Acetylenic and Ethylenic Iodonium Salts and Their Reactions with a Carbanion[1,2]

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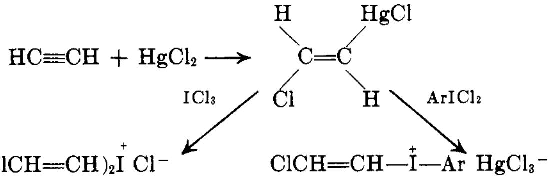
Phenyl(β-phenylethynyl)iodonium chloride, from iodosobenzene dichloride and lithium phenylacetylide, decomposes at room temperature to iodobenzene and chlorophenylacetylene. In solution this salt adds hydrogen chloride to give a new salt, phenyl(α-chlorostyryl)iodonium chloride. The latter cation has been isolated as the stable fluoroborate and chloride and as the much less stable iodide. The acetylenic and ethylenic iodonium salts react with the anion of 2-phenyl-1,3-indandione to give 2-phenyl-2-phenylethynyl-1,3-indandione and 2-phenyl-2-(α-chlorostyryl)-1,3-indandione, respectively, in good yield.

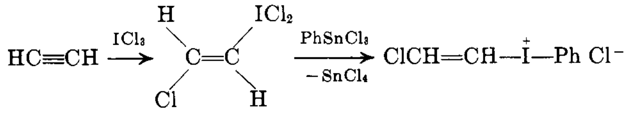
The synthesis, physical properties, and reactions of diaryliodonium salts have been much investigated. For example, reaction of the diaryliodonium cation with organic and inorganic nucleophiles,[4] including carbanions,[5] to give arylated products has been studied in detail, and mechanisms for this arylation have been proposed.[4b,5b]

$$Ar_2I^+ + X^- \longrightarrow ArX + ArI$$

In contrast to this increasing knowledge of diaryliodonium salts, little is known about iodonium salts not having two aryl groups. A few substituted vinyliodonium salts have been prepared; thus, reaction of *trans*-chlorovinylmercuric chloride with iodine trichloride gave bis(*trans*-2-chlorovinyl)iodonium chloride)[6] in low yield, while reaction of this organomercury compound with an aryliodoso dichloride gave the corresponding aryl(*trans*-chlorovinyl)iodonium chloride.[7,8]



Phenyl(*trans*-chlorovinyl)iodonium chloride was also obtained[7] by reaction of *trans*-chlorovinyliodoso dichloride with phenylstannic chloride. Under these conditions *trans*-iodovinyliodoso dichloride gave only diphenyliodonium chloride, acetylene, and stannic chloride. The authors[6,7] report that all these iodonium salts gave acetylene near their melting points, on prolonged heating in water or dilute acid and even at room temperature in the presence of aqueous base or dry pyridine. Besides the polarographic reduction of the aryl(*trans*-chlorovinyl)iodonium salts[8] few other reactions of these compounds have been investigated.



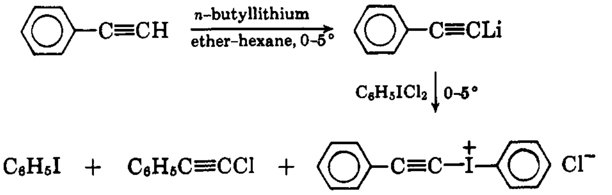
It was found in this laboratory[9] that aryliodoso dichlorides react with aryllithium compounds at low temperatures to give diaryliodonium salts. One reaction path involved conversion of the first-formed iodonium chloride by the organolithium compound to a trisubstituted iodine, which was then cleaved by another equivalent of the aryliodoso dichloride.

$$\begin{tikzcd}
ArLi + ArICl_2 \arrow[r, "ether", "-70^\circ"'] & Ar_2I^+Cl^- \arrow[d, "ArLi"', "-LiCl"] \\
2Ar_2I^+Cl^- & Ar_3I \arrow[l, "ArICl_2"']
\end{tikzcd}$$

The aim of the present research was to adapt this reaction to the synthesis of vinyl- and ethynyliodonium salts and to study the properties and reactions of these new iodonium salts with a carbanion.

Results and Discussion

Phenyl(β-phenylethynyl)iodonium Chloride.—This compound, prepared from lithium phenylacetylide and iodosobenzene dichloride, is the first reported acetylenic iodonium salt. This compound was characterized by its analysis and by its infrared spectrum, which indicated a carbon–carbon triple bond by the presence of a band at 2170 cm.$^{-1}$.



I (12–20%)

No other iodonium salt (bisphenylethynyliodonium or diphenyliodonium chloride) was isolated from the reaction. Other products identified by vapor phase chromatography were phenylacetylene, iodobenzene, and chlorophenylacetylene.[10] The latter two were the major components in the mixture. Iodobenzene and

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[2] Publication XXV in the series on Iodonium Salts. Paper XXIV: F. M. Beringer, L. Kravetz, and G. B. Topliss, *J. Org. Chem.*, **30**, 1141 (1965).

[3] National Institutes of Health Postdoctoral Fellow, 1963–1965.

[4] (a) F. M. Beringer, A. Brierly, M. Drexler, E. M. Gindler, and C. C. Lumpkin, *J. Am. Chem. Soc.*, **75**, 2708 (1953); (b) F. M. Beringer and R. A. Falk, *J. Chem. Soc.*, 4442 (1964).

[5] (a) F. M. Beringer, P. S. Forgione, and M. D. Yudis, *Tetrahedron*, **8**, 49 (1960); (b) F. M. Beringer, S. A. Galton, and S. J. Huang, *J. Am. Chem. Soc.*, **84**, 2819 (1962); (c) F. M. Beringer and P. S. Forgione, *Tetrahedron*, **19**, 739 (1963); *J. Org. Chem.*, **28**, 714 (1963); (d) F. M. Beringer and S. A. Galton, *ibid.*, **28**, 3417 (1963).

[6] (a) R. Kh. Freidlina, E. M. Brainina, and A. N. Nesmeyanov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 647 (1945) (in English); *Chem. Abstr.*, **40**, 4686 (1946); (b) A. N. Nesmeyanov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 239 (1945); *Chem. Abstr.*, **40**, 2122 (1946).

[7] E. M. Brainina and R. Kh. Freidlina, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 623 (1947); *Chem. Abstr.*, **42**, 5863 (1948).

[8] E. L. Colichman and H. P. Maffei, *J. Am. Chem. Soc.*, **74**, 2744 (1952); E. L. Colichman and J. T. Matschiner, *J. Org. Chem.*, **18**, 1124 (1953).

[9] F. M. Beringer, J. W. Dehn, Jr., and M. Winicov, *J. Am. Chem. Soc.*, **82**, 2948 (1960).

[10] R. Truchet, *Ann. chim.*, [10] **16**, 309 (1931).

chlorophenylacetylene, isolated from the mixture by preparative vapor phase chromatography, were identified by their infrared spectra; the latter showed a band at 2230 cm.$^{-1}$ characteristic of a triple bond. Chlorophenylacetylene has a tendency to polymerize at higher temperatures. However, it was possible under v.p.c. conditions (column temperature 130°) to obtain a pure sample for determination of retention time and infrared spectrum. Sodium fusion showed the presence of chlorine but no iodine. This sample was identical in its retention time and infrared spectrum with that of an authentic sample of chlorophenylacetylene, prepared from lithium phenylacetylide and chlorine in ether at −10°.

Phenyl(β-phenylethynyl)iodonium chloride (I), on standing at room temperature for some hours, decomposed spontaneously to iodobenzene and chlorophenylacetylene in the ratio of 1:1, as determined by vapor phase chromatography. The decomposition is believed to be a nucleophilic displacement, in one or two steps, by chloride ion on the acetylenic α-carbon.

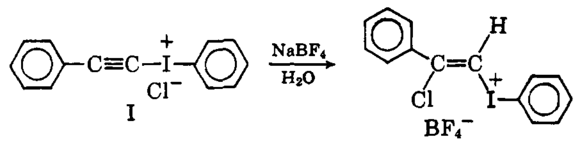
$$C_6H_5C{\equiv}C{-}\overset{+}{I}{-}C_6H_5 + Cl^- \xrightarrow{\text{(over-all)}} C_6H_5C{\equiv}CCl + C_6H_5I$$

This is one of the few reported examples of this reaction type. One such example is the reaction[11-13] of haloalkynes with sodium thiolates to form acetylenic thioethers; another is the reaction with tertiary phosphines[13,14] and tertiary amines.[15]

$$RC{\equiv}CX + \left[\begin{array}{l} R'S^- \xrightarrow[-25^\circ]{\text{DMF}} RC{\equiv}CSR' \quad + X^- \\ P(R')_3 \longrightarrow RC{\equiv}C\overset{+}{P}(R')_3 + X^- \\ LiN(R')_2 \longrightarrow RC{\equiv}CN(R')_2 + LiX \\ 2N(R')_3 \longrightarrow RC{\equiv}CN(R')_2 + \overset{+}{N}(R')_4X^- \end{array}\right.$$

$$R = H, (CH_3)_3, Ph$$
$$X = Br, Cl$$

Phenyl(α-chlorostyryl)iodonium Salts.—Attempts to prepare the fluoroborate of the phenyl(β-phenylethynyl)iodonium ion (I) by stirring the chloride in aqueous sodium fluoroborate overnight gave a new iodonium salt, phenyl(α-chlorostyryl)iodonium fluoroborate (II). This iodonium salt is stable at room temperature and was converted to the stable chloride and the unstable iodide by metathesis. This reaction indicates that this acetylenic bond is quite susceptible to nucleophilic addition; indeed, it was not possible to recrystallize iodonium salt I even from such aprotic solvents as chloroform without its conversion to the chloride of salt II. The geometry of iodonium salt II has not been established. However, the position of the chlorine was shown to be β, as outlined in the following section. In this reaction chloride ion may attack the β-position of the acetylenic bond to give a stabilized carbanion, which then can abstract a proton from the solvent. If the chloride ion attacks on the α-position, displacement rather than addition occurs, as was seen in the previous section. Since the yield of the fluoroborate is only 50% and since decomposition to oily products was evident in the reaction, it is possible that the two pathways are competitive. Table I summarizes the iodonium salts and their melting points obtained in this study.



I

II, 50%

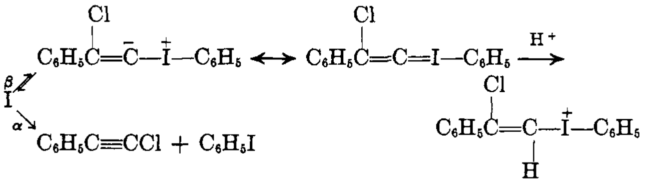


TABLE I

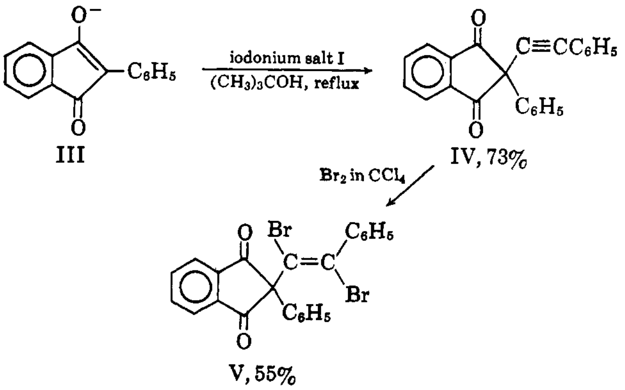
ACETYLENIC AND ETHYLENIC IODONIUM SALTS

Cation	Anion	% yield	M.p., °C.
I	Cl^-	12–20	83–84 dec.
II	BF_4^-	50[a]	173–174 dec.
II	Cl^-	88[b]	149–150 dec.
II	I^-	100[b]	124–125 dec.

[a] Yield based on preparation from iodonium salt I. [b] Yield based on metathesis from the fluoroborate of II.

Ethynylation and Vinylation of the Carbanion of 2-Phenyl-1,3-indandione.—To confirm their structures and to investigate their reactivities toward carbanions, the acetylenic iodonium salt I and the ethylenic iodonium salt II were treated with 2-phenyl-1,3-indandione (III) in the presence of sodium *t*-butoxide in refluxing *t*-butyl alcohol. This system was chosen for study because the analogous phenylation has been studied in detail,[5b] including preparative phenylation in 93% yield.

Anion III with iodonium salt I gave in 73% yield a new compound 2-phenyl-2-phenylethynyl-1,3-indandione (IV); no 2,2-diphenyl-1,3-indandione was obtained. Chromatographic work-up of the reaction mixture gave in addition to compound IV only iodobenzene, a trace of chlorophenylacetylene, and a trace of a dehydro dimer of III,[16] also obtained from the phenylation reaction.[5b]



III

IV, 73%

V, 55%

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[11] G. R. Ziegler, C. A. Welch, C. E. Orzech, S. Kikkawa, and S. I. Miller, *J. Am. Chem. Soc.*, **85**, 1648 (1963).

[12] A. K. Kuriakose and S. I. Miller, *Tetrahedron Letters*, 905 (1962).

[13] S. I. Miller, C. E. Orzech, C. A. Welch, G. R. Ziegler, and J. I. Dickstein, *J. Am. Chem. Soc.*, **84**, 2020 (1962).

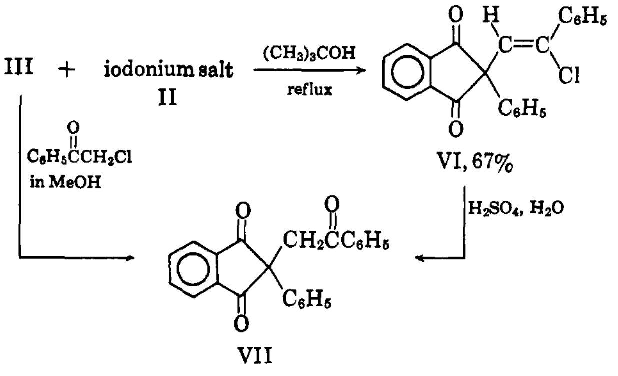
[14] H. G. Viehe and E. Franchimont, *Chem. Ber.*, **95**, 319 (1962).

[15] H. G. Viehe and M. Reinstein, *Angew. Chem.*, **76**, 537 (1964); H. G. Viehe, S. I. Miller, and J. I. Dickstein, *ibid.*, **76**, 573 (1964).

[16] F. M. Beringer, S. A. Galton, and S. J. Huang, *Tetrahedron*, **19**, 809 (1963).

Compound IV added bromine across the triple bond to give 2-phenyl-2-(α,β-dibromostyryl)-1,3-indandione (V). Analysis and infrared, ultraviolet, and n.m.r. data confirm the structures of both compounds IV and V.

Anion III under identical conditions with the iodonium cation II (both as the chloride and the fluoroborate) gave exclusively 2-phenyl-2-(α-chlorostyryl)-1,3-indandione (VI), a new compound, in 67% yield.

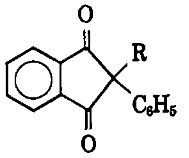


The structure of VI and the position of the chlorine in both compounds VI and II were proven by hydrolysis of VI with sulfuric acid to 2-phenyl-2-phenacyl-1,3-indandione (VII), which was independently synthesized from anion III and phenacyl chloride.

A summary of these substitution reactions is given in Table II.

TABLE II

NEW 2,2-DISUBSTITUTED 1,3-INDANDIONES



R	Compd.	% yield	M.p., °C.
$-C{\equiv}CC_6H_5$	IV	73	114–115
$-\overset{Br}{\overset{\mid}{C}}{=}\underset{\underset{Br}{\mid}}{C}C_6H_5$	V	55	170–171
$-\overset{H}{\overset{\mid}{C}}{=}\underset{\underset{Cl}{\mid}}{C}C_6H_5$	VI	67	116–117
$-CH_2\overset{O}{\overset{\|}{C}}C_6H_5$	VII	60	171–172

Details of spectral data are given in the Experimental section; some special comments follow.

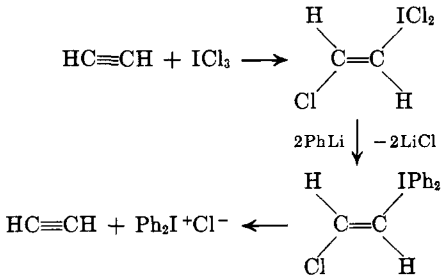
The infrared spectrum of all the 1,3-indandiones[5b,d,16] including compounds IV–VI show a characteristic doublet in the carbonyl region at 1710 and 1740 cm.$^{-1}$, while compound VII shows the same doublet plus an extra carbonyl peak at 1680 cm.$^{-1}$ due to the phenacyl carbonyl group.

The n.m.r. spectra similarly show a characteristic doublet[5d] for the ring protons of the 1,3-indandione system in the region τ 2.1–2.5; the phenyl ring protons appear as a multiplet centered around τ 2.8–3.2. The methylene protons in compound VII give a single peak at τ 6.1, while the olefinic proton in compound VI gives a single peak at τ 3.9. In comparison to compound VI the olefinic proton in the corresponding iodonium salt II is shifted downfield to τ 2.25. This strong deshielding suggests that this proton is in close proximity to the positive iodine.

It is not possible now to say definitely whether substitution by the carbanion occurs by direct nucleophilic displacement on the acetylenic or olefinic carbon[4b] or by an electron-transfer free-radical mechanism analogous to that proposed[5b] for the phenylation of carbanion III.

When vinyllithium was treated with iodosobenzene dichloride at −70°, the only isolable salt was diphenyliodonium chloride (5%). Likewise, chlorovinyliodoso dichloride with phenyllithium gave under identical conditions about 28% of the diphenyliodonium salt as a mixture of the chloride and bromide; no vinyliodonium salt was isolated. In both cases the diphenyliodonium salt probably arises from decomposition of a trisubstituted iodine.[9]

$$2H_2C{=}CHLi + 2PhICl_2 \xrightarrow{-2LiCl} (H_2C{=}CH)_2I{-}Ph +$$
$$PhICl_2 \longrightarrow (H_2C{=}CH)_2I^+Cl^- + Ph_2I^+Cl^-$$



Experimental[17]

Starting Materials.—Phenylacetylene and 2-phenyl-1,3-indandione were purchased from Aldrich Chemical Co. Phenacyl chloride was purchased from Eastman Organic Chemicals Co., while *n*-butyllithium was obtained from the Foote Mineral Co. *t*-Butyl alcohol from Matheson Coleman and Bell was distilled from calcium hydride before use. Iodine trichloride was purchased from K & K Laboratories, Inc. Iodosobenzene dichloride[18] and phenyllithium[19] were prepared according to described procedures. Vinyllithium[20] was prepared from tetravinyltin (Metal and Thermit Corporation) and *n*-butyllithium in hexane, filtered under nitrogen, and dissolved in ether, or was bought as a tetrahydrofuran solution from the Lithium Corporation of America. Chlorovinyliodoso dichloride[21] was prepared from acetylene and iodine trichloride in 15% hydrochloric acid according to reported procedure.

Phenyl(β-phenylethynyl)iodonium Chloride (I).—To a solution of 15.3 g. (0.15 mole) of phenylacetylene in 200 ml. of anhydrous ether at 0–5° there was added dropwise under nitrogen 92 ml. of a 1.6 *N* solution of *n*-butyllithium (0.15 mole). With the reaction temperature at 0–5°, 35 g. (0.127 mole) of iodosobenzene dichloride was added slowly through Gooch tubing over 30

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[17] Analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Infrared spectra were taken on a Perkin-Elmer Model 521 grating spectrophotometer and a Perkin-Elmer 137 Infracord spectrophotometer. N.m.r. spectra were run on a Varian high resolution spectrometer at a frequency of 60 Mc./sec., in carbon tetrachloride, unless otherwise noted, using tetramethylsilane as internal standard. Gas chromatography was done on Wilkins Aeroprep-A700 and Perkin-Elmer, Model 154D, gas chromatographs. Melting points were taken in capillary tubes and were corrected.

[18] H. J. Lucas and E. R. Kennedy, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 482.

[19] J. C. W. Evans and C. F. H. Allen, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 517.

[20] D. Seyferth and M. A. Weiner, *J. Am. Chem. Soc.*, **83**, 3583 (1961).

[21] A. N. Nesmeyanov and R. Kh. Freidlina, *Compt. rend. acad. sci. URSS*, **31**, 892 (1941); *Chem. Abstr.*, **37**, 868 (1943).

min. with stirring. While a white solid formed almost immediately, stirring was continued for 3 hr., when no more iodosobenzene dichloride was detected by testing with potassium iodide solution for oxidizing power. During the reaction the temperature was allowed to rise to about 10°. With the mixture held at 0–5°, 150 ml. of water was added slowly with stirring. The undissolved solid was collected, washed with water, suspended in acetone and again in water, and washed with acetone and finally with ether. After drying in the desiccator for about 2 hr., 8.5 g. (2.5 mmoles, 20%) of phenyl(β-phenylethynyl)iodonium chloride (I), a white solid, m.p. 83–84° dec., was obtained. This solid could not be recrystallized, because in solutions of chloroform or methanol it was converted to iodonium salt II, described later. Satisfactory analysis, however, was obtained on a sample purified only as described above and dried thoroughly over P_2O_5 under vacuum.

Anal. Calcd. for $C_{14}H_{10}ClI$: C, 49.37; H, 2.96; Cl, 10.41; I, 37.26. Found: C, 49.17; H, 3.13; Cl, 10.46; I, 36.95.

The ether and water layers obtained after filtration of the iodonium salt were separated; the ether layer was dried over magnesium sulfate and concentrated to a small volume at room temperature. This liquid was analyzed by vapor phase chromatography at 130°, using helium as the carrier gas on a silicone oil "C"-type column. Besides a mixture of low-boiling components, not separated, there were found phenylacetylene, iodobenzene, and a higher boiling compound. Iodobenzene and the higher boiling material were isolated by preparative gas chromatography. Infrared spectrum confirmed the identity of iodobenzene by comparison with that of an authentic sample. The higher boiling component was identified as chlorophenylacetylene.[22] Its infrared spectrum showed a band at 2230 cm.$^{-1}$ characteristic of a carbon–carbon triple bond, along with the characteristic substitution pattern at 750 and 685 cm.$^{-1}$ for monosubstituted benzenes; it was identical with that of an authentic sample prepared below. Sodium fusion gave a positive test for chlorine and a negative test for iodine. The ratio of iodobenzene to chlorophenylacetylene judged from the areas under the peaks was about 1:1. Some polymerization of chlorophenylacetylene did occur under these conditions to give much higher boiling materials, which probably were not removed from the column under these conditions or detected on the chromatograms.

Iodonium salt I decomposed on standing at room temperature overnight, even under vacuum, to give iodobenzene and chlorophenylacetylene in the ratio of 1:1 as determined by gas chromatography. It was, therefore, stored in an evacuated container at 0° or below and used for further reactions usually within 1 or 2 days.

Chlorophenylacetylene.—To a solution of 15.3 g. (0.15 mole) of phenylacetylene in 100 ml. of ether at 0° there was added 92 ml. of a 1.6 *N* solution of *n*-butyllithium (0.15 mole) in hexane. The mixture was cooled to about −10° in an ice–salt bath, and with stirring a slow stream of chlorine was passed over the reaction surface, keeping the temperature below −3°. White crystals of lithium chloride began to form immediately and were filtered after about 2 hr. The filtrate was concentrated to a yellow oil in the hood at room temperature. The residue showed only one component on vapor phase chromatography, identical in its retention time and infrared spectrum with chlorophenylacetylene obtained in the above reaction. This oil was distilled at 30° (0.3 mm.) to give 15.6 g. (0.12 moles, 77%) of colorless product.

Anal. Calcd. for C_8H_5Cl: C, 70.35; H, 3.69; Cl, 25.96. Found: C, 70.13; H, 3.90; Cl, 26.16.

Phenyl(α-chlorostyryl)iodonium Salt (II).—A suspension of 4 g. (11.7 mmoles) of iodonium salt I in 100 ml. of water containing 20 g. of sodium fluoroborate was stirred overnight at room temperature. A yellow gummy material was isolated by decantation and dissolved in acetone. The acetone solution was diluted with ether, and the white crystals were collected, washed with ether, and dried to give 2.5 g. (5.85 mmoles, 50%) of **phenyl(α-chlorostyryl)iodonium fluoroborate**, m.p. 172–173° dec.; after two recrystallizations from acetone–ether its melting point was 173–174° dec.

Anal. Calcd. for $C_{14}H_{11}BClF_4I$: C, 39.25; H, 2.59; B, 2.53; Cl, 8.28; F, 17.74; I, 29.62. Found: C, 38.99; H, 2.65; B, 2.59; Cl, 8.19; F, 17.64; I, 29.33.

The infrared spectrum showed, besides bands characteristic of monosubstituted benzenes, a very large broad band at 1200–1000 cm.$^{-1}$ characteristic of the BF_4^- anion; this band was also found in the known diphenyliodonium fluoroborate,[23] whose spectrum was run for comparison.

To a solution of 1.0 g. (2.32 mmoles) of the above prepared fluoroborate of II in 5 ml. of acetone there was added a solution of aqueous sodium chloride, and the mixture was diluted with water to about 50 ml. The white precipitate was collected, washed with water, and dried to give 773 mg. (2.0 mmoles, 88%) of **phenyl(α-chlorostyryl)iodonium chloride**, m.p. 141–142° dec. After two recrystallizations from chloroform–ether the melting point was raised to 149–150° dec. The ultraviolet absorption spectrum had a broad band at λ_{max}^{MeOH} 268 mμ (ϵ 10,800).

Anal. Calcd. for $C_{14}H_{11}Cl_2I$: C, 44.59; H, 2.94; Cl, 18.81; I, 33.66. Found: C, 44.42; H, 3.15; Cl, 18.68; I, 33.85.

The n.m.r. spectrum of this compound in deuterated chloroform shows a doublet centered around τ 1.73 assigned to the *ortho* protons on the phenyl ring adjacent to the positive iodine, a multiplet centered around τ 2.70 due to all the other ring hydrogens in both phenyl rings, and a singlet at τ 2.25 assigned to the olefinic proton on the carbon adjacent to the positive iodine and consequently strongly deshielded.[24]

Phenyl(α-chlorostyryl)iodonium iodide, m.p. 124–125° dec., was obtained as a cream-colored solid from the fluoroborate in about quantitative yield by metathesis with aqueous potassium iodide. No solvent was found that dissolved this material at room temperature, and in hot solvents it decomposed. Decomposition was noted even at room temperature after standing for 2 or 3 days. Purification by suspension in water twice, then twice in acetone, finally washing with ether, and drying over P_2O_5 under vacuum gave a satisfactory analysis.

Anal. Calcd. for $C_{14}H_{11}ClI_2$: C, 35.89; H, 2.37; Cl, 7.57; I, 54.17. Found: C, 36.06; H, 2.27; Cl, 7.72; I, 54.05.

Reaction of Phenyl(β-phenylethynyl)iodonium Chloride (I) with 2-Phenyl-1,3-indandione (III).—To a solution of 115 mg. (5 mg.-atoms) of sodium in 25 ml. of *t*-butyl alcohol there was added 1.1 g. (5 mmoles) of 2-phenyl-1,3-indandione. To this red solution at room temperature with stirring and under nitrogen 1.7 g. (5 mmoles) of iodonium salt I was added, and the mixture was heated to gentle reflux. Within 5–10 min. the red color was discharged, and the mixture turned light orange. Most of the solvent was evaporated on a steam bath, and the residue was chromatographed on a Florisil (200 g.) column prepared in hexane. The hexane eluate after evaporation of some of the solvent showed, on vapor phase chromatography, only iodobenzene.

The benzene eluate after removal of solvent and trituration with ether–methanol gave 1.18 g. (3.67 mmoles, 73%) of pale yellow crystals of **2-phenyl-2-phenylethynyl-1,3-indandione (IV)**, m.p. 92–93°. This compound, after three recrystallizations from methanol, had a melting point of 114–115°. The ultraviolet absorption maximum was λ_{max}^{MeOH} 227 mμ (ϵ 44,400) with a shoulder at 245 mμ.

Anal. Calcd. for $C_{23}H_{14}O_2$: C, 85.69; H, 4.38; mol. wt., 322. Found: C, 85.92; H, 4.28; mol. wt., 339.

The infrared spectrum did not show a band in the triple-bond region (2300–2000 cm.$^{-1}$); its absence is probably due to the lack of an appreciable dipole in this disubstituted carbon–carbon triple bond.[25] Carbonyl bands characteristic of the 1,3-indandione system appear at 1710 and 1740 cm.$^{-1}$, with a shoulder at 1760 cm.$^{-1}$, also observed in 2,2-diphenyl-1,3-indandione.[5b]

The n.m.r. spectrum supports the assigned structure. Besides the characteristic doublet for the protons on the 1,3-indandione ring at τ 2.18, the only other peaks observed were those arising from the protons on the two phenyl rings giving a rather simple absorption band centered around τ 2.82.

Concentration of the ether eluate gave 20 mg. of a white solid, whose infrared spectrum was identical with that of a **dehydro dimer of III.**[5b,16] About 25 mg. of unchanged III was recovered from the methanol eluate.

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[22] For the properties of chlorophenylacetylene, see ref. 6 and 11.

[23] F. M. Beringer, R. A. Falk, M. Karniol, I. Lillien, G. Masullo, M. Mausner, and E. Sommer, *J. Am. Chem. Soc.*, **81**, 342 (1959).

[24] The abnormal deshielding of the *ortho* protons by iodine has been described [L. M. Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, p. 63; and more recently: H, Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961); P. C. Lauterbur, *ibid.*, **38**, 1406 (1963); J. Martin and B. P. Dailey, *ibid.*, **39**, 1722 (1963)]. The effect of the positive charge on iodine on the ring hydrogens has been studied in the diphenyliodonium salts by us and will be submitted for publication shortly.

[25] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 58–60.

Bromination of 2-Phenyl-2-phenylethynyl-1,3-indandione.—To a hot solution of 400 mg. (1.24 mmoles) of compound IV in carbon tetrachloride there was added a solution of bromine in carbon tetrachloride, with heating on a steam bath until no more discharge in color was observed. The solvent was then evaporated, and the residue was triturated with methanol. The yield of **2-phenyl-2-(α,β-dibromostyryl)-1,3-indandione** (V), a white solid, was 330 mg. (0.69 mmole, 55%), m.p. 160–164°. After recrystallization three times from ethanol it melted at 170–171°. The ultraviolet absorption maximum was $\lambda_{\max}^{\mathrm{MeOH}}$ 229 mμ (ε 49,800).

Anal. Calcd. for $C_{23}H_{14}Br_2O_2$: C, 57.29; H, 2.93; Br, 33.15. Found: C, 57.01; H, 2.76; Br, 32.90.

The n.m.r. spectrum showed a doublet at τ 2.54 for the absorption of the 1,3-indandione ring protons and a multiplet centered around τ 3.22 for the protons on the two phenyl rings.

Reaction of Phenyl(α-chlorostyryl)iodonium Chloride (II) with 2-Phenyl-1,3-indandione (III).—The same procedure was followed as in the reaction of iodonium salt I with the anion of III as described above, using 115 mg. (5 mg.-atoms) of sodium in *t*-butyl alcohol, 1.1 g. (5 mmoles) of III, and 1.88 g. (5 mmoles) of II. Chromatography of the reaction mixture after removal of solvent and trituration of the residue with methanol gave in the benzene eluate 1.20 g. (3.35 mmoles, 67%) of **2-phenyl-2-(α-chlorostyryl)-1,3-indandione (VI)** as pale yellow crystals melting, after two recrystallizations from methanol, at 116–117°. The ultraviolet absorption spectrum showed two maxima: $\lambda_{\max}^{\mathrm{MeOH}}$ 227 mμ (ε 49,000) and 252 mμ (ε 28,800).

Anal. Calcd. for $C_{23}H_{15}ClO_2$: C, 76.99; H, 4.21; Cl, 9.88. Found: C, 77.01; H, 4.18; Cl, 9.86.

The other fractions gave only trace amounts of material, not identified.

The same compound VI was obtained in 57% yield when the fluoroborate rather then the chloride of iodonium salt II was used.

The protons on the 1,3-indandione ring in the n.m.r. spectrum of VI appear as the usual doublet at τ 2.28, those of the two phenyl rings appear as a multiplet centered around τ 2.80, while the one olefinic proton gives a single peak at τ 3.90.

2-Phenyl-2-phenacyl-1,3-indandione (VII).—A solution of sodium methoxide was prepared from 1.15 g. (0.05 g.-atom) of sodium in 200 ml. of dry methanol. To this solution there was added 11.1 g. (50 mmoles) of 2-phenyl-1,3-indandione (III) and 7.73 g. (50 mmoles) of phenacyl chloride, and the mixture was refluxed overnight. The dark red mixture was concentrated to a thick oil on a steam bath, the residue was diluted with 200 ml. of water, and the insoluble yellow oily crystals were filtered. The obvious presence of a lachrymator and the infrared spectrum indicated some unchanged phenacyl chloride in the solid. Suspension of this solid in methanol yielded 3.63 g. (10.6 mmoles, 59% based on moles of III used) of flaky white crystals of 2-phenyl-2-phenacyl-1,3-indandione (VII), having a melting point after two recrystallizations from methanol of 171–172°. The ultraviolet spectrum showed two maxima: $\lambda_{\max}^{\mathrm{MeOH}}$ 226 mμ (ε 48,100) and 246 mμ (ε 27,500).

Anal. Calcd. for $C_{23}H_{16}O_3$: C, 81.18; H, 4.74. Found: C, 81.05; H, 4.51.

The infrared spectrum of VII showed three bands in the carbonyl region: 1710 and 1740 cm.$^{-1}$ for the 1,3-indandione and 1680 cm.$^{-1}$ for the phenacyl carbonyl absorption.

The n.m.r. spectrum showed the doublet for the 1,3-indandione ring hydrogens at τ 2.28, a multiplet centered about τ 2.80 for the hydrogens on the two phenyl rings, and a single peak for the methylene protons at τ 6.10.

The red aqueous filtrate from the above work-up was acidified with concentrated hydrochloric acid, and the white solid was collected to give 7.0 g. (32 mmoles, 64%) of unchanged 2-phenyl-1,3-indandione (III), identified by comparison of its infrared spectrum with that of an authentic sample.

Hydrolysis of 2-Phenyl-2-(α-chlorostyryl)-1,3-indandione (VI) with Sulfuric Acid.—A solution of 500 mg. (1.55 mmoles) of compound VI in 5 ml. of concentrated sulfuric acid was allowed to stand at room temperature for 0.5 hr. The dark brown solution was then poured over 100 ml. of water–ice mixture, and 525 mg. of a red-brown solid was collected. This solid was chromatographed on a Florisil (100 g.) column prepared in hexane and was eluted with hexane, benzene, chloroform, and ether successively. The benzene eluate, after removal of the solvent and trituration of the residue with methanol, gave 263 mg. (0.78 mmole, 50%) of **2-phenyl-2-phenacyl-1,3-indandione (VII)**, m.p. 169–170° after one recrystallization from methanol. The melting point was not depressed on admixture with an authentic sample, and the infrared spectrum was superimposable on that of compound VII prepared above.

The ether eluate yielded an orange-red amorphous solid which was not characterized.

Reaction of Vinyllithium with Iodosobenzene Dichloride.—A suspension of 27.5 g. (0.1 mole) of iodosobenzene dichloride in 100 ml. of tetrahydrofuran (distilled from $LiAlH_4$) was cooled to −70° in a Dry Ice–acetone bath. Dropwise with stirring under nitrogen, 55 ml. of a 1.73 *N* solution (0.1 mole) of vinyllithium in tetrahydrofuran was added. Soon after the solution became yellow, a white solid precipitated. After the addition, the cooling bath was removed, the mixture was diluted to 1000 ml. with ether, and 10.2 g. of a white solid was collected. This solid was stirred into water with cooling, and the insoluble material was collected and washed with ether to give 800 mg. (2.53 mmoles, 5%) of **diphenyliodonium chloride**, which was recrystallized once from methanol to a melting point of 224–225° dec.; lit.[26] m.p. 228–229° dec. The infrared spectrum of this compound was identical with that of an authentic sample.

Similar results were obtained when to an ether solution of vinyllithium prepared according to Evans and Allen[19] there was added solid iodosobenzene dichloride through Gooch tubing, with stirring under nitrogen at −70°. The solid obtained was collected, suspended in chloroform, and stirred with water containing sodium fluoroborate. The small amount of diphenyliodonium fluoroborate[23] obtained was identified by infrared spectrum.

Reaction of Chlorovinyliodoso Dichloride with Phenyllithium.—A solution of 12.6 g. (48.6 mmoles) of chlorovinyliodoso dichloride in 100 ml. of ether was cooled to −70° in a Dry Ice–acetone bath. With stirring under nitrogen, 37 ml. of a 1.34 *N* solution of phenyllithium in ether (48.6 mmoles) was added dropwise over 0.5 hr. After the addition was complete, the reaction mixture was stirred 30 min. at −70° and then allowed to warm to room temperature. A mixture of 8.49 g. of orange and white solids formed, which was collected and washed with ether. This solid was cooled in ice, suspended in 50 ml. of ice–water, collected, and suspended in acetone to give an orange solution and a white solid. This was collected to give 2.29 g. (about 28%) of a mixture of diphenyliodonium chloride and bromide, m.p. 230–235° dec. Fractional crystallization of this mixture from methanol gave a sample of **diphenyliodonium bromide**, m.p. 246–247° dec. (lit.[9] m.p. 233–234° dec.), and **diphenyliodonium chloride**, m.p. 224–225° dec. (lit.[26] m.p. 228–229° dec.). The infrared spectra were identical with those of authentic samples.

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