ing to a small, magnetically driven centrifugal pump with a polypropylene head, through a small flask containing pH meter probes and back to the electrolysis cell. The calomel electrode used for pH measurements was separated from the catholyte by an agar plug prepared from 3% agar in 10% aqueous tetramethylammonium chloride. The anode compartment was made from a coarse sintered-glass filter funnel with the walls removed and stem lengthened. A layer of fresh hot solution of 3% agar in 10% aqueous tetramethylammonium chloride was poured onto the anode side of the sintered glass for each experiment. The cell was cooled with an isopropyl alcohol bath to which Dry Ice was added as needed.

General Procedure.—The electrolyses were carried out as follows. Acid (0.15 mol) was neutralized with ammonium hydroxide and diluted to about 250 ml. To this solution was added 18.6 g of boric acid or 20 g of $(NH_4)H_2PO_4$, if a buffer was used. The solution was diluted to 300 ml and adjusted to pH 6 with ammonium hydroxide or dilute hydrochloric acid. This solution, along with 200 ml of benzene, was added to the electrolysis cell. The anolyte consisted of 10% tetramethylammonium chloride with some ammonium hydroxide added to keep the solution basic. The catholyte was stirred vigorously to maintain a good emulsion.

After the solution had been cooled to about 10°, the electrolysis was started with the current set at 0.8 A (current density about 10 mA/cm^2). During the electrolysis the temperature was maintained near 10° and the pH was kept at 6 ± 0.2 by the addition of dilute HCl. After 0.5 hr, the electrolysis was stopped, an internal standard was added to the benzene, and that solution was analyzed by gas chromatography for the desired aldehyde. It was on this basis that the current efficiencies shown in Table I were determined.

In a longer experiment using salicylic acid with boric acid present, the electrolysis was carried out at 1.5 A for 5 hr. After each hour, the mercury pool was replaced because of the large amount of mercury foam which had formed on the surface.

Analysis.—After the electrolysis, the benzene was separated and analyzed for salicylaldehyde as below. The aqueous catholyte was divided into two equal portions. One-half was acidified to pH 1 with concentrated HCl and extracted with ether. Gas chromatographic analysis of the ether solution for saligenin indicated that a 4% current efficiency to saligenin was obtained. The other portion of the catholyte was taken to pH 9 with NaOH, diluted, and analyzed for salicylate with a salicylate ion selective electrode[19] by the known addition technique[20] and comparing to known solutions containing approximately the same composition. Of the initial salicylic acid, 90% was accounted for either as unreacted salicylic acid, salicylaldehyde (80% yield, 50% current efficiency), or saligenin.

The analyses of the aldehydes except for hydroxy aldehydes were carried out on a 10 ft × $^1/_8$ in. gas chromatography column packed with 10% Carbowax 20M on Chromosorb G using biphenyl or naphthalene as internal standards.

Salicylaldehyde, saligenin, *p*-hydroxybenzaldehyde, and vanillin were treated in benzene (or ether) solution with Regisil [bis(trimethylsilyl)trifluoroacetamide] and then analyzed by gas chromatography on a 10 ft × $^1/_8$ in. column packed with 10% SE-52 on Chromosorb W using naphthalene or biphenyl as the internal standards.[21]

Acknowledgment.—The author wishes to thank Mr. W. O. Jackson for technical assistance and Drs. M. M. Baizer and D. A. Tyssee for helpful discussions.

(19) W. M. Haynes and J. H. Wagenknecht, *Anal. Lett.*, **4**, 491 (1971).

(20) Orion Newsletter, July 1969, p 9.

(21) Since this paper was submitted, an article has appeared [J. A. Harrison and D. W. Shoesmith, *J. Electroanal. Chem.*, **32**, 125 (1971)] showing significant improvements in the yields of aldehydes in the reduction of aromatic acids by Udupa's method[6b] (rotating Cu amalgam cathode). This was accomplished by replacing metal ions with tetramethylammonium ions and by adding ethanol to the catholyte.

Exchange of Aryl Ligands to Polyvalent Iodine[1]

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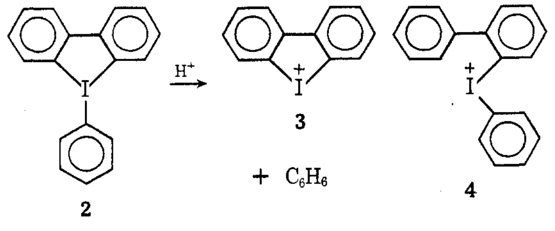
By treatment with aryllithium reagents (RLi) and then acid, diaryliodonium salts ($Ar_2I^+X^-$) have been converted to ArI^+X^- and $R_2I^+X^-$. With $[RLi]/[Ar_2I^+]$ near unity, a triaryliodine can be isolated. The product ratio from its acid cleavage reflects the relative susceptibility of Ar and R to protodeiodination and the selectivity of the reagent. Results include cases where Ar_2 = 2,2′-biphenylene (*i.e.*, Ar_2I^+ is the dibenziodolium ion) and R = C_6H_5, and where Ar = 4-chlorophenyl and R = C_6H_5. With $[RLi]/[Ar_2I^+] > 1$, aryl groups can be exchanged through three- and four-coordinated iodine intermediates, such as $Ar_2R_2I^-Li^+$. Treatment of the reaction mixture with acid gives iodonium salts whose amounts depend on the equilibria and on the cleavage ratios. Successful replacements include $4\text{-}ClC_6H_4$ by C_6H_5 and C_6H_5 by $4\text{-}(CH_3)_2NC_6H_4$ and by 2,2′-biphenylene.

Wittig and Clauss[2] reported the formation of the unstable triphenyliodine (**1**) by the addition of 1 equiv of phenyllithium solution to an ether suspension of a diphenyliodonium halide at −80°. Similarly, when a dibenziodolium halide **3** was treated with phenyllithium at 0°, a more stable triaryliodine, 5-phenyl-5*H*-dibenziodole (**2**), was produced.[3,4] Treatment of triaryliodines **1** and **2** with acids had been reported to regenerate the starting iodonium salts.[2,3] However, in a recent investigation of the acid cleavage of 5-phenyl-5*H*-dibenziodole (**2**) we found that, in addition to the starting cyclic dibenziodolium salt (**3**), a new acyclic 2-biphenylylphenyliodonium salt (**4**) was also formed.[1] The dependence of the product distribution on the protonic or Lewis acid used has been reported.[1]



We should now like to note that this two-step process, formation of a triaryliodine and its cleavage by acid, may be used to replace one aryl group with another in a

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(1) (a) Preceding paper: F. M. Beringer and L. L. Chang, *J. Org. Chem.*, **36**, 4055 (1971). (b) Taken from the dissertation of Lydia L. Chang submitted to the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Chemistry), 1971. (c) Supported by National Institutes of Health, 1968–1969, through Grant No. 5-SO5-FR-07063-04.

(2) G. Wittig and K. Clauss, *Justus Liebigs Ann. Chem.*, **578**, 136 (1952).

(3) K. Clauss, *Chem. Ber.*, **88**, 268 (1955).

(4) Diphenyliodonium chloride and *n*-butyllithium form an unstable trivalent organoiodine which decomposes in solution at approximately −40°: F. M. Beringer, J. W. Dehn, Jr., and M. Winicov, *J. Amer. Chem. Soc.*, **82**, 2948 (1960).

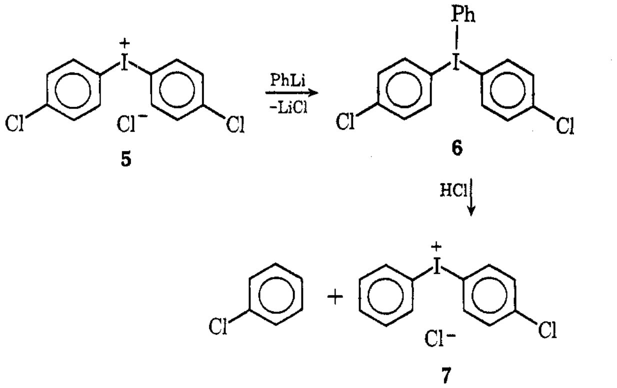
TABLE I

EXCHANGE OF ARYL GROUPS ATTACHED TO POLYVALENT IODINE.
REACTION[a] OF ARYLLITHIUM WITH IODONIUM SALTS, FOLLOWED BY QUENCHING

Ar_2I^+	RLi	[RLi]/[Ar_2I^+]	Time, min	Quenching reagent	% R in iodonium product[b]	Other products
$(4\text{-}ClC_6H_4)_2I^+$	PhLi	1	15	HCl	50[c]	*d*
$(4\text{-}ClC_6H_4)_2I^+$	PhLi	1	15	PhCOOH	50[e]	*f*
$(4\text{-}ClC_6H_4)_2I^+$	PhLi	1.3	30	PhCOOH	77	*g*
$(4\text{-}ClC_6H_4)_2I^+$	PhLi	1.46	30	CO_2 then HCl	76	*h, i*
$(4\text{-}ClC_6H_4)_2I^+$	PhLi	2.3	30	PhCOOH	86	*j*
$(4\text{-}ClC_6H_4)_2I^+$	PhLi	4	30	PhCOOH	100[k]	*l*
$(4\text{-}ClC_6H_4)_2I^+$	PhLi	4	30	CO_2 then HCl	100[k]	*m*
Ph_2I^+	$4\text{-}ClC_6H_4Li$	1	30	CO_2 then HCl	0[n]	*o*
Ph_2I^+	$4\text{-}(CH_3)_2N\text{-}C_6H_4Li$	4	30	CO_2 then HCl	100[p]	*q, r*

[a] All reactions were run in diethyl ether at Dry Ice–acetone temperature under argon. [b] Based on the amount of RI from the pyrolysis of the mixture of iodonium iodides. [c] The product was pure 4-chlorodiphenyliodonium cation precipitated as iodide (86%). [d] Chlorobenzene in 83.5% yield based on the milliequivalents of chlorophenyl group that exchanged. [e] The product was 4-chlorodiphenyliodonium cation precipitated as iodide (89%). [f] Chlorobenzene in 86% yield. [g] Chlorobenzene in 73% yield. [h] Benzoic acid in 27% yield based on the unreacted phenyllithium. [i] 4-Chlorobenzoic acid in 21% yield based on the 4-chlorophenyl group that exchanged. [j] Chlorobenzene in 58% yield. [k] The product was pure diphenyliodonium cation precipitated as the iodide (87%). [l] Chlorobenzene in 77% yield. [m] 4-Chlorobenzoic acid in 70% yield determined as the methyl ester by vpc. [n] Diphenyliodonium cation in 69% yield recovered as the iodide. [o] 4-Chlorobenzoic acid in 74% yield determined as the methyl ester by vpc. [p] Pure 4,4′-di(dimethylamino)diphenyliodonium iodide in 72.5% yield. [q] Benzoic acid in 28.6% yield determined as the methyl ester. [r] 4-Dimethylaminobenzoic acid in 43% yield.

diaryliodonium salt. Thus bis(4-chlorphenyl)phenyliodine (**6**), obtained from 4,4′-dichlorodiphenyliodonium chloride (**5**) and 1 equiv of phenyllithium, gave on cleavage with hydrogen chloride unsymmetrical 4-chlorodiphenyliodonium chloride (**7**). The preferential cleavage of the 4-chlorophenyl group is striking, but no explanation is advanced now.



Consideration of this two-step process for aryl exchange on iodine led to the formulation of another possible route. Central to this idea was the likelihood that in a triaryliodine the large iodine atom, with unfilled d orbitals, would accept another ligand as from an aryllithium.

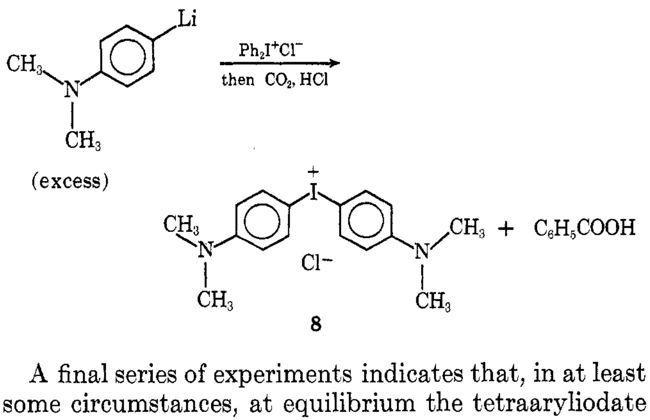
$$\begin{matrix} Ar_3I \\ + RLi \end{matrix} \rightleftharpoons \begin{matrix} Ar_3\bar{I}R \\ Li^+ \end{matrix} \rightleftharpoons \begin{matrix} Ar_2IR \\ + ArLi \end{matrix}$$

Further, it seemed probable that such a tetraryliodate ion would also be in equilibrium with a new triaryliodine and aryllithium. The triaryliodine might be formed *in situ*, as before, and then allowed to exchange with aryllithium reagent.

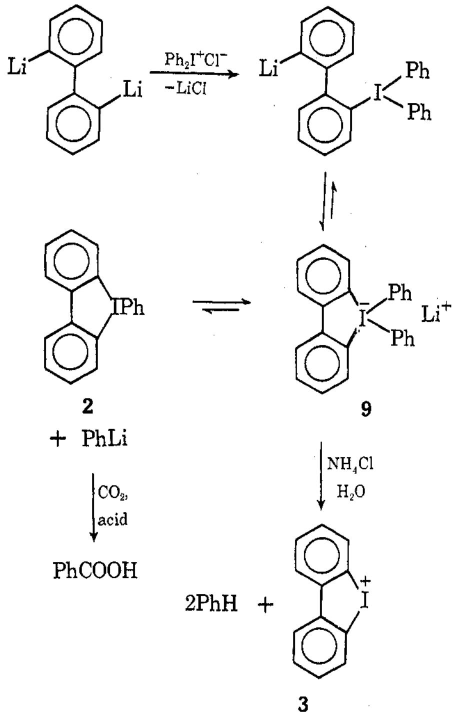
$$\begin{tikzcd} \begin{matrix} Ar_2I^+X^- \\ + 2RLi \end{matrix} \arrow[r, "-LiX"] & \begin{matrix} Ar_2IR \\ + RLi \end{matrix} \arrow[d, shift left] \\ & Ar_2\bar{I}R_2Li^+ \arrow[u, shift left] \arrow[d, shift left] \\ \begin{matrix} X^-\overset{+}{I}R_2 \\ + 2ArLi \end{matrix} \arrow[r, "-LiX"] & \begin{matrix} ArIR_2 \\ + ArLi \end{matrix} \arrow[u, shift left] \end{tikzcd}$$

In the first successful example of this aryl exchange, 4,4′-dichlorodiphenyliodonium chloride (**5**) was treated with excess phenyllithium in various ratios; quenching with acid then gave mixtures of iodonium salts bearing phenyl and 4-chlorophenyl groups. As the excess of phenyllithium increased, the replacement of 4-chlorophenyl groups was more extensive (Table I); with a fourfold excess of phenyllithium the exchange was essentially complete. If the reaction mixtures containing excess phenyllithium were treated with carbon dioxide before acidification, 4-chlorobenzoic acid was formed along with benzoic acid.

In another exchange reaction, of more synthetic interest, the phenyl groups in the readily available diphenyliodonium chloride were replaced; treatment with excess 4-dimethylaminophenyllithium followed by acidification gave a previously unknown salt, 4,4′-di(dimethylamino)diphenyliodonium chloride (**8**).



A final series of experiments indicates that, in at least some circumstances, at equilibrium the tetraaryliodate ion may be formed in substantial amount from the triaryliodine and aryllithium. When a suspension of diphenyliodonium chloride in tetrahydrofuran was treated with a slight excess of 2,2′-dilithiobiphenyl at low temperature, a bright citrus-yellow suspension resulted, which gave a good yield (74%) of dibenziodolium iodide (**3**) after acidification but only 2% of benzoic acid after carbonation and acidification. This shows the absence of substantial amounts of aryllithium in the reaction mixture and supports the formulation of a tetraaryliodate intermediate (**9**), in which the diphenyliodonium ion has accepted a new bidentate ligand.



It is hoped that the further development of this approach utilizing tetraryliodate ions will open up the synthesis of new organoiodines bearing two, three, or four aryl or other organic groups.

Experimental Section

Analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Gas chromatography was done on 6-ft columns, packed with 20% OV-1 on 60/80 Chromosorb W with an Aerograph 1520-A gas chromatograph. Melting points were taken in capillary tubes on a Thomas-Hoover apparatus and are corrected.[5] All reactions involving organolithium reagents or triaryliodines were performed in an inert atmosphere.

Diphenyliodonium chloride,[6] 4,4-dichlorodiphenyliodonium chloride,[7] dibenziodolium chloride,[8] 4-dimethylaminodiphenyllithium,[9] 4-chlorophenyllithium,[10] and 2,2′-dilithiobiphenyl[11] were prepared by previously reported procedures. 5-Phenyl-5*H*-dibenziodole, prepared according to Clauss,[3] is sensitive to air and heat but may be kept for a few days in a vacuum desiccator at 0°.

Reaction of 5-Phenyl-5*H*-dibenziodole (2) with Hydrogen Chloride.—A solution of **2** was prepared under argon, standardized with benzoic acid,[1] and used for reaction immediately.

When a solution of 1.84 mmol of **2** in 50 ml of tetrahydrofuran was added to a solution of 3.44 mmol of hydrogen chloride in tetrahydrofuran, a white precipitate formed immediately. After stirring for 30 min, the solid was collected, washed with tetrahydrofuran, dried, and weighed (0.63 g). After this white solid was redissolved in 100 ml of hot water and treated with concentrated potassium iodide solution, the pale yellow mixed iodonium iodides that precipitated were collected, washed with water, and dried. This mixture was then heated at 200° for 5 min to give a dark oil, which was shown by vpc to contain 0.79 mmol of iodobenzene, 0.75 mmol of 2-iodobiphenyl, and 0.79 mmol of 2,2′-diiodobiphenyl, indicating 0.79 mmol (50%) of 2-biphenylylphenyliodonium ion (**4**) and 0.79 mmol (50%) of dibenziodolium ion (**3**) in the product mixture.[1]

4,4′-Dichlorodiphenyliodonium Chloride (5) with Phenyllithium.—To a suspension of **5** (1.23 g, 3.18 mmol) in 5 ml of anhydrous ether, 2 ml of 1.59 *M* phenyllithium solution (3.18 mmol) was added dropwise at −73°. The bright citrus-yellow mixture was stirred for 0.5 hr at −73° and treated with 20 ml (11 mmol) of 0.52 *M* hydrogen chloride in ether, giving a white precipitate. The mixture was stirred for 0.5 hr while warming to room temperature. The precipitate was collected, dissolved in hot water, and treated with potassium iodide to give 1.26 g (2.86 mmol, 90%) of 4-chlorodiphenyliodonium iodide, mp 160° dec. Vpc analysis of the products of pyrolysis of this iodonium iodide showed 1.00 equiv of iodobenzene for each 1.01 equiv of 4-chloroiodobenzene.

Anal. Calcd for $C_{12}H_8I_2Cl$: C, 32.77; H, 2.03; I, 57.40; Cl, 7.80. Found: C, 32.46; H, 1.98; I, 57.69; Cl, 7.75.

The ethereal mother liquor was washed with dilute NaOH solution and dried over $MgSO_4$, and was shown to contain 2.63 mmol (83.5%) of chlorobenzene.

When the above reaction was run with a 1:4 mole ratio of salt **5** to phenyllithium, pure diphenyliodonium iodide was obtained in 81% yield, mp 176° dec (lit.[5] mp 182–183° dec). Pyrolysis gave iodobenzene only. The infrared spectrum was in accord with that of an authentic sample.

Reactions run at mole ratios between 1:1 and 1:4 of **5** and phenyllithium, after quenching with acid, gave mixtures of 4-chlorodiphenyliodonium and diphenyliodonium salts; see Table I. The per cent of iodobenzene from the pyrolysis of the iodonium iodides was used as the per cent of the exchange reaction.

To demonstrate that 4-chlorophenyllithium was present in the reaction mixture, quenching with carbon dioxide was performed as in the following example. Through the citrus-yellow mixture from 2.38 mmol of **5** and 3.5 mmol of phenyllithium in anhydrous ether, stirred at −73° for 0.5 hr, dry carbon dioxide gas was passed for 15 min with vigorous stirring. The resulting mixture was treated with 10 mmol of hydrogen chloride in ether. The white solid was collected, dissolved in hot water, and treated with KI to give 0.31 g of iodonium iodides, which decomposed on pyrolysis to 2.65 mmol of iodobenzene and 0.84 mmol of 4-chloroiodobenzene, indicating 76% of phenyl groups in the iodonium salts.

The organic phase was separated into acidic and nonacidic components by extraction with dilute NaOH. The aqueous phase was separated and neutralized with dilute HCl to give a white solid. The mixture was then extracted three times with ether, esterified with diazomethane in ether, and analyzed by vpc to give 0.23 mmol (27% based on the millimoles of unreacted phenyllithium) of methyl benzoate and 0.82 mmol (21% based on the milliequivalents of 4-chlorophenyl groups exchanged) of methyl 4-chlorobenzoate.

Diphenyliodonium Chloride and 4-Chlorophenyllithium.—Reaction between 0.733 g (2 mmol) of diphenyliodonium chloride and 2.2 mmol of 4-chlorophenyllithium in ether was carried out under the same conditions as described above. After quenching and usual work-up, 0.560 g (1.38 mmol, 69%) of diphenyliodonium iodide was isolated. The acidic organic product was esterified with diazomethane to give 1.48 mmol (67.3%) of methyl 4-chlorobenzoate.

Quenching a solution of 2.2 mmol of 4-chlorophenyllithium with carbon dioxide under the same reaction conditions gave 1.63 mmol (74.1%) of 4-chlorobenzoic acid (analyzed on vpc as methyl ester).

Diphenyliodonium Chloride with 4-Dimethylaminophenyllithium.—A suspension of 1.27 g (4 mmol) of diphenyliodonium chloride in ether and 20 mmol of 4-dimethylaminophenyllithium solution was allowed to react under the conditions described above. The resulting citrus-yellow suspension was subsequently quenched with carbon dioxide and hydrogen chloride in ether to give a pale yellow suspension. After the addition of

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(5) F. M. Beringer, *et al.*, *J. Amer. Chem. Soc.*, **81**, 342 (1959).

(6) F. M. Beringer, E. J. Geering, I. Kuntz, and M. Mausner, *J. Phys. Chem.*, **60**, 141 (1956).

(7) F. M. Beringer, M. Drexler, E. M. Gindler, and C. C. Lumpkin, *J. Amer. Chem. Soc.*, **75**, 2705 (1953).

(8) J. Collette, D. McGreer, R. Crawford, F. Chubb, and R. B. Sandin, *ibid.*, **78**, 3819 (1956).

(9) H. Gilman and I. Banner, *ibid.*, **62**, 344 (1940).

(10) H. Gilman in "Organic Reactions," Vol. VIII, Wiley, New York, N. Y., 1954, p 285.

(11) F. M. Beringer and R. A. Nathan, *J. Org. Chem.*, **34**, 685 (1969).

100 ml of water, two clear phases were separated. Treating the aqueous phase with concentrated potassium iodide solution gave a crude yellow solid. Recrystallization from ethanol gave 1.43 g (2.9 mmol, 72.5%) of fine yellow crystalline flakes of 4,4′-di(dimethylamino)diphenyliodonium iodide, mp 159° dec.

Anal. Calcd for $C_{16}H_{20}N_2I_2$: C, 38.87; H, 4.05; N, 5.66; I, 51.42. Found: C, 39.22; H, 3.91; N, 5.59; I, 51.38.

The infrared spectrum (KBr) has aliphatic C–H stretching at 2900 cm^{-1}, CH_3–N stretching at 2805 cm^{-1}, CH_3 rocking at 1500 and 1440 cm^{-1}, and an aromatic para-disubstitution pattern at 805 cm^{-1}.

The aqueous filtrate was then neutralized with dilute sodium hydroxide solution to give an off-white precipitate, which after recrystallization from water gave 1.02 g (6.1 mmol, 43% based on unexchanged 4-dimethylaminophenyllithium) of 4-dimethylaminobenzoic acid, mp 239–240° (lit.[12] mp 240–241°).

The acidic product in the organic phase was separated by acid–base extractions and esterified with diazomethane to give 0.595 g of methyl benzoate (2.29 mmol, 28.6% based on the milliequivalents of phenyl group in the starting diphenyliodonium salt, 57.2% based on the millimoles of diphenyliodonium chloride).

Dibenziodolium Iodide from Diphenyliodonium Chloride and 2,2′-Dilithiobiphenyl.—To a white suspension of 1.27 g (4 mmol) of diphenyliodonium chloride in 40 ml of tetrahydrofuran at −73°, there was added 4.25 mmol of 2,2′-dilithiobiphenyl in ether. The resulting bright yellow semitransparent solution was stirred at −73° for 15 min and filtered rapidly into aqueous potassium iodide with stirring. The pale yellow solid that separated between two phases was collected, washed with ether and water, and dried to give 1.2 g (2.86 mmol, 71.5%) of dibenziodolium iodide, mp 220° dec (lit.[13] mp 210–215°). The infrared spectrum was in agreement with that of an authentic sample. The pyrolysis product was pure 2,2′-diiodobiphenyl, identified by vpc peak enhancement with an authentic sample. Analysis of the ether layer also showed 27% of biphenyl, apparently arising from unreacted 2,2′-dilithiobiphenyl.

When a similar reaction mixture was treated first with carbon dioxide and then with aqueous acid, the yield of benzoic acid was only 2%.

Registry No.—**2**, 32174-73-5; **5**, 34220-01-4; phenyllithium, 591-51-5; diphenyliodonium chloride, 1483-72-3; 4-chlorophenyllithium, 14774-78-8; 4-dimethylaminophenyllithium, 13190-50-6; 4,4′-di(dimethylamino), diphenyliodonium iodide, 34220-05-8.

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(12) C. A. Bischoff, *Ber.*, **22**, 343 (1889).

(13) L. Mascarelli and G. Benati, *Gazz. Chim. Ital.*, **38**, 619 (1908).

Oxidation of Arylpropenes by 2,3-Dichloro-5,6-dicyanoquinone[1]

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Oxidation of anethole, estragole, or 1-phenylpropene by DDQ in benzene gives mono- and/or bis(arylpropenyl) ethers of dichlorodicyanohydroquinone (DDHQ). These highly reactive intermediates can be further oxidized by DDQ to arylpropenals, converted to allylically rearranged alkyl arylpropenyl ethers by alcoholysis, or converted to arylpropenyl chlorides by treatment with HCl. No esr or CIDNP evidence for free-radical intermediates could be detected, and it is assumed from solvent and substituent kinetic effects that the initial oxidation involves hydride ion abstraction by DDQ. Exclusive incorporation of ^{18}O-labeled water into the aldehyde oxidation product implicates an acetal intermediate in this transformation. The allylic rearrangement which takes place on alcoholysis is postulated to proceed *via* a cyclic S_N2' mechanism in which hydrogen bonding of the alcohol to the departing hydroquinone anion determines the geometry of the transition state.

In addition to its widespread use for the introduction of conjugated double bonds in steroidal ketones and hydroaromatic systems,[4] 2,3-dichloro-5,6-dicyanoquinone (DDQ) has been used to generate stable carbonium ions (*e.g.*, cycloheptatrienyl and triphenylcyclopropenyl) and free radicals (*e.g.*, perinaphthenyl) from the parent hydrocarbons.[5] In cases where an intermediate ion or radical is of lower stability and simple dehydrogenation to an alkene is blocked, the intermediate may either undergo rearrangement (*e.g.*, 1,1-dimethyltetralin to 1,2-dimethylnaphthalene[6]) or collapse to a covalent adduct (*e.g.*, 2,2-dimethylindan,[7] diphenylmethane[8]). We have characterized the reaction of DDQ with arylpropenes, which falls into the latter category. Because of the ability of DDQ to abstract either hydride ions or hydrogen atoms, we have also investigated briefly the mechanism of this reaction, as well as that of the oxidation to arylpropenals by excess DDQ. Finally, we have explored some synthetically useful transformations based on these reaction.

Results and Discussion

Reactions of DDQ with *trans*-1-(*p*-methoxyphenyl)-propene (anethole), 3-(*p*-methoxyphenyl)propene (estragole), *trans*-1-phenylpropene, 2-phenylpropene, and *p*-methoxystyrene were carried out under a variety of conditions. Intensely colored molecular complexes formed immediately in all cases, but oxidation rates varied widely; the reactions could be conveniently followed by observing the disappearance of color and precipitation of the quinone reduction product, 2,3-dichloro-5,6-dicyanohydroquinone (DDHQ). Reaction of anethole with tetrachloro-*p*-benzoquinone (chloranil) in benzene was also carried out for comparative purposes; in this case, no oxidation occurred within 5 days at room temperature. Since oxidation of anethole by DDQ under these conditions proceeds measurably within 1 sec (see below), it can be concluded that DDQ is at least 10^5 times as reactive as chloranil in this case.

2-Phenylpropene was not oxidized by DDQ within 8 days under the above conditions, nor was any po-

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(1) Abstracted from the Ph.D. thesis of F. E. Lutz, University of Hawaii, 1970. Parts of this work have been published in preliminary form[2,3] and presented at the 26th Northwest Regional Meeting of the American Chemical Society, Bozeman, Mont., June 17, 1971. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the U. S. Public Health Service, National Institutes of Health, for support of this research.

(2) F. E. Lutz and E. F. Kiefer, *Tetrahedron Lett.*, 4851 (1970).

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(8) H.-D. Becker, *J. Org. Chem.*, **34**, 1203 (1969).