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Computational study of the catalytic olefination reaction

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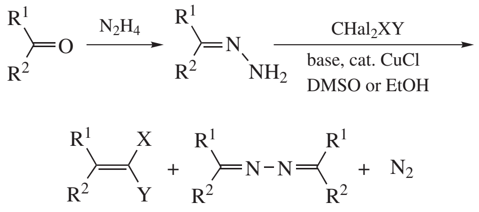
Catalytic olefination of hydrazones was computed to proceed with effective activation barrier of 19.9 kcal mol^{-1}. Initially the catalyst-assisted abstraction of Cl$^-$ anion from CCl_4 occurs that is accompanied by simultaneous C–C bond formation; then proton is eliminated by ammonia present in the reaction mixture yielding a neutral intermediate; the second CuCl-assisted abstraction of Cl$^-$ anion from CCl_3 group is followed by synchronous reaction that affords the olefination product and releases N_2 together with CuCl·HCl.

Creation of new carbon–carbon bonds is a key problem of organic chemistry. Olefination of carbonyl compounds is one of the most versatile approaches for preparation of alkenes from aldehydes or ketones. Development of this area in past decades provided a variety of reliable synthetic protocols.[1] Nevertheless, taking into account the synthetic potential of these methods, the search for new carbonyl olefination reactions is steadily continued.

In 1999 some of us reported, that N-unsubstituted hydrazones of aldehydes and ketones could be transformed into alkenes by treatment with polyhalogenated alkanes in the presence of a base and catalytic amounts of copper salts (Scheme 1).[2] Symmetrical azines were the only side products of the reaction. The reaction revealed a wide synthetic scope allowing one to prepare various alkenes including fluorinated and functionalized ones.[3] Simple experimental procedure depriving of organometallic or toxic organophosphorous compounds, affordable price and availability of starting materials, high yields and stereoselectivity were the distinct advantages of this reaction.

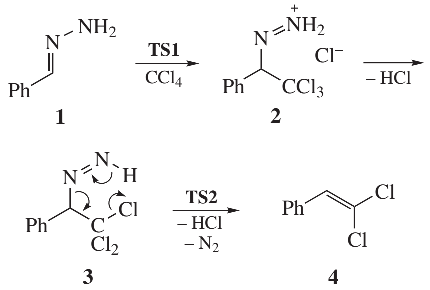


R^1 = Ar, Alk, R^2 = Alk, H
Hal = Cl, Br X = F, Cl, Br, H
Y = F, Cl, Br, CN, CO_2Et

Scheme 1

Two mechanistic schemes were proposed previously for catalytic olefination reaction[4] involving the intermediate formation of either carbene or radical species. Here we report a simple mechanism found by state-of-art DFT calculations[†] that involves neither carbene nor radical intermediates, which may have important implications for the further synthetic improvements.

We reckoned that the simplest pathway for the formation of olefin from hydrazone **1** would be an electrophilic attack of CCl_4 on the double C=N bond followed by abstraction of HCl from the resulting intermediate **2** and synchronous release of N_2 and HCl from the intermediate **3** (Scheme 2).



Scheme 2

A transition state for the rate-limiting stage of the non-catalyzed reaction (Figure 1) was found from a scan approaching CCl_4 molecule to the molecule of hydrazone **1**. The transition state **TS1** features a trigonal planar CCl_3 fragment and slightly

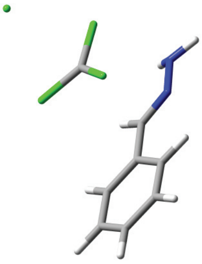


Figure 1 Transition state **TS1** for the first stage of the non-catalyzed reaction. The imaginary frequency ν = 89.5i.

[†] Computations were carried out using the latest long-range corrected hybrid functional with damped atom-atom dispersion (WB97XD)[5] as implemented in the GAUSSIAN 09 software package.[6] All atoms were modelled at the 6-31G(d) level of theory. The solvent influence has been accounted for by performing optimizations in the CPCM force field (DMSO).

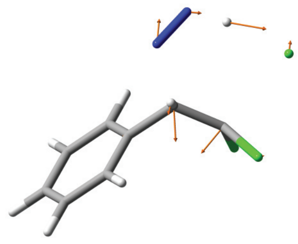
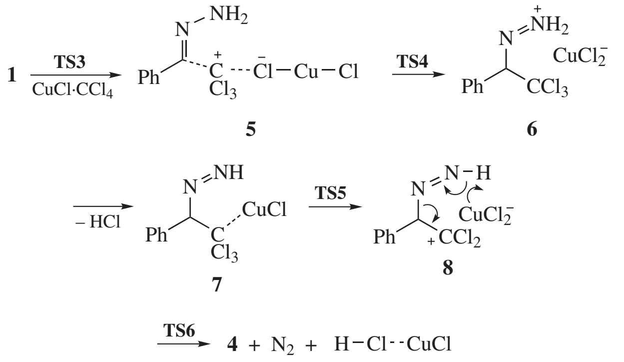


Figure 2 Transition state **TS2** for the second stage of the non-catalyzed reaction showing the displacement vectors. The imaginary frequency $\nu = 416.8i$.

non-planar terminal nitrogen atom. The activation barrier is high enough (51.0 kcal mol^{-1}) that is in accord with the practical impossibility of the non-catalyzed reaction. On the other hand, after the abstraction of HCl from initially formed salt **2**, the reaction becomes exogonic for 7.1 kcal mol^{-1} that indicates the possibility of this pathway in a catalytic reaction.

Scanning the distance between the NH proton and one of the chlorine atoms in **3** afforded the transition state for the second stage of the non-catalyzed reaction (Figure 2), which is a synchronous process involving simultaneous movement of six reaction centers. Hydrogen chloride released after this stage is quenched with ammonia present in the reaction mixture.[‡]



Scheme 3

The catalytic pathway for the olefination reaction is shown in Scheme 3. Under catalytic conditions, each of the two stages becomes stepwise that leads to the significant decrease of the effective activation barrier (Figure 3). Further formation of C–C bond requires relatively low activation barrier and yields the iminium salt **6**. Elimination of HCl with ammonia results in the metastable intermediate **7**. The next stage, the abstraction of Cl$^-$ from the CCl$_3$ group, is rate-limiting in the catalytic process with activation barrier of 19.9 kcal mol^{-1}. It is followed by the facile concerted formation of the product **4** and regenerating the catalyst in the form of the HCl adduct (see Figure 4).

Potential profiles for the catalytic and non-catalytic reactions are shown in Figure 3. The effective Gibbs energy of activation (19.9 kcal mol^{-1}) is in a reasonable agreement with the experimentally optimized reaction conditions (4 h at ambient temperature). Thus, the studies designated to use the acquired mechanistic insights for the optimization of the reaction conditions and extending the scope are underway.

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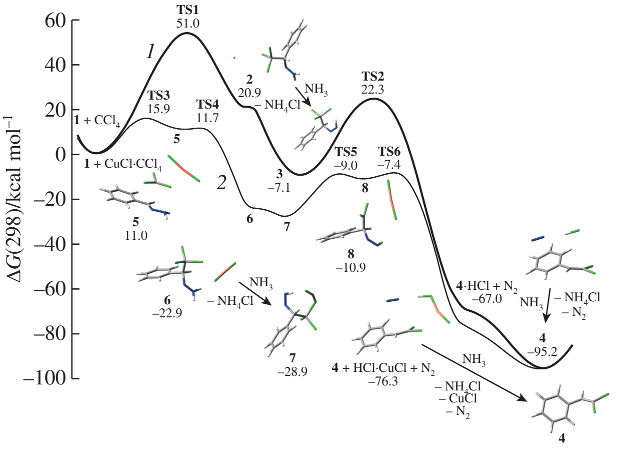

Figure 3 Potential Gibbs energy profiles for the (*1*) non-catalyzed and (*2*) catalyzed olefination reaction. The numbers indicate free energies at 298 K in kcal mol^{-1}. Computations were carried out at the WB97XD/6-31G*/CPCM(DMSO) level of theory.

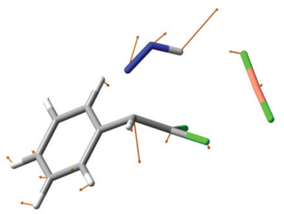

Figure 4 Transition state **TS6** for the olefination reaction catalyzed with CuCl, showing the displacement vectors. The imaginary frequency $\nu = 187.7i$.

Online Supplementary Materials

Supplementary data associated with this article (Cartesian coordinates of all computed compounds and transition states) can be found in the online version at doi:10.1016/j.mencom.2014.11.008.

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[‡] We also considered the non-catalytic reaction in the triplet state. The triplet intermediate **2** can be formed in two stages *via* an extremely unstable transition state (36.0 kcal mol^{-1} less stable than **TS1**). Moreover, the triplet transition state could not be found for the second stage of the reaction since the corresponding energy scan exhibited only the steady rise of the energy without achieving any maximum.