Studies on Chrysanthemic Acid. IV.[1] Photochemical Behavior of Chrysanthemic Acid and Its Derivatives

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Chrysanthemic acid (**1a**), ethyl chrysanthemate (**1b**), chrysanthemol (**1c**), chrysanthemamide (**1d**), and dihydrochrysanthemo-δ-lactone (**2**) were directly irradiated in solutions with high-pressure mercury lamps. β,β-Dimethyl-γ-isobutenyl-γ-butyrolactone (**5**) was isolated from **1a**, **1b**, and **1d** as a recyclization product after initial cyclopropane ring cleavage. As a photofragmentation products of the cyclopropane ring, ethyl β,β-dimethylacrylate (ethyl senecioate, **3**) from **1b** and β,β-dimethylallyl alcohol (prenol, **8**) from **1c** were produced in considerable yields, respectively. **1c** was photoisomerized to 2-isopropenyl-5-methyl-4-hexen-1-ol (lavandulol, **9**), presumably *via* a 1,4-hydrogen migration of the initially produced diradical intermediate (**15a**). Similar isomerization of **2** afforded β-isopropenyl-δ,δ-dimethyl-δ-pentanolactone (**11**). The cleavage positions of the cyclopropane ring in these reactions could be rationalized in terms of a stabilizing effect of the substituent on the intermediate diradicals.

In previous papers,[1] we have reported the reactivity of the isobutenyl and carboxyl group in chrysanthemic acid (**1a**). Our present interest is focused on the photochemical behavior of the cyclopropyl moiety of **1a** and its derivatives **1b**, **1c**, **1d**, and **2**. Although pyrolytic rearrangements of **1a**,[2] **1b**, and **1c**,[3] and the carbonium ion-promoted ring cleavages of **1c**[4] and **1d**[1b,c] have been reported, there are apparently no reports on the photochemical behavior of **1a** and its derivatives.[5]

Results

Irradiation of ethyl chrysanthemate **1b** (*cis/trans* isomer ratio: 1/2.5)[6] in *n*-hexane for 150 hr with a 100-W high pressure mercury lamp afforded an oily product, which was distilled to give three main fractions. The first fraction was a very volatile oil, which was characterized as ethyl β,β-dimethylacrylate (ethyl senecioate, (**3**), on the basis of its ir spectrum and the fact that its alkaline hydrolysis afforded known crystalline senecioic acid (**4**). The second fraction with a boiling point range of 52–56° (6 mm) was identified as recovered **1b** by vpc and ir analysis. The *cis/trans* isomer ratio of the recovered **1b** was shown to be the same as that of starting **1b** (1/2.5) by nmr analysis.[7] The third fraction boiling at 61–95° (0.15 mm) afforded colorless needles on further purification by chromatography. This product was characterized as the known β,β-dimethyl-γ-isobutenyl-γ-butyrolactone (**5**) on the basis of its melting point,[8] its analysis, and its ir and nmr data.

When irradiation was carried out with a 500-W high pressure mercury lamp under similar conditions, **1b** afforded a large amount of undistillable side products together with a mixture of **3** and **5** in a ratio similar to that obtained by photolysis with a 100-W lamp. The results of the photolysis in different solvents with a 100-W lamp are summarized in Table I; on photolysis in acetone, **1b** afforded the corresponding oxetane derivative **7a**[9] and a small amount of **3**.

TABLE I

PHOTOLYSIS OF ETHYL CHRYSANTHEMATE (**1b**)[a]

Solvent	Concn, *M*	Irradiation time, hr	Conversion,[b] %	Product ratio **3**	**5**	**7a**
n-Hexane	0.1	150[c]	80	6	1.5	
Ethanol	0.15	105	20	1	0	
Acetone	0.1	65	70	2	0	5[d]

[a] Irradiation was carried out with a 100-W high pressure mercury lamp (see Experimental Section). [b] Estimated by peak area on vpc. [c] *Ca.* 75% conversion was obtained after 100 hr. [d] As a crude oxetane fraction.

Direct irradiation of chrysanthemol (**1c**) in *n*-hexane with a 500-W high pressure mercury lamp afforded two main products in about 20% yield each, together with a large quantity of nondistillable products, which were not further identified. One of the products, a volatile liquid, was characterized as β,β-dimethylallyl alcohol (prenol, **8**) after conversion to its phenylurethan derivative.[10] The higher boiling product was identified as 2-isopropenyl-5-methyl-4-hexen-1-ol (lavandulol, **9**) by comparison of its ir spectrum and its vpc retension time with those of an authentic specimen.[11]

The photolysis of **1a** in *n*-hexane and of **1d** in ether both afforded a γ-lactone **5** in 15 and 10% yields, respectively. The corresponding fragmentation products such as senecioic acid and senecioamide were not detected in both cases.

Photolysis of dihydrochrysanthemo-δ-lactone **2** in *n*-hexane with a 100-W lamp afforded a complex mixture of several products, from which a cyclopropane ring opened δ-lactone **11** was isolated by preparative vpc. The structure of **11** was assigned as β-isopropenyl-δ,δ-dimethyl-δ-pentanolactone, on the basis of its ir, nmr, and mass spectral data (see Experimental Section).

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[1] (a) Part I: T. Sasaki, S. Eguchi and M. Ohno, *J. Org. Chem.*, **33**, 676 (1968). (b) Part II: T. Sasaki, S. Eguchi, and M. Ohno, *Tetrahedron Lett.*, 927 (1968). (c) Part III: T. Sasaki, S. Eguchi, and M. Ohno, *Tetrahedron*, **25**, 2145 (1969).

[2] L. Crombie, S. H. Harper, and R. A. Thompson, *J. Sci. Food Agr.*, **2**, 421 (1951).

[3] G. Ohloff, *Tetrahedron Lett.*, 3795 (1965).

[4] (a) R. B. Bates and S. K. Paknikar, *ibid.*, 1453 (1965); (b) L. Crombie, R. P. Houghton, and D. K. Woods, *ibid.*, 4553 (1967).

[5] A substituent effect on the photocleavage of the cyclopropane ring might be expected, by comparison with the results of known photoreactions of 2,2-dimethyl-3-isobutenyl-1-phenylcyclopropane (**1e**). See H. Kristinsson and G. S. Hammond, *J. Amer. Chem. Soc.*, **89**, 5970 (1967).

[6] A mixture of *cis–trans* isomers was used for the photolysis. Sensitized *cis–trans* photoisomerizations of **1a** and its esters have been reported by us.[1a]

[7] The same isomer ratio was also obtained for the recovered **1b** after photolysis in ethanol and in acetone.

[8] F. Korte, D. Scharf, and K. H. Buechel, *Ann. Chem.*, **664**, 97 (1963).

[9] For the formation of oxetane derivatives with benzophenone, see ref 1a.

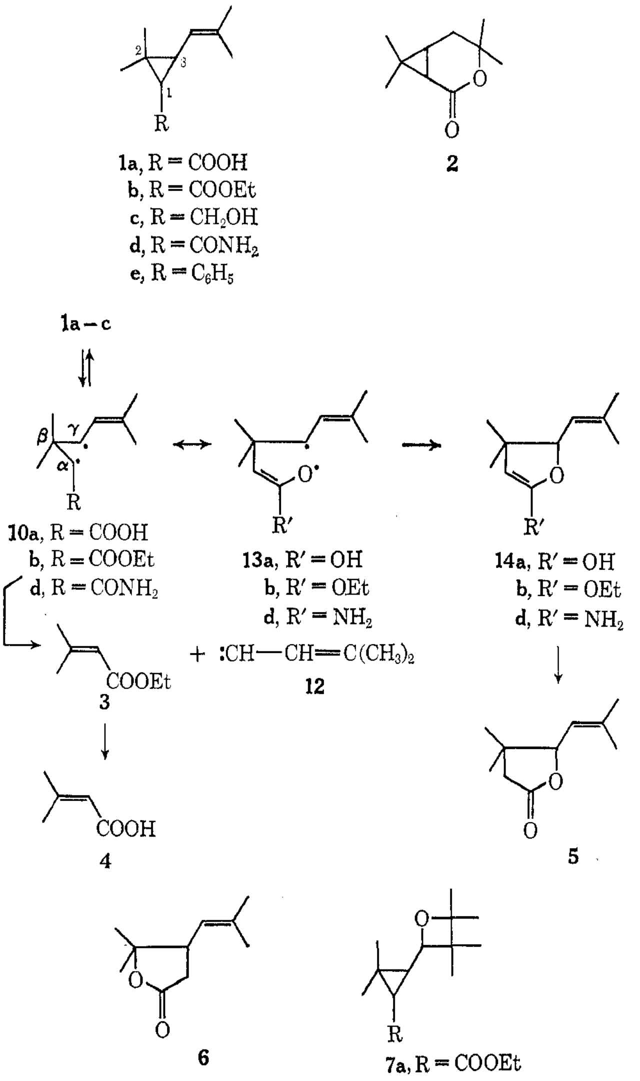
[10] T. Lennartz, *Chem. Ber.*, **76**, 841 (1943).

[11] S. M. Baba, H. H. Mathur, and S. C. Bhattacharyya, *Tetrahedron*, **22**, 903 (1966), and references cited therein.

Discussion

Mechanisms for the formation of **3** and **5** from **1b** are proposed in Scheme I; initial cyclopropane ring cleavage at the 1,3 bond leads to the formation of a resonance-stabilized diradical intermediate **10b**, which is capable of recyclization to **1b** or to **14b** *via* an enolate radical **13b**. **14b** can be converted to **5** by further irradiation[12] and/or by hydrolysis. The formation of **5** from **1a** and **1d** can be explained similarly. Further bond rupture of **10b** between the β and γ positions produces the fragmentation product **3** and presumably a vinylcarbene **12**.[13]

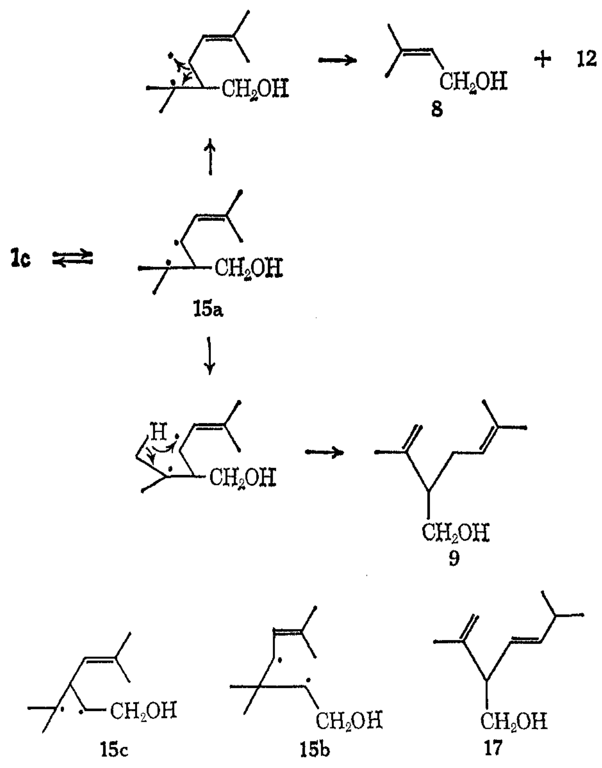
SCHEME I



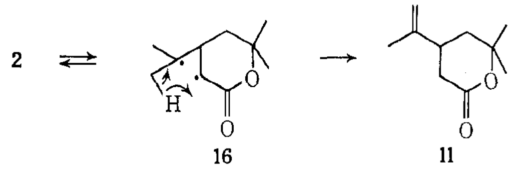
The formation of **8** and **9** from **1c** suggests a process involving diradical intermediate **15a**, which implies an initial 2,3 bond fission as shown in Scheme II. The possibility of initial 1,3 bond fission to **15b** as another process for formation of **8** cannot be ruled out, however.

The possible mechanism for the formation of **11** from **2** is depicted in Scheme III: cyclopropane ring cleavage of **2** at the 1,2 bond gives rise to a diradical intermediate **16** which can be converted to **11** *via* a 1,4 hydrogen migration.

SCHEME II



SCHEME III



The observed position of the cyclopropane ring cleavage can be rationalized in terms of the relative stabilities of the possible intermediate diradicals. The ethoxycarbonyl, carboxyl, and carbamoyl groups in **1b**, **1a**, and **1d**, respectively, will interact with the radical at C-1 by conjugation, and thus favor 1,3 bond cleavage resulting in the formation of **10b**, **10a**, and **10d**, respectively. The lower reactivity of **1b** in ethanol than in *n*-hexane might be attributable to stabilization of the diradical intermediate by the polar solvent, since the uv spectrum of **1b** in ethanol is similar to that in cyclohexane (Figure 1).

1c, having a saturated group at C-1, was cleaved at the 2,3 bond. The diradical intermediate **15a** is again assumed to be the most stable among three possible diradicals, **15a**, **15b**, and **15c**.[14]

Similarly, we could visualize the 1,2 bond cleavage of **2** as a process leading to the formation of the most stable diradical **16** in the system. It may be noted that the fates of the excited molecules or the diradical-like intermediates are considerably influenced by the C-1 substituent.

In the photolysis of **1e**, having a C-1-phenyl substituent, the ratio of fragmentation product (β,β-di-

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[12] For example, see E. Murad, *J. Amer. Chem. Soc.*, **83**, 1327 (1961).

[13] Formation of **12** could not be demonstrated by isolation of 3,3-dimethylcyclopropene or by trapping with appropriate olefins, although its formation was suggested by isolation of a hydrocarbon which might have been produced by polymerization of **12** or of 3,3-dimethylcyclopropene. Another possible process for the formation of **3** and **12**, the initial 2,3 bond fission followed by 1,3 bond rupture, cannot be ruled out, however.

[14] For concurrent 1,6 and 1,7 bond fissions of 2-carene-4α-methanol by direct irradiation, see P. J. Kropp, *ibid.*, **89**, 1126 (1967).

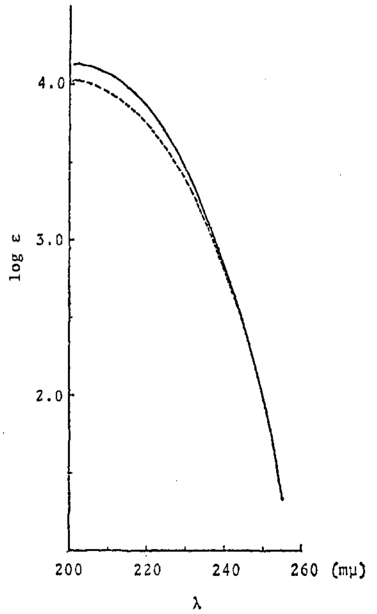

Figure 1.—Ultraviolet absorption spectrum of ethyl chrysanthemate (**16**): in cyclohexane, ——; in ethanol, - - - -.

methylstyrene) to cyclization product (bicyclo[2.1.0]pentane derivative) to recyclization product *via* the C-1 substituent (1-isobutenyl-2,2-dimethylindan) has been reported to be 1/6/2.[5] In the photolysis of **1b**, this ratio (ethyl senecioate to bicyclo[2.1.0]pentane derivative to β,β-dimethyl-γ-isobutenyl-γ-butyrolactone) is 6/0/1.5. In the photolysis of **1a** and **1d**, only the recyclization product *via* the conjugated substituent at C-1 could be produced, but no bicyclo[2.1.0]pentane derivatives or fragmentation products could be detected.

The photocleavage of the cyclopropane ring is quite different from the pyrolytic one. Thermolysis of **1a** results in the formation of pyrocin **6** *via* 1,2 bond cleavage,[2] while pyrolysis of **1b** affords the 2,3 bond cleaved product,[3] both being different from the photolytic 1,3 bond cleavage. **1c**, having no conjugated C-1 substituent, has been reported to give a double-bond isomer of lavandulol, **17**, on pyrolysis,[3] which implies the occurrence of the 2,3 bond fission followed by a simultaneous or a subsequent 1,6 hydrogen migration, in contrast to the 1,4 hydrogen migration *via* **15a** on photolysis. The electronically excited molecule might be more reactive than the thermally excited one to cause the fragmentation to **8**. Although the thermal rearrangement of vinylcyclopropanes to -cyclopentenes has been well documented,[15] no photolytic formation of cyclopentene derivatives from **1a**–**1d** could be observed, in agreement with the photolytic results of **1e**.[5]

Experimental Section[16]

Photolysis of Ethyl Chrysanthemate (1b). A. In *n*-Hexane.—A solution of 19.6 g (0.1 mol) of **1b**[6] in 1 l. of *n*-hexane was irradiated at room temperature under a slow nitrogen stream with a 100-W high pressure mercury lamp (UM-102, Ushio Denki Co., Tokyo), using a cylindrical quartz jacket cooled by running water. Irradiation was continued for 150 hr, at which 80% conversion was obtained, by vpc analysis. The product was a complex mixture (at least 10 peaks on the vpc), from which the main products were separated as follows: After removal of the solvent by distillation through a 40-cm Widmer column, the oily residue was fractionated through a 10-cm spinning-band column under reduced pressure to give three main fractions. The first fraction, trapped at −70° from vapors of a distillation flask at 60° under 20 mm, was 4.5 g (35%) of crude **3**: ir (neat) 1720 (C=O) and 1655 (C=C) cm^{-1}; hydrolysis of **3** with 10% aqueous potassium hydroxide solution afforded senecioic acid **4** as colorless needles (methanol–benzene), mp 68–69° (lit.[17] mp 67.8–68.3°). The second fraction of bp 52–57° (6 mm) was 3.0 g (20% recovery) of recovered **1b**, which was identified *via* vpc, ir, and nmr. The *cis*/*trans* isomer ratio was estimated as 1/2.5 by nmr (100 MHz). The third fraction was 3.0 g of a viscous oil: bp 60–95° (0.15 mm); ir (neat) 1770 cm^{-1} (γ-lactone). Further purification on a silica gel (Mallinckrodt, 100 mesh) column eluting with benzene afforded 0.4 g of an oily hydrocarbon, which exhibited no carbonyl ir bands, and therefore was discarded, and 1.65 g (10%) of pure β,β-dimethyl-γ-isobutenyl-γ-butyrolactone **5**, which on cooling at −70° in *n*-hexane, solidified to colorless needles: mp 46–49° (lit.[8] mp 49°); ir ($CHCl_3$) 1770 (γ-lactone), 1670, and 850 cm^{-1} (trisubstituted olefin); nmr ($CDCl_3$) τ 4.77 (broad d, 1, J = 9.5 Hz, CH=C), 5.17 (d, 1, J = 9.5 Hz, -OCH–), 7.52 and 7.70 (AB q, each 1, J = 17 Hz, $-CH_2CO-$), 8.17 and 8.26 [broad s, each 3, $C=C-(CH_3)_2$], and 8.86 and 8.90 [each s, each 3, $C(CH_3)_2$].

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.53; H, 9.94.

The fourth fraction of bp 95–120° (0.15 mm) was 2.5 g of a viscous oil, which was unidentified because of the difficulty of purification. The distillation residue amounted to 2.3 g.

Irradiation of 22.05 g (0.11 mol) of **1b** in 1.1 l. of *n*-hexane with a 500-W lamp for 32 hr under similar conditions afforded 6.2 g (40%) of **3**, 2.8 g (14%) of **5**, 3.9 g (18% recovery) of recovered **1b**, and 6.5 g of nondistillable residue.

B. In Ethanol.—A solution of 29.4 g (0.15 mol) of **1b** in 1 l. of ethanol was irradiated under similar conditions for 105 hr. Work-up as above afforded 2.1 g (11%) of **3** and 24.0 g (80%) recovery) of recovered **1b** (Table I). No γ-lactone **5** could be detected by vpc analysis or by ir.

C. In Acetone.—A solution of 19.6 g (0.1 mol) of **1b** in 1 l. of acetone was irradiated similarly for 65 hr. After removal of the solvent, the residual oil was fractionated as above to give 1.9 g (12%) of **3**, 5.3 g (27% recovery) of recovered **1b** of bp 50–55° (6 mm), 6.8 g (33%) of the oxetane fraction, and 3.3 g of nondistillable residue. The oxetane fraction was further purified on a silica gel column. Eluting with benzene containing 1 vol.% of acetone gave 5.0 g of **7a** as an oil, which was still not pure enough, as shown by the presence of an ir absorption band at 1620 (shoulder, C=C of the impurities), besides those at 1720 (C=O) and 970 (oxetane) cm^{-1}. A portion (0.62 g) of this oil was stirred overnight at room temperature with 10 ml of 3% aqueous sodium hydroxide solution. After neutralization with 10% hydrochloric acid, the product was taken up with ether (four 20-ml portions). Removal of the solvent afforded 0.48 g (75%) of an oil which crystallized on cooling. Recrystallization from petroleum ether (bp 40–60°) afforded colorless needles of the oxetane acid **7b**: mp 154–156°; ir (KBr) 3200–2400 and 1700 (COOH), and 980 (shoulder, oxetane) cm^{-1}; nmr ($CDCl_3$) τ −0.80 (broad s, 1, COOH), 6.06 (d, 1, J = 10.0 Hz, $-\overline{\mathrm{CCOC}}$-H),[18] 8.13 (d, 1, J = 5.5 Hz, C-1 H),[19] 8.39 (q, 1,

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(15) This isomerization has been explained by a process *via* a diradical intermediate: M. R. Willcott and V. H. Cargle, *J. Amer. Chem. Soc.*, **89**, 723 (1967) and references cited therein.

(16) All melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. Microanalyses were carried out on a Yanagimoto C. H. N. Corder Model MT-1. Ir spectra were recorded on a JASCO Model IR-S ir spectrophotometer, and uv spectra on a JASCO Model ORD/UV-5 spectrophotometer. Nmr spectra were obtained with Varian A-60 and HA-100 spectrometers using TMS as the internal standard, and mass spectra with a JEOL Model JMS-01SG mass spectrometer at 75 eV of electron energy. Vpc analyses were performed on a Yanagimoto gas chromatograph Model GCG-220 using a 7-ft column packed with PG-6000 at 100–200°, vpc separations on a JEOL JGC-750T preparative gas chromatograph using a 10-ft column (coil-form, 6-mm i.d.) packed with acid-washed Chromosorb W at 170°.

(17) B. R. Thomas and J. J. Sudborough, *J. Chem. Soc.*, 101, 326 (1912).

(18) D. R. Arnold, R. L. Hirman, and A. H. Glick, *Tetrahedron Lett.*, 1425 (1964).

(19) This coupling constant is in the range postulated for the *trans* configuration, though **7a** may be a mixture of *cis* and *trans* isomers; see ref 1a.

J = 10.0 Hz and 5.5 Hz, C-3 H), 8.64, 8.71, 8.82 and 8.88 (each s, *ca.* 18, 6 CH_3).

Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, C, 69.13; H, 10.21.

Photolysis of Chrysanthemol (1c) in *n*-Hexane.—A solution of 17.1 g (0.11 mol) of **1c**[20] in 1.1 l. of *n*-hexane was irradiated with a 500-W high pressure mercury lamp for 28 hr. The crude product was distilled through a 10-cm spinning-band column after removal of the solvent through a 40-cm Widmer column. The first liquid fraction of bp 47–68° (19 mm) consisted of prenol **8**, 2.4 g (25%): ir (neat) 3400 (OH), 1670 and 830 (C=CH) cm^{-1}. Its phenylurethan derivative had mp 62–64° (lit.[10] mp 64°). The second oily fraction of bp 52–53° (1.5 mm) was characterized as lavandulol (**9**), 3.3 g (20%), by comparison with an authentic specimen[11] *via* vpc and ir. The residue, 4.6 g, was nondistillable.

Photolysis of Chrysanthemic Acid (1a) in *n*-Hexane.—A solution of **1a** (3.36 g, 0.02 mol) in 200 ml of *n*-hexane was irradiated with a 100-W lamp for 70 hr. After removal of the solvent, the oily residue was dissolved in 30 ml of *n*-hexane and the solution was extracted with 5% aqueous potassium hydroxide solution (three 20-ml portions). The orgnaic layer was dried (Na_2SO_4). Removal of the solvent left 0.55 g (16%) of an oil, which afforded colorless crystals of **5**, mp 46–49°, on cooling. The combined alkaline extracts were neutralized with 10% hydrochloric acid and the resultant oil was taken up with chloroform (three 30-ml portions). Work-up afforded 2.3 g (68% recovery) of a viscous oil, which was identified as recovered **1a** by comparison with an authentic sample *via* vpc and ir. No trace of senecioic acid **4** was detected by vpc analysis of the crude product. Furthermore, it was found that photodecarboxylation of **1a** had occurred during the photolysis to less than 3% as determined by titration of the evolved carbon dioxide with aqueous sodium hydroxide solution.

Photolysis of Chrysanthemamide (1d) in Ether.—A solution of 3.34 g (0.02 mol) of **1d**[1c] in 200 ml of ether was irradiated with a 100-W lamp for 90 hr. After removal of the solvent, the residual oil was purified on alumina (neutral, activity grade III), eluting with *n*-hexane, benzene, and ether, successively. The *n*-hexane fraction afforded 0.3 g of oily hydrocarbon which was discarded. The benzene and ether fractions gave a mixture (2 g) of **5** and recovered **1d** on vpc. Further purification of this mixture on a silica gel column (with dichloromethane) gave pure **1d** and **5** both in 10% yields.

Photolysis of Dihydrochrysanthemo-δ-lactone (2) in *n*-Hexane.—A solution of 3.36 g (0.02 mol) of **2**[2] in 200 ml of *n*-hexane was irradiated with a 100-W lamp for 90 hr. The crude oily product obtained after removal of the solvent was purified on a silica gel column eluting with *n*-hexane and benzene, successively. The *n*-hexane fraction gave 0.44 g of an oily hydrocarbon which was discarded because of the absence of carbonyl bands in the ir spectrum. The first benzene fraction afforded 1.16 g of a compound, which was shown to be acidic by the presence of carboxyl absorption bands in the ir spectrum. It showed three large peaks on vpc and could not be identified because of difficulties in obtaining pure materials. Further elution with benzene gave 0.74 g (20%) of β-isopropenyl-δ,δ-dimethyl-δ-pentanolactone (**11**) after purification by preparative vpc: ir (neat) 1720 (δ-lactone), 1640 and 890 (C=CH) cm^{-1}; nmr ($CDCl_3$) τ 5.12 and 5.20 (partly overlapped s, 2, C=CH), 8.22 (broad s, 3, $C=CCH_3$), 8.52 and 8.55 [s, 6, $C(CH_3)_2$], and 7.00–8.20 (m, *ca.* 5, methine and methylene protons); mass spectrum (75 eV) m/e (rel intensity) 168 (5.1, M^+) and 68 (100, $C_5H_8^+$). Further elution with benzene gave 0.43 g (13% recovery) of recovered **2**.

Registry No.—**1a**, 10453-89-1; **1b**, 97-41-6; **1c**, 5617-92-5; **1d**, 22841-81-2; **2**, 22841-82-3; **7b**, 22841-83-4.

Acknowledgment.—We are very grateful to Dr. T. Nishida of the Nippon Electric Varian Ltd. and to Mr. K. Watanabe of JEOL Co. for running nmr spectra and vpc separations.

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

Fragmentation without Rearrangement of the *p*-Fluoro Label in the Mass Spectra of Some Six-Membered Heterocycles

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Scrambling results by the *p*-fluoro-labeling technique are reported for a pentaarylpyridine, a tetraarylpyrazine, and a triaryl-*as*-triazine. There is little or no randomization of the label before each of the major fragmentations of the molecular ions. Such results are discordant with the statistical randomization of molecular ions of six-membered aromatic compounds found by deuterium-labeling studies. The discrepancy could suggest that the valence-isomer formation of six-membered rings postulated previously to occur on electron impact is not the mechanism of randomization; another mechanism, less likely but preserving this previous suggestion, is also proposed.

The degree of hydrogen scrambling before fragmentation of some six-membered aromatic ring compounds in the mass spectrometer is essentially complete, and mechanisms of scrambling have been suggested which resemble the photochemical transformation of benzene into valence tautomers.[2,3] In addition, there is scrambling of hydrogen in decomposing molecular ions of thiophene, but not in those of furan, in the mass spectrometer; the extent of scrambling is a function of the particular decomposition of the molecular ion.[4] These results are each the product of deuterium-labeling studies, and have therefore several explanations: they may indicate rearrangement of the carbon skeleton through intermediates similar to the photochemical intermediates,[2,3] but they might merely indicate that hydrogen atoms migrate about an essentially intact heavy-atom skeleton. Several examples have now been offered in support of the latter mechanism in special cases.[5,6]

We have recently suggested an inexpensive companion method to deuterium replacement of protium, the *p*-fluoro label.[7] In this method, the *p*-fluorophenyl substituent replaces an unsubstituted phenyl substituent; in typical examples the *p*-fluoro substituent

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[1] Fellow of the Alfred P. Sloan Foundation, 1969–1971.

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[5] S. Safe, *Chem. Commun.*, 534 (1969).

[6] M. M. Bursey and T. A. Elwood, *J. Amer. Chem. Soc.*, **91**, 3812 (1969).

[7] M. M. Bursey, R. D. Rieke, T. A. Elwood, and L. R. Dusold, *ibid.*, **90**, 1557 (1968).