ARTICLE

A Molecular Electron Density Theory Study of the Mechanism of the Reaction Between Bromotrichloromethane and Triethylphosphite.

M.E. Belghiti

ABSTRACT: In present study we employed the method to determine certain thermodynamic descriptors, transition states, global reactivity Indicatorlike the energies of the highest occupied and lowest unoccupied molecular orbitals (, respectively), the difference between the two( ) gaps, electronic chemical potential μ, chemical hardness , global electrophilicity index and global nucleophilicity index N, and local reactivity like the electrophilic and nucleophilic Parr functions, as the most relevant indices forof the reaction between bromotrichloromethane and triethylphosphite . In vibrational frequencies calculation, no imaginary frequency was shown. Our results show that triethylphosphite behaves as a nucleophile, while bromotrichloromethane behaves as an electrophile. The nucleophilic attack takes place preferentially at the halogen(Br or Cl) atom of the bromotrichloromethane rather than at the carbon atom. The reaction is exothermic, polar and regioselective. These results are comparable to those obtained experimentally.

Key Words: *Bromotrichloromethane; ; Reactivity indices;Parr functions; Transition state; Triethylphosphite.*

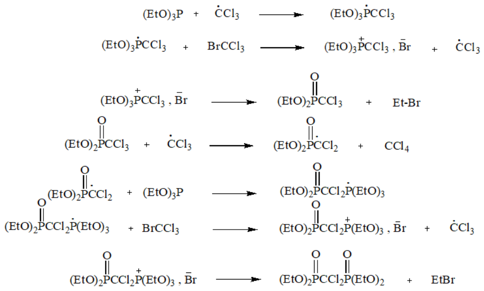
INTRODUCTION

The reaction between the trivalent phosphorus derivates and certain polyhalogenoalkanes leads to the formation of a number of products[1,2], some of which have numerous applications in industry [3]and biology [4]. The nature of the products obtained varies considerably depending on the structure of the reactants, which suggests that there are significant variations in the reaction mechanism [5,6].

The reactivity of trivalent phosphorus with regard to polyhalogenomethanes in general and tetrachloromethane in particular has already been the subject of several studies [7,8].This reactivity varies according to the nature of the substituents carried by the phosphorus atom and increases as its electro positivity increases.

$$(i-PrO)_3P \rangle (EtO)_3P \rangle (MeO)_3P \rangle (EtO)_2POPh \rangle (PhO)_2POEt \rangle (PhO)_3P$$

A number of reaction mechanisms have been proposed to describe these reactions[9-11]. Kamai and Egorova were the first to study the reaction between triethylphosphite(EtO)_3 PandBrCCl_3, in 1946[12].At room temperature, this reaction is extremely vigorous and is complete in a few minutes. According to Griffin [13], and to Cadogan and Bunyan [14],the reaction involves a radical chain mechanism as shown below:



These authors present this reaction mechanism without describing how the trichloromethyl radical is formed fromBrCCl_3at the initial stage.In order to clarify this, Bakkas [15]carried out a controllable thermic reaction between triethylphosphiteand at 60°C,using heptane as solvent. The reaction led to the formation of a very complex mixture. He proposed an ionic reaction mechanism starting with mono-electron transfer from phosphite to bromotrichloromethane.However nucleophilic attack at the halogen, whether this is chlorine or bromine, appears the most probable in view of the results obtained in our laboratory.

At the same time, a number of theories have been put forward to explain chemical reactivity in general. The most widely used are transition state theory [16]and frontier molecular orbital theory [17]. Recently new chemical concepts and reactivity indices derived from density functional theory (DFT) have emerged as powerful tools for the prediction of reactive sites in molecular systems [18,19]. Some of these concepts are already familiar to chemists, e.g. electronic chemical potential μ and electronegativity . New concepts such as electrophilicity and chemical hardness have been derived from the fundamental equations of DFT.

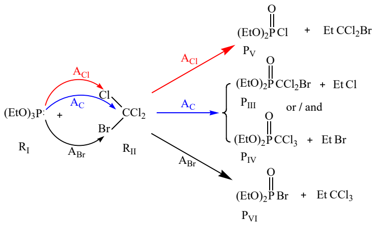


Figure 1.Reaction betweenbromotrichloromethaneBrCCl_3andtriethylphosphite(EtO)_3 P.

Our aim in this work was to carry out a theoretical study, using basis set ,of the reaction between BrCCl_3 and(EtO)_3 P in order to determine whether the phosphorus atom, which behaves here as a nucleophile, attacks the bromine(A_Br), the chlorine (A_Cl) or the carbon(A_C) of the bromotrichloromethane, which behave as electrophilic centres(Fig.1).

Method of calculation

FWe employed the method[20,21] to study the mechanism and equilibrium

---

Laboratory of Nernst Technology, 163 Willington Street, Sherbrook, J1H5C7, Quebec, Canada.

Correspondence: M.E. Belghiti,Laboratory of Nernst Technology, 163 Willington Street, Sherbrook, J1H5C7, Quebec, Canada., Tel/Fax: +1(819)6400530 : E-mail: elbelghiti10@gmail.com

Received: June 29, 2020, Accepted: July 10, 2020, Published: July 29, 2020

geometries of the reaction between bromotrichloromethane and triethylphosphite, as well as the transition states corresponding to the three attacksA_C,A_BrandA_Cl. We localised the transition states and confirmed their existence by the presence of a single imaginary frequency in the Hessian matrix. The Intrinsic Reaction Coordinate (IRC) [22]was calculated and plotted in order to show that the transition stateis indeed linked to the two minima (reactantsand products). Enthalpy, entropy and free energy were calculated using standard statistical thermodynamics. All calculations were carried out using the level of theorywith Gaussian 09Wsoftware[23].

In order to determine the electrophilic/nucleophilic nature of the reactants, we calculated the µ (electronic chemical potential) and □ (global hardness). These two statistical valuesdirectly extracted from the output files such as the energy of the lowest unoccupied molecular orbital ( ), energy of the highest occupied molecular orbital ( ), as & respectively [24]. The global electrophilicityindex ( )is also defined as the energy stabilisation due to charge transfer[25]. It has been shown that the nucleophilic nature of a molecule can be determined without taking account of its electron density [26]. The nucleophilicity index Nis expressed in terms of the of tetracyanoethylene(TCE)as [27].

The global Reactivity indices were calculated from the energies in the base state of the molecules using the level of theory. Static indices of (local electrophilicity)[28]and (local nucleophilicity) [26] can reliably predict the most favoured reaction between the electrophile and the nucleophilein the formation of a chemical bond between two atoms. Indices of & are given by the expressions & , respectively, where & are obtained by analysis of the Mulliken atomic spin density of the anion and the cation [29].

Results and discussion

Thermodynamicstudy

In order to understand the reactivity of triethylphosphite□(EtO)□_3 Pin relation to bromotrichloromethane □BrCCl□_3(Fig.1) we employed level of theoryto calculatethe variations in reaction energy□ΔE□_r, reaction standard enthalpy□ΔH□_rand reaction free enthalpy ΔG_rcorresponding to the formation of the compounds P_III ,P_IV ,P_V and P_VI(Table 1).

		$\Delta(TS_C - TS_{Cl})$kcal/mol	$\Delta(TS_C - TS_{Br})$kcal/mol	$\Delta(TS_{Br} - TS_{Cl})$kcal/mol	K_{Cl}/K_C	K_{Br}/K_C
$(EtO)_3P + BrCCl_3$	A_{Cl}/A_C	18.83	…..	6.27	6.38 10^{13}	…..
	A_{Br}/A_C	…..	12.55		…..	1.59 10^9

Table 1.Calculated valuesof the reaction energy□ΔE□_r, reaction standard enthalpy□ΔH□_r and reaction free enthalpyΔG_r (Kcal□(mol).)

As Table 1 shows, □ΔG□_ris always negative, whatever the mode of attack. This means that these reactions are not only possible, but also thermodynamically preferred. The value of □ΔG□_r corresponding to the formation ofcompoundP_VIis greater in absolute terms than that corresponding to the formation of compoundP_V, showing that compoundP_VIis more stable thermodynamicallythan compoundP_Vand that the phosphorusattacksthe bromine rather than the chlorine.

We found that the formation of compoundsP_IIIand P_IVwhich result from an attackat the carbonatom□(A□_C) is thermodynamicallyless favoured than the formation of compoundsP_VandP_VI. Free enthalpy of formation of these last two is greater in absolute terms than that of productsP_IIIandP_IV, showing that the most favourable site for the attackis the halogen (Cl or Br) rather than the carbon.

We also found that the value of□ΔE□_rcorresponding to the formation of compoundP_VIis greater in absolute terms than that corresponding to the formation of compoundP_(V), which confirms that the most favoured site of attackis the bromine atom.

Frontier molecular orbitals

[31]M. E. Belghiti, A. Dafali, Y. Karzazi, M.Bakass, H. Elalaoui-Elabdallaoui, L. O. O lasunkanmie, E. E. Ebenso., Applied Surface Science, 491 (15) (2019) 707-722.

[32]M.E. Belghiti, S. Echihi, A. Mahsoune, Y. Karzazi, A. Aboulmouhajir, A. Dafali, I. Bahadur., Journal of Molecular Liquids., 261 (2018) 62-75.

Frontier molecular orbitals theory(FMOT) requires that the orbitals to be considered in the interaction between two molecules should be the (nucleophile) of one molecule reacting with the (electrophile) of a second molecule chosen in such a way that the energy difference is as small as possible [30]. The & are directly obtainable, alongside with the ( ) from the computational output. The has served as a simple measure of kinetic stability[31]. A molecule with a small energy gap value is chemically reactive[32].Pearson showed that the energy gap value represents the chemical hardness of the molecule.3,5 Zhou and Parr discussed the chemical reactivity of cyclic p-electronic systems using the of the reactant and the transition state.The & of triethylphosphite,and bromotrichloromethane are calculated by level of theoryand depicted in Fig.2.The orbital diagram (Fig.2) gives a good qualitative indication of the reactivity between the LUMO of and the HOMO of .

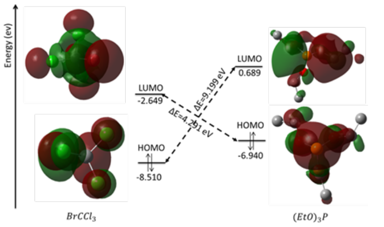


Figure 2.Orbital diagram of triethylphosphite and the bromotrichloromethane□BrCCl□_3.

Localisation of the molecular orbitals of triethylphosphite and bromotrichloromethane (Fig.2) shows that the is very concentrated around the phosphorus atom while the is concentrated around the bromine atom, indicating that the nucleophilic attack by the phosphorus atom takes place primarily at the bromine atom.

Chemical concepts and reactivity indices based on DFT

Predicting the nature of the reaction mechanism and the electrophilic/nucleophilic character of the reaction

In order to determine which reactant behaves as a nucleophile (electron donor) and which as an electrophile (electron acceptor), we calculated the energy gap for each pair of reactants (Table 2).

Reactants	E_{LUMO}	E_{HOMO}	$\lvert E_{HOMO} - E_{LUMO(BrCCl_3)} \rvert$	$\lvert E_{HOMO(BrCCl_3)} - E_{LUMO} \rvert$
$(EtO)_3P$	0.689	-6.940	4.291	9.199
$BrCCl_3$	-2.649	-8.510		

Table 2. Difference between the two possible energy ( ) gaps combinations for triethylphosphite and the polyhalogenoalkaneBrCCl3 (eV).

From the Table 2, its can be seen that the |E_HOMO-E_(LUMO(Br□CCl□_3)) |gap are smaller than the

|E_HOMO(□BrCCl□_3) -E_LUMO |gap and thusthat triethylphosphitebehaves as a nucleophile in this reaction, while bromotrichloromethane behaves as an electrophile.

Theoretical study of the|E_HOMO-E_LUMO |differences of and allows us to predict whether the interaction between these two reactants is NED (Normal Electron Demand) or IED (Inverse Electron Demand) in character. Global indices based on conceptual DFT/B3LYP [18]are effective tools for studying the reactivityof polar interactions.

We analysed the reactivity at various sites in the reactants using the static global propertiesof triethylphosphite and bromotrichloromethane, namelyelectronic chemical potential µ,chemical hardness □,global electrophilicityindex □and global nucleophilicityindex N (Table3).

Reactants	E_{LUMO}	E_{HOMO}	μ	η	ω	N	$\Delta\omega$
$(EtO)_3P$	0.689	-6.940	-3.125	7.629	0.640	2.428	….
$BrCCl_3$	-2.649	-8.510	-5.579	5.861	2.655	0.858	2.015

Table 3. electronic chemical potentialμ,Hardness, electrophilicity andglobal nucleophilicityNof and BrCCl_3.

We found thatBrCCl_3behave as electrophile (electron acceptor), whiletriethylphosphitebehaves as a nucleophile (electron donor). BrCCl_3has the highest electrophilicityindex(=2.655 eV)and the lowest nucleophilicityindex(N=0.858 eV). Furthermore, the electronic chemical potential of

(EtO)_3 Pis higher than that of BrCCl_3 (μ=- 5.579 eV), indicatingthat electrons are transferred from (EtO)_3 Pto BrCCl_3.

The difference in electrophilicity(Δ=2.015 eV)between BrCCl_3and(EtO)_3 Pindicates that this reaction is highly NED in character.

Predicting the local reactivity of thereactants

According to Chattaraj's polar model[31,32], the local philicity indices_Kand N_Kcan reliably predict the most favoured interaction between two polar centres. The most favoured interactionis that associated with the highest local electrophilicityindex_Kof the electrophileand the highest local nucleophilicityindexN_Kof the nucleophile.

We used DFT/B3LYP/6-311G(d,p) to calculate the Parr functions (&)of the two reactants, and from these we calculated the values of local nucleophilicity N_Kfor(EtO)_3 Pand local electrophilicity _Kfor BrCCl_3,in order to predict the most likely electrophile/nucleophileinteraction throughout the reaction pathway, and thus to explain the regioselectivity of the reaction. Table 4 shows the most active sites in the reactants. The bromine atomBr is the most electrophilicsite in BrCCl_3 (_Br=0.345 eV), while the phosphorusatom P is the mostnucleophilic site in (EtO)_3 P (N_P=0.990 eV). We can therefore deduce that the most favoured reaction takes place between the phosphorusatom P of (EtO)_3 Pand the bromine atom Br of BrCCl_3.

	$(EtO)_3P$				$BrCCl_3$				
	P_1	O_2	O_3	O_4	C_1	Br_2	Cl_3	Cl_4	Cl_5
P_K^+					0.236	0.345	0.139	0.140	0.140
P_K^-	0.399	0.026	0.275	0.222					
ω_K					0.626	0.915	0.369	0.371	0.371
N_K	0.990	0.064	0.682	0.551					

Table4. Parr functions (&), localelectrophilicity_Kand local nucleophilicityN_K of and BrCCl_3using DFT at the level of theory.

Electrostatic potential

3D-distribution of MEPs is highly useful in predicting the reactive sites behavior of the triethylphosphite and the polyhalogenoalkane. Weanalysed the MEPs and found that our results confirmed the electrophilic nature of bromine.The electrostatic potential at a pointris defined as the electrostatic interaction energy of an imaginary charge of+1.0 a.u with all the nuclei and electrons in a molecular system. This is expressed as:

$$V_{PES}(r) = \sum_A \frac{Z_A}{|R_A - r|} - \int \frac{p(r')}{|r' - r|} dr'$$

Areas of negative electrostatic potentialare susceptible to electrophilic attack, while areas of positive potential are more susceptible to nucleophilic attack[33-35]. Theoretical determinationof electrostatic potentialusing DFT at level are summarized in Figure3, shows that the main interaction takes place between the bromine, which is the most electrophiliccentre of BrCCl_3, and the phosphorusof (EtO)_3 P, which is the most reactive and nucleophilic s

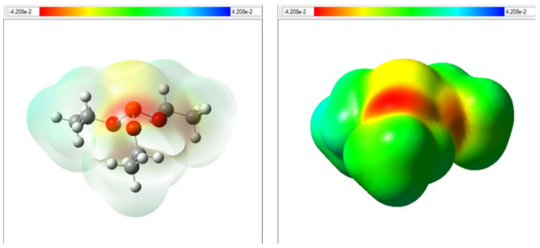
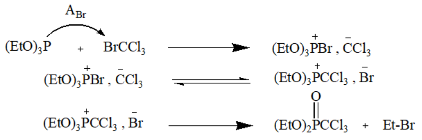


Figure 3.Molecular Electrostatic Potentials (MEPs)surfaces of(EtO)_3 P andBrCCl_3using DFT at the level of theory. (Red: most negative electrostatic potential,Blue: most positive electrostatic potentialand Green: moderately positive electrostatic potential)

Example of a nucleophilic attackat the bromine atom

(EtO)_3 Preacts with BrCCl_3to give a complex mixture of phosphorus-containing and polyhalogenated products, the exact composition of which depends on the experimental conditions, and in particular on the mode of attackof the phosphorusonBrCCl_3 (A_(Br,) A_Cl,or A_C). The simultaneous formation of bromateand chlorate phosphorus derivatives, respectively[(EtO)_2 P(O)Br,(EtO)_2 P(O) CBrCl_2]and[(EtO)_2 P(O) CCl_3,(EtO)_2 P(O)Cl],shows that these modes of attackare competitive.

For example, the formation of trichloromethylphosphonate(EtO)_2 POCCl_3results from a nucleophilic attack on the bromine atom as shown in the following diagram:



The phosphite tends to react with brominerather than with chlorinebecause of the energy difference between theC-BrandC-Clbonds [36] (Table5). The strength of the bond is directly related to its length: the longer the bond, the weaker it is.

Molecules	Bonds	Distances(Å)	Bondenergies(Kcal/mol)
CCl_4	$C-Cl$	1.9872	490.0347
$BrCCl_3$	$C-Cl$	1.7888	491.9235
	$C-Br$	1.9743	437.4369
Br_2CCl_2	$C-Cl$	1.9879	493.8625
	$C-Br$	1.9837	439.8653

Table5.Interatomicdistanceandbondenergyofcertainpolyhalogenomethanes calculated by B3LYP/6-311G(d,p)basis set.

Kinetic study of the nucleophilicattack of (EtO)_3 Pon BrCCl_3 (A_(C),A_Cl and A_Br)

In order to determine the nature of the nucleophilic attack by the phosphorusatom on BrCCl_3 (A_Cl,A_C and A_Br), we calculated the energy of the reactants and the products formed, relative energy, energy of the transition states(TS_(C),TS_Cl and TS_Br), energy difference of the transition states and the ratiosK_ClK_C and K_BrK_C of the reactions betweenBrCCl_3and (EtO)_3 P.

Comparison of the three nucleophilic modes of attack by the phosphorusatom on the bromine, chlorine and carbon atoms(A_(C),A_Cl and A_Br)

The potential energy surface corresponding to the two nucleophilic modes of attackon the bromine and carbonatoms during the reaction between BrCCl_3and (EtO)_3 P(Figure 4) shows that the energy of the transition state correspondingto the bromine attack(TS_Br)is 0.0118a.u. (equivalent to 7.4046 Kcal/mol) lower thanthatcorresponding to the carbonattack(TS_(CCl_3)). The activation energies corresponding to the two modes of attackare 43.4675kcal/mol for A_Brand 50.9035kcal/mol forA_C. It follows thatthe attackon the bromine atomis kinetically favoured relative to the attackon the carbon atom.

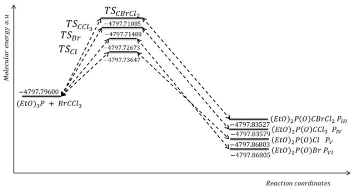


Figure 4.Energy profile in a.u.of the reaction betweenBrCCl_3and(EtO)_3P.

Figure 4 shows that for the twomodes of attack(A_Cl and A_C)the transition state energy for the chlorine attack(TS_Cl)is 0.0256a.u.higherthatfor the carbon attack (TS_(BrCCl_2))(equivalent to 16.0642 kcal/mol). Activation energies for the two modes of attackare 37.3556kcal/mol for A_Cland 53.4324kcal/mol for A_C. This indicates that the attackon the chlorineatom is preferred to the attackon the carbon atom.The transition state(TS_Cl) (corresponding to the attackon the chlorine atom) for an activation energy of 37.3556 kcal/molis 6.1119 kcal/mol lower than(TS_Br) (corresponding to the attack on thebromine atom). This shows that the productsresulting from the attack at the chlorine atom arekinetically preferred.The four transition state structures optimized using basis set are depicted in Fig.5.

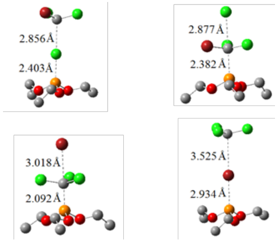


Figure 5.Bond lengths of the transition states in the reaction between

triethyl phosphite and bromotrichloromethane.

Determination of the reaction pathway (IRC)

We determined the changes in the molecular systemduring the reaction between BrCCl_3and (EtO)_3 P, calculating the intrinsic reaction coordinate (IRC) in order to show that in each case the transition state is indeed linked to the minima of the reactantsand the products.

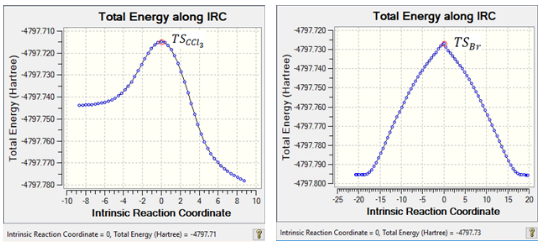


Figure 6.IRC of the reaction betweenBrCCl_3and (EtO)_3 P calculated using DFT/B3LYP/6-311G(d,p)(A_BrA_C).

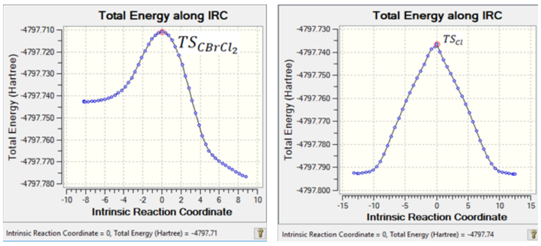


Figure 7.IRC of the reaction between BrCCl_3and (EtO)_3 Pcalculated using DFT/B3LYP/6-311G(d,p)(A_Cl(A_C)).

We can deduce from this theoretical study that :

- the three nucleophilic modes of attack by (EtO)_3 P on BrCCl_3 (A_C ,A_Cl and A_Br) are all thermodynamically possible;
- even though the local electrophilicity of carbon (0.236 eV) is greater than that of chlorine (0.140 eV), the attack at A_C is discouraged by the steric hindrance around the chlorine and bromine atoms;
- the attack on the carbon atom A_C is kinetically unfavorable given the very high ratio of the speed constants of the different nucleophilic modes of attack (K_Cl(K_C and K_Br(K_C)) (Table 6

Table 6 shows that:

- The ratio K_BrK_C is greater than the ratio K_ClK_C , showing that the formation of the products resulting from the attack on the bromine atom is kinetically preferred to the formation of the products resulting from the attack on the chlorine atom. In other words, the substitution of a bromine atom in place of chlorine increases the kinetic constant K_Brrelative to K_Cand K_Cl, confirming that the attack on the bromine atom is more favoured.
- The energy difference Δ(TS_Br-TS_Cl) is smaller than Δ(TS_C-TS_Br) and Δ(TS_C-TS_Br), showing that the products resulting from the attack on the halogen (chlorine or bromine) are kinetically favoured relative to the products resulting from the attack on the carbon atom.

Table6.Energy difference between the transition states and the ratio K_ClK_C and K_BrK_C of the reactions between(EtO)_3 P andBrCCl_3, calculated using DFT/B3LYP/6-311G(d,p).

Conclusion

We used DFT (density functional theory) with the standard base 6-311G(d,p) and the B3LYP functionalto determine the variation in free enthalpy ΔG_r and show that whatever the mode of attackby the phosphorus (ACl, ACand ABr) on BrCCl_3,the corresponding variationsin free enthalpyΔG_rare negative.This shows that these nucleophilic attacks are thermodynamically possible.

Calculation of the global indices shows that(EtO)_3 Pbehaves as a nucleophile whileBrCCl_3behaves as an electrophile.The experimentally determined regioselectivity was also confirmed by the local electrophilicityand nucleophilicityindices kand Nk.

The variation in reaction enthalpyΔHr is highlyexothermicfor the reaction leading to theformation of compoundVI, showing that this reactionis preferred since the products formed are stableand their formation releases energy.

Localisation of the HOMOof (EtO)_3 Pand the LUMO ofBrCCl_3shows that the phosphorusatom is the most nucleophilic centre of(EtO)_3 P, while bromine is the most electrophiliccentre of BrCCl_3.

Calculation of the transition states shows that the kinetic products of the reaction between BrCCl_3and (EtO)_3 Pare formed by the attack on the halogen atomsbromine and chlorine, with a preference for bromine.

REFERENCES

1. Waschbüsch R., Carran J., Savignac, P., Tetrahedron52 (1996) 14199-14216.
2. Barhoumi. A, Zeroual. A, Bakkas. S and El Hajbi. A. Journal of Computational Methods in Molecular Design, 5 (2015) 8-15.
3. Timokhin B. V., Russian Chemical Reviews59 (1990) 193-203.
4. Halazy S., Ehrhard A., Eggenspiller A., Berges-Gross V., Danzin C.,Tetrahedron52 (1996) 177-184.
5. Kosolapoff G. M., J. Am. Chem. Soc.69 (1947) 2112-2113.
6. Dmitriev V. I., Kozlov E. S., Timokhin B. V., Dubenko L. G., Kalabina A. V., ZhurnalObshcheiKhimii50 (1980) 2230-2233.
7. Barhoumi. A, Bakkas. S and El Hajbi. A. Mor. J. Chem. 4 (2016) 639-650.

8. Crofts P. C., Downie I. M.,J. Chem. Soc. (1963) 2559-2560.
9. Kosolapoff G. M.,J. Amer. Chem. Soc.69 (1947) 1002-1003.
10. Bakkas S., Julliard M., Chanon M., Tetrahedron 43 (1987) 501-512.
11. Bakkas S., Mouzdahir A., Khamliche L., Julliard M., PéralezE., Chanon M., Phosphorus,Sulfur and Silicon157 (2000) 211-224.
12. Kamai G., E. GorovaL. P., J. Gen. Chem. (U.S.S.R.)16(1946)1521.
13. Griffin, C. E. chem and ind. (London), (1958) 415.
14. Bunyan P. J., Cadogan J. I. G., J. Chem. Soc.(1962) 2953-2958.
15. Bakkas S., Thèse de Doctorat d'Etat, Université d'Aix Marseille III,(1984).
16. Eyring H., J. Chem. Phys.3 (1935) 107-115.
17. Fukui K., Theory of Orientation and Stereoselection, Springer-Verlag, Berlin / Heidelberg / New York, (1975).
18. Geerlings P., De Proft F., Langenaeker W., Chem. Rev.103 (2003) 1793-1874.
19. Pearson R. G., J. Chem. Ed.76 (1999) 267-275.
20. Lee C., Yang W., Parr R. G., Phys. Rev. B37 (1988) 785-789.
21. Becke A. D., J. Chem. Phys.98 (1993) 5648-5652.
22. Schlegel H. B., Geometry optimization on potential energy surface, in: D. R. Yarkony, (ed.), Modern Electronic Structure Theory, World Scientific Publishing, Singapore, (1995) 459-500.
23. Frisch M. J. et al, Gaussian Inc., Wallingford CT, (2009).
24. Parr R. G., Yang W., Density-functional theory of atoms and molecules, Oxford University Press, New York / Oxford, (1989).
25. Parr R. G., Pearson R. G., J. Am. Chem. Soc.105 (1983) 7512-7516.
26. Pérez P., Domingo L. R., Duque-Noreña M., Chamorro E., J. Mol. Struct. (Theochem) 895 (2009) 86-91.
27. Domingo L. R., Chamorro E., Pérez P., J. Org. Chem.73 (2008) 4615-4624.
28. Domingo L. R., Aurell M. J., Pérez P., Contreras R., J. Phys. A106 (2002) 6871-6875.
29. Domingo L. R., Pérez P., Sáez J. A., RSC Advances3 (2013) 1486-1494.
30. Rivail, J. L., Elémentsde chimie quantique à l'usage des chimistes, Deuxième édition, Savoirs Actuels, Inter-Editions / CNRS Editions, (1994).
31. Ess D. H., Jones G. O., Houk K. N., Adv. Synth. Catal.348 (2006) 2337-2361.
32. Chattaraj P. K., Sarkar U., Roy D. R., Chem. Rev. 106 (2006) 2065-2091.
33. PetrucciR. H., Harwood W. S., HerringG. E., Madura J. D.,General Chemistry: Principles and Modern Applications, 9th Ed., New Jersey, Pearson Education, Inc., (2007).
34. Csizmadia I. G., Theory and Practice of MO Calculations on Organic Molecules, Elsevier, Amsterdam(1976).
35. OxtobyD.W., Gillis H. P., Campion A.,Principles of Modern Chemistry, 6th Ed.,Thomson/Brooks Cole, Belmont, CA (2007).
36. Meyers C.Y., Catalysis in Organic Synthesis (C), Academic Press Inc., London, (1977) 260-278.