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LETTERS

# A Simple Preparation of Iodoarenes, Iodoalkenes and Iodoalkynes by Reaction of Organolithiums with 2,2,2-Trifluoro-1-iodoethane

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***Abstract*:** Organolithium anions, generated either by deprotonation or lithium-bromine exchange, when quenched with 2,2,2-trifluoro-1-iodoethane produce cleanly the synthetically useful iodoarenes, iodoalkenes and iodoalkynes. © 1999 Elsevier Science Ltd. All rights reserved.

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The preparation of iodoarenes, -alkenes and -alkynes is of increasing interest, in particular to those working in the fields of Pd-catalysed coupling reactions[1] and synthetic free-radical chemistry.[2] In general direct arene halogenation with $I_2$ is not possible and alternative methods relying on direct quenching of organometallic species with iodine are employed. Such approaches are also useful for the preparation of iodoalkenes and iodoalkynes. Organolithiums are easily prepared by deprotonation,[3] lithium-halogen exchange[4] or by other methods[5] before being treated directly with iodine, though in some cases transmetallation[6] is effected prior to the quench. For deprotonation of terminal alkynes Grignard reagents[7] and weaker organic bases such as morpholine[8] have also been employed. Alternative sources of "$I^+$" to molecular iodine have been employed,[9] such as 1,2-diiodoethane.[10] In connection with another project we needed a very clean source of "$I^+$" that was not able to act as a one-electron oxidant with sensitive organolithiums. We reasoned that $F_3CCH_2I$ would very cleanly fashion ArI and volatile $CH_2{=}CF_2$ upon reaction with ArLi due to the driving force for LiF formation.

**Table 1. Lithiation/iodination reactions with $F_3CCH_2I$.**

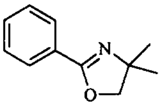
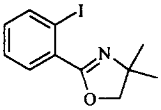
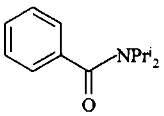
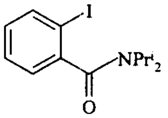
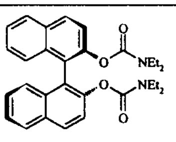
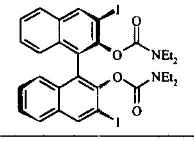
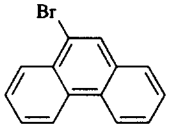
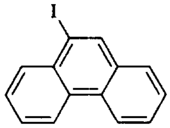
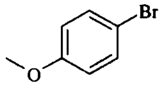
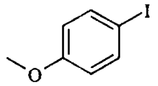
| ENTRY(a) | SUBSTRATE | PRODUCT | YIELD / % (b) |
|---|---|---|---|
| 1[11] |  |  | 51 (73) |
| 2[12] |  |  | 79 |
| 3[13] |  |  | 79 |
| 4 |  |  | 72[14] (c) |
| 5 |  |  | 51 (87) |

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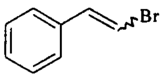
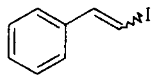
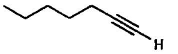
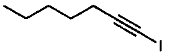
Table 1. Continued.

| ENTRY[(a)] | SUBSTRATE | PRODUCT | YIELD / % [(b)] |
|---|---|---|---|
| **6** |  |  | **64**[1] |
| **7** |  |  | **43**[15] |

**Notes:**

(a) For entries **1-3** metallation was achieved according to the reference indicated. For entries **4-7** lithium-bromine exchange was effected by the action of *n*-BuLi on the bromo substrate for 10 minutes at –78 °C in THF. (b) Unoptimized yields are quoted (crude yields in parentheses). MS and NMR data (and melting point where appropriate) for the products were correlated with data from the literature source indicated. For entries **1-3** the products were fully characterized by NMR. MS and elemental analysis and /or HRMS. (c) After removal of the reaction solvent, the product was purified directly by recrystallization from ethanol.

The reactions all proceeded cleanly and in general the crude material, after removal of volatile organic components, could be used directly (Table 1). 1-Lithioheptyne (entry 7) was an exception as the resulting iodo product is significantly volatile and distillation resulted in a suppressed isolated yield. However GC inspection of the reaction mixture revealed a single product. This method should ultimately compare favourably with the silver acetylide-NIS method[9d] for the preparation of iodoalkynes, as in this particular example the higher yields reported (65-86%) are not disadvantaged by the problem of product volatility. Dilithio compounds reacted equally well as mono anions (entries 2 and 3), in this case fashioning valuable starting materials for 1,1'-binaphthyl chemistry. We note that bis(chloromercuri)ferrocene has been reacted with NIS to give di-iodoferrocene in only 42% yield,[16] which was however a much higher yield than if molecular iodine was employed. Our clean, high-yielding iodination of a dilithio species (entry 3) prompts further investigation into the synthetic utility of this procedure with particular application to oxidation-sensitive substrates.

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