amine[18] on Chromosorb.[19] The retention times of some alkylpyridines on this substrate have been determined[20] and it was observed that the values of 2- and 4-isomers differ greatly, the 4-isomers having longer retention times. It is interesting to note that 2-ethylpyridine has a smaller retention time than 4-picoline. This could be ascribed to the hindrance to solvation of the 2-substituted pyridines on the polar solvent. A complete separation of the starting material and the reaction product was in such cases achieved. The column was kept at 150°. Helium was used as a carrier gas. In the case of 4-alkylpyridines homologs, a shorter column—about 10 feet—could be used, since the separation is quite large; for the lower 2-alkylpyridine homologs, an additional 10-foot column improved the separation. The pressure of the carrier gas was changed from 10 to 30 lb./sq. inch according to the increase in length of the column.

Acknowledgment.—The authors wish to thank Mr. Ed. M. Lewicki for technical assistance.

EVANSTON, ILL.

---

(18) Visco Products Co., Inc., Houston, Texas.

(19) Johns–Manville Corporation.

(20) A. W. Decora and G. V. Dinneen, Paper presented before the Analytical Division, American Chemical Society Meeting, September, 1958, Chicago, Ill.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Diaryliodonium Salts. XIV. Reactions of Organometallic Compounds with Iodosobenzene Dichlorides and with Iodonium Salts[1,2]

BY F. MARSHALL BERINGER[3] JOSEPH W. DEHN, JR., AND MURRAY WINICOV

RECEIVED NOVEMBER 30, 1959

At low temperatures aryllithium compounds react with aryliodoso dichlorides in ether, tetrahydrofuran or toluene to give 20–50% of diaryliodonium salts. More aryllithium compound or arylmagnesium halide converts the iodonium salt to a triaryliodine, from which the iodonium salt can be recovered in good yield by cleavage with acid. A triaryliodine or an alkyldiaryliodine allowed to warm to 0° or above in ether gives products formed by decomposition to iodo compounds and free radicals, which may react with each other or with solvent.

Introduction.—Three steps may be considered in the reactions of organometallic compounds (RM) with iodine(III) chlorides.

$$RM + ICl_3 \longrightarrow RICl_2 + MCl \qquad (A)$$

$$RM + RICl_2 \longrightarrow R_2ICl + MCl \qquad (B)$$

$$RM + R_2ICl \longrightarrow R_3I + MCl \qquad (C)$$

Reaction A is exemplified by the formation of *trans*-2-chlorovinyliodoso dichloride from the corresponding mercuric chloride by treatment with iodine trichloride.[4] There are few examples of reaction A alone, as in most cases it is followed by reaction B to give an iodonium salt; *e.g.*, bis-(*trans*-2-chlorovinyl)-mercury with iodine trichloride gave bis-(*trans*-2-chlorovinyl)-iodonium chloride[4] while both diphenylmercury and phenylstannic chloride with iodine trichloride gave diphenyliodonium chloride.[5]

Reaction B has been run with organometallic compounds of mercury,[5,6] silver,[7] tin[5] and magnesium.[8] Reactions with phenylstannic chloride[5] were convenient and successful while those with Grignard reagents[8] gave iodonium salts in only trace amounts. For example, iodosobenzene dichloride with ethylmagnesium bromide gave ethylbenzene and iodobenzene and with phenylmagnesium bromide gave biphenyl, iodobenzene and a trace of a diphenyliodonium salt.

The appearance of ethylbenzene, biphenyl and iodobenzene suggests the further reaction of the Grignard reagent with the iodonium salt formed in the initial reaction. Examples of reaction C are the formation at low temperature of triphenyliodine[9,10] from diphenyliodonium iodide and phenyllithium and of phenyl-2,2′-biphenylyliodine[11] from 2,2′-biphenylyliodonium iodide and phenyllithium. Both trisubstituted iodines are yellow. The latter cyclic trisubstituted iodine was relatively stable to 100°, while triphenyliodine decomposed above 0° to give, as one product, biphenyl.

In 1953, it was reported[12] from these laboratories that ethereal methylmagnesium iodide, ethylmagnesium bromide, phenylmagnesium bromide and phenyllithium at 0° or above gave with diphenyliodonium bromide toluene (59%), ethylbenzene (37%) and biphenyl (33 and 46%). At that time it was thought that these products probably arose from nucleophilic attack of the organometallic compound on the 1-carbon of the diphenyliodonium ion. The alternative route of formation *via* trisubstituted iodines was not explicitly considered.

The first aim of the present work was to investigate the synthesis of diaryliodonium salts from aryliodoso dichlorides and organolithium or magnesium compounds at low temperatures. The second aim was to investigate further the products of the reaction of diphenyliodonium chloride in ether with Grignard reagents.

---

(1) This paper is taken from the M.S. thesis of Murray Winicov and the Ph.D. dissertation of Joseph W. Dehn, Jr., and was presented in part at the New York City Meeting of the American Chemical Society in September, 1957 (Abstracts of Papers, p. 36P).

(2) Preceding paper: F. M. Beringer and I. Lillien, THIS JOURNAL, **82**, 725 (1960).

(3) Visiting Associate Professor, Yale University, 1958–1959.

(4) A. N. Nesmeyanov, *Bull. acad. sci. U.R.S.S., Classe Sci. Chim.*, 239 (1945); *C. A.*, **40**, 2122 (1946).

(5) R. K. Freidlina and A. N. Nesmeyanov, *Compt. rend., acad. sci. U.R.S.S.*, **29**, 567 (1940); *C. A.*, **35**, 3614 (1941).

(6) C. Willgerodt, *Ber.*, **30**, 56 (1897); **31**, 915 (1898).

(7) C. Willgerodt, *ibid.*, **28**, 2107 (1895); J. Thiele and H. Haakh, *Ann.*, **369**, 131 (1909).

(8) H. Hepworth, *J. Chem. Soc.*, **119**, 1244 (1921).

(9) G. Wittig and M. Rieber, *Ann.*, **562**, 187 (1949).

(10) G. Wittig and K. Clauss, *ibid.*, **578**, 136 (1953).

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

(12) F. M. Beringer, A. Brierley, M. Drexler, E. M. Gindler and C. C. Lumpkin, THIS JOURNAL, **75**, 2708 (1953).

Results and Discussion

The Synthesis of Diaryliodonium Salts.—A single reaction of iodine trichloride with phenyllithium gave only a very small yield (1%) of diphenyliodonium salt. More successful were the reactions of phenyliodoso dichloride with phenyllithium at low temperatures (Table I).

TABLE I

DIPHENYLIODONIUM BROMIDE FROM PHENYLIODOSO DICHLORIDE AND PHENYLLITHIUM AT LOW TEMPERATURES[a]

Solvent	Temp., °C.	Molar ratio[b]	Yield, % Crude	Yield, % Crystd.
Ether	−76 to −70	1	..	19
	−65 to −55	1	27	22
	−70 to −55[c]	1	47	33
	Dry Ice-bath	3	..	29
	−76 to −60	3	..	35
	−67 to −55[c]	3	49	31
THF[d]	−65 to −55	1	23	18
Toluene	−71 to −65	1	39	31

[a] Unless otherwise noted the ethereal solution of phenyllithium and lithium bromide was added to the phenyliodoso dichloride. [b] Molar ratio of phenyllithium to phenyliodoso dichloride. [c] Inverse addition. [d] Tetrahydrofuran.

A reaction of phenyliodoso dichloride with phenylmagnesium chloride in tetrahydrofuran at −72 to −60° gave 3% of diphenyliodonium bromide. The reason for the superiority of the lithium reagent is not presently known.

One aspect of Table I requires further comment: the use in some reactions of phenyllithium in excess of that required by the stoichiometry of reaction B. Under these conditions the first-formed iodonium salt was converted to triphenyliodine (reaction C) from which the iodonium salt could be recovered by cleavage with acid (reaction D).

$$(C_6H_5)_3I + HX \longrightarrow (C_6H_5)_2I^+X^- + C_6H_6 \qquad (D)$$

In practice there was only a small increase in yield. In a control experiment diphenyliodonium chloride treated at low temperature first with phenyllithium and then with hydrogen chloride gave back 64% of iodonium salt as the bromide; 84% of diphenyliodonium bromide was recovered from crystallization under comparable conditions.

Another possible synthesis of diphenyliodonium salts is the reaction of triphenyliodine with phenyliodoso dichloride (reaction E). In a two-step reaction phenyliodoso dichloride was first converted to yellow, crystalline triphenyliodine which

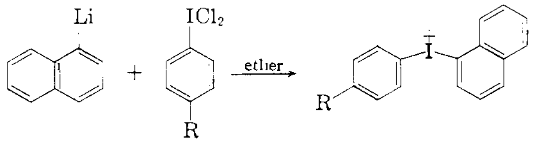
$$(C_6H_5)_3I + C_6H_5ICl_2 \longrightarrow 2(C_6H_5)_2I^+Cl^- \qquad (E)$$

then was cleaved with an equivalent of phenyliodoso dichloride to the iodonium salt, isolated as the crude bromide (47%).

Two symmetrical salts were prepared by the addition of a substituted phenyliodoso dichloride to a similarly substituted phenyllithium. Both 4,4′-dimethyl- and 4,4′-dichlorodiphenyliodonium bromide were obtained in 30% yield after crystallization.

Some preliminary attempts to prepare naphthyliodonium salts by reaction B have been successful. Reactions of 1-naphthyllithium with phenyliodoso dichloride and with *p*-chlorophenyliodoso dichloride have given the unsymmetrical salts in 28 and 34% yields after crystallization.[13,14]

The related reaction in which 1-naphthyliodoso dichloride[13] is treated with an aryllithium compound is made difficult by the instability of this iodoso dichloride, which may decompose exothermically minutes after collection and washing on a Büchner funnel. The best yield by this route has been 8% of 1,1′-dinaphthyliodonium salt.



As 2-naphthyliodoso dichloride[15] is of about the same stability as the phenyl derivative, 2-naphthyliodonium salts[15] may be prepared both from this iodoso dichloride and from 2-naphthyllithium. The two reagents together gave 2,2′-dinaphthyliodonium salts (7%).

Thus diaryliodonium salts may be prepared from iodoso dichlorides by treatment not only with the relatively unreactive mercury and tin compounds but also with the reactive lithium compounds.

Diphenyliodonium Halides with Grignard Reagents.—When dry diphenyliodonium chloride or bromide was added to ethereal Grignard reagent near the boiling point, there was local boiling and a fleeting yellow coloration. Addition below 0° gave a yellow-orange precipitate, which lost its color on stirring at room temperature.

Products from the reactions of Grignard reagents with diphenyliodonium chloride or bromide are given in Table II.

It is proposed that the variety of products obtained arises from the decomposition of trisubstituted iodines to iodo compounds and free radicals, which react with each other and with the solvent.[16]

$$\begin{array}{l}
(C_6H_5)_2IR + MgX_2 \longleftarrow (C_6H_5)_2I^+X^- + RMgX \\
\qquad\big\downarrow \\
C_6H_5\cdot + R\cdot \longrightarrow C_6H_5C_6H_5 + C_6H_5R + RR \\
\quad C_6H_5I + RI \qquad\qquad C_6H_6 + RH + RH_{-1} \\
\\
\qquad C_6H_5\cdot\ (\text{or } R\cdot) \longrightarrow C_6H_6\ (\text{or } RH) \\
\quad CH_3CH_2OCH_2CH_3 \qquad\qquad CH_3\dot{C}HOCH_2CH_3
\end{array}$$

The data of Table II indicate that there is a tendency for R· to be formed rather than $C_6H_5\cdot$; *i.e.*, the C_6H_5I/RI ratio is always greater than two.

---

(13) 1-Naphthylphenyliodonium salts have been made from 1-naphthyliodoso dichloride and diphenylmercury: C. Willgerodt and P. Schlosser, *Ber.*, **33**, 692 (1900).

(14) Similar salts substituted in the phenyl group have been prepared by the condensation of 1-iodosonaphthalene with substituted iodoxybenzenes in the presence of silver oxide: C. Willgerodt and W. Ernst, *ibid.*, **34**, 3406 (1901); C. Willgerodt and K. Damman, *ibid.*, **34**, 3678 (1901); C. Willgerodt and W. Bergdolt, *Ann.*, **327**, 286 (1903); C. Willgerodt and P. Lewino, *J. prakt. Chem.*, [2] **69**, 321 (1904).

(15) 2-Naphthylphenyliodonium chloride was prepared from 2-naphthyliodoso dichloride and diphenylmercury: C. Willgerodt, *Ber.*, **31**, 915 (1898). The 2-naphthyliodoso dichloride is more stable than the 1-isomer but less stable than the phenyl derivative.

(16) A related reaction scheme helps to explain some of the products from diphenyliodonium ions with carbanions from di- and triketones: [F. M. Beringer, P. S. Forgione and M. D. Yudis, *Tetrahedron*, **8**, 49 (1960)] and from esters [P. S. Forgione, Ph.D. dissertation, 1960].

TABLE II

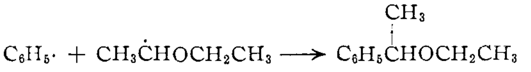
PRODUCTS FROM THE REACTIONS OF DIPHENYLIODONIUM HALIDES WITH GRIGNARD REAGENTS IN ETHER

Starting materials and products in millimoles[a, b]										
RMgX from RX		$Ph\overset{+}{I}Ph\ Y^-$ Y^-		Temp., °C.	PhI	PhH	PhPh	PhR	RI	$PhCH(OC_2H_5)CH_3$
CH_3I	200	Cl	100	− 5	90	85	. .	10	. .	
CH_3Br	200	Cl	160	35	135	50	10	40	. .	20
C_2H_5Cl	100	Cl	100	5	70	45	5	15	. .	
C_2H_5Br	200	Cl	100	− 5	80	95	5	15	20	
C_2H_5Br	100	Cl	100	35	80	60	5	15	Trace	
C_2H_5Br	200	Br	140	35	130	130	. .	20	10	
C_2H_5Br	200	Cl	200[c]	−40	130	120	15	20	25	
C_2H_5I	100	Cl	100	5	75	55	10	10	Trace	
i-C_3H_7Br	200	Cl	160	35	155	95	10	25	. .	10
t-C_4H_9Cl	100	Cl	100	35	95	70	5	0–10	. .	5
n-$C_8H_{17}Br$	100	Cl	130[d]	35	90	35	10	. .	. .	5

[a] Values rounded off to the nearest five millimoles. The leaders (. .) signify that none of the substance was found. [b] Four [c]odobenzene fractions were analyzed to determine the amount of $PhCH(CH_3)OCH_2CH_3$; these are shown in the last column. [d] Iodonium salt was recovered (20 mmoles); also, a considerable amount of what is believed to be butane was collected. Twenty millimoles of octene-1 was recovered.

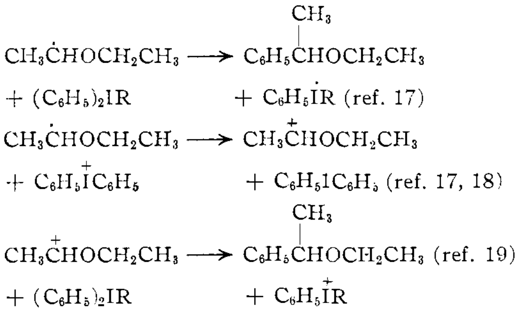
Next, it is seen that more phenyl radicals abstract a hydrogen from the ether than couple with another radical. The number of millimoles of iodobenzene recovered is close to that of the starting reagent present in smaller amount. Furthermore, the material balance for the other phenyl group, the sum of the millimoles of benzene and alkylbenzene and twice the millimoles of biphenyl, is often 80–100% of the theoretical. In accord with these observations, reactions in which alkyl iodides were formed also produced larger amounts of products other than iodobenzene.

It has been found that some of the missing phenyl groups are in the ethyl ether of methylphenylcarbinol which arises from interaction with solvent. The simplest route for its formation would be radical coupling. Alternatively, this product might



$$C_6H_5\cdot + CH_3\dot{C}HOCH_2CH_3 \longrightarrow C_6H_5CH(CH_3)OCH_2CH_3$$

have been formed from trisubstituted iodine by attack of solvent radical or its derived carbonium ion.[17–19]



$$CH_3\dot{C}HOCH_2CH_3 + (C_6H_5)_2IR \longrightarrow C_6H_5CH(CH_3)OCH_2CH_3 + C_6H_5\dot{I}R \text{ (ref. 17)}$$

$$CH_3\dot{C}HOCH_2CH_3 + C_6H_5\overset{+}{I}C_6H_5 \longrightarrow CH_3\overset{+}{C}HOCH_2CH_3 + C_6H_5IC_6H_5 \text{ (ref. 17, 18)}$$

$$CH_3\overset{+}{C}HOCH_2CH_3 + (C_6H_5)_2IR \longrightarrow C_6H_5CH(CH_3)OCH_2CH_3 + C_6H_5\overset{+}{I}R \text{ (ref. 19)}$$

Finally, it should be noted that in the present work the yields of alkylbenzenes (Table II) are substantially lower than those previously reported.[12] Since the present work is on a larger scale and has more efficient separation and analysis of products, the previously reported[12] yields of alkylbenzenes must be revised downward.

Acknowledgment.—F. M. B. wishes to acknowledge the hospitality of Yale University, where this article was written during a year's appointment, 1958–1959, and generous support by the Alfred P. Sloan Foundation, Inc. We are indebted to the Interchemical Corp. for analyses performed in their laboratories.

Experimental[20]

Starting Materials.—Commercial iodobenzene was redistilled before use. 4-Iodotoluene, 4-chloroiodobenzene and 1-iodonaphthalene were used as received from Distillation Products, Inc. 2-Iodonaphthalene was prepared from the corresponding naphthylamine.[21,22] The dichlorides of these iodo compounds were prepared by known procedures[13,15,23,24] and were generally used soon after isolation.

1-Naphthyliodoso dichloride[13] is unstable and was used immediately after preparation. Apparently the best preparation to date was carried out using propionic acid as solvent, as described below. Acetic acid was used as solvent in some experiments; in one, α-naphthyliodoso dichloride isolated in 68% yield spontaneously decomposed very rapidly and violently before it could be used. In attempts to chlorinate 1-iodonaphthalene in carbon tetrachloride, ether and hexane, the product decomposed rapidly *in situ* before it could be isolated.

1-Iodonaphthalene (5.08 g., 20 mmoles) in 25 ml. of propionic acid was treated with chlorine at 0–5° over 1 hour. The bright yellow precipitate was collected rapidly, washed with 300 ml. of cold ether and used immediately; see preparation of di-1-naphthyliodonium bromide.

Diphenyliodonium chloride[25] and bromide[24] were prepared directly from benzene. Ethereal solutions of organomagnesium halides and organolithium compounds (except 4-chlorophenyllithium, 1-naphthyllithium and 2-naphthyllith-

---

[17] For discussions of the formation and reactions of diphenyliodine and related radicals see (a) H. E. Bachofner, F. M. Beringer and L. Meites, THIS JOURNAL, **80**, 4269 (1958); (b) F. M. Beringer, E. M. Gindler, M. Rapoport and R. J. Taylor, *ibid.*, **81**, 351 (1959).

[18] The oxidation of solvent radical by iodonium ion was proposed in ref. 17b and is analogous to oxidation by diazonium ion: D. F. DeTar and M. N. Turetsky, *ibid.*, **77**, 1745 (1955).

[19] This electrophilic attack on a trisubstituted iodine is similar to reactions D and E in the text and the reaction of triphenyliodine with triphenylboron (ref. 10).

[20] Capillary melting points were taken in a Hershberg apparatus. For a discussion of techniques and their effects on observed ranges of melting and decomposition see F. M. Beringer, R. A. Falk, M. Karniol, I. Lillien, G. Masullo, M. Mausner and E. Sommer, THIS JOURNAL, **81**, 342 (1959).

[21] J. Schmidlin and M. Huber, *Ber.*, **43**, 2829 (1910).

[22] L. C. Raiford and H. P. Lankelma, THIS JOURNAL, **47**, 1118 (1925).

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

[24] F. M. Beringer, M. Drexler, E. M. Gindler and C. C. Lumpkin, THIS JOURNAL, **75**, 2705 (1953).

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

ium) were made from the alkyl or aryl halide with magnesium or lithium. 4-Chlorophenyllithium,[26] 1-naphthyllithium[27a] and 2-naphthyllithium[27] were formed by the interaction of *n*-butyllithium[28] with 4-bromochlorobenzene, 1-bromonaphthalene and 2-bromonaphthalene.

The alkyl halides were of the highest purity commercially available (Distillation Products, Inc., or Matheson Co., Inc.) and were redistilled before use. Merck magnesium turnings were used for the first runs; later, Dow magnesium of very high purity became available. With the latter, slightly higher yields of Grignard reagents were obtained. The ether and other solvents used were the best grades obtainable and were used without further purification.

The preparation of aryllithium compounds and their reactions with aryliodoso dichlorides were all conducted under an atmosphere of dry nitrogen.

Iodosobenzene Dichloride.—Iodobenzene (102 g., 0.5 mole) was treated with chlorine in 150 ml. of cold, dry chloroform by the method of Lucas and Kennedy[23] to give 130.2 g. (97%) of iodosobenzene dichloride, m.p. 104–107°; reported m.p. 115–127°,[29] 110–136°,[30] 120–121°.[31]

Triphenyliodine.—To 106.5 mmoles of phenyllithium in 200 ml. of anhydrous ether at −60° under nitrogen 14.65 g. (0.0533 mole) of iodosobenzene dichloride was added gradually. While first additions dissolved, in time bright yellow crystals of triphenyliodine formed from deep yellow solution. The reaction was stirred 30 min. longer at −70 to −65°.

Diphenyliodonium Bromide from Triphenyliodine with Iodosobenzene Dichloride.—An additional 14.7 g. (0.0533 mole) of iodosobenzene dichloride was added gradually at −70° to the above mixture. The yellow crystals gradually changed over 45 min. to a white precipitate. The reaction was allowed to stir another 50 hours (over a weekend) and come slowly to room temperature. The thick white precipitate was collected and washed with 75 ml. of ether to give 30 g. of solid which was suspended in 100 ml. of water and ground with a mortar and pestle. The aqueous suspension was filtered and washed with 50 ml. of water to give 18.2 g. (47%) of crude diphenyliodonium bromide, which was recrystallized from 1000 ml. of water to yield 12.57 g. (32.7%), m.p. 229–230°. One gram of this salt was recrystallized from 60 ml. of methyl alcohol to give 0.65 g. of **diphenyliodonium bromide**, m.p. 233–234°; reported m.p. 208°,[24] 208–209°,[20] 210°,[32] 230°.[33]

Anal. Calcd. for $C_{12}H_{10}IBr$: C, 39.92; H, 2.79. Found: C, 40.42; H, 2.92.

Diphenyliodonium Bromide from Triphenyliodine with Hydrogen Chloride.—To 2.75 g. (10 mmoles) of iodosobenzene dichloride suspended in 15 ml. of anhydrous ether at −60° under nitrogen, 31 mmoles of phenyllithium in ether was added. Practically all the solid dissolved in about 3 min., and after about 8 min. yellow crystals precipitated. After 2 hours the yellow solid was allowed to settle, the supernatant liquid was decanted, and the solid was washed by decantation with 25 ml. of cold anhydrous ether. (Lithium hydroxide in the supernatant and wash liquids was titrated with 11.3 mmoles of hydrochloric acid, which is the excess phenyllithium employed.) Another 25 ml. of cold anhydrous ether was added to the residual solid and with stirring 32 mmoles of hydrogen chloride in ether was added gradually. The yellow needles immediately changed to a white precipitate. The bath was filled with Dry Ice, and the reaction mixture was stirred overnight and allowed to come gradually to room temperature. The thick white precipitate was filtered, suspended in 30 ml. of ether, filtered again and washed with ether. The 3.18 g. obtained was suspended in 15 ml. of water, filtered, washed, and then recrystallized from 80 ml. of water to give 1.04 g. (29%) of **diphenyliodonium bromide** as white needles, m.p. 223–226°.

Anal. Calcd. for $C_{12}H_{10}IBr$: C, 39.92; H, 2.79. Found: C, 40.00, 40.10; H, 2.79, 2.68.

Reaction of Diphenyliodonium Chloride with Phenyllithium and its Recovery.—To 11.07 g. (35 mmoles) of diphenyliodonium chloride in 80 ml. of anhydrous ether 70 mmoles of phenyllithium in ether was added dropwise at −70°. The solution and the precipitate gradually changed to a bright yellow. After 2 hr., 83 mmoles of hydrogen chloride in ether solution was added dropwise at below −60°. The resulting white precipitate was stirred 30 min. at −70° and then allowed to stand overnight and gradually come to room temperature. The product was filtered, washed with ether, and recrystallized from 600 ml. of water to yield 8.10 g. (22.4 mmoles) of **diphenyliodonium bromide** as white needles, m.p. 219–221°. There was thus 64% of recovery of the diphenyliodonium cation.

Iodine Trichloride with Phenyllithium.—Treatment of 23.4 g. (100 mmoles) of iodine trichloride in 400 ml. of ether under nitrogen at −60° with 200 mmoles of ethereal phenyllithium was followed by prolonged stirring at −70° and warming to room temperature. The usual work-up gave 2.94 g. of red-brown solid. Crystallization from water gave 0.73 g. of impure, light yellow **diphenyliodonium iodide**, m.p. 147–153°. Recrystallization from methanol gave 0.40 g. (1 mmole, 1%) of colorless crystals, m.p. 156–157°; no depression of m.p. on admixture with an authentic sample.

Iodosobenzene Dichloride with Phenylmagnesium Chloride.—To 27.5 g. (100 mmoles) of iodosobenzene dichloride in 200 ml. of tetrahydrofuran under nitrogen at −60° there was gradually added 100 mmoles of a tetrahydrofuran solution of phenylmagnesium chloride[34] at −70 to −60°. After 45 minutes the color of the initially deep bright blue solution began to change to green and to fade, while precipitation of a white solid commenced. After 44 hours at this temperature and warming to room temperature the precipitate was collected, ground with 20 ml. of water, collected again, washed with water and dried to give 2.54 g. (8 mmoles, 8%) of **diphenyliodonium chloride**, m.p. 204–209°. Crystallization from water and once from methanol gave 0.45 g. (1.4 mmoles, 1.4%) of colorless crystals, m.p. 223–224°.

4,4′-Dimethyldiphenyliodonium Bromide.—To 100 mmoles of *p*-tolyllithium in 200 ml. of ether at −60° 28.9 g. (100 mmoles) of *p*-tolyliodoso dichloride, m.p. 94–97,[35] was added. The precipitate was bright yellow initially but then became colorless. The precipitate was collected and washed with water to give 16.1 g. (41.4 mmoles, 41%) of crude **4,4′-dimethyldiphenyliodonium bromide**, m.p. 176.5–178.5°. Crystallizations from water and methanol (three times) raised the m.p. to 181–182°[36]; reported m.p. 171–173°,[20] 178°.[37]

Anal. Calcd. for $C_{14}H_{14}IBr$: C, 43.21; H, 3.62. Found: C, 42.82; H, 3.56.

4,4′-Dichlorodiphenyliodonium Bromide.—To 4-chlorophenyllithium prepared from 100 mmoles each of 4-bromochlorobenzene and *n*-butyllithium in 100 ml. of ether there was added 30.94 g. (100 mmoles) of 4-chlorophenyliodoso dichloride, m.p. 110–112,[38] at −60° over 10 minutes. The yellow precipitate had made the mixture too thick to stir, so an additional 100 ml. of ether was added. After an additional 10 minutes at −60° the precipitate became colorless. The temperature rose to −22° over 48 hr. and then to ambient. The collected solid (35.5 g.) was ground with 100 ml. of water, collected again, washed with water and dried to give 21.6 g. (50.2 mmoles, 50%) of crude **4,4′-dichlorodiphenyliodonium bromide**. Crystallization from three liters of water gave 13.1 g. (30.5 mmoles, 31%) of salt, m.p. 187–189°; two further crystallizations from methanol raised the m.p. to 189–190°; reported m.p. 187–188°,[20] 190°,[39] 204–205°.[20]

Anal. Calcd. for $C_{12}H_8Cl_2BrI$: C, 33.52; H, 1.88. Found: C, 33.33, 33.38; H, 2.06, 1.91.

---

(26) H. Gilman, W. Langham and F. W. Moore, THIS JOURNAL, **62**, 2327 (1940).

(27) (a) H. Gilman and F. W. Moore, *ibid.*, **62**, 1843 (1940); (b) H. Gilman and C. G. Brannen, *ibid.*, **72**, 4280 (1950).

(28) H. Gilman, "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 285; H. Gilman, *et al.*, THIS JOURNAL, **71**, 1499 (1949).

(29) C. Willgerodt, *Ber.*, **41**, 1097 (1908).

(30) W. Caldwell and E. A. Werner, *J. Chem. Soc.*, **91**, 240 (1907).

(31) J. C. Nichol and R. B. Sandin, THIS JOURNAL, **67**, 1307 (1945).

(32) M. O. Forster and J. H. Schaeppi, *J. Chem. Soc.*, **101**, 382 (1912).

(33) C. Hartman and V. Meyer, *Ber.*, **27**, 502 (1894).

(34) H. E. Ramsden, A. E. Balint, W. R. Whitford, J. J. Walburn and R. Cserr, *J. Org. Chem.*, **22**, 1202 (1957).

(35) Reported m.p. 88–90°: R. M. Keefer and L. J. Andrews, THIS JOURNAL, **80**, 277 (1958).

(36) See discussion of this melting point in Experimental section of ref. 20.

(37) J. McCrae, *Ber.*, **28**, 97 (1895).

(38) Reported[31] m.p. 115°.

(39) L. Wilkinson, *Ber.*, **28**, 99 (1895).

Di-1-naphthyliodonium Bromide.—To roughly 20 mmoles of ethereal 1-naphthyllithium (from 20 mmoles each of 1-bromonaphthalene and *n*-butyllithium) there was added roughly 20 mmoles of 1-naphthyliodoso dichloride (from 20 mmoles of 1-iodonaphthalene). The yellow color persisted after 3 hours at −60° and 42 hours between −60 and −40°. The reaction mixture was treated at −70° with 40 mmoles of ethereal hydrogen chloride (to convert any tri-1-naphthyliodine to the iodonium salt). After 2 hours at this temperature, the white mixture was warmed to ambient. The collected precipitate was ground with 12 ml. of water, filtered, washed with water and dried to give 0.71 g. (1.54 mmoles, 8%) of crude **di-1-naphthyliodonium bromide**, m.p. 145–147°. Crystallization from methanol raised the m.p. to 149–151°.

Anal. Calcd. for $C_{20}H_{14}BrI$: C, 52.09; H, 3.06. Found: C, 51.91; H, 3.12.

Phenyl-1-naphthyliodonium Bromide.—To roughly 100 mmoles of ethereal 1-naphthyllithium (from 100 mmoles each of 1-bromonaphthalene and *n*-butyllithium) there was added 27.5 g. (100 mmoles) of phenyliodoso dichloride at −75°. After 0.5 hour the yellow color had disappeared, but stirring at −75 to −45° was continued for 48 hours. The precipitate was collected, ground with 150 ml. of water, collected, washed with water and dried to give 22.6 g. (55 mmoles, 55%) of crude **phenyl-1-naphthyliodonium bromide**, m.p. 148–156°. One crystallization from water and two from methanol raised the m.p. to 168–169°.

Anal. Calcd. for $C_{16}H_{12}BrI$: C, 46.74; H, 2.94. Found: C, 46.74; H, 2.94.

4-Chlorophenyl-1-naphthyliodonium Bromide.—The reaction was run and worked up as for the preceding experiment (except that 4-chlorophenyliodoso dichloride was used) and gave 27.1 g. (60.8 mmoles, 61%) of crude **4-chlorophenyl-1-naphthyliodonium bromide** as a light yellow solid. While three crystallizations from water gave colorless crystals, m.p. 150–154°, a further crystallization from methanol raised the m.p. to 161–162°.

Anal. Calcd. for $C_{16}H_{11}BrClI$: C, 43.13; H, 2.49. Found: C, 43.32; H, 2.63.

Reactions with Iodonium Salts

General Procedure.—About 250 ml. of ethereal solution of Grignard reagent was prepared in the usual way from 0.1 mole of alkyl or aryl halide and 0.1 g. atom of magnesium. To the cooled solution, iodonium salt was added in about 3-g. portions. Each addition caused superficial ether boiling and a fleeting yellow coloration. Addition of excess iodonium salt (over the molar equivalent) did not cause further boiling. The iodonium salt dissolved in the ethereal solution. A heavy sticky white solid of smaller total bulk appeared from the solution as addition was continued. Depending on the state of subdivision, this new solid sometimes appeared to be a second, heavier liquid phase. Stirring was usually continued for 0.5 hour after the addition was complete.

Several of the reactions were carried out with the Grignard solution kept under 0° by an ice–salt-bath. The iodonium salt was added at intervals sufficiently spaced apart to prevent any disturbance at the surface of the ether. In these reactions an intensely yellow-orange colored precipitate formed during the addition, which reverted to a white sticky solid upon stirring at room temperature. No apparent evolution of heat accompanied this transition.

To the reaction mixtures 5–10 ml. of 10% sulfuric acid was added dropwise, causing vigorous boiling. The ether layer was separated, washed twice with bicarbonate solution and dried over anhydrous sodium sulfate or potassium carbonate before distillation. A small amount of free iodine was usually present in the ether layer at this point.

The dried ether solutions containing the reaction products were first distilled to remove ether using a 21-ball Snyder column. When the volume was reduced to about 35 ml., the solution was transferred to a 50-ml. flask and the distillation was continued utilizing a smaller, 8-ball column. From some runs biphenyl was isolated from the small residue.

Identification of the Products.—Preliminary identification of liquids was made on the basis of boiling point, density and refractive index. The infrared spectrum of most of the cuts and residues was taken on a Beckman single beam automatic recording infrared spectrophotometer between 15.0 and 2.3 μ. Reference spectra of pure benzene, alkylbenzenes and iodobenzene were taken under the same operating conditions. Semi-quantitative estimates were made on the basis of these standards. Biphenyl was identified by recrystallization of residues from methanol and determining the capillary melting point and mixed melting point with an authentic sample.

Diphenyliodonium Chloride with Methylmagnesium Bromide.—Using the procedure described previously, 50 g. (160 mmoles) of diphenyliodonium chloride was added to 200 mmoles of methylmagnesium bromide in 300 ml. of ether with moderate ice-bath cooling to prevent excessive ether boiling. The reaction was "decomposed" with 10 g. of sulfuric acid in 100 ml. of aqueous solution, washed twice with 5% sodium bicarbonate, twice with water, dried over anhydrous sodium sulfate and distilled in a 21-ball Snyder column to remove the ether. A sample of the recovered ether did not give a positive test for methyl iodide using alcoholic silver nitrate acidified with nitric acid. The 43.0 g. of product remaining after the ether was removed was further fractionated in an 8-ball Snyder column to give three main cuts (benzene, toluene, iodobenzene and a biphenyl-containing residue). Infrared analysis of the iodobenzene (cut 3) fraction in this experiment and in three others noted in Table II indicated that the same impurity (identified as ethyl α-phenylethyl ether) was present in all four cases. Superimposed on the normal iodobenzene spectrum in each case were strong peaks at 1104, 701, 762 and 2990 cm.$^{-1}$ (arranged in order of decreasing strength).

Isolation of Ethyl α-Phenylethyl Ether from the Iodobenzene Cut.—To 1.5 g. of magnesium turnings (60 mg. atoms) in a 50-ml. two-necked flask were added 20 ml. of anhydrous ethyl ether. A 5.0-ml. portion of the iodobenzene (cut 3) fraction was added to the flask, and the Grignard reaction was initiated with a drop of methyl iodide. In about 1 minute the reaction started and refluxed without added heat for about 30 minutes. The mixture was allowed to stand one week at room temperature before "decomposing" with 25 ml. of 1 *N* sulfuric acid. After washing and drying in the usual manner, the ether solution was distilled in a micro-apparatus yielding 1.2 ml. of an oil of distillation range 170–200°, predominantly at 185°; $d^{25}{}_{25}$ 1.00; infrared spectrum of a 10.0% w./v. solution of this material in carbon disulfide was qualitatively identical with an authentic sample of 7.5% w./v. ethyl α-phenylethyl ether in the same solvent with respect to exactness of position and relative heights of the characteristic peaks. A slight amount of extraneous absorption in the recovered sample was classified as "very weak" and was ascribable to a trace of unreacted iodobenzene. The amount of this ether found by isolation and infrared analysis agreed with the amount calculated using the 1104 cm.$^{-1}$ ether peak in the untreated iodobenzene (cut 3) fraction. The other three values shown in Table II were similarly obtained using the absorption at 1104 cm.$^{-1}$ as the analytical peak. Mislow[40] has reproduced the spectrum of ethyl α-phenylethyl ether in carbon tetrachloride; the use of this solvent which absorbs very strongly in the 760 cm.$^{-1}$ region resulted in a spectrum which is qualitatively similar to that obtained in this study, but in which the peak at 762 cm.$^{-1}$ was completely masked. This ether has a reported b.p. 78° (20 mm.), $d^{25}{}_4$ 0.9131.

BROOKLYN, N. Y.

---

[40] K. Mislow, THIS JOURNAL, **73**, 3954 (1951).