# Preparation, Characterisation, and some Properties of Secondary Enamines

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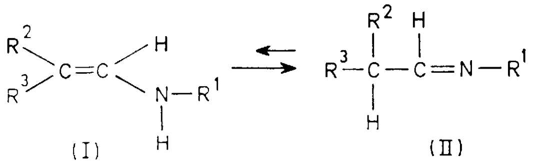
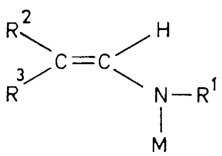
*Summary* Partial methanolysis of organo-tin or -magnesium salts of imines leads to secondary enamines which are stable in aprotic media allowing the study of their physical and chemical properties.

SECONDARY enamines (I) are thermodynamically unstable since they exist in equilibrium with the tautomeric imines (II). Except in some cases[1] the imino-form is the only detectable form [equation (1)].


(I) (II) (1)

We report on the physical and chemical properties of secondary enamines which can be obtained in relatively stable form when generated in strictly aprotic media.

We have previously reported the preparation of organotin enamines (III) and imines (IV) ($M = SnBu_3$) by three different routes.[2] As expected, these compounds are very sensitive to protolysis (*e.g.*, methanolysis) giving the corresponding imines (II). However, when an insufficient amount of methanol (75% of the theoretical amount) is used, the kinetic product of the reaction, the secondary enamine (I), is quantitatively obtained. These enamines are stable in the organotin media, and can be extracted from the reaction mixture under reduced pressure and trapped at − 80 °C. As the enamines are the only volatile component of the reaction mixture, they can be obtained very pure.


(III)

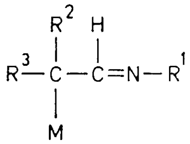
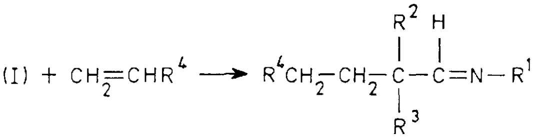

(IV)

TABLE 1. $^1$H N.m.r. and i.r. spectroscopic data of some secondary enamines (I).

| (I) | | | N.m.r. (δ/p.p.m.) | | | | | I.r. (ν/cm$^{-1}$) | |
|---|---|---|---|---|---|---|---|---|---|
| $R^1$ | $R^2$ | $R^3$ | $R^1$ | $R^2$ | $R^3$ | CH | NH | N–H | C=C |
| Me | Me | Me | 2·5 | | 1·35—1·45 | 5·25 | 2·45 | 3360 | 1675 |
| Et | Me | Me | 1·15 ($CH_2$); 2·8 (Me) | | 1·45—1·55 | 5·3 | 2·3 | 3360 | 1670 |
| Pr$^i$ | Me | Me | 0·95 (Me); 2·9 (CH) | | 1·4—1·5 | 5·5 | 2·4 | 3360 | 1670 |
| Bu$^i$ | Me | Me | 0·8 (Me); 1·5 (CH); 2·5 ($CH_2$) | | 1·3—1·4 | 5·3 | | 3360 | 1672 |
| Bu$^i$ | Et | H | 2·7 ($CH_2$) | 4·25 (CH) | | 5·5 | | 3380 | |
| Bu$^i$ | Me | H | 2·65 ($CH_2$) | 4 (CH) | | 5·45 | | 3360 | |

Using this method, secondary enamines were also obtained from other metallic systems, *e.g.*, the magnesium salts of imines used for the Stork alkylation.[3] In order to obtain pure enamines, a high boiling solvent (tetraglyme) was used in these reactions. Methanolysis using MeOD gives *N*-deuteriated enamines with ν(N–D) 2500 cm$^{-1}$.

The secondary enamines are quite stable at − 80 °C (imine content, 25% after 18 h); they can, however, be characterised at room temperature (when total isomerisation takes 1 h) and the results are shown in Table 1.



$$(I) + CH_2{=}CHR^4 \longrightarrow R^4CH_2{-}CH_2{-}C(R^2)(R^3){-}C(H){=}N{-}R^1 \qquad (2)$$

(V)

In order to investigate the reactivity of enamines, they were subjected to a set of reactions which imines are known to undergo *via* the enamine tautomer,[4] *e.g.*, electrophilic addition of alkenes [equation (2)]. As expected, the enamines underwent fast, exothermic reaction at 0 °C, leading, besides some polymerisation, to the expected adducts (V) (Table 2). In the cases of the corresponding imines, the reaction is either very slow (24 h, at 80 °C) or does not take place. *N*-Deuteriated enamines give adducts (V) having a deuterium atom in the α position with respect to the $R^4$ group.

TABLE 2. Reaction of enamines (I) with alkenes to give the adducts (V).

| M in (III) | $R^1$ | $R^2$ | $R^3$ | $R^4$ | yield of (V)/%[a] |
|---|---|---|---|---|---|
| MgCl | Pr$^i$ | Me | Me | CN | 65 |
| MgCl | Pr$^i$ | Me | Me | COMe | 42 |
| MgCl | Pr$^i$ | Me | Me | $CO_2Et$ | 32 |
| MgCl | Me | Me | Me | CN | 41 |
| MgCl | Me | Me | Me | CN | 46 (from MeOD) |
| MgCl | Et | Me | Me | CN | 30 |
| $SnBu_3$ | Et | Me | Me | CN | 37 |
| $SnBu_3$ | Me | Me | Me | CN | 40 |
| $SnBu_3$ | Pr$^i$ | Me | Me | CN | 27 |
| $SnBu_3$ | Et | Me | H | CN | 30 |
| $SnBu_3$ | Bu$^i$ | Me | H | CN | 30 |
| $SnBu_3$ | Pr$^i$ | Me | H | CN | 44 |

[a] The yields are for pure adducts after two distillations based on MeOH.

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[4] M. Pfau and C. Ribiere, *Bull. Soc. chim. France*, 1971, 2584.