Anal. Calcd for $C_{19}H_{23}N_2O_2 \cdot I$: C, 51.92; H, 5.51; N, 6.38. Found: C, 51.68; H, 5.61; N, 6.32.

α,α′-Diphthalimido-o-xylene.—A mixture of 500 g (1.9 mol) of α,α′-dibromo-o-xylene, 1 kg (5.4 mol) of potassium phthalimide, and 3.78 l. of DMF was stirred and refluxed for 16 hr. The mixture was then cooled to approximately 100° and diluted with an equal volume of water. The precipitate was then filtered, washed well with water, ethyl alcohol, and ether, consecutively, and air-dried to give 606 g (81%) of white, fluffy crystals, mp 275° (lit.[15] mp 277°).

α,α′-Diamino-o-xylene Dihydrochloride.—A slurry of 200 g (0.51 mol) of α,α′-diphthalimido-o-xylene was made in 7 l. of 1-butanol. To this was added 48.5 ml (0.98 mol) of 99% hydrazine hydrate and the mixture was stirred and refluxed for 16 hr. With continued stirring and refluxing, 100 ml (1.12 mol) of concentrated HCl was added and reflux was continued for 24 hr. At this time approximately one-half the solvent was evaporated *in vacuo*. The white solid formed was filtered and then triturated with 500 cc of water. The water was stripped *in vacuo* and the residue was triturated with methanol. After filtration the white solid was recrystallized from 4:1 ethanol–water to give 89.5 g (84%) of white crystals, mp >300° (lit.[15] mp >300°).

Preparation of Dihydro-2,4-benzodiazepines.—A solution of 2.0 g (0.015 mol) of α,α′-diamino-o-xylene (prepared from the dihydrochloride by extraction with $CHCl_3$ of a strongly alkaline aqueous solution) in 40 ml of ethyl alcohol was refluxed overnight with 1.8 g (0.015 mol) of ethyl acetimidate hydrochloride. The solution was cooled overnight to give 1.7 g (59%) of **4,5-dihydro-3-methyl-1H-2,4-benzodiazepine hydrochloride** as white crystals, mp 283°.

To a solution of 2.0 g (0.015 mol) of α,α′-diamino-o-xylene in 25 ml of methyl alcohol was added 2.3 g (0.015 mol) of ethyl chloroacetimidate hydrochloride. The solution was allowed to stand overnight. The solution was then added dropwise with stirring to a large excess of ether to give 1.8 g (53%) of 3-chloromethyl-4,5-dihydro-1H-2,4-benzodiazepine hydrochloride, mp 255°.

2,3,4,5-Tetrahydro-1H-2,4-benzodiazepin-3-one (XIX).—To a solution of 6.0 g (0.044 mol) of α,α′-diamino-o-xylene in 150 ml of THF was added 7.5 g (0.046 mol) of N,N′-carbonyldiimidazole in 100 cc of THF dropwise with ice cooling. The solution was then allowed to stand overnight at room temperature. The white solid was filtered to give 6.0 g (84%), mp 300°.

4,5-Dihydro-3-dimethylaminomethyl-1H-2,4-benzodiazepine Dihydrochloride.—The pH of a concentrated aqueous solution of 3-chloromethyl-2,5-dihydro-1H-2,4-benzodiazepine hydrochloride (10.0 g, 0.043 mol) was adjusted to approximately 9. The precipitate was collected on a filter, washed well with water, air-dried, and recrystallized from ethyl acetate to give 4.5 g (54%) of the free base, mp 235–240°.

Anal. Calcd for $C_{10}H_{11}N_2Cl$: C, 61.70; H, 5.70; N, 14.39. Found: C, 61.98; H, 5.76; N, 14.58.

To a saturated solution of dimethylamine in methyl alcohol (15 ml) was added 4.5 g of the chloromethyl free base. The solution was refluxed for 0.5 hr. This was then made acidic with ethanolic hydrogen chloride and the solid formed was recrystallized from ethyl alcohol to give 5.0 g (78%) of white crystals, mp 239–241°.

3-Amino-4,5-dihydro-1H-2,4-benzodiazepine Hydrochloride (XXI).—A slurry of 7.5 g (0.046 mol) of XIX in 30 ml of $POCl_3$ was heated on a water bath for 3 hr. The excess reagent was evaporated *in vacuo* and the solid triturated with ethyl acetate and filtered to give 11.0 g (72%) of XX, mp 215°. This material was added in portions to 200 ml of liquid ammonia. The slurry was stirred while the ammonia was allowed to evaporate naturally at room temperature over a 3-hr period. The remaining solid was slurried in water, made strongly basic with saturated KOH, and extracted with chloroform. The extracts were dried over K_2CO_3 and evaporated to an oil. This was dissolved in ethanol and made acidic with ethanolic hydrogen chloride. The solution was evaporated to give white crystals which were recrystallized from ethanol–methanol to give 5.0 g (76%) of XXI, mp 279–281°.

Acknowledgment.—The authors wish to take this opportunity to thank Mr. Dorfman and all members of this microanalytical and spectral staff for the physical data reported herein.

Studies on Chrysanthemic Acid. I. Some Reactions of the Isobutenyl Group in Chrysanthemic Acid

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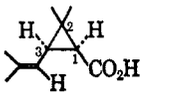
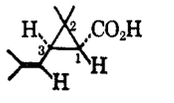
Diphenyloxetane derivatives were prepared by photocycloaddition of *cis*- and *trans*-chrysanthemic acid (**1a** and **1b**) to benzophenone. Oxidation of the *cis* isomer (**1a**) with lead tetraacetate afforded an olefinic γ-lactone (**11**), which was hydrolyzed to the corresponding olefinic hydroxy acid (**12**). The *trans* isomer (**1b**) gave an epoxide (**7**) by oxidation with monoperphthalic acid, while the *cis* isomer did not react at all with this reagent. Amino functions were introduced into the isobutenyl group by applying the Ritter reaction to **1a** and **1b** and by ring opening of **7** with dimethylamine.

A number of ester derivatives of chrysanthemic acid[1] have been reported mainly because of interest in their insecticidal activity.[2] It is known that the isobutenyl group of chrysanthemic acid is rather unreactive toward cycloaddition reactions; **1a** and **1b** give only a trace of pyrazoline esters even with excess amounts of diazomethane[3] and, furthermore, Diels–Alder additions with maleic anhydride or cyclopentadiene and the dichlorocarbene addition thereto are all unsuccessful.[4]

In this paper we describe the results of some reactions carried out successfully on the isobutenyl group of **1a** and **1b**, including the photocycloaddition with benzophenone, oxidations with lead tetraacetate and monoperphthalic acid, and the Ritter reaction.



1a



1b

Results and Discussion

Photocycloaddition.—Irradiation of **1a** with benzophenone in benzene or methanol afforded in low

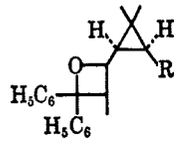
(1) Chrysanthemum monocarboxylic acid, 2,2-dimethyl-3-isobutenylcyclopropane-1-carboxylic acid (the *cis* isomer (**1a**) and the *trans* isomer (**1b**)).

(2) For example, see (a) Y-L. Chen and W. F. Barthel, *J. Am. Chem. Soc.*, **75**, 4287 (1953); (b) W. F. Barthel and B. H. Alexander, *J. Org. Chem.*, **23**, 1012 (1958); (c) W. F. Barthel, U. S. Patent, 2,857,309 (1958); *Chem. Abstr.*, **53**, 8528*d* (1959); (d) T. Mitsui and T. Nagase, *J. Sci. Res. Inst.* (Tokyo), **50**, 76 (1956); *Chem. Abstr.*, **51**, 7639*d* (1957); (e) T. Mitsui, M. Kitahara, and T. Nagase, *J. Sci. Res. Inst.* (*Tokyo*), **50**, 80 (1956); *Chem. Abstr.*, **51**, 7639*e* (1957).

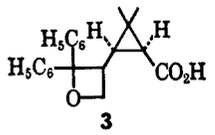
(3) I. G. M. Campbell and S. H. Harper, *J. Chem. Soc.*, 283 (1945).

(4) T. Sasaki, S. Eguchi, and M. Ohno, unpublished observation.

yields a new acid, to which the *cis*-oxetane structure **2a** was assigned on the basis of analytical data and the infrared spectrum which showed the presence of carboxyl (3300–2700 and 1690 cm^{-1}), phenyl (1600, 760 and 710 cm^{-1}), and oxetane (997 cm^{-1}).[5] The isomeric structure **3** was excluded because the nmr spectrum showed a signal at τ 5.03 (1 H, d, J = 9.5 cps), indicating the presence of a hydrogen α to the oxetane ring oxygen.[6] The postulated structure was supported by the generally accepted mechanism for oxetane formation by photocycloaddition.[7] The *cis* relationship of the carboxyl group to the oxetane ring in **2a** was supported also by the nmr spectrum which had a signal at τ 8.20 (1 H, d) assignable to C-1-H. $J_{H_1-H_2}$ (8.5 cps) was in the range of that postulated for the *cis* configuration.[8]



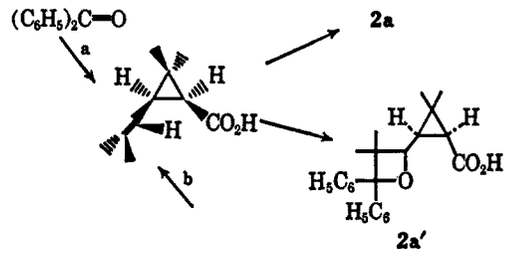
2a, R = CO_2H
b, R = CO_2CH_3
c, R = CH_2OH



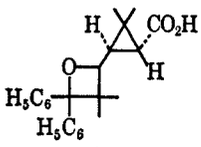
3

The methyl ester **2b** was prepared either by photocycloaddition of methyl chrysanthemate to benzophenone or by direct methylation of **2a**. Reduction of **2b** with lithium aluminum hydride afforded the corresponding oxetane alcohol **2c** of mp 125–126°, the infrared spectrum of which (CCl_4) showed the presence of free hydroxyl (3640 cm^{-1}) and dimeric hydroxyl group (3490 cm^{-1}),[9] indicating the absence of an intramolecular hydrogen bond between the hydroxyl group and oxetane ring oxygen. This fact supported structure **2a** rather than **2a'**, either of which could have been produced depending on the direction of attack side, a or b, by benzophenone on the isobutenyl group (Scheme I).

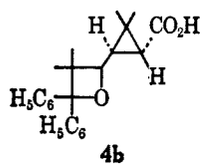
SCHEME I



Irradiation of **1b** under the same condition as that of **1a** furnished **2a** and, because of the unsharp melting point, what appeared to be a mixture of isomeric acids, probably **4a** and **4b**, because of $J_{H_1-H_2}$ (5.0 cps).



4a



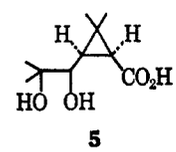
4b

Irradiation of methyl chrysanthemate (a mixture of *cis* and *trans* isomers in a ratio of 4:6) in the presence of benzophenone also afforded a mixture of *cis*- and *trans*-oxetane esters which was separated by chromatography.

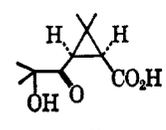
Photosensitized *cis–trans* Isomerization.—The photosensitized *cis–trans* isomerization of cyclopropane derivatives has attracted considerable attention recently.[10] The formation of a *cis*-oxetane acid from **1b** could be explained by assuming photoisomerization of **1b** prior to reaction. To establish this point the photoisomerization of chrysanthemic acid and methyl chrysanthemate was studied in the presence of benzophenone and confirmed at least qualitatively, but no photostationary state could be observed for simultaneous occurrence of side reactions.

Oxidations of 1a and 1b with Monoperphthalic Acid and Lead Tetraacetate.—Oxidation of the isobutenyl group in **1a** and **1b** with potassium permanganate has been reported to afford glycol **5** and hydroxy ketone **6**.[11]

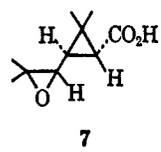
Oxidation of **1b** with monoperphthalic acid afforded an epoxide **7** of mp 145–146°, but **1a** was not oxidized under the same condition. The difference could be explained as follows (**8**): the approach of the reagent to the b side of **1b** might be hindered by the methyl group at C-2, but not from an a side, while in **1a**, both sides will be more or less blocked by the carboxyl at C-1 and the methyl group at C-2.



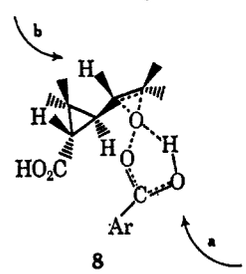
5



6



7



8

Lead tetraacetate oxidation of **1a** in benzene afforded an oil to which, because of infrared bands at

(5) R. N. Jones and C. Sandorfy in "Technique of Organic Chemistry," Vol. IX, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p 436.

(6) D. R. Arnold, R. L. Hirman, and A. H. Glick, *Tetrahedron Letters*, No. 22, 1425 (1964).

(7) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 208.

(8) The coupling constants for *cis* hydrogens in cyclopropane derivatives are known to be larger than those for *trans* hydrogens and the same thing can be said for the values of J_{cis} and J_{trans} of chrysanthemic acid derivatives given: (a) J. D. Graham and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 2249 (1962); (b) D. J. Patel, M. E. H. Howden, and J. D. Roberts, *ibid.*, **85**, 3218 (1963); (c) U. Schöllkopf, G. L. Lehman, J. Paust, and H. D. Härtl, *Chem. Ber.*, **97**, 1527 (1964); (d) T. Shono, T. Morikawa, A. Oku, and R. Oda, *Tetrahedron Letters*, No. 14, 791 (1964).

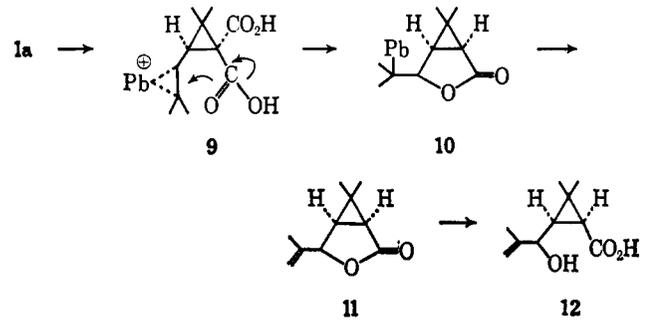
(9) Reference 5, p 417.

(10) (a) W. von E. Doering and M. Jones, Jr., *Tetrahedron Letters*, No. 12, 791 (1963); (b) G. W. Griffin, E. J. O'Connel, and H. A. Hammond, *J. Am. Chem. Soc.*, **85**, 1001 (1963); (c) W. G. Brown and J. F. Neumer, *Tetrahedron*, **22**, 473 (1966).

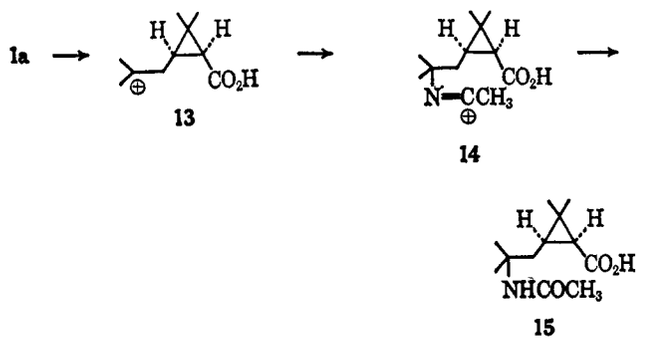
(11) (a) M. Matsui, K. Yamashita, and M. Miyano, *Bull. Agr. Chem. Soc. Japan*, **20**, 89 (1956); (b) M. Matsui and H. Yoshioka, *Agr. Biol. Chem.* (Tokyo), **28**, 32 (1964).

1760 (γ-lactone), 1650 and 899 (C=CH_2) cm^{-1}, structure **11** was assigned. This assignment was confirmed by hydrolysis of **11** to crystalline **12** which had infrared bands at 3400 (OH), 3200–2500 and 1710 (CO_2H), 1640 and 904 (C=CH_2) cm^{-1} and nmr signals at τ 3.53 (2 H, s, OH and CO_2H), 5.00 and 5.15 (2 H, each s, C=CH_2), 5.55 (1 H, d, J = 9.5 cps, O–C–H), 8.16 (3 H, s, C=C–CH_3), 8.34 (1 H, d, J = 9.0 cps, C-1-H), 8.63 (1 H, t, J = 9.0 cps, C-3-H), 8.71 and 8.78 (6 H, s, *gem*-dimethyls at C-2).

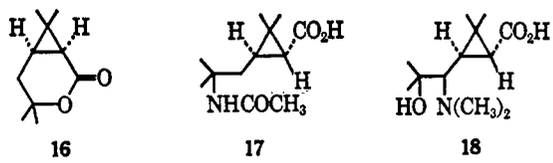
The formation of **11** from **1a** could be explained in the manner postulated from the oxidation of norbornenecarboxylic acid with lead tetraacetate,[12] differing only in the formation of an olefin instead of an acetate during the last step.



Some Amino Derivatives of 1a and 1b.—The Ritter reaction[13] of **1a**, treatment of **1a** with acetonitrile in an acidic medium, afforded an acetylamino derivative **15**, the structure of which was confirmed by analytical and spectral data.



The facile formation of the δ-lactone[14] **16** from **1a** indicates that the tertiary carbonium ion **13** seems to be stable enough to produce an immonium intermediate **14** which could be hydrolyzed to **15**. The Ritter reaction of **1b** with acetonitrile under similar conditions afforded the corresponding acetylamino derivative **17**.



On the other hand, epoxide **7** was heated with dimethylamine at 125° for 16 hr to give the corresponding dimethylamino derivative **18**, in which the direction of the epoxide ring opening was determined by the presence of a signal at τ 7.20 (1 H, d, J = 10.0 cps) in the nmr spectrum.

Experimental Section[15]

Photocycloaddition of Chrysanthemic Acids.—A solution of 0.84 g (5.0 mmoles) of **1a** and 0.90 g (5.0 mmoles) of benzophenone in 200 ml of benzene was irradiated at room temperature under nitrogen stream with a 100-w high-pressure mercury lamp (UM-102, Ushio Denki Co., Tokyo, Japan), using a cylindrical quartz jacket which was cooled by a water stream. Irradiation was continued for 8 hr, until benzophenone disappeared upon thin layer chromatography (Kieselgel G, Merck). The reaction mixture was extracted ten times with 5% aqueous sodium hydroxide in 10-ml portions and the combined alkaline extracts were neutralized with hydrochloric acid (1:1). The separated oil was extracted twice with 20-ml portions of ether and the combined extracts were concentrated to give a sticky residue which was treated with methanol to afford white solids. Three recrystallizations from aqueous acetone gave 100 mg (5.8%) of **2a** as colorless plates: mp 250–251° dec; ν_{max}^{KBr} 3200–2400, 1690, 1600, 997, 760, and 710 cm^{-1}; nmr (CD_3SOCD_3) τ 2.25–2.75 (10 H, c, phenyl protons), 5.03 (1 H, t, J = 9.0 cps, –C–C–O–C–H), 8.20 (1 H, d, J = 8.5 cps, C-1-H), 8.56 (1 H, t, J = 9.0 cps, C-3-H), 8.82, 8.84, and 8.95 (12 H, *gem*-dimethyls at C-2 and oxetane ring).

Anal. Calcd for $C_{23}H_{26}O_3$: C, 78.82; H, 7.48. Found: C, 78.39; H, 7.61.

The yield of **2a** was raised to 11.6% by using twice as much benzophenone as **1a**, methanol as a solvent, and a shorter irradiation time (1.5 hr).

The brownish oil which was obtained by acidification of the alkaline extract from the irradiated mixture of 0.84 g of **1b** and 0.90 g of benzophenone in 200 ml of benzene afforded white solids from aqueous acetone, from which plates (87 mg, 5.0%) of mp 249–251° dec and prisms (52 mg, 3.0%) of mp 178–185° were obtained by fractional recrystallization from aqueous acetone. The former crystals were identified with **2a** by no depression of the mixture melting points, the same R_f values on thin layer chromatography, and the superimposition of the infrared spectrum with those of **2a**. The latter crystals were the *trans*-oxetane acid: ν_{max}^{KBr} 3200–2500, 1690, 1600, 995, 770, 755, and 710 cm^{-1}, nmr ($CDCl_3$) τ 2.24–2.78 (10 H, c, phenyl protons), 5.03 (1 H, d, J = 8.5 cps, –C–C–O–C–H), 8.28 (1 H, d, J = 5.0 cps, C-1-H), 8.52 (C-3-H, superimposed with a signal at τ 8.60), 8.60, 8.81, and 8.95 (12 H, *gem*-dimethyls at C-2 and oxetane ring).

Anal. Calcd for $C_{23}H_{26}O_3$: C, 78.82; H, 7.48. Found: C, 78.86; H, 7.34.

In every run examined, the formation of benzpinacol produced by photoreduction of benzophenone was observed expectedly.

Photocycloaddition of Methyl Chrysanthemate.—After removal of the solvent from the irradiated mixture of 1.82 g (10.0 mmoles) of methyl chrysanthemate (a mixture of *cis* and *trans* isomer in a ratio of 4:6) and 1.82 g (10.0 mmoles) of benzophenone in 200 ml of benzene, the oily residue was dissolved in benzene and chromatographed on 80 g of silica gel (Kieselgel, Merck). The first fractions eluted with benzene gave 210 mg (5.7%) of benzpinacol, besides 0.756 g (41.5% recovery) of crude methyl chrysanthemate. The second fractions afforded 285 mg (7.7%) and **2b**: mp 112–113° (from *n*-hexane); ν_{max}^{KBr} 1720, 1600, 995, 750, and 710 cm^{-1}; nmr

(12) R. M. Moriarty, H. G. Walsh, and H. G. Gopal, *Tetrahedron Letters*, No. 36, 4363 (1966), and references cited there.

(13) (a) J. Ritter and P. Minieri, *J. Am. Chem. Soc.*, **70**, 4045 (1948); (b) J. Ritter and J. Kalish, *ibid.*, **70**, 4048 (1948); (c) F. Benson and J. Ritter, *ibid.*, **71**, 4128 (1949); (d) L. Hartzel and J. Ritter, *ibid.*, **71**, 4130 (1949); (e) R. Lusskin and J. Ritter, *ibid.*, **72**, 5577 (1950).

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

(15) All melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. Microanalyses were carried out on a Yanagimoto C.H.N. Corder, Model MT-1. The infrared spectra were recorded on a JASCO Model IR-S infrared spectrophotometer and nmr spectra were obtained with a Hitachi high-resolution nmr spectrometer, Model H-6013, at 60 Mc. Unless otherwise specified, nmr data are reported in τ values relative to tetramethylsilane as the internal standard, and broad or complex signals in the aromatic region are reported as a range, designated as c, singlet as s, doublet as d, triplet as t, quartet as q, and multiplet as m.

($CDCl_3$) τ 2.21–2.72 (10 H, c, phenyl protons), 4.98 (1 H, d, J = 9.0 cps, $-\overset{|}{C}-\overset{|}{C}-O-\overset{|}{C}-H$), 6.17 (3 H, s, CO_2CH_3), 8.17 (1 H, d, J = 8.5 cps, C-1-H), 8.52 (1 H, t, J = 9.0 cps, C-3-H), 8.79 and 8.92 (12 H, s, *gem*-dimethyls at C-2 and oxetane ring).

Anal. Calcd for $C_{24}H_{28}O_3$: C, 79.09; H, 7.74. Found: C, 79.40; H, 7.70.

The same ester was obtained in 67% yield by methylation of **2a** by the general procedure with diazomethane in ether.

The third fractions amounted to 777 mg (21.3%) as an oily material, ν_{max}^{KBr} 1730 (ester C=O), 1600, 765, 750, and 710 (phenyl) and 995 (oxetane ring) cm^{-1}. A portion of this oil was hydrolyzed by warming at 70–80° in 0.8 *N* methanolic sodium hydroxide for 5 hr to give prisms of mp 180–190° (from aqueous acetone); its melting point and infrared spectrum were very close to those of *trans*-oxetane acid.

Anal. Calcd for $C_{23}H_{26}O_3$: C, 78.82; H, 7.48. Found: C, 78.20; H, 7.46.

The fractions eluted with chloroform afforded 0.55 g of an oil which was unidentified.

Oxetane Alcohol 2c.—To a mixture of 600 mg (15.8 mmoles) of lithium aluminum hydride in 15 ml of dry ether was added a solution of 110 mg (0.302 mmole) of **2b** in 10 ml of dry ether at room temperature with stirring and stirring was continued for 1 hr. After decomposition of excess reagent by adding water under cooling, the ether layer was washed with 20% aqueous sodium hydroxide and water, dried over Na_2SO_4, and concentrated to dryness to give crude crystals of **2c**, which was recrystallized from chloroform–light petroleum (bp 40–60°) to afford 31 mg (30.3%) of colorless prisms: mp 125–126°; $\nu_{max}^{CCl_4}$ 3640, 3490, 1600, 1495, 990, and 710 cm^{-1}.

Anal. Calcd for $C_{23}H_{28}O_2$: C, 82.10; H, 8.39. Found: C, 81.85; H, 8.35.

Photosensitized *cis–trans* Isomerization.—In the course of the photocycloaddition of **1a** and **1b** to benzophenone, the reaction mixture was examined with thin layer chromatography (Kieselgel G, 5% methanol–benzene, and I_2) and the formation of the corresponding isomers was observed clearly at R_f 0.22 (**1a**) and R_f 0.16 (**1b**) after irradiation for 1.5 hr.

An equimolar solution of methyl chrysanthemate (pure *trans* isomer) and benzophenone in CCl_4 was irradiated and at an appropriate time interval the aliquot was directly taken into a 0.1-mm solution cell in order to take the infrared spectrum. For the measurement of *cis–trans* conversion the bands used were at 1365 (characteristic of the *trans* isomer) and 1085 (characteristic of the *cis* isomer) cm^{-1}. Irradiation for 1 hr afforded a mixture of 15% of *cis* and 85% of *trans* isomers. A dark brown color appeared gradually and the infrared spectrum after 3 hr of irradiation showed a very complex spectrum, indicating side reactions had occurred simultaneously.

Oxidation of 1b with Monoperphthalic Acid.—A solution of 0.84 g (5.0 mmoles) of **1b** and monoperphthalic acid (5.0 mmolar equiv)[16] in 50 ml of ether was refluxed for 5 hr. The solvent was removed *in vacuo* to afford white solids, from which the chloroform-soluble portion was extracted. The extract was concentrated to dryness and the residue was recrystallized from benzene to give needles of **7**, 0.20 g (21.3%): mp 145–146°; ν_{max}^{KBr} 3300–2600, 1715, 1230, and 810 cm^{-1}; nmr ($CDCl_3$) τ 7.50 (1 H, d, J = 8.0 cps, $-\overset{|}{C}-O-\overset{|}{C}-H$), 8.46 (1 H, d, J = 5.8 cps, C-1-H), 8.66–8.72 (13 H, C-3-H and *gem*-dimethyls at C-2 and epoxide ring).

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.12; H, 8.75. Found: C, 65.19; H, 8.75.

(16) D. Swern, *Org. Reactions*, **7**, 392 (1953).

Oxidation of 1a with Lead Tetraacetate.—A mixture of 1.68 g (10.0 mmoles) of **1a** and 6.65 g (15.0 mmoles) of lead tetraacetate (a commercial sample was dried *in vacuo* before use) in 50 ml of dry benzene was refluxed for 20 hr. The cooled mixture was washed with water several times, dried over Na_2SO_4, and evaporated *in vacuo* to give an oily residue (2.0 g), which was dissolved in benzene and chromatographed on silica gel (60 g). The fractions eluted with 50% chloroform–benzene afforded 0.478 g of **11** as an oil which had infrared bands at 1760 (γ-lactone) and 1650 and 899 ($C=CH_2$) cm^{-1}. All of this oil was hydrolyzed by stirring with 5% aqueous sodium hydroxide at room temperature to give 120 mg (25%) of **12** as colorless needles, mp 101–102° (from acetone–light petroleum (bp 40–60°)).

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.13; H, 8.82.

From the fractions eluted with chloroform 0.43 g of crude **1a** was recovered.

Ritter Reaction of 1a and 1b with Acetonitrile.—A mixture of 0.41 g (2.5 mmoles) of **1a**, 5.0 ml of acetonitrile, 5.0 ml of glacial acetic acid, and 0.1 ml of concentrated sulfuric acid was stirred at room temperature for 20 hr. The mixture was poured into an ice–water mixture and extracted four times with 20-ml portions of chloroform. The combined extracts were washed with water, dried over Na_2SO_4, and evaporated to dryness to give a sticky residue which was treated with a small amount of water and kept in a refrigerator for a week. The solid mass was crystallized from benzene–*n*-hexane mixture to give 105 mg (18.5%) of **15** as fine needles: mp 153–154°; ν_{max}^{KBr} 3280, 3300–2400, 1687, 1650, and 1558 cm^{-1}; nmr ($CDCl_3$) τ −0.84 (1 H, s, CO_2H), 4.12 (1 H, s, NH), 7.91–8.04 (5 H, CH_2 and $NCOCH_3$), 8.46 (1 H, d, J = 9.0 cps, C-1-H), 8.63 and 8.80 (13 H, C-3-H, *gem*-dimethyls at C-2 and α-C of NH).

Anal. Calcd for $C_{12}H_{21}O_3N$: C, 63.41; H, 9.31; N, 6.16. Found: C, 62.86; H, 9.48; N, 6.37.

Similarly, 0.41 g (2.5 mmoles) of **1b** was treated with acetonitrile and the worked-up product amounted to 0.387 g as an oil which exhibited infrared bands at 3300, 1690, 1650, and 1550 cm^{-1}. A portion of this oil was treated with S-benzylthiuronium chloride in alkaline aqueous ethanol to give a white solid which was recrystallized from aqueous dioxane and aqueous ethanol to give prisms of mp 165–167°; ν_{max}^{KBr} 3300–2400, 3300 (shoulder), 1645, 1572, and 1550 cm^{-1}.

Anal. Calcd for $C_{20}H_{31}O_3N_3S$: C, 61.05; H, 7.94; N, 10.68. Found: C, 60.87; H, 7.71; N, 10.55.

Ring-Opening Reaction of 7 with Dimethylamine.—A mixture of 0.37 g (2.0 mmoles) of **7** and 3.0 ml of dimethylamine (30% aqueous solution) was heated for 16 hr at 125° in a sealed tube. After cooling, the mixture was washed with ether. The aqueous layer was concentrated to dryness to give crude crystals of **18** which were recrystallized from methanol as plates (hygroscopic): mp 181–182°; ν_{max}^{KBr} 3600–2400 (broad), 1625, and 1580 cm^{-1}; nmr (D_2O)[17] τ 7.20 (1 H, d, J = 10.0 cps, N–C–H), 7.22 (6 H, s, $N(CH_3)_2$), 8.42 (1 H, d, J = 6.0 cps, C-1-H), 8.69–8.96 (13 H, C-3-H, *gem*-dimethyls at C-2 and α-C of OH).

Anal. Calcd for $C_{12}H_{23}O_3N\cdot H_2O$: C, 58.27; H, 10.19; N, 5.66. Found: C, 58.16; H, 10.31; N, 5.83.

Registry No.—**1a**, 15259-78-6; **1b**, 15259-79-7; **2a**, 15266-74-7; **2b**, 15266-75-8; **2c**, 15314-06-4; **4a**, 15259-84-4; **7**, 15266-76-9; **11**, 15266-77-0; **12**, 15259-80-0; **15**, 15259-81-1; **17** S-benzylthiuronium salt, 15259-82-2; **18**, 15259-83-3.

(17) Acetone was used as an internal reference.