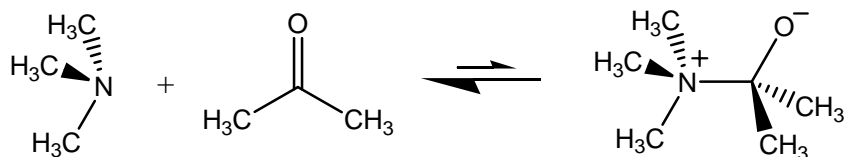


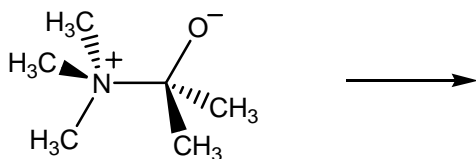
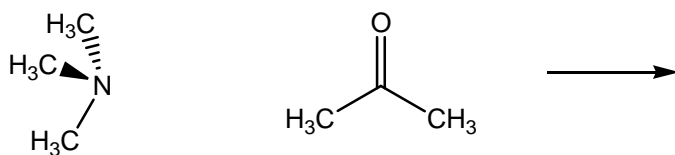
## Workshop 1

The covalent adduct of a trialkylamine and a ketone isn't stable, and would normally revert to starting materials:

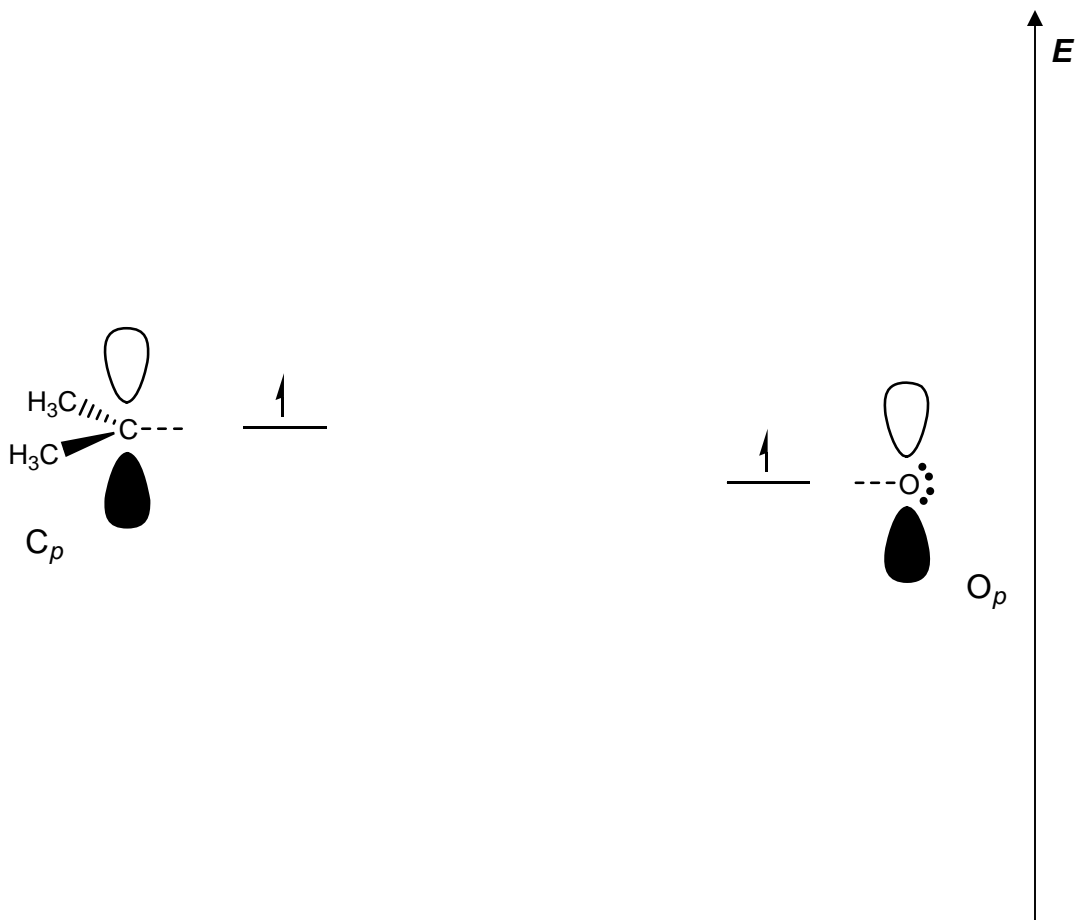


Nevertheless, even though the equilibrium lies far to the left, the reversible process shown above does occur spontaneously.

- a. Using “electron pushing”, illustrate how electron pairs move in both the forward and reverse reactions shown above.

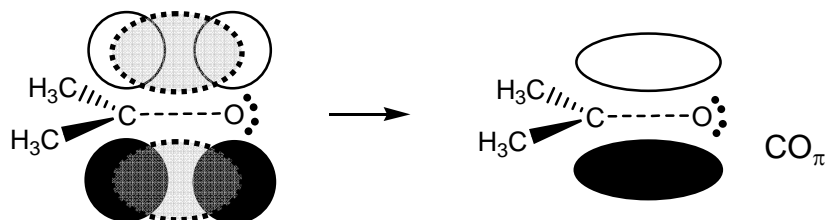


- b. In the forward reaction, a lone pair of electrons occupying a non-bonding molecular orbital on nitrogen ( $N_{lp}$ ) interacts with an empty  $\pi^*$  antibonding orbital of the acetone carbonyl ( $CO_{\pi^*}$ ). **Illustrate the  $CO_{\pi}$  and  $CO_{\pi^*}$  orbitals** by “mixing” a  $C_p$  orbital with an  $O_p$  orbital on the next page.



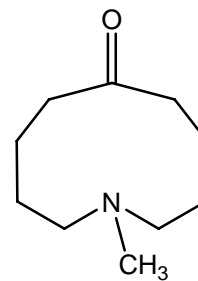
Some things to keep in mind:

- You start with two orbitals, so you should end with two orbitals.
- I drew the oxygen orbital lower in energy than the carbon orbital. Why?
- Spatially, the closer halves of the two  $p$  orbitals get used up to make the bonding  $\text{CO}_\pi$  orbital. What does that leave behind for the  $\text{CO}_{\pi^*}$  orbital? (What does it look like compared to the  $\text{CO}_\pi$  orbital below?)



- After mixing two parent orbitals, each product orbital looks more like the parent that is closer in energy, and less like the parent that is farther away in energy. What does that mean for the orbital density near C and O in the two products? (Which product orbital has more  $\text{C}_p$  in it, and which has more  $\text{O}_p$ ?)

- c. Hans Beat Bürgi and Jack Dunitz, back in the 1970's, determined X-ray crystal structures of molecules in which a trialkylamine and a ketone were physically tethered together such that they were forced to interact.<sup>1</sup> For example, the structure of the molecule **1** showed that the lone pair of the nitrogen was interacting with the  $\text{CO}_{\pi^*}$  orbital of the carbonyl. (They went on to say that this data illustrated how a free nucleophile might attack a carbonyl.)



**1**

Based on what you know about the shapes and densities of the  $\text{N}_{\text{lp}}$  and  $\text{CO}_{\pi^*}$  orbitals, draw what you think the 3-dimensional structure of **1** might look like. Don't worry about the two alkane tethers—just draw these as wavy lines. Most importantly, what do you think the relative positions and orientations of the amine and carbonyl groups are?

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<sup>1</sup> Bürgi, H. B.; Dunitz, J. D. *Acc. Chem. Res.* **1983**, *16*, 153-161.