A DFT study of the mechanism and regioselectivity of the reaction between diethyl trichloro-methyl phosphonate and diphenyl methyl phosphinite

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Abstract

The reaction of diethyl trichloro-methyl phosphonate (C1) with diphenyl methyl phosphinite (C2), has been scrutinized within the Density Function Theory at the B3LYP/6-311(d,p) computational level. The regiosomeric reaction paths involving the two center of compound (C1) have been studied. DFT calculations account for the high regioselectivity in the chlorine atom, in complete agreement with the experimental outcomes.

Keywords: diphenyl methyl phosphinite, diethyl trichloro-methyl phosphonate, DFT/B3LYP/6-311 G(d,p), regiosomeric, regioselectivity.
1. Introduction

It has been shown in the literature that most polyhalogenomethanes such as tetrachloromethane and chloroform, react with trialkylphosphites using only one halogen atom [1-2]. Other highly electrophilic polyhalogenoalkanes, such as dichloromethylene [3], N-(trichloromethyl)-dialkylamine [4], substitute two or even three of their halogenated atoms for dialkylphosphonyl groups. The activity of halogen in position increases with the introduction of an electroattractor group. This is the case of trichloro-acetonitrille(\(\text{CCl}_3\text{CN}\)) which involves the three chlorine atoms by reacting with phosphites [5].

\[
\begin{align*}
3(\text{RO})_2\text{P} + \text{CCl}_3\text{CN} & \rightarrow [(\text{RO})_3\text{P}]_3\text{C} - \text{CN} + 3\text{R} - \text{Cl}
\end{align*}
\]

Scheme 1. Reaction between trichloro-acetonitrille and trialkylphosphite.

According to this mechanism, Sagina and Kukhar [5] expected trichloro-methyl phosphonate to act in the same way as trichloro-acetonitrille despite the low electron acceptor power of the dialkylphosphonyl group compared to the nitrile function. They showed that between 120°C and 130°C, in the absence of solvent and catalyst, bisphosphonate III is formed with a yield of 82% from equivalent proportions of (\(\text{RO})_2\text{P}\) and \(\text{CCl}_3\text{PO(OR)}_2\).

\[
\begin{align*}
(\text{RO})_2\text{P} + \text{CCl}_3\text{P(OR)}_2 & \rightarrow (\text{RO})_2\text{PCCl}_3\text{P(OR)}_2 + \text{R-Cl}
\end{align*}
\]

Scheme 2. Reaction between trichloro-methyl phosphonate and trialkylphosphite.

Since phosphonate II was obtained from phosphite \((\text{RO})_2\text{P}\) and excess tetrachloromethane [6], it was reported that bisphosphonate is also formed by reacting one mole \(\text{CCl}_4\) and two moles phosphite\((\text{RO})_3\text{P}\).

\[
\begin{align*}
2(\text{RO})_2\text{P} + \text{CCl}_4 & \rightarrow (\text{RO})_2\text{PCCl}_3\text{P(OR)}_2 + 2(\text{R-Cl})
\end{align*}
\]

Scheme 3. Reaction between tetrachloromethane and trialkyl phosphate.

The mechanism proposed by Sagina and Kukhar [5] for the formation of dichloro-methylene bisphosphonate is a \(\text{SN}_2\)-type nucleophilic attack on carbon which excludes a radical mechanism. As bisphosphonate III was never previously demonstrated in the reaction of \(\text{CCl}_4\) and \((\text{EtO})_2\text{P}\), Bakkas et al. [7-9] experimentally re-examined the reaction of \(\text{Ia and II}\) reactants and showed that according to Scheme 4:

- This reaction does not lead to biphosphonate \(\text{III}\) but to phosphonate \(\text{IV}\) among other phosphorous compounds.
- Biphosphonate \(\text{III}\) reactant, or its derivatives are obtained when \(\text{Ia and II}\) reacts in the presence of ultraviolet radiation according to a radical mechanism.

It was subsequently concluded that the thermal reaction of triethylphosphite \(\text{Ia}\) with diethyl trichloro-methyl phosphonate \(\text{II}\) was a nucleophilic attack of \(\text{Ia}\) reactant one of the chlorine atoms of compound \(\text{II}\).

\[
\begin{align*}
(\text{EtO})_2\text{P} + \text{Cl} - \text{CCl}_3\text{P(OEt)}_2 & \rightarrow (\text{EtO})_2\text{PCCl}_3\text{P(OEt)}_2 + \text{Et-Cl}
\end{align*}
\]

Scheme 4. Reaction between diethyltrichloro-methylphosphonate \(\text{CCl}_3\text{PO(OEt)}_2\) and triethylphosphite \((\text{EtO})_3\text{P}\).
The reaction of diphenyl methyl phosphinite with diethyl trichloro-methyl phosphonate is performed at room temperature instead of 80°C [8]. This confirms that phosphinite $Ib$ is more reactive than phosphite $(EtO)_2P$ vis-à-vis diethyl trichloro-methyl phosphonate $II$. As a comparison, we theoretically studied by the method DFT/B3LYP/6-311G(d,p) the reaction of $CCl_3PO(OEt)_2$ with $Ph_2POCH_3$ in order to specify its reaction mechanism. In other words, does phosphinite, considered as a nucleophilic donor, attack $A_C$ carbon or chlorine $A_{Cl}$ of diethyl trichloro-methyl phosphonate which is supposed to be electrophilic acceptor according to Scheme 5.

$$\begin{align*}
(PH_2)POCH_3 + CCl_2P(OEt) & \rightarrow (PH)PCl_2P(OEt) + CH_3-Cl \\
(PH_2)POCl + (EtO)_2PCl_2-CH_3 & \rightarrow (PH)PCl_2P(OEt) + CH_3-Cl
\end{align*}$$

Scheme 5. Reaction between diethyl trichloro-methyl phosphonate $CCl_3PO(OEt)_2$ and diphenyl methyl phosphinite $Ph_2POCH_3$.

2. Calculation methodology
This study was conducted using Gaussian 09 software[10]. The equilibrium mechanism and geometries of the reaction of diethyl trichloro-methyl phosphonate with diphenyl methyl phosphinite, as well as the transition states corresponding to the two attacks $A_C$ and $A_{Cl}$, were studied via the DFT method using the standard base 6-311G(d,p). We used the B3LYP function in which the exchange energy is calculated by the three-parameter of Becke method and the correlation by Lee, Yang and Parr method [11-21]. The transition states were located and their existence was confirmed by the presence of a single imaginary frequency in the Hessian matrix. The Intrinsic Reaction Coordinate (IRC) [22] was calculated and plotted to show that the transition state is well connected to the two minima of reagents and products. Enthalpy, entropy and free energy values were calculated using standard statistical thermodynamics. It has been established that the DFT calculation method is one of the most efficient for this type of organic molecules [23].

3. Results and Discussion

3.1. Structural and Electronic Properties Studies

3.1.1. Geometrical Parameters of the Reagent
The optimized geometry obtained by the functional B3LYP and the base 6-311G(d,p) and the numbering of the atoms of the most stable conformation of the diethyltrichloro-methylphosphonate $CCl_3PO(OEt)_2$ are shown in Figure 1.
From this optimized structure, we determined the lengths, energies and angles of the bonds involved in this reaction. The results obtained are given in Table 1.

**Table 1.** Geometric parameters (in Angströms and Degrees) optimized by DFT/B3LYP/6-311G(d, p) of the reagent CCl$_3$PO(OME)$_2$.

<table>
<thead>
<tr>
<th>Reagents</th>
<th>CCl$_3$PO(OME)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
<td>Distances</td>
</tr>
<tr>
<td>Distances and energies between bound atoms</td>
<td>R(1,2)</td>
</tr>
<tr>
<td></td>
<td>R(1,3)</td>
</tr>
<tr>
<td></td>
<td>R(1,22)</td>
</tr>
<tr>
<td></td>
<td>R(1,4)</td>
</tr>
<tr>
<td>Valence angles formed by three bound atoms</td>
<td>A(1,2,3)</td>
</tr>
<tr>
<td></td>
<td>A(2,1,4)</td>
</tr>
<tr>
<td></td>
<td>A(2,1,22)</td>
</tr>
<tr>
<td></td>
<td>A(3,1,4)</td>
</tr>
<tr>
<td></td>
<td>A(3,1,22)</td>
</tr>
<tr>
<td></td>
<td>A(4,1,22)</td>
</tr>
</tbody>
</table>

The results obtained show that the chlorine atoms of polyhalogenoalkane CCl$_3$PO(OME)$_2$ do not have the same reactivity to the most reactive site of the phosphorus compound (Ph)$_2$POCH$_3$.

### 3.1.2. Electronic Properties

Mulliken charges arise from the Mulliken Population Analysis (MPA) [24] and provide a means of estimating partial atomic charges from calculations carried out by the DFT/B3LYP/6-311G(d,p). Atomic charges were also determined using Natural Population analysis (NPA) [25] using the B3LYP/6-311G(d,p) level. All net charges of the most reactive polyhalogenoalkane CCl$_3$PO(OME)$_2$ sites calculated by the method DFT/B3LYP/6-311G(d,p) was presented in Table 2. A review of the distribution of these net charges revealed the following findings:

- The carbon atom is an electron-rich site because its net charge is negative
- The three chlorine atoms are electron-deficient sites because their positive charges are unevenly distributed over them due to the difference in their chemical environment.

We deduce from this analysis that carbon is defined as a nucleophilic donor while chlorine is more active against nucleophilic attack.

**Table 2.** Net charges of the most reactive polyhalogenoalkane CCl$_3$PO(OME)$_2$ sites calculated by DFT/B3LYP/6-311G(d,p).

<table>
<thead>
<tr>
<th>Reagents</th>
<th>CCl$_3$PO(OME)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atoms</td>
<td>C$_1$</td>
</tr>
<tr>
<td>Natural charges (NPA)</td>
<td>-0.494</td>
</tr>
<tr>
<td>Mulliken charges (MPA)</td>
<td>-0.559</td>
</tr>
</tbody>
</table>
3.2. Study of frontier orbitals

The concept of frontier orbitals is a useful tool to analyze the reactivity of molecules in terms of interactions of molecular orbitals of reactants. Indeed, this concept simplifies the problem by considering only the most important interactions [26]. During the interaction between two reagents, the orbitals considered are the HOMO (Highest Occupied Molecular Orbitals) of one and the LUMO (Lowest Vacant Molecular Orbitals) of the other. These frontier orbitals are chosen so that the energy gap \((E_{\text{LUMO}} - E_{\text{HOMO}})\) between them is as low as possible [27]. In general, the closer the orbitals of the reagents are, the stronger the interaction between these orbitals, the more the stabilizing effect increases. We studied here the reaction of diethyl trichloro-methylphosphonate \(\text{CCl}_3\text{PO(OEt)}_2\) with diphenyl methyl phosphinite \(\text{Ph}_2\text{POCH}_3\) according to Scheme 2. Using the calculation method DFT/B3LYP/6-311G(d,p), we calculated the energy gap \((E_{\text{LUMO}} - E_{\text{HOMO}})\) for the two possible combinations between the two reagents. The goal of this part of our studies was to enhance the understanding of the reactivity of diphenyl methyl phosphinite to diethyl trichloro-methylphosphonate. As shown in Figure 2, the orbital diagram provides a good qualitative indication of the reactivity of our system. The main interaction is found between the LUMO of diethyl trichloro-methyl phosphate and the HOMO of diphenyl methyl phosphinite.

![Energy gap between nucleophilic HOMO and electrophilic LUMO calculated by B3LYP/6-311G(d,p).](image)

Figure 2. Energy gap between nucleophilic HOMO and electrophilic LUMO calculated by B3LYP/6-311G(d,p).

The location of the molecular orbitals as well as the energy gap between HOMO of diphenyl methyl-phosphinite (nucleophilic donor) and LUMO of diethyl trichloro-methyl phosphonate (electrophilic acceptor) calculated by B3LYP/6-311G(d,p) are given in Figure 2. From the analysis of the diagram in Figure 2 we conclude that orbital is highly condensed at the phosphorus atom while the LUMO is condensed at the chlorine atom. This indicates that the nucleophilic attack of the phosphinite is mainly carried on the chlorine atom. The analysis of the reaction for the two modes of attack \((A_C\) and \(A_{Cl}\)) correctly explains the experimentally observed regioselectivity [8].

3.3. Analysis of overall reagent properties

In order to highlight the nucleophilic donor or electrophilic acceptor character of the two reagents, we have calculated the energy gaps between HOMO and LUMO of the reagents. The results of this study are shown in Table 3. The results show that the gap \(|E_{\text{HOMO(Ph}_2\text{POCH}_3)} - E_{\text{LUMO}}|\) is smaller than the gap \(|E_{\text{HOMO}} - E_{\text{LUMO(Ph}_2\text{POCH}_3)}|\) and therefore diphenyl methyl phosphinite acts as a nucleophilic donor while diethyl trichloro-methyl phosphonate serves as an electrophile acceptor. The theoretical study, dedicated to the calculation of energy
differences $HOMO/LUMO$ the $Ph_2POCH_3$ and $CCl_3PO(OEt)_2$ allows to predict the NED (Normal Electron Demand) or IED (Inverse Electron Demand) character of the interaction between these reagents. It is important to note here that the global indices defined in the framework of the conceptual DFT/B3LYP [28] are efficient tools to study the reactivity of polar interactions. The global static properties namely: electronic chemical potentials $\mu$, chemical hardness $\eta$, global electrophilicity indices $\omega$ and global nucleophilicity indices $N$ of diphenyl methyl phosphinite and trichloromethyl phosphonate are chemical properties that allows to analyze the reactivity of the reagent sites. In order to highlight the electrophile/nucleophile character of the reagents, we calculated the electronic chemical potential $\mu$ and the global hardness $\eta$. These two statistical quantities can be calculated from the energies of the $HOMO$ and $LUMO$ molecular orbital frontiers. They are given as $\mu = \frac{E_{HOMO} - E_{LUMO}}{2}$ and $\eta = E_{LUMO} - E_{HOMO}$ respectively [29].

The global electrophilicity index $\omega = \frac{\mu^2}{2\eta}$ [30] is also defined as the energy stabilization due to charge transfer. It has been shown that the nucleophilicity of a molecule can be related to its ability to neglect its electron density [31].

The nucleophilicity index $N$ is expressed as a function of the $HOMO$ energy of tetracyano-ethylene (TCE) in the form $N = E_{HOMO(TCE)} - E_{HOMO}$ [32]. Table 4 gives the energies $HOMO$ and $LUMO$, electronic chemical potential $\mu$, hardness $\eta$, global electrophilicity $\omega$, global nucleophilicity $N$ and the global electrophilicity gap $\Delta \omega$ of the reagents $CCl_3PO(OEt)_2$, $(EtO)_3P$ and $CCl_3PO(OEt)_2$.

$E_{HOMO(TCE)} = -9.368 \text{ eV}$ calculated by DFT/B3LYP/6-311G (d,p).

$\Delta \omega = \omega(CCl_3PO(OEt)_2) - \omega(Ph_2POCH_3)$

### Table 3: Energy gap between the two possible combinations $HOMO/LUMO$ for diethyltrichloro-methyl phosphonate $CCl_3PO(OEt)_2$ and diphenyl methyl phosphinite $Ph_2POCH_3$ (the eV values).

<table>
<thead>
<tr>
<th>Reagents</th>
<th>$E_{LUMO}$</th>
<th>$E_{HOMO}$</th>
<th>$E_{HOMO} - E_{LUMO}$</th>
<th>$E_{HOMO} - E_{LUMO}(Ph_2POCH_3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Ph_2POCH_3$</td>
<td>-0.899</td>
<td>-6.131</td>
<td>4.7</td>
<td>7.438</td>
</tr>
<tr>
<td>$CCl_3PO(OEt)_2$</td>
<td>-1.431</td>
<td>-8.337</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

### Table 4. $HOMO$ and $LUMO$ energies, electronic chemical potential $\mu$, hardness $\eta$, global electrophilicity $\omega$, global nucleophilicity $N$ and the global electrophilicity gap $\Delta \omega$ of the reagents $CCl_3PO(OEt)_2$ and $CCl_3PO(OEt)_2$ (the values in eV).

<table>
<thead>
<tr>
<th>Reagents</th>
<th>$E_{LUMO}$</th>
<th>$E_{HOMO}$</th>
<th>$\mu$</th>
<th>$\eta$</th>
<th>$\omega$</th>
<th>$N$</th>
<th>$\Delta \omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CCl_3PO(OEt)_2$</td>
<td>-1.431</td>
<td>-8.337</td>
<td>-4.884</td>
<td>6.906</td>
<td>1.727</td>
<td>1.031</td>
<td>..</td>
</tr>
<tr>
<td>$Ph_2POCH_3$</td>
<td>-0.899</td>
<td>-6.131</td>
<td>-3.515</td>
<td>5.232</td>
<td>1.180</td>
<td>3.237</td>
<td>0.547</td>
</tr>
</tbody>
</table>

Analysis of the data given in Table 4 shows that diethyl trichloro-methyl phosphonate acts as an electrophilic acceptor while diphenyl methyl phosphinite serves as a nucleophilic donor. Indeed, diethyl trichloro-methyl phosphonate has the highest electrophilicity index ($\omega = 1.727$ eV) and the lowest nucleophilicity index ($N = 1.031$ eV). In addition, the chemical electron potential of the reagent $Ph_2POCH_3$ is at a higher energy value than that of diethyltrichloro-methyl phosphonate ($\mu = -4.884$ eV), i.e. a stream of electrons flowing from $Ph_2POCH_3$ to $CCl_3PO(OEt)_2$ will stabilise the system. The nucleophilicity of diphenyl methyl phosphinite and the electrophilicity of diethyltrichloro-methyl phosphonate have been well confirmed, implying that the electron transfer will be accomplished to the diethyl trichloro-methyl phosphonate. In conclusion, in this reaction diethyl trichloro-methyl phosphonate acts as an electrophile. In addition, the small difference in electrophilicity $\Delta \omega$ between $CCl_3PO(OEt)_2$ and $Ph_2POCH_3$ reagents indicates a low polar character.
3.4. Thermodynamic study

We have studied the reaction of diethyl trichloro-methyl phosphonate $CCl_2PO(OEt)_2$ with diphenyl methyl phosphinite $Ph_2POCH_3$ according to Figure 2. Using the calculation method DFT/B3LYP/6-311G(d,p), we determined the energy variations $\Delta E_r$, enthalpy $\Delta H_r$, free enthalpy $\Delta G_r$ of the formation reaction of the products $P_C$ and $P_{Cl}$. The values of these different thermodynamic quantities have been grouped together in Table 5. The aim of this part of our studies is to enhance understanding the reactivity of diphenyl methyl phosphinite with diethyl trichloro-methyl phosphonate.

Table 5: Calculated values (Kcal/mole) of the variations of reaction energy $\Delta E_r$, of the variations of reaction enthalpy $\Delta H_r$ and of the variations of free reaction enthalpy $\Delta G_r$.

<table>
<thead>
<tr>
<th>Systems</th>
<th>Product</th>
<th>$\Delta H_r$</th>
<th>$\Delta E_r$</th>
<th>$\Delta G_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(Ph)_2POCH_3 + CCl_2PO(OEt)_2$</td>
<td>$P_C$</td>
<td>-14.843</td>
<td>-15.845</td>
<td>-12.001</td>
</tr>
<tr>
<td></td>
<td>$P_{Cl}$</td>
<td>-46.238</td>
<td>-47.081</td>
<td>-44.397</td>
</tr>
</tbody>
</table>

As shown in Table 4, the free enthalpy variations $\Delta G_r$ of the reactions regardless of the attack mode are all negative. Therefore, these reactions are spontaneous and thermodynamically favored. Moreover, we have noticed that the value of the variation in free enthalpy of the reaction $\Delta G_r$, which corresponds to the formation of the compound, $P_{Cl}$, is greater in absolute value than $\Delta G_r$ of the reaction for the formation of the compound $P_C$. We note that the formation of the product $P_C$ which results from an attack on the carbon $A_C$ is thermodynamically disadvantaged compared to the formation of the compound $P_{Cl}$. The free enthalpy of formation of the latter is greater in absolute value than that of the product $P_C$. This shows that the most favourable site of attack is halogen Cl instead of carbon. We also found that the value of $\Delta E_r$ which corresponds to the reaction of formation of the $P_{Cl}$ compound is greater in absolute value than that of the reaction of formation of the $P_C$ compound. This again confirms that the most favorable site of attack is the chlorine atom.

3.5. Kinetic study of the attack modes ($A_C$ and $A_{Cl}$)

In order to highlight the type of nucleophilic attack on the phosphorus atom of $Ph_2POCH_3$ on $CCl_2PO(OEt)_2(A_C$ or $A_{Cl}$), we determined the reagent energies, the product energies and the energies of the transition states (TS$_{Cl}$ and TS$_{C}$) of the reaction of $CCl_2PO(OEt)_2$ with $Ph_2POCH_3$. Figure 3 shows the energy profile for the reaction between diethyl trichloro-methyl phosphonate and diphenyl methyl phosphinite. The area of the potential energy SEP (the energy that depends on the geometry of a system, i.e. spatial coordinates) relative to the two modes of attack shows that: the energy of the transition state corresponding to the attack on the chlorine atom TS$_{Cl}$ is 7 Kcal/mol below the energy of the transition state corresponding to the attack on the carbon TS$_{C}$ (Figure 3). The activation energies corresponding to the two modes of attack are $\Delta E_{Cl}^a = 40$ Kcal/mol for $A_C$ and $\Delta E_{Cl}^a = 33$ Kcal/mol for $A_{Cl}$. Therefore, the attack on the chlorine atom is kinetically more favored than the attack on the carbon atom.
Figure 3. Energy profile in (Kcal/mol) for the reaction between diethyl trichloro-methyl phosphonate and diphenyl methyl phosphinite.

Otherwise, the structure of the transition state associated with the reaction path $A_{Cl}$ is more stable than that associated with the reaction path $A_C$, the two transition state structures optimized by DFT/B3LYP/6-311G(d,p) are also shown in Figure 3. As shown in Figure 4, the diphenyl methyl phosphinite tends to react more with chlorine than with carbon because of the difference in length between the $P - Cl$ and $P - C$ bonds at the $d(P - Cl) < d(P - CCl_2)$ transition state.

Figure 4. Bond lengths for the transition states of the reaction of diphenyl methyl phosphinite with diethyl trichloro-methyl phosphonate.

3.6. Analysis of the reaction path (IRC)

In order to ensure that the transition states are correct, we studied the evolution of the molecular system along the reaction path between diphenyl methyl phosphinite and diethyl trichloro-methyl phosphonate. The results obtained are given in Figure 5. When performing the IRC calculation, it is important to ensure that the transition state is related to the minima (reagents and products).
Figure 5: The IRC of the reaction between diphenyl methyl phosphinite and diethyltrichloro-methyl phosphonate calculated by DFT/B3LYP/6-311G(d,p).

We can deduce via this theoretical study that:

- both modes of nucleophilic attack of $\text{Ph}_2\text{POCH}_2$ on $\text{CCl}_3\text{PO(Or)}_2$ ($A_C$ and $A_C'$) are thermodynamically possible. The products obtained from the attack on the chlorine atom are more favoured kinetically and thermodynamically.

- attack on the carbon atom $A_C$ is kinetically disadvantaged due to the very high value of the ratio of the rate constants of the two nucleophilic attack modes ($K_{C1}/K_{C} = 3.327 \times 10^5$).

In order to make all these theoretical results homogeneous and consistent with the experimental results [8], we propose a reaction mechanism whose first step is a nucleophilic attack on the chlorine of $\text{CCl}_3\text{PO(Or)}_2$ leading to the product $P_1$ ion pair. The carbanion $(\text{EtO})_2\text{PO(Cl)}_2^-$ that is sufficiently stable can exchange with chlorine and give the other pair of $P_2$ ions as it can attack the phosphonium ion and give the product IV according to the Arbusov reaction (3) (Scheme 6).

![Scheme 6: Proposed reaction mechanism for the reaction of $\text{Ph}_2\text{POCH}_2$ with $\text{CCl}_3\text{PO(Or)}_2$.](image-url)
4. Conclusion

In this work, we have demonstrated by the DFT method via the standard base 6-311G(d,p) and the functional B3LYP, by determining the variation of free enthalpies $\Delta G_{r}$, whatever the mode of attack of the phosphorus ($A_{C}$ and $A_{P}$) on $\text{CCl}_3\text{PO(OEt)}_2$, the corresponding variations of free enthalpies $\Delta G_{r}$ are negative. This shows that these nucleophilic attacks are thermodynamically possible. The calculation of the global indices shows that the reagent $\text{Ph}_2\text{POCH}_3$ acts as nucleophilic donor and the diethyl trichloro-methyl phosphonate $\text{CCl}_3\text{PO(OEt)}_2$ serves as electrophilic acceptor. The difference in electrophilicity $\Delta \delta$ is small, we are talking about a non-polar process. The reaction for the formation of product $P_{Cl}$ is very exothermic, showing that this reaction is more favored because the products formed are stable and their formation releases energy. The location of the molecular orbitals $\text{HOMO}$ of diphenyl methyl phosphinite and $\text{LUMO}$ of diethyl trichloro-methyl phosphonate indicates that the phosphorus atom is the nucleophilic centre, while chlorine is the electrophilic site of $\text{CCl}_3\text{PO(OEt)}_2$. Thermodynamic and kinetic studies show that the stable products of the reaction of diethyl trichloro-methyl phosphonate $\text{CCl}_3\text{PO(OEt)}_2$ with diphenyl methyl phosphinite $\text{Ph}_2\text{POCH}_3$ are the products from the attack on the halogen Cl.

References


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