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 (λ_{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.

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Photochemical Reactions of Methyl Phenoxyacetates

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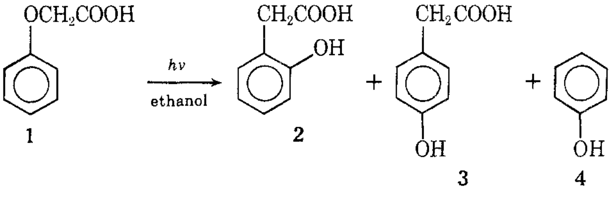
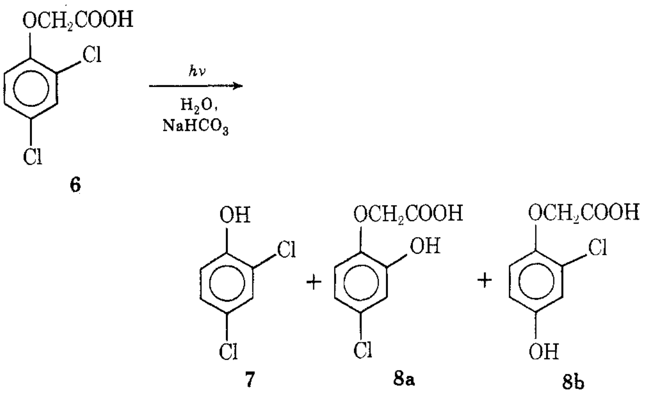
The photochemical reactions of methyl 2,4-dichlorophenoxyacetate (9), 4- and 2-chlorophenoxyacetates (10 and 11), and phenoxyacetate (14) have been investigated. These compounds were found to participate in a photochemical sequence of reactions which begins with 9 and ends with methyl 2- and 4-hydroxyphenylacetates (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.

Irradiation (Vycor filtered) of methyl 4-chlorophenoxyacetate (**10**) under the same conditions as photolysis of **9** resulted in 36% conversion of the starting material in 1 hr. The same isolation procedure yielded the methyl esters of 2-hydroxyphenylacetic[6] (**12**, 40%), 4-hydroxyphenylacetic (**13**, 21%), and phenoxyacetic (**14**, 10%) acids along with phenol (**4**, 10%). A dark material, insoluble in organic solvents, was also formed in this reaction. Irradiation of methyl 2-chlorophenoxyacetate (**11**) under the same conditions as **10** produced the same result.

Similar photolysis (Vycor filtered) of methyl phenoxyacetate (**14**) resulted in complete consumption of **14** in 30 min and the formation of methyl 2-hydroxyphenylacetate (**12**, 58%), methyl 4-hydroxyphenylacetate (**13**, 25%), and phenol (**4**, 12%).

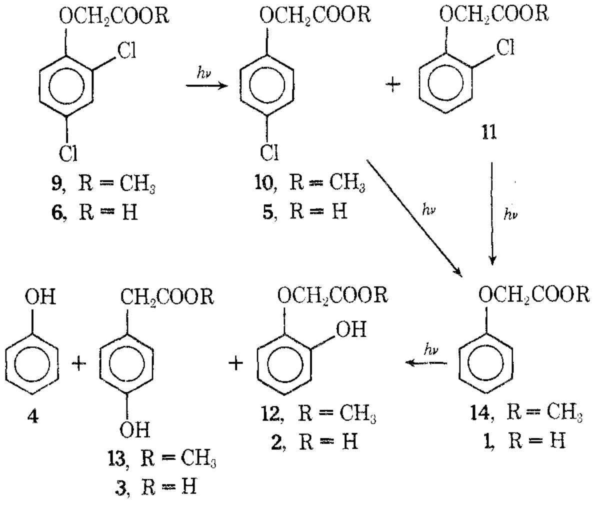
Methyl 2-hydroxyphenylacetate (**12**) did not rearrange to methyl 4-hydroxyphenylacetate (**13**) under the photolysis conditions.

Pyrex-filtered irradiation of methyl 2,4-dichlorophenoxyacetate (**9**) under the conditions described above required 90 hr for a 20% conversion of **9**; however, only the methyl esters of 4- and 2-chlorophenoxyacetic acids (**10** and **11**) were formed in 51 and 39% yields, respectively. The same result was obtained when irradiation of **9** was conducted using water as the solvent. A small amount of hydrolysis of **9** was observed under these conditions. Neither methyl 4-chlorophenoxyacetate (**10**) nor methyl phenoxyacetate (**14**) was reactive when the Pyrex filter was used.

Discussion

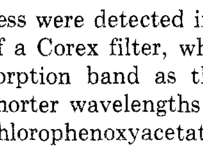
The photoproducts arising from irradiation of the various phenoxyacetates (**9–11** and **14**) suggest that a sequence of photochemical changes, such as that outlined in Scheme I, is operative. For such a series of transformations to represent correctly the photochemical reactivity of these compounds (**9–11** and **14**) it is necessary to demonstrate first that the proposed changes are possible and second that, as well as can be determined, they are the only pathways of reaction. The first is certainly the easier of these two requirements to demonstrate. Photolysis of methyl 2,4-dichlorophenoxyacetate (**9**) and each of the other phenoxyacetates shown in Scheme I produces the succeeding products in the reaction sequence; thus, the postulated pathway (Scheme I) connecting these compounds (**9–14**) is a possible one. To show that this sequence is the only one being followed is more difficult to do and requires careful examination of each of the several reaction stages.

Scheme I
Proposed Reaction Sequences



Consider the initial step in the reaction sequence in Scheme I ($R = CH_3$), the conversion of methyl 2,4-dichlorophenoxyacetate (**9**) into methyl 4- and 2-chlorophenoxyacetates (**10** and **11**). The question one must ask concerning this first photochemical process is whether **9** is converted exclusively into **10** and **11**. One way in which this question could be answered would be to prevent the further photochemical reaction of **10** and **11** and then determine whether products **12–14** are still capable of forming. With any arbitrary group of compounds such an approach might be impossible or, at least, extremely difficult. In the case of methyl 2,4-dichlorophenoxyacetate (**9**) and methyl 4- and 2-chlorophenoxyacetates (**10** and **11**), however, the fortunate situation exists that the uv absorption of **9** begins at longer wavelength than **10** and **11** (Figure 1); hence, selective absorption of light by **9** is possible. In practice this selective absorption is achieved by use of a Pyrex filter. Pyrex-filtered photolysis of **9** yields only **10** and **11**. This result clearly points to the first step in the reaction sequence shown in Scheme I ($R = CH_3$) being a required one.

It is, of course, possible that the higher energy radiation incident upon the reaction mixture when the Vycor filter is used causes a new reaction pathway to be operative, perhaps one in which methyl 2,4-dichlorophenoxyacetate (**9**) rearranges to give compounds such as the chlorinated phenols **16**, **17**, or **18**. These systems would then suffer photochemical chlorine loss to produce methyl 2- and 4-hydroxyphenylacetates (**12** and **13**). Two factors argue against a new reaction pathway. First, no intermediates such as **16–18** corresponding to a new rearrangement process were detected in the photolysis mixtures. Second, use of a Corex filter, which allows excitation in the same absorption band as the Pyrex filter but at the somewhat shorter wavelengths necessary to permit methyl 4- and 2-chlorophenoxyacetates (**10** and **11**) and methyl phenoxyacetate (**14**) to absorb light (Figure 1), yielded the same reaction products as with the Vycor filter. Since it seems unlikely that a change in excitation energy within the same absorption band would stimulate a new major reaction pathway and since no new products (*e.g.*, **16–18**) indicative of a new pathway were detected, little justification exists for proposing a type of reactivity for methyl 2,4-dichlorophenoxyacetate (**9**) other than that which has been shown to exist (Scheme I). The conclusion reached from consideration of all the evidence pertaining to the photochemical reaction of **9** is that its conversion into **10** and **11** appears to be the only pathway operative.



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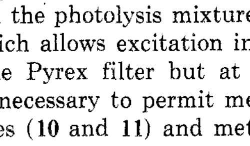

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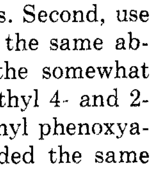

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Turning next to the second transformation in this sequence, the conversion of methyl 4- and 2-chlorophenoxyacetates (**10** and **11**) into methyl phenoxyacetate (**14**), one has greater difficulty in establishing with certainty that **10** and **11** are converted only into **14**. In this case, unfortunately, selective light absorption by either **10** or **11** and not **14** is possible, in theory, but not experimentally feasible (Figure 1). There is ample reason to believe, however, that **14** is the only primary photoproduct from irradiation of **10** or **11**. When either **10** or **11** is irradiated, a small amount of **14** is formed along with the photoproducts

Table I
Photochemical Reactions of Methyl Phenoxyacetates

Compd	Filter	Irradiation time, hr	Per cent conversion	Per cent yield of photoproducts 10	11	14	4	12	13
Methyl 2,4-dichlorophenoxyacetate (**9**)	Vycor	1.5	46	16	7	1	9	42	18
Methyl 2,4-dichlorophenoxyacetate (**9**)	Corex	6.0	32	28	16	10	3	25	12
Methyl 4-chlorophenoxyacetate (**10**)	Vycor	1.0	36			10	10	49	21
Methyl 2-chlorophenoxyacetate (**11**)	Vycor	1.0	36			10	10	50	20
Methyl phenoxyacetate (**14**)	Vycor	0.5	100				12	58	25
Methyl 2,4-dichlorophenoxyacetate (**9**)[a]	Pyrex	90.0	20	51	39				
Methyl 4-chlorophenoxyacetate (**10**)	Pyrex	180.00	0	No reaction					
Methyl phenoxyacetate (**14**)	Pyrex	180.0	0	No reaction					

[a] The same result was obtained with water as a solvent in nitrogen or air atmosphere.

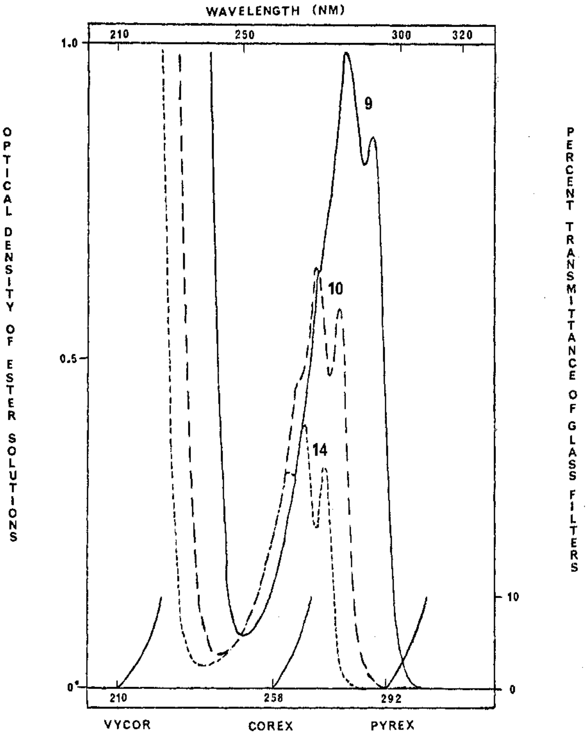

Figure 1. Absorption curves for methyl 2,4-dichlorophenoxyacetate (**9**, —), 4-chlorophenoxyacetate (**10**, --), and phenoxyacetate (**14**, ---) and minimum transmission wavelengths for Vycor, Corex, and Pyrex filters.

methyl 2- and 4-hydroxyphenylacetates (**12** and **13**) and phenol (**4**). The ratio of photoproducts **12**, **13**, and **4** to each other is independent of the choice of **10** or **11** as the starting material. Such behavior certainly suggests a common intermediate in these two reactions. Further strengthening this common intermediate proposal and directly implicating methyl phenoxyacetate (**14**) as the intermediate is the fact that photolysis of **14** produces the photoproducts **12**, **13**, and **4** in the same ratio as obtained from 4- and 2-chlorophenoxyacetates (**10** and **11**).

Recognizing now that the methyl phenoxyacetates (**9**–**11** and **14**) appear to follow a particular sequence of reactions[9] and that the wavelength of light incident upon them determines which compounds are reactive, it is possible for one to return to the variety of photochemical reactivities reported for phenoxyacetic acid derivatives and attempt to understand how these different reactions relate to each other. First, the report by Pinhey and Rigby[4] that 2,4-dichlorophenoxyacetic acid (**6**) produces a complex mixture upon unfiltered irradiation is understandable in light of the findings made here on the photochemistry of methyl 2,4-dichlorophenoxyacetate (**9**), where under similar conditions all members in the reaction sequence (Scheme I) were isolated. A second finding described in the literature, the rearrangement of phenoxyacetic acid (**1**) to 2- and 4-hydroxyphenylacetic acids (**2** and **3**) and phenol (**4**),[3] appears to be the same process as the photoreaction observed in this study for methyl phenoxyacetate (**14**) and represents simply the final step in the sequence shown in Scheme I. This particular process bears a close analogy to the photo-Fries reaction.[10] The fact that photolysis of one intermediate in this sequence, 4-chlorophenoxyacetic acid (**5**),[4] is reported to give only 2-hydroxyphenylacetic acid (**2**) and phenol (**4**) indicates that **1**, like its methyl ester (**14**), is much more reactive than its ring-substituted derivatives; hence, little of the intermediate unsubstituted acid remained after photolysis.[11]

Experimental Section

Synthesis of Reactants and Photoproducts. The starting materials used in this research and the independently obtained samples required for photoproduct identification were either commercially available[12] or were synthesized from commercially available acids by a standard procedure.[13]

General Irradiation and Isolation Procedures. The photochemical reactions conducted in connection with this research were done using a 450-W Hanovia high-pressure quartz mercury-vapor lamp which had been lowered into a water-cooled quartz immersion well. A filter (Vycor, Corex, or Pyrex) was placed between the reaction mixture, which was contained in a Model 6515 Ace photochemical reaction vessel, and the light source. The esters (3.00 mmol) were dissolved in 350 ml of methanol and continuously stirred during photolysis. Prepurified nitrogen was passed through the solution prior to irradiation and a slow stream of nitrogen continued during photolysis.

After irradiation, the solvent was removed by fractional distillation *in vacuo* below 35°. Simple distillation allowed some of the more volatile products to be carried over in the distillate. Nmr and ir spectra were taken on the crude reaction mixtures prior to separation and compared with the spectra of the isolated products in an effort to detect any change brought about by the chromatography conditions. With the exception of methyl 2-hydroxyphenylacetate (**12**), which was partially converted into 2-cumaranone (**15**) during separation, all the starting materials and photoproducts were shown to be stable under the isolation conditions.

The reaction mixtures were separated into their individual components and collected for identification using a Varian Aerograph Model 90-P gas chromatograph containing a 0.25 in. × 5 ft column packed with 10% OV-1 on 80–120 mesh Chromosorb W. The column temperature was 170° and the helium flow rate was

40 ml/min. The retention times of the various starting materials and photoproducts under these conditions follow: phenol (**4**), 3 min; methyl phenoxyacetate (**14**), 7 min; methyl 2-hydroxyphenylacetate (**12**), 10 min; methyl 4-hydroxyphenylacetate (**13**), 13 min; methyl 4-chlorophenoxyacetate (**10**), 16 min; methyl 2-chlorophenoxyacetate (**11**), 16 min; and methyl 2,4-dichlorophenoxyacetate (**9**), 25 min. Each photoproduct was identified by comparison of its nmr and ir spectra with those of an independently obtained sample. The product yields are given in Table I and are determined using only the starting material reacted for calculation. The yields were obtained from integrated recorder curves after response to each compound had been measured and corrections made for varying responses.

Specific Irradiations. The general procedures described in the previous section were followed in each case. The essential information is given in Table I.

Ultraviolet Spectra of Methyl Phenoxyacetates and Transmission Curves for Light Filters. The uv spectra shown in Figure 1 were determined on 0.0022 *M* solutions of the three methyl phenoxyacetates in methanol using a Cary 14 uv spectrometer. The transmission curves for the three light filters shown in Figure 1 were determined on the actual filters used in irradiations by a Beckman Dk 2a uv spectrometer.

Registry No. 9, 1928-38-7; **10**, 4841-22-9; **11**, 6956-85-0; **14**, 2065-23-8.

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(2) O. M. Aly and S. D. Faust, *J. Agr. Food Chem.*, **12**, 541 (1964); G. R. Bell, *Botan. Gaz.*, **118**, 133 (1956); C. R. Aandres and R. J. Dario, *Rev. Dep. Quim., Univ. Nac. Colomb.*, **4**, 26 (1969); *Chem. Abstr.*, **74**, 124481e (1971).

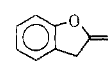
(3) D. P. Kelly and J. T. Pinhey, *Tetrahedron Lett.*, 3427 (1964).

(4) J. T. Pinhey and R. D. G. Rigby, *Tetrahedron Lett.*, 1267 (1969).

(5) D. G. Crosby and H. O. Tutlass, *J. Agr. Food Chem.*, **14**, 596 (1966).

(6) R. W. Binkley and T. R. Oakes, *Chemosphere*, in press.

(7) Methyl 2-hydroxyphenylacetate (**12**) cyclized to 2-coumaranone (**15**) to varying extents during glc analysis. The yield reported for **12** has been corrected for this conversion.



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(8) In the Vycor-filtered reactions even at low conversions color developed in the reaction mixtures and a significant amount of the incident radiation was not being absorbed by the starting material. This situation prevented reliable quantum yield determinations.

(9) A somewhat similar observation has been made by E. A. Caress and I. E. Rosenberg, *J. Org. Chem.*, **36**, 769 (1971).

(10) (a) J. C. Anderson and C. B. Reese, *J. Chem. Soc.*, 1781 (1963). (b) For a recent review, see D. Bellus, *Advan. Photochem.*, **8**, 109 (1971). (c) This similarity has been noted previously by Pinhey, *et al.*, in their complete paper on aromatic ether photochemistry: D. P. Kelly, J. T. Pinhey, and R. D. G. Rigby, *Aust. J. Chem.*, **22**, 977 (1969).

(11) A small but unspecified amount of phenoxyacetic acid (**1**) was also found (ref 4). 4-Hydroxyphenylacetic acid (*3*) was not reported (ref 4); however, since only the volatile materials were analyzed, it would not have been detected.

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The Molecular Geometry of β-Pinene as Deduced from the Crystal and Molecular Structure of *cis*-Pinocarvyl *p*-Nitrobenzoate†

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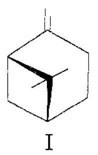
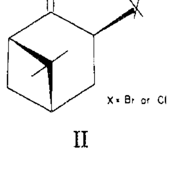
The crystal structure of *cis*-pinocarvyl *p*-nitrobenzoate (abbreviated name, *cis*-PNB), a derivative of β-pinene, has been determined from three-dimensional X-ray data obtained near the temperature of liquid nitrogen. The unit cell was monoclinic with the following dimensions: at approximately −193°, a = 10.583 ± 0.006 Å, b = 6.740 ± 0.003 Å, c = 10.443 ± 0.009 Å, β = 90.46 ± 0.15°; at approximately 22°, a = 10.904 ± 0.012 Å, b = 6.778 ± 0.006 Å, c = 10.906 ± 0.009 Å, β = 91.77 ± 0.27°. Systematic absences occurred for 0k0 when k was odd, indicating space group $P2_1$. The *p*-nitrobenzoate geometry is similar to that found in other *p*-nitrobenzene derivatives. The cyclobutane ring in the *cis*-pinocarvyl portion of the molecule is normal (internal dihedral angle 141°), leading to severe steric interactions between C-3 and C-7. These interactions are minimized in *cis*-PNB through a decreased puckering in the C-2,C-3,C-4 end of the molecule. The observed C-3···C-7 distance is 2.72 Å. Since the same interactions exist in β-pinene, it is postulated that the *cis*-pinocarvyl grouping and β-pinene have very similar molecular geometries. *cis*-PNB exhibits pseudo-mirror molecular symmetry, C-10 being the only nonhydrogen atom not related to another atom by the mirror plane.



I

β-Pinene (I) and related bicyclic terpenes undergo cyclobutane ring opening to yield monocyclic or acyclic molecules and cyclobutane ring expansion to form bornane or fenchane compounds.[1-3] Such rearrangements dominate β-pinene chemistry, suggesting that the original bicyclic ring system is relatively unstable.

It has been postulated that the rigid cyclobutane ring leads to severe distortions in the rest of the bicyclic system. Support for this idea is found in the reported crystal structures of chloro-3-nopinone and bromo-3-nopinone (II).[4] In these structures the cyclobutane ring is normal, but the angle between plane C-2,C-3,C-4 and the best



II

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† From theses submitted by R. A. M., J. A. H., and W. E. S. in partial fulfillment of the requirements of The Institute of Paper Chemistry for the degree of Doctor of Philosophy from Lawrence University, Appleton, Wis.