mura, S. Sato, and Y. Kishida, *Tetrahedron Lett.*, 2739 (1968).
(19) C. Weygand, E. Bauer, and H. Hennig, *Ber.*, **62**, 562 (1929).
(20) C. L. Bickel and R. Morris, *J. Amer. Chem. Soc.*, **73**, 1786 (1951).
(21) R. D. Abell, *J. Chem. Soc.*, **79**, 928 (1901).
(22) E. E. Royals and K. C. Brannock, *J. Amer. Chem. Soc.*, **75**, 2050 (1953); **76**, 3041 (1954).
(23) D. L. Storm and T. A. Spencer, *Tetrahedron Lett.*, 1865 (1967).
(24) K. v. Auwers, *Justus Liebigs Ann. Chem.*, **415**, 169 (1918).
(25) Melting point determinations were done with sealed capillaries in an oil bath preheated to 120°.
(26) T. Morel and P. E. Verkade, *Recl. Trav. Chim. Pays-Bas*, **70**, 35 (1951).
(27) H. Wynberg, *J. Amer. Chem. Soc.*, **80**, 364 (1958).
(28) A. W. Johnson, *J. Chem. Soc.*, 895 (1946).

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# Baeyer–Villiger Oxidation of $\Delta^{1(9)}$-Octalone-2 and $\Delta^{1(8)}$-Indanone-2[1]

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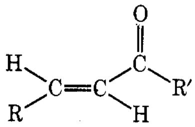
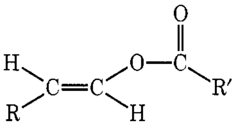
The reactions of $\Delta^{1(9)}$-octalone-2 and $\Delta^{1(8)}$-indanone-2 with trifluoroperacetic acid and *m*-chloroperbenzoic acid have been investigated under a variety of reaction conditions. The reaction conditions which were varied included temperature, reaction time, acidity, and equivalents of oxidizing agent used. Product distributions are reported. Oxidations using trifluoroperacetic acid gave complex product mixtures which resulted from reactions of the initially formed products with more trifluoroperacetic acid or with the trifluoroacetic acid which was produced during the reaction. Varying the above-mentioned variables did not greatly simplify the problem. Oxidation reactions using *m*-chloroperbenzoic acid gave the simplest product mixtures; *e.g.*, $\Delta^{1(9)}$-octalone-2 gave exclusively an epimeric mixture of epoxy lactones when 2 equiv of the peracid was used.

The outcome of the Baeyer–Villiger oxidation of $\alpha,\beta$-unsaturated ketones, given by the general formula **1**, seems to be highly dependent upon the nature of the ketone and the reaction conditions used.[2] The primary oxidation products, enol esters (**2**) and epoxy ketones (**4**), are rarely isolated. In general the major product is the epoxy ester (**3**), which is no doubt derived from the enol ester (**2**).[3]



**1**



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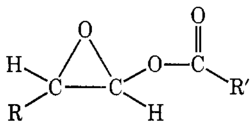

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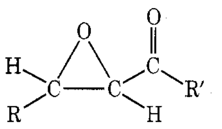
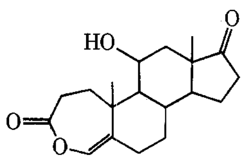
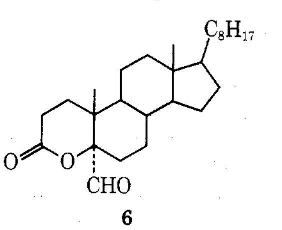


**4**

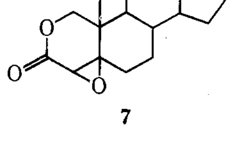
Several $\Delta^4$-3-keto steroids have been subjected to Baeyer–Villiger oxidation reactions. The reaction of perbenzoic acid with 11$\beta$-hydroxyandrost-4-ene-3,17-dione in the presence of anhydrous perchloric acid in chloroform gave a 60% yield of the enol lactone **5**.[4] In contrast to this, oxidation of cholest-4-en-3-one with trifluoroperacetic acid (TFPAA) gave what was reported as a good yield of **6**.[5] It has been shown that the aldehyde lactone **6** resulted from the acid-catalyzed rearrangement of an intermediate epoxy lactone.[6] This has been confirmed by the oxidation of testosterone acetate with perbenzoic acid, in which all of the intermediates were isolated and characterized.[7]



**5**



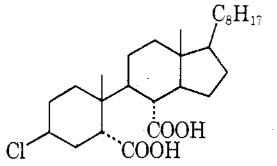
**6**



**7**

Although hydrogen peroxide oxidation of $\alpha,\beta$-unsaturated ketones usually leads to the formation of epoxy ketones, it has been found that in the presence of a catalytic amount of selenium dioxide $\Delta^4$-3-keto steroids are converted into enol lactones.[8]

The alkaline hydrogen peroxide oxidation of *A*-nortestosterone leads to the formation of **7**, presumably *via* the epoxy ketone which is subsequently converted to **7**.[9] The oxidation of 3$\beta$-chlorocholest-5-en-7-one with TFPAA gave **8**.[10]

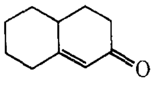


**8**

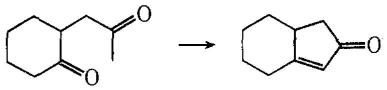
In contrast to the data available concerning the above, very few data are available which deal with the Baeyer–Villiger oxidation of simple $\alpha,\beta$-unsaturated ketones. Oxidation of 2-cyclohexenone with TFPAA yielded a small amount of 2-hydroxyadipic acid.[11] Reaction of 3-phenyl-2-cyclopentenone with perbenzoic acid gave 4-oxo-4-phenylbutanoic acid.[12]

In view of the lack of information available on the Baeyer–Villiger oxidation of simple $\alpha,\beta$-unsaturated cyclic ketones, and, in view of the fact that in most instances a rather complex mixture of products was obtained, this work was carried out to develop processes which would give good yields of intermediates such as **13**, **20**, **21**, and **24** (see Scheme I). In our case these intermediates were always isolated as stereoisomeric pairs. An attempt was made to correlate product distributions with the reaction conditions employed. Also, the use of "buffered" oxidation reaction conditions (TFPAA and disodium hydrogen phosphate) in the oxidation of $\alpha,\beta$-unsaturated ketones seems not to have been thoroughly studied. Since it appears that the presence of the trifluoroacetic acid, produced during reactions using TFPAA, may be responsible for the formation of complex reaction product mixtures, the use of *m*-chloroperbenzoic acid (CPBA) could lead to more of the primary oxidation products since the *m*-chlorobenzoic acid which is formed during the reaction is a weaker acid than trifluoroacetic acid, and would probably lead to fewer side reactions.

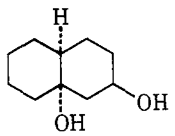
Two $\alpha,\beta$-unsaturated ketones were used in this study. $\Delta^{1(9)}$-Octalone-2 (**9**) was prepared following the procedure of Stork.[13] Details pertaining to the purification of **9** may be found in the Experimental Section. $\Delta^{1(8)}$-Indanone-2 (**11**) was formed by the intramolecular Aldol condensation of the $\gamma$-diketone **10**,[14] which was made from cyclohexanone morpholine enamine and bromoacetone.[15]



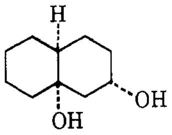
**9**



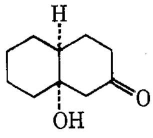
The expected primary oxidation products for the peracid oxidation of **9** were the epoxy ketones **12a** and **12b** and the enol lactone **13** (see Scheme I). An authentic sample of **12a** was readily prepared by the alkaline hydrogen peroxide epoxidation at 20° of the $\alpha,\beta$-unsaturated ketone **9**, which produced a single isomer. The stereochemistry of the product was determined by reduction of the epoxy ketone with lithium aluminum hydride to a mixture of diols **14a** and **14b**. The known diol[16] **14a** was isolated in 33% yield. The diol **14a** was oxidized to the known hydroxy ketone **15**.[16] The material remaining after the isolation of **14a** also gave **15** upon oxidation, lending credence to the fact that reduction of **12a** produced both **14a** and **14b**.



**14a**



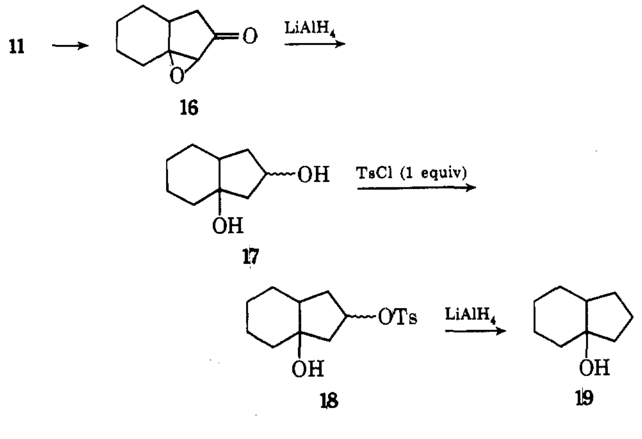
**14b**



**15**

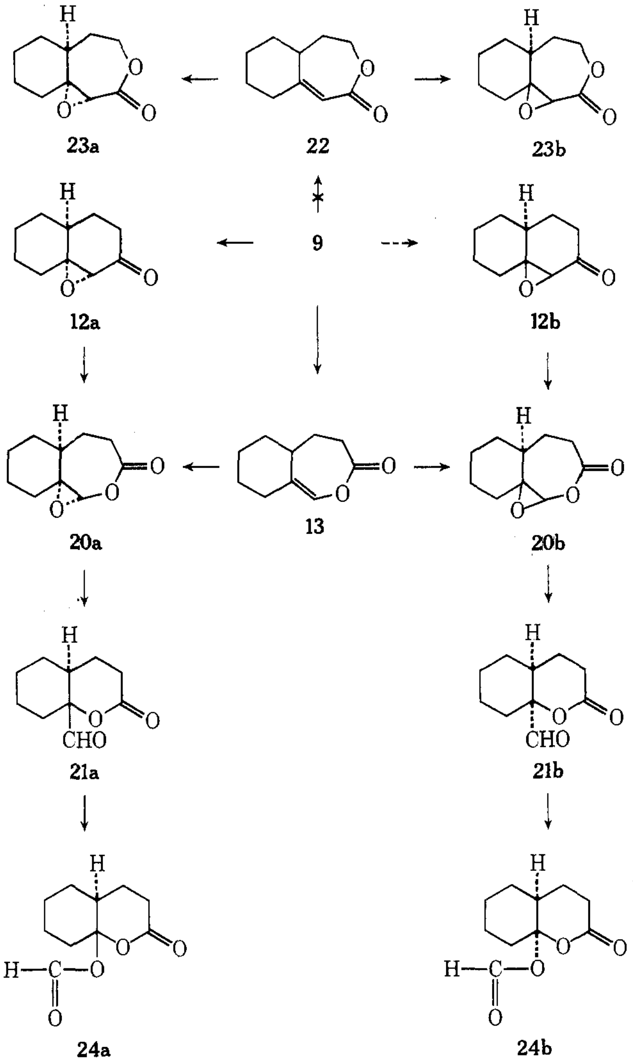
Alkaline hydrogen peroxide oxidation of **9** at 40° resulted in a 9:1 mixture of **12a** and **12b**. The cis:trans ratio was determined from the nmr integral of the oxirane ring proton ($\delta$ 2.98 for **12a** and 3.12 for **12b**).

The epoxy ketone **16** was synthesized by the procedure used for the preparation of **12a** and the stereochemistry of **16** was determined by conversion to the known[17] *cis*-3a-indanol (**19**).



**Scheme I**

**The Baeyer-Villiger Oxidation of $\Delta^{1(9)}$-Octalone-2 (9)**



Compounds **9** and **11** were oxidized using both 85% CPBA and TFPAA. The reactions were run under various reaction conditions. The variables were temperature, equivalents of oxidizing reagent, reaction times, and, in those cases where TFPAA was used, the presence or absence of disodium hydrogen phosphate. In certain instances, all of the oxidizing reagent was added at one time and in other reactions it was added intermittently. The results and exact experimental conditions employed are indicated in Table I for the oxidation of **9** and Table II for the oxidation of **11**. The product distributions were determined from the nmr spectra of the crude reaction products by measuring the relative areas of signals which were characteristic of the molecules present. Scheme I summarizes the results of the Baeyer-Villiger oxidation of **9**. The relationship indicated by the dashed arrow is only suppositional while those indicated by solid arrows have been observed.

The isolation and characterization of the various intermediates and products in the oxidation of **9** was accomplished as follows. The components of the crude product mixture were separated by elution chromatography. Since an authentic sample of **12a** had already been prepared (*vide supra*), it was readily identified as one of the products. The epoxy ketone **12a** was present only when **9** was treated with 1 equiv of CPBA. For reactions using TFPAA as the oxidizing agent, **12a** was not observed to be present, indicating that **12a** either did not form or it reacted

**Table I**
**The Effect of Type and Amount of Oxidizing Reagent, Reaction Time, Temperature, and Acidity on Product Distributions from the Baeyer–Villiger Oxidation of $\Delta^{1(9)}$-Octalone-2 (9)**

| | | | | | | Product composition, % | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Expt | Oxidation reagent | Buffered[a] | Temp, °C | Equiv of oxid reagent used | Reaction time, hr | 9 | 12a | 13 | 20a | 20b | 21a | 21b | 24 |
| 1a | TFPAA | + | −6 | 1 | 24 | 77 | | 16 | 5 | | | 2 | |
| 1b | TFPAA | + | −6 | 2[c] | 48 | 54 | | 20 | 18 | | 1 | 7 | |
| 1c | TFPAA | + | −6 | 3[c] | 72 | 35 | | 16 | 29 | | 8 | 12 | |
| 2a | TFPAA | + | 10 | 1 | 24 | 59 | | 11 | 19 | | 4 | 7 | |
| 2b | TFPAA | + | 10 | 2[c] | 48 | 18 | | 6 | 24 | | 20 | 14 | 18 |
| 2c | TFPAA | + | 10 | 3[c] | 72 | | | | 24 | | | 10 | 66 |
| 3a | TFPAA | + | 25 | 1 | 24 | 52 | | 14 | 16 | | 1 | 13 | 4 |
| 3b | TFPAA | + | 25 | 2[c] | 48 | 15 | | 6 | 4 | | 38 | 26 | 11 |
| 3c | TFPAA | + | 25 | 3[c] | 72 | | | | | | 41 | 29 | 30 |
| 4 | TFPAA | + | 10 | 3[b] | 90 | 29 | *d* | 22 | 37 | | 3 | 5 | 4 |
| 5a | TFPAA | − | 10 | 1 | 24 | 58 | | 11 | | | 19 | 11 | 1 |
| 5b | TFPAA | − | 10 | 2[c] | 48 | 17 | | | | | 44 | 29 | 10 |
| 5c | TFPAA | − | 10 | 3[c] | 72 | | | | | | 42 | 18 | 40 |
| 6 | CPBA | − | −7 | 1 | 24 | 30 | 2 | 36 | 16 | 16 | | | |
| 7 | CPBA | − | 25 | 1 | 24 | 38 | 17 | 7 | 20 | 18 | | | |
| 8 | CPBA | − | 25 | 2 | 24 | | | | 52 | 48 | | | |

[a] + means buffered, − means unbuffered. [b] All of the oxidizing agent was added at one time. [c] One equivalent of the oxidizing agent was added every 24 hr. [d] Trace amounts of **12a** were probably formed, since **12a** was subsequently detected during chromatography (see Experimental Section).

**Table II**
**The Effect of Type and Amount of Oxidizing Reagent, Reaction Time, Temperature, and Acidity on Product Distributions from the Baeyer–Villiger Oxidation of $\Delta^{1(8)}$-Indanone-2 (11)**

| | | | | | | Product composition, % | | | |
|---|---|---|---|---|---|---|---|---|---|
| Expt | Oxidation reagent | Temp, °C | Equiv of oxid reagent used | Reaction time, hr | Buffered | 11 | 30 | 31 | 32 |
| 9 | TFPAA | 10 | 3[a] | 90 | + | 64 | 36 | | |
| 10 | TFPAA | 25 | 1 | 24 | + | 70 | 9 | 20 | 1 |
| 11 | CPBA | 25 | 1 | 24 | − | 84 | 16 | | |
| 12 | CPBA | 25 | 2[a] | 24 | − | 57 | 43 | | |

[a] All of the oxidizing agent was added at one time.

rapidly under the reaction conditions. The trans epoxy ketone **12b** was never detected in any of the product mixtures, indicating that it did not form or that its rate of reaction with acid exceeded its rate of formation.

A second product was identified as having structure **13** on the basis of the following spectral data: ir $\nu_{C=O}$ 1758, $\nu_{C=C}$ 1662 cm$^{-1}$; nmr $\delta$ 6.00 (s, 1, vinyl H). Had oxygen insertion occurred on the other side of the carbonyl group leading to the formation of **22** the ir absorptions would have been at a longer wavelength. Furthermore, as shown by several examples cited earlier, **13** is entirely consistent with the normal mode of the peracid oxidations of $\alpha,\beta$-unsaturated ketones.

The epoxy lactone **20a** was prepared by the oxidation of **12a** with CPBA. The nmr spectrum of the product of this oxidation was inconsistent with **23a**. The chemical shift of the oxirane ring proton in **23a** would probably have a value close to that of the oxirane ring proton in **12a**, *i.e.*, $\delta$ 2.98. Additionally, the chemical shift of the methylene protons adjacent to the ether type oxygen should have a value of $\delta$ 3.5–4.0. In actuality none of the signals expected for **23a** are observed. On the contrary, the signal at $\delta$ 4.88 is in good agreement with what is expected for the oxirane ring proton in the epoxy lactone **21a**. The possibility that the trans epoxy lactone **20b** might be formed from **12a** can be eliminated since the stereochemistry of the ring fusion is rigid and not directly involved in the reaction. The epoxy lactone **20a** was observed in product mixtures involving the use of CPBA as the oxidizing agent and also in product mixtures where TFPAA buffered with disodium hydrogen phosphate was used. The epoxy lactone **20a** was not observed in product mixtures where unbuffered TFPAA was used, suggesting that **20a** is unstable under acidic conditions. That **20a** undergoes an acid-catalyzed rearrangement was established (*vide infra*).

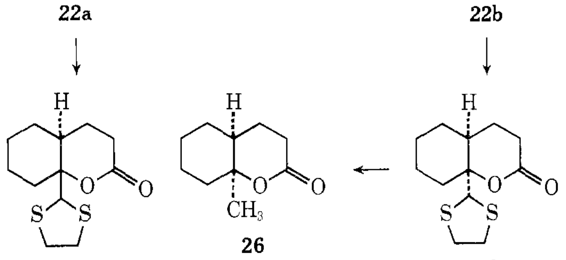
When **13** was treated with 1 equiv of CPBA, equal amounts of **20a** and **20b** were formed. The epoxy lactone **20b** was assigned the trans ring juncture on the basis of its synthesis and because it had spectral properties very similar to those of the cis isomer **20a**. Compound **20b** was only observed in reaction mixtures in which **9** had been oxidized with CPBA.

Also, oxidations employing TFPAA yielded products which showed absorptions in the nmr spectrum at $\delta$ 9.6 and 9.8. This suggests that the products contain aldehydic protons. By analogy with the already established acid-catalyzed rearrangement for a steroidal system containing a similar functionality,[7] the rearrangement of **20a** and **20b** yields **21a** and **21b**. Evidence supporting this rearrangement was obtained by treatment of **20a** with a catalytic amount of *p*-toluenesulfonic acid which gave a single product (**21a**) having an nmr signal at $\delta$ 9.8. Consistent with this structure are selected spectral data: ir $\nu_{CH}$ (aldehydic) 2730, $\nu_{C=O}$ (aldehyde and lactone) 1746 cm$^{-1}$. Additionally, the elemental analysis was consistent with the empirical formula $C_{10}H_{14}O_3$.

Treatment of a 50:50 mixture of **20a** and **20b** with a catalytic amount of *p*-toluenesulfonic acid resulted in a 50:50 mixture of **21a** and **21b**. These data along with the previously established stereospecific rearrangement of the cis isomer **20a** suggest that **20b** undergoes a stereospecific rearrangement to yield **21b**.

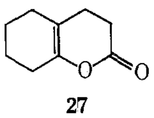
A fifth product (isomeric pair) was detected in product mixtures which resulted when **9** was oxidized with TFPAA. These products were assigned structures **24a** and **24b** on the basis of their nmr spectrum, which showed singlets at δ 8.24 and 8.39 which are attributable to the formate protons. Also, a mixture of **24a** and **24b** could be prepared by TFPAA or CPBA oxidation of a mixture of **21a** and **21b**.

The stereochemistry of **21a** and **21b** was established in the following manner. A mixture of two dithioacetals was obtained upon treatment of a 1:1 mixture of **21a** and **21b** with 1,2-ethanedithiol. The nmr chemical shifts of the methinyl protons (originally the aldehydic protons) of the 1,3-dithiolane rings of the mixture of dithioacetals were at δ 4.7 and 4.9. The dithioacetal **25b** (nmr signal at δ 4.9, *vide infra*) was prepared in pure form by treating the mixture of aldehyde lactones **21a** and **21b** with 1,2-ethanedithiol for a short period of time and then washing the crude product mixture with aqueous $Na_2CO_3$. The stereochemistry of **25b** was determined by its conversion to the known lactone **26**.[18] In order to determine which aldehyde lactone was derived from **20a** and which one from **20b**, the aldehyde lactone **21a**, prepared from **20a**, was converted into the corresponding dithioacetal **25a** and it indeed gave an nmr signal at δ 4.7. The data imply that the stereochemical relationships are those shown in Scheme I. The mechanism for these rearrangements is analogous to that reported for the rearrangement of the epoxy lactone derived from $\Delta^4$-cholesten-3-one.[6]



25a 26 25b

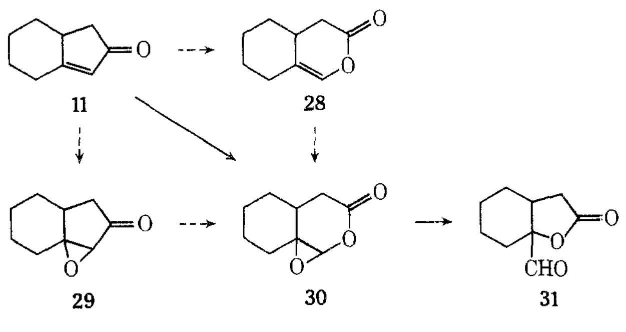
Finally, in certain reactions involving oxidation with TFPAA, minor amounts of **27** were isolated. The enol lactone **27** could not be detected by nmr in the product mixtures because it does not give rise to a characteristic nmr absorption. However, it could be isolated by careful chromatography of the reaction products (see Experimental Section).



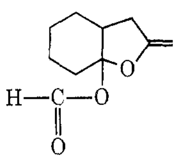
27

Scheme II outlines the results of the Baeyer-Villiger oxidation of $\Delta^{1(8)}$-indanone-2 (**11**). Oxidation of **11** was not investigated to the same extent as was the oxidation of **9**. The structural assignments were based on analogy with the products obtained from the oxidation of **9**. The primary oxidation products **28** and **29** were not detected in any of the product mixtures, although one or both of them are undoubtedly formed as intermediates in the pathway to the epoxy lactone **30**, which is observed in buffered oxidations using TFPAA as well as in oxidations using CPBA. The aldehyde lactone **31** is observed only for oxidations with unbuffered TFPAA and is undoubtedly the product of an acid-catalyzed rearrangement of **30**. A compound detected in some of the product mixtures using TFPAA as the oxidizing agent may have the structure **32** as suggested by analogy with the oxidation of **9**.

**Scheme II**
**The Baeyer-Villiger Oxidation of $\Delta^{1(8)}$-Indanone-2**



11 28 29 30 31



32

The data in Table I are meant to illustrate the complex product mixtures which are obtained when using TFPAA. Several of the experiments have been duplicated but the exact product distribution cannot be predicted with any degree of regularity. This may be due to several factors. First, the thermal instability of the epoxy lactones which restricted us to nmr as our method of analysis and the nmr integral has its limitations. Second, exact reproducibility cannot be expected readily because of the heterogeneous reaction mixtures which were used. The data do, however, permit some conclusions to be drawn. The use of TFPAA with or without added $Na_2HPO_4$ does not give the intermediates **13**, **20**, or **21** as major products. All cases where TFPAA has been used in this study have resulted in product mixtures in which the components could be separated only by elution chromatography. Also, the use of CPBA gave **20** (epimeric mixture) in good yield. This material could then be used to prepare pure **21**, which in turn could be converted to **24** all in good yield. The only reason **21** and **24** could not be isolated in nearly quantitative yield was because of their sensitivity to the hydrolytic work-up which was used.

## Experimental Section[19]

**Cyclohexanone Morpholine Enamine.** The method of Stork[13] was employed (81% yield), bp 109–111° (12 mm) [lit.[13] bp 104–106° (12 mm)].

**$\Delta^{1(9)}$-Octalone-2 (9).** The synthesis was performed as described by Stork,[13] bp 66–68° (0.05 mm) [lit.[13] bp 66° (0.05 mm)]. The crude product (74% yield) consisted of approximately 80% of the $\Delta^{1(9)}$ isomer and about 20% of the $\Delta^{9(10)}$ isomer (nmr analysis). Low-temperature (Dry Ice-acetone bath) recrystallization from hexane gave a product which consisted of 94% of the $\Delta^{1(9)}$ isomer and 6% of the $\Delta^{9(10)}$ isomer as indicated by nmr. Ir confirmed the presence of some of the $\Delta^{9(10)}$ isomer.

An attempt to fractionally distil the 80:20 octalone mixture at atmospheric pressure using a 16 × 250 mm column packed with glass helices resulted in extensive decomposition of the octalones. Distillation at 12 mm using the same column resulted in no significant separation of the two isomers.

The 80:20 octalone mixture (0.7 g) was separated by elution chromatography on a 20 × 300 mm column packed with silica gel. The column was successively eluted with 300 ml of hexane, 500 ml of 2% ethyl acetate in hexane, and finally 5% ethyl acetate in hexane. A forerun of 500 ml of solvent was eluted before 16 40-ml fractions were collected. The forerun consisted only of solvent. Fractions 5–7 (0.077 g) were identified as virtually pure $\Delta^{9(10)}$-octalone-2. Fractions 9–16 (0.615 g) were identified as pure $\Delta^{1(9)}$-octalone-2 (**9**) by the absence of saturated carbonyl in the ir and by an aliphatic to vinyl proton ratio of 13:1 ± 5% in the nmr.

The 80:20 octalone mixture apparently contained a third component because of a signal at δ 3.6 in the nmr. A sample of the 80:20 octalone mixture (50 ml) was very slowly distilled and the first 1-ml fraction, bp 103–111° (12 mm), was found to be enriched in the compound responsible for the δ 3.6 nmr signal. This fraction (0.7 g) was placed on a 20 × 300 mm silica gel column and successively eluted with 200 ml of hexane, 200 ml of 2% ethyl acetate in hexane, 200 ml of 5% ethyl acetate in hexane, and finally 10% ethyl acetate in hexane. A forerun of 400 ml of solvent was eluted before 24 40-ml fractions were collected. The forerun consisted only of solvent. The first two materials to elute from the column were identified as octalones. The third component to elute, fractions 20–24 (0.481 mg), was identified by ir, nmr, and mass spectra as 1-morpholino-3-butanone. The spectra of this material were identical with those of an authentic sample prepared by another route.[20] Removal of this contaminant from the crude 80:20 octalone mixture was accomplished by bubbling HCl into a solution of 40 g of octalone mixture in 50 ml of hexane until no further precipitation occurred. The solid hydrochloride salt was collected by filtration, the filtrate was successively washed with water, 5% aqueous $NaHCO_3$ solution, and water, and the octalones were recovered by distillation. The hydrochloride salt of 1-morpholino-3-butanone was recrystallized from ethanol and had mp 148–149° (lit.[21] mp 149°).

**Bromoacetone.** The procedure of Catch[22] was used with the exception that both the original aqueous layer and the MgO and water slurry were extracted with ether and the additional material obtained was added to the crude product prior to distillation. The desired product was obtained in 48% yield after distillation: bp 37–45° (12mm) [lit.[22] bp 63–65° (50 mm)]; ir $\nu_{C=O}$ 1720 cm$^{-1}$; nmr $\delta$ 2.28 (s, 3 H), 3.88 (s, 2 H).

**1-(2-Oxocyclohexyl)propanone (10).** The synthesis was carried out according to the procedure of Baumgarten[15] with the exception that steam distillation was not employed as a means of isolating the crude product. At the end of the heating period the reaction mixture was cooled, the aqueous and organic layers were separated, and the aqueous layer was extracted with ether. The organic extracts were combined and dried, and the solvent was removed on a rotary evaporator. The residue was distilled to yield the product in 21% yield: bp 70–72° (0.04 mm) [lit.[15] bp 91–93° (1.1 mm)]; ir $\nu_{C=O}$ 1712 and 1620 cm$^{-1}$ (doublet); nmr $\delta$ 1.1–2.5 (9 H), 2.14 (s, 3 H), 2.90 (m, 2 H).

**$\Delta^{1(8)}$-Indanone-2 (11).** Cyclization of **10** according to the procedure of Islam and Raphael[14] afforded the desired product in 88% yield after distillation: bp 51–53° (0.02 mm) [lit.[14] bp 88° (4 mm)]; ir $\nu_{CH}$ (vinylic) 3070, $\nu_{C=O}$ 1710, $\nu_{C=C}$ 1623 cm$^{-1}$; uv $\lambda_{max}$ 230 nm ($\epsilon$17,600); nmr $\delta$ 0.8–2.9 (11 H), 5.62 (s, 1 H); mass spectrum *m/e* (rel intensity) 136 (52), 108 (69), 95 (37), 93 (50), 91 (45), 80 (48), 79 (100), 77 (52), 66 (40), 53 (34), 51 (50).

**Conversion of $\Delta^{1(9)}$-Octalone-2 (9) to *cis*-1,9-Epoxydecalone-2 (12a).** The conversion of 3 g of **9** was performed as outlined by Wasson and House[23] and gave 2.36 g (72%) of **12a:** bp 74–76° (0.03 mm); ir $\nu_{C=O}$ 1710 cm$^{-1}$; nmr $\delta$ 1.1–2.5 (13 H), 2.98 (s, 1 H); mass spectrum *m/e* (rel intensity) 166 (34), 111 (61), 95 (67), 93 (34), 81 (31), 67 (100), 55 (47).

**Conversion of *cis*-1,9-Epoxydecalone-2 (12a) to *cis*-2,9-Decalindiol (14a).** A solution of 0.6 g (0.0036 mol) of **12a** in 10 ml of THF was added dropwise to an ice bath cooled slurry of 0.205 g (0.0054 mol) of $LiAlH_4$ in 20 ml of THF. The reaction mixture was allowed to come slowly to room temperature and stirring was continued for a total of 18 hr. At the end of this time the reaction mixture was treated successively with 0.2 ml of water, 0.2 ml of 15% aqueous NaOH, and 0.6 ml of water. The salts were removed by filtration and the filtrate was concentrated on a rotary evaporator to give 0.6 g of an oil–solid mixture. Recrystallization from benzene yielded 0.2 g (33%) of **14a,** mp 158–160° (lit.[16] mp 159–160°). Evaporation of the mother liquors gave 0.4 g of an oil suspected to be the epimeric cis diol **14b.** This was confirmed when both **14a** and the oil were oxidized separately with Jones reagent to the same product, *cis*-9-hydroxydecalone-2 (**15**). Spectral data for **14a** are as follows: ir $\nu_{OH}$ 3400 cm$^{-1}$; nmr $\delta$ 0.9–2.1 (14 H), 3.30 (m, 1 H), 3.71 (m, 1 H), 3.90 (s, 1 H), 4.20 (d, 1 H); mass spectrum *m/e* (rel intensity) 170 (21), 152 (91), 109 (80), 98 (100), 96 (35), 55 (40), 43 (48), m* 136.0.

**Conversion of *cis*-2,9-Decalindiol (14a) to *cis*-9-Hydroxydecalone-2 (15).** The conversion of 0.200 g of **14a** was performed according to the procedure of Prelog and Smith[16] to give 0.150 g (75%) of **15:** mp 130–131° (lit.[16] mp 131–132°); ir $\nu_{OH}$ 3390, $\nu_{C=O}$ 1710 cm$^{-1}$; nmr $\delta$ 1.1–1.9 (10 H), 2.26 (m, 4 H), 2.41 ($\nu_{AB}$ for AB pattern, $\delta$ 2.12 $\nu_A$, 2.69 $\nu_B$, $J$ = 14.3 Hz, 2 H); mass spectrum *m/e* (rel intensity) 168 (67), 150 (56), 122 (87), 111 (90), 108 (38), 98 (100), 97 (40), 55 (88), 43 (57), m* 134.0.

**Conversion of $\Delta^{1(8)}$-Indanone-2 (11) to *cis*-1,8-Epoxy-1*H*,8*H*-dihydroindanone-2 (16).** The conversion was performed in the same manner as the conversion of **9** to **12a**, 2.72 g of **11** giving 1.5 g (60%) of **16:** bp 68–70° (0.05 mm); ir $\nu_{CH}$ (epoxy) 3050, $\nu_{C=O}$ 1755 cm$^{-1}$; nmr $\delta$ 0.8–2.7 (11 H), 3.11 (s, 1 H); mass spectrum *m/e* (rel intensity), 142 (9), 95 (100), 67 (55).

**Preparation of *cis*-3a-Indanol (19) from *cis*-1,8-Epoxy-1*H*,8*H*-dihydroindanone-2 (16).** The epoxy ketone **16** (0.260 g, 0.0017 mol) in 2 ml of THF was added to a slurry of 0.100 g (0.0036 mol) of $LiAlH_4$ in 4 ml of THF at 5°. The reaction mixture was allowed to warm to room temperature and stirred for 17 hr. It was then diluted with ether, and 0.1 ml of $H_2O$, 0.1 ml of 15% aqueous NaOH, and 0.3 ml of $H_2O$ were added successively. The precipitate was removed by filtration and the filtrate was concentrated to give 0.29 g of crude diol **17.** *p*-Toluenesulfonyl chloride (0.358 g, 0.0019 mol) dissolved in 2 ml of pyridine was added to the crude **17** (0.0018 mol) at 5°. The solution was then poured onto ice and dilute HCl and the product was extracted with ether. The extract was washed successively with dilute HCl, aqueous $NaHCO_3$, and water. After drying and removal of the solvent, 0.43 g of crude monotosylate **18** (oil) was obtained.

The crude tosylate dissolved in 3 ml of THF was added to a slurry of 0.2 g of $LiAlH_4$ in 8 ml of THF at ~0°. The mixture was stirred at room temperature for 1 hr and then under reflux for 20 hr. After the mixture was cooled in an ice bath and diluted with ether, 0.2 ml of $H_2O$, 0.2 ml of 15% aqueous NaOH, and 0.6 ml of $H_2O$ were successively added. The precipitate was removed by filtration. After removal of the solvent, 0.14 g of **19** was obtained. Sublimation of the crude product gave crystals, mp 51–51.5° (lit.[17] mp 49°). The ir spectrum was identical with that reported.[17]

**Trifluoroperacetic Acid.** Preparation was according to the method outlined by Lewis.[24]

**Oxidation of $\Delta^{1(9)}$-Octalone-2 (9) with TFPAA.** Five separate oxidations were performed, each experiment involving a change in one or more of the following parameters: temperature, acidity, reaction time, and equivalents of oxidizing reagent employed. In four of the five experiments the additional equivalents of oxidizing reagent were added at known time intervals during the course of the reaction. In the remaining experiment TFPAA was added at one time.

The composition of the crude product from each of the experiments was determined from an nmr integral by choosing characteristic sharp signals for each of the compounds produced in the reaction and comparing the relative areas of these signals. The crude product compositions for the five reactions are presented in Table I along with the reaction parameters.

Since all five experiments were run in the same fashion, the experimental details of only one will be given.

A solution at 10° of 1 equiv (5.2 g) of TFPAA in 40 ml of $CH_2Cl_2$ was added slowly to a mixture of 6.0 g (0.04 mol) of **9** and 57 g of anhydrous $Na_2HPO_4$ in 200 ml of $CH_2Cl_2$ at 10°. The reaction mixture was kept at 10° and stirring was continued for 24 hr. At the end of this time a 3-ml aliquot was withdrawn from the reaction flask, concentrated, and analyzed by nmr and a second equivalent TFPAA was added. After stirring at 10° for another 24 hr, a second aliquot was withdrawn and a third equivalent of TFPAA was added. After stirring at 10° for an additional 24 hr (total reaction time 72 hr), the salts were removed by filtration, and the filtrate was dried and then concentrated on a rotary evaporator to give 4 g of crude product mixture (for composition see Table I).

The crude product (0.6 g) from expt 1 (see Table I) was placed on a 20 × 300 mm silica gel column and successively eluted with 200 ml of hexane, 200 ml of 2% ethyl acetate in hexane, 500 ml of 5% ethyl acetate in hexane, and finally 10% ethyl acetate in hexane. A forerun of 300 ml of solvent was eluted before 32 40-ml fractions were collected. The forerun consisted only of solvent. Fractions 5–9, 0.097 g (containing some solvent), were identified by ir and nmr as about 90% enol lactone **13** and 10% epoxy ketone **12a.** Fractions 11–14, 0.191 g (containing some solvent), were identified as recovered starting material. Fractions 19–25, 0.166 g (containing some solvent), were sublimed (30°, 0.005 mm) to yield 0.157 g of epoxy lactone **20a.** Fractions 27–31, 0.054 g (containing some solvent), were identified as a mixture of the aldehyde lactones **21a** and **21b** and were distilled, bp 108–11° (0.5 mm).

A chromatography performed after a repetition of the above experiment resulted in the isolation of 0.05 g of material in fractions 3–4. The material was distilled (bp 66°, 0.004 mm) and was identified as the enol lactone **27**: ir $\nu_{C=O}$ 1766, $\nu_{C=C}$ 1713 cm$^{-1}$; nmr $\delta$ 1.64 (m, 4 H), 2.12 (m, 6 H), 2.58 (t, 2 H); mass spectrum *m/e* (rel intensity) 152 (79), 124 (42), 96 (50), 82 (44), 67 (100).

**Oxidation of $\Delta^{1(8)}$-Indanone-2 (11) with TFPAA.** These oxidations were performed in the same manner as the oxidations of **9** with TFPAA. The crude product distributions were also determined in the same fashion and are tabulated in Table II.

**Oxidation of $\Delta^{1(9)}$-Octalone-2 (9) with CPBA.** This reaction was run first using 1 equiv and then 2 equiv of the peracid. The procedure for both experiments was the same and will be given only for the oxidation employing 1 equiv of the peracid.

To a solution at room temperature of 0.2 g (0.00134 mol) of **9** in 50 ml of $CH_2Cl_2$ was added dropwise with stirring a solution of 0.281 g of 85% CPBA (0.00134 mol of peracid) in 15 ml of $CH_2Cl_2$ and stirring was continued for a total of 24 hr. The reaction mixture was then extracted with 5% aqueous $NaHCO_3$ solution until the extracts remained basic and washed with water. The organic solution was dried and the solvent was removed on a rotary evaporator to yield 0.180 g of crude product. The crude product composition was determined from the nmr integral in the same manner as it was in the experiments using TFPAA as the oxidizing reagent. The results are listed in Table I.

For the experiment involving 2 equiv of CPBA, 2.0 g of **9** gave 2.03 g (84%) of isomeric epoxy lactones **20a** and **20b** as the only product. In an attempt to separate the mixture of epoxy lactones using a silica gel column and 10% ethyl acetate in hexane as the solvent, the trans isomer **20b** decomposed. The cis isomer **20a** eluted from the column in pure form: ir $\nu_{CH}$ (epoxy) 3022, $\nu_{C=O}$ 1748 $cm^{-1}$; nmr $\delta$ 1.1–2.2 (11 H), 2.54 (m, 2 H), 4.88 (s, 1 H).

*Anal.* Calcd for $C_{10}H_{14}O_3$: C, 65.92; H, 7.74. Found: C, 66.07; H, 7.83.

**Oxidation of $\Delta^{1(8)}$-Indanone-2 (11) with CPBA.** These oxidations were performed and product distributions were determined in the same manner as outlined for the oxidations of **9** with CPBA. All oxidations gave approximately 100% crude yield. The results are listed in Table II.

**Conversion of the Epoxy Lactone 20a to the Aldehyde Lactone 21a.** *p*-Toluenesulfonic acid monohydrate (0.002 g) was dissolved in 20 ml of benzene. Benzene (4 ml) was removed by distillation to remove water from the solution. The epoxy lactone **20a** (0.150 g) was added and the solution was stirred at room temperature for 10 hr. The reaction mixture was washed with 5% aqueous $NaHCO_3$ and water and dried. After removal of the benzene, the residue was distilled to yield 0.112 g (75%) of **21a**: bp 94–95° (0.005 mm); ir $\nu_{CH}$ (aldehydic) 2730, $\nu_{C=O}$ (aldehyde and lactone) 1745 $cm^{-1}$; nmr $\delta$ 1.1–2.3 (11 H), 2.58 (m, 2 H), 9.83 (d, 1 H, $J$ = 1.1 Hz); mass spectrum $m/e$ (rel intensity) 182 (2), 153 (31), 125 (48), 98 (64), 83 (41), 81 (46), 79 (54), 67 (76), 55 (100), 44 (67).

*Anal.* Calcd for $C_{10}H_{14}O_3$: C, 65.92: H, 7.74. Found: C, 65.73, H, 7.84.

**Conversion of the Aldehyde Lactones 21a and 21b to the Formate Lactones 24a and 24b with TFPAA.** A solution of TFPAA (0.00055 mol) in 10 ml of $CH_2Cl_2$ at 5° was added slowly to a cooled, stirred mixture of 0.100 g (0.00055 mol) of a 50:50 mixture of **21a** and **21b** and 0.470 g (0.003 mol) of anhydrous $Na_2HPO_4$ in 15 ml of $CH_2Cl_2$. The temperature of the cooling bath was maintained at 12° and the reaction mixture was stirred for 24 hr, after which time a 10-ml aliquot was withdrawn and concentrated and an nmr spectrum was obtained. The nmr spectrum showed the starting material to be 60% converted to a 50:50 isomeric mixture of diesters **24a** and **24b** on the basis of characteristic singlets at $\delta$ 8.22 and 8.38. The nmr sample was returned to the reaction vessel and 0.470 g of anhydrous $Na_2HPO_4$ was added followed by addition of a second equivalent of peracid in 10 ml of $CH_2Cl_2$. The cooling bath was maintained at 12° and the reaction mixture was stirred for another 24 hr, after which time the nmr spectrum of a second aliquot showed the conversion to be complete. The reaction mixture was filtered and the filtrate was rapidly washed with cold (5°), 10% aqueous $NaHCO_3$ and water and dried. The solvent was removed on a rotary evaporator and the residue was distilled, bp 85–87° (0.005 mm), to yield 0.063 g (60%) of a 50:50 mixture of **24a** and **24b**: ir $\nu_{C=O}$ 1750 (broad, formate and lactone); nmr $\delta$ 8.22 (s) and 8.38 (s) (the two peaks integrate to one H), 1.2–2.8 (13 H).

**Conversion of *cis*-1,9-Epoxydecalone-2 (12a) to the Epoxy Lactone 20a.** To a solution at 25° of 1.0 g (0.006 mol) of **12a** in 100 ml of $CH_2Cl_2$ was added slowly with stirring a solution at 25° of 1.40 g (0.006 mol of peracid) of 85% CPBA in 50 ml of $CH_2Cl_2$. The reaction progress was monitored by observing the diminution of the characteristic singlet attributable to the epoxide ring proton of **12a** in the nmr spectrum. After 48 hr, all monitor spectra indicated that the reaction had stopped, so an additional 1.40 g (0.006 mol of peracid) of 85% CPBA was added, and after an additional 24 hr nmr analysis showed the reaction to be complete. The reaction mixture was washed with 100 ml of 10% aqueous $NaHCO_3$ and then with 100 ml of water. After drying, the solvent was removed on a rotary evaporator and the residue was sublimed to yield 0.780 g (71%) of the cis epoxy lactone **20a**, mp 96–97°.

**Oxidation of the Enol Lactone 13 with CPBA.** To an ice bath cooled solution of 0.150 g (0.0009 mol) of **13** in 20 ml of $CH_2Cl_2$ was added slowly with stirring a cool (5°) solution of 0.210 g (0.0009 mol of peracid) of 85% CPBA in 20 ml of $CH_2Cl_2$. The solution was allowed to come to room temperature and stirring was continued for a total of 12 hr, after which time an nmr spectrum indicated that all of **13** had been consumed. The reaction mixture was washed twice with 40 ml of 5% aqueous KOH and once with 40 ml of water. After drying, the solvent was removed on a rotary evaporator and the residue was sublimed to yield 0.145 g (89%) of a 50:50 mixture of the isomeric epoxy lactones **20a** and **20b** as indicated by nmr.

**Conversion of 21a and 21b to 24a and 24b with CPBA.** To a solution at 12° of 0.100 g (0.00055 mol) of a 50:50 mixture of **21a** and **21b** in 15 ml of $CH_2Cl_2$ was added a solution at 5° of 0.170 g (0.00066 mol, 1.2 equiv of peracid) of 85% CPBA in 10 ml of $CH_2Cl_2$. The homogeneous solution was stirred at 12° for 24 hr. The reaction mixture then was washed rapidly with two 20-ml portions of cold 10% aqueous $NaHCO_3$, rinsed with 20 ml of water, and dried. The solvent was removed on a rotary evaporator, and the residue was distilled to yield 0.092 g (85%) of a 50:50 mixture of **24a** and **24b**.

**Reaction of the Aldehyde Lactones 21a and 21b with 1,2-Ethanedithiol.** A 1:1 mixture (0.1 g, 0.00055 mol) of **21a** and **21b**, 1 ml (excess) of 1,2-ethanedithiol, and a small crystal of *p*-toluenesulfonic acid were added to 2 ml of benzene and this solution was kept at room temperature for 24 hr. An nmr spectrum showed the presence of two singlets (in the ratio of 1:1) at $\delta$ 4.7 and 4.9 and these were assigned to the methinyl proton in the 1,3-dithiolane rings of **25a** and **25b**, respectively

On another occasion the reaction mixture was diluted with ether 20 min after mixing the reagents and then washed with aqueous $NaHCO_3$, dried, and concentrated to give **25b**. The fate of the product derived from **21a** was not determined.

**Desulfurization of the Dithioacetal 25b.** The crude **25b** prepared above was treated with 4 g of Raney Ni (W-2) in 10 ml of dioxane at 85° for 1 hr. The catalyst was removed by filtration, and after removal of the solvent a product was obtained whose ir and nmr spectral properties were identical with those reported for **26**.[18]

**Preparation of the Dithioacetal 25a from the Aldehyde Lactone 21a.** The procedure used for the preparation of **25a** was identical with that used for the preparation of the mixture **25a** and **25b** above. The chemical shift of the methinyl proton of the 1,3-dithiolane ring of **25a** was $\delta$ 4.7.

**Registry No. 9,** 1196-55-0; **10,** 6126-53-0; **11,** 39163-29-6; **12a,** 42393-90-8; **13,** 42393-91-9; **14a,** 42393-92-0; **15,** 42393-93-1; **16,** 42393-94-2; **19,** 13366-92-2; **20a,** 42393-95-3; **20b,** 42393-64-6; **21a,** 42393-96-4; **21b,** 42393-97-5; **24a,** 42393-98-6; **24b,** 42393-99-7; **25b,** 42394-00-3; **27,** 700-82-3; bromoacetone, 598-31-2

## References and Notes

(1) Taken in part from the M.S. Thesis of R. E. Ellwanger, University of Wyoming, July 1972.
(2) H. Walton, *J. Org. Chem.*, **22**, 1161 (1957).
(3) G. B. Payne and P. H. Williams, *J. Org. Chem.*, **24**, 284 (1959).
(4) E. Caspi, Y. W. Chang, and R. I. Dorfman, *J. Med. Pharm. Chem.*, **5**, 714 (1962).
(5) J. T. Pinhey and K. Schaffner, *Tetrahedron Lett.*, 601 (1965).
(6) J. T. Pinhey and K. Schaffner, *Aust. J. Chem.*, **21**, 1873 (1968).
(7) M. Gorodetsky, N. Danieli, and Y. Mazur, *J. Org. Chem.*, **32**, 760 (1967).
(8) E. Caspi and S. N. Balasubrahmanyam, *Experientia*, **19**, 396 (1963).
(9) S. D. Levine, *J. Org. Chem.*, **31**, 3189 (1966).
(10) A. M. Nicaise and R. Bourbon, *Bull. Soc. Chim. Fr.*, 1552 (1970).
(11) E. E. Smissman and F. B. Block, *J. Amer. Pharm. Ass., Sci. Ed.*, **48**, 526 (1959).
(12) T. Yokoyama and N. Izui, *Bull. Chem. Soc. Jap.*, **38**, 1501 (1965).
(13) G. Stork, *et al.*, *J. Amer. Chem. Soc.*, **85**, 207 (1963).
(14) A. M. Islam and R. A. Raphael, *J. Chem. Soc.*, 4086 (1952).
(15) H. E. Baumgarten, P. L. Creger, and C. E. Villars *J. Amer. Chem. Soc.*, **80**, 6609 (1958).
(16) V. Prelog and H. E. Smith, *Helv. Chim. Acta*, **42**, 2624 (1959).
(17) H. Christol and G. Solladié, *Bull. Soc. Chim. Fr.*, 3193 (1966).
(18) P. A. Tardella and G. DiMaio, *Tetrahedron*, **23**, 2285 (1967).
(19) Microanalyses were performed by Chemalytics Inc., Tempe, Ariz. A Perkin-Elmer grating infrared spectrophotometer, Model 621, and a Beckman spectrophotometer, Model IR-10, were used for the determination of the infrared (ir) spectra. Liquids were run as liquid films between sodium chloride plates, and solids were run as solid dispersions in potassium bromide pellets. A Varian Associates HA-100 spectrometer was used to determine the nuclear magnetic resonance (nmr) spectra; deuteriochloroform or carbon tetrachloride were the solvents, and tetramethylsilane was the internal standard.

The nmr data are reported as chemical shifts in δ units followed by s = singlet, d = doublet, dd = doublet of doublets, t = triplet, or m = multiplet and the relative number of protons attributable to the signal reported. A Beckman DB spectrophotometer was used for the determination of the ultraviolet (uv) spectra. Samples were run as solutions in 95% ethanol in 1-cm quartz cells. Uv data are reported as wavelength of maximum absorption ($\lambda_{max}$) followed by the molar absorptivity. Melting points were determined with a Fisher-Johns melting point apparatus and are corrected. Boiling points are uncorrected. Mass spectra were determined with a Varian MAT CH-5 spectrometer. The mass spectral data are reported for $M\cdot^{+}$ and fragment ions over 30% of the base peak. Important metastable peaks are denoted by m*. Unless otherwise specified, reagents were obtained from regular commercial sources. $MgSO_4$ was the drying agent used.

(20) N. C. Ross and R. Levine, *J. Org. Chem.*, **29**, 2346 (1964).

(21) N. Grier and S. J. Lederer, French Patent 1,347,339 (1963); *Chem. Abstr.*, **60**, 10693*h* (1964).

(22) J. R. Catch, D. R. Elliott, D. H. Hey, and E. R. H. Jones, *J. Chem. Soc.*, 272 (1948).

(23) R. L. Wasson and H. O. House in "Organic Syntheses," Collect. Vol. IV, N. Rabjohn, Ed., Wiley, New York, N. Y., 1963, p 552.

(24) S. N. Lewis in "Oxidation," Vol. I, R. L. Augustine, Ed., Marcel Dekker, New York, N. Y., 1969, p 217.

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# Photochemical Reactions of Methyl Phenoxyacetates

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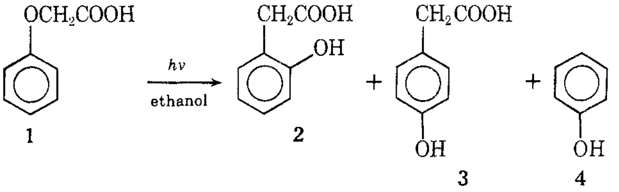
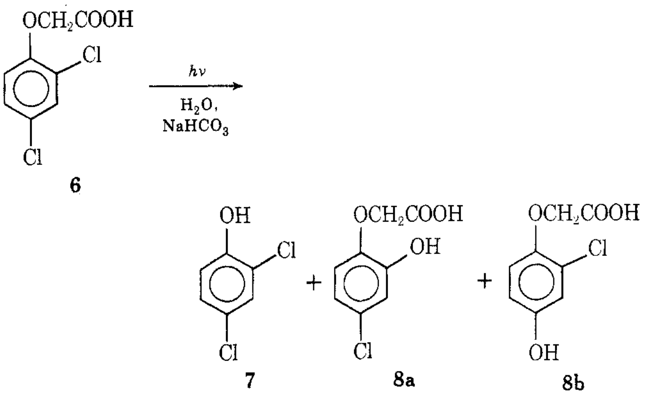
The photochemical reactions of methyl 2,4-dichlorophenoxyacetate (9), 4- and 2-chlorophenoxyacetates (10 and 11), and phenoxyacetate (14) have been investigated. These compounds were found to participate in a photochemical sequence of reactions which begins with 9 and ends with methyl 2- and 4-hydroxyphenylacetates (12 and 13). The existence of this reaction sequence when combined with the relative reactivities of its various members and the dependence of reaction on the wavelength of excitation explains the variety of photochemical behaviors which have been observed for phenoxyacetic acids and their derivatives.

The chlorinated phenoxyacetic acids and esters represent one of the commercially and socially most important groups of organic compounds due to their extensive use in weed control.[1] Stimulated by a desire to understand the natural photochemical decay of these substances, a number of researchers have examined the light-induced reactions of these systems;[2-6] interestingly, the majority of research has been directed toward the parent acids rather than their esters even though the esters are also widely used. Much of the work on the chlorinated phenoxyacetic acids has led to partial identification of photoproducts and to observations of color and pH changes caused by irradiation.[2] Several studies have, however, resulted in more complete product identification; thus, some detailed photochemical understanding of these systems is presently available.

Several years ago Kelly and Pinhey reported that the parent compound in this series, phenoxyacetic acid (1), experienced a photochemical rearrangement to yield 2- and 4-hydroxyphenylacetic acids (2 and 3) and phenol (4).[3] It was further reported that the products 2 and 4 (and a small amount of 1) were formed when 4-chlorophenoxyacetic acid (5) was irradiated; however, 2,4-dichlorophenoxyacetic acid (6, the most interesting of these from a herbicidal point of view) produced a complex mixture from which nothing other than phenol (4) was detected.[4] Crosby and Tutlass[5] observed that upon irradiation under somewhat different conditions 2,4-dichlorophenoxyacetic acid (6) assumed a much different reaction course from the unsubstituted and 4-chloro derivatives (1 and 5). No rearrangement took place; instead, substitution and homolysis products 7, 8a, and 8b were formed. These products then experienced further reaction. From the results of these two research groups it was clear that some unidentified factor was exercising a deciding influence over the photochemistry of the various phenoxyacetic acids.





More recently it has been shown that photochemical reaction of a series of 2,4-dichlorophenoxyacetic acid esters under conditions simulating those occurring naturally results in replacement of chlorine by hydrogen as the only observable reaction process.[6] Since this result appeared to be still another type of photochemical behavior in the phenoxyacetic acid system, we decided to examine the photochemistry of one of these esters (the methyl) in greater depth in an effort to uncover some of the basic factors responsible for its reactivity.

## Results

Vycor-filtered irradiation of 3.00 mmol of methyl 2,4-dichlorophenoxyacetate (9) in 350 ml of methanol for 1.5 hr with a 450-W Hanovia mercury vapor lamp under nitrogen caused the reaction of 46% of the starting material to produce, after glc separation, the methyl esters of 4-chlorophenoxyacetic acid (10, 16%), 2-chlorophenoxyacetic acid (11, 7%), 2-hydroxyphenylacetic acid (12, 42%),[7] 4-hydroxyphenylacetic acid (13, 18%), and phenoxyacetic acid (14, 1%) as well as phenol (4, 9%). A dark, insoluble tar presumably accounted for the remaining reacted starting material.[8] The products were each identified by comparison with independently obtained materials.