Lucibufagins. 2. Esters of 12-Oxo-2β,5β,11α-trihydroxybufalin, the Major Defensive Steroids of the Firefly *Photinus pyralis* (Coleoptera: Lampyridae)\(^1\)\(^a\)

Jerrold Meinwald,\(^*\)\(^1\) David F. Wiemer,\(^*\)\(^b\) and Thomas Eisner\(^*\)\(^c\)

*Contribution from the Department of Chemistry and the Section of Neurobiology and Behavior, Cornell University, Ithaca, New York 14853. Received July 28, 1978*

**Abstract:** Fireflies of the species *Photinus pyralis* (Coleoptera: Lampyridae) are shown to contain a group of closely related steroidal pyrones, named lucibufagins, which serve a defensive role. The five major steroids from this insect are characterized as esters (5, 6, 7, 11, 12) of 12-oxo-2β,5β,11α-trihydroxybufalin (9), chiefly on the basis of detailed spectral analyses. Selective proton decoupling \(^1\)C NMR experiments played a key role in making these structural assignments. These insect-derived steroids are the first bufadienolides to be isolated and characterized from an invertebrate source.

**Introduction**

The remarkable ability of fireflies (sometimes also called lightning bugs or glowworms) to produce light signals has been celebrated by poets and musicians. \(^1\) Biologists, \(^2\) biochemists, \(^3\) and organic chemists \(^4\) have studied the origin and meaning of these beetles' signals in depth. We have become interested in the chemical defenses of fireflies, and have recently reported that two locally available species, *Photinus ignitus* and *P. marginellus*, contain mixtures of at least three bufadienolides, for which we proposed the generic name lucibufagins. \(^5\) These steroids were shown to render the fireflies distasteful to birds. \(^6\)

We now report the complete structures of five lucibufagins isolated from *P. pyralis*. \(^7\) These insect steroids are the first insect-derived bufadienolides to be fully characterized. Data on their deterrent effect on birds and ants will be described elsewhere.

**Results and Discussion**

Employing the extraction procedure previously described, \(^7\) ~2.8 g of crude steroid was isolated from ~28 000 freeze-dried, lanternnecotomized animals (\*P. pyralis\*). \(^8\) This extract was further fractionated by column chromatography, which afforded five compounds (initially designated as A, B, C, D, and E) in order of increasing retention volume) in the ratio of 2:1:20:8:3. The major component, compound C, crystallized spontaneously, providing over 1 g of pure material. We focused our first efforts on determining the structure of this compound.

The infrared spectrum of C contains significant bands at 1635 and 1535 cm\(^{-1}\) (C=C), while its ultraviolet spectrum has a single maximum at 298 nm (\(ε \approx 5500\)). The ultraviolet absorption, together with the observation of a set of three interacting protons in the low-field region of the \(^1\)H NMR spectrum of C (Figure 1), indicates the presence of a conjugated system. The chemical shifts and coupling constants of the three low-field protons agree closely with those reported for 5-substituted 2-pyrones \(^9\) and, upon consideration of all of the spectral data, the presence of this pyrone moiety in C is clear. \(^10\) \(^11\) The chemical ionization mass spectrum (CIMS) of C establishes a molecular weight of 532, leaving 437 amu to be accounted for by the single substituent on the pyrone ring.

Our initial interpretation of the \(^1\)H NMR spectrum led to the hypothesis that C contains two quaternary methyl groups, two secondary acetoxyl groups, and a tertiary and two secondary hydroxyl groups. The \(^13\)C NMR spectrum shows 28 resonances and confirms the presence of two acetates (δ 20.5, 20.7, 168.8, and 169.2). This accounts for two of a total of five sp\(^3\) carbons bearing an oxygen substituent. In addition, a set of five resonances (δ 114.9, 120.9, 147.5, 149.8, and 162.5) agree well with expectations for the α-pyrone unit. \(^12\) Finally, a signal observed at δ 212.8 revealed the presence of a ketonic carbonyl group. With 28 carbons directly observed and 10 oxygens implied from the \(^13\)C NMR spectrum of C, the molecular formula C\(_{28}\)H\(_{36}\)O\(_{10}\) (mol wt 532) is required by its mass spectrum. Aside from the nine carbon resonances of the pyrone and acetate units, the remaining 19 signals present a pattern which suggests that C contains a saturated steroid nucleus, a conclusion consistent with the molecular formula and with the presence of two upfield methyl singlets in its \(^1\)H NMR spectrum.

Steroidal pyrones, previously isolated only from certain toads and a small group of plants, \(^13\) often possess desirable cardiotonic properties. This class of steroids, the bufadienolides, is characterized by a cis-anti-trans-syn-cis stereo skeleton bearing β- and 14β-oxygen substituents and a 17β-pyrono substituent. We assumed (and later confirmed) the presence of these same features in compound C, placing an acetoxyl group at the C-3 position (vide infra) to derive the part structure 1.

The electron impact mass spectrum (EIMS) of C, although dominated by cleavage of the acetyl groups (m/e 43), does contain useful fragments of higher molecular weight. In addition to the weak molecular ion (m/e 532), diagnostic peaks were observed at m/e 123, 135, 136, 191, 201, and 204. The three lower molecular weight fragments in this group are characteristic of bufadienolides which are devoid of oxygen substituents at C-15, -16 and -17. \(^14\) The three remaining ions, also prominent in the mass spectrum of arenobufagin (2), have...
been assigned structures which include the pyrone ring, the 14-hydroxylated D ring, and the C-12 carbonyl group on the basis of high resolution mass spectrometry. The mass spectrum of C therefore suggests the presence of a carbonyl group at C-12 as well as the usual C-14 hydroxyl group.

Treatment of C with methanolic ammonia gave a deacetylated steroid whose mass spectrum was instructive. A molecular ion at m/e 448 (11%) was detected, as well as the characteristic peaks at m/e 123, 135, 136, 191, 201, and 204, previously observed in the mass spectrum of C itself. High resolution mass measurements established the anticipated molecular formula C$_{24}$H$_{32}$O$_8$ for this deacetylated product, and confirmed the compositions of four important fragment ions (Table I). Of these, the m/e 191 and 204 fragments, previously characterized as 3 and 4 by Pettit et al., are particularly important because they provide direct support for the presence of C-12 carbonyl and C-14 hydroxyl functions, and for the absence of oxygen substituents at C-15, -16 and -17.

In order to establish the positions of the remaining oxygen substituents, it was necessary to resolve an apparent discrepancy between the $^1$H and the $^{13}$C NMR spectra. Off-resonance decoupling experiments established that of the five sp$^3$ carbon atoms bonded to oxygen, two bear no protons (δ 84.1 (s) and 73.1 (s)), and three bear a single proton (δ 72.8 (d), 70.0 (d), and 67.8 (d)). However, our initial interpretation of the $^1$H NMR spectrum had suggested that four oxygen substituents were secondary and only one tertiary. In order to resolve this conflict, we conducted selective proton decoupling experiments,
carefully controlled to decouple single protons. These experiments revealed that the protons found at \( \delta 5.5, 5.1 \) (2 CHOAc), and 4.4 (CHOH) are bonded to the carbons appearing at \( \delta 70.0, 67.8, \) and 72.8 ppm, respectively. However, the remaining downfield proton (\( \delta 4.1 \)) was found to be joined to a carbon which absorbs at \( \delta 40.4 \) (d), a position too far upfield to represent an oxygen-bearing carbon. Thus it can be concluded that compound C contains two secondary acetoxy functions, one secondary hydroxyl group, and therefore two tertiary hydroxyls (one of which is already known to be at C-14). The nature of the methine proton which appears at \( \delta 4.1 \) (d of d, \( J = 9, 6 \) Hz) remains to be explained.

A more detailed examination of the \(^1H\) NMR spectral data allows determination of the positions of the remaining functional groups, and leads ultimately to the assignment of structure 5 to C. Of the remaining protons geminal to oxygen, one appears at \( \delta 4.40 \) as a doublet of doublets (\( J = 10, 3 \) Hz) which simplifies to a doublet (\( J = 10 \) Hz) upon addition of D\(_2\)O. This simple splitting pattern places this hydroxy group at C-11; the diaxial arrangement of the C-11 and C-9 protons is apparent from the large coupling constant, and necessitates the equatorial (\( \alpha \)) placement of the hydroxyl group. With this result in hand, it becomes possible to assign the position of the remaining (tertiary) hydroxyl group. Of the four possible tertiary sites (C-5, C-8, C-9, and C-17), two (C-9 and C-17) already have been eliminated on the basis of \(^1H\) NMR and mass spectral data. Introduction of an \( 8\beta \)- or \( 5\alpha \)-hydroxyl group is known to result in dramatic deshielding of the angular methyl groups\(^{15} \) and is not compatible with the observed chemical shifts. Thus the \(^1H\) NMR spectrum appears most consistent with the \( 5\beta \) placement of this tertiary hydroxyl group.

![Structure of the compound](image)

The two secondary acetoxy groups can be located by inspection of the coupling patterns and chemical shifts of their geminal protons. The doublet observed at \( \delta 5.53 \) (Figure 1) is too narrow to include a diaxial coupling. This signal is most easily accounted for by the assignment of one acetoxy group to the \( 3\beta \) position, an oxygenation pattern almost universally observed in bufadienolides.\(^8\) It is interesting to note that in eight known \( 3\beta \)-acetoxybufadienolides the \( 3\alpha \) proton appears at \( \delta 5.09 \pm 0.02.\) In bufadienolides which also bear a \( 5\beta \)-hydroxyl substituent, intramolecular hydrogen bonding has been invoked to explain a marked deshielding of the \( 3\alpha \) proton (\( \delta 5.28 \pm 0.01.\))\(^{15} \) as well as a more modest deshielding of the acetate methyl (\( \delta 2.09 \) vs. 2.04).\(^{15} \)

In compound C, one acetate methyl is observed at \( \delta 2.10, \) in accord with expectations for this type of interaction. The \( 3\alpha \) proton, however, appears even further downfield than expected (\( \delta 5.55.\)) This implies that still another electron-withdrawing group is nearby; the only possibility is the one remaining acetoxy group. The proton geminal to this final acetoxy group appears at \( \delta 5.10 \) as a doublet of triplets (\( J = 12, 4, 3 \) Hz), suggesting one diaxial coupling and two axial-equatorial couplings. Of the remaining positions on the A and B rings, this pattern can be achieved only by placement of the acetoxy group at the \( 2\beta \) position, leading unambiguously to structure 5. While all the functional groups are well accommodated for in this structure, the origin of the \(^1H\) NMR absorption at \( \delta 4.1 \) was not immediately apparent. However, the spectral studies of arenobufagin (2) described below resolved this problem.

In the \(^1H\) NMR spectrum of 2 there are signals easily attributable to the 11\( \alpha \) proton (\( \delta 3.45, d, J = 10, 3 \) Hz) and to the 11-hydroxyl proton (\( \delta 3.82, d, J = 3 \) Hz, exchanges with D\(_2\)O). These signals correspond closely in chemical shift and coupling pattern to the analogous protons of 5. Furthermore, by using the observed chemical shifts of arenobufagin's angular methyl groups as base values and employing the empirical rules of Gsell and Tamm\(^{15} \) to incorporate the effects of acetylation of C-3 and hydroxylation at C-5, it is possible to calculate the expected chemical shifts for the angular methyl groups of 5. The calculated (C-18, \( \delta 0.95; \) C-19, \( \delta 1.20 \)) and the observed values (C-18, \( \delta 0.89; \) C-19, \( \delta 1.20 \)) agree well, providing additional support for the position and stereochemistry of the function groups.\(^{17} \)

The \(^1H\) NMR spectrum of 2 contains two overlapping absorptions at \( \delta 4.10.\) Acetylation results in a downfield shift of \( \sim 1 \) ppm for one of these signals, presumably the \( 3\alpha \) proton, while the second signal, whose splitting pattern can now be seen (d of d, \( J = 9, 6 \) Hz), is unaffected. This absorption can be attributed only to the C-17 proton, strongly deshielded by proximity to the C-12 carbonyl group. Similar deshielding of a 17\( \alpha \) proton in a 12-keto cardenolide has been reported in the case of sarverogenin (13).\(^{18} \) The analogous \( \delta 4.1 \) signal in the

![Structure of compound 5](image)

\(^{1H}\) NMR spectrum of 5 can therefore be assigned with confidence to the 17\( \alpha \) proton in this C/D cis-fused 12-ketobufadienolide.

To help assign the \(^13C\) resonances in 5, the \(^13C\) NMR spectrum of 2 was recorded. Many of the resonances could be assigned by comparison with pyrone\(^12\) and cardenolide\(^{19} \) models. Close agreement is observed between the spectra of 2 and 5, and thus many assignments can be made (Figure 2).

The signals attributed to C-11-C-24, except for C-19, are assigned by comparison with pyrone\(^12\) and cardenolide\(^{19} \) models. Close agreement is observed between the spectra of 2 and 5, and thus many assignments can be made (Figure 2).

The calculated (C-18, \( \delta 0.95; \) C-19, \( \delta 1.20 \)) and the observed values (C-18, \( \delta 0.89; \) C-19, \( \delta 1.20 \)) agree well, providing additional support for the position and stereochemistry of the function groups.\(^{17} \)

The \(^1H\) NMR spectrum of 2 contains two overlapping absorptions at \( \delta 4.10.\) Acetylation results in a downfield shift of \( \sim 1 \) ppm for one of these signals, presumably the \( 3\alpha \) proton, while the second signal, whose splitting pattern can now be seen (d of d, \( J = 9, 6 \) Hz), is unaffected. This absorption can be attributed only to the C-17 proton, strongly deshielded by proximity to the C-12 carbonyl group. Similar deshielding of a 17\( \alpha \) proton in a 12-keto cardenolide has been reported in the case of sarverogenin (13).\(^{18} \) The analogous \( \delta 4.1 \) signal in the
familiar series of fragment ions which are diagnostic for the pyrone ring plus the C-12 carbonyl and C-14 hydroxyl functions. In common with the mass spectra of 5, 6, and 7, the base peak in the mass spectrum of A (m/e 43) results from cleavage of an acetyl moiety, but a new peak at m/e 71 (43%) implies the presence of a larger acyl group as well. This is confirmed by the 13C NMR spectrum of A, which exhibits 30 signals, 26 of which find close counterparts in the spectrum of 5 and four of which can be ascribed to an isobutyrate residue in place of one of the two acetate functions in 5. The low-field portion of the 1H NMR spectrum of A is virtually identical with that of 5, indicating acylation of both the 2β- and 3β-hydroxy groups, while the upfield region contains two new doublets, as expected for the methyl groups of an isobutyrate ester. In order to determine which acyl group was at C-2 and which at C-3, samples of the monoacetates 6 and 7 were each treated with isobutyryl chloride and the course of the acylation was followed by LC. In the case of 6, the initial product had a retention time (Rt) identical with that of A, and this was further esterified to yield a bisisobutyrate (10) of slightly longer Rt. In contrast, the initial product from 7 did not agree in Rt with A, and a new bis ester was produced. Treatment of A itself with isobutyryl chloride afforded a bisisobutyrate (10) indistinguishable from that obtained from 6. A can therefore be assigned structure 11. In a completely analogous fashion, B was shown to be the 2-acetate 3-propionate (12) (see the Experimental Section for details).

These five steroids (5, 6, 7, 11, and 12) are the first bufadienolides to be isolated and characterized from an arthropod source. In view of the known biological properties of the bufadienolide family, and our preliminary bioassays, which revealed that these steroids render fireflies distasteful to birds, it seems clear that these compounds have a defensive value to the fireflies. The other biological properties of these bufadienolides, as well as their distribution among the Lampyridae and related animals, are subjects under active investigation.

Experimental Section

Melting points were recorded on a Thomas-Hoover melting point...
apparatus and are uncorrected. Ultraviolet spectra were obtained on a Cary 14 spectrophotometer and infrared spectra (in CHCl₃) were recorded with a Perkin-Elmer 257 grating infrared instrument. The 90-MHz 1H NMR spectra were obtained on a Varian EM-390 instrument while the 250-MHz spectrum of 5 was recorded at the NIH NMR Facility for Biomedical Studies, Mellon Institute, Pittsburgh. Deuteriochloroform was used as solvent unless otherwise noted and chemical shifts are reported in parts per million downfield from (CH₃)₄Si. Routine 13C NMR spectra were obtained on a Varian CFT-20 spectrometer with the following parameters representing a typical set of conditions: spectral width, 4000 Hz; acquisition time, 1.023 s; pulse width, 10 μs; data points, 8192. Chemical shifts are reported in parts per million downfield from the (CH₃)₄Si using the CFT-20 spectrometer with the following parameters representing a typical set of conditions: spectral width, 4000 Hz; acquisition time, 1.023 s; pulse width, 10 μs; data points, 8192. Chemical shifts are reported in parts per million downfield from (CH₃)₄Si.

Isolation of 5, 6, 7, 11, and 12. Freeze-dried and lanternectomized F. parisi (28000 animals, ~280 g) were suspended in dichloromethane (3 L) and allowed to stand at 0°C for 2 days.23 The mixture was filtered, and the resulting solution containing vacuum-dried 100% hexane to afford an oily residue. After this residue was washed with hexane, the resulting solution was concentrated in vacuo to afford a glass which resisted crystallization. This material, which had spontaneously crystallized after chromatography, was purified by column chromatography (silica gel; 3:3:4 acetone-water, 2), 472 (1), 454 (2), 436 (5), 412 (6), 394 (18), 376 (24), 358 (25), 221 (14), 204 (25), 201 (2), 191 (2), 175 (6), 135 (7), 123 (5), 123 (3), 123 (2), 123 (3), 123 (4), 47 (10).

Treatment of compound 11 with butyric anhydride (0.5 mL) was added to a solution of the diacetate 5 (53 mg, 0.1 mmol) in pyridine (1 mL) and the resulting solution heated at 65°C for 2 h. After removal of the volatile material in vacuo, the residue was purified by flash chromatography on silica gel; 3:3:4 acetone-chloroform-hexane to afford the triacetate 9 (48 mg, 84%; mp 109–111°C). 'H NMR δ 0.36 (3, s), 1.18 (3, s), 1.34–1.4 (16, m), 1.97 (3, s), 2.07 (3, s), 2.13 (3, s), 4.06 (1, d, J = 9, 6 Hz), 5.20 (1, d, J = 12, 3, 5 Hz), 5.50 (1, d, J = 12, 5 Hz), 5.57 (1, br), 6.30 (1, d, J = 10 Hz), 7.34 (1, d, J = 2, 7 Hz), 7.77 (1, d, J = 9, 6 Hz), 8.42 (1, d, J = 12, 3, 5 Hz), 10.02 (1, br, d). EIMS (70 eV) m/e (rel intensity) 574 (M⁺, 1), 556 (M⁺ – H₂O, 1), 514 (1), 496 (1), 412 (2), 394 (4), 376 (1), 220 (8), 205 (28), 204 (2), 191 (20), 175 (6), 135 (2), 137 (2), 63 (11), 63 (4), 16 (10).

Treatment of both monoacetates 6 and 7 with Ac₂O-pyridine in a similar manner afforded the same triacetate (TLC, LC, and 1H NMR).

12-Oxo-23,32-di-O-acetyl-5,11a-trihydroxybufalin (9). Diacetate 5 (100 mg, 0.2 mmol) was dissolved in methanol saturated with ammonia and the resulting solution stirred at room temperature for 4 h. Evaporation of the volatile material in vacuo afforded the deacetylated product 9 (84 mg, 95%). Purification by column chromatography (silica gel; 9:1 chloroform-methanol gave 9 as a white solid (mp 168–170°C) accompanied by a second component which appeared to be the 11-oxo-12-hydroxy isomer. 'H NMR (CDCl₃) δ 0.80 (3, s), 1.03 (3, s), 1.21–2.4 (14, m), 5.77 (1, br), 6.30 (1, d, J = 10 Hz), 7.34 (1, d, J = 2, 7 Hz), 7.77 (1, d, J = 9, 6 Hz), 8.42 (1, d, J = 12, 3, 5 Hz), 10.02 (1, br, d). EIMS (70 eV) m/e (rel intensity) 448 (M⁺, 11), 430 (M⁺ – H₂O, 16), 412 (M⁺ – 2H₂O, 25), 404 (10), 394 (18), 387 (19), 369 (24), 214 (44), 208 (20) (36), 191 (41), 175 (44), 149 (100), 136 (20), 135 (37), 123 (20), 123 (22), 123 (23), 123 (24)

Treatment of compound 11 with isobutyryl chloride under identical conditions also gave compound 10, while the analogous reaction of 7 afforded a different compound.

12-Oxo-23-α,32-β-isobutyryl-5,11a-trihydroxybufalin (10). Isobutyryl chloride (100 μL) was added dropwise to a solution of 6 (100 mg, 0.2 mmol) in pyridine (1 mL) and portions of the resulting solution were removed periodically for LC analysis. During the course of this reaction, the concentration of 6 decreased and a product with Rf identical with that of 11 was observed. As the reaction neared completion, only a second product of slightly longer Rf was detected. Evaporation of the volatile material in vacuo and purification of the residue by column chromatography gave 10 as a glass (55 mg, 74%). The 1H NMR spectrum of 10 was very similar to that of the triacetate 9, except that two acetate methyl group resonances were replaced by butyrate signals (δ 1.19 (6, d, J = 7 Hz), 1.20 (6, d, J = 7 Hz), 5.27 (2, sept, J = 7 Hz); EIMS (70 eV) m/e (rel intensity) 630 (M⁺, 0.1), 612 (M⁺ – H₂O, 0.1), 394 (5), 204 (5), 201 (2), 191 (12), 175 (19), 153 (4), 135 (3), 123 (4), 47 (10).

Treatment of compound 11 with isobutyryl chloride under identical conditions also gave compound 10, while the analogous reaction of 7 afforded a different compound.

12-Oxo-23-α,32-β-isobutyryl-5,11a-trihydroxybufalin (10). Isobutyryl chloride (100 μL) was added dropwise to a solution of 6 (100 mg, 0.2 mmol) in pyridine (1 mL) and portions of the resulting solution were removed periodically for LC analysis. During the course of this reaction, the concentration of 6 decreased and a product with Rf identical with that of 11 was observed. As the reaction neared completion, only a second product of slightly longer Rf was detected. Evaporation of the volatile material in vacuo and purification of the residue by column chromatography gave 10 as a glass (55 mg, 74%). The 1H NMR spectrum of 10 was very similar to that of the triacetate 9, except that two acetate methyl group resonances were replaced by butyrate signals (δ 1.19 (6, d, J = 7 Hz), 1.20 (6, d, J = 7 Hz), 5.27 (2, sept, J = 7 Hz); EIMS (70 eV) m/e (rel intensity) 630 (M⁺, 0.1), 612 (M⁺ – H₂O, 0.1), 394 (5), 204 (5), 201 (2), 191 (12), 175 (19), 153 (4), 135 (3), 123 (4), 47 (10).

Treatment of compound 11 with isobutyryl chloride under identical conditions also gave compound 10, while the analogous reaction of 7 afforded a different compound.

12-Oxo-23-α,32-β-isobutyryl-5,11a-trihydroxybufalin (10). Isobutyryl chloride (100 μL) was added dropwise to a solution of 6 (100 mg, 0.2 mmol) in pyridine (1 mL) and portions of the resulting solution were removed periodically for LC analysis. During the course of this reaction, the concentration of 6 decreased and a product with Rf identical with that of 11 was observed. As the reaction neared completion, only a second product of slightly longer Rf was detected. Evaporation of the volatile material in vacuo and purification of the residue by column chromatography gave 10 as a glass (55 mg, 74%). The 1H NMR spectrum of 10 was very similar to that of the triacetate 9, except that two acetate methyl group resonances were replaced by butyrate signals (δ 1.19 (6, d, J = 7 Hz), 1.20 (6, d, J = 7 Hz), 5.27 (2, sept, J = 7 Hz); EIMS (70 eV) m/e (rel intensity) 630 (M⁺, 0.1), 612 (M⁺ – H₂O, 0.1), 394 (5), 204 (5), 201 (2), 191 (12), 175 (19), 153 (4), 135 (3), 123 (4), 47 (10).
Identity of the Chain-Carrying Species in Halogenations with Bromo- and Chloroarylalkoxyiodinanes: Selectivities of Iodinanyl Radicals

Ronald L. Amey and J. C. Martin*

Contribution from Roger Adams Laboratory, School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801. Received October 11, 1978

Abstract: The free-radical halogenation of substituted toluenes by haloiodinanes 2a-b and 3a-b in benzene solvent is highly selective for benzylic hydrogens. The process involves cyclic iodinanyl radicals, except in the case of 3b, which appears to react via a bromine atom chain. The essentially identical values of \( \nu^* \) for 2a (-1.46) and 2b (-1.48) are consistent with there being a common chain-carrying species for both bromination and chlorination. Identical \( \nu^* \) values were not observed for 3a (-1.31) and 3b (-1.55 vs. Br. -1.58). Such iodinanyl radicals, unlike those derived from phenyliodine dichloride, are constrained to a C=O angle far smaller than 180°, allowing an opportunity to study the effects of bonding on radical selectivities. The intermediacy of iodinanyl radicals in free-radicals chlorinations is further supported by evidence from photoinitiated reactions of iodinanyl radicals. The allylic chlorinations of \( \alpha \)C-1-O angle far smaller than 1

Introduction

Organic compounds of tricoordinate iodine(III) may be generally designated as hypervalent iodine species and more specifically as iodinanes. The formation of iodine-centered radical intermediates from such iodinanes, since it involves breaking weak bonds to iodine, is expected to be an energetically favorable process.