Experimental Section

Materials.—All alkyl halides were commercially available; they were redistilled before use. Propyl tosylate was prepared by the usual method; methyl tosylate and ethyl tosylate were obtained from commercial sources, and were recrystallized prior to use. Phosphonates were prepared by the Michaelis–Arbuzov reaction and by transalkylation. Many of the phosphonates are new compounds; the rather routine identification by nmr was based upon peak position, intensity, and multiplicity. Table V contains useful phosphonate data.

Analysis Procedure.—All phosphonates were analyzed by glpc, using a 5 ft × ⅛ in. stainless steel column containing 4% QF-1 (fluorosilicone) on 80/100 mesh acid-washed and silanized Chromosorb G. Alkyl iodides were analyzed on a 3 ft × 0.25 in. copper column containing 18% tricresyl phosphate on 60/80 mesh untreated firebrick. Two columns were used for preparative work involving phosphonates, a 3 ft × 0.25 in. copper column containing 20% Carbowax 20M on 60/80 mesh untreated firebrick, and a 6 ft × 0.25 in. copper column containing 5% UCON LBX 550 on 80/100 mesh acid-washed and silanized Chromosorb G. A Micro-Tek chromatograph equipped with glass-lined injector block and thermal conductivity detectors was used for both analytical and preparative work. Thermal conductivity response factors are included in Table V; the estimated values are either interpolations or extrapolations from known values.

Reaction Procedure.—The reactions below are representative.

A. Reaction of Diethyl Ethylphosphonate with Methyl Tosylate.—A mixture of 1.66 g (0.01 mol) of diethyl ethylphosphonate and 9.3 g (0.05 mol) of methyl tosylate contained in a 25-ml pear-shaped flask equipped with thermometer, reflux condenser, and drying tube was heated at *ca.* 140° for 3.5 hr. The phosphonate mixture was then separated from the tosylate mixture by vacuum distillation at 0.3–0.5 mm. Glpc analysis of an ether solution of the distillate indicated that the product distribution was 43% dimethyl ethylphosphonate, 46% methyl ethyl ethylphosphonate, and 11% diethyl ethylphosphonate. The over-all recovery of phosphonate was 95%. Analysis of the residual tosylate mixture by nmr indicated a methyl tosylate–ethyl tosylate ratio of 2.8:1, the value predicted from the phosphonate distribution.

B. Reaction of Dimethyl Methylphosphonate with Propyl Iodide.—A mixture of 0.62 g (0.005 mol) of dimethyl methylphosphonate and 1.133 g (0.0067 mol) of propyl iodide was heated in an oil bath at 130 ± 0.5° in a heavy-walled tube for 140 hr. Analysis of the product indicated 17.5% dimethyl methylphosphonate, 49.7% methyl propyl methylphosphonate, and 32.8% dipropyl methylphosphonate; the over-all recovery was 93%. Analysis of the alkyl halides indicated 85.9% methyl iodide and 14.1% propyl iodide, with an over-all recovery of 96%.

C. Preparation of Dipropyl Methylphosphonate.—A mixture of 6.2 g (0.05 mol) of dimethyl methylphosphonate and 51 g (0.30 mol) of propyl iodide was allowed to react in a heavy-walled tube for 96 hr at 130°. The tube was then opened, the contents was placed in a distillation apparatus, and the methyl iodide was distilled. The phosphonate–propyl iodide mixture was then returned to the tube, and additional propyl iodide was introduced such that 0.3 mol was again present. After 48 hr at 130°, the tube was again opened and the product distilled. In this manner, 7 g (78%) of a material boiling at 86–87° (6 mm) was obtained, $n^{20}{}_D$ 1.4201 [lit.[22] bp 95–96° (10 mm), $n^{20}{}_D$ 1.4200]. Analysis by glpc indicated a purity of 99.5%.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Diaryliodonium Salts from Aryllithium Reagents with *trans*-Chlorovinyliodoso Dichloride[1,2]

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Received August 2, 1968

A new synthetic route to symmetrical diaryliodonium salts used the low-temperature reaction of *trans*-chlorovinyliodoso dichloride with 2 equiv of aryllithium and gave fair to excellent yields of diphenyliodonium, di-*p*-tolyliodonium, di-1-naphthyliodonium, di-2-naphthyliodonium, di-9-anthryliodonium, and dibenziodolium salts. An extension of this method allows the synthesis of unsymmetrical diaryliodonium salts.

Synthesis of diaryliodonium salts[4] is generally accomplished by the electrophilic attack of a polyvalent

$$Ar\overset{+}{I}OH + Ar'H \xrightarrow{-H_2O} Ar\overset{+}{I}Ar'$$

$$ArICl_2 + Ar'Li \xrightarrow[-Cl^-]{-LiCl} Ar\overset{+}{I}Ar'$$

iodine species on an aromatic system.[5,6] These syntheses cannot be used, however, if the iodoso compounds cannot be prepared or if they are not stable; 1-naphthyliodoso dichloride is one such example.[6]

Our new approach involved the following steps: (a) preparation of a compound Cl–Z–ICl_2, such that Z represents a masking group inert to ArLi under the reaction conditions; (b) reaction of Cl–Z–ICl_2 with 2 equiv of ArLi, forming Cl–Z–IAr_2; and (c) removal of Z to form $Ar_2I^+Cl^-$. Several considerations lead to the selection of the group –CH=CH– as Z; the reactions can now be formulated more specifically.

There were four reasons for believing in the possibility of the final ionic elimination: (a) the intermediate phenyl(β-chlorovinyl)iodonium chloride with base yields acetylene,[7] (b) the large size of the IAr_2

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[1] Publication in the series on Iodonium Salts. Preceding paper: F. M. Beringer and P. Bodlaender, *J. Org. Chem.*, **33**, 2981 (1968).

[2] Supported by National Science Foundation Grant GP-4425.

[3] Taken from the dissertation of R. A. Nathan to be submitted to the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the Ph.D. degree.

[4] Polyvalent organoiodine compounds: D. F. Banks, *Chem. Rev.*, **66**, 243 (1966).

[5] J. B. Briody, *J. Chem. Soc.*, *B*, 93 (1968).

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

[7] Aryl(*trans*-chlorovinyl)iodonium salts and bis(*trans*-chlorovinyl)iodonium salts are known.[8,9] The authors report that all of these iodonium salts liberate acetylene near their melting points or with acid or base.

Table I

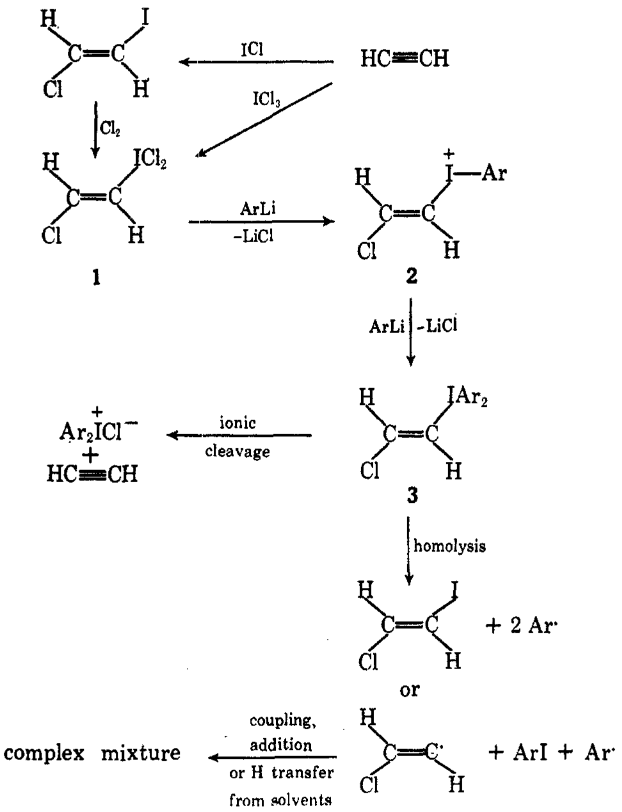
Diaryliodonium Salts from ArLi and *trans*-Chlorovinyliodoso Dichloride

Product				
Cation	Anion	Solvent for ArLi[a]	Mp, °C[b]	% yield
Ph_2I^+	I^-	Benzene	172–173 dec	100
$(p\text{-Tolyl})_2I^+$	I^-	Diethyl ether	157–159 dec	73
$(1\text{-Naphthyl})_2I^+$	Cl^-, Br^-	Toluene or ether–benzene		55
$(2\text{-Naphthyl})_2I^+$	Cl^-, Br^-	Ether–toluene		55
$(9\text{-Anthryl})_2I^+$	Cl^-, Br^-	Ether–toluene		32
Dibenziodolium	Cl^-, Br^-	Ether–toluene		39

[a] In all cases toluene was the solvent for *trans*-chlorovinyliodoso dichloride; 2 equiv of ArLi were used. [b] All melting points are corrected.

Scheme I

Synthesis of Symmetrical Diaryliodonium Salts



group might favor elimination, (c) the IAr_2 group should be electron releasing while chlorine is electron attracting, and (d) the third carbon–iodine bond should be weak, *cf.* decomposition of triphenyliodine at about 5°. In any case it has been known for some 20 years that triaryliodines[10] decompose readily and in certain cases give excellent yields of diaryliodonium salts.[10,11]

Results and Discussion

We have found that, when aryllithium reagents are added to solutions of *trans*-chlorovinyliodoso dichloride (**1**) produced either by the addition of iodine trichloride to acetylene[12] or by the chlorination of *trans*-chloroiodoethylene,[13] we are able to isolate good yields of the symmetrical diaryliodonium salt. It is believed that the substitution of aryl groups takes place in a stepwise manner as shown in Scheme I.

Work in this laboratory has shown that depending on reaction conditions triaryliodines can decompose to give a multitude of products, presumably through a free-radical mechanism, in addition to ionic reorganization to the iodonium salt.

Because of its presumed instability, no attempt has been made to isolate intermediate **3.**

It is difficult to envision **2** undergoing ionic elimination under the reaction conditions,[7] as the leaving iodine should be initially neutral and able to release electrons. An unsuccessful attempt was made to realize the reverse reaction, *i.e.*, the addition of iodosobenzene dichloride to acetylene to form **2.**

Using the following general procedure, we have prepared in fair to excellent yields diphenyliodonium, di-*p*-tolyliodonium, di-1-naphthyliodonium, di-2-naphthyliodonium, di-9-anthryliodonium,[14] and dibenziodolium salts; see Table I.

In general best yields of iodonium salt were obtained by the dropwise addition of a solution of the aryllithium in an appropriate solvent to a toluene solution of the *trans*-chlorovinyliodoso dichloride under argon at Dry Ice–acetone temperatures. This temperature was then maintained for 1–3 hr before the reaction mixture was allowed to come slowly to room temperature. Stirring of the resulting suspension was then continued for approximately 1 week.

We have found that, if the dropwise addition of the aryllithium solution to the diethyl ether solution of iodoso dichloride was carried out at ice–salt temperatures or above instead of in a Dry Ice–acetone bath, low yields of iodonium salt were obtained. However, it was not necessary to maintain the reaction mixture at this temperature more than 2 hr following addition of the aryllithium. It was advantageous, though, to stir the resulting suspension at room temperature for up to 1 week. Shorter reaction times gave noticeably smaller yields. When we varied the relative amounts of *trans*-chlorovinyliodoso dichloride and aryllithium through the range 1:1 to 1:4 equiv, we found as expected an optimum yield when 2 equiv of the aryllithium solution

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(8) (a) R. Kh. Freidlina, E. M. Brainina, and A. N. Nesmeyanov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 647 (1945); *Chem. Abstr.*, **40,** 4686 (1946); (b) A. N. Nesmeyanov, *ibid.*, 239 (1945); *Chem. Abstr.*, **40,** 2122 (1946); (c) E. M. Brainina and R. Kh. Freidlina, *ibid.*, 623 (1947); *Chem. Abstr.*, **42,** 5863 (1948).

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

(10) G. Wittig and M. Rieber, *Ann. Chem.*, **562,** 187 (1949); G. Wittig and K. Claus, *ibid.*, **578,** 141 (1952).

(11) K. Claus, *Chem. Ber.*, **88,** 268 (1955).

(12) L. B. Howell and W. A. Noyes, *J. Amer. Chem. Soc.*, **42,** 991 (1920); A. N. Nesmeyanov and R. Kh. Friedlina, *Compt. Rend. Acad. Sci. URSS,* **31,** 892 (1941); *Chem. Abstr.*, **37,** 868 (1943).

(13) J. Thiele and H. Haakh, *Ann. Chem.*, **369,** 131 (1909).

(14) Previously unreported compound.

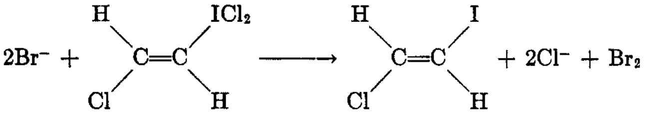
was allowed to react with 1 equiv of iodoso dichloride. The presence of light did not seem to have any effect on the yield of iodonium salt.

The availability of low-temperature solvent systems unreactive toward aryllithium reagents is limited; however, we have compared the reactions in diethyl ether, toluene, tetrahydrofuran, and pentane. No diphenyliodonium salt could be isolated from reactions run in pentane or tetrahydrofuran, but the yields from reactions in toluene were frequently over 80%. When dry diethyl ether was used as a solvent the yields were erratic and usually below 50%.

Phenyllithium is available in various solvents either commercially or by synthesis in the laboratory. In the early phases of our study we found, as noted above, that toluene or a toluene–benzene mixture was a solvent system that gave markedly better yields than benzene–ether or ether. It was thought that these results could most likely be extended to the case of the other aryllithiums. Thus we generated the aryllithium in toluene or benzene; as this precipitated and could not be transferred accurately to the iodoso dichloride, it was suspended, and the iodoso dichloride was added to the suspension at Dry Ice–acetone temperatures. In duplicate runs for each of three aryllithium reagents, after addition to the iodoso dichloride, stirring for 4 days, and work-up, there was no evidence of iodonium salt. In a duplicate set of experiments the aryllithium was prepared in toluene and the resulting suspension was warmer and diluted with toluene until solution occurred. This was then added in the usual manner to a toluene solution of *trans*-chlorovinyliodoso dichloride. Iodonium salt was isolated after 1 week but the yields were only approximately one-half those obtained previously in the presence of diethyl ether. Although various possible explanations come to mind, we have no evidence as the the true nature of this phenomenon.

We found that with the exception of the diphenyliodonium salts the diaryliodonium salts were too insoluble in all solvents tested to be recrystallized. Thus, as the reactions generally gave products as a mixture of the iodonium chloride and bromide, a method of conversion into a single analytically pure salt was sought. As the iodonium salts were sensitive to prolonged heating, use of a Soxhlet apparatus was not possible. They were also sensitive to acid; thus treatment with anhydrous hydrofluoric acid, sulfuric, nitric, and acetic acids caused immediate decomposition. Grinding with aqueous silver nitrate had no effect, presumably because of low solubility. Finally, however, conversion into analytically pure bromide or iodide was accomplished by stirring the iodonium salt with a large excess of the appropriate lithium or potassium halide in boiling methanol.

Alternatively, a mixture of iodonium salts could be avoided if the reaction was performed in the presence of a large excess (approximately 100 mol equiv) of anhydrous lithium salt. When lithium bromide was used, care was taken to bring the toluene solution of the *trans*-chlorovinyliodoso dichloride to Dry Ice–acetone temperatures prior to adding the anhydrous salt; otherwise bromide ion may reduce the iodoso dichloride. Analytically pure iodonium perchlorate was obtained when the reactions were carried out in the presence of silver or lithium perchlorate; however, the yields obtained with the former reagent were low.



The thermal decomposition of diaryliodonium salts generally gives high yields of aryl halides, apparently from the nucleophilic attack by the anion on the cation.[15,16] We decomposed in this manner samples of

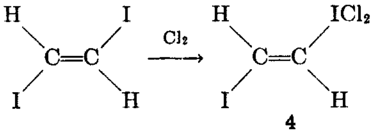
$$\mathrm{Ar\overset{+}{I}Ar\ X^- \xrightarrow{\Delta} ArI + ArX}$$

di-1-naphthyliodonium iodide, di-2-naphthyliodonium iodide, and di-9-anthryliodonium bromide. In each case vpc analysis of the reaction mixture using the peak enhancement method with authentic samples showed only the expected products.

If Scheme I is indeed representative of the mechanism involved, one would expect that the treatment of the known compound phenyl(*trans*-chlorovinyl)iodonium trichloromercurate(II) with 1 equiv of phenyllithium would give diphenyliodonium trichloromercurate(II). This has been shown to be the case.

An extension of this method allows the preparation of an unsymmetrical salt; thus, treatment of **2** with 1 equiv of 1-naphthyllithium has given phenyl(1-naphthyl)iodonium chloride.

For a successful heterolysis of the β-X-vinyldiaryliodine, presumably the "better" the leaving group, X, the larger the proportion of ionic cleavage (*i.e.*, iodonium salt). We have investigated the corresponding *trans*-iodovinyliodoso dichloride (**4**)[13] prepared by the chlorination of *trans*-diiodoethylene; as it was found to be unstable and particularly difficult to work with, it was not further investigated.



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Work is currently underway in this laboratory to define more closely the mechanism and scope of this synthetic procedure.

Experimental Section

Analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Gas chromatography was done on 6-ft columns packed with 20% SE-30 on Chromsorb W with an Aerograph 1520 gas chromatograph. Melting points were taken in capillary tubes on a Thomas–Hoover apparatus and corrected. The technique involved in taking the melting points of iodonium salts has previously been discussed.[16]

Starting Materials.—Iodine trichloride was purchased from City Chemical Co. *p*-Bromotoluene and 2-bromonaphthalene were purchased from Distillation Products Industries. 1-Bromonaphthalene and 9-bromoanthracene were purchased from Aldrich Chemical Co. Anhydrous lithium perchlorate and silver perchlorate and *n*-butyllithium in hexane (Lithium Corp. of America) was purchased from Alpha Inorganics. Lithium ribbon

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[15] (a) F. M. Beringer, M. Drexler, E. M. Gindler, and C. C. Lumpkin, *J. Amer. Chem. Soc.*, **75**, 2705 (1953); (b) F. M. Beringer and M. Mausner, *ibid.*, **80**, 4535 (1958); (c) L. Mascarelli and G. Benati, *Gazz. Chim. Ital.*, **38**, 619 (1908).

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

(high purity) was purchased from Foote Mineral Co. Acetylene and prepurified grade argon were supplied by Matheson. The toluene and benzene were reagent grade. The anhydrous diethyl ether was analytical grade as supplied by Mallinckrodt. The can was opened immediately before use and sealed with a rubber septum. The ether was transferred with a syringe previously flushed well with argon. Any ether not used immediately after opening the can was considered no longer suitable as solvent and was used as wash during the work-up procedure. 2,2′-Diiodobiphenyl was prepared by thermal decomposition of dibenziodolium iodide followed by sublimation as reported previously.[15c]

***trans*-Chlorovinyliodoso Dichloride.**—Acetylene was bubbled through the bright orange solution of 20–25 g of iodine trichloride in 45–50 ml of concentrated hydrochloric acid and 100 ml of ice water. About every 2 hr the yellow precipitate was removed by filtration, with the filtrate returned to the gas-washing bottle for further treatment with acetylene. (The solution should not be stored for use at another time.) The *trans*-chlorovinyliodoso dichloride was suction dried on the filter for 20–30 min. Frequently decomposition of the iodoso dichloride occurred during drying. The iodoso dichloride should not be washed with water before drying, as this seemed to speed decomposition. If the iodoso dichloride was not collected about every 2 hr, it frequently became tacky and was no longer suitable for use. Generally, fresh *trans*-chlorovinyliodoso dichloride was prepared for each set of reactions; however, it was sometimes prepared and stored at low temperatures (−20° or below). If stored in this manner the iodoso dichloride retained complete reactivity for at least 2 months.

Aryllithium Reagents.—Phenyllithium in 70:30 benzene–ether (Lithium Corp. of America) was purchased from Alpha Inorganics. *p*-Tolyllithium was prepared as reported previously.[6]

1-Naphthyllithium in Ether–Benzene.—To a stirred solution of 20.7 g (100 mmol) of 1-bromonaphthalene in 100 ml of anhydrous ether held at 15° under argon 100 mmol of *n*-butyllithium solution in hexane or benzene was added dropwise over 15 min. Stirring was continued for 15–30 min at room temperature. Benzene or toluene was added in 10-ml portions (*via* syringe) with stirring until the heated suspension turned to a clear brown solution (approximately 100 ml of hydrocarbon required).

1-Naphthyllithium in Toluene.—To 20.7 g (100 mmol) of 1-bromonaphthalene dissolved in 300 ml of toluene under argon 100 mmol of *n*-butyllithium solution in hexane was added dropwise over 15 min with stirring at 40–45°. Stirring was continued for 30 min at 45°.

2-Naphthyllithium.—To 20.7 g (100 mmol) of 2-bromonaphthalene dissolved in 100 ml of anhydrous ether and 100 ml of toluene under argon 100 mmol of *n*-butyllithium solution was added dropwise over 15 min at room temperature, with additional stirring for 15 min at that temperature. Stirring the cloudy solution at 45–55° for 30 min gave a clear brown solution.

9-Anthryllithium.—To 15.4 g (60 mmol) of 9-bromoanthracene in 100 ml of anhydrous ether and 50 ml of toluene under argon 60 mmol of *n*-butyllithium solution was added dropwise over about 15 min at room temperature; stirring was continued for 15 min. Stirring the yellow-orange suspension at 80° while 200 ml of toluene was added gave after 0.5 hr a clear brown solution.

2,2′-Dilithiobiphenyl.—To 10.15 g (50 mequiv) of 2,2′-diiodobiphenyl in 50 ml of diethyl ether and 50 ml of toluene 50 mmol of *n*-butyllithium in hexane was added dropwise over 15 min at room temperature. Stirring under argon was continued for 1 hour.

Reactions Forming Iodonium Salts. Diphenyliodonium Iodide and Di-*p*-tolyliodonium Iodide.—A solution of 2.5 g (9.5 mmol) of *trans*-chlorovinyliodoso dichloride in 100 ml of toluene in a three-necked flask flushed well with argon and equipped with a magnetic stirrer and a pressure-equalizing addition funnel was cooled to equilibrium temperature (*ca.* −70°) in a Dry Ice–acetone bath. Freshly titrated aryllithium solution (20 mmol) was added dropwise with stirring over 10–15 min. The Dry Ice–acetone bath was maintained for 1–3 hr and then allowed to come slowly to room temperature. After 1 week of stirring the precipitate was collected, washed with small portions of ether and acetone, and dissolved in a minimum of hot water (*ca.* 300 ml). Addition of a concentrated solution of 2–3 g of potassium iodide to the filtered, cooled solution precipitated diaryliodonium iodide. After cooling and washing with small amounts of ether and acetone, the solid was dried overnight in a vacuum desiccator. A typical yield of diphenyliodonium iodide was 3.82 g (94%), mp 172–173° (lit. mp 172–175°,[17] 175–176°,[18] 182°,[19] 159–162° [20]). A typical yield of di-*p*-tolyliodonium iodide was 3.21 g (73%), mp 157–159° (lit. mp 172–174°,[21] 143–156°,[22] 146° [23]).

1-Naphthyl-, 2-Naphthyl-, and 9-Anthryliodonium and Dibenziodolium Salts.—A 500-ml reaction kettle equipped with a magnetic stirrer and pressure equalizing addition funnel was flushed well with argon and maintained under a positive argon pressure. *trans*-Chlorovinyliodoso dichloride (2.5 g, 9.5 mmol) in 150 ml of toluene was added to the kettle and placed in a Dry Ice–acetone bath. After equilibration 20 mequiv of aryllithium solution was added dropwise with stirring over a 10–15-min period. After the addition was completed, the ice bath was maintained for 1–3 hr before the reaction was allowed to come slowly to room temperature. Stirring was continued for 1 week after which the solid was collected, washed well with acetone and ether, suspended in 100 ml of cold water for 3 hr, and recollected. The iodonium salt was washed again with ether and acetone, suction dried for 30 min, and dried overnight in a vacuum desiccator. The iodonium salt obtained was a mixture of the iodonium chloride and bromide. Based on the elementary analyses (C, H, Cl, and Br) the percentage of iodonium chloride and bromide was determined and thus the total per cent yields. Typical yields of di-1-naphthyliodonium chloride bromide were 35–55% (ten reactions). Typical yields of di-2-naphthyliodonium chloride bromide were 27–55% (five reactions). Yields of dibenziodolium chloride bromide were 32 and 39% (two reactions). Typical yields of di-9-anthryliodonium chloride bromide were 22–32% (four reactions). In one case we obtained analytically pure di-9-anthryliodonium bromide, 1.25 g (22%), mp 125–126.5° dec.[14]

Anal. Calcd for $C_{28}H_{18}IBr$: C, 59.91; H, 3.24. Found: C, 59.91; H, 3.36.

A sample of di-9-anthryliodonium bromide was decomposed at 130°. Vpc analysis on a 6-ft 20% SE-30 columns showed only two peaks. These were approximately the same size and were identified as 9-bromoanthracene and 9-iodoanthracene by the peak-enhancement method with authentic samples.

Di-1-naphthyliodonium Chloride.—A reaction carried out as above with aryllithium prepared from 1-iodonaphthalene, gave 1.57 g (40%) of di-1-naphthyliodonium chloride, mp 177–179.5° dec.[14]

Di-1-naphthyliodonium Bromide.—In a stirred reaction run as described above at −70°, 52 g (60 mmol) of anhydrous lithium bromide was placed in the flask. The collected iodonium salt was washed well with absolute ethanol, acetone, and ether, triturated with water, and dried to give 1.51 g (34.5%) of white crystalline di-1-naphthyliodonium bromide, mp 163–164° dec (lit.[6] mp 149.4–151.4°).

Anal. Calcd for $C_{20}H_{14}IBr$: C, 52.09; H, 3.07; I, 27.52; Br, 17.33. Found: C, 51.90; H, 2.98; I, 27.42; Br, 17.20.

Di-2-naphthyliodonium Perchlorate.—In a similar reaction, after bringing the reaction flask to Dry Ice–acetone temperature 50 g of anhydrous lithium perchlorate was added before adding the aryllithium solution. Work-up gave 2.18 g (45%) and 3.11 g (65%) of di-2-naphthyliodonium perchlorate in duplicate runs, mp 157.5–162.5° dec.[14]

Anal. Calcd for $C_{20}H_{14}IClO_4$: C, 49.98; H, 2.94; I, 26.40; Cl, 7.38; O, 13.34. Found: C, 49.86; H, 3.10; I, 26.56; Cl, 7.64; O, 13.00.

1- and 2-Naphthyliodonium Iodides.—To a 0.5-g sample of the naphthyliodonium chloride bromide suspended in 300 ml of boiling methanol 5 g of potassium iodide was added, and the hot solution was stirred for 6 hr. After cooling, the collected solid was washed with ether and acetone, stirred with 100 ml of cold water for 3 hr, collected, and resuspended in cold water for 1 hr. The di-1-naphthyliodonium iodide was collected, washed with ether and acetone, and dried *in vacuo* to give a colorless salt of mp 132.5–134.5° dec.[14]

Anal. Calcd for $C_{20}H_{14}I_2$: C, 47.08; H, 2.77. Found: C, 47.44; H, 2.92.

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[17] R. L. Datta and J. K. Choudhury, *J. Amer. Chem. Soc.*, **38**, 1079 (1916); H. J. Lucas and E. R. Kennedy, *Org. Syn.*, **22**, 52, 69, 72 (1942).

[18] C. Hartmann and V. Meyer, *Ber.*, **27**, 426, 502, 1592 (1894).

[19] C. Willgerodt, *ibid.*, **30**, 56 (1897).

[20] P. F. D. Shaw, *J. Chem. Soc.*, 443 (1951).

[21] H. Abbes, *Ber.*, **28**, 84 (1895).

[22] H. Peters, *J. Chem. Soc.*, **81**, 1350 (1902).

[23] J. McCrae, *Ber.*, **28**, 97 (1895).

After thermal decomposition of this salt at 150° vpc analysis showed one peak (on 6-ft 20% SE-30 columns), which was shown to be 1-iodonaphthalene by the peak enhancement method with an authentic sample.

Di-2-naphthyliodonium iodide, mp 151–154° dec (lit.[24] mp 147°), was prepared similarly.

Anal. Calcd for $C_{20}H_{14}I_2$: C, 47.08; H, 2.77. Found: C, 47.09; H, 2.91.

Again thermal decomposition at 200° showed one peak on vpc analysis; this was shown to be 2-iodonaphthalene by the peak-enhancement method with an authentic sample.

Diphenyliodonium Trichloromercurate(II).—To 5.6 g (10 mmol) of phenyl(*trans*-chlorovinyl)iodonium trichloromercurate-(II)[8c] suspended in 80 ml of toluene at Dry Ice–acetone temperature under an argon atmosphere, 10 mmol of phenyllithium solution was added slowly with stirring; the ice bath was allowed to "melt." After 1 day at room temperature the precipitate was collected and recrystallized from 300 ml of water. The white crystalline diphenyliodonium trichloromercurate(II) was collected and dried to give 4.3 g (73%), mp 177–180° (lit. mp 168–170°,[8a] 172–175°[18]).

Phenyl(1-naphthyl)iodonium Chloride.—To 440 mg (1.5 mmol) of phenyl(*trans*-chlorovinyl)iodonium chloride suspended in 30 ml of toluene at Dry Ice–acetone temperatures under an argon atmosphere, 1.5 mmol of 1-naphthyllithium solution was slowly added with stirring, thereafter allowing the ice bath to "melt." After 3 days at room temperature the solid was collected, suspended in 25 ml of cold water for 3 hr, recollected, washed with acetone and ether, and dried under vacuum to give 151 mg (27.5%) of phenyl(1-naphthyl)iodonium chloride, mp 170–171° (lit.[25] mp 168°).

Registry No.—**1,** 18964-25-5; di-9-anthryliodonium bromide, 18963-90-1; di-1-naphthyliodonium chloride, 18963-91-2; di-2-naphthyliodonium perchlorate, 18963-92-3; di-1-naphthyliodonium iodide, 18963-93-4.

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Intermediates in Nucleophilic Aromatic Substitution. VI.[1] Formation of Meisenheimer Complexes of the Isomeric 2,4,6-Cyanodinitroanisoles

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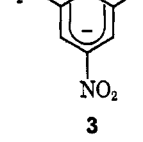
Received August 5, 1968

The rate constants for the formation and decomposition of the 1,1-dimethoxy Meisenheimer complexes **3** and **5** formed by the reaction of methoxide ion with 2-cyano-4,6-dinitroanisole (**1**) and 2,4,6-trinitroanisole (**6**), respectively, in methanolic solution have been determined at three different temperatures, allowing a determination of K, k_1, and k_2 and the energies and entropies of activation for the reactions. A similar study of the 1,1-dimethoxy complex **4** formed from 4-cyano-2,6-dinitroanisole (**2**) has been carried out. These data indicate that the relative order of stabilities of the complexes is **5** > **3** > **4** and that the replacement of a *p*-nitro group by a cyano group has a much more serious effect on the stability of the complex than the corresponding replacement of an *o*-nitro group, *i.e.*, $K_5/K_3 = 6.5$, $K_5/K_4 = 60$. Both the forward and reverse reactions for these complexes are dependent to a greater extent on changes in the entropies than in the enthalpies of activation. The entropy of activation for the formation of **3** is *ca.* 15 eu higher than that for either **4** or **5**, implying a much less extensively solvated transition state for the formation of **3**. The rate of decomposition of complex **3** in H_2O and D_2O has been determined over the pH range 5.27–10.80 at 25.00°. The lesser stability of **3** relative to **5** is further demonstrated by its higher rate of decomposition (k_2^0 for **3** = $15k_2^0$ for **5**); a significant deuterium isotope effect on the entropy of this reaction is observed. The formation and decomposition of **3** was also followed in CH_3OD and the solvent isotope effect on the equilibrium constant (K^H/K^D) was found to be 0.45, an apparently typical value for nucleophilic aromatic substitution reactions. The structures of complexes **3**, **4**, and **5** have been substantiated by studies of the pmr spectra of both the isolated and *in situ* generated complexes. In the *in situ* generation of **3** and **4** by the reaction of methanolic methoxide ion with **1** and **2** in DMSO-d_6 solution, the formation of unstable transients is observed. The initial attack of methoxide ion is at an unsubstituted ring position to yield 1,3-dimethoxy complexes, *i.e.*, 1,3-dimethoxy-2-cyano-4,6-dinitrocyclohexadienylide (**10**) from **1** and 1,3-dimethoxy-4-cyano-2,6-dinitrocyclohexadienylide (**12**) from **2**. The lifetimes of the transient complexes **10** and **12** are dependent on methanol concentration.

The formation of complexes by the addition of methanolic sodium methoxide to solutions of 2-cyano-4,6-dinitroanisole (**1**) and 4-cyano-2,6-dinitroanisole (**2**) has been observed and the electronic spectra of the complexes have been reported.[3] More recently, the proton magnetic resonance (pmr) spectra of the solid complexes of **1**, potassium 1,1-dimethoxy-2-cyano-4,6-dinitrocyclohexadienylide (**3**),[4] and **2**, potassium 1,1-dimethoxy-4-cyano-2,6-dinitrocyclohexadienylide (**4**),[5]



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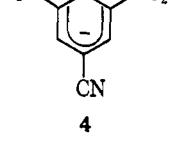

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in DMSO-d_6 solution have been obtained. The observed electronic and pmr spectra of complexes **3**[4] and **4**,[5] generated *in situ*, suggested that these complexes

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