Cl with NH_3), and a white solid separated gradually. The product was filtered off, washed with dichloromethane, and recrystallized from aqueous acetone as white needles (840 mg, 33%)—a mixture of **17a** and **b**, m.p. 136–139°.[1] (Found: C, 56·03; H, 6·19; N, 5·44. $C_{12}H_{16}O_3NCl$ requires: C, 55·92; H, 6·27; N, 5·44%).

In the above reaction, removal of excess oxalyl chloride and the solvent after the addition of oxalyl chloride was complete (ca. 20 min), and treatment of the residue with MeOH afforded NH_4Cl in 50% yield.

The reactions of *cis*-**5a**, m.p. 88–89° (lit.[15] 93°) and *trans*-**5b**, m.p. 126–127° (lit.[15] 126°) with oxalyl chloride afforded the same product **17a, b** in 26 and 20% yields, respectively, which was confirmed by their m.ps, IR and NMR spectra.

Decomposition reactions of **17a, b**

A. *In ammonia-acetone.* Addition of 257 mg (1·00 mmole) of **17a, b** in 5 ml ammoniacal acetone (ca. 18 N) afforded a white ppt, which was filtered off and washed with light pet ether (b.p. 40–65°) to give 80 mg (91%) of oxamide.[16] The filtrate and washings were combined, concentrated, washed with 10% HCl (5 ml × 4) after addition of 30 ml light pet ether, and dried (Na_2SO_4). Removal of the solvent gave an oily residue which was purified on a silica-gel column to give 120 mg of crude **18** as an oil: IR (neat) 1700 (CO), 1630 and 1590 (sh, C=C), 890 (C=CH_2) cm^{-1}; UV max (EtOH) 212 mμ (log ε ca. 4·1) and 257 (ca. 3·6); NMR ($CDCl_3$) τ 3·03 (1 H, s, CH=C), 4·00 and 4·95 (each 1 H, broad s, C=CH_2), 7·71 (2 H, s, —CH_2—), 8·17 (3 H, s, C=CMe), and 8·81 (6 H, s, —CMe_2); mass spectrum *m/e* (rel. intensity %) 150 (M^+, 14), 149 (100), 135 (17), 107 (17), and 69 (37).

The 2,4-dinitrophenyl hydrazone of **18**, m.p. 233–235° (from chloroform after chromatography on a silica-gel column), showed the following IR (KBr): 3300 (NH), 1625 (C=N, C=C), 1595 (C=C, phenyl), 905 (C=CH_2) cm^{-1}; UV max (THF) 378 mμ (log ε 4·40) and 450 (infl., 3·08). (Found: C, 58·09; H, 5·52; N, 17·07. $C_{16}H_{18}O_4N_4$ requires: C, 58·17; H, 5·49; N, 16·96%).

B. *In acidic methanol.* A soln of **17a, b** (257 mg) in 5 ml MeOH was treated with 100 mg conc H_2SO_4 and the mixture was kept at room temp for 1 day. Insoluble material was filtered off and the filtrate was concentrated to an oily residue the spectral data of which (IR, UV, NMR, and mass) are very similar to those of the ammonolysis product except contamination with methyl oxalate. Treatment of this residue with 2,4-dinitrophenyl hydrazine reagent[17] gave the corresponding hydrazone of **18** identified with the former product by a mixed m.p. measurement and comparisons of IR and NMR spectra.

C. *In 2,4-dinitrophenyl hydrazine reagent.* 2,4-Dinitrophenyl hydrazone of **18** was also obtained in 30% yield by treatment of **17** with the 2,4-dinitrophenyl hydrazine reagent.[17]

D. *In ethanolic potassium hydroxide.* Treatment of **17** with 3% ethanolic KOH after work-up also gave **18** which was characterized as its 2,4-dinitrophenyl hydrazone.

Reaction of chrysanthemanilide (**19**) *with oxalyl chloride.* To a soln of 243 mg (1·00 mmole) chrysanthemanilide (ca. 1:1-mixture of *cis*- and *trans*-isomers, m.p. 100–104°, lit.[17] m.p. 125° for the *cis*-isomer and 111° for the *trans*-isomer) in 5 ml dichloromethane was added 200 mg (1·58 mmole) oxalyl chloride under ice-cooling. After stirring for 3 hr at room temp, during which time HCl gas was evolved gradually, removal of the solvent and the excess oxalyl chloride gave an oily residue of the corresponding O-acylated product: IR (neat) 1825, 1745, and 1700 (C=O and C=N) cm^{-1} (no NH band). This residue was dissolved in 5 ml MeOH and the soln was stirred at room temp for 24 hr, and removal of the solvent left a sticky residue, from which solid anilinium hydrochloride was obtained in 50% yield as a material insoluble in chloroform. The chloroform-soluble portion was a mixture of **19**, and dimethyl oxalate (IR, VPC, and TLC analysis).

The reactions of **19** with oxalyl chloride in dichloromethane for 1 day and in 1,2-dichloroethane for 2 hr both being heated under reflux affording similar results.

Reaction of N*-methyl chrysanthemanilide* (**20**) *with oxalyl chloride.* Compound **20** was prepared from **2** and N-methylaniline as an oil: IR (neat) 1650 (CO), 1600, 1500, 700 (phenyl), and 855 (CH=C) cm^{-1}. (Found: C, 79·24; H, 9·27; N, 5·40. $C_{17}H_{23}ON$ requires: C, 79·33; H, 9·01; N, 5·44%).

The treatment of 500 mg (1·94 mmole) of **20** with 600 mg (4·7 mmoles) oxalyl chloride in 1,2-dichloroethane at room temp for 1 day and by heating under reflux for 12 hr yielded only the starting anilide **20**.

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