than 2% of the mixture, by coinjection with an authentic sample;[29] also, no trace of an aromatic singlet below $\delta$ 6.8 was detected by NMR.

From **3l**. The residue (99%) was essentially pure **2-*tert*-butyl-1-naphthol (5l)**, identified by comparison with an authentic sample.[30] This material was $\geq$99% pure by GC, and no trace of a singlet below $\delta$ 6.8 was detected by NMR.

From (impure) **3n**. The residue (75%) was essentially pure **2-bromo-1-naphthol (5n)**, identified by comparison with an authentic sample.[31] This material was $\geq$98% pure by GC ($t_R$ 5.69 min at 280 °C), and no trace of a singlet below $\delta$ 6.8 was detected by NMR.

From (impure) **3o** after chromatography, **2-(ethoxycarbonyl)-1-naphthol (5o)** (15%). The presence of this material as well as a small amount of **3-(ethoxycarbonyl)-1-naphthol (7o)** was detected in the crude product by GC (**5o**:**7o** = 98:2, $t_R$ 2.82 and 6.26 min, respectively, at 240 °C) by comparison with authentic materials.[1]

**Acknowledgment**. We are grateful to P. E. Crawford, R. A. Quas de Penno, D. Timby, and K. F. Blom for their assistance in obtaining spectral data. We also thank D. C. Spellmeyer for helpful discussions on the semiempirical molecular orbital calculations.

**Registry No.** **1a**, 62495-31-2; **1h**, 136131-34-5; **1i**, 136131-35-6; **1j**, 136131-36-7; **3a**, 136131-37-8; **3b**, 136131-38-9; **3c**, 136131-39-0; **3d**, 19061-32-6; **3e**, 136131-40-3; **3f**, 136131-50-5; **3g**, 136131-41-4; **3h**, 136131-42-5; **3i**, 136131-43-6; **3j**, 136131-44-7; **3k**, 136131-45-8; **3l**, 136131-46-9; **3m**, 136131-49-2; **3n**, 136131-47-0; **3o**, 136131-48-1; **4a**, 136131-51-6; **4b**, 136131-52-7; **4c**, 136131-53-8; **5a**, 136131-54-9; **5b**, 136131-55-0; **5c**, 136131-56-1; **5d**, 32849-41-5; **5e**, 129957-20-6; **5f**, 62456-32-0; **5g**, 36441-32-4; **5h**, 109380-82-7; **5i**, 136131-57-2; **5j**, 136131-58-3; **5k**, 7469-77-4; **5l**, 27286-81-3; **5n**, 771-15-3; **5o**, 33950-71-9; **6a**, 136131-59-4; **6b**, 136131-60-7; **6c**, 136131-61-8; **7d**, 51149-87-2; **7e**, 136131-62-9; **7f**, 52927-23-8; **8g**, 123239-69-0; **7h**, 136131-63-0; **7i**, 136131-64-1; **7j**, 136131-65-2; **7k**, 13615-40-2; **7o**, 91307-39-0; 3-furancarboxaldehyde, 498-60-2; 4-bromoanisole, 104-92-7; $\alpha$-(4-methoxyphenyl)-3-furanmethanol, 136131-66-3; 1-bromo-4-(1,1-dimethylethyl)benzene, 3972-65-4; 1-bromo-4-(trifluoromethyl)benzene, 402-43-7; 2-amino-1,1′-(biphenyl), 90-41-5; $\alpha$-oximino-2-phenylacetanilide, 136131-67-4; 2-amino-3-methylbenzoic acid, 4389-45-1; 2-amino-3-phenylbenzoic acid, 4445-39-0; 6-amino-2-(methoxycarbonyl)benzoic acid, 103259-06-9; anthranilic acid, 118-92-3; 3-methylfuran, 930-27-8; 3-(1,1-dimethylethyl)furan, 7040-42-8; 3-bromofuran, 22037-28-1; ethyl 3-furancarboxylate, 614-98-2; 3-phenylfuran, 13679-41-9.

**Supplementary Material Available:** Tabulated spectral data and analytical results for **1h–j**, **3b–o**, **5a–j**, and **7a–j** (6 pages). Ordering information is given on any current masthead page.

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# Reaction of Enol Silyl Ethers and Enol Acetates with Copper(II) Nitrate–Iodine: Synthesis of $\alpha$-Iodo Ketones

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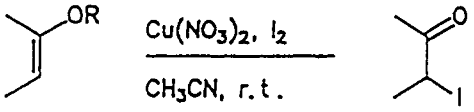
During the last few years a number of methods for the preparation of $\alpha$-iodo ketones[1] from ketones, enol acetates, and enol silyl ethers have been reported. Although some of them represent a significant advance in this field,[2,3] there are still some disadvantages due, for instance, to the use of highly toxic reagents, such as thallium(I) acetate,[4] or to some substrate limitations.[5,6] At present, the most general method available consists of the sequential treatment of enol silyl ethers with silver acetate–iodine, followed by triethylammonium fluoride.[7] However, new efficient and cheaper methods for the preparation of these compounds are still desirable, in view of the extensive use of $\alpha$-iodo carbonyl compounds in the synthesis of electrophilic $\alpha$-oxo alkyl radicals.[8]

This paper reports a new and convenient procedure for the preparation of $\alpha$-iodo ketones from the corresponding enol silyl ether or enol acetate with $I_2$ and copper(II) nitrate under mild reaction conditions, according to the following equation:



1 2

R = $SiMe_3$, Ac

Treatment of the enol derivative **1** with 1 molar equiv of copper(II) nitrate and 1 molar equiv of iodine in $CH_3CN$ at rt for a few minutes affords the corresponding $\alpha$-iodo ketone in very good yield. The results, displayed in Table I, clearly show the general applicability of the procedure. Under the same conditions, i.e., copper(II) nitrate and $I_2$, anisole gives iodoanisole in 64% yield after 24 h, while no ring iodination occurs by this procedure during the short time needed to obtain the corresponding $\alpha$-iodo ketone in the case of compounds **1d** and **1h**. Moreover, the direct treatment of the enol silyl ether of cyclohexanone with molecular iodine without the copper salt does not afford any detectable trace of iodo ketone after 4 h. From these observations we can probably say that copper(II) nitrate plays a dual role in this reaction. First of all, it promotes the iodination process acting as a Lewis acid catalyst, and then it reoxidizes iodide ions back to iodine, analogous to a scheme that has been already proposed by Baird et al.[9] for the synthesis of aryl iodides. Although it is known that both copper(I) and copper(II) salts show Lewis acid properties capable of polarizing the iodo group and facilitating cleavage of the silyl group,[10] copper(II) is also a good oxidant. For this reason an alternative hypothesis has to be considered, in which the species involved in the process is $I^+$, which is generated from $I_2$ by oxidation with copper nitrate, as postulated in the synthesis of $\alpha$-iodo ketones by electrochemical procedures[11] or by use of the *m*-chloroperoxybenzoic acid/sodium iodide reagent.[3]

In conclusion, iodination of trimethylsilyl enol ethers and enol acetates with copper(II) nitrate and $I_2$ represents a

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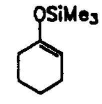
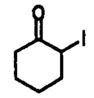
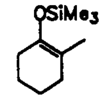
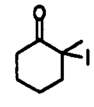
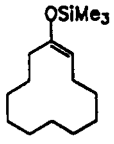
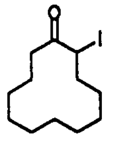
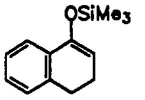
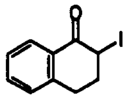
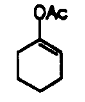
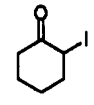
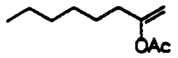
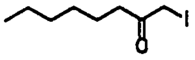
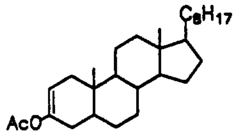
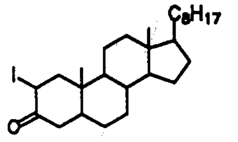
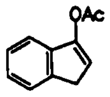
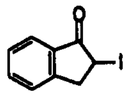
**Table I. Preparation of $\alpha$-Iodo Ketones from Enol Silyl Ethers and Enol Acetates with Copper(II) Nitrate and Iodine**

| substrate | product | yield[a] (%) |
|---|---|---|
|  1a |  2a | 100 |
|  1b |  2b | 100 |
|  1c |  2c | 85 |
|  1d |  2d | 85 |
|  1e |  2a | 100 |
|  1f |  2f | 90 |
|  1g |  2g | 100 |
|  1h |  2h | 100 |

[a] Isolated yield.

convenient procedure for the regiospecific synthesis of $\alpha$-iodo ketones. This method supplements the others already reported and recommends itself for the simplicity, the mild conditions needed, and the high yields obtained.

## Experimental Section

Enol acetates and enol silyl ethers were prepared according standard procedures.[11,12] All known compounds were identified by comparison of their IR, $^1$H NMR, and MS spectra with the published data,[14] except for compound **1h**, which has been synthesized for the first time.

**1*H*-Inden-3-yl acetate (1h)** was prepared according to the method of ref 11 and purified by column chromatography on silica gel (hexane/ethyl acetate (10:1)): mp 46–47 °C; IR (neat) 1775, 1710 cm$^{-1}$; $^1$H NMR (80 MHz, CDCl$_3$) $\delta$ 7.5–7.1 (m, 4 H), 6.32 (t, $J$ = 2 Hz, 1 H), 3.40 (d, $J$ = 2 Hz, 2 H), 2.32 (s, 3 H); MS $m/z$ 174. Anal. Calcd for $C_{11}H_{10}O_2$: C, 74.84; H, 5.78. Found: C, 74.92; H, 5.55.

**Preparation of $\alpha$-Iodo Ketones 2. 2-Iodocyclododecanone (2c).** To a solution of $I_2$ (0.157 g, 1.25 mmol) and $Cu(NO_3)_2 \cdot H_2O$ (0.301 g, 1.25 mmol) in 5 mL of $CH_3CN$ was added (trimethylsiloxy)cyclododecene (0.317 g, 1.25 mmol).[18] After 5 min, the reaction mixture was diluted with pentane (10 mL), washed with saturated sodium thiosulfate solution (10 mL), and then dried ($Na_2SO_4$). After concentration the residue was crystallized from methanol to give 0.326 g (85%) of pure 2-iodocyclododecanone, mp 53–54 °C (lit.[7] mp 52–52.5 °C).

Reaction times for enol silanes and enol acetates were 5 and 15 min, respectively. In those cases in which yields of 100% are reported, it means that no further purification was done. The purity of the products was checked by $^1$H NMR and GC. No trace of starting material or other products different from the corresponding iodo ketone were detected. Products **2g**, **2d**, and **2h** have been crystallized; compound **2f** has been purified by flash chromatography on silica gel (hexane/ethyl acetate (8:2)).

**2$\alpha$-Iodo-5$\alpha$-cholestan-3-one (2g)**: mp 131.5–132.5 °C (lit.[16] mp 132–133 °C).

**2-Iodo-1-tetralone (2d)**: mp 77–78 °C (lit.[2] mp 76–78 °C).

**2-Iodo-1-indanone (2h)**: mp 69–70 °C (lit.[17] mp 68–70 °C).

**Acknowledgment.** This work has been carried out in the framework of the Progetto Finalizzato CNR Chimica Fine II.

**Registry No.** **1a**, 6651-36-1; **1b**, 19980-35-9; **1c**, 51584-36-2; **1d**, 38858-72-9; **1e**, 1424-22-2; **1f**, 26735-84-2; **1g**, 1255-89-6; **1h**, 19455-83-5; **2a**, 35365-19-6; **2b**, 77256-25-8; **2c**, 69381-33-5; **2d**, 41099-31-4; **2f**, 63641-50-9; **2g**, 2516-55-4; **2h**, 113021-30-0; $Cu(NO_2)_2$, 3251-23-8; $I_2$, 7553-56-2; PhOMe, 100-66-3; iodoanisole, 35745-35-8.

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(14) For compounds **1a**, **2a**, **1c**, **2c**, see ref 7; **1b**, **2b**, ref 15; **1d**, **2d**, **1e**, **1f**, **2f**, ref 2; **1g**, **2g**, refs 4, 16; **2h**, ref 17.

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(18) For the acetate **1g** 2 mL of $CH_2Cl_2$ was added to achieve the complete solubilization of the substrate.

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# Benzoin Enediol Dianion and Hydroxide Ion in DMSO: A Single Electron Transfer Reduction System Driven by the Irreversible Benzilic Acid Rearrangement

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In a study of nucleophilic reactions of ketone enolate ions with the sterically constrained ($Z$)-$\alpha$,$\beta$-dibenzoylstyrene (1) in DMSO, a reductive side reaction was found.[1] The competing reduction was proposed to occur by elec-

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(1) Taken in part from: Robinson, J. M. M.S. Thesis, Louisiana Tech University, 1969.