

SYNTHESIS, STRUCTURE, AND SELF-OXIDATION OF ALKYNYL(PHENYL)IODONIUM PERIODATES

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Synthesis and characterization of alkynyl(phenyl)iodonium periodate (**2**) are described; on standing at room temperature, the product undergoes the carbon-carbon triple bond cleavage by self-oxidation with the counter anion, IO_4^- .

KEYWORDS alkynyliodonium periodate; X-ray analysis; self-oxidation; carboxylic acid; ligand exchange; triple bond cleavage

Alkynyl(phenyl)iodonium salts are versatile intermediates in organic synthesis.¹⁻⁶ Conjugate addition of nucleophiles to the β -carbon offers a useful route for the synthesis of cyclopentenones, polysubstituted furans, and β -heteroatom-substituted alkenyliodonium salts.¹⁻³ The ligand exchange reaction of *tert*-butylethynyl group at trivalent iodine with 2-lithiofuran yielding aryl(2-furyl)iodonium tosylates has been reported.⁴ Because of the high leaving ability of the phenyliodonium group, alkynyl(phenyl)iodonium salts formally serve as reactive, alkynyl cation equivalents and afford substitution products by the reaction with some nucleophiles, with concomitant reductive elimination of iodobenzene.^{5,6} Here we report a synthesis and an X-ray structure analysis of hitherto unknown alkynyl(phenyl)iodonium periodates, which undergo self-oxidation by the counter anion yielding carboxylic acids.

The required alkynyl(phenyl)iodonium tetrafluoroborates (**1**) were prepared from 1-alkynes and/or alkynyltrimethylsilanes according to the method developed by us.^{5,7} When a solution of 3,3-dimethyl-1-butynyl(phenyl)iodonium tetrafluoroborate (**1d**) in dichloromethane was vigorously shaken two times with a saturated aqueous solution of sodium periodate (20 equiv.) using a separatory funnel, a ligand exchange took place and the iodonium periodate (**2d**) was obtained as colorless plates in 96% yield. A broad, strong band at $980\text{--}1120\text{ cm}^{-1}$ characteristic of the BF_4^- anion, which appeared in the IR spectrum of **1d**, disappeared and instead strong bands at 855 and 845 cm^{-1} assigned to IO_4^- appeared in **2d**.⁸ Similarly, alkynyliodonium periodates (**2a-c**) were prepared in high yields (**2a**: 98%, **2b**: 91%, **2c**: 94%).

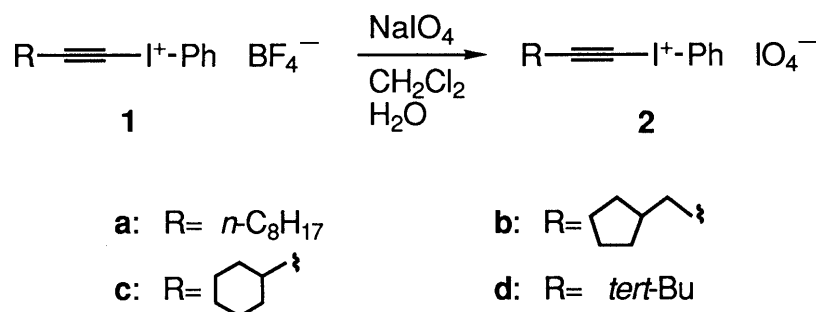
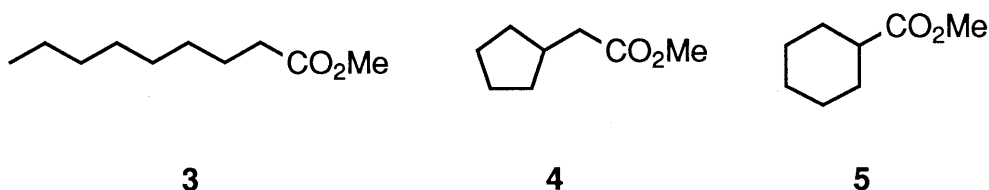


Chart 1

The periodate (2d) was stable on standing at room temperature for a few days, because of a large steric demanding by the tert-butyl group; however, the other periodates (2a-c) readily underwent the carbon-carbon triple bond cleavage by self-oxidation with the counter anion, IO_4^- , yielding the corresponding carboxylic acids. Standing 1-decynyl-(phenyl)iodonium periodate (2a) at room temperature over night followed by the treatment with diazomethane afforded methyl nonanoate (3) in 35% yield. With 2b and 2c, methyl cyclopentylacetate (4) and methyl cyclohexylcarboxylate (5) were obtained in 40 and 37% yields, respectively. When 2a was treated with 5 equiv. of sodium periodate in dichloromethane-water for 24 h at room temperature and then with diazomethane, the yield of 3 increased up to 52%.



X-ray study of 2d revealed that the I(1) atom is bonded by C(1) [2.006(13) Å], C(7) [2.124(9) Å], and O(1) [2.618(9) Å] which are arranged in a distorted T-shape geometry [$\angle \text{C}(1)\text{--I}(1)\text{--C}(7) = 93.1(4)^\circ$, $\angle \text{C}(1)\text{--I}(1)\text{--O}(1) = 172.4(4)^\circ$, $\angle \text{C}(7)\text{--I}(1)\text{--O}(1) = 81.1(3)^\circ$] as seen in other trivalent organoiodine compounds (Fig. 1).^{9,11} The I(1)–O(1) bond is very long, compared with the computed covalent single bond length of 1.99 Å,¹² and there is no significant difference among the I–O bond lengths [1.74(1)–1.78(1) Å] of the periodate group. These indicate that the molecule to has an ionic character similarly to phenylethynyl(phenyl)iodonium tosylate (I–O = 2.56 Å).¹³ The bond lengths of I(1)–C(1) and I(1)–C(7) are compatible with the corresponding ones of trimethylsilylethynyl(phenyl)iodonium tetrafluoroborate¹⁴ and phenylethynyl(phenyl)iodonium tosylate.¹³ Two molecules, related by an inversion center in the crystal, form the bimolecular unit bound by the secondary bonds, I(1)–O(1') [3.387(9) Å] and I(1)–O(2') [3.235(10) Å], as shown in

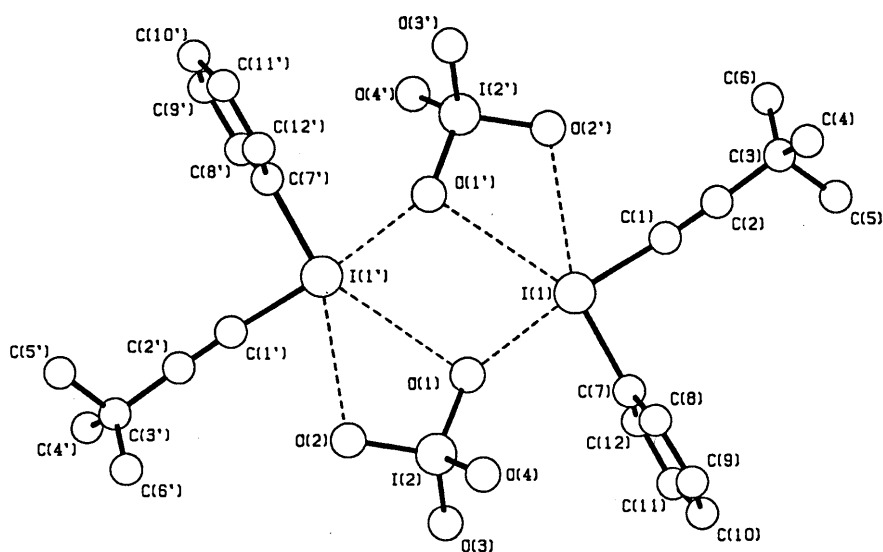


Fig. 1. Structure of the Bimolecular Unit Formed around an Inversion Center in the Crystal of 2d
Symmetry related atoms in one of the pair are primed in the other.

Fig. 1. The results suggest that the molecule adopts a distorted trigonal bipyramidal configuration with the I(1)-C(1), I(1)-C(7), and I(1)-O(1) bonds, the apical positions being occupied by C(1) and O(1).

Thus, the stable alkynyliodonium periodate (2d), which has two iodine atoms of different oxidation states in the molecule, namely trivalent and heptavalent iodines, was synthesized and the structure was unambiguously established by X-ray diffraction.

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- 8) Selected physical and spectroscopic data for 2d, mp 114-115°C (dec., from dichloromethane-hexane). IR_{max}^{KBr} cm⁻¹: 3075, 2970, 2175, 2145, 1470, 1440, 1250, 985, 855, 845, 820, 740, 730 cm⁻¹. ¹H-NMR(in CDCl₃)δ: 1.24 (9H, s), 7.40-7.75 (3H, m), 8.00-8.15 (2H, m). ¹³C-NMR(in CDCl₃)δ: 20.3(s), 29.8(q), 116.6(s), 118.9(s), 132.5(d), 132.6(d), 133.7(d). Fast atom bombardment MS m/z : 285 (M⁺-IO₄).
- 9) Crystal data for 2d, C₁₂H₁₄O₄I₂, M_w = 476.1, monoclinic, P2₁/c, a = 12.028(5), b = 6.178(3), c = 21.201(10) Å, β = 93.39(5)°, V = 1573(1) Å³, D_c = 2.010 g cm⁻³, Z = 4, F(000) = 896, Mo-K_α radiation (λ = 0.7107 Å), μ(Mo-K_α) = 40.5 cm⁻¹. The intensity data were collected on a Rigaku AFC-5R diffractometer in the range 0.2 ≤ 2θ ≤ 47.0°. Of 2316, 2037 unique reflections were observed [|F_o| > 3σ(F_o)]. Three standard reflections monitored every 100 reflections showed no significant change during data collection. The structure was solved by the conventional heavy-atom method and refined by the block-diagonal least-squares technique of positional and anisotropic thermal parameters of non-H atoms. H atoms could not be located in a difference electron density map. Absorption corrections were applied by an empirical method.¹⁰⁾ The final R and R' were 0.056 and 0.074 for 2010 reflections, respectively. The weighting scheme was w = [σ²(F_o) + 0.00433|F_o|²]⁻¹ for the observed reflections with w^{1/2}|ΔF| > 4.0 and w = 0 otherwise.
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