Synthesis, Structure, and Reactions of a Benziodolium Cation

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The 3-butyl-2-phenylbenziodolium cation has been synthesized by the low-temperature reaction of *trans*-chlorovinyliodoso dichloride and *trans*-1-lithio-2-*o*-lithiophenyl-1-phenyl-1-hexene. The iodonium ion underwent attack by nucleophiles (Cl^-, I^-, and CH_3O^-) exclusively at the 2 position to give a mixture of *cis*- and *trans*-stilbenes. Reaction of the iodonium ion with water in the absence of oxygen gave 2-*o*-iodophenyl-1-phenyl-1-hexanone, which has been independently synthesized by hydrolysis of *trans*-1-iodo-2-*o*-iodophenyl-1-phenyl-1-hexene. Reaction of the iodonium ion with oxygen in water gave 2-hydroperoxy-2-*o*-iodophenyl-1-phenyl-1-hexanone, which was thermally cleaved to benzoic acid and 1-*o*-iodophenyl-1-pentanone. The latter compound has been independently synthesized by addition of butylmagnesium chloride to *o*-iodobenzaldehyde followed by oxidation of the resulting alcohol with the Jones reagent. The α-hydroperoxy ketone was reduced by sodium borohydride or sodium iodide to 2-hydroxy-2-*o*-iodophenyl-1-phenyl-1-hexanone, which was oxidatively cleaved with lead tetraacetate in benzene to benzoic acid and 1-*o*-iodophenyl-1-pentanone. Mechanisms of some of these transformations are discussed. The crystal structures of 3-butyl-2-phenylbenziodolium chloride and dibenziodolium tetrafluoroborate are reported. Correlations between structure and reactivity of these compounds are discussed. Numerous attempts to form an iodolium cation finally gave, by the reaction of 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene with *trans*-chlorovinyliodoso dichloride, a low yield of 2,3,4,5-tetraphenyliodolium chloride.

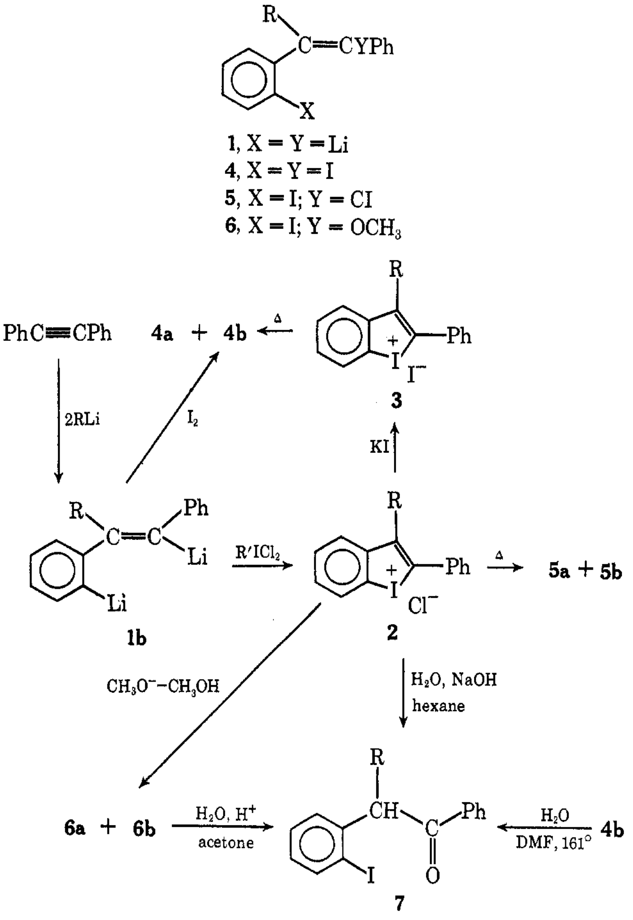
In previous papers[4] there has been reported a new route to symmetrical diaryliodonium salts *via* the low-temperature reaction of *trans*-chlorovinyliodoso dichloride with 2 equiv of aryllithium reagent. Fair to excellent yields of the diphenyl-, di-*p*-tolyl-, di-1-naphthyl-, di-2-naphthyl-, di-9-anthryl-, 2,2′-biphenylene-, di-2-thienyl-, and di-2-furanyliodonium salts were obtained. Attempts to form iodonium salts with one or two bonds to sp^3 carbon were unsuccessful. We have now extended the synthesis to yield an interesting heterocyclic arylvinyliodonium salt and have studied its ring-opening reactions. We have determined its crystal structure and also, for comparison, that of dibenziodolium (2,2′-biphenyleneiodonium) tetrafluoroborate.

Results

Mulvaney and coworkers[5] have reported the addition to and metalation of diphenylacetylene with *n*-butyllithium in ether to give *trans*-1-lithio-2-*o*-lithiophenyl-1-phenyl-1-hexene (**1b**). The low-temperature reaction of **1b** with *trans*-chlorovinyliodoso dichloride in ether gave in 26% yield 3-butyl-2-phenylbenziodolium chloride (**2**), converted by metathesis to 3-butyl-2-phenylbenziodolium iodide (**3**) (Scheme I). The nmr spectrum of **2** in CD_2Cl_2 shows a downfield shift of the 8 proton expected of protons ortho to the iodonium group.[6] This proton appears as a doublet at τ 1.05, with further splitting evident. By comparison, the proton ortho to uncharged iodine in *trans*-1-iodo-2-*o*-iodophenyl-1-phenyl-1-hexene (**4b**), synthesized by reaction of **1b** with iodine, appears at τ 2.14. The C=C ir stretching bands in both **2** and **3** are very weak or absent as expected for tetrasubstituted olefins.[7]

SCHEME I

SYNTHESIS AND REACTIONS OF BENZIODOLIUM SALTS[a]



R = *n*-butyl
R′ = *trans*-2-chlorovinyl

[a] In text, cis isomers are **a** and trans isomers are **b**.

Reactions of Salts 2 and 3.—Decomposition of **2** at its melting point gave an equimolar mixture of *cis*- and *trans*-stilbenes. Decomposition of **3** gave 42% of the *cis*- and 58% of the *trans*-stilbene. The mass spectrum of the melt from **3** was identical with that from **4b**, apparently indicating equilibrium of the *cis*- and *trans*-stilbenes upon electron impact. These

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[3] Taken in part from the dissertation of H. Jaffe, submitted to the Faculty of the Polytechnic Institute of Brooklyn, in partial fulfillment of the requirements for the degree of Ph.D., 1971; NDEA Fellow, 1966–1969.

[4] F. M. Beringer and R. A. Nathan, *J. Org. Chem.*, **34**, 685 (1969); **35**, 2095 (1970).

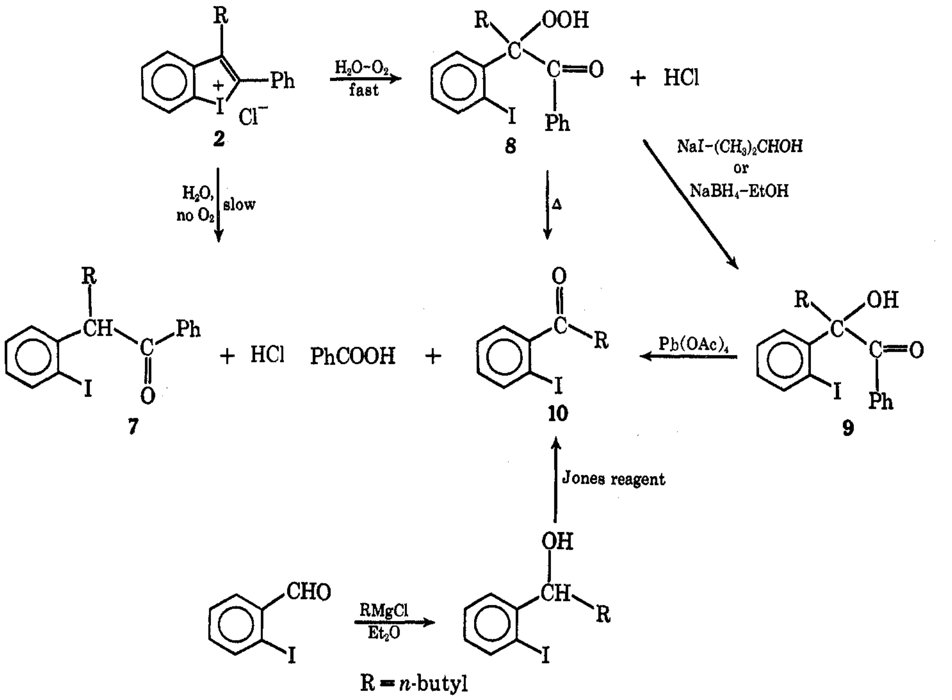
[5] J. E. Mulvaney, Z. G. Gardlund, S. L. Gardlund, and D. J. Newton, *J. Amer. Chem. Soc.*, **88**, 476 (1966).

[6] F. M. Beringer and S. A. Galton, *J. Org. Chem.*, **31**, 1648 (1966).

[7] L. J. Bellamy, "Infra-red Spectra of Complex Molecules," Wiley, New York, N. Y., 1962.

SCHEME II

OXIDATIVE HYDROLYSIS OF A BENZIODOLIUM SALT



halogenated stilbenes display M and M − halogen peaks.

Reaction of **2** with sodium methoxide in anhydrous methanol gave an equimolar mixture of *cis*- and *trans*-2-iodophenyl-1-methoxy-1-phenyl-1-hexene (**6a** and **6b**), which was separated by glpc. (The mass spectra of these isomers are identical and display molecular ions.) The mixture of vinyl ethers undergoes acid-catalyzed hydrolysis to 2-*o*-iodophenyl-1-phenyl-1-hexanone (**7**), independently synthesized by high-temperature hydrolysis of diiodo compound **4b**. Reaction of **2** with sodium hydroxide gives ketone **7**, apparently by tautomerization of the first-formed enols.

Reaction of Iodonium Salt 2 with Water and Oxygen.—When a suspension of **2** is stirred in distilled water at room temperature in the presence of oxygen, a novel oxidative hydrolysis occurs rapidly (*ca.* 1-2 hr) to give 2-hydroxyperoxy-2-*o*-iodophenyl-1-phenyl-1-hexanone (**8**). The uptake of oxygen is almost quantitative as measured by the Warburg respirometer. Under the same conditions but in the absence of oxygen a very slow (*ca.* 1 month) hydrolysis to ketone **7** occurs in almost quantitative yield. The structure of α-hydroperoxy ketone **8** is based on microanalysis, ir and nmr spectroscopy, reduction to 2-hydroxy-2-*o*-iodophenyl-1-phenyl-1-hexanone (**9**), and thermal cleavage to benzoic acid and 1-iodophenyl-1-pentanone (**10**) (Scheme II). The ir spectrum of **8** displays on OH band at 3300 and a C═O band at 1668 cm^{-1}. The nmr of **8** in acetone-d_6 displays a one-proton singlet (D_2O exchangeable) at τ −1.13 for the strongly deshielded hydroperoxy proton.[8]

Brief exposure to sodium borohydride in ethanol at room temperature reduced **8** to hydroxy ketone **9**. Neither the carbonyl group nor the iodine[9] was affected under these conditions. Treatment of **8** with solium iodide in acetone also gave **9**.

Hydroxy ketone **9** is oxidatively cleaved with lead tetraacetate to benzoic acid and ketone **10**. The ir spectrum of **9** is almost identical with that of **8** except for a slight shift of the C═O band to 1662 cm^{-1} and a larger shift of the OH band to 3450 cm^{-1}. The nmr spectrum in $CDCl_3$ is similar to that of **8** except for a dramatic upfield shift of the OH peak to a one-proton, D_2O-exchangeable, singlet at τ 5.17. The mass spectrum displays major peaks at *m/e* 289, 231, 203, 105, 77, and 76. The molecular ion at 394 was not observed. We propose α cleavage as the major fragmentation pathway to account for these peaks. By comparison, the mass spectrum of benzoin displays major peaks at *m/e* 107 ($PhCHOH^+$, α cleavage), 105 ($PhC{=}O^+$, α cleavage), and 77 (Ph^+).

Ketone **9** is cleaved by lead tetraacetate in refluxing benzene to benzoic acid and ketone **10**, synthesized independently by Jones reagent oxidation of the alcohol resulting from addition of *n*-butylmagnesium chloride to *o*-iodobenzaldehyde.

Crystal Structures of the Dibenziodolium and Benziodolium Salts.—In Figure 1 the molecular parameters of dibenziodolium tetrafluoroborate are reported. The standard deviations of the bond lengths and angles are 0.015 Å and 0.2°, respectively. The molecule is planar; deviations from the mean molecular plane are less than 0.03 Å. The molecule has an almost exact C_2 symmetry; this symmetry is even extended to the mode of thermal vibrations of the atoms (see Figure 1a). The bond angle C–I–C of 83° is appreciably smaller than the corresponding angle in the structure of di-

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[8] Hydroperoxy protons characteristically show low-field nmr absorption: S. Fujiwara, M. Katayama, and S. Kamio, *Bull. Chem. Soc. Jap.*, **32**, 657 (1959).

[9] The reduction of aryl iodides by lithium aluminum hydride and sodium borohydride has recently been reported: H. C. Brown and S. Krishnamurthy, *J. Org. Chem.*, **34**, 3918 (1969); H. M. Bell, C. W. Vanderslice, and A. Spehar, *ibid.*, **34**, 3923 (1969).

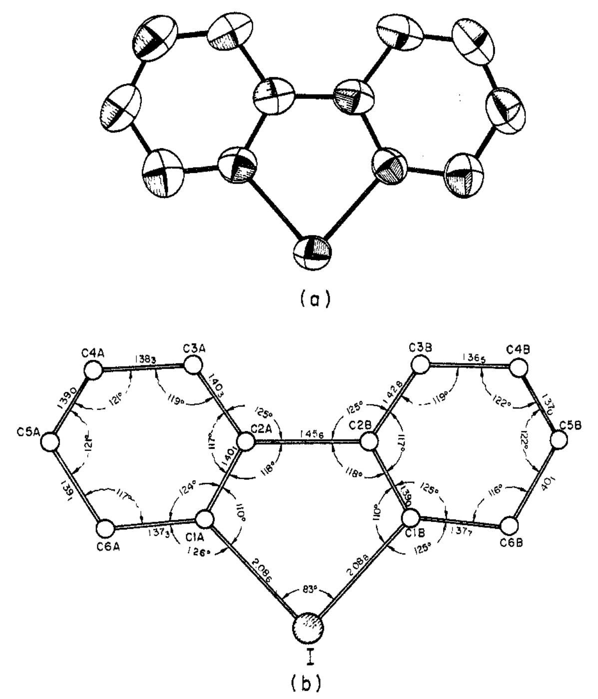
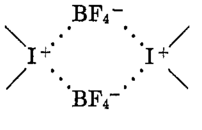


Figure 1.—The dibenziodolium ion: (a) modes of thermal atomic vibrations; (b) molecular conformational parameters.

phenyliodonium chloride[10] (93°). The bond lengths C–I$^+$ are almost the same as the normal C–I bonds (2.10–2.15 Å). Relevant are the distortions from 120° of some bond angles of the phenyl rings (up 5–6°). Dibenziodolium ions are held together pairwise by two BF$_4^-$ ions. Groups with almost identical distances I$^+\cdots$BF$_4^-$ (3.65 Å) are formed in this way around inversion centers.[11]



In Figure 2 the molecular parameters of 3-butyl-2-phenylbenziodolium chloride (2) are reported. The standard deviations of these parameters are the same as in 11. Except for the phenyl group and the butyl group the molecule is planar within the standard deviations. The phenyl group bonded to C7 forms an angle of 52° with the plane of the benziodolium moiety. Also the butyl group has a nearly planar full-extended conformation and its mean plane forms an angle of 76° with the plane of the benziodololium moiety. The bond length C7–C8 (1.34 Å) shows the olefinic character of this bond. In spite of the different environment on the two sides of I$^+$ in 2 the two Cl bond lengths are identical within the standard deviations.

In 3-butyl-2-phenylbenziodolium chloride the two nonequivalent I$^+\cdots$Cl$^-$ distances are quite different (3.22 and 2.95 Å) as in the case of diphenyliodonium chloride,[10] indicating a different character of the bonds.[11] These are the first crystal structures of heterocyclic aryliodolium salts reported so far.

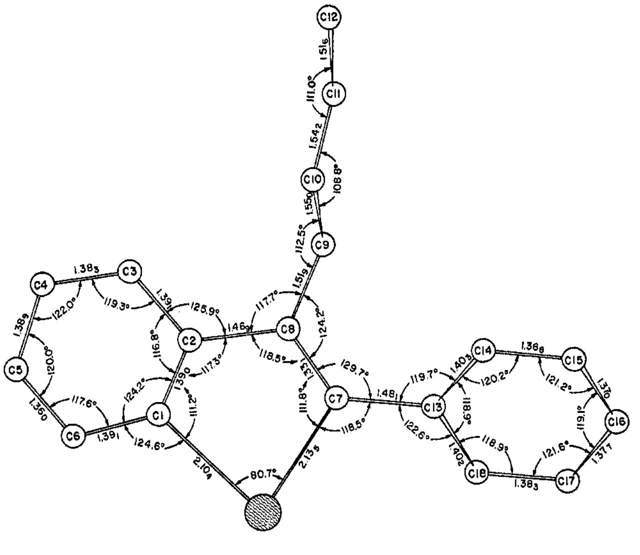
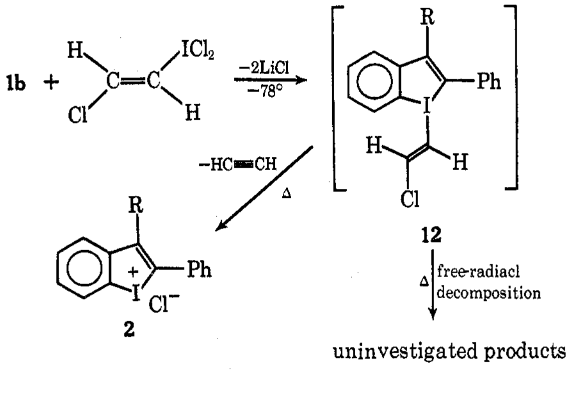


Figure 2.—Molecular conformation parameters of the 3-butyl-2-phenylbenziodolium ion.

Discussion

The synthesis of 2 from the reaction of *trans*-chlorovinyliodoso dichloride and dilithium compound **1b** probably proceeds *via* the trivalent organoiodine intermediate 12. Analogous intermediates have been proposed in the synthesis of diaryliodonium salts from the reaction of *trans*-chlorovinyliodoso dichloride and aryllithium reagents.[4] Upon warming to room temperature 12 is believed to undergo two modes of decomposition.[4] Ionic elimination gives acetylene and the desired product, iodonium salt 2. The major mode of decomposition is apparently a free-radical cleavage of the bonds to iodine yielding a complex mixture of products (Scheme III).

SCHEME III
DECOMPOSITION OF INTERMEDIATE 12



We have seen that 3-butyl-2-phenylbenziodolium cation undergoes attack by nucleophiles exclusively at the 2 position to give almost equal amounts of *cis*- and *trans*-stilbenes. In no case was any product of attack at the 9 position observed. The following mechanism (Scheme IV) might best account for these results. Attack of the nucleophile at the 2 position from above or below the plane of the ring can occur with

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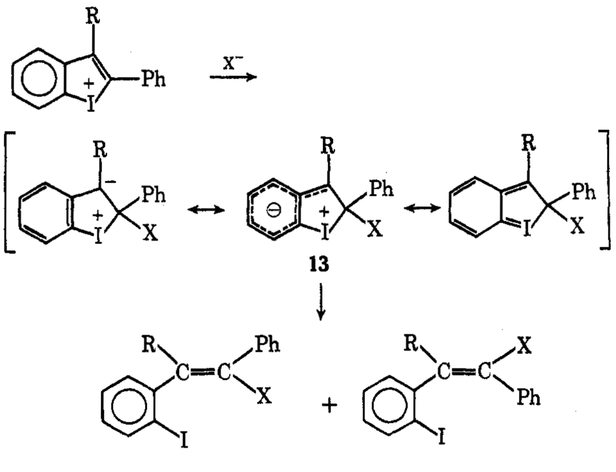
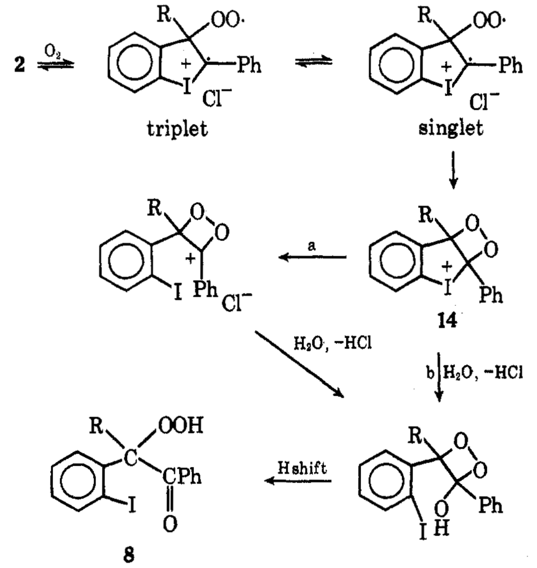
(10) T. L. Khotsyanova, *Dokl. Akad. Nauk SSSR*, **110**, 7 (1956) [*Chem. Abstr.*, **52**, 4282*h* (1958)]; T. L. Khatsyanova and Yu. T. Struckhov, *Zh. Fiz. Khim.*, **26**, 644, 669 (1952) [*Chem. Abstr.*, **49**, 6684*e* (1952)].

(11) The tables of observed and calculated structure factors, the positional and thermal parameters and crystallographic projections of compounds **2** and **11** will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

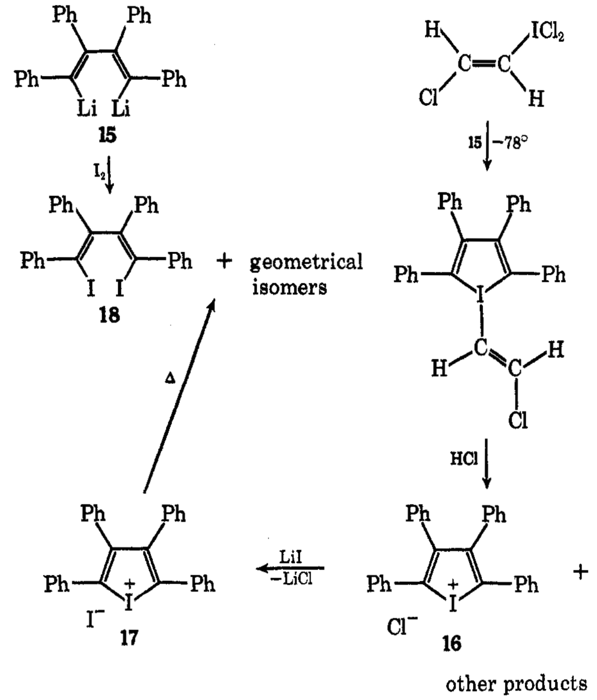
SCHEME IV
REACTION OF THE 3-BUTYL-2-PHENYLBENZIODOLIUM ION WITH NUCLEOPHILES



SCHEME V
REACTION OF THE BENZIODOLIUM ION WITH OXYGEN



SCHEME VI
SYNTHESIS AND REACTIONS OF TETRAPHENYLIODOLIUM SALTS



equal probability to give a dipolar intermediate (**13**). Delocalization of the negative charge into the aromatic ring and into the d or f orbitals of iodine might help stabilize the intermediate. E1 elimination of the $-I^{+}-$ group would give equal amounts of the cis and trans isomers. By contrast, attack at the 9 position would involve disruption of the aromatic system, while backside displacement of the $-I^{+}-$ group would be expected to give only the *cis*-stilbene. The proposed mechanism is in accord with the X-ray results which show no electronic interaction between the α-vinyl group and any of the aromatic groups.

The formation of α-hydroperoxy ketone **8** from **2** might involve addition of triplet oxygen to the double bond to give a cyclic peroxide intermediate (**14**, Scheme V). In this addition, the iodine might facilitate conversion of an initially formed 1,4 diradical with spins unpaired to one with spins paired[12] which then closes to **14**. The latter, which contains a sp^3 carbon bonded to a positive iodine,[13] would be expected to undergo SN1-like heterolysis (pathway a) or, less likely, SN2-like displacement of the $-I^{+}-$ group by water (pathway b) to give intermediates which rearrange to the observed product. The very slow rate of formation of ketone **7** in the absence of oxygen excludes any mechanism for the formation of **8** involving addition of oxygen to an intermediate enol.[14]

The thermal decomposition of **8** to benzoic acid and ketone **10** is characteristic of α-hydroperoxy ketones.[15] Pritzkow[16a] has proposed that such cleavages are acid catalyzed and proceed by a mechanism similar to that involved in the conversion of cumyl hydroperoxide to phenol and acetone.[16b]

Tetraphenyliodolium Salts.—The procedure used to form the benziodolium chloride (**2**) has been adapted, by the use of 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene (**15**) as the dilithio reagent, to give in low yield 2,3,4,5-tetraphenyliodolium chloride (**16**), the first salt having an iodolium cation without a fused ring (Scheme VI). The tetraphenyliodolium chloride and iodide reacted at the melting point to give 1-halo-4-iodo-1,2,3,4-tetraphenyl-1,3-butadienes, whose mass spectra showed peaks at M^{+}, $M^{+} - X$, $M^{+} - I$, $M^{+} - X - I$, and ions related to 1,2,3-triphenylnaphthalene and 1,2-diphenylnaphthalene.

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[12] Transitions between the singlet and triplet states are facilitated by a heavy atom, especially if the electron is located in an orbital close to the heavy atom: N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967, p 50.

[13] The only aliphatic iodonium salt to be isolated, dimethyliodonium hexafluoroantimonate, undergoes immediate hydrolysis when exposed to moisture: G. A. Olah and J. R. Demember, *J. Amer. Chem. Soc.*, **92**, 718 (1970).

[14] Addition of oxygen to stabilized enols is known to give α-hydroperoxy ketones: for example, R. C. Fuson and H. L. Jackson, *ibid.*, **72**, 1637 (1950).

[15] For example, D. B. Sharp, L. W. Patton, and S. E. Whitcomb, *ibid.*, **73**, 5600 (1951); E. P. Kohler, M. Tishler, and H. Potter, *ibid.*, **57**, 2517 (1935).

[16] (a) W. Pritzkow, *Chem. Ber.*, **88**, 572 (1954). (b) J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, New York, N. Y., 1964, p 432.

A comparison between the molecular structures of **11** and **2** shows that the nature of the groups bonded to the iodolium ring do not affect to an appreciable extent the conformation of the iodonium group C–I$^+$–C. The different reactivity of the bonds C1–I and C7–I in 3-butyl-2-phenylbenziodolium ion appears to be due simply to the different chemical environments on the two sides of I$^+$.

Experimental Section

Analyses were performed by Galbraith Laboratories, Knoxville, Tenn., or by Chermalytics, Inc., Tempe, Ariz. Gas chromatography was done on 6- or 10-ft columns packed respectively with 20% OV1 or 4% SE-30 on Chromosorb W with an Aerograph 1520 gas chromatograph or on 2-m columns packed with 1.5% SE-30 on Chromosorb W with a Perkin-Elmer 154 vapor fractometer. Peak areas were measured by planimetry. Melting points were taken in capillary tubes on a Thomas-Hoover apparatus. Melting and boiling points are uncorrected. Infrared spectra were taken on Perkin-Elmer 521 and 337 grating infrared spectrophotometers. Nmr spectra were taken on a Varian Associates Model A-60 instrument. Chemical shifts are reported in parts per million (τ) downfield from tetramethylsilane. Mass spectra were taken at 80 eV on a Hitachi Perkin-Elmer RMU-6E instrument. Oxygen absorption was measured by a mercury-calibrated Warburg respirometer corrected with a thermobarometer.

Starting Materials.—Iodine trichloride was purchased from City Chemical Co. or Alpha Inorganics, Inc. Organolithium compounds were purchased from Alpha Inorganics, Inc., and standardized before use by the method of Gilman and Cartledge.[17] *n*-Butylmagnesium chloride in THF was purchased from Alpha Inorganics, Inc. Lithium wire was purchased from Lithium Corp. of America. Diphenylacetylene was synthesized by the method of Cope, Smith, and Cotter[18] or purchased from Aldrich Chemical Co. Acetylene and prepurified argon were supplied by Matheson. The anhydrous ether was analytical grade as supplied by Mallinchrodt; only cans opened immediately before use and sealed with a septum were used. Methanol was dried by distillation from magnesium and stored over molecular sieves. Benzene and toluene were dried by distillation and stored over molecular sieves.

***trans*-Chlorovinyliodoso Dichloride.**—The procedure of Beringer and Nathan[4] was modified as follows. Through a solution of 100 g (0.427 mol) of ICl_3 in 160 ml of HCl, diluted to three times its original volume with ice and contained in an ice water bath, acetylene was bubbled. After 1.0–1.5 hr the bright yellow crystals were collected by vacuum filtration; the filtrate was returned for further treatment with acetylene. The yellow solid was washed with water until the filtrate was colorless, pressed on the filter to remove excess water, and air-dried on the filter for 30–45 min to give dry *trans*-chlorovinyliodoso dichloride. The cycle was repeated one or two times to give a total yield of 37.5 g (34%). The dried solid was used immediately or was stored in amber bottles in a Dry Ice box. *Caution: trans*-Chlorovinyliodoso dichloride is a hazardous material subject to spontaneous decomposition with the evolution of noxious vapors, especially if it appears reddish in places. Such material is to be discarded immediately. The compound should not be handled with metal spatulas. Several sealed bottles have exploded upon warming to room temperature. Not more than *ca.* 10 g of the compound should be stored in a 1-oz bottle. Sealed cold bottles should be warmed to room temperature behind a safety shield under the hood and opened with caution.

***trans*-1-Lithio-2-*o*-lithiophenyl-1-phenyl-1-hexene (1b).**—The procedure of Mulvaney, *et al.*,[5] was modified as follows. To 332[19] ml of anhydrous ether there was added 143 ml of 2.23 M *n*-butyllithium (0.320 mol) in hexane and then a solution of 25.0 g (0.140 mol) of diphenylacetylene in 100 ml of anhydrous ether. The resulting solution was stirred for 24 hr[20] under argon to give an orange-red solution of *trans*-1-lithio-2-*o*-lithiophenyl-1-phenyl-1-hexene (**1b**).

3-Butyl-2-phenylbenziodolium Chloride (**2**).—The above solution was added dropwise over 1 hr to a stirred solution of 47.5 g (.183 mol) of *trans*-chlorovinyliodoso dichloride in 300 ml of anhydrous ether under argon cooled in a Dry Ice–acetone bath. The resulting yellow suspension was kept cold for an additional 3 hr and then allowed to warm to room temperature overnight.

The reaction mixture was filtered, washed with ether, suspended in water, filtered, and dried on the filter to give 11.5 g of an off-white powder.[21] Recrystallization from 300 ml of benzene[22] (heated funnel) gave 8.10 g (14.6,[23] 26.2%[24]) of yellow crystals of 3-butyl-2-phenylbenziodolium chloride (**2**): mp 151.5–152.5° dec; ir (KBr) 3054, 2960, 2928, 2867, 1570, 1483, 1460, 1439, 1429, 1375, 1108, 1073, 1028, 1000, 850, 772, 762, 750, 715, 692, 652, 648, 635, 552, and 418 cm^{-1}; nmr (CD_2Cl_2) τ 1.05 (d with further splitting evident, 1, proton ortho to –I$^+$–), 2.15–2.69 (m, 8, other aromatic H), 7.32 (broad t, 2, $CH_2CH_2CH_2CH_3$), and 8.10–9.47 (m, 7, other aliphatic H).

Anal. Calcd for $C_{18}H_{18}ICl$: C, 54.49; H, 4.58; Cl, 8.94; I, 31.98. Found: C, 54.76; H, 4.57; Cl, 8.72; I, 32.04.

When 41.6 g (.160 mol) of *trans*-chlorovinyliodoso dichloride was used, the yield of **2** was only 1.74 g (3.1,[23] 5.7%[24]).

When 400 ml of dry toluene were used instead of the 300 ml of ether, the yield of **2** was 7.71 g (13.9,[23] 25.0%[24]).

3-Butyl-2-phenylbenziodolium Iodide (**3**).—To a solution of 30.0 g of NaI in 75 ml of 50% aqueous acetone (v:v) cooled to room temperature there was added .75 g (1.9 mmol) of 3-butyl-2-phenylbenziodolium chloride (**2**). The reaction flask was stoppered and vigorously stirred in the dark for 15 hr. Filtration followed by washing with water gave an orange-yellow solid. Recrystallization from 30 ml of acetone gave 0.43 g (three crops, 46%) of 3-butyl-2-phenylbenziodolium iodide (**3**). The iodide was not indefinitely stable at room temperature and was stored in the cold to retard decomposition: mp 121–122° dec (tube in at 120° and heated at 1–2°/min); ir (KBr) essentially the same as for **2**.

Anal. Calcd for $C_{18}H_{18}I_2$: C, 44.28; H, 3.72; I, 51.99. Found: C, 44.37; H, 3.78; I, 51.86.

Decomposition of 3-Butyl-2-phenylbenziodolium Chloride (**2**).—A small amount of **2** was heated at its melting point until the entire sample had decomposed to a pale yellow oil. Analysis by glpc (4% SE-30, 10 ft × 0.25 in., 190°, 84 ml/min He) indicated 51.0% isomer A, with shorter retention time, and 49.0% isomer B, with longer retention time. By comparison with the glpc data for **4a** and **4b** (see below), isomer B is probably the *trans*-1-chloro-2-*o*-iodophenyl-1-phenyl-1-hexene (**5b**) and isomer A the cis isomer. Data for this mixture follows: ir (neat) 3055, 2956, 2928, 2870, 2858, 1485, 1458, 1438, 1424, 1373, 1225, 1069, 1010, 890, 752, 736, 722, 691, 676, 638, 592, 583, 560, and 521 cm^{-1}; mass spectrum (decomposition in the instrument) *m/e* 398 (M$^+$ for ^{37}Cl), 396 (M$^+$ for ^{35}Cl), 361 (M$^+$ − Cl), 355 (M$^+$ − $CH_3CH_2CH_2$ for ^{37}Cl), 353 (M$^+$ − $CH_3CH_2CH_2$ for ^{35}Cl), 317, 234 (M$^+$ − Cl − I), 213, 192, 191, (M$^+$ − Cl − I − $CH_3CH_2CH_2$), 190, 189, 178, 91, 77 (Ph$^+$), and 57.

Anal. Calcd for $C_{18}H_{18}ICl$: C, 54.49; H, 4.58; Cl, 8.94; I, 31.98. Found: C, 54.64; H, 4.52; Cl, 8.99; I, 32.22.

Decomposition of 3-Butyl-2-phenylbenziodolium Iodide (**3**).—A small amount of **3** was heated at its melting point until the entire sample had decomposed to a reddish oil. Analysis by glpc (4% SE-30, 10 ft × 0.25 in., 190°, 84 ml/min He) indicated 57.9% of *trans*-1-iodo-2-*o*-iodophenyl-1-phenyl-1-hexene (**4b**) with longer retention time and 42.1% of the cis isomer **4a** (*vide infra*) with shorter retention time: ir (neat) 3058, 2959, 2929, 2871, 2861, 1485, 1461, 1442, 1429, 1378, 1218, 1120, 1109, 1073, 1059, 1031, 1013, 1001, 868, 852, 759, 749, 731, 723, 698, 662, 648, 640, 580, 549, 522, and 442 cm^{-1}; mass spectrum (decomposition in the instrument) identical with that of **4b**.

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[17] H. Gilman and F. K. Cartledge, *J. Organometal. Chem.*, **2**, 447 (1964).

[18] A. J. Cope, D. S. Smith, and R. J. Cotter, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 377.

[19] The volume of ether is enough to dilute the hexane threefold in the final solution.

[20] The yield of **1b** was determined by quenching an aliquot of the reaction mixture with water and analyzing for the resulting *trans*-α-*n*-butylstilbene by glpc (1.5% SE-30, 2 m × 0.25 in., 190°) with triphenylmethane as an internal standard. An average yield of 55.6% was found after 24 hr. Analysis after 45 hr showed no significant change in the yield. *trans*-α-*n*-Butylstilbene was prepared by the method Mulvaney, *et al.*[5]

[21] *Caution:* this powder is an irritant to the nose and throat. It should be handled under the hood.

[22] Alternately, this material can be recrystallized from acetone.

[23] Yield based on diphenylacetylene.

[24] Yield based on **1b**.

***trans*-1-Iodo-2-*o*-iodophenyl-1-phenyl-1-hexene (4b).**—A solution of **1b** was prepared as described above from 25.0 g (140 mmol) of diphenylacetylene in 100 ml of anhydrous ether, 142 ml of 2.24 *M* (320 mmol) of *n*-butyllithium in hexane, and 325 ml of anhydrous ether. To the solution at 0–5° a solution of iodine in anhydrous ether was added dropwise with stirring until the purple color of iodine persisted (30 min); *ca.* 56 g (0.22 mol) of iodine in 300 ml of anhydrous ether was required. After warming to room temperature the reaction mixture was poured into an equal volume of water. The ether layer was separated, washed with water, dried ($MgSO_4$), and evaporated to give 52.7 g of a dark oil which was distilled with a short path apparatus at 0.07 mm. To prevent decomposition a pot temperature of 210° was not exceeded. Purity of fractions (*ca.* 4 ml) was monitored by glpc (1.5% SE-30, 2 m × 0.25 in., 230°). Fractions 1–4, bp 25–154° (15.6 g), were mainly unreacted diphenylacetylene. Fraction 5, bp 154–156° (5.9 g), was largely **4b**. Fractions 6–8, bp 156–163° (20.9 g, *ca.* 30.6%), were **4b** (95% purity) as viscous pale yellow oils. Recrystallization of fractions 6–8 from methanol afforded white crystals of *trans*-1-iodo-2-*o*-iodophenyl-1-phenyl-1-hexene (**4b**). Attempted crystallization of fraction 5 gave an oil which partially solidified upon slow evaporation of the solvent at room temperature and standing for several months. Absorption of the excess oil with paper towels followed by recrystallization of the crude solid from methanol gave additional pure crystals of **4b**: mp 59–61°; ir (KBr) 3053, 2953, 2926, 2867, 1482, 1457, 1437, 1424, 1228, 1210, 1115, 1105, 1067, 1029, 1010, 936, 839, 756, 732, 723, 702, 671, 655, 633, 572, and 438 cm^{-1}; nmr (CCl_4) τ 2.14 (d with further splitting evident, 1, proton ortho to iodine), 2.42–3.28 (m, 8, other aromatic H), 7.23–8.11 (m, 2, $CH_2CH_2CH_2CH_3$), and 8.40–9.61 (m, 7, other aliphatic H); mass spectrum *m/e* 488 (M^+), 361 ($M^+ - I$), 318 ($M^+ - I - CH_3CH_2CH_2$), 234 ($M^+ - 2I$), 205 ($M^+ - 2I - CH_3CH_2$), 192, 191 ($M^+ - 2I - CH_3CH_2CH_2$), 189, 131, 130, 91, and 77 (Ph^+).

Anal. Calcd for $C_{18}H_{18}I_2$: C, 44.28; H, 3.72; I, 51.99. Found: C, 44.29; H, 3.74; I, 52.02.

Reaction of 2 with Sodium Methoxide in Anhydrous Methanol.—To a solution of 0.130 g (2.41 mmol) of sodium methoxide in 20 ml of anhydrous methanol, **2** (0.400 g, 1.01 mmol) was added. The resulting yellow solution was stirred in the dark for 75 min to give a nearly colorless solution. Ether and water were added to form two layers which were separated. The ether layer was washed twice with saturated $NaHCO_3$ solution, dried ($MgSO_4$), and evaporated to give 0.370 g of a yellow oil. The aqueous phase, which was neutral to pH paper, was combined with the $NaHCO_3$ washings, acidified with HCl, and extracted with ether. The ether extract was dried ($MgSO_4$) and evaporated to give 6.3 mg (5.1%) of benzoic acid.[25] Analysis of the yellow oil by glpc (20% OV1, 6 ft × 0.25 in., 195°, 100 ml/min He) indicated 92% of a mixture of *cis-* and *trans*-2-*o*-iodophenyl-1-methoxy-1-phenyl-1-hexene (**6a** and **6b**), 4% 1-*o*-iodophenyl-1-pentanone (**10**),[25] and 4% of unidentified materials. The mixture of isomers consisted of 48.7% isomer A, with shorter retention time, and 51.3% isomer B, with longer retention time. Samples of the isomer mixture were collected by preparative glpc (same conditions) for microanalysis and nmr. Samples of each isomer were collected for ir and mass spectroscopy. All samples were highly viscous pale yellow oils: ir (isomer A, neat) 3051, 2957, 2930, 2870, 2858, 2830, 1638, 1595, 1486, 1459, 1440, 1425, 1263, 1252, 1234, 1124, 1104, 1072, 1054, 1025, 1012, 773, 758, 742, 730, 697, and 648 cm^{-1}; ir (isomer B, neat) 3054, 2958, 2932, 2871, 2858, 2834, 1650, 1595, 1486, 1458, 1440, 1424, 1287, 1266, 1245, 1127, 1102, 1070, 1058, 1010, 758, 742, 731, 700, 644, and 629 cm^{-1}; mass spectrum (isomer A) *m/e* 392 (M^+), 349 ($M^+ - CH_3CH_2CH_2$), 222, 207, 192, 191, 179, 178, 121, 165, 161, 121, 115, 105, 91, 89, 77 (Ph^+), and 51; mass spectrum (isomer B) identical with that of isomer A; nmr (both isomers) (CCl_4) τ 2.02–3.48 (m, 9, aromatic H), 6.60 (s, 1.5, OCH_3), 6.86 (s, 1.5, OCH_3), 7.46–8.11 (m, 2, $CH_2CH_2CH_2CH_3$), and 8.20–9.52 (m, 7, other aliphatic H).

Anal. Calcd for $C_{19}H_{21}IO$: C, 58.17; H, 5.40. Found: C, 58.10; H, 5.39.

Hydrolysis of 6a and 6b to 7.—To a solution in 10 ml of acetone of 0.100 g of the crude yellow oil mentioned in the previous reaction there was added 1.5 ml of 35% $HClO_4$, and the resulting solution was refluxed for 1 hr. After the mixture was cooled to room temperature, ether and water were added to form two layers which were separated. The aqueous layer was extracted with ether, and the combined organic phase was washed with saturated $NaHCO_3$ solution, dried ($MgSO_4$), and evaporated to give 91 mg of a pale yellow brown oil. Analysis by glpc (20% OV1, 6 ft × 0.25 in., 210°, 108 ml/min He) indicated 92% 2-*o*-iodophenyl-1-phenyl-1-hexanone (**7**), 6% 1-*o*-iodophenyl-1-pentanone (**10**),[25] and 2% unidentified materials. Ketone **7**, collected by preparative glpc (same conditions), was identical (mass spectroscopy) with an authentic sample.

Reaction of 2 with NaOH.—A flask was charged with 0.397 g (1.00 mmol) of **2**, 0.100 g (2.50 mmol) of NaOH, 7 ml of water, and 7 ml of hexane. After 30 min of reflux all the solid had reacted to give a yellow hexane solution and a cloudy water phase. To the cooled reaction mixture were added ether and water, and the layers were separated. The organic layer was washed with water containing 1 drop of HCl, dried ($MgSO_4$), and evaporated to give 0.356 g of a viscous yellow oil. Analysis by glpc (20% OV1, 6 ft × 0.25 in., 220°, 104 ml/min He) indicated 74% 2-*o*-iodophenyl-1-phenyl-1-hexanone (**7**), 0.6% 1-*o*-iodophenyl-1-pentanone (**10**),[25] 3.3% of *ca.* an equal mixture of *cis-* and *trans*-1-chloro-2-*o*-iodophenyl-1-phenyl-1-hexene (**5a** and **5b**), and 22.3% of various unidentified products. Ketone **7** was collected by preparative glpc (same conditions) and found to be identical (ir and mass spectroscopy) with an authentic sample.

Reaction of 2 with H_2O in the Absence of Oxygen.—A Carius tube was charged with 150 mg (3.78 mmol) of **2** and 4 ml of water. The tube was degassed *via* four freeze–thaw cycles (0.07 mm), sealed, and shaken in the dark for 30 days after which time all the solid had changed to an oil. The ethereal extract was washed with saturated $NaHCO_3$ solution, dried ($MgSO_4$), and concentrated to give 0.127 g of a colorless oil. Analysis by glpc (20% OV1, 6 ft × 0.25 in., 210°, 108 ml/min He) indicated 97% 2-*o*-iodophenyl-1-phenyl-1-hexanone (**7**), 1% 1-*o*-iodophenyl-1-pentanone (**10**),[25] and 2% unidentified materials. Preparative glpc (same conditions) gave a sample of ketone **7** identical (ir and mass spectroscopy) with an authentic sample.

2-Hydroperoxy-2-*o*-iodophenyl-1-phenyl-1-hexanone (8). Method A.—A suspension of 100 mg (0.252 mmol) of **2** in 12 ml of water was vigorously stirred in the dark under a balloon of oxygen for 17 hr. After ether was added to the resulting white suspension to give two clear layers, these were filtered to remove a small amount (*ca.* 1 mg) of unreacted starting material. The layers were separated, and the aqueous phase was extracted with ether. The aqueous phase was strongly acid (HCl). The combined ether phase was washed with saturated $NaHCO_3$ solution, dried ($MgSO_4$), and evaporated at reduced pressure to give 0.097 g (94%) of a white solid. Recrystallization from 15 ml of ether–hexane (1:3) gave 58.6 mg (57%) of 2-hydroperoxy-2-*o*-iodophenyl-1-phenyl-1-hexanone (**8**) as white crystals (two crops). The crystals were stored in the freezer, since decomposition was evident after several days at room temperature: mp 93–94.5° dec; ir (KBr) 3300 (OH) 3063, 2950, 3917, 2867, 1668 (C=O), 1592, 1575, 1462, 1441, 1424, 1321, 1302, 1292, 1267, 1250, 1230, 1181, 1097, 1022, 1009, 968, 861, 858, 761, 732, 708, 698, 683, 656, 643, 619, 568, 535, and 449 cm^{-1}; nmr (acetone-d_6) τ −1.13 (s, 1, OOH, exchangeable with D_2O), 1.94–3.22 (m, 9, aromatic H), 7.18–7.45 (m, 2, $CH_2CH_2CH_2CH_3$), and 8.28–9.55 (m, 7, other aliphatic H).

Anal. Calcd for $C_{18}H_{19}IO_3$: C, 52.70; H, 4.67; I, 30.92. Found: C, 52.73; H, 4.65; I, 30.67.

Method B.—A flask was charged with 2.25 g (5.68 mmol) of **2**, 75 ml of water, 125 ml of hexane, and 5 drops of concentrated HCl The reaction mixture was refluxed for 30 min with vigorous stirring, filtered hot to remove any unreacted starting material, and cooled to room temperature. Ether was added until the precipitated solid dissolved, and two clear layers resulted. Workup as before (method A) gave a waxy solid that was triturated with a minimum amount of hexane to give 1.72 g (74%) of a white solid. Recrystallization from 180 ml of ether–hexane (1:3) gave 1.25 g of (54%) of **8** (two crops).

2-*o*-Iodophenyl-1-phenyl-1-hexanone (7).[26]—A sealed tube containing 200 mg (0.505 mmol) of **4b** and 2.00 ml of 30% aqueous DMF and protected from light was heated in an oil bath at 161 ± 2° for 308 hr. The tube was cooled to room temperature and opened. Ether and water were added to form two layers which

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[25] These products probably arise from decomposition of α-hydroperoxy ketone **8** which is formed by reaction of **2** with water and oxygen present.

[26] This procedure is similar to those described in L. L. Miller and D. A. Kaufman, *J. Amer. Chem. Soc.*, **90**, 7282 (1968).

were separated. The aqueous layer was extracted with ether and the combined organic phase was extracted several times with water. The dried organic phase ($MgSO_4$) was evaporated to give 0.161 g of an oil. Analysis by glpc (20% OV1, 6 ft × 0.25 in., 205°, 88 ml/min He) indicated 47.5% 2-*o*-iodophenyl-1-phenyl-1-hexanone (**7**), 46.2% unreacted diiodo compound **4b**, and 6.3% of various unidentified materials. Preparative glpc (same conditions) gave pure 2-*o*-iodophenyl-1-phenyl-1-hexanone (**7**) as a viscous colorless oil: ir (neat) 3059, 2958, 2930, 2870, 2860, 1680 (C=O), 1591, 1575, 1555, 1460, 1444, 1430, 1342, 1280, 1253, 1230, 1200, 1176, 1008, 968, 984, 934, 750, 715, 699, 683, 652, 582, and 545 cm^{-1}; nmr (CCl_4) τ 1.89–3.42 (m, 9, aromatic H), 5.07–5.40 (m, 1, tertiary H), and 7.59–9.38 (m, 9, $CH_2CH_2CH_2CH_3$); mass spectrum m/e 378 (M^+), 322, 251 ($M^+ - I$), 217, 165, 115, 106, 105 ($PhC{=}O^+$), 91, 90, 77 (Ph^+), and 51.

Anal. Calcd for $C_{18}H_{19}IO$: C, 57.16; H, 5.07. Found: C, 57.06; H, 5.22.

1-*o*-Iodophenyl-1-pentanone (10).—To a solution of 4.84 g (19.0 mmol) of *o*-iodobenzaldehyde in 50 ml of dry ether there was added dropwise over a period of 40 min 7.00 ml (21.0 mmol) of 3.00 *M* *n*-butylmagnesium chloride in tetrahydrofuran. After the reaction mixture had been refluxed for 2 hr, the cooled white suspension was poured into water. Acidification with H_2SO_4 followed by addition of ether and water gave two layers which were separated. The aqueous layer was extracted with ether and the combined ether phase was washed with water, dried ($MgSO_4$), and evaporated to give 5.49 g of an oil. Infrared spectroscopy indicated the absence of carbonyl bands and the presence of an OH band at 3338 cm^{-1}. To the oil dissolved in 40 ml of acetone, the Jones reagent[27a] was added dropwise with stirring until the brown color persisted. After excess reagent had been destroyed with $NaHSO_3$ solution and the reaction mixture had been filtered, the green residue was washed with several portions of acetone. To the combined filtrate, ether and water were added, forming two layers, which were separated. The aqueous layer was extracted with ether, and the combined ether phase was washed with water, saturated $NaHCO_3$ solution, and again water, then dried ($MgSO_4$), and evaporated to give 4.41 g of a yellow oil. Analysis by glpc (20% OV1, 6 ft × 0.25 in., 160°, 88 ml/min He) indicated 47% 1-*o*-iodophenyl-1-pentanone (**10**), 34% *o*-iodobenzaldehyde, and 20% of various unidentified materials. Ketone **10** was purified by preparative glpc (same conditions) to give an analytical sample as a pale yellow oil: ir (neat) 3059, 2960, 2935, 2873, 1696 (C=O), 1588, 1556, 1459, 1426, 1399, 1377, 1351, 1341, 1275, 1245, 1205, 1049, 1020, 1013, 1004, 978, 969, 756, 728, 666, and 636 cm^{-1}; nmr (CCl_4) τ 2.18 (d with further splitting evident, 1, proton ortho to iodine), 2.46–3.20 (m, 3, other aromatic H), 7.18 (t, 2, $CH_2C{=}O$), and 8.01–9.33 (m, 7, other aliphatic H); mass spectrum m/e 288 (M^+), 246, 231 ($M^+ - CH_2CH_2CH_2CH_3$), 203 ($M^+ - C{=}O - CH_2CH_2CH_2CH_3$), 161 ($M^+ - I$), 105, 104, 91, 77, 76, 75, 74, 57, 51, and 50.

Anal. Calcd for $C_{11}H_{13}IO$: C, 45.85; H, 4.55. Found: C, 45.89; H, 4.48.

The formation of *o*-iodobenzaldehyde in 34% yield apparently reflects substantial reduction[28] of the starting material by the Grignard reagent followed by subsequent oxidation by the Jones reagent.

Thermal Decomposition of 8 in Heptane.—A suspension of 1.26 g (3.07 mmol) of **8** in 50 ml of heptane was refluxed for 20 min. Solvent removal gave an oil which partially solidified on standing. The semisolid was taken up in ether and extracted several times with saturated $NaHCO_3$ solution. The ether phase was dried ($MgSO_4$) and evaporated to give 0.91 g of a yellow oil. The $NaHCO_3$ extracts were acidified and extracted twice with ether. The extracts were dried ($MgSO_4$) and evaporated to give 230 mg (62%) of a white solid identified as benzoic acid. Recrystallization from hexane gave white crystals whose ir spectrum (KBr) was identical with that of an authentic sample of benzoic acid, mp and mmp 121–122° (lit.[29a] mp 121°).

The yellow oil was distilled with a short-path apparatus to give 530 mg (60%) of a pale yellow oil, bp 85° (0.07 mm). Preparative glpc (20% OV1, 6 ft × 0.25 in., 160°, 104 ml/min He) gave analytically pure 1-*o*-iodophenyl-1-pentanone (**10**) identical (ir and mass spectroscopy) with an authentic sample.

Analysis of 8 by Iodometry.[30]—A weighed sample of *ca.* 40–50 mg of **8** was dissolved in 25 ml of 2-propanol in an iodine flask. Several small pieces of Dry Ice were added, followed by 10 drops of glacial acetic acid and several drops of saturated KI solution. The stopper was set in place and sealed with 2-propanol. The flask was gently heated on a steam bath for 15 min to give a dark brown solution of iodine. To the hot solution were added 25 ml of water and several small pieces of Dry Ice. Immediate titration with 0.025 *N* $Na_2S_2O_3$ to the disappearance of the iodine color allowed calculation of the molecular weight of **8**, calcd 410, found 425 (average of three determinations).

Reduction of 8. Method A.—To a solution of 388 mg (0.946 mmol) of **8** in 20 ml of absolute ethanol was added 71.1 mg (1.88 mmol) of $NaBH_4$. After the reaction mixture had been stirred at room temperature for 5 min, the excess $NaBH_4$ was decomposed by several drops of acetic acid. Ether and water were added to form two layers which were separated. The aqueous layer was extracted with ether. The combined ether phase was extracted with saturated $NaHCO_3$ solution, washed with water, dried ($MgSO_4$), and evaporated to give 310 mg of a semisolid. Trituration with a minimum of hexane gave 250 mg (67%) of 2-hydroxy-2-*o*-iodophenyl-1-phenyl-1-hexanone (**9**). Recrystallization from hexane gave an analytical sample: mp 102–103°; ir 3450 (OH), 3062, 2936, 2924, 2865, 1661 (C=O), 1591, 1570, 1457, 1443, 1430, 1418, 1378, 1370, 1287, 1261, 1240, 1217, 1178, 1162, 1139, 1021, 1010, 978, 971, 965, 841, 792, 758, 730, 716, 702, 689, 659, 640, 620, 535, and 441 cm^{-1}; nmr ($CDCl_3$) τ 2.02–3.18 (m, 9, aromatic H), 5.17 (s, 1, OH, exchangeable with D_2O), 7.64 (broad t with further splitting evident, 2, $CH_2CH_2CH_2CH_3$), and 8.37–9.47 (m, 7, other aliphatic H); mass spectrum m/e 289 ($M^+ - PhCO$), 233, 231 ($C_6H_4ICO^+$), 203 ($C_6H_4I^+$), 143, 133, 120, 91, 78, 77 (Ph^+), 76 ($C_6H_4\cdot^+$), 71, and 57.

Anal. Calcd for $C_{18}H_{19}IO_2$: C, 54.84; H, 4.86; I, 32.19. Found: C, 54.88; H, 4.81; I, 32.02.

Method B.—To a solution of 646 mg (1.58 mmol) of **8** in 50 ml of acetone there were added 3 drops of acetic acid and 1 ml of a saturated acetone solution of NaI. The solution was refluxed gently on a steam bath for 15 min, cooled to room temperature, and treated with $Na_2S_2O_3$ solution to destroy the liberated iodine. Water and ether were added to form two layers which were separated. The aqueous layer was extracted with ether, and the combined ether phase was extracted with saturated $NaHCO_3$ solution, dried ($MgSO_4$), and evaporated to give 590 mg of a yellow oil. Trituration with a minimum amount of pentane and cooling gave 280 mg (45%) of **9**. Recrystallization from hexane gave analytically pure **9**, identical (ir and mass and nmr spectroscopy) with a sample prepared by method A, mp and mmp 102–103°.

Anal. Calcd for $C_{18}H_{19}IO_2$: C, 54.84; H, 4.86; I, 32.19. Found: C, 54.57; H, 4.87; I, 32.19.

Oxidative Cleavage of 9 with Lead Tetraacetate.—To a solution of 78.4 mg (0.119 mmol) of **9** in 5 ml of dry benzene was added 133 mg (0.300 mmol) of $Pb(OAc)_4$. After 1 hr of reflux the off-white suspension was cooled to room temperature and several drops of ethylene glycol were added to destroy any excess reagent. The reaction mixture was filtered, and the residual salts were washed with several portions of benzene. To the combined benzene filtrate were added ether and water to form two layers which were separated. The organic layer was extracted twice with saturated $NaHCO_3$ solution, washed with water, dried ($MgSO_4$), and evaporated to give 51.4 mg of a yellow oil. The $NaHCO_3$ extracts were acidified and extracted twice with ether. The ether extracts were dried ($MgSO_4$) and evaporated to give 8.1 mg (33%) of benzoic acid. Recrystallization from hexane gave white crystals identical (ir) with an authentic sample, mp and mmp 119.5–120° (lit.[29a] mp 121°). Reduction of the reflux time to 0.5 hr increased the yield of benzoic acid to 50%.

The yellow oil was purified by preparative glpc (20% OV1, 6 ft × 0.25 in., 160°, 104 ml/min He) to give 24.6 mg (43%) of analytically pure 1-*o*-iodophenyl-1-pentanone (**10**) identical (ir and mass spectroscopy) with an authentic sample.

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[27] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. 1, Wiley, New York, N. Y., 1967: (a) p 142; (b) p 817.

[28] Reduction by the Grignard reagent accompanies its addition to hindered carbonyl compounds: D. J. Cram and G. S. Hammond, "Organic Chemistry," McGraw-Hill, New York, N. Y., 1964, p 316.

[29] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," Wiley, New York, N. Y., 1964: (a) p 313; (b) p 147.

[30] Based on procedures in A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience, New York, N. Y., 1954, p 52.

Attempted cleavage of **9** with periodic acid in THF[27b] was unsuccessful, possibly because of steric hindrance to the formation of the intermediate ester.[29b]

Measurement of the Absorption of Oxygen by 2.[31]—A sample of *ca.* 4–5 mg of **2** was accurately weighed to ±0.1 mg and added to the Warburg flask containing 4.00 ml of water, pH 2.00 buffer or 0.05 *M* KCl solution, previously equilibrated at 24.7 ± 0.10°. The apparatus was quickly assembled, the stirrer was started, and readings were taken and corrected with the thermobarometer. Typical results follow.

Fluid	% reaction	Approximate time of reaction, hr
Water	96	1.5–2.5
pH 2.00	95	5–6
0.05 *M* KCl	95	6

Determination of the Crystal Structures of 3-Butyl-2-phenylbenziodolium Chloride (2) and Dibenziodolium Tetrafluoroborate (11) by X-Ray Analysis.—Dibenziodolium tetrafluoroborate (**11**) was prepared according to the method of Beringer and Chang,[32] by metathesis of the iodonium chloride with silver tetrafluoroborate in 20% H_2O–80% MeOH followed by recrystallization from water. Single crystals (needles) of **11** and **2** were chosen with dimensions 0.15 × 0.30 × 0.10 mm and 0.10 × 0.30 × 0.10 mm, respectively. A Picker four-circle automated diffractometer was used for the collection of 1527 independent reflections in the case of **11** and 2175 in the case of **2** to a 2θ angle at 45°. A 2θ–θ scan mode was used. Mo Kα radiation was used. From Weissenberg photographs the space groups $P\bar{1}$ and $C2/c$ (later confirmed) have been assigned to compounds **11** and **2**, respectively. The unit cell parameters have been determined by least-squares refinement of the setting angles of 12 reflections. The resulting crystal data are reported in Table I. The structures have been solved by Patterson method and refined by least-squares calculations to R values of 0.036 and 0.031 for **11** and **2**, respectively. $R = \Sigma w|\Delta F|/\Sigma wF_o$, $w = 1/(A + BF_o + CF_o^2)$, with $A = 0.11111$, $B = 1/18F_{o(\min)}$, $C = 2(18F_{o(\min)} \cdot F_{o(\max)})$.[33] The refinement was performed using anisotropic thermal parameters for all the nonhydrogen atoms. The hydrogens were included assuming their geometrically calculated positions. Absorption corrections have been done assuming the crystals are cylinders. We used the atomic scattering factors of Moore.[34] The tables of observed and calculated structure factors are available."

TABLE I

CRYSTAL DATA FOR **11** AND **2**

Dibenziodolium Tetrafluoroborate

a = 10.168 ± 0.004 Å
b = 10.081 ± 0.004 Å
c = 7.238 ± 0.003 Å
α = 110° 46 ± 3 min
β = 105° 11 ± 2 min
γ = 106° 2 ± 2 min

Space group $P1$
$Z = 2$
V = 610.9 Å^3
D_x = 2.00 g cm^{-3}
D_{obsd} = 1.97 g cm^{-3}
μ = 26.8 cm^{-1} (Mo Kα)

3-Butyl-2-phenylbenziodolium Chloride

a = 28.310 ± 0.019 Å
b = 7.646 ± 0.005 Å
c = 17.547 ± 0.014 Å
β = 121° 50 ± 3 min

Space group $C2/c$
$Z = 8$
V = 3227.0 Å^3
D_x = 1.64 g cm^{-3}
D_{obsd} = 1.63 gm^{-3}
μ = 21.6 cm^{-1} (Mo Kα)

Tetraphenyliodolium Chloride (16).—A suspension of 1,4-dilithiotetraphenyl-1,3-butadiene (**15**)[35] was prepared under argon rom 26.7 g (150 mmol) of diphenylacetylene, 1.05 g (150 mg-atoms) of lithium wire in 75 ml of anhydrous ether. The suspension was transferred *via* a syringe (equipped with an 18-gauge needle) to an addition funnel and added dropwise over a period of 45 min to a stirred solution of 20.8 g (80.0 mmol) of *trans*-chlorovinyliodoso dichloride in 350 ml of anhydrous ether under argon at −78°. Small portions of ether were used to facilitate the transfers. After the resulting yellow suspension had been stirred for 15 min, excess ether–HCl complex was added dropwise. The greenish suspension that resulted was warmed to room temperature, filtered, washed with ether, suspended in water, filtered, dried, suspended in ether, filtered, and dried. The yellow solid was stirred in 50 ml of methylene chloride for 15 min to give a fine white powder suspended in a brownish green solution. Vacuum filtration through two layers of filter paper and a fine sintered-glass funnel gave 862 mg of a white powder. Slow dilution of the clear methylene chloride filtrate with a large volume of hexane caused precipitation of 963 mg (2.5%) of crude tetraphenyliodolium chloride as a pale yellow solid. Addition of ether dropwise to a solution of the crude salt in a minimum of tetrahydrofuran precipitated an analytically pure sample as an off-white solid. If insufficient ether were added to cause immediate precipitation, the pure salt could be obtained as off-white fluffy crystals by cooling the solution overnight: mp 140.5–141.5° dec (tube in at 135° and heated at *ca.* 1–2°/min); ir 3076, 3062, 3032, 1594, 1570, 1480, 1439, 1277, 1172, 1152, 1068, 1024 998, 952, 913, 872, 791, 779, 753, 726, 700, 690, 628, 622, 561, and 552 cm^{-1}; nmr (CD_2Cl_2) 2.62–3.18 (m, Ar H).

Anal. Calcd for $C_{28}H_{20}ICl$: C, 64.82; H, 3.89; I, 24.46. Found: C, 64.71; H, 3.96; I, 24.64.

Tetraphenyliodolium Iodide.—To a solution of 57 mg (0.11 mmol) of crude tetraphenyliodolium chloride in a minimum amount of acetone there was added a solution of excess anhydrous lithium iodide in acetone. Tetraphenyliodolium iodide precipitated as an orange powder: mp 133.0–133.5° dec to red liquid (tube in at 125° and heated at *ca.* 1–2°/min); ir essentially identical with that of tetraphenyliodolium chloride.

Anal. Calcd for $C_{28}H_{20}I_2$: C, 55.10; H, 3.30; I, 41.59. Found: C, 55.18; H, 3.27; I, 41.67.

Decomposition of the Tetraphenyliodolium Salts.—Tetraphenyliodolium chloride was decomposed in the mass spectrometer: *m/e* 520 (M^+ for ^{37}Cl), 518 (M^+ for ^{35}Cl), 483 (M^+ − Cl), 393 (M^+ − 1 for ^{37}Cl), 391 (M^+ − 1 for ^{35}Cl), 356 (M^+ − I − Cl), 355 ($C_{27}H_{19}^+$), 279 (M^+ − I − Cl − Ph), 278 ($C_{21}H_{14}\cdot^+$), 178 ($PhC{\equiv}CPh\cdot^+$), 77 (Ph^+).

Tetraphenyliodolium iodide was similarly decomposed in the mass spectrometer yielding the following mass spectrum which is identical with that obtained from 1,4-diiodo-1,2,3,4-tetraphenyl-1,3-butadiene:[36] *m/e* 610 (M^+), 483 (M^+ − I), 356 (M^+ − 21), 355 ($C_{27}H_{19}^+$), 279 (M^+ − 21 − Ph), 278 ($C_{21}H_{14}\cdot^+$), 178 ($PHC{\equiv}CPh\cdot^+$), and 77 (Ph^+).

Registry No.—**2**, 32730-78-2; **3**, 32730-79-3; **4a**, 32721-29-2; **4b**, 32721-30-5; **5a**, 32721-31-6; **5b**, 32721-32-7; **6a**, 32721-33-8; **6b**, 32721-34-9; **7**, 32730-80-6; **8**, 32730-81-7; **9**, 32730-82-8; **10**, 32730-83-9; **11**, 18116-06-8; **16**, 34143-18-5; **17**, 34143-19-6.

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[31] Based on procedures in W. W. Umbrieit, R. H. Burris, and J. F. Stauffer, "Manometric Techniques," 4th ed, Burgess Publishing Co., Minneapolis, Minn., 1964.

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