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Energetics of Iodine Ate Complexes, Intermediates in the Iodine/Magnesium Exchange on 1,1-Diiodoalkanes

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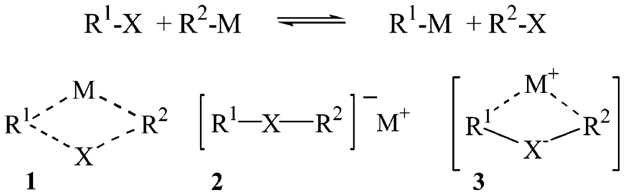
On reaction of 1,1-diiodoalkanes with Grignard reagents at −78 °C, long-lived α-iodoalkyl iodine ate complexes were generated as observable intermediates. Their lifetime depends on the nature of the Grignard reagent and the nature of the 1,1-diiodoalkane. An α-bromoalkyl iodine ate complex was observable only when generated from a 1-bromo-1-iodoalkane with allyl−MgX. The energetic situations and factors that affect the lifetime of such ate complexes are discussed.

Introduction

Despite the importance of the halogen/metal exchange reaction (Scheme 1) in preparative chemistry, its mechanistic aspects are far from being clear.[1] Transition states such as **1** have been discussed, intermediates such as the ate complex **2** have been postulated,[2] and, if carbon−halogen bond formation precedes carbon-metal bond formation, the transition state of the halogen−metal exchange reaction may resemble the arrangement **3**, which corresponds to a contact ion pair between the ate complex anion and the metal cation.[3] All these mechanistic scenarios may be discussed in the framework of the general scheme depicted in Figure 1.

Scheme 1



The detailed reaction course depends on the relative energy of the arrangements **2** and **3** (be they contact ion pairs, solvent-separated ion pairs, or dissociated ions) with respect to the energy of the starting system. When such an arrangement is strongly destabilized relative to the starting system, situation A prevails, and when the arrangement is more stable than the starting system, situation C holds, in which the ate complex **2** may become an observable intermediate. Situation B describes the case in which the ate complex **2** would be a reactive intermediate in the halogen/metal exchange process.

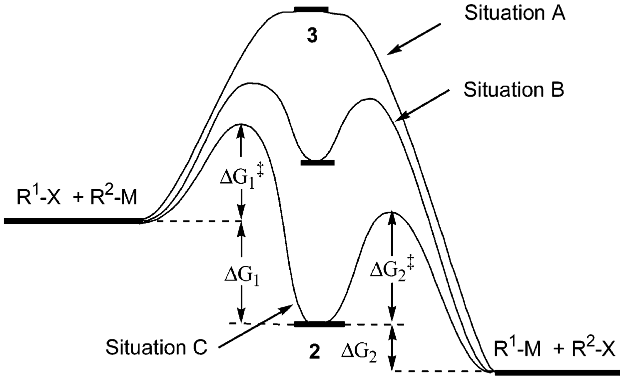
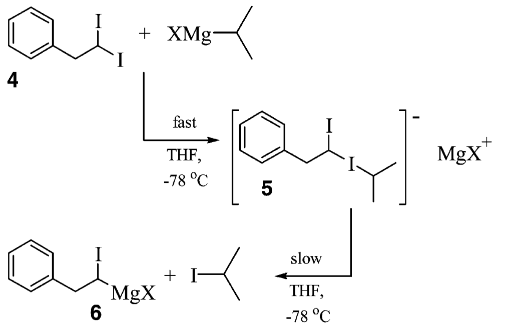


Figure 1. Possible energy schemes for halogen/metal exchange reactions.

Scheme 2



Short-Lived and Long-Lived Ate Complexes

We encountered a situation C case in the iodine/magnesium exchange reaction of the 1,1-diiodoalkane **4** (Scheme 2).[4,5] This reaction is characterized by a bimolecular first step with $k_1 = (5.4 \pm 0.4) \times 10^{-2}$ L mol^{-1} s^{-1} at −78 °C in THF followed by a second step to give **6**,[6] which is pseudo first order in **5** with $k_2 =$

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(1) Bailey, W. F.; Patricia, J. J. *J. Organomet. Chem.* **1988**, *352*, 1−46.

(2) Wittig, G.; Schöllkopf, U. *Tetrahedron* **1958**, *3*, 91−93.

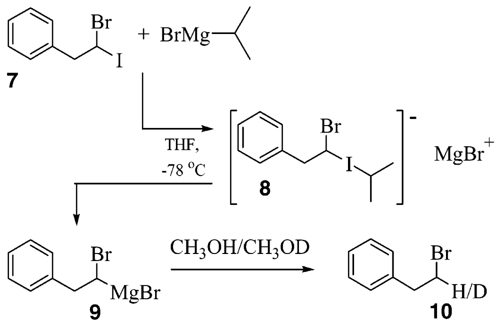
(3) Reich, H. J.; Bevan, M. J.; Gudmundsson, B. O.; Puckett, C. L. *Angew. Chem.* **2002**, *114*, 3586−3589; *Angew. Chem., Int. Ed.* **2002**, *41*, 3436−3439.

(4) (a) Schulze, V.; Brönstrup, M.; Böhm, V. P. W.; Schwerdtfeger, P.; Schimeczek, M.; Hoffmann, R. W. *Angew. Chem.* **1998**, *110*, 869−871; *Angew. Chem., Int. Ed.* **1998**, *37*, 824−826. (b) Hoffmann, R. W.; Brönstrup, M.; Müller, M. *Org. Lett.* **2003**, *5*, 313−316.

(5) Böhm, V. P. W.; Schulze, V.; Brönstrup, M.; Müller, M.; Hoffmann, R. W. *Organometallics* **2003**, *22*, 2925−2930.

10.1021/om0210210 CCC: $25.00

Scheme 3



$(4.2 \pm 0.8) \times 10^{-4}\ \mathrm{s}^{-1}$ for a concentration of $[\mathrm{Mg}^{2+}]_{\mathrm{total}} = 0.225\ \mathrm{mol\ L}^{-1}$.

We have now found a situation B case in the corresponding reaction of the bromo iodo compound **7** with isopropylmagnesium bromide (Scheme 3). No color indicative of the ate complex **8** is generated when the reactants are mixed at −78 °C. The Grignard reagent **9**[6] was formed within less than 1 min, as evidenced by the formation of **10** (95%) after quenching with CH_3OH.

Quenching of the reaction mixture after 1, 60, or 120 min with a 1:1 mixture of CH_3OH/CH_3OD[5] showed that **9**[6] is protonated with an apparent isotope effect $k_H/k_D = 1.5$: cf. the corresponding value for **6**[6] of 1.1. When, however, isopropylmagnesium bromide was added to a mixture of **7** and 40 equiv of CH_3OH/CH_3OD (1:1), the product **10**, obtained in 95% yield, had a much lower deuterium content, corresponding to an apparent isotope effect k_H/k_D of 9.0. This indicates that the ate complex **8** is formed under these conditions just as a reactive intermediate that may be intercepted in situ by protonolysis and that can be characterized by the apparent isotope effect. These results show that the α-bromine atom in **8** does not convey as much thermodynamic or kinetic stability to the ate complex as does the α-iodine atom in **5**. This has to do with the ability of the α-halogen atom to stabilize a negative charge that resides predominantly on the α-carbon atoms of the ate complex.[7] Since there are two α-carbon atoms in the ate complex **2**, stabilizing effects could come from either side. This is demonstrated in the reaction of **7** with allylmagnesium bromide at −78 °C in THF. On combination of the reactants an intensive lemon yellow color was generated that lasted for more than 5 h at this temperature.

When the decolorized mixture was quenched with CH_3OD, the expected product **10** was obtained in only 28% yield (Scheme 4). The main product (62%) was compound **12**, which arose by reaction of **9** with allyl iodide formed in the iodine/magnesium exchange. The iodide liberated in the latter step furthermore entered into a nucleophilic substitution of the carbenoid **9**[8,9] to give **6**, which in the end gave rise to 11% of the iodo compound **13**. This follow-up chemistry has been confirmed in a separate experiment starting from **9**[6] and allyl iodide.

Scheme 4

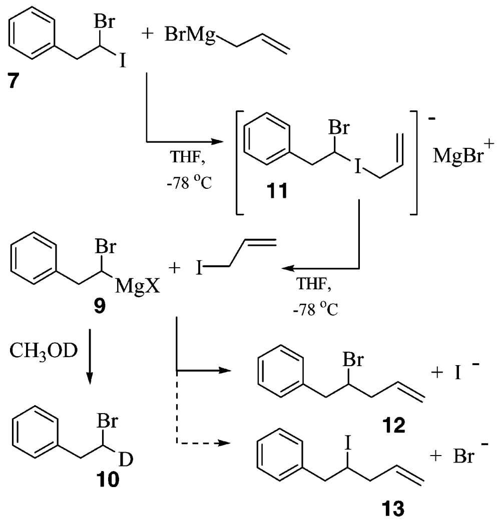
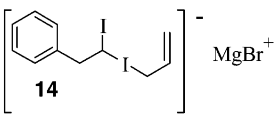


Chart 1



Of relevance here is the increased stability of the ate complex **11** versus that of **8**. Likewise, when the diiodoalkane **4** was treated with allylmagnesium bromide, an intense orange color developed, which we ascribe to the long-lived ate complex **14** (Chart 1).

Workup after decolorization (12 h) provided 49% of compound **13** by a follow-up chemistry as described above: reaction of **6**[6] with allyl iodide indeed formed **13** in 75% yield.

Variation of the Initial Grignard Reagent

Encouraged by these results, we tested a variety of Grignard reagents $\mathrm{R}^2\mathrm{M}$ to enter into an iodine/magnesium exchange with compound **4** and to affect the thermodynamic and kinetic stability of the ate complex intermediates. The outcome depends on the overall free energy change of the halogen/metal exchange ($= \Delta G_1 + \Delta G_2$ in Figure 1), the thermodynamic stability of the ate complex intermediate ($= \Delta G_1$), and the kinetic stability of the intermediate ($= \Delta G_2^{\ddagger}$). Of course, if either $\Delta G_1^{\ddagger}$ is too high or if $\Delta G_1 + \Delta G_2$ is too positive, no reaction will occur.

The overall free energy change in the halogen/metal exchange depends mainly on the basicity of R^2 relative to that of R^1. The stability of the ate complex intermediates **2** will somehow depend on the basicity of R^1 and R^2 but much more so on the ability of R^1 and R^2 to stabilize a negative charge on their α-carbons.[7] Hence, when the Grignard reagent $\mathrm{R}^2\mathrm{M}$ is changed, the changes in ΔG_1 and in ΔG_2 will not necessarily be in unison.

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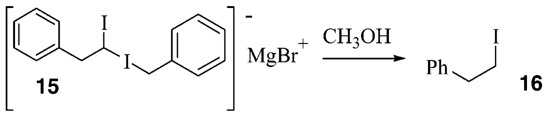
(6) When we speak of **6** (or related species), we refer to the Grignard solution obtained by iodine/magnesium exchange of the diiodoalkane **4.** In the present study we have not ascertained what the major species in solution is, **6** or—more likely[5]—a bis(α-iodoalkyl)magnesium species resulting from a Schlenk equilibrium.

(7) Boche, G.; Schimeczek, M.; Cioslowski, J.; Piskorz, P. *Eur. J. Org. Chem.* **1998**, 1851−1860.

(8) Miller, W. T.; Whalen, D. M. *J. Am. Chem. Soc.* **1964**, *86*, 2089−2090.

(9) (a) Köbrich, G.; Ansari, F. *Chem. Ber.* **1967**, *100*, 2011−2020. (b) Charreau, P.; Julia, M.; Verpeaux, J.-N. *J. Organomet. Chem.* **1989**, *379*, 201−210. (c) Satoh, T.; Takano, K.; Ota, H.; Someya, H.; Matsuda, K.; Yamakawa, K. *Tetrahedron* **1998**, *54*, 5557−5574. (d) Hoffmann, R. W.; Nell, P.; Leo, R.; Harms, K. *Chem. Eur. J.* **2000**, *6*, 3359−3365.

Scheme 5



We have seen the result on going from isopropyl Grignard reagent to allyl Grignard reagent in the reaction with the standard diiodoalkane **4**. When benzyl Grignard reagent is used, a long-lived (ca. 30 h) yellow color resulted on reaction with the diiodoalkane **4**, indicating a large thermodynamic (ΔG_1) and kinetic ($\Delta G_2^{\ddagger}$) stability of the ate complex **15** (Scheme 5). The overall conversion to product **16** remained low (33%) independent of reaction time. This suggests that $\Delta G_1 + \Delta G_2$ is slightly endothermic.

A related situation is encountered on reaction of **4** with phenylmagnesium bromide: a yellow color developed rather slowly, reaching a moderate intensity after ca. 1 h. Thus, $\Delta G_1^{\ddagger}$ is larger than in the reaction of **4** with isopropylmagnesium bromide.[10] The yellow color persisted for days at −78 °C. After quenching of the (still yellow) solution with methanol, 67% of **4** and 33% of **16** could be isolated. This indicates a situation D (cf. Figure 2) case, with the formation of the ate complex **17** being slightly endothermic (Scheme 6). A reviewer pointed out that this interpretation for the "low conversion" is not necessarily the only one, because there is the possibility that ate complexes such as **15** and **17** could be protonated not only at the α-iodo-bearing carbon atom but concurrently also at the benzylic (**15)** or the ipso carbon atom of the phenyl group (in **17**). Such a protonation would release the diiodoalkane **4** and hence suggest a "low conversion".

When (*p*-fluorophenyl)MgX or C_6F_5MgX was combined with **4** at −78 °C, no color developed and no reaction occurred. Apparently the basicity of the latter Grignard reagents is too low (a situation E case) to initiate the iodine/magnesium exchange. As the reaction between **4** and C_6F_5MgBr to give **6** and C_6F_5I can be considered to be endothermic, the reverse process should be exothermic. Indeed, when C_6F_5I was allowed to react with a solution of **6**,[6] quenching after 7 days provided a 70% yield of **4** (Scheme 7). Thus, the iodine/magnesium exchange reaction is proceeding in this direction, yet the absence of any color indicates that the ate complex **18** has no sufficient thermodynamic stability to reach an observable stationary concentration.

Special attention was given to the system shown in Scheme 8, in which the overall exchange would be degenerate and, hence, thermoneutral.

As mentioned before,[5] no color was observed on mixing the reactants, despite the fact that the ate complex **19** might enjoy thermodynamic stability similar to that of the ate complex **5**. If the absence of the characteristic color in the above reaction is not for thermodynamic reasons, it could be due to an unfavorable kinetic situation. To probe this aspect, we carried out crossover experiments as delineated in Scheme 9.

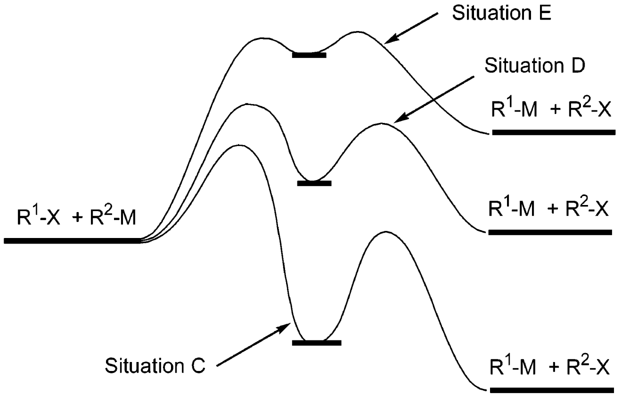
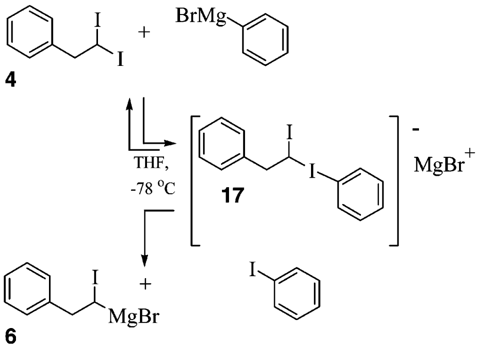
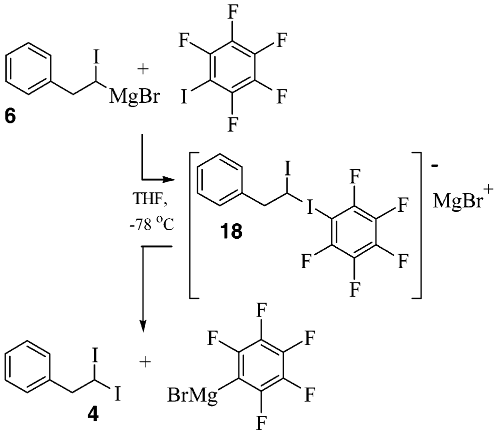


Figure 2. Possible energetics (schematic) on reaction of an alkyl iodide with different Grignard reagents.

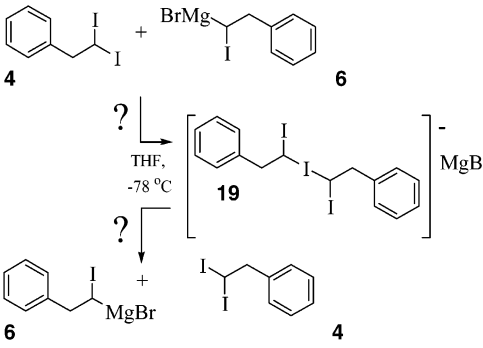
Scheme 6



Scheme 7



Scheme 8



Crossover was attempted both from the side of **20** and **6**[6] and from the side of **22**[6] and **4**. Since we could not guarantee that the solution of **6** would be free either of excess diiodoalkane **4** or traces of isopropylmagnesium bromide, we intentionally used in one case a solution of **6** that had excess diiodoalkane **4** and in another case a solution that had excess isopropylmagnesium bromide.

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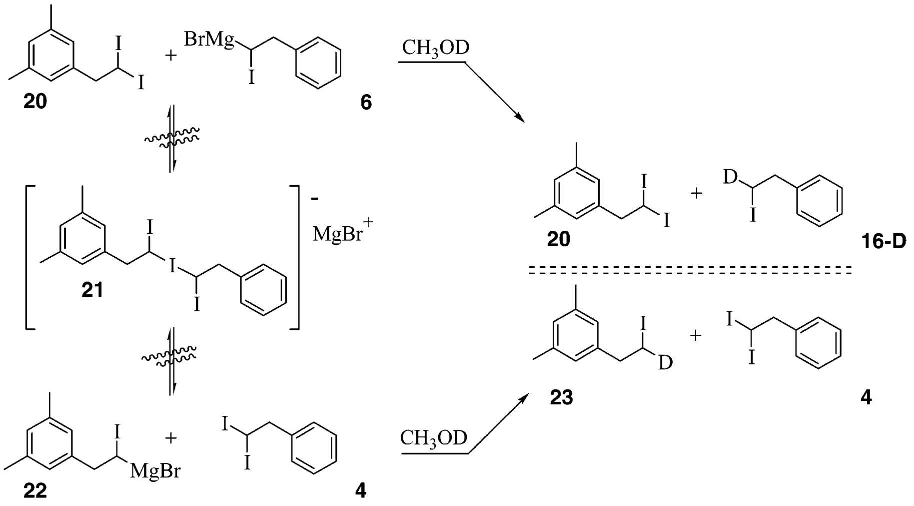
(10) Wiberg, K.; Sklenak, S.; Bailey, W. F. *J. Org. Chem.* **2000**, *65*, 2014−2021.

Scheme 9



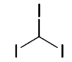
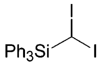
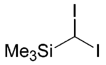
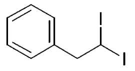
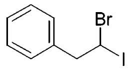
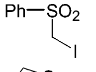
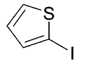
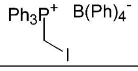
The consequence of this is that in the case of non-crossover not two, but three of the possible four products **4**, **16**, **20**, and **23** are formed. Crossover should in turn lead to all four products. The reactions were carried out for 17 h at −78 °C and led in each experiment to only three products. Thus, there is no crossover between the two systems; i.e., the quasi-symmetrical ate complex **21** is not being reached under these reaction conditions. Given the presumed thermodynamic stability of **19** (or **21**), the failure to generate **19** must be due to a lack of reactivity (basicity) of the α-iodoalkyl Grignard-reagents. The activation barrier $\Delta G_1^{\ddagger}$ is apparently too high.

Summarizing the reactions of the diiodoalkane **4** with various Grignard reagents, we have encountered the mechanistic situations C−E depicted in Figure 2. We have also found a case in which the kinetic barrier to the formation of an ate complex (**19**) was too high to observe any reaction.

Variation of the Diiodoalkane

The stabilization and, hence, the ability to observe α-iodoalkyl iodine ate complexes as long-lived intermediates in the iodine/magnesium exchange reaction on 1,1-diiodoalkanes depends on the ability of the substituent on the α-carbon atoms to stabilize a negative charge. Thus, there should be noticeable substituent effects also on the side of the 1,1-diiodoalkane starting materials. Such effects have been qualitatively noted in the reaction of numerous 1,1-diiodoalkanes (and some related compounds) with isopropylmagnesium chloride. Relevant examples are compiled in Tables 1 and 3.

Table 1. Occurrence or Nonoccurrence of a Transient Yellow Color in Iodine/Mg Exchange Reactions with Isopropyl Grignard Reagents at −78 °C in THF[a]

Entry Nr.	Substrate	Period for decolourisation (min)	Yield of Protonolysis Product after I/Mg-exchange
1		ca. 450	n.d.
2	 **24**	50	95
3	 **25**[11]	12	n.d.
4	 **4**	120	95
5	 **7**	0	95
6	 **26**[12]	0	95
7	 **27**	0	n.d.
8	 **28**	ca. 180	77

[a] $[Mg^{2+}]_{total}$ = 0.09 M. n.d.= not determined.

Looking at a variety of 1,1-diiodoalkanes or α-hetero-substituted iodoalkanes that undergo an iodine/magnesium exchange reaction at −78 °C in THF (Table 1), it is interesting to note in which cases ate complexes can visually be detected by their color. Iodoform forms a very long-lived ate complex.[13] Whereas the silyl derivatives **24** and **25** generate ate complexes that are less persistent than that (compound **5**) formed from the diiodoalkane **4**, the bromoiodoalkane **7** (as discussed above), the sulfone **26**, and iodothiophene **27** readily undergo iodine/magnesium exchange reactions, but no color can be detected, corresponding to situation B cases (cf. Figure 1). Reaction of isopropylmagnesium chloride with the (iodomethyl)phosphonium salt **28** should give rise to an internally Coulomb-stabilized ate complex. The long-lived deep yellow color generated in this reaction supports such a notion.

It is tempting to correlate the ability to form ate complexes with the reduction potential of the iodoalkane, which should parallel the LUMO energy of the C−I σ*-orbital. The few data we have, however, do not support this assumption (cf. Table 2).

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(11) Seyferth, D.; Lambert, R. L., Jr.; Hanson, E. M. *J. Organomet. Chem.* **1970**, *24*, 647−661.

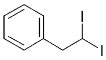
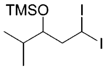
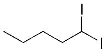
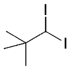
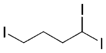
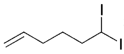
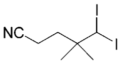
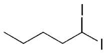
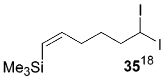
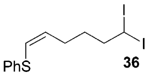
(12) Jonczyk, A.; Pytlewski, T. *Synthesis* **1978**, 883−885.

(13) (a) Seyferth, D.; Lambert, R. L., Jr. *J. Organomet. Chem.* **1973**, *54*, 123−130. (b) Hoffmann, R. W.; Müller, M.; Menzel, K.; Gschwind, R.; Schwerdtfeger, P.; Malkina, O. L.; Malkin, V. G. *Organometallics* **2001**, *20*, 5310−5313.

Table 2. Peak Potential for the First Cyclic Voltammetric Reduction Wave in Acetonitrile on a Glassy-Carbon Electrode Using Tetrabutylammonium Tetrafluoroborate as Supporting Electrolyte, vs SCE[14]

compd	redn potential (V vs sce)
26	−1.75
4	−1.74
25	−1.69

Table 3. Persistence of the Yellow Color That Arises from Reaction of the 1,1-Diiodoalkanes with Isopropyl Grignard Reagents at −78 °C in THF

Entry Nr.	Substrate	$[Mg_{total}]$, mol l^{-1}	Period for decolourisation (min)	Yield of Protonolysis Product after I/Mg-exchange
1	 **4**	0.09	120	95
2	 **29**[15]	0.26	120	85
3	 **30**[16]	0.04	120	n.d.
4	 **31**[17]	0.09	75	45
5	 **32**	0.09	140	99
6	 **33**	0.09	30	96
7	 **34**	0.09	4	78
8	 **30**[16]	0.65	3 [a)]	92
9	 **35**[18]	0.38	3 [a)]	95
10	 **36**	0.34	>>300 [a)b)]	34

[a] In THF/Et_2O (3.5:1). [b] Observation from a single experiment; n.d. = not determined.

Looking next at the persistence of iodine ate complexes generated from various 1,1-diiodoalkanes (cf. Table 3), we note that the phenyl group in **5** has no special significance, as the color generated from simple aliphatic 1,1-diiodoalkanes such as **29** and **30** by reaction with isopropyl Grignard reagent lasts for about the same period (cf. entries 1−5 in Table 3). Steric effects, if they are present, remain small (cf. entries 3 and 4 in Table 3). Substituent effects (electronic?) of groups which are in a 1,5-relationship on the diiodoalkane group appear to be more marked (cf. entries 6, 7, and 8−10 in Table 3). The lifetime of the ate complex derived from **36** has been observed in a single experiment to be exceptionally long.

Experimental Section

1. General Remarks. All temperatures quoted are uncorrected. All reactions with organometallic reagents were carried out in flame-dried glassware under an argon atmosphere. The concentration of Grignard reagent solutions was determined by titration with menthol against 1,10-phenanthroline as indicator[19] or after hydrolysis with 1 M hydrochloric acid by back-titration with 0.1 M NaOH.[20] Boiling range of petroleum ether: 40−60 °C. ^1H NMR, ^{13}C NMR: Bruker ARX-200, AC-300, WH-400, DRX-400, AM-400, AMX-500. Analytical gas chromatography: Siemens Sichromat 3, 30 m × 0.3 mm quartz capillary column with DB 5, 1 bar He. Flash chromatography: silica gel SI 60, E. Merck KGaA, Darmstadt, 40−63 μm.

2. Reaction of 1-Bromo-1-iodo-2-phenylethane (7) with Isopropylmagnesium Bromide. A solution of isopropylmagnesium bromide (1.1 M in THF, 0.29 mL, 0.32 mmol) was added dropwise at −78 °C into a solution of 1-bromo-1-iodo-2-phenylethane (**7**;[21] 100 mg, 0.32 mmol) in THF (3 mL). No coloration was observed. After the mixture was stirred for 3 h at −78 °C, methanol (35 μL, 1 mmol) was added. Water (10 mL) was added, and the mixture was extracted with *tert*-butyl methyl ether (3 × 10 mL). The combined organic layers were dried (Na_2SO_4) and concentrated. The crude product was purified by flash chromatography with pentane to furnish the product **10** (54 mg, 91%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ 3.07 (t, J = 7.7 Hz, 2H), 3.47 (t, J = 7.7 Hz, 2H), 7.04−7.27 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 32.8, 39.4, 126.9, 128.6, 128.6, 138.9. Anal. Calcd for C_8H_9Br (185.1): C, 51.92; H, 4.90. Found: C, 52.08; H, 5.03.

3. Reaction of 1-Bromo-1-iodo-2-phenylethane (7) with Allylmagnesium Bromide. A solution of allylmagnesium bromide (1.0 M in diethyl ether, 0.35 mL, 0.35 mmol) was added dropwise at −78 °C into a solution of 1-bromo-1-iodo-2-phenylethane (**7**;[21] 100 mg, 0.32 mmol) in THF (3 mL). This led to an intense lemon yellow coloration that persisted for >5 h. After the mixture was stirred for 12 h at −78 °C, methanol (35 μL, 1 mmol) was added into the decolorized solution. GC analysis of the crude solution indicated the presence of 28% of **10**, 62% of **12**, and 11% of **13**.

For a control experiment allyl iodide (54 mg, 0.32 mmol) was added to a solution of **9** generated as described in (2). Workup and GC analysis as above showed the presence of 60% of **10**, 17% of **16**, 15% of **12**, and 8% of **13**.

Preparation of Authentic Samples of 12 and 13. 4-Hydroxy-5-phenyl-1-pentene. Tin(II) chloride (6.77 g, 30 mmol) and sodium iodide (4.50 g, 30 mmol) were added at 0 °C into a solution of phenylacetaldehyde (2.40 g, 20 mmol) and allyl chloride (1.68 g, 22 mmol) in DMF (120 mL). After the mixture was stirred for 2 h at 0 °C and 12 h at room temperature, aqueous NH_4F solution (30%, 30 mL) and *tert*-butyl methyl ether (50 mL) were added. After this mixture was stirred for 1 h, the layers were separated and the aqueous layer was extracted with *tert*-butyl methyl ether (3 × 50 mL). The combined extracts were washed with brine (50 mL), dried ($MgSO_4$), and concentrated. Flash chromatography of the residue with petroleum ether/ethyl acetate (10:1) furnished the product alcohol (1.72 g, 53%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.77 (broad d, J = 2.4 Hz, 1H), 2.22−2.40 (m, 2H), 2.74 (dd, J = 13.6 and 7.9 Hz, 1H), 2.84 (dd, J = 13.6 and 5 Hz, 1H), 3.84−3.96 (broad m, 1H), 5.12−5.22 (m, 2H), 5.80−5.97 (m, 1H), 7.20−7.39 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 41.2, 43.3, 71.7, 118.0, 126.4, 128.5, 129.4, 134.7,

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(14) These potentials were kindly measured by the group of Prof. W. R. Dolbier, Department of Chemistry, University of Florida, Gainesville, FL 32611-7200.

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138.4. Anal. Calcd for $C_{11}H_{14}O$ (162.2): C, 81.44; H, 8.70. Found: C, 81.24; H, 8.72.

4-Bromo-5-phenyl-1-pentene (12). CBr_4 (424 mg, 1.28 mmol) is added at 0 °C to a solution of the above alcohol (148 mg, 0.91 mmol) in dichloromethane (10 mL). After the mixture was stirred for 15 min at 0 °C, a solution of triphenylphosphane (670 mg, 2.55 mmol) in dichloromethane (4 mL) was added and stirring was continued for 1 h at 0 °C and 12 h at room temperature. Saturated aqueous NH_4Cl solution (10 mL), aqueous $Na_2S_2O_3$ solution (20%, 3 mL), and petroleum ether (20 mL) were added. The layers were separated, and the aqueous layer was extracted with petroleum ether (3 × 10 mL). The combined extracts were washed with brine (5 mL), dried (Na_2SO_4), and concentrated. Flash chromatography of the residue with petroleum ether/ethyl acetate (30:1) furnished the product **12** (147 mg, 72%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ 2.48−2.70 (m, 2H), 3.09−3.22 (m, 2H), 4.21 (d pseudo-q, $J = 7.2$ and 5.0 Hz, 1H) 5.09−5.18 (m, 2H), 5.88 (dd pseudo-t, $J = 17.1$, 10.3, and 6.8 Hz, 1H), 7.10−7.52 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 42.2, 44.9, 55.4, 118.1, 126.8, 128.4, 129.2, 134.7, 138.4. Anal. Calcd for $C_{11}H_{13}Br$ (225.1): C, 58.69; H, 5.82. Found: C, 58.52; H, 5.80.

4-Iodo-5-phenyl-1-pentene (13). Triphenylphosphane (1.57 g, 6.0 mmol) and imidazole (0.51 g, 7.5 mmol) were added at 5 °C into a solution of the above alcohol (811 mg, 5.0 mmol) in THF (50 mL). The mixture was stirred for 12 h at room temperature. Saturated aqueous NH_4Cl solution (20 mL), aqueous $Na_2S_2O_3$ solution (20%, 10 mL), and petroleum ether (50 mL) were added. The layers were separated, and the aqueous layer was extracted with petroleum ether (3 × 50 mL). The combined extracts were washed with brine (30 mL), dried (Na_2SO_4), and concentrated. Flash chromatography of the residue with petroleum ether/ethyl acetate (30:1) furnished the product **13** (1.17 g, 86%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ 2.58−2.60 (m, 2H), 3.18 (dd, $J = 14.4$ and 7.2 Hz, 1H), 3.26 (dd, $J = 14.4$ and 7.8 Hz, 1H), 4.29 (d pseudo-q, $J = 7.3$ and 5.5 Hz, 1H), 5.10−5.22 (m, 2H), 5.87 (dd pseudo-t $J = 17.0$, 10.2, and 6.8 Hz, 1H), 7.17−7.36 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 35.7, 43.4, 46.5, 117.9, 126.8, 128.4, 128.9, 136.2, 139.5. Anal. Calcd for $C_{11}H_{13}I$ (272.1): C, 48.55; H, 4.81. Found: C, 48.53; H, 4.75.

4. Reaction of 1,1-Diiodo-2-phenylethane (4) with Allylmagnesium Bromide. A solution of allylmagnesium bromide (1.0 M in diethyl ether, 0.56 mL, 0.56 mmol) was added dropwise at −78 °C into a solution of 1,1-diiodo-2-phenylethane (**4**;[21] 100 mg, 0.28 mmol) in THF (3 mL). This led to an intense orange-yellow coloration that persisted for >5 h. After the mixture was stirred for 12 h at −78 °C, methanol (35 μL, 1 mmol) was added into the decolorized solution. Workup as above was followed by flash chromatography with pentane/*tert*-butyl methyl ether (10:1) to furnish 37 mg (49%) of **13**.

For a control allyl iodide (141 mg, 0.84 mmol) was added to a solution of **6** generated as described in (2). The mixture was stirred for 12 h at −78 °C. Methanol quench and workup as above furnished after flash chromatography 114 mg 75% of **13**.

5. 1,1-Diiodo-2-(3,5-dimethylphenyl)ethane (20). A solution of hexamethyldisilazane (4.20 mL, 20.0 mmol) in THF (7 mL) was cooled to −78 °C. *n*-Butyllithium (1.57 M in hexane, 12.7 mL, 20.0 mmol) was added, and the mixture was allowed to reach room temperature. A solution of diiodomethane (8.84 g, 33.0 mmol) in THF (20 mL) was cooled to −105 °C. One equivalent of the lithium hexamethyldisilazide solution was added dropwise over 1 h. After the mixture was stirred for 1.5 h at −105 °C, a solution of 3,5-dimethylbenzyl bromide[22] (5.93 g, 29.8 mmol) in THF (10 mL) was added dropwise at −100 °C. The mixture was allowed to reach room temperature over 12 h. Saturated aqueous NH_4Cl solution (50 mL) was added, the layers were separated, and the aqueous layer was extracted with *tert*-butyl methyl ether (3 × 50 mL). The combined organic layers were dried ($MgSO_4$) and concentrated. The crude product was purified by flash chromatography with petroleum ether to give 7.72 g (67%) of the product **20**. ^1H NMR (200 MHz, $CDCl_3$): δ 2.24 (s, 6H), 3.56 (d, $J = 7.4$ Hz, 2H), 6.62 (s, 2H), 6.88 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ −26.1, 21.3, 54.3, 126.6, 129.1, 138.0, 139.5. Anal. Calcd for $C_{10}H_{12}I_2$ (386.0): C, 31.12; H, 3.13. Found: C, 31.14; H, 3.23.

6. Preparation of 1,1-Diiodoalkanes. 1,1,3-Triiodobutane (32). Lithium hexamethyldisilazide (1 M in THF, 18.8 mL, 18.8 mmol) was added dropwise at −120 °C over 15 min into a solution of diiodomethane (5.00 g, 18.8 mmol) and 1,3-diiodopropane (15.0 g, 46.3 mmol) in THF (150 mL). The solution was allowed to reach room temperature over 10 h. Saturated aqueous NH_4Cl solution (20 mL) was added, and the mixture was extracted with *tert*-butyl methyl ether (3 × 20 mL). The combined extracts were washed with $Na_2S_2O_3$ solution (20%, 20 mL) and water (2 × 20 mL), dried ($MgSO_4$), and concentrated. Flash chromatography with pentane afforded the product **32** as a pink oil (2.04 g, 25%). ^1H NMR (200 MHz, $CDCl_3$): δ 1.94 (m, 2H), 2.45 (m, 2H), 3.17 (t, $J = 6.6$ Hz, 2H), 5.11 (t, $J = 6.2$ Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ −28.9, 3.1, 35.0, 48.3. Exact mass for $C_4H_7I_3$: calcd, *m*/*z* 435.7682; found (HRMS EI), *m*/*z* 435.7676.

1,1-Diiodo-5-hexene (33). Hydrazine hydrate (5.0 g, 0.1 mol) was added to a solution of 5-hexenal[23] (ca 10 mmol) in methanol (5 mL). After the mixture was stirred for 1 h, water (20 mL) was added. The layers were separated, and the aqueous layer was extracted with dichloromethane (3 × 20 mL). The solution was concentrated, and the residue was taken up in diethyl ether (20 mL). Triethylamine (9 mL) was added, and iodine was added in small portions to the point that the iodine color persisted. Saturated aqueous $Na_2S_2O_3$ solution (20 mL) was added, and the mixture was extracted with *tert*-butyl methyl ether (3 × 20 mL). The combined extracts were concentrated. Flash chromatography of the residue with pentane furnished the diiodo alkane **33** (438 mg, 13%) as a colorless liquid. ^1H NMR (300 MHz, $CDCl_3$): δ 1.53 (tt, $J = 7.5$ and 7.5 Hz,, 2H), 2.11 (td, $J = 7.2$ and 6.9 Hz, 2H), 2.35 (dt, $J = 8.7$ and 6.5 Hz, 2H), 4.99 (dd, $J = 10.3$ and 1.4 Hz, 1H), 5.03 (dd, $J = 17.1$ and 1.4 Hz, 1H), 5.11 (t, $J = 6.5$ Hz, 1H), 5.77 (ddt, $J = 17.1$, 10.3, and 6.7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ −25.7, 31.0, 31.6, 47.6, 115.5, 137.6. Anal. Calcd for $C_6H_{10}I_2$ (335.9): C, 21.45; H, 3.00. Found: C, 21.22; H, 3.03.

4,4-Dimethyl-5,5-diiodopentanenitrile (34). 4,4-Dimethyl-5-oxopentanenitrile[24] (630 mg, 5.0 mmol) was converted into compound **34** as described above. Flash chromatography of the residue with pentane/*tert*-butyl methyl ether (1:1) furnished 1.48 g (81%) of **34** as a slightly yellowish oil. ^1H NMR (300 MHz, $CDCl_3$): δ 1.14 (s, 6H), 1.92 (t, $J = 8.4$ Hz, 2H), 2.32 (t, $J = 8.4$ Hz, 2H), 5.13 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ −4.1, 12.8, 24.7, 34.6, 39.3, 119.2. Anal. Calcd for $C_7H_{11}I_2N$ (363.0): C, 23.16; H, 3.05; N, 3.86. Found: C, 23.02; H, 3.01; N, 3.85.

2-(5-(Phenylthio)pent-4-en-1-oxy)tetrahydro(2*H*)-pyran. *n*-Butyllithium (1.22 M in hexane, 84.5 mL, 103 mmol) was added dropwise at 0 °C into a solution of 2-(pent-4-en-1-oxy)tetrahydro(2*H*)pyran[25] (16.8 g, 0.1 mol) in THF (1 L). Methyl iodide (6.5 mL, 105 mmol) was added to a solution of diphenyl disulfide (22.98 g, 104 mmol) in THF (0.4 L). The latter solution was added at 0 °C over 2 h to the former solution. The mixture was allowed to reach room temperature over 15 h. Saturated aqueous NH_4Cl solution (100 mL) and water (300 mL) were added, the layers were separated, and

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the aqueous layer was extracted with *tert*-butyl methyl ether (3 × 300 mL). The combined extracts were washed with brine (300 mL), dried (Na_2SO_4), and concentrated. Flash chromatography of the residue with pentane/*tert*-butyl methyl ether (12:1) containing 1% of triethylamine furnished the thioether (18.1 g, 65%) as a slightly yellowish liquid. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.49−1.90 (m, 8H), 2.57 (t, J = 7.0 Hz, 2H), 3.49 (dd, J = 9.8 and 6.0 Hz, 1H), 3.44−355 (m, 1H), 3.86 (dd, J = 9.8 and 6.3 Hz, 1H), 3.80−3.91 (m, 1H), 4.56−4.62 (m, 1H), 7.11−7.21 (m 1H), 7.24−7.43 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 16.1, 19.4, 25.3, 28.7, 30.5, 62.0, 64.9, 65.6, 98.6, 99.1, 125.6, 125.9, 128.9, 133.5. Anal. Calcd for $C_{16}H_{20}O_2S$ (363.0): C, 69.53; H, 7.29. Found: C, 69.50; H, 7.30.

5-(Phenylthio)pent-4-en-1-ol. *p*-Toluenesulfonic acid monohydrate (0.82 g, 4.4 mmol) was added to a solution of the above THP ether (15.20 g, 55 mmol) in methanol (960 mL) and water (10 mL). After the mixture was stirred for 20 h, potassium carbonate (4.80 g) was added. After this mixture was stirred for 30 min, the mixture was partitioned between water (1 L) and *tert*-butyl methyl ether (2 L). The layers were separated, and the aqueous layer was extracted with *tert*-butyl methyl ether (200 mL). The combined organic layers were dried (Na_2SO_4) and concentrated. Flash chromatography of the residue with pentane/*tert*-butyl methyl ether (1:1) furnished the alcohol (8.95 g, 84%) as a colorless liquid. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.82 (tt, J = 6.6 and 6.6 Hz, 2H), 2.14 (broad s, 1H), 2.56 (t, J = 7.0 Hz, 2H), 3.75 (t, J = 6.2 Hz, 2H), 7.18−7.20 (m, 1H), 7.27−7.41 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 16.7, 31.2, 61.3, 65.3, 98.9, 125.7, 126.1, 129.0, 133.3. Anal. Calcd for $C_{11}H_{12}OS$ (192.3): C, 68.71; H, 6.29. Found: C, 68.46; H, 6.32.

(4*Z*)-5-(Phenylthio)pent-4-en-1-ol. A solution of diisobutylaluminum hydride (1.0 M in pentane, 136 mL, 136 mmol) was added over 1 h at −15 °C to a solution of the above alcohol (8.71 g, 45 mmol) in diethyl ether (190 mL). The mixture was heated for 5 days to 40 °C. It was poured onto aqueous NaOH (2.0 M, 300 mL) at 0 °C. The layers were separated, and the aqueous layer was extracted with *tert*-butyl methyl ether (3 × 300 mL). The combined organic layers were dried (Na_2SO_4) and concentrated. Flash chromatography of the residue with pentane/*tert*-butyl methyl ether (1:1) containing 1% of triethylamine furnished the alkene (6.72 g, 76%) with a 96:4 *Z*:*E* ratio. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.62−1.81 (tt, J = 6.8 and 6.8 Hz, 2H), 2.22 (broad s, 1H), 2.33 (tdd, J = 7.5, 7.5, and 1.3 Hz, 2H), 3.64 (t, J = 6.5 Hz, 2H), 5.81 (dt, J = 9.3 and 7.3 Hz, 1H), 6.22 (dt, J = 9.3 and 1.3 Hz, 1H), 7.19−7.27 (m, 1H), 7.29−7.40 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 25.5, 31.7, 62.1, 123.7, 126.3, 128.9, 129.0, 132.2, 136.0. Anal. Calcd for $C_{11}H_{14}OS$ (194.3): C, 68.00; H, 7.26. Found: C, 67.88; H, 7.19.

(1*Z*)-5-Iodo-1-(phenylthio)-1-pentene. Iodine (293 mg, 1.16 mmol) was added in small portions at 0 °C into a solution of triphenylphosphane (303 mg, 1.16 mmol) and imidazole (79 mg, 1.2 mmol) in dichloromethane (2 mL). The resulting yellow suspension was stirred for 5 min. A solution of the above alcohol (150 mg, 0.77 mmol) in dichloromethane (1 mL) was added, and the mixture was stirred for 3 h in the dark. Water (3 mL) was added, and the layers were separated. The aqueous layer was extracted with dichloromethane (3 × 4 mL), and the combined organic layers were washed with aqueous $Na_2S_2O_3$ solution (20%, 3 mL). The solution was dried ($MgSO_4$) and quickly concentrated from a bath at 0 °C. Flash chromatography of the residue with pentane furnished the iodide (217 mg, 93%) with a 89:11 *Z*:*E* ratio. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.99 (tt, J = 7.1 and 7.1 Hz, 2H), 2.36 (dt, J = 7.3 and 7.3 Hz, 2H), 3.22 (t, J = 7.0 Hz, 2H), 5.76 (dt, J = 9.3 and 7.3 Hz, 1H), 6.27 (dt, J = 9.3 and 1.2 Hz, 1H), 7.15−7.40 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 6.2, 30.0, 32.8, 124.7, 126.1, 128.6, 128.9, 130.3, 135.8. Anal. Calcd for $C_{11}H_{13}IS$ (304.2): C, 43.43; H, 4.31. Found: C, 43.42; H, 4.20.

(1*Z*)-6,6-Diiodo-1-(phenylthio)-1-hexene (36). A solution of hexamethyldisilazane (0.18 mL, 0.85 mmol) in THF (0.8 mL) was cooled to −35 °C. *n*-Butyllithium (1.47 M in hexane, 0.58 mL, 0.85 mmol) was added, and the mixture was allowed to reach 0 °C. After this mixture was cooled to −110 °C, a solution of diiodomethane (218 mg, 0.85 mmol) in THF (0.75 mL) was added over 3 min. After the mixture was stirred for 1.5 h at −105 °C, a solution of the above alkyl iodide (200 mg, 0.66 mmol) in THF (0.75 mL) was added dropwise. The mixture was allowed to reach room temperature over 12 h. The mixture was poured into saturated aqueous NH_4Cl solution (3 mL), aqueous $Na_2S_2O_3$ solution (20%, 3 mL), and diethyl ether (10 mL). The layers were separated, and the aqueous layer was extracted with diethyl ether (2 × 20 mL). The combined organic layers were dried (Na_2SO_4) and quickly concentrated from a bath at 0 °C. Flash chromatography of the residue with pentane furnished **36** (158 mg, 54%) with a 89:11 *Z*:*E*-ratio. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.61 (tt, J = 7.3 and 7.3 Hz, 2H), 2.31 (dt, J = 6.9 and 6.9 Hz, 2H), 2.40 (dt, J = 8.3 and 6.6 Hz, 2H), 5.16 (t, J = 6.4 Hz, 1H), 5.78 (dt, J = 9.1 and 7.3 Hz, 1H), 6.26 (dt, J = 9.1 and 1.1 Hz, 1H), 7.25−7.40 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$): δ −26.0, 26.9, 30.9, 47.4, 124.4, 126.4, 128.9, 129.0, 131.4, 135.9. Anal. Calcd for $C_{12}H_{14}I_2S$ (444.1): C, 32.45; H, 3.18. Found: C, 32.68; H, 3.30.

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