

# Hypervalent Iodine in Carbon-carbon Bond Forming Reactions. A New Reaction of Hypervalent Iodine Compounds and Organolithium Reagents

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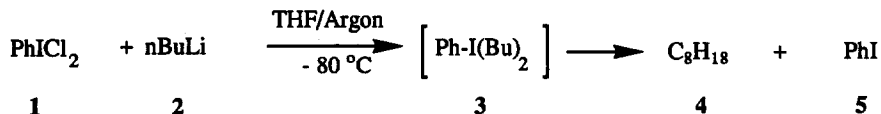
**Abstract:** Hypervalent iodine compounds react with organolithium reagents instantaneously even at -80°C resulting in the formation of hydrocarbons. Our findings indicate that the carbon-carbon bond formation is the result of ligand exchange and second displacement on the carbon bonded to iodine.

## Introduction

Hypervalent iodine compounds<sup>1</sup> as reagents play an increasingly useful role in synthetic organic chemistry.<sup>2</sup> There is a group of reagents (iodobenzene diacetate, iodobenzene bis(trifluoroacetate), 2-iodosobenzoic acid, hydroxy(tosyloxy)iodobenzene (Koser-reagent)) which are available for functional group transformation<sup>3</sup> and also for use in natural product synthesis.<sup>4</sup> Ligand coupling<sup>5</sup> on various heteroatoms, e.g. sulfur,<sup>6</sup> phosphorus,<sup>7</sup> tellurium,<sup>8</sup> bismuth and lead<sup>9</sup> is well documented in the chemical literature. Iodine, in principle would have several advantages over other heteroatoms because it is non-toxic compared to the others and easy to handle. There is evidence, that hypervalent iodine can be used for this purpose.<sup>10</sup> With this background we decided to study the reaction between hypervalent iodine<sup>III</sup> compounds and organolithium reagents.

## Results and discussion

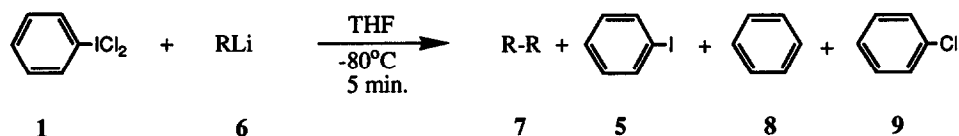
We conceived that a ligand exchange and coupling might take place on iodine, *via* the proposed<sup>2d</sup> intermediate (3), resulting in the formation of a new carbon-carbon bond. The iodobenzene thus formed could be recycled (Scheme 1).



Scheme 1

Indeed, iodobenzene dichloride (1), freshly prepared by the method of Willgerodt,<sup>11</sup> reacted instantly in a cold tetrahydrofuran solution (-80°C, dark, under argon) with *n*-butyllithium. The products formed were measured after aqueous work-up by glc with an internal reference (for the calculation of the yields see Experimental). This reaction was then studied with other lithium reagents (Table 1).

Table 1. Reaction of organolithium reagents with iodobenzene dichloride (1).



| Entry | R group in RLi    | RLi/PhICl <sub>2</sub><br>molar ratio | Products (%) <sup>a</sup> |    |    |   |
|-------|-------------------|---------------------------------------|---------------------------|----|----|---|
|       |                   |                                       | 7                         | 5  | 8  | 9 |
| 1     | <i>n</i> -butyl   | 2.2                                   | 85                        | 0  | 70 | 8 |
| 2     | <i>n</i> -butyl   | 2.0                                   | 63                        | 25 | 50 | 7 |
| 3     | <i>sec</i> -butyl | 2.3                                   | 70                        | 50 | +  | + |
| 4     | <i>t</i> -butyl   | 2.0                                   | 30                        | 65 | 10 | 7 |

<sup>a</sup>determined by glc

These preliminary experiments showed that significant formation of *n*-octane took place. Thus, the trivial, and perhaps more expected reaction, formation of butyl chloride, chloride ion and iodobenzene was not seen. Similarly results were obtained using 4-methoxyiodobenzene dichloride. This latter compound was very unstable and decomposed fairly rapidly at room temperature<sup>12</sup>.

Product analysis revealed that varying amounts of the expected hydrocarbons were formed, accompanied by the expected iodobenzene (and benzene). Relatively small amounts of chlorobenzene, butylbenzene, iodobutane were also found. Minor products (p-dichlorobenzene, p-iodochlorobenzene) were also identified in small amounts. The formation of the latter compounds indicated a more complex mechanism than shown in Scheme 1.

Comparable data in Table 1 show that hydrocarbon (7) formation decreases in the primary > secondary > tertiary order. Using 10 % molar excess of *n*-butyllithium (entry 1 in Table 1) no iodobenzene (5) was detected. This experiment showed that the consumption of butyllithium is faster than it would have been expected on the basis of the reaction in Scheme 1. This finding and the product analysis of these reactions suggest that the iodobenzene effectively competes for the *n*-butyllithium with iodobenzene dichloride.

It is also worth noting, that because of the possibility of the known exchange reactions between the halo-compounds and lithium reagents, the BuLi + BuI reaction can also contribute to the *n*-octane formation.

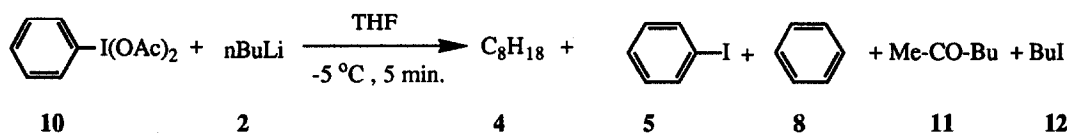
The following blank experiments were carried out. Using identical reaction conditions (THF, - 80°C, argon, 5 min.) iodobenzene was reacted with *n*-butyllithium (molar ratio= 1:1). The reaction mixture was analysed by glc, 30 % *n*-octane, 40 % butylbenzene, 8% iodobutane and the unreacted iodobenzene were measured. Similarly, the reaction of the *n*-butyllithium and iodobutane produced 100 % *n*-octane.

These blank experiments showed clearly, that iodobenzene is indeed an effective competitor for the *n*-butyllithium. Also the nBuLi + nBuI reaction (very fast even at - 80°C) can produce the corresponding *n*-octane quantitatively.

We then examined a number of phenyliodine<sup>III</sup> reagents. We expected that iodobenzene diacetate would afford butyl methyl ketone on attack by butyllithium. Instead, with a 2:1 butyllithium to iodobenzene diacetate ratio, an 80 % yield of *n*-octane was obtained. Iodobenzene bis-trifluoroacetate and dibenzoate gave lesser amounts of *n*-octane, but the Koser reagent also gave a good yield.

In order to increase lipophilicity and low temperature solubility and decrease the competition of the aromatic iodo compound (cf. iodobenzene) that is produced in the coupling reaction we have synthesized the more hindered 2,6-dimethyl-4-*tert*-butyl-iodobenzene-diacetate. In the case of a 1:2 iodine compound - *n*-butyllithium ratio, only 32% of *n*-octane was formed, together with 2-hexanone (16%), butyl iodide (7%), 3,5-dimethyl-*tert*-butylbenzene (35%), the expected 2,6-dimethyl-4-*tert*-butyl-iodobenzene (but only 48%), 2,2',6,6'-tetramethyl-4,4'-*bis-tert*-butyl-biphenyl (10%), 2,6-dimethyl-4-*tert*-butyl-*n*-butylbenzene (10%) and 5-methyl-5-hydroxy-nonane (4%). The *n*-octane yield was increased to 80% in the reaction when the iodine reagent - *n*-butyllithium ratio was increased to 4:1. However, the complex product mixture obtained in the first reaction and the higher *n*-octane yield in the latter with unsubstituted iodobenzene diacetate (93%) suggests, that this hypervalent iodine compound could not be the ideal reagent. Also, the presence of 3,5-dimethyl-*tert*-butylbenzene (24%), measured in the reaction with 4:1 reagent ratio suggests that even the steric hindrance introduced could not eliminate the unwanted competition of the iodobenzene derivative for the reagent, *n*-butyllithium.

We decided then to concentrate on the diacetate and to try to understand the mechanism of the reaction. Table 2 summarizes the results.

**Table 2.** Reaction of iodobenzene diacetate with *n*-butyllithium.

| Entry | 10/2<br>molar ratio | Products (%)         |                 |    |    |    |
|-------|---------------------|----------------------|-----------------|----|----|----|
|       |                     | 4                    | 5               | 8  | 11 | 12 |
| 1     | 0.4                 | 95                   | 65              | +  | +  | +  |
| 2     | 0.5                 | 83                   | 71              | 17 | 9  | 4  |
| 3     | 1.0                 | 43 (86) <sup>a</sup> | + <sup>b</sup>  | 1  | 2  | <1 |
| 4     | 2.0                 | 23 (92) <sup>a</sup> | + <sup>b</sup>  | 1  | 1  | <1 |
| 5     | 4.0                 | 12 (96) <sup>a</sup> | 12 <sup>b</sup> | <1 | <1 | <1 |

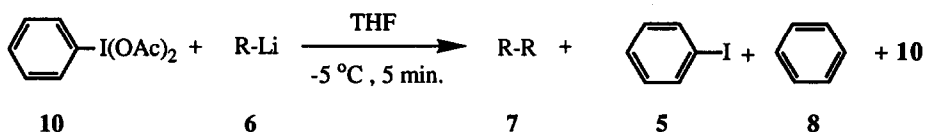
<sup>a</sup> yields in brackets calculated with respect to **2**.

<sup>b</sup>**10** is also detected by <sup>1</sup>H NMR.

+ detected but not measured.

Iodobenzene diacetate is fairly soluble in THF between -10 and +25 °C, so we studied its reaction at -5 °C. Changing the molar ratio of iodobenzene diacetate to *n*-butyllithium from 1:2 to 4:1 we found that the yield of *n*-octane was increased up to 96% (calculated with respect to **2**) and the formation of benzene, butyl methyl ketone and iodobutane decreased (see entry 2 vs. 5 in Table 2). In this way we were able to suppress the competition reaction of benzene formation during the course of the reaction. A careful GC-MS study revealed that these reaction mixtures do not contain any trace of butyl acetate, however small amount of butyl methyl ketone was identified. Running the <sup>1</sup>H NMR spectra of the reaction mixtures (entries 3, 4 and 5) unreacted iodobenzene diacetate was detected.

We have also studied the reaction of iodobenzene diacetate with other organolithium reagents, the results of these experiments are summarized in Table 3.

**Table 3.** Reaction of iodobenzene diacetate with organolithium reagents.

| R   | 10/6<br>molar ratio | Products (%)         |    |       |                 | Mass Balance (%) |                 |
|-----|---------------------|----------------------|----|-------|-----------------|------------------|-----------------|
|     |                     | 7                    | 5  | 8     | 10 <sup>a</sup> | Ph               | Bu              |
| nBu | 4                   | 12 (96) <sup>b</sup> | 12 | trace | 86              | 98               | 96              |
| sBu | 4                   | 8 (64) <sup>b</sup>  | 11 | 3     | 82              | 96               | 80 <sup>c</sup> |
| tBu | 4                   | 2 (16) <sup>b</sup>  | 8  | 4     | 84              | 96               | 96 <sup>d</sup> |

<sup>a</sup>average value (determined by <sup>1</sup>H NMR and iodometric titration)

<sup>b</sup>yields in brackets calculated with respect to 6

<sup>c</sup>16% C4 saturated hydrocarbon was also measured (with respect to 6)

<sup>d</sup>40% C4 saturated and 40% C4 unsaturated hydrocarbon is also measured (with respect to 6)

We found, that the optimal molar ratio of iodobenzene diacetate to *n*-butyllithium is 4:1 (see Table 2), consequently these experiments were also performed with this molar ratio. Comparable data in Table 3 show that hydrocarbon (7) formation decreases in the primary>secondary>tertiary order. In the reaction mixture of iodobenzene diacetate and *tert*-butyllithium we measured considerable amounts of C4 saturated and unsaturated hydrocarbons. Using the combined <sup>1</sup>H NMR measurement and iodometric titration of the final reaction mixtures we determined the unreacted amounts of iodobenzene diacetate. In this way finally we were able to calculate the mass balance of these reactions.

To prove the possible mechanism of these reactions we decided to determine the total mass balance for the reaction of iodobenzene diacetate and *n*-butyllithium.

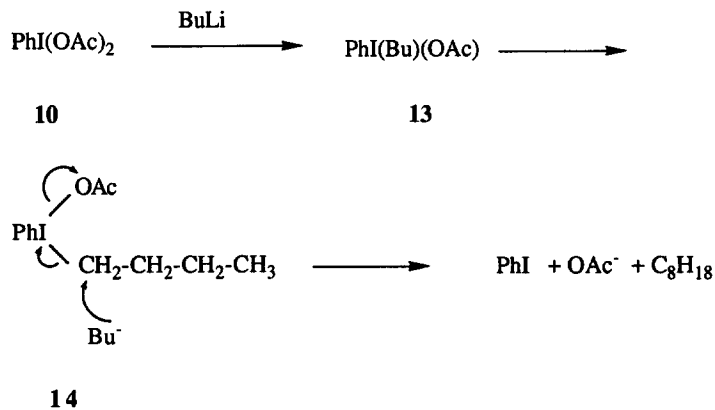
The final reaction mixture (from a molar ratio of iodobenzene diacetate : *n*-butyllithium = 1 : 2) was studied by quantitative glc analysis, we measured 83 % *n*-octane, 71 % iodobenzene, 17 % benzene, 4 % iodobutane and

9 % butyl methyl ketone, respectively. We have also determined and measured 83 % lithium acetate and 12 % lithium iodide. Another blank experiment revealed that iodobenzene diacetate can oxidize lithium iodide quantitatively to iodine. Based on these measurements we calculated the mass balance for this reaction as follows: mass balance (%): phenyl > 98, butyl 96, acetate 100, iodide > 87, lithium 95.

One can presume that iodobenzene dichloride is more reactive than iodobenzene diacetate in these reactions. In an NMR tube we did a preliminary experiment reacting iodobenzene dichloride (1 mmol), iodobenzene diacetate (1 mmol) and *n*-butyllithium (2 mmol) in THF-d<sub>6</sub>. Running the <sup>1</sup>H NMR spectrum of this reaction mixture revealed, that both hypervalent iodine reagents were consumed at about similar extent. To explain this observation we did a blank experiment. We measured the <sup>13</sup>C-NMR spectra of the iodobenzene diacetate and iodobenzene dichloride alone, then we mixed them together and ran the <sup>13</sup>C-NMR again. The assignment of the C1 carbon signals is very easy. In the case of iodobenzene diacetate δ(C1): 121.55, for the corresponding dichloride δ(C1): 125.32 ppm respectively. This 'mixed spectrum,' however, showed three C1 signals in this range, with the relative intensities of 1:2:1. These signals are: 125.21 (1), 122.84 (2) and 121.60 (1). We can see also three sets of signals of the CH carbons of the phenyl ring. These data showed that on mixing these two hypervalent iodine reagents together, we can observe an immediate ligand exchange; consequently we could not do any real competition experiments with *n*-butyllithium.

The results in Table 2 show that when the iodobenzene diacetate is in excess by 4 to 8 times the theoretical amount the reaction becomes very efficient for the production of *n*-octane. It is not easy to understand why the displacement of one acetate by a butyl group should activate so much the displacement of the second acetate. This is what would be required if the ligand coupling mechanism of Scheme 1 were to operate.

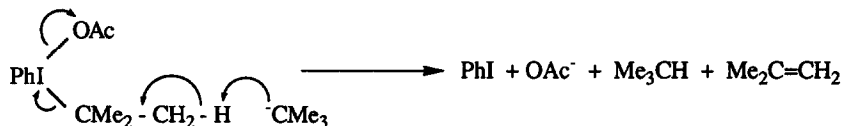
The only hypothesis which could sustain ligand coupling would be rapid ligand exchange, as seen for iodobenzene diacetate and dichloride (see above). An exchange process could produce iodobenzene dibutyl which could ligand couple as fast as it was formed.



### Scheme 2

Another hypothesis, which seems to us to be more attractive, is shown in Scheme 2. Here the replacement of one acetate gives an intermediate which reacts rapidly with a second butyllithium on the carbon atom attached to iodine in an S<sub>N</sub>2-type process.

This hypothesis will also explain the results observed with the secondary and tertiary butyllithiums (Table 3). *tert*-Butyllithium gave very little di-*t*-butyl. An S<sub>N</sub>2-type reaction on a tertiary carbon (cf. **14**) would not be expected to be a major pathway. The major hydrocarbons from the reaction were isobutene and isobutane (40% each). These would be expected products from the bimolecular fragmentation process shown in **15** (Scheme 3).

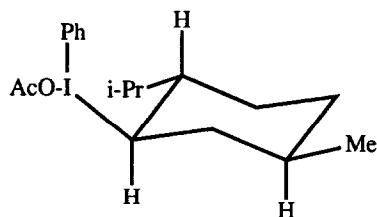
**15**

Scheme 3

*sec*-Butyllithium does afford a significant amount (64%) of di-*sec*-butyl as well as butane. We did not detect butene at the level present, but the presence of the butane suggest that the mechanism in Scheme 3 is operative.

The simplest procedure for the detection of an S<sub>N</sub>2 reaction is to demonstrate inversion of configuration at the carbon center attached. In the case in point a secondary alkyl lithium of stable configuration would be needed.

Walborsky<sup>13</sup> has shown that many cyclopropyllithium species are configurationally stable. However, we found in the publication of Glase and Selman<sup>14</sup> that menthyllithium species under defined conditions are also stable. Since we had menthol to hand we examined this first. The optically active (+)-menthyllithium, prepared from a lithium-sodium alloy and (-)-menthyl chloride,<sup>14,15</sup> gives no significant coupling reaction. The main coupling is the Wurtz coupling that can be observed without the addition of any hypervalent iodine reagent. (However, menthyllithium is formed and not consumed by the sluggish Wurtz coupling. Upon quenching with water menthane is obtained indicating the formation and presence of menthyl lithium.) The product ratio is the same in each experiment. In the presence of iodobenzene diacetate there is a relative increase in the amount of menthene. This finding indicates a reaction similar to the *tert*-butyllithium case. These observations suggest that the first intermediate after mixing (+)-menthyllithium with iodobenzene diacetate is the equatorial iodine compound **16**.

**16**

The second acetoxy group could be replaced on the iodine to form the dimethyl-iodobenzene. This would be required by the true ligand coupling reaction. However, a displacement on the iodine-bearing carbon of **16** by another menthyl anion seems sterically improbable. It would be possible from the (not favored) axial derivative. This may be the explanation that no coupling is observed in the presence of iodobenzene diacetate; hence this is not a ligand coupling reaction.

## Experimental

Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer 881 spectrophotometer. UV-VIS spectra were recorded on a Beckman DU-7 spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were determined for solutions in deuteriochloroform (unless specified otherwise) with TMS internal reference on Varian XL 200 instrument. Gas chromatography (glc) measurements were performed on a Chrompack Packard Model 493 glc instrument or a Hewlett-Packard 5890 II glc system equipped with a FID detector and a DB-5 and/or a GS-Q fused capillary columns (30 m each) using nitrogen as a carrier gas. GC-MS data were obtained on a Hewlett-Packard 5890 II GC-MS system with a 5971 mass selective detector. Microanalyses were performed by Atlantic Microlab, Inc., Norcross, Georgia. Solvent were used either as purchased or dried and purified by standard methods, under dry, pure nitrogen or argon. Organolithium reagents were always freshly titrated using the double titration method.<sup>16</sup> A reference compound (hexamethyl-ethane) and starting materials were purchased from Aldrich Chemical Co., Inc., Milwaukee, Wisconsin.

### Typical procedure:

The given hypervalent iodine reagent (1 mmol) was dissolved in freshly distilled dry tetrahydrofuran (5.0 ml) and cooled to -80 or -5 °C under argon. Then it was treated with a hydrocarbon (pentane, hexanes) solution of the organolithium compounds (molar ratios in Table 1, 2 and Table 3). The reaction mixture was then stirred at this temperature. After the reaction (times in the Tables) water was added into the flask (5.0 ml) and the glc reference compound. Then this mixture was extracted with ether (2 x 5 ml), dried over anhydrous magnesium sulfate and the hydrocarbon content was measured by glc.

### Calculation of yields:

Standard solutions in diethyl ether were prepared, which contained 1 mmols of n-octane, iodobenzene, benzene and iodobutane, and 1 mmol of naphthalene as an internal reference compound. Using the glc measurement based on the corresponding area percent individually established correction factors were calculated for each compounds.

After the reaction 1mmol of naphthalene was added into the reaction mixture and glc analysis was performed. Based on the corresponding area percent the yields were calculated (using the previously established correction factors) with respect to the iodobenzene diacetate or organolithium reagents depending on the molar ratio used.

### Determination of the mass balance

First we determined the "active " iodobenzene diacetate content of this commercially available reagent. Based on the iodometric titration<sup>17</sup> it is 97-98 % pure, however titration with 0.1 N sodium-hydroxide solution showed only 92-93 % acetate content. This is in agreement with its  $^1\text{H}$ -NMR spectrum, which showed 7-8 % iodobenzene content.

The reaction mixture of iodobenzene diacetate and n-butyllithium (molar ratio = 1 : 2) was evaporated to dryness and taken in  $\text{D}_2\text{O}$  (DSS was used as internal reference). Authentic lithium acetate was also taken in  $\text{D}_2\text{O}$ . Running the  $^1\text{H}$  NMR spectra of these samples, we measured the chemical shift of the acetate methyl group (authentic lithium acetate  $\delta$ : 1.907 ppm, reaction mixture (evaporated)  $\delta$ : 1.911 ppm).



Based on these results we can say that our mixture does contain lithium acetate. Using methyl- $\alpha$ -D-glucopyranoside as internal standard, we did a quantitative  $^1\text{H}$  NMR experiment as well, in this way we measured 83 % lithium acetate content in our sample.

We repeated the reaction using identical conditions. The reaction mixture was evaporated, the residue was dissolved in 10 % nitric acid and excess amount of silver nitrate solution was added. The LiI precipitate was filtered off and dried. According to this experiment 12 % lithium iodide was formed in the reaction.

Preparation of 2,6-dimethyl-4-*tert*-butyl-iodobenzene diacetate. This was carried out similarly to the general procedure.<sup>18</sup> Yield: 27%, m.p. 163°C (dec.) (from hexane); IR ( $\text{CHCl}_3$ ) 3003, 2968, 1645, 1269  $\text{cm}^{-1}$ ; UV(THF) 289, 247 nm;  $^1\text{H}$  NMR ( $\delta$ ,ppm): 1.32 (s, 9H), 1.98 (s, 6H), 2.74 (s, 6H), 7.27 (s, 2H);  $^{13}\text{C}$  NMR ( $\delta$ ,ppm): 20.33, 27.04, 31.10, 34.82, 125.51, 129.33, 140.93, 155.78, 176.45; calcd. for  $\text{C}_{16}\text{H}_{23}\text{IO}_4$ : C:47.30, H: 5.71, I: 31.24; found; C: 47.37, H: 5.72, I: 31.33%. 3,4-Dimethylhexane as a reference compound was prepared from the reaction of *sec*-butyl iodide with *sec*-butyllithium. Yield: 50 %; b.p.114-117 °C. (Lit. 116.5 °C<sup>19</sup>).

**Determination of isobutane and isobutene by glc:** Freshly titrated *tert*-butyllithium (1 mmol) was treated with 5 ml of water and extracted with ether (2x2ml). Then the organic phase was separated, p-xylene (1 mmol) was added and a glc analysis was performed on a 30 m GS-Q column. A correction factor was calculated based on area percents. After the reaction of iodobenzene diacetate with *tert*-butyllithium, p-xylene (1 mmol) was added to the final mixture and glc analysis was performed. Using the previously established correction factor the isobutane content was calculated. We found another peak close to isobutane. This was isobutene which had the same area percent.

**Activated lithium-sodium alloy<sup>14</sup>:** Lithium metal (6.8 g, 0.96 mole) was melted in paraffin oil at 200°C. A few drops of oleic acid was added followed by sodium metal (0.13 g). The mixture was stirred for 2 h at this temperature and cooled down to room temperature while vigorously shaken. The shots of the solidified alloy were filtered under argon and washed with a large amount of dry ether. Then the shots were dried for five hours in oil pump vacuum and flushed with pure, dry argon. This lithium can be stored under dry argon for several weeks without the loss of activity.

**Synthesis of (+) menthyllithium<sup>14</sup> and reaction with iodobenzene diacetate:** To a stirred mixture of lithium-sodium alloy (0.28 mol) in dry n-pentane (15 ml) (-)-menthyl chloride (0.02 mol) was added in small portions during 5 h at room temperature. Additional stirring (10 h) and filtration afforded a solution of (+)-menthyllithium<sup>16</sup> (0.61 mmol/ml, 55% yield). This lithium compound was reacted with iodobenzene diacetate as described in the typical procedure (10 min, -80°C, then 2 h at room temperature). Analysis by glc and GC-MS: 45 % menthane, 8 % menthene, 2 % menthyl chloride and 37 % of 3 major dimethyl compounds (ratio 2 : 2.5 : 1). Analysis of the reaction mixture of the blank experiment (hydrolysis of 1 ml organolithium compound) showed the presence of 55 % menthane, 7 % menthene, 4 % menthyl chloride, 22 % major dimethyl products (ratio 2 : 2.5 : 1).

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