ARTICLE

Article 1

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Research Article

Homolytic phosphorylation of unsaturated compounds as a method for the synthesis of organo-Phosphoric

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Abstract : In the structure of olefin, the introduction of halogen, of alkoxy groups acyl and other, influence the process of homolytic addition and performance in the phosphonates. The movement of the double bond toward the center of the molecule of olefin (composed non- saturated) makes it difficulté. The Addition (2-hexene, 2-heptene compared to 1-hexene and 1-heptene) and the cyclohexene is less reactive. The addition of the phosphite in diethyl cyclohexene initiated by UV rays is characterized significantly by the effect of induction. The introduction of the halogen atom (chlorine, fluorine, etc.) increases the reactivity of the olefin. As well as the vinyl chloride reacts with the phosphite of dimethyl to 145-155°C in the presence of peroxides of the alkyl to give β-chloroethyl dimethyl phosphonate with the yield 85%.

Key words: phosphonate, cyclohexene, β-chloroethyl, Alcoxy-acyle

Resume : La structure de l'oléfine, l'introduction d'halogène, de groupes alcoxy-acyle et autres, influencent le déroulement du processus d'addition homolytique et le rendement en phosphonates. Le mouvement de la double liaison vers le centre de la molécule d'oléfine (composé non- saturé) rend difficile l'addition (2-hexène, 2-heptène comparés à 1-hexène et 1-heptène). Le cyclohexène est moins réactif. L'addition du phosphite de diéthyle au cyclohexène initié par les rayons UV est caractérisée de façon significative par l'effet d'induction. L'introduction de l'atome d'halogène (chlore, fluor, etc.) augmente la réactivité de l'oléfine. Ainsi le chlorure de vinyle réagit avec le phosphite de diméthyle à 145-155°C en présence des peroxydes d'alkyle pour donner β-Chloroéthyle diméthyle phosphonate de rendement 85%.

Mots clés : Phosphonate, Cyclohexène, β-Chloroéthyle, Alcoxy-acyle

1. INTRODUCTION

The synthesis of design phosphoric by the method of homolytic phosphorylation of phosphites of dialkyl, phosphines, has been the subject of particular attention[1-5]. The addition reaction includes the homolytic steps, one of which is the initiation takes place in the presence of substances capable of generating, in certain specific conditions, radicals[6-9]. The particular character of the reaction gives an indication of a low relative selectivity, the wide spectrum of isomeric products obtained. During the initiation of the action of light or ionizing emissions, it is appropriate to analyze meticulously the possibility of rupture the homolytic bond because a priori, this fact alone, cannot be considered as the demonstration of homolytic processes. A serious argument in favor of the homolytic mechanism of the reactions of derived from phosphorus may serve the strict dependence of the kinetics of the chain reaction, it has observed in Organic Chemistry[10,11]. In organic chemistry, it is appropriate to have in the idea, that can take place in a parallel manner, several mechanisms, as well homolytic hétérolytiques that leading to the same final products[12-18]. In addition, a slight modification of the conditions of the reaction (concentration, temperature, pressure, uncontrolled waste etc.) is likely to change so well known the importance of such or such other direction, leading to the same products. Mention should be made of such mechanisms in which, the homolytic stages and hétérolytiques are consecutive. With the exception of the cases as well listed, there are reactions to homolytic drop down through the intermediate stages ion-radical or even through an intermediate situation of polarization High. They have traits similar to hétérolytiques process. To study the process of homolytic phosphorylation, it uses the methods known: the chromatographic method (gas/liquid chromatography), paramagnetic resonance, nuclear, chemical polarization of the kernel, ultraviolet and other[18-28]

2. MATERIEL ET METHODES

The study of any chemical process is essential to establish the kinetics, the mechanism and its rules of conduct. Most often, the establishment of the rules of conduct of any reaction passes through the definition of its speed. For a homogeneous reaction, the RK speed is measured by the variation MK of component per unit of time. Either:

$$r_k = \left| \frac{-dmk}{Vd\tau} \right| = \left| \frac{d(\frac{mk}{V})}{d\tau} \right| = \left| \frac{dCk}{d\tau} \right| \quad \text{... (2.1)}$$

Dmk : Variation of the mass of the component;

V : volume ;

dτ : variation of the time ;

Ck : concentration of the component k.

In practice, on the value of RK influence several factors to the number of the most important, we must mention: the temperature T, the pressure p, the concentration of the reacting body, the quantity of initiators etc.

Thus, the equation 2.1 take the form 2.2 and it is called the kinetic equation of the reaction

$$r_k = r_k (x) \qquad \text{or}$$

$$r_k = k_j * \pi * C^{mki}_{Ak} \qquad \dots (2.2)$$

Where kj : rate constant of the reaction;

$m_{1j}, m_{2j}, \dots m_{nj}$: The order of the reaction by the reagents $A_1, A_2, \dots A_k$.

Nevertheless, in practice and in the light of the complexity of the equation 2.3, it adopts the principle of Baudenstein. The task of the definition of the order and thus the speed of the reaction, is reduced to the definition of the order of the component to more small concentration and the Equation 2.3 take the form:

$$\mathbf{r_{kj} = k_j * C^m} \qquad \dots (2.3)$$

Where m : The order of the reaction of the compound at low concentration;

C: its concentration.

Kinetic equations of the process of phosphorylation of vinyl esters and allyl of carboxylic acids : For the purposes of highlighting the rule of conduct of the process of homolytic phosphorylation of allyl and vinyl acetate by the phosphite of dimethyl, the reaction has been conducted at different temperatures; the variation of the concentration of the Esters non saturated in function of time has been determined. The experiments were conducted at 130°, 140°, 150°C with the molar ratios of phosphite of dimethyl: ROAc : (ROAR): tertio-Bu_2O_2 300:100:5.

The chemical equations of the phosphorylation reaction homolytic can be presented in the form

$$r = \frac{dC}{dt} = kC_A^{m_1} * C_B^{m_2} * C_D^{m_3} \qquad \dots(2.4)$$

C_A: concentration of the ester non saturated;

C_B: concentration of dimethyl phosphite (excess)

C_D: concentration of the tertio-Bu_2O_2.

m_1, m_2, m_3 : The order of the reaction, respectively, by the vinyl acetate (allyl acetate etc.), dimethyl phosphite and the tertio-Bu_2O_2.

In the light of the equation 2.4 and under, of the principle of stationary of Baudenstein, the order of the reaction should be that of the Initiator tertio-Bu_2O_2, which is the smallest. However, it has been established that during the transformations, the concentration of this substance has remained virtually unchanged and the equation 2.4. is reduced to the form

$$\mathbf{r = k * C^m = k * C_A^{m_1}} \qquad \dots(2.5)$$

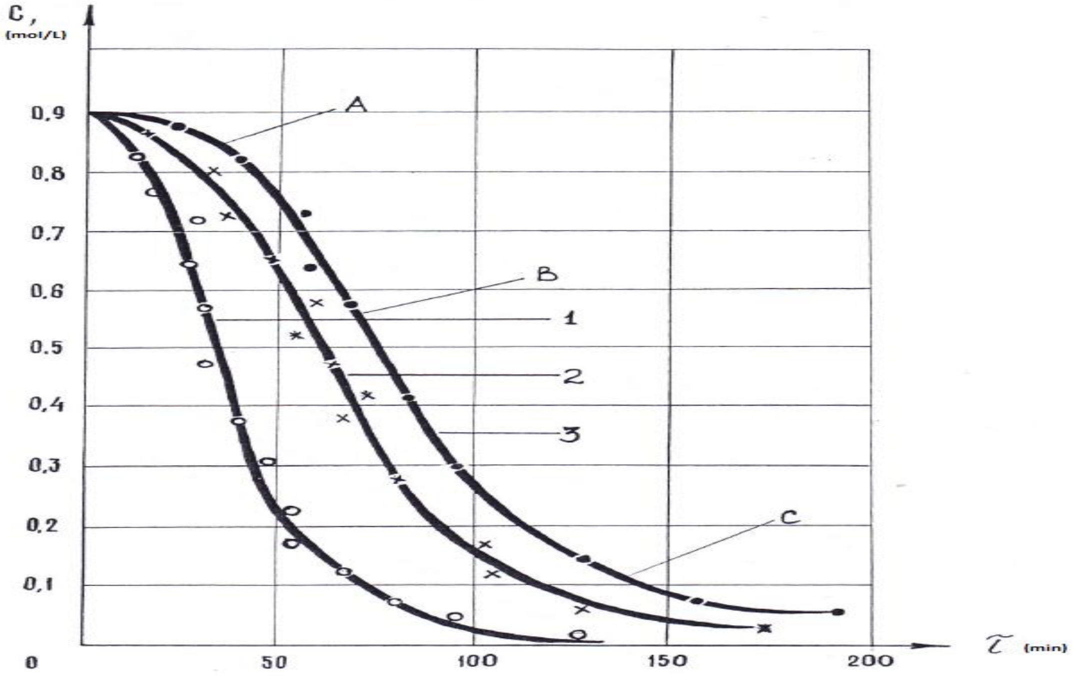
C_A = C - concentration of the ester unsaturated,

$m = m_1$ - The order of the reaction by this compound.

3. RESULTS

Study of the kinetics of the process of homolytic phosphorylation of Compounds, Non- saturated by different methods : By the method of nuclear magnetic resonance, it has been possible to establish the variation of the concentration of the ester is unsaturated in function of the time and in accordance with the equation 2.3, the curve c= F(τ) 2.4.1.1 for a different temperature has been developed From the figure 1, it is clear that the conduct of the reaction of homolytic phosphorylation depends on the temperature. In effect, with the increase of the temperature, the curve **C=F(τ)** tends more and more toward a straight line. There is thus no doubt that the elevation of the temperature in the conditions of the reaction, induces a great speed of decomposition of the Initiator that increases the concentration of radicals at the beginning of the process. This state of things considerably reduces the induction time to finally increase the speed of the addition. The more one can judge the complex character of the process by the form "s" of all curves kinetics, anything that characterizes the radical mechanism of a complex process. If the form "s" of kinetic curves is a serious argument in favor of those that the reaction proceeds by the radical mechanism, this finding in him alone is not sufficient to justify the radical mechanism of the reaction[6].

The quantitative processing of kinetic curves of the **Fig.1** has allowed to determine graphically the order of the reaction. The determination of the order of the reaction, of the constant speed has been made possible by the treatment of kinetic curves of **Figures 2 and 3** and the results are recorded in the **table1.**



1 : 150°C (○) **2** : 140°C (x) **3** : 130°C (●)

Figure 1: kinetic curves of the process of homolytic phosphorylation of the acetate of allyl by the phosphite of dimethyl in the presence of the peroxide of tertio-butyl (method of Nuclear Magnetic Resonance)

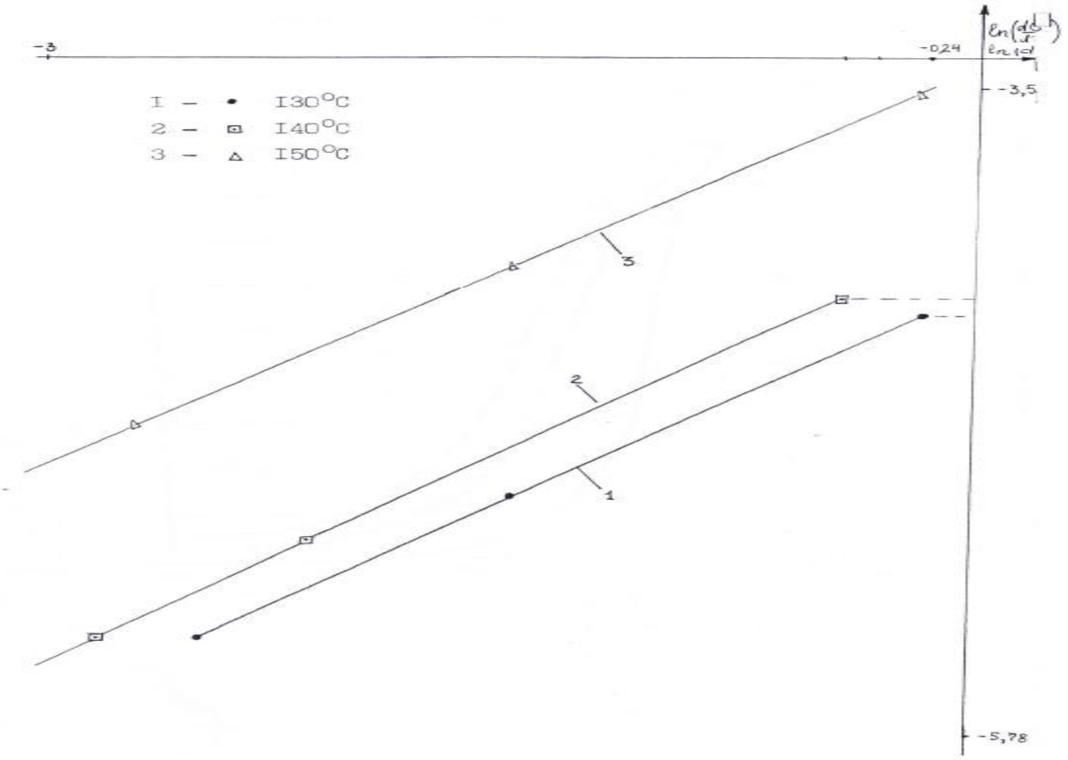


Figure 2 : Graphical determination of the order of the reaction (method of Nuclear Magnetic Resonance)

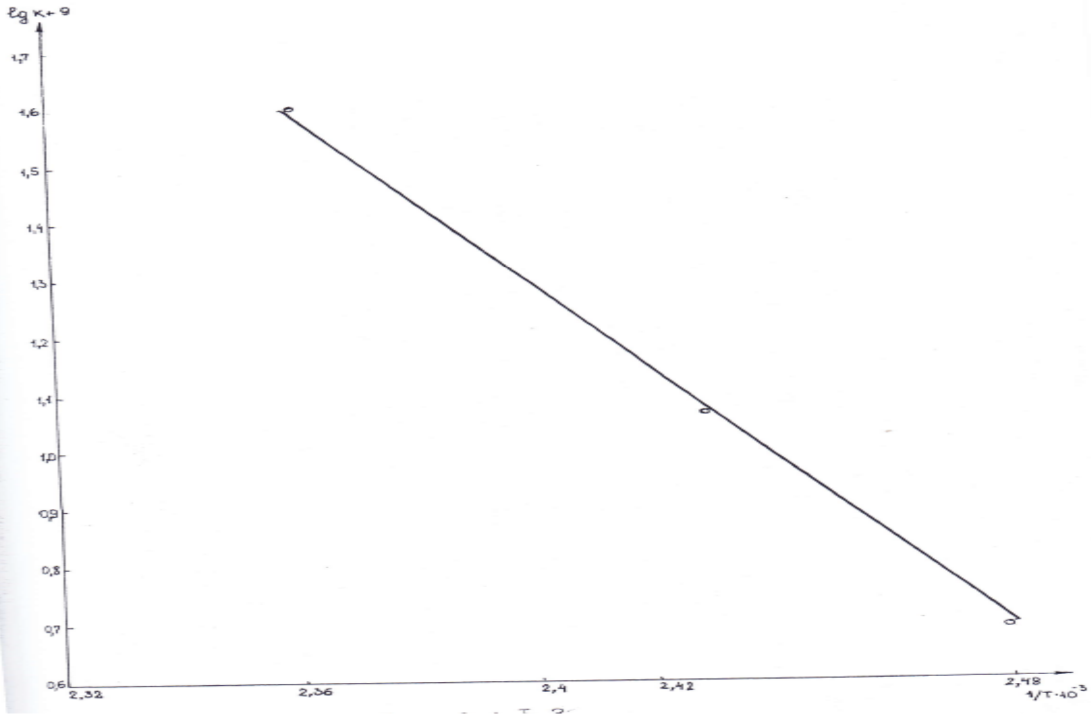


Figure 3 : Variation of the constant speed depending on the temperature of the homolytic phosphorylation of the acetate of allyl, in the presence of tertio-Bu_2O_2

Table 1. kinetic parameters and activation of the homolytic phosphorylation of the acetate of allyl, in the presence of the peroxide of tertio-butyl.

Temperature of the process *(°C)*	**Rate constants** ***K.105 In S-1***	**Order of reaction** ***M***	**Energy of activation *k J/mol, Eact***	**Log has S-1**	**Entropy of activation *In Eu, $\Delta S^\#$***	**Enthalpy of activation *kJ/ mol, H $\Delta^\#$***	**Free energy of activation *kJ/ mol, $\Delta G^\#$***
130	17	0.477	58.52	3,279	192,78	110,07	128,66
140	19	0.781	58.52	3,279	195,33	112.4	131,67
150	28	0.898	58.52	3,279	195,41	113.7	137,47

The speed of the process for any concentration of unsaturated describes the equation of the form:

$$\mathbf{r = k * C^m = k * C^{0,477 ....0,898}} \qquad \textbf{... (3.6)}$$

With r: the speed of the reaction;

k : Constant of speed;

C: concentration of the ester non- saturated;

m : 0.477…0.898: the order of the reaction.

Of the equations of Arrhénius Eyring and Davidson[4], after the determination of the rate constant, it becomes easy to evaluate the entropy of activation ΔS≠, the enthalpy of activation and the free energy of activation ΔH≠ and ΔG≠

The **equation 3.6** has a particular form which reflects the complex nature of the addition reaction.

In total, the serious argument in favor of the mechanism homolytico-radical of the reaction are used and the shape of the Curves kinetics as well as the kinetic equation, update.

Analysis of the compartments of the Kinetic curves of the process of phosphorylation of the Esters Non-saturated with carboxylic acids : The analysis (the Observation) of the shape of the curves of the **Figure 4** has allowed to deduct the important characteristic below: each curve can be divided into three parts.

The analysis of each compartment of the Curves presents a great interest (kinetic analysis and thermodynamics). It was to this end assessed the value of the energy of activation, and the thermodynamic characteristics of each compartment.

The evaluation of the thermodynamic values has been carried out according to the equation of Ey ring.

$$\mathbf{\Delta G^{\neq} = 4,576 * T * [10,319 + logT - logk]} \qquad \textbf{.... (3.7)}$$

With $\Delta G^\#$: free energy of activation in kJ/mol;

T: Temperature in °K;

K : constant speed of process in S-1.

$$\Delta S^{\neq} = 4,576 * \log\frac{\mathbf{k}}{\mathbf{T}} + \log\frac{\mathbf{kE}}{\mathbf{T}} - 49,21 \qquad \text{…(3.8)}$$

With $\Delta S^{\#}$: free energy of activation in kJ/mol;

E: energy of activation of the process in kJ/mol.

The main characteristics of each compartment are reflected in the **tables 1, and 2.**

The data in **Table 1** show for Part A of the curves which follows:

The speed of the process grows with the elevation of the temperature;

The activation energy is to 146.3 kJ/mol (35 kcal/mol), which, according to [1, 35, 45, 51,69, 109] Corresponds to the energy of decomposition of the initiator, the tertio-Bu_2O_2. We can conclude that the party has corresponded to the stage of the initiation of the process.

The number of pre-exponential has been 1,61014, it is clear that a large number of radicals (molecules) participate in the reaction to this step. We can therefore conclude that it is the step of the generation of radicals.

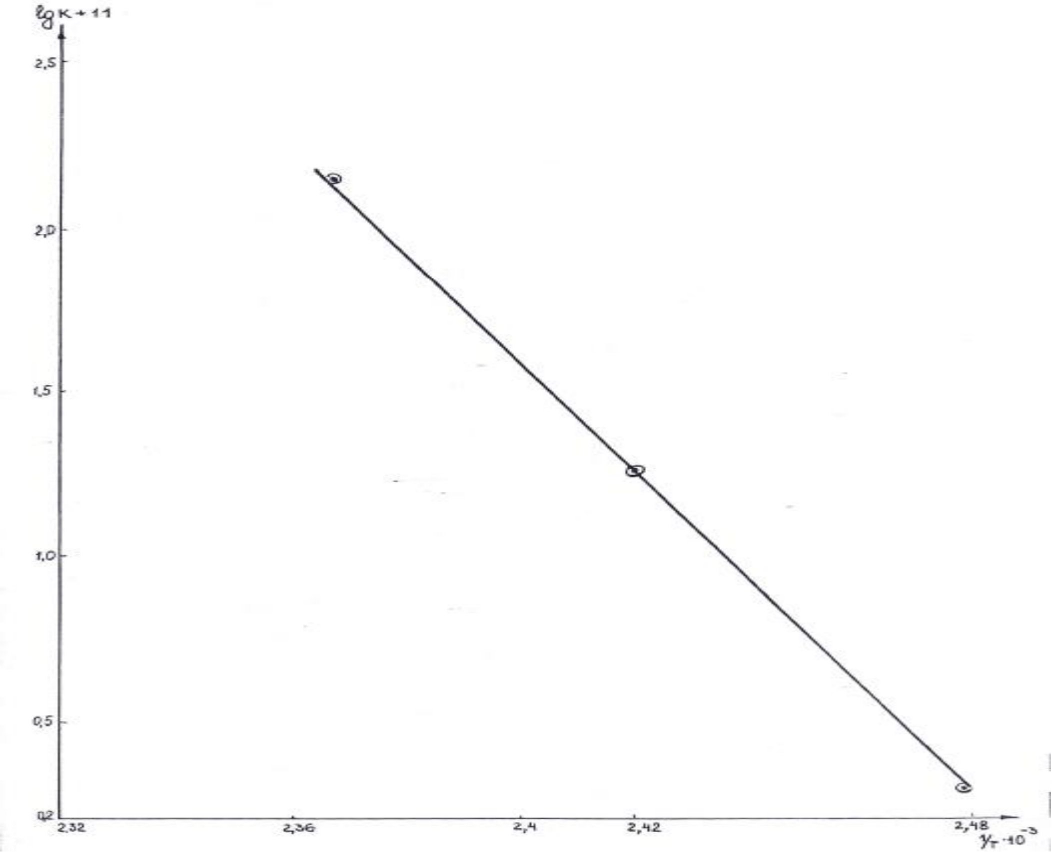


Figure 4: variation of rate constants as a function of temperature at the homolytic phosphorylation of the acetate of allyl by the phosphite of dimethyl on the compartment has kinetic curves.

Table: 2: kinetic parameter and the activation of the process of homolytic phosphorylation of the acetate of allyl acetic acid on the Compartment A.

Temperature of the process *(°C)*	**Rate constants** ***K.105 In S-1***	**Energy of activation *k*** ***J/mol, Eact***	**Log has S-1**	**Entropy of activation** ***In Eu, ΔS#***	**Enthalpy of activation *kJ/*** ***mol, H Δ#***	**Free energy of activation *kJ/*** ***mol, ΔG#***
130	2.15	146.3	14,31	4.36	135.6	135,59
140	7.38	-"-	14.38	4.65,	142,87	134,80
150	12,13	-"-	14,16	3.59	142,78	136,43

1. ΔG≠ ΔH≠ = Eact., it is allowed to assume that the whole energy expended will in the decomposition of the initiator, therefore the≅ tertio-Bu2O2.
2. It was also noted that the higher the temperature , the less the induction period is large:

$$t_{ind_{150}} < t_{ind_{140}} < t_{ind_{130}}$$

Because of this evidence, it is desirable for the conduct of the reaction around 140 -150°C given that the induction period is significantly reduced around this temperature regime.

The formation of radicals from the peroxide and the phosphite occurs by the diagram:

$$\mathbf{(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)_3CO^{\bullet}}$$

$$\mathbf{(CH_3)_3CO^{\bullet} \longrightarrow CH^{\bullet}{}_3 + CH_3–C(O)–CH_3}$$

$$\mathbf{CH_3^{\bullet} + H–P(O)(OCH_3)_2 \longrightarrow CH_4 \quad + {}^{\bullet}P(O)(OCH_3)_2}$$

On the Part B of the **Figure 4** and observing the data in the **table.2**, we can say:

1. The higher the temperature, the greater the speed of the reaction; the activation energy is equal to 31,77 kJ/mol, which represents significantly the energy of avulsion (extraction) of the hydrogen atom in the molecule of phosphite of dimethyl ;
2. The comparison of the apparent activation energies in parts A and B shows that EB is very much lower than EA, or 4.6 times less;
3. The value of the number of pre-exponential has demonstrated that participating particles to the reaction are reduced : 1,76.1011 time!
4. $\Delta S_A^{\neq}$ >, the process is fairly well oriented on the part B and can be schematized as follows:$\Delta S_B^{\neq}$

$$^{\bullet}P(O)(OCH_3)_2 + CH_3C(O){-}O{-}CH_2{-}CH{=}CH_2 \longrightarrow (CH_3O)_2P{-}CH_2{-}C^{\bullet}H{-}CH_2{-}O{-}C(O){-}CH_3$$

$$(CH_3O)_2P{-}CH_2{-}C^{\bullet}H{-}CH_2{-}O{-}C(O){-}CH_3 + H{-}P(O)(OCH_3)_2 \longrightarrow (CH_3O)_2P(O){-}CH_2{-}CH_2{-}CH_2{-}O{-}C{-}CH_3 + {}^{\bullet}P(O)(OCH_3)_2$$

DISCUSSION

In a reactor at 4 passes of 0.25 liter of capacity fitted with Stirrer, of fridge thermometer inverse of a dropping funnel and a bubbler for the introduction of inert gas, add 80 ml phosphite of dimethyl freshly distilled and maintained the temperature of 155-160°C with an intense unrest in the atmosphere of nitrogen. after than add 0.4 ml of peroxide of di-tertio-butyl (molar ratio of vinyl acetate: phosphite of dimethyl peroxide:=1.00:5.00:0.02) at the end of the closing , the mixture is agitated for a further 30 minutes at the same temperature (155-160°C), the excès of phosphite of dimethyl unreacted is extracted by using the bain marie of boiling water to residual pressure[8] of 20mm Hg. Reactant is then distilled under vacuum and gathering of the Fraction to téb. 108-110 (4mm Hg). The 2- dimethoxy-phosphoryl ethyl ester of acetic acid is again distilled (purified) with 1g of sodium bicarbonate to extract the traces of phosphite of dimethyl[7] Performance 36.0g-(86.7%) =1,4365.

The 3-dimethoxy-phosphoryl ester of acetic acid is obtained in conditions similar with 25ml of acetate of allyl, 100ml phosphite and dimethyl 0,8ml of peroxide of di-tertio-butyl (molar ratio of 1.0: 4.68: 0.02). 41,3performance g either (84.8%) $n_D^{20}n_D^{20}$ =1,4415, téb.=109-112 (4mm Hg) 19,6g (0,100mole) 2-dimethoxy- phosphoryl ethyl ester of acetic acid and 1 ml of concentrated hydrochloric acid are boiled in 100ml of ethanol to 99% purity for eight (08) hours. The after evaporation of reactant again distilled under vacuum and we obtains 12.8g of 2-dimethoxy phosphoryl -ethanol performance of 83.1% with the following characteristics: téb.=110-112°C (3mm Hg); n_D^{20} =1,4432.

This body is obtained in conditions similar in reacting 21,0g (0,100mole) of 3-dimethoxy-phosphoryl ethyl ester of acetic acid with 1 ml of hydrochloric acid and 100ml of ethanol 99% purity. Performance[5] 15.8g- 75.2%

Téb.= 119-122°C (3mm of Hg) n_D^{20} =1,4480.

In 20g (0,102mole) of 2-dimethoxy-phosphoryl ethyl ester of acetic acid heated to 155-160°C, we introduced during four (04) hours of clock the anhydrous chloride of hydrogen to the speed[9] of 40-50ml/minute.

It cools the product entirely crystallized and recrystallized in a mixture of carbon tetrachloride-ethanol (1:1) and one obtains 11.3g of a product white crystalline solid, tf =72-74°C; yield 76.7%.

CONCLUSION

The reaction of homolytic phosphorylation of the Esters Non-saturated with carboxylic acids has been studied on the case of vinyl acetate, benzoate, vinyl acetate of allyl and benzoate of allyl .The study has shown that the esters non saturated of vinyl have a reactivity significantly higher than their counterparts in the allyl. It was about the same, established that the nature of the compound non-saturated plays an important role in the process of decomposition of the Initiator (peroxides) in the phosphite of dimethyl at relatively low temperatures (low) . The kinetic equation of the process of phosphorylation of the Esters Non-saturated with carboxylic acids in the presence of peroxides has been established. On the basis of the kinetic equation obtained and kinetic curves obtained, the radical character of the mechanism of the reaction has been demonstrated (proved). It has been established that the limiting stage of the process of homolytic phosphorylation of the Esters Non-saturated with carboxylic acids is the stage of development of the chain with the participation of intermediate structures cycliquesplus or less stable capable of the évulsion (extraction) of the hydrogen atom in the molecule of dimethyl phosphite.

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