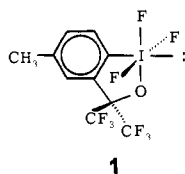


An Alkoxyaryltrifluoroperiodinane. A Stable Heterocyclic Derivative of Pentacoordinated Organoiodine(V)¹

Sir:

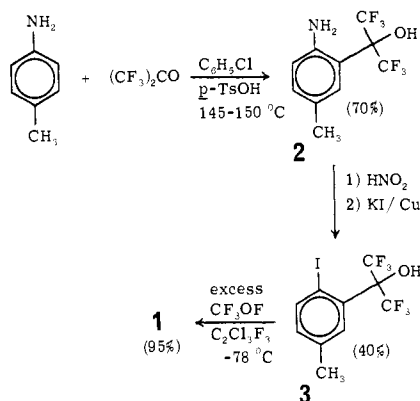
Iodine pentafluoride has been known since 1870² and a few organic derivatives, in which one of the fluorine ligands has been replaced by a perfluoroalkyl or a perfluoroaryl group, have been prepared.³ In 1972 Oates and Winfield reported⁴ a series of derivatives of IF₅ in which fluorines were replaced by simple alkoxy ligands. These were unstable above 20 °C. The only analogous compound reported with an aryl ligand other than pentafluorophenyl is C₆H₅IF₄,⁵ a compound sufficiently reactive that its characterization was left incomplete.

We now report the isolation and characterization of periodinane **1**,⁶ a stable compound including, in a five-membered



ring, an alkoxy ligand and a simple aryl ligand to iodine(V). In sharp contrast to its acyclic analogues, heterocyclic periodinane **1** is a stable compound showing a reactivity pattern which we ascribe to a strong stabilizing influence of the five-membered ring. The synthesis of **1** was effected by the route of Scheme I.

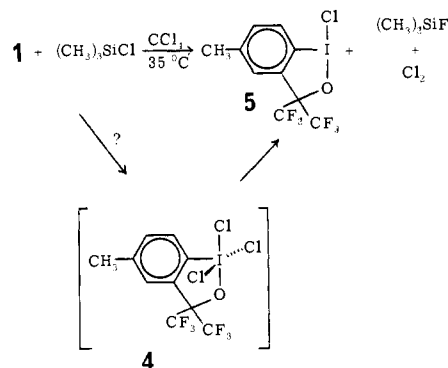
Scheme I



The product was recrystallized from C₂Cl₃F₃ to give **1**, mp 191–193 °C dec.¹⁰ The crystalline material is stable indefinitely at room temperature. The ¹⁹F NMR doublet at δ 13.20 ppm¹⁰ and triplet at δ 41.57 ppm¹⁰ ($J_{FF} = 116$ Hz) are assigned to the nonequivalent fluorines attached to iodine, consistent with the postulated octahedral structure depicted for **1**. Although other structures for **1** are consistent with the available spectral data (for example, one which places the alkoxy ligand opposite the electron pair), the structure illustrated is preferred on the basis of structures reported for several phosphorus analogues.¹¹

Solid periodinane **1** is unreactive toward atmospheric moisture at room temperature. It disappears slowly (4 days) in acetonitrile-*d*₃, as evidenced by ¹⁹F and ¹H NMR spectra. The periodinane in CD₃CN solution etches glass. No reaction products from **1** have been identified.

The addition of trimethylsilyl chloride (3 or more equiv) to a suspension of **1** in CCl₄ at 35 °C forms chloroiodinane¹² **5**, trimethylsilyl fluoride, and chlorine,¹³ possibly via **4**. Iodinane **5** was identified by comparison of the isolated material with authentic **5**, prepared from iodo alcohol **3** and *tert*-butyl hy-



pochlorite. The success of this ligand exchange reaction suggests that planned studies of analogous reactions, such as that with alkoxytrimethylsilanes, will make a wide variety of periodinanes accessible.

The exceptionally low reactivity of **1**, in comparison with its acyclic analogues, suggests the importance for pentacoordinate iodine(V) species of the stabilizing "five-membered ring effect", for which evidence may be adduced in the chemistry of pentacoordinate phosphorus(V),¹⁴ tetracoordinate sulfur(IV),¹⁵ hexacoordinate sulfur(VI),⁹ and tricoordinate iodine(III).¹⁶ Further studies on the structure and reactivity of periodinanes are currently underway in this laboratory.

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- Anal. (C₁₀H₈F₉O) C, H, I. IR (Fluorolube mull): 1575 (s), 1460 (s), 1380 cm⁻¹ (w). ¹H NMR (CD₃CN): δ 2.56 (s, 3, CH₃), 7.73 (s, 1, H ortho to C(CF₃)₂), 7.89 (d, 1, H para to C(CF₃)₂, $J = 8$ Hz), 8.29 (d, 1, H ortho to I, $J = 8$ Hz). ¹⁹F NMR (CD₃CN): δ 13.20 (d, 2, F cis to oxygen, $J_{FF} = 116$ Hz), 41.57 (t, 1, F trans to oxygen, $J_{FF} = 116$ Hz), 74.30 (t, 6, CF₃, $J_{FCF_3} = 8$ Hz). ¹⁹F NMR chemical shifts reported in parts per million upfield from CFCl₃ standard. Mass spectrum (10 eV) m/e (rel intensity): 440 (14.9, M⁺), 421 (2.0, M - F), 402 (2.0, M - 2F), 371 (100, M - CF₃).
- For example, hexacoordinate phosphorus ions such as R₂PF₄⁻ and RHPF₄⁻, have been shown to exist with the more apophilic ligands disposed trans to each other. See (A) E. O. Bishop, P. R. Carey, J. F. Nixon, and J. R. Swain, *J. Chem. Soc. A*, 1074 (1970); (b) R. G. Cavell and J. F. Nixon, *Proc. Chem. Soc. London*, 229 (1964); (c) J. Jander, D. Börner, and U. Engelhardt, *Justus Liebig's Ann. Chem.*, **726**, 19 (1969).
- Anal. (C₁₀H₈ClF₉O) C, H, Cl. Melting point: 179–180 °C. IR (KBr): 1279 (m), 1225 (s), 1169 (s), 1149 (s), 1120 (s), 750 (s), 370 cm⁻¹ (s). ¹H NMR (CDCl₃, 220 MHz): δ 2.55 (s, 3, CH₃), 7.50 (s, 1, H ortho to C(CF₃)₂), $W_{1/2} = 9$ Hz), 7.63 (d, 1, H para to C(CF₃)₂, $J = 9$ Hz), 7.90 (d, 1, H ortho to I, $J = 9$ Hz). ¹⁹F NMR (CDCl₃): δ 76.13 (d, CF₃, $J = 1.38$ Hz). Mass spectrum (70 eV) m/e (rel intensity): 418 (40, M⁺), 383 (24.0, M - Cl), 349 (100, M - CF₃), 314 (27.5, M - Cl, CF₃), 245 (91.8, M - 2CF₃, Cl).
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 (16) For a qualitative comparison of iodine reactivities, compare the following: (a) C. Willgerodt, *J. Prakt. Chem.*, [2] **33**, 154 (1886); (b) G. P. Baker, F. G. Mann, N. Sheppard, and A. J. Tetlow, *J. Chem. Soc.*, 3721 (1965); (c) W. C. Agosta, *Tetrahedron Lett.*, 2681 (1965).

Ronald L. Amey, J. C. Martin*

The Roger Adams Laboratory, University of Illinois
 Urbana, Illinois 61801

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Triplet Carbonyl-Olefin Charge-Transfer Complexes. A CNDO Treatment

Sir:

Several reports have appeared recently in which the postulated exciplexes of n, π^* formaldehyde and ammonia have been examined theoretically.¹ However, in spite of the mounting evidence for the existence of $^3n, \pi^*$ carbonyl-olefin exciplexes,² their existence has not been confirmed by any theoretical treatment.³ Our interest in carbonyl-olefin photochemistry⁴ has prompted us to apply the CNDO method to an investigation of excited-state complexes in these systems.

The exciplexes of $^3n, \pi^*$ carbonyl compounds with olefins are thought to exhibit moderate charge-transfer (CT) character. Therefore the propensity of quinones to serve as electron acceptors might be expected to facilitate exciplex formation and to lead to high exciplex stabilization energies.⁵ In the hopes that the existence of these more stable exciplexes might be more easily demonstrated than those arising from simple carbonyl compounds, we have examined the *p*-benzoquinone-ethylene ensemble by the CNDO method.

Calculations were performed for a large variety of geometries of the *p*-benzoquinone-ethylene system.⁶ The procedure chosen was to use CNDO/2 to calculate ground-state (closed-shell singlet) energies as a function of geometry, and to calculate the singlet-triplet energy differences by CNDO/S, which is known to represent these quantities best.⁷ Approaches along a vector connecting the carbonyl oxygen with the center of the ethylene double bond, both in the plane of the carbonyl π orbitals (geometries 1 and 3, Figure 1) and in the plane of the nonbonding orbitals (geometries 2 and 4, Figure 1), were examined systematically at distances of less than 2.00 Å. No matter what the direction of ethylene approach in the front oxygen hemisphere (angles 90-180°, Figure 1) the lowest singlet state was found to cross from the conventional ground state (little or no CT) to a CT state at separations of between 1.85 and 2.00 Å. In this crossing region the lowest triplet state drops below the singlet states (Figures 2 and 3a). In all four approach geometries, 1-4, a family of triplet minima as a function of the angle of approach, α , could be assembled into a trough around the carbonyl oxygen. The minima of the cross sections of these troughs drop in energy, increase in depth below the singlet state, and move closer to the carbonyl oxygen as the approach angle α goes from 90 to 180°. At 180°, approach geometries 1 and 2 converge to form a trough minimum which constitutes an *n* complex 5: $D_{\min} = 1.86$ Å, $\Delta E_{TS} = -19.7$ kcal/mol. In the same fashion approach geometries 3 and 4 converge to form another trough minimum which constitutes a π complex 6: $D_{\min} = 1.90$ Å, $\Delta E_{TS} = -17.3$ kcal/mol. Rotation about the carbonyl axis interconverts these two trough minima across an energy barrier of 7.7 kcal/mol.

It is encouraging to note that this type of complex is not

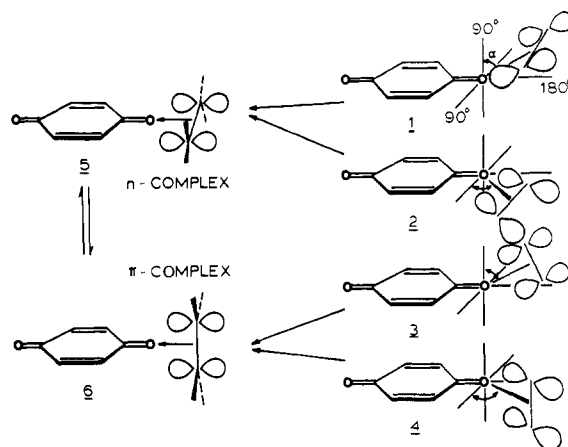


Figure 1. Carbonyl-olefin approach geometries, 1-4, and complex minimum geometries, 5 and 6.

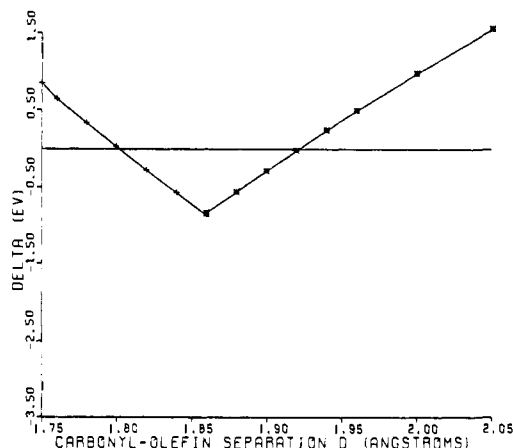


Figure 2. Energy differences, ΔE_{TS} , between the lowest triplet, 3B_1 ($\dots 5b_1 12a_1$), and the lowest singlet state for approach geometry 5: to the right of the minimum 1A_1 ($\dots 12a_1 4b_1$) (conventional singlet), to the left of the minimum 1A_1 ($\dots 11a_1 5b_1$) (CT singlet).

Table I. CT Properties of Carbonyl-Olefin Complexes

	<i>p</i> -Benzoquinone-ethylene		Formaldehyde-ethylene	
	5	6	<i>n</i> complex	π complex
Electrons transferred	0.4648	0.4707	0.4277	0.4647
Dipole moment, D	11.06	10.83	3.72	4.21

peculiar to *p*-benzoquinone, since the formaldehyde-ethylene⁶ ensemble displays this same type of behavior in the 180° geometry: for the analogous *n* complex, $D_{\min} = 1.92$ Å, $\Delta E_{TS} = -2.0$ kcal/mol (Figure 3b); for the analogous π complex, $D_{\min} = 1.94$ Å, $\Delta E_{TS} = -0.2$ kcal/mol.

Both the *p*-benzoquinone and formaldehyde complexes are strongly CT in nature (see Table I) with the carbonyl component serving as the acceptor and the olefin as the donor. It should be noted that about the same amount of charge is transferred in all cases, but that the quinone complexes 5 and 6 have much higher dipole moments. The favorable delocalization of the transferred charge into the quinone π system accounts for these high moments and also probably accounts for the unusual stabilities of the triplet quinone complexes relative to the formaldehyde complexes where the transferred charge is of necessity localized on the carbonyl group. Since these complexes have little n, π^* character we tend to agree with Wagner, who has noted^{2c} that photochemical species of this type should be classified as CT complexes rather than exciplexes.

The existence of CT complexes with these end-on geometries