More dramatic and of much more importance is the reaction of zinc with dihalomethanes. Zinc metal prepared by potassium reduction reacts rapidly with diiodomethane, and when this is reacted in the presence of cyclohexene, a Simmons–Smith reaction occurs to yield bicyclo[4.1.0]heptane. A wide variety of conditions were tried but a maximum yield of 25–30% was realized. This zinc also reacted rapidly with dibromomethane but only a 5% yield of bicyclo[4.1.0]heptane was obtained. The zinc prepared by lithium reduction, in contrast, gave excellent results. The zinc powder was prepared in the usual manner by lithium reduction in glyme. The solution was allowed to settle and then the glyme was removed via a syringe. The black powders can be washed with fresh dry glyme to remove the bulk of the naphthalene. Finally, the remaining glyme is removed with the aid of a vacuum pump. Anhydrous diethyl ether is then injected into the flask. Cyclohexene (0.5 equiv, based on zinc) is then injected into the reaction followed by the slow (10–15 min) addition of dibromomethane (1.0 equiv, based on zinc). The reaction is somewhat exothermic during the addition. The solution is then refluxed for 6 h, yielding 94% bicyclo[4.1.0]heptane and 6% cyclohexene. Dichloromethane appears to be unreactive under these conditions, and diiodomethane due to its very high reactivity gives somewhat erractic results. Thus dibromomethane is the reagent of choice. The Simmons–Smith reaction can be extended to even more unreactive dihalides. Reaction of 1,1-dibromoethane with cyclohexene under the above conditions produces both *exo*-7-methylbicyclo[4.1.0]heptane (12%) and *endo*-7-methylbicyclo[4.1.0]heptane (12%).

The zinc powders prepared by potassium reduction have been previously shown to be very useful in the Reformatsky reaction.[11] Similarly, the zinc powders prepared by lithium reduction lead to near quantitative yields in this reaction. As in the Simmons–Smith reaction, once the zinc powders are prepared the glyme is removed and replaced with diethyl ether. Ethyl α-bromoacetate (0.1 equiv) is added to the zinc powder at ice bath temperatures. A mixture of cyclohexanone and the remaining ethyl α-bromoacetate are added dropwise over 15 min.[12] The reaction mixture is then stirred at room temperature for 1 h and the quenched with aqueous acid. Analysis by GLC and isolation indicated near quantitative yields (yields ranged from 95% to 98%) of the β-hydroxy esters. The reaction proceeds equally well with aldehydes.

The reaction can also be carried out with ethyl α-chloroacetate. The only change in reaction conditions is that the reaction is refluxed for 2 h instead of being stirred at room temperature for 1 h. Yields are in the range of 85–90%.

Earlier we had also reported the preparation of highly reactive magnesium metal powders prepared by the reduction of magnesium halides, using potassium or sodium.[1,3,4] We now report that magnesium powders of equal reactivity can be readily and conveniently prepared by using lithium along with an electron carrier as the reducing agent. The highly reactive magnesium is prepared by the reduction of anhydrous magnesium chloride with 2 equiv of lithium and a small amount of naphthalene or biphenyl (10% based on the number of moles of lithium) in freshly distilled glyme or tetrahydrofuran under an argon atmosphere.[13] The solution is stirred vigorously at room temperature for 24 h. After complete reduction, the highly reactive magnesium appears as a dark gray to black powder, which slowly settles when stirring is stopped. Grignard reagents or other reactions can be prepared right in the reaction vessel by injecting the appropriate halide. If desired, the magnesium powder can be washed with fresh solvent to remove the electron carrier as described for zinc. Also, one can add a variety of other solvents if it is desired to carry out a reaction in a solvent other than glyme or THF. Grignard reagents prepared from this magnesium appear to react as normal Grignard reagents prepared from magnesium turnings. For example, they react with CO_2 to give the corresponding acid and add to ketones to give the corresponding alcohol.

In summary, high reactive zinc and magnesium powders are easily and safely prepared by lithium reduction of the corresponding salts. These metals are of equal or in the case of zinc superior reactivity to those metals prepared by potassium or sodium reduction. We will report the full details of these metals in the near future.

Acknowledgment. We gratefully acknowledge support of this work by the U.S. Army Office (supported work on zinc) and the Division of Chemical Sciences, Department of Energy (Contract No. DE-AC02-80ER10603, supported work on magnesium).

Registry No. Zinc, 7440-66-6; zinc chloride, 7646-85-7; magnesium, 7439-95-4; magnesium chloride, 7786-30-3; lithium, 7439-93-2.

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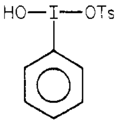
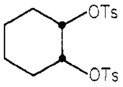
Functionalization of Alkenes and Alkynes with [Hydroxy(tosyloxy)iodo]benzene. Bis(tosyloxy)alkanes, Vinylaryliodonium Tosylates, and Alkynylaryliodonium Tosylates

Summary: [Hydroxy(tosyloxy)iodo]benzene (1) reacts with various alkenes to give bis(tosyloxy)alkanes and with various alkynes to give either vinylaryliodonium tosylates or alkynylaryliodonium tosylates. In the presence of 1, 1,1-diphenylethylene undergoes oxidative rearrangement and phenyliodination.

Sir: We report that [hydroxy(tosyloxy)iodo]benzene (1)[1-6] reacts with various alkenes to give bis(tosyloxy)alkanes and, in one case, a vinylaryliodonium salt and a product of oxidative rearrangement. With various alkynes, either vinylaryliodonium tosylates or alkynylaryliodonium tosylates are obtained.



1



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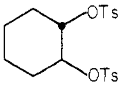

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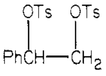
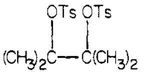


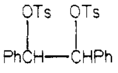
$$\mathrm{PhCH(OTs){-}CH_2(OTs)}$$

4



$$\mathrm{(CH_3)_2C(OTs){-}C(OTs)(CH_3)_2}$$

5



$$\mathrm{PhCH(OTs){-}CH(OTs)Ph}$$

6

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(1) O. Neiland and B. Karele, *J. Org. Chem. USSR* (*Engl. Transl.*), 6, 889 (1970).

(2) G. F. Koser and R. H. Wettach, *J. Org. Chem.*, **42**, 1476 (1977).

(3) G. F. Koser, R. H. Wettach, J. M. Troup, and B. A. Frenz, *J. Org. Chem.*, 41, 3609 (1976).

(4) G. F. Koser and R. H. Wettach, *J. Org. Chem.*, **45**, 1542 (1980).

(5) G. F. Koser, R. H. Wettach, and C. S. Smith, *J. Org. Chem.*, **45**, 1543 (1980).

(6) G. F. Koser and R. H. Wettach, *J. Org. Chem.*, **45**, 4988 (1980).

0022-3263/81/1946-4324$01.25/0

Table I. Melting Points of Bis(tosyloxy)alkanes, Vinylaryliodonium Tosylates, and Alkynylaryliodonium Tosylates[a]

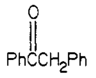
compd	mp, °C	compd	mp, °C
2 (from 1)	128–130 (α form), 115–117 (β form)	8	112–113 dec
2 (authentic)	128–130	9	92.5–95.5
3 (authentic)	108–110.5	11	156–157.5
4	116–118	12	152–154
5[b]	68 dec	13	124–125.5
6[c]	variable dec between 116 and 131	14[d]	147.5–149
		17	119–122 dec
		18	125–127.5 dec

[a] Satisfactory combustion analytical data (±0.4%) for C and H (all entries) and I (8, 11, 12, 13, 17, 18) were provided. [b] Unstable compound, see the text. [c] From *trans*-stilbene. [d] A satisfactory iodine analysis has not yet been obtained.

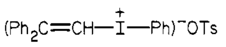
When a mixture of 1 (3.90 g) and cyclohexene (25 mL) was stirred for 1.5 h at room temperature, *cis*-1,2-bis(tosyloxy)cyclohexane (2) was isolated in 38% yield following the work up. The gross structure of 2 was established by elemental (C, H) and ^{1}H NMR analysis and the stereochemistry by spectral (IR, ^{1}H NMR) comparisons with authentic 2 and its trans isomer 3. The authentic ditosylates were prepared by treatment of *cis*- and *trans*-1,2-cyclohexanediols[7,8] with tosyl chloride in pyridine.[9,10]

The bis(tosyloxy)lation reaction extends to other alkenes. Thus, [hydroxy(tosyloxy)iodo]benzene was observed to react alternatively with styrene (CH_2Cl_2, 12.5 h, room temperature), tetramethylethylene (CH_2Cl_2, 0.5 h, 2–5 °C), and *trans*- and *cis*-stilbenes (CH_2Cl_2, 2 weeks, room temperature) to give the corresponding *vic*-ditosylates 4 (62.5%), 5 (18%), and 6 (51% from *trans*-stilbene, 58% from *cis*-stilbene). 2,3-Bis(tosyloxy)-2,3-dimethylbutane (5) decomposes slowly at room temperature, and a satisfactory elemental analysis for this compound has not yet been obtained. However, the ^{1}H NMR spectrum ($CDCl_3$) of 5 is clearly consistent with the assigned structure: δ 1.60 (s, 12 H); 2.37 (s, 6 H); 6.97–7.77 (AA′BB′ m, 8.4 H).

p-Toluenesulfonic acid was formed as a significant byproduct in the reactions of 1 with tetramethylethylene, *trans*-stilbene, and *cis*-stilbene, the yields by isolation being 66%, 17%, and 21%, respectively.[11] However, possible corresponding products of alkene oxidation (e.g., epoxides) were not identified. In the reaction of [hydroxy(tosyloxy)iodo]benzene with 1,1-diphenylethylene (CH_2Cl_2, 30 min, 5–10 °C), on the other hand, the formation of *p*-toluenesulfonic acid (76% yield) was attended by the production of deoxybenzoin (7), isolated in 65% yield. In addition, phenyl (β,β-diphenylvinyl)iodonium tosylate (8), a previously unreported vinyliodonium salt, was obtained in 5% yield.


$\mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_2Ph}$

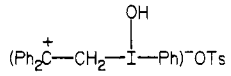
7


$(\mathrm{Ph_2C{=}CH{-}\overset{+}{I}{-}Ph})^{-}\mathrm{OTs}$

8

$\mathrm{PhCH_2CH(OTs)_2}$

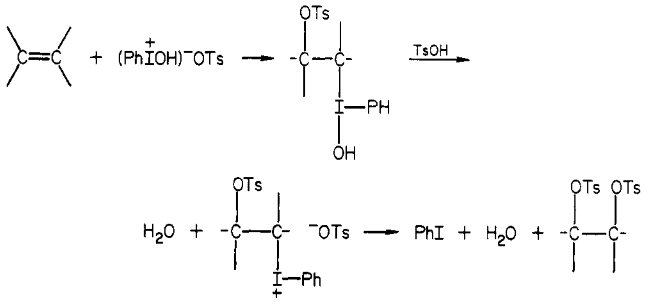
9


$(\mathrm{Ph_2\overset{+}{C}{-}CH_2{-}\overset{OH}{\overset{|}{I}}{-}Ph})^{-}\mathrm{OTs}$

10

With styrene as substrate, a curious medium effect was observed. Thus, while 1 reacted with styrene in dichloromethane to give the *vic*-ditosylate 4, the reaction of 1 with neat styrene eventuated in the isomeric *gem*-ditosylate 9 (62%) and *p*-toluenesulfonic acid (~10%).

Previous studies of the reactions of 1 with anisole,[1] iodoarenes,[4] and (trimethylsilyl)arenes[5] are consistent with its formulation as an ion-pair species in solution (i.e., $\mathrm{PhIOH^{+}\,^{-}OTs}$). Thus, a *plausible* mechanism for the bis(tosyloxy)lation reactions described herein is one involving the following steps: (1) electrophilic addition of $\mathrm{PhIOH^{+}\,^{-}OTs}$ to the double bond of the alkene, (2) dehydroxylation of the >I–OH function of the adduct with *p*-toluenesulfonic acid present in the reaction medium, and (3) nucleophilic displacement of iodobenzene by tosylate ion in the intermediate alkyliodonium tosylate. Although the processes affording toluenesulfonic acid have not yet been identified, it seems clear that toluenesulfonic acid ultimately originates from 1. Thus, 2 mol of 1 is required for the production of 1 mol of bis(tosyloxy)alkane, and reported yields are calculated on that basis. The combination of trans addition in step 1 and S_N2 displacement in step 3 would explain the cis stereochemistry in 2 derived from 1 and cyclohexene. The stereochemistry of the reactions of 1 with *cis*- and *trans*-stilbenes has not yet been clarified, but preliminary indications are that mixtures of stereoisomers of 6 are obtained from both substrates.



It seems likely that the addition of 1 to 1,1-diphenylethylene would give the ionic species 10 which could then serve as a common precursor to deoxybenzoin and the vinyliodonium salt 8.

When [hydroxy(tosyloxy)iodo]benzene was allowed to react with alkynes, stable vinyliodonium salts derived from the addition of 1 to the carbon–carbon triple bond were obtained. After 19 days at room temperature, a mixture of 1 and 2-butyne yielded phenyl[α,β-dimethyl-β-(tosyloxy)vinyl]iodonium tosylate (11, 62% by isolation). The 60-MHz ^{1}H NMR spectrum of 11 is somewhat complicated in the methyl region, but the 300-MHz ^{1}H NMR spectrum ($CDCl_3$)[12] exhibits four sharply defined methyl singlets at

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[7] F. V. Brutcher, Jr., and G. Evans III, *J. Org. Chem.*, 23, 618 (1958).

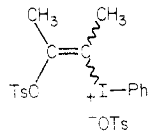
[8] S. Winstein, *J. Am. Chem. Soc.*, 64, 2791 (1942).

[9] M. Fieser and L. F. Fieser, "Reagents for Organic Synthesis", Vol. 1, Wiley, New York, 1967, p 1180.

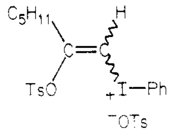
[10] The authentic *cis*- and *trans*-1,2-bis(tosyloxy)cyclohexanes melted at 128–130 and 108–110.5 °C, respectively. Two polymorphs of *cis*-1,2-bis(tosyloxy)cyclohexane were obtained from the reaction of 1 with cyclohexene which, after mechanical separation, melted at 115–117 and 128–130 °C respectively. A solidified melt of the low-melting modification showed slight decomposition and remelted at 125–127 °C. The IR spectra (KBr) of both polymorphs are identical with one another and with that of authentic 2 but different from that of authentic 3.

[11] Yields of *p*-toluenesulfonic acid reported herein are based on its formulation as a monohydrate although higher hydrates may actually be formed.

[12] Recorded by Mr. Everett R. Santee at The University of Akron's NMR center.



11



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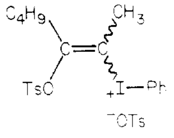

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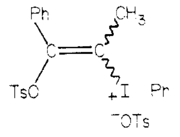
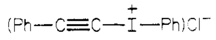


14

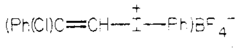
δ 2.19, 2.28, 2.38, and 2.42 as expected for the assigned structure. [Hydroxy(tosyloxy)iodo]benzene reacted likewise with 1-heptyne (CH_2Cl_2, reflux, 26 h), 2-heptyne (CH_2Cl_2, reflux, 2 days), and phenylmethylacetylene (CH_2Cl_2, reflux, 2 days) to give the corresponding phenyl[β-(tosyloxy)vinyl]iodonium tosylates **12** (57% crude), **13** (42% crude, 32% after recrystallization), and **14** (56.5% after recrystallization). The stereochemistry (i.e., *E* and *Z*) of these new vinyliodonium salts remains to be elucidated, and compounds **12**, **13**, and **14** may well be mixtures of regioisomers.

We are aware of only one report of the isolation of an alkynyliodonium salt in the chemical literature. In 1965, Beringer and Galton described the isolation of phenyl(β-phenylethynyl)iodonium chloride (**15**) in yields of 12–20% from the reaction of β-phenylethynyllithium with (dichloroiodo)benzene ($PhICl_2$) in ether/hexane.[13] They indicated that, "on standing at room temperature for some hours", **15** decomposed to iodobenzene and chloroacetylene, and, in aqueous sodium tetrafluoroborate, **15** was converted to phenyl(β-chloro-β-phenylvinyl)iodonium tetrafluoroborate (**16**).



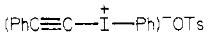
$(\mathrm{Ph{-}C{\equiv}C{-}\overset{+}{I}{-}Ph})\mathrm{Cl}^-$

15



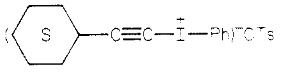
$(\mathrm{Ph(Cl)C{=}CH{-}\overset{+}{I}{-}Ph})\mathrm{BF}_4^-$

16



$(\mathrm{PhC{\equiv}C{-}\overset{+}{I}{-}Ph})^-\mathrm{OTs}$

17



18

When [hydroxy(tosyloxy)iodo]benzene was mixed with phenylacetylene and brought to reflux for 10 min, phenyl(β-phenylethynyl)iodonium tosylate (**17**) was isolated in 60% yield following the workup and is a moderately stable solid at room temperature. The reaction of **1** with cyclohexylacetylene (CH_2Cl_2, 6 days, room temperature) afforded a 5% yield of phenyl(β-cyclohexylethynyl)iodonium tosylate (**18**), a new alkynyliodonium salt. Compounds **17** and **18** were characterized by elemental (C, H, I) and ^{1}H NMR and IR spectroscopic analyses. As expected, both exhibit infrared absorption in the carbon–carbon triple bond region. A sample of **18** (mp 125–7.5 °C) after storage for seven months under ambient conditions exhibited a melting point of 126–128 °C dec.

Registry No. **1**, 27126-76-7; **2**, 5433-22-7; **3**, 5433-21-6; **4**, 1886-71-1; **5**, 79069-18-4; **6** isomer 1, 79069-19-5; **6** isomer 2, 36439-55-1; **7**, 451-40-1; **8**, 79069-21-9; **9**, 79069-22-0; **11**, 79069-24-2; **12**, 79069-26-4; **13**, 79069-28-6; **14**, 79069-30-0; **17**, 79069-32-2; **18**, 79069-34-4; cylohexene, 110-83-8; *cis*-1,2-cyclohexanediol, 1792-81-0; *trans*-1,2-cyclohexanediol, 1460-57-7; styrene, 100-42-5; *cis*-stilbene, 645-49-8; *trans*-stilbene, 103-30-0; *p*-toluenesulfonic acid, 104-15-4; 1,1-diphenylethylene, 530-48-3; 2-butyne, 503-17-3; 1-heptyne, 628-71-7; 2-heptyne, 1119-65-9; phenylmethylacetylene, 673-32-5; phenylacetylene, 536-74-3; cyclohexylacetylene, 931-48-6.

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(13) F. M. Beringer and S. A. Galton, *J. Org. Chem.*, 30, 1930 (1965).