

SYNLETT Spotlight 103

Molecular Iodine

Compiled by Shun-Yi Wang



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

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Introduction

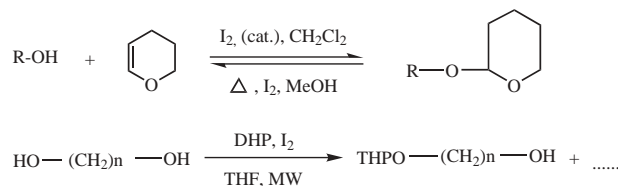
The use of molecular iodine in organic synthesis has been known for a long time, such as in the Grignard reaction. In recent years, molecular iodine has received considerable attention as an inexpensive, non-toxic, readily available

catalyst for various organic transformations under very mild and convenient conditions to afford the corresponding products in excellent yields with high selectivity. This is because of the mild Lewis acidity of iodine.

Abstracts

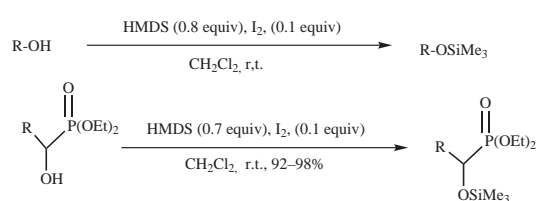
(A) Kumar and co-workers used a catalytic amount of iodine for the rapid tetrahydropyranylation of alcohols and phenols in high yields at room temperature. Depyranylation is effected by refluxing with iodine in methanol for few hours.¹

Similarly, selective protection of one hydroxyl group as its tetrahydropyranyl ether in 1,*n*-symmetrical diols is achieved by iodine-catalyzed reaction of the diol with dihydropyranyl ether under microwave irradiation.^{2,3}



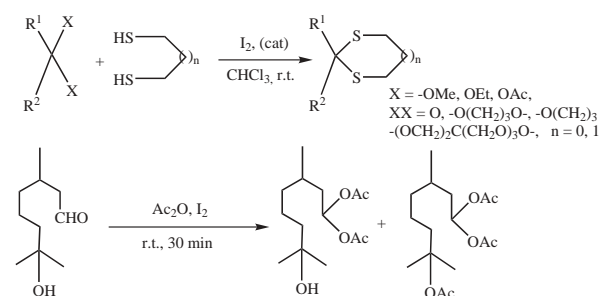
(B) Karimi described a new protocol for the mild and rapid trimethylsilylation of a wide variety of alcohols using HMDS and a catalytic amount of iodine.⁴

Iodine was also shown to catalyze the procedure for the immediate conversion of various α -hydroxyphosphonates to α -trimethylsilyloxyphosphonates under neutral conditions using HMDS.⁵

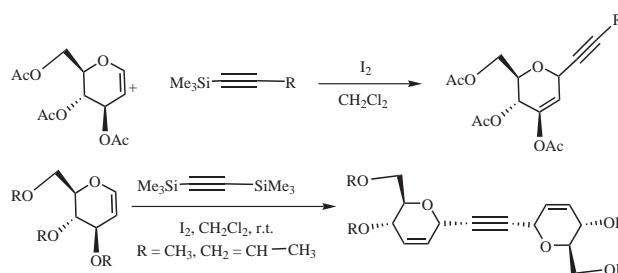


(C) Banik et al. reported a facile and convenient iodine-catalyzed thioketalization for various carbonyl compounds in high yield.⁶ The reactions can also be performed without solvent, using a catalytic amount of iodine supported on a neutral alumina surface.⁷

Nabajyoti et al. reported that iodine can catalyze the reaction of RCHO (R = alkyl, alkenyl, aryl, 2-furyl) with Ac₂O to give RCH(OAc)₂.⁸

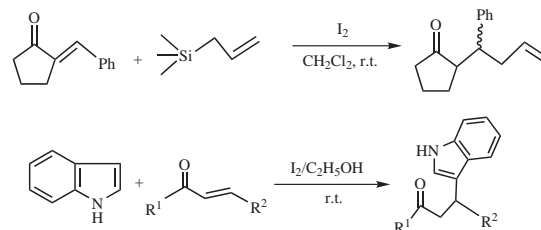


(D) Iodine has been employed as a catalyst to promote the *O*-glycosidation^{9a} and recently *C*-glycosidation of allyltrimethylsilane.^{9b} The use of iodine in the *C*-glycosidation of tri-*O*-acetyl-D-glucal and silylacetylene with various types of R groups at the other end of the acetylene moiety has also been reported.^{9c}

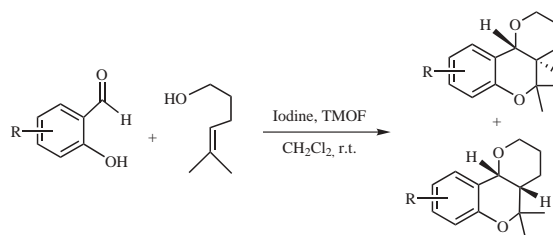


(E) α,β -Unsaturated ketones smoothly undergo conjugate addition with allyltrimethylsilane in the presence of a catalytic amount of elemental iodine under very mild and convenient conditions to afford the corresponding Michael adducts in high yields and with high selectivity.¹⁰

Our group has also developed a simple, convenient and efficient protocol for 3-(3-oxoalkyl)indoles using a catalytic amount of I₂ under mild conditions at room temperature.¹¹

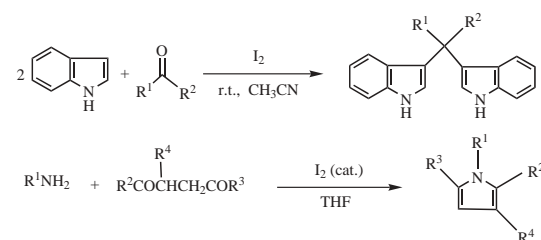


(F) Elemental iodine has been utilized as an efficient catalyst for the intramolecular [4+2] cycloaddition of *o*-quinomethanes generated in situ from *o*-hydroxybenzaldehydes and unsaturated alcohols. The reaction takes place in the presence of trimethyl orthoformate to afford the corresponding *trans*-annulated pyrano[3,2-*c*]benzopyrans in high yields and with high diastereoselectivity.¹²



(G) Molecular iodine also catalyzes an efficient and highly rapid synthesis of bis(indolyl)methanes under mild conditions.¹³

A simple synthesis of substituted pyrroles using iodine-catalyzed modified Paal–Knorr methods has been accomplished in excellent yields.¹⁴



References

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