LONG-RANGE POLAR EFFECT ON THE C–ON BOND HOMOLYSIS IN (*tert*-BUTYL[1-(DIETHYLPHOSPHONYL)-2,2-DIMETHYLPROPYL]-AMINOXYL) SG1-BASED ALKOXYAMINES

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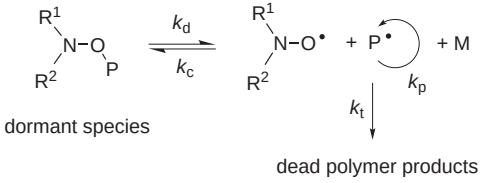
Dedicated to Professor Otto Exner on the occasion of his 80th birthday for his outstanding contribution to physical organic chemistry and to the development of linear free energy relationships.

Alkoxyamines and persistent nitroxyl radicals are important regulators of nitroxide-mediated radical polymerization. Because the polymerization times decrease with the increasing rate constant of the homolysis of the C–ON bond between the polymer chain and the nitroxyl moiety, the factors influencing the cleavage rate constant are of considerable interest. Because alkyl acrylate monomers are among the most used in polymerization, we present the measures of the rate constants (k_d) of the C–ON bond cleavage for new SG1 based alkoxyamine models containing *para*-substituted aromatic acrylates (4-XC_6H_4OC(O)C(Me)H-SG1). It appears that the values of k_d increase with the electron-withdrawing properties of the *para*-substituent groups (4-X) of the ester SG1-based alkoxyamines.

Keywords: Universal electrical effect; SG1-based alkoxyamines; Living/controlled polymerization; Polar molecular state effect; Homolysis rate constants; Radical polymerization.

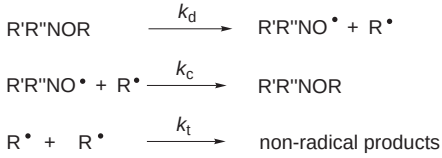
Thanks to the seminal works of Rizzardo[1] and Georges[2], it is now possible to prepare polymers with definite molecular weights and architectures and low polydispersity indexes (PDI) using the process called nitroxide-mediated polymerization (NMP)[3]. The free radical polymerization can be performed through reversible deactivation of growing polymer radicals with stable or persistent radicals such as nitroxyl radicals[4]. The easiest way to trigger the polymerization is to use thermally unstable alkoxyamines prepared beforehand. The growth of the polymer radicals P$^\bullet$ involves successive deactivation-dissociation cycles, in which they are alternately trans-

formed into alkoxyamines (dormant species) and re-activated by thermal homolysis (Scheme 1).



SCHEME 1

Due to the persistent radical effect[5] (Scheme 2), the rate of polymerization in such system depends on the equilibrium constant $K = k_d/k_c$. If K is too small, the polymerization becomes very sluggish or inhibited, whereas if K is too large, the polymerization is too fast and the control very poor or a non-controlled radical polymerization occurs[6].

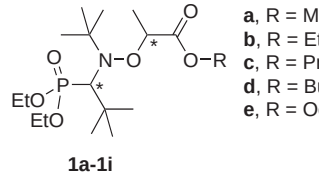


SCHEME 2

Fischer et al.[6,7] have shown that, for NMP to be efficient, the equilibrium constant $K = k_d/k_c$ should vary roughly from 10^{-7} to 10^{-11} mol l^{-1}. Therefore, k_d and k_c have to be in a narrow range i.e. $10^{-3} < k_d < 1$ s^{-1} and $10^6 < k_c < 10^9$ l mol^{-1} s^{-1}. Since k_d and k_c depend on the alkoxyamine structure and k_c varies in general within a narrow range (10^5–10^9 l mol^{-1} s^{-1} from room temperature to 120 °C), while k_d varies within a wide range (10^{-9}–1 s^{-1} at 120 °C)[8,9a], it is crucial to know the effect of the structure of the alkoxyamine on k_d.

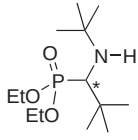
Hence, it has been shown that the activation energy (E_a) of the homolysis gives a good estimate of the value of the bond dissociation enthalpy (BDE) of the C–ON bond in alkoxyamines[9]. We[8c,g,9] and others[8a,b,d–f,j–m,10] have shown that the C–ON bond in alkoxyamines was strengthened by anomeric effects[8a,9f,10d] (e.g., due to a heteroatom bound to the carbon) and polar effects[8f,9a,10a,11] (due to an electron-withdrawing group bound to the nitrogen atom) or weakened by the steric strain and polar effects of both alkyl and nitroxyl fragments[8a,c,f,g,9a,10,11]. Furthermore, stabilization of the released alkyl radical and of the nitroxyl radical (due to an intramolecular hydrogen bond) also weakens the C–ON bond[8,a,c,f,g,i–q,9a,10,11]. It has been shown that almost all nitroxide-mediated polymerizations performed with TEMPO [12] or

DBNO [12] alkoxyamines suffer severe limitations[13]. That led our group[8g,14] to develop a new family of alkoxyamines (Scheme 3) containing a nitroxyl moiety with a phosphoryl group in β-position, SG1 (*tert*-butyl[1-(diethylphosphonyl)-2,2-dimethylpropyl]aminoxyl) **4**. Because acrylate monomers are of high interest for the industry, we have recently studied[15,16] the influence of the alkyl ester group on the value of k_d for a series of alkoxyamines **1** (Scheme 3). It was pointed out that the values of k_d decreased with the increasing size of the alkyl group[15,16], but the substituted phenyl groups (**1h** and **1j**) exhibited an unexpected reactivity, i.e. the values of k_d were higher than those for **1a** although it can rightly be assumed that the phenyl group is bulkier than the methyl group[15]. That surprising reactivity was explained by an increase in the polarity of the phenyl ring compared with that of the alkyl groups. This assumption is confirmed hereafter with the study of the influence of the *para*-substituted (4-X) phenyl ring on the values of k_d for the alkoxyamines **2** (Scheme 3).



1a-1i

a, R = Me
b, R = Et
c, R = Pr
d, R = Bu
e, R = Oct
f, R = i-Pr
g, R = t-Bu
h, R = Ph
i, R = CH_2Ph
j, R = C_6H_4F-4
k, R = CEt_3



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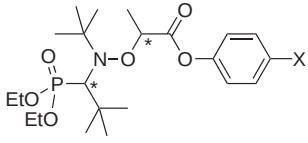
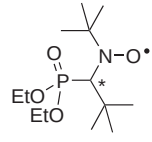


2a-2h

a, X = *t*-Bu
b, X = Me
c, X = OMe
d, X = H
e, X = F
f, X = CF_3
g, X =CN
h, X = NO_2



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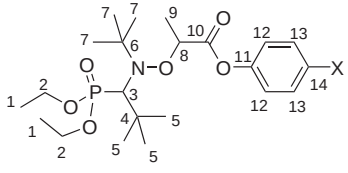

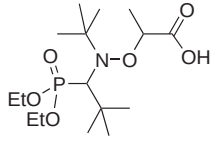

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SCHEME 3

EXPERIMENTAL

Solvents for synthesis, triethylamine, 4-(dimethylamino)pyridine (DMAP), thionyl chloride ($SOCl_2$), *N*,*N*-dimethylaniline (DMA), and *para*-substituted phenols were purchased from Aldrich and used as received. TEMPO was purchased from Acros and sublimed. *tert*-Butylbenzene was purchased from Aldrich and purified by conventional procedure[17]. Amine **3** was prepared as previously described[14] and used as internal standard for kinetic experiments. Nitroxyl radical **4** (SG1) was kindly provided by Atofina and alkoxyamines **5** and **2f** were prepared as already described[15]. NMR experiments were performed in $CDCl_3$ on a 300 Avance Bruker spectrometer (^{1}H 300 MHz, ^{13}C 75.48 MHz and ^{31}P 121.59 MHz) in the Centre Regional de RMN in Marseille. Chemical shifts are given in ppm (δ-scale) with TMS as internal reference for ^{1}H NMR, $CDCl_3$ (internal reference) for ^{13}C NMR and H_3PO_4 85% (external reference) for ^{31}P NMR. Coupling constants (*J*) are given in Hz. Elemental analyses were made in the Service Commun de Micro Analyse Université d'Aix-Marseille 3. Reactions were monitored by TLC (60 F 240 silica gel plates, eluent ethyl acetate–pentane 1:1), with UV and phosphomolybdic acid detection. Alkoxyamines were purified by chromatography (60 Silicagel, 70–230 mesh, Merck), eluent ethyl acetate–pentane 3:1.

General Procedure

A solution of **5** (4.0 g, 11.0 mmol) in CH_2Cl_2 was degassed by nitrogen bubbling for 10 min. Then, $SOCl_2$ (3 equiv., 2.4 ml, 33.0 mmol) was added under nitrogen atmosphere. The mixture was stirred at room temperature for 45 min and the excess of $SOCl_2$ was removed under vacuum (0.1 mb) to yield alkoxyamine **6**. Crude **6** was diluted in ether and then a 20 ml ether solution of alcohol (2 equiv.), Et_3N (1 equiv., 1.5 ml, 11 mmol) and DMAP (0.4 equiv., 0.3 g, 2.4 mmol) was added under nitrogen atmosphere. A white solid precipitated and the mixture was stirred at room temperature for 4 h. The white solid was filtered off and the solvent removed to yield oil. The oil was dissolved in 30 ml of ether, then washed 3 times with 15 ml of NH_4Cl 5% aqueous solution, 3 times with 15 ml of a saturated sodium carbonate aqueous solution and with water to reach a neutral pH. The organic layer was dried over anhydrous $MgSO_4$ and the solvent removed to yield oil which was purified by chromatography to afford alkoxyamines **2a**–**2h**.

4-tert-Butylphenyl 2-({tert-butyl[1-(diethoxyphosphoryl)-2,2-dimethylpropyl]amino}oxy)propanoate (**2a**). Alkoxyamine **5** (4.00 g, 10.9 mmol), $SOCl_2$ (2.4 ml, 32.7 mmol), 4-*tert*-butylphenol (1.7 g, 21.8 mmol), triethylamine (1.5 ml, 10.9 mmol), DMAP (0.3 g, 2.4 mmol). Yellowish viscous oil. Yield 43% (2.42 g) of both diastereoisomers (56:44). For $C_{26}H_{46}NO_6P$ (499.6) calculated: 62.50% C, 9.28% H, 2.80% N; found: 62.89% C, 9.07% H, 2.68% N. ^{31}P NMR: 23.95 (dia1); 24.46 (dia2). ^{1}H NMR: 1.19–1.32 m, 48 H (H1, H5, H7, dia1+2); 1.66 d, 3 H (J_{HH} = 6.0, H9, dia1); 1.69 d, 3 H (J_{HH} = 6.0, H9, dia2); 2.17 s, 18 H (*t*-Bu, dia1+2); 3.32 d, 1 H (J_{PH} = 24.0, H3, dia1); 3.42 d, 1 H (J_{PH} = 24.0, H3, dia2); 3.85–4.40 m, 8 H (H2, dia1+2); 4.83 q, 1 H (J_{HH} = 6.0, H8, dia1); 4.91 q, 1 H (J_{HH} = 6.0, H8, dia2); 6.81–7.41 m, 8 H (H12, H13, dia1+2). ^{13}C NMR: 15.89 d, 2 C (J_{PC} = 6.8, C1, dia1+2); 16.20 d, 2 C (J_{PC} = 6.0, C1, dia1+2); 17.60 (C9, dia2); 19.15 (C9, dia1); 27.73, 6 C (C7, dia2); 29.27 d, 3 C (J_{PC} = 5.3, C5, dia1); 30.05 d, 3 C (J_{PC} = 6.0, C5, dia2); 31.06 3 C ($C(CH_3)_3$, dia1); 31.32 3 C ($C(CH_3)_3$, dia2); 34.01 (C-$(CMe)_3$, dia2); 34.06 (C-$(CMe)_3$, dia1); 34.97 d (J_{PC} = 4.5, C4, dia2); 35.33 d (J_{PC} = 6.0, C4, dia1); 58.58 d (J_{PC} = 7.5, C2, dia1); 58.85 d (J_{PC} = 7.5, C2, dia2); 61.16 (C6, dia2); 61.52 (C6, dia1); 61.72 d (J_{CP} = 6.8, C2, dia1); 61.85 d (J_{CP} = 6.8, C2, dia2); 69.06 (J_{CP} = 139.0, C3, dia2);

69.36 (J_{CP} = 140.0, C3, dia1); 76.58 (C8, dia2); 82.38 (C8, dia1); 120.24 2 C (C13, dia1); 120.51 2 C (C13, dia2); 125.78 2 C (C12, dia2); 125.95 2 C (C12, dia1); 147.77 (C14, dia1); 147.96 (C14, dia2); 148.35 (C11, dia1); 155.08 (C11, dia2); 170.63, 2 C (C10, dia2); 172.09 (C10, dia1).

4-Methylphenyl 2-({tert-butyl[1-(diethoxyphosphoryl)-2,2-dimethylpropyl]amino}oxy)propanoate (**2b**). Alkoxyamine **5** (4.00 g, 10.9 mmol), $SOCl_2$ (2.4 ml, 32.7 mmol), 4-methylphenol (2.13 g, 21.8 mmol), triethylamine (1.5 ml, 10.9 mmol), DMAP (0.3 g, 2.4 mmol). White powder. Yield 40% (2.13 g) of both diastereoisomers (77:23). For $C_{23}H_{40}NO_6P$ (457.6) calculated: 60.38% C, 8.81% H, 3.06% N; found: 60.61% C, 8.94% H, 3.08% N. ^{31}P NMR: 23.91 (s, dia1); 24.47 (s, dia2). ^{1}H NMR: 1.19 m, 36 H (H5, H7, dia1+2); 1.21–1.34 m, 12 H (H1, dia1+2); 1.65 d, 6 H (J_{HH} = 6.0, H9, dia2); 1.68 d, 6 H (J_{HH} = 6.0, H9, dia1); 2.32 s, 3 H (Me, dia2); 2.34 s, 3 H (Me, dia1); 3.30 d, 1 H (J_{PH} = 24.0, H9, dia1); 3.41 d, 1 H (J_{PH} = 24.0, H9, dia2); 3.87–4.30 m, 8 H (H2, dia1+2); 4.80 q, 1 H (J_{HH} = 6.0, H8, dia1); 4.89 q, 1 H (J_{HH} = 6.0, H8, dia2); 6.94–7.19 m, 8 H (H12, H13, dia1+2). ^{13}C NMR: 16.20 d, 2 C (J_{PC} = 6.8, C1, dia1+2); 16.50 d, 2 C (J_{PC} = 6.0, C1, dia1+2); 17.86 2 C (C9, dia1+2); 19.40 2 C (Me, dia1+2); 20.78 6 C (C7, dia1+2); 29.56 d, 3 C (J_{PC} = 6.0, C5, dia1); 30.39 d, 3 C (J_{PC} = 6.0, C5, dia2); 35.21 d (J_{PC} = 5.3, C4, dia2); 35.60 d (J_{PC} = 5.3, C4, dia1); 58.75 d (J_{PC} = 6.8, C2, dia1); 59.03 d (J_{PC} = 7.5, C2, dia2); 61.40 (C6, dia2); 61.78 (C6, dia1); 61.87 d (J_{PC} = 6.0, C2, dia1); 61.95 d (J_{CP} = 6.0, C2, dia2); 69.28 (J_{CP} = 139.0, C3, dia2); 69.60 (J_{CP} = 139.0, C3, dia1); 76.66 (C8, dia2); 82.63 (C8, dia1); 120.86 2 C (C12, dia1); 121.15 2 C (C12, dia1); 129.75 2 C (C13, dia2); 129.90 2 C (C13, dia1); 135.14 (C14, dia2); 135.53 (C14, dia1); 148.13 (C11, dia1); 148.18 (C11, dia2); 171.11 (C10, dia2); 172.55 (C10, dia1).

4-Methoxyphenyl 2-({tert-butyl[1-(diethoxyphosphoryl)-2,2-dimethylpropyl]amino}oxy)propanoate (**2c**). Alkoxyamine **5** (4.00 g, 10.9 mmol), $SOCl_2$ (2.4 ml, 32.7 mmol), 4-methoxyphenol (2.7 g, 21.8 mmol), triethylamine (1.5 ml, 10.9 mmol), DMAP (0.3 g, 2.4 mmol). Yellowish viscous oil. Yield 28% (1.48 g) of both diastereoisomers (54:46). For $C_{23}H_{40}NO_7P$ (473.6) calculated: 58.34% C, 8.51% H, 2.96% N; found: 58.55% C, 8.37% H, 3.02% N. ^{31}P NMR: 24.16 (dia1); 24.68 (dia2). ^{1}H NMR: 1.18 s, 18 H (H7, dia1+2); 1.19 s, 18 H (H5, dia1+2); 1.20–1.35 m, 12 H (H1, dia1+2); 1.62 d, 3 H (J_{HH} = 6.0, H9, dia1); 1.65 d, 3 H (J_{HH} = 6.0, H9, dia2); 3.31 d, 1 H (J_{HP} = 24.0, H3, dia1); 3.41 d, 1 H (J_{HP} = 24.0, H3, dia2); 3.78 s, 3 H (OMe, dia2); 3.80 s, 3 H (OMe, dia1); 3.88–4.32 m, 8 H (H2, dia1+2); 4.80 q, 1 H (J_{HH} = 6.0, H8, dia1); 4.87 q, 1 H (J_{HH} = 6.0, H8, dia2); 6.85–7.08 m, 8 H (H12, H13, dia1+2). ^{13}C NMR: 16.31 d, 2 C (J_{PC} = 7.5, C1, dia1+2); 16.63 d, 2 C (J_{PC} = 6.0, C1, dia1+2); 18.50 (C9, dia2); 19.53 (C9, dia1); 28.12 6 C (C7, dia1+2); 30.17 3 C (C5, dia1); 30.98 3 C (C5, dia2); 35.32 (C4, dia1); 35.77 (C4, dia2); 55.68 2 C (OMe, dia1+2); 58.91 d, 2 C (J_{PC} = 6.0, C2, dia1+2); 61.54 (C6, dia1); 61.91 (C6, dia2); 62.01 d, 2 C (J_{CP} = 6.0 C2, dia1+2); 69.72 (J_{CP} = 140.0, C3, dia1); 69.70 (J_{CP} = 140.0, C3, dia2); 77.10 (C8, dia2); 82.72 (C8, dia1); 114.43, 114.59 4 C (C13, dia1+2); 122.06, 122.37 4 C (C12, dia1+2); 143.94, 144.12 2 C (C14, dia1+2); 157.22, 157.43 (C11, dia1+2); 172.93 2 C (C10, dia1+2).

4-Fluorophenyl 2-({tert-butyl[1-(diethoxyphosphoryl)-2,2-dimethylpropyl]amino}oxy)propanoate (**2e**). Alkoxyamine **5** (4.00 g, 10.9 mmol), $SOCl_2$ (2.4 ml, 32.7 mmol), 4-fluorophenol (2.44 g, 21.8 mmol), triethylamine (1.5 ml, 10.9 mmol), DMAP (0.3 g, 2.4 mmol). Yellowish viscous oil. Yield 43% (3.61 g) of both diastereoisomers (1:1). Diastereoisomer *RR*/*SS*: ^{31}P NMR: 24.0. ^{1}H NMR: 1.19 s, 9 H (H7); 1.20 s, 9 H (H5); 1.22–1.34 m, 6 H (H1); 1.70 d, 3 H (J_{HH} = 6.0, H9); 3.44 d, 1 H (J_{PH} = 24.0, H3); 3.93–4.32 m, 4 H (H22); 4.92 q, 1 H (H8, J_{HH} = 6.0); 7.02–7.09 m, 4 H (H12, H13). ^{13}C NMR: 16.21 d (J_{PC} = 6.8, C1); 16.50 d (J_{PC} = 6.0, C1); 17.97 (C9); 28.03 3 C (C7); 30.26 d, 3 C (J_{PC} = 6.0, C5); 35.08 d (J_{CP} = 4.5, C4); 59.19 d

(J_{CP} = 7.5, C2); 61.25 (C6); 61.90 d (J_{CP} = 7.5, C2); 69.61 d (J_{CP} = 140.0, C3); 77.10 (C8); 115.71 d, 2 C (J_{CF} = 23.0, C13); 122.73 d, 2 C (J_{CF} = 8.3, C12); 146.10 d (J_{CF} = 2.3, C11); 160.01 d (J_{CF} = 243.0, C14); 170.82 (C10). Diastereoisomer *RS*/*SR*: ^{31}P NMR: 23.64. ^{1}H NMR: 1.18 s, 9 H (H7); 1.20 s, 9 H (H5); 1.27–1.33 m, 6 H (H1); 1.68 d, 3 H (J_{HH} = 6.0, H9); 3.32 d, 1 H (J_{PH} = 24.0, H3); 3.89–4.33 m, 4 H (H2); 4.82 q, 1 H (H8); 7.04–7.07 m, 4 H (H12, H13). ^{13}C NMR: 16.06 d (J_{PC} = 6.0, C1); 16.37 d (J_{PC} = 6.0, C1); 19.18 (C9); 28.86 3 C (C7); 29.48 d, 3 C (J_{PC} = 6.0, C5); 35.46 d (J_{CP} = 6.0, C4); 58.69 d (J_{CP} = 7.5, C2); 61.50 (C6, dia1); 61.67 (C6); 61.71 d (J_{CP} = 6.0, C2); 69.44 d (J_{CP} = 139.0, C3); 82.26 (C8); 115.95 d, 2 C (J_{CF} = 24.0, C13); 122.50 d, 2 C (J_{CF} = 8.3, C12); 146.07 d (J_{CF} = 2.3, C11); 160.10 d (J_{CF} = 243.0, C14); 172.20 (C10).

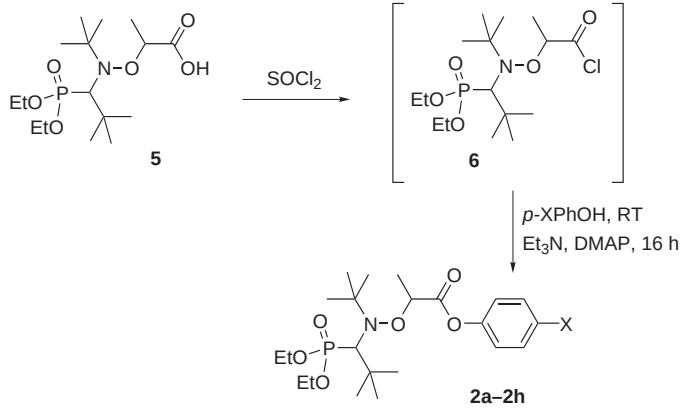
4-Trifluoromethylphenyl 2-({tert-butyl[1-(diethoxyphosphoryl)-2,2-dimethylpropyl]amino}oxy)propanoate (**2f**). Alkoxyamine **5** (4.00 g, 10.9 mmol), $SOCl_2$ (2.4 ml, 32.7 mmol), 4-(trifluoromethyl)phenol (3.50 g, 21.8 mmol), triethylamine (1.5 ml, 10.9 mmol), DMAP (0.3 g, 2.4 mmol). Yellowish viscous oil. Yield 43% (3.61 g) of both diastereoisomers (1:1). ^{31}P NMR: 23.64 (s, dia1); 24.02 (dia2). ^{1}H NMR: 1.19 s, 18 H (H7, dia1+2); 1.20 s, 18 H (H5, dia1+2); 1.22–1.34 m, 12 H (H1, dia1+2); 1.66 d, 3 H (J_{HH} = 6.0, H9, dia1); 1.70 d, 3 H (J_{HH} = 6.0, H9, dia2); 3.33 d, 1 H (J_{PH} = 24.0, H3, dia1); 3.44 d, 1 H (J_{PH} = 24.0, H3, dia2); 3.93–4.32 m, 8 H (H2, dia1+2); 4.82–4.92 m, 2 H (H8, dia1+2); 7.21–7.66, m, 8 H (H12, H13, dia1+2). ^{13}C NMR: 16.21 d, 2 C (J_{PC} = 6.8, C1, dia1+2); 16.50 d, 2 C (J_{PC} = 6.0, C1, dia1+2); 17.97 (C9, dia2); 19.31 (C9, dia1); 28.00 3 C (C7, dia2); 28.03 3 C (C7, dia1); 29.67 d, 3 C (J_{PC} = 6.0, C5, dia1); 30.43 d, 3 C (J_{PC} = 6.0, C5, dia2); 35.25 d (J_{CP} = 4.5, C4, dia2); 35.63 d (J_{CP} = 5.2, C4, dia1); 58.97 d (J_{CP} = 7.5, C2, dia1); 59.19 d (J_{CP} = 7.5, C2, dia2); 61.50 (C6, dia1); 61.90 d (J_{CP} = 7.5, C2, dia1); 61.89 (C6, dia2); 61.99 d (J_{PC} = 7.5, C2, dia2); 69.24 d (J_{CP} = 139.0, C3, dia2); 69.61 d (J_{CP} = 140.0, C3, dia2); 77.1 (C8, dia2); 82.32 (C8, dia1); 121.81 2 C (C12, dia1); 122.13 2 C (C12, dia2); 123.80 q (J_{CF} = 270.0, CF_3, dia2); 123.93 q (J_{CF} = 270.0, CF_3, dia1); 126.67 q, 2 C (J_{CF} = 3.8, C13, dia2); 126.87 q, 2 C (J_{CF} = 3.8, C13, dia1); 127.95 q (J_{CF} = 33.0, C14, dia2); 128.30 q (J_{CF} = 33.0, C14, dia1); 152.93 (C11, dia2); 153.14 (C11, dia1); 170.58 (C10, dia2); 171.88 (C11, dia1).

4-Cyanophenyl 2-({tert-butyl[1-(diethoxyphosphoryl)-2,2-dimethylpropyl]amino}oxy)propanoate (**2g**). Alkoxyamine **5** (4.00 g, 10.9 mmol), $SOCl_2$ (2.4 ml, 32.7 mmol), 4-hydroxybenzonitrile (2.68 g, 21.8 mmol), triethylamine (1.5 ml, 10.9 mmol), DMAP (0.3 g, 2.4 mmol). Yellow powder. Yield 41% (2.16 g) of both diastereoisomers (60:40). For $C_{23}H_{37}N_2O_6P$ (468.5) calculated: 58.96% C, 7.96% H, 5.98% N; found: 59.22% C, 8.06% H, 6.02% N. ^{1}P NMR: 23.86 (dia1); 24.38 (dia2). ^{1}H NMR: 1.18 8 H (H7, dia1+2); 1.20 8 H (H5, dia1+2); 1.23–1.35 m, 6 H (H1, dia1+2); 1.63 d, 3 H (J_{HH} = 9.0, H9, dia1); 1.68 d, 3 H (J_{HH} = 6.0, H9, dia2); 3.33 d, 1 H (J_{HH} = 27.0, H3, dia2); 3.43 d, 1 H (J_{HH} = 27.0, H3, dia1); 3.90–4.35 m, 4 H (dia1+2); 4.85 q, 1 H (J_{HH} = 6.0, H8, dia2); 4.86 q, 1 H (J_{HH} = 9.0, H9, dia1); 7.22–7.72 m, 4 H (H12, H13, dia1+2). ^{13}C NMR: 16.32 d, 4 C (J_{PC} = 7.5, C1, dia1+2); 16.60 d, 2 C (J_{PC} = 6.0, C1, dia1); 16.64 d, 2 C (J_{PC} = 6.0, C1, dia2); 18.10 (C9, dia1); 19.31 (C9, dia2); 28.09 3 C (C7, dia1); 28.12 3 C (C7, dia2); 29.79 d, 3 C (J_{PC} = 5.3, C5, dia2); 30.51 d, 3 C (J_{PC} = 6.0, C5, dia1); 35.33 d (J_{CP} = 4.6, C4, dia1); 35.60 d (J_{CP} = 5.2, C4, dia2); 59.10 d (J_{CP} = 6.8, C2, dia2); 59.30 d (J_{CP} = 6.8, C2, dia1); 61.62 (C6, dia1); 61.95 d (J_{CP} = 7.5, C2, dia2); 62.00 (C6, dia2); 62.03 d (J_{PC} = 5.2, C2, dia1); 69.77 d (J_{CP} = 138.8, C3, dia1); 70.11 d (J_{CP} = 138.8, C3, dia2); 77.30 (C8, dia2); 82.24 (C8, dia1); 106.68 (C14, dia1); 110.07 (C14, dia2); 118.22 (CN, dia2); 118.47 (CN, dia2); 122.54 2 C (C12, dia2); 122.93 2 C (C12, dia1); 133.68 2 C (C13, dia1); 133.84 2 C (C13, dia2); 153.77 (C11, dia2); 154.03 (C11, dia1); 170.39 (C10, dia1); 171.62 (C11, dia2).

4-Nitrophenyl 2-({tert-butyl[1-(diethoxyphosphoryl)-2,2-dimethylpropyl]amino}oxy)propanoate (**2h**). Alkoxyamine **5** (4.00 g, 10.9 mmol), $SOCl_2$ (2.4 ml, 32.7 mmol), 4-nitrophenol (2.94 g, 21.8 mmol), triethylamine (1.5 ml, 10.9 mmol), DMAP (0.3 g 2.4 mmol). Orange solid. Yield 45% (2.5 g) of both diastereoisomers (56:44). For $C_{22}H_{37}N_2O_8P$ (488.5) calculated: 54.09% C, 7.63% H, 5.73% N; found: 54.16% C, 7.62% H, 5.74% N. ^{31}P NMR: 23.84 (dia1); 24.12 (dia2). ^{1}H NMR: 1.18 s, 18 H (H7, dia1+2); 1.20 s, 18 H (H5, dia1+2); 1.23–1.34 m, 12 H (H1, dia1+2); 1.66 d, 3 H (J_{HH} = 6.0, H9, dia1); 1.67 d, 3 H (J_{HH} = 6.0, H9, dia2); 3.34 d, 1 H (J_{PH} = 27.0, H3, dia1); 3.44 d, 1 H (J_{PH} = 27.0, H3, dia2); 3.91–4.32 m, 8 H (H2, dia1+2); 4.87 bq, 2 H (H8, J_{HH} = 6.0, dia1+2); 7.27–8.30 m, 8 H (H12, H13, dia1+2). ^{13}C NMR: 16.14 d, 2 C (J_{PC} = 6.8, C1, dia1+2); 16.42 d, 2 C (J_{PC} = 5.3, C1, dia2); 16.44 d, 2 C (J_{PC} = 6.0, C1, dia1); 17.90 (C9, dia2); 19.09 (C9, dia1); 27.88 3 C (C7, dia2); 27.91 3 C (C7, dia1); 29.62 d, 3 C (J_{PC} = 6.0, C5, dia1); 30.33 d, 3 C (J_{PC} = 6.0, C5, dia2); 35.12 d (J_{PC} = 4.5, C4, dia2); 35.50 d (J_{PC} = 5.3, C4, dia1); 58.94 d (J_{PC} = 7.5, C2, dia1); 59.14 d (J_{PC} = 7.5, C2, dia2); 61.41 (C6, dia2); 61.77 d (J_{PC} = 7.5, C2, dia1); 61.82 (C6, dia1); 61.80 d (J_{PC} = 7.5, C2, dia2); 69.06 d (J_{PC} = 139.5, C3, dia2); 69.41 d (J_{PC} = 139.0, C3, dia1); 77.21 (C8, dia2); 82.02 (C8, dia1); 122.08 2 C (C12, dia1); 122.48 2 C (C12, dia2); 124.97 2 C (C13, dia2); 125.15 2 C (C13, dia1); 145.18 (C14, dia2); 145.34 (C14, dia1); 155.03 (C11, dia1); 153.24 (C11, dia2); 170.06 (C10, dia2); 171.26 (C10, dia1).

RESULTS

To avoid copper wastes and because all 2-bromopropanoic acid esters were not commercially available, alkoxyamines **2a**–**2h** were prepared as depicted in Scheme 4. Preparations of **2d** and **2e** were given in a previous work[15].



SCHEME 4

Alkoxyamine **5** was treated with $SOCl_2$ to yield the corresponding acyl chloride **6**. Then a phenol was added to afford the required alkoxyamines **2a**–**2h**.

Due to the presence of two chiral centers in the molecule (see Scheme 2) two isomers were obtained for each alkoxyamine **2a**–**2h**. ^{31}P NMR signals do not exhibit significant changes when varying the 4-X substituent of the

phenyl group in the ester function. Therefore, with regard to the absolute configuration attributed to **1a** [18], it was assumed that the ^{31}P NMR shifts of ca. 24.7 and 24.0 ppm corresponded to the *RR*/*SS* and *RS*/*SR* diastereoisomers, respectively (see Experimental and Table I).

TABLE I
^{31}P NMR shifts δ, homolysis rate constants k_d and activation energies E_a for alkoxyamines **2a**–**2h**

2	T, °C[a]	δ, ppm[b]		$k_d \times 10^4$, s^{-1} [c]		E_a, kJ mol^{-1} [d,e]		$k_d^{120} \times 10^4$, s^{-1} [e]	
		RR/SS	*SR/RS*	*RR/SS*	*SR/RS*	*RR/SS*	*SR/RS*	*RR/SS*	*SR/RS*
a	101	24.6	24.0	1.3	4.7	130.9	127.2	9.5	29.7
(X=*t*-Bu)	102			1.4	4.1				
b	99	24.5	24.0	1.5	4.2	130.1	127.1	12.2	30.6
(X=Me)	100			1.6	3.9				
c	99	24.5	24.0	1.4	4.0	129.9	126.8	13.0	33.6
(X=OMe)	100			1.5	4.1				
d	100	24.5	23.9	1.4	3.6	129.9	126.7	13.0	34.6[f]
(X=H)	101			1.5	4.7				
e	100	24.3	24.0	1.8	4.6	129.2	126.4	16.1	38.0[g]
(X=F)	101			2.1	4.7				
	100			2.4	5.0				
	101				5.8[h]				
f	100	24.3	24.0	3.2	7.9	127.5	125.5	27.1	50.0
(X=CF_3)	102			3.5	6.3				
	100			3.9	8.3				
g	100	24.3	24.0	4.1	6.5	126.8	125.3	33.6	53.2
(X=CN)	100			4.2	7.3				
h	101	24.5	24.0	5.2	7.9	126.4	125.1	38.0	56.4
(X=NO_2)	101			5.5	8.0				

[a] Temperature ±1 °C. [b] Amine **3** as internal standard in C_6D_6/*tert*-butylbenzene δ 31.0 ppm. [c] Errors were less than 5%. [d] E_a ±2 kJ mol^{-1}. [e] See the text. [f] Measured at 110 °C in lit.[15]. [g] Values given in lit.[15]. [h] Pure diastereoisomer.

Kinetic measurements were performed by monitoring the alkoxyamine concentration using ^{31}P NMR as previously described[19]. All experiments were carried out twice at ca. 100 °C in the presence of an excess of TEMPO as alkyl radical scavenger. Thanks to the ^{31}P NMR method, the homolysis rate constants k_d of both diastereoisomers were measured in a single NMR experiment (Eq. (*1*)).

$$\ln \frac{[\text{alkoxyamine}]_t}{[\text{alkoxyamine}]_0} = -k_d\, t \qquad (1)$$

The activation energies E_a were estimated using the average frequency factor 2.4×10^{14} s^{-1} defined in the literature[8j,f,9a], and then all the k_d were re-estimated at 120 °C to be consistent with the literature. Values of k_d, ^{31}P NMR shifts, temperatures and E_a values are gathered in Table I.

Assuming that the steric hindrance of a benzene ring does not depend on the size of the *para*-substituent, the changes observed in the values of k_d are therefore due to either the electron-withdrawing or electron-donating properties of the *para*-substituent or to the benzene ring itself. Electron-withdrawing or electron-donating properties are split into two families, i.e. localized (inductive/field or universal) electrical effects or delocalized effects[20]. In our series, the universal electrical effect[21] is expressed by the Hammett constants $\sigma_{U,X}$ or $\sigma_{U,4-XC_6H_4}$ for the X substituents or for the whole aromatic substituent, respectively. The latter is given[22] by Eq. (*2*).

$$\sigma_{U,4-XC_6H_4} = 0.138\sigma_{U,X} + 0.137\sigma^0_{R,X} + 0.120 \qquad (2)$$

The delocalization effect is often described by the Hammett constants σ_R: with our series of alkoxyamines **2**, $\sigma_{R,X}$ is used for the X substituents of a benzene ring and $\sigma_{R,4-XC_6H_4}$ is used to take into account the effect of the whole aromatic substituent. The latter is given[22] by Eq. (*3*).

$$\sigma_{R,4-XC_6H_4} = 0.180\sigma_{U,X} + 0.111\sigma^0_{R,X} - 0.0988 \qquad (3)$$

with $\sigma_{U,X}$ the Hammett constant for the universal electrical (localized) effect of an X group and $\sigma^0_{R,X}$ the Hammett constant for the normalized delocalized effect of an X group[20]. Classically, although the Hammett constant $\sigma_{p,X}$ is a composite constant of $\sigma_{U,X}$ and $\sigma_{R,X}$, it is often used to describe the influence of a *para*-substituent of the aromatic ring on the reactivity[20]. The stabilization of the unpaired electron by delocalization onto the benzene ring is disregarded because DFT calculations on the 1-(phenoxy)carbonylethyl ($C_6H_4OC(O)CHMe^{\bullet}$) radical show no unpaired electron density onto the benzene ring[23]. All Hammett constants are listed in Table II.

There is a fair correlation (Eqs (*4a*) and (*4b*)) between log k_d and $\sigma_{U,4-XC_6H_4}$ at 100 °C, as shown in Fig. 1; the slight scatter of experimental data is certainly due to the differences of temperatures (see Table I). The $\sigma_{U,4-XC_6H_4}$ values appeared to be the most suitable (vide infra). Thus, a plot of the logarithm of the re-estimated rate constant k_d at 120 °C was preferred (Fig. 2 and Eqs (*5a*) and (*5b*) in Table III) for each of the parameters given in Table II.

TABLE II
Hammett σ constant values $\sigma_{U,4-XC_6H_4}$, σ_U, σ_R, $\sigma_{R,4-XC_6H_4}$ and σ_p

X	$\sigma_{U,4-XC_6H_4}$ [a]	σ_U [b]	σ_R [b]	$\sigma_{R,4-XC_6H_4}$ [a]	σ_P [b]
a (X=*t*-Bu)	0.09	–0.02	–0.18	–0.08	–0.02
b (X=Me)	0.10	–0.01	–0.16	–0.13	–0.17
c (X=OMe)	0.11	0.29	–0.58	–0.19	–0.27
d (X=H)	0.12	0.00	0.00	–0.11	0.00
e (X=F)	0.13	0.45	–0.48	–0.07	0.06
f (X=CF_3)	0.19	0.38	0.11	–0.01	0.54
g (X=CN)	0.21	0.51	0.08	0.01	0.66
h (X=NO_2)	0.23	0.65	0.25	0.03	0.78

[a] $\sigma_{U,4-XC_6H_4}$ and $\sigma_{R,4-XC_6H_4}$ values are given by Eqs (*2*) and (*3*), respectively; $\sigma^0_{R,X}$ values are given in lit.[20]. [b] $\sigma_{U,X}$, $\sigma_{R,X}$ and $\sigma_{p,X}$ values are given in lit.[20].

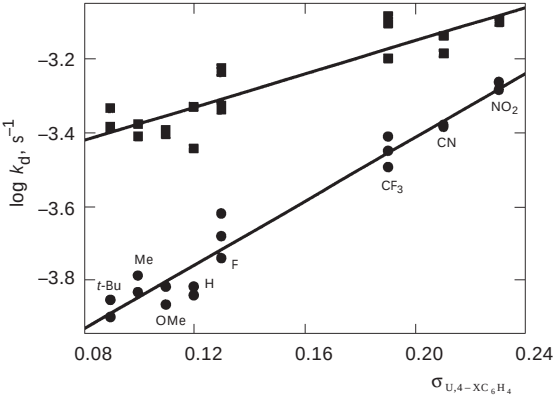


FIG. 1
Plot of log k_d vs $\sigma_{U,4-XC_6H_4}$ for alkoxyamines **2a**–**2h** at 100 °C: ● *RR*/*SS* and ■ *RS*/*SR* diastereoisomers

TABLE III
Coefficient and statistical data for the correlations of log k_d with Hammett constants

Equations[a]	Hammett constants	log $k_{d,0}$ [b,c]	ρ[c]	R^2 [d]	s[e]	t, % [f]
(*5a*)	$\sigma_{U,4-XC_6H_4}$	–2.70(0.01)	2.05(0.09)	0.99	0.01	99.99
(*6a*)	σ_U	–2.51(0.03)	0.37(0.09)	0.76	0.06	99.53
(*7a*)	$\sigma_{R,4-XC_6H_4}$	–2.31(0.03)	1.27(0.33)	0.74	0.06	99.38
(*8a*)	σ_P	–2.45(0.01)	0.26(0.02)	0.96	0.03	99.99
(*9a*)	σ_R	–2.37(0.04)	0.25(0.12)	0.44	0.10	92.68
(*5b*)	$\sigma_{U,4-XC_6H_4}$	–3.35(0.03)	4.13(0.19)	0.99	0.03	99.99
(*6b*)	σ_U	–2.96(0.07)	0.75(0.18)	0.76	0.13	99.53
(*7b*)	$\sigma_{R,4-XPh}$	–2.57(0.07)	2.52(0.69)	0.71	0.14	99.14
(*8b*)	σ_P	–2.84(0.02)	0.52(0.05)	0.94	0.06	99.99
(*9b*)	σ_R	–2.68(0.07)	0.51(0.25)	0.44	0.19	92.65

[a] *a* and *b* are for *RS*/*SR* and *RR*/*SS* diastereoisomers, respectively. [b] log $k_{d,0}$ is the *y*-intercept. [c] Numbers in brackets are the errors. [d] R^2 is the square of the linear regression coefficient. [e] *s* is the standard deviation. [f] *t* is the Student *t*-test.

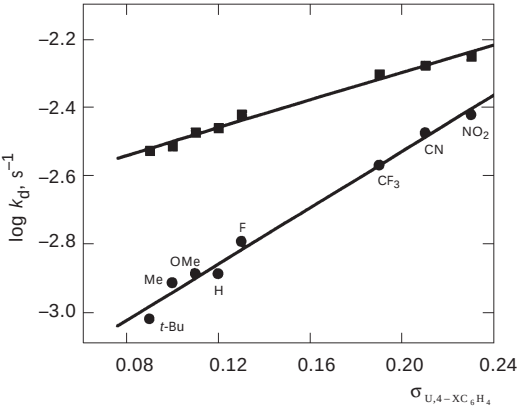


FIG. 2
Plot of log k_d vs $\sigma_{U,4-XC_6H_4}$ for alkoxyamines **2a**–**2h** at 120 °C: ● *RR*/*SS* and ■ *RS*/*SR* diastereoisomers

For *RS*/*SR* diastereoisomers:

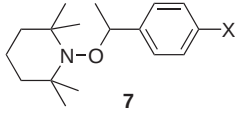
$$\log (k_d/s^{-1}) = -3.6(\pm 0.1) + 2.3(\pm 0.3)\,\sigma_{U,4-XC_6H_4} \qquad R^2 = 0.90 \qquad (4a)$$

For *RR*/*SS* diastereoisomers:

$$\log (k_d/s^{-1}) = -4.3(\pm 0.1) + 4.3(\pm 0.2)\,\sigma_{U,4-XC_6H_4} \qquad R^2 = 0.96 \qquad (4b)$$

DISCUSSION

The *para*-substituent on the benzene ring of an ester alkoxyamine **2** exerts a weak but unambiguously long-range effect on the values of k_d (Table I). Such effect has already been observed by Marque et al.[8f] with *para*-substituted aromatic TEMPO-alkoxyamines of type **7** (Chart 1). However, the aromatic ring was directly bound to the reactive center which is more sensitive to the *para*-substituent on the aromatic ring (Chart 1).



7

CHART 1

The correlation of log k_d with σ_U (universal electrical effect) and σ_R (delocalization effect) are not fair enough (Eqs (*6*) and (*9*) in Table III) because the electron-withdrawing or electron-donating capacities of the X group are certainly buffered by the presence of an aromatic ring bound to the oxygen atom (vide infra). Furthermore, orders of the substituents as a function of σ_U and σ_R does not match the order given by the k_d values (Chart 2). Because σ_p and $\sigma_{R,4-XC_6H_4}$ (Eq. (*3*)) are composite constants of σ_U and σ_R^0, it is not surprising to observe a high degree of correlation of $\sigma_{R,4-XC_6H_4}$ and σ_p with log k_d (Eqs (*7*) and (*8*) in Table III). Nevertheless, the correlations between k_d and σ_p and $\sigma_{R,4-XC_6H_4}$ have to be disregarded because σ_p and $\sigma_{R,4-XC_6H_4}$ are generally used when the reactive center is directly linked to the aromatic ring as for the alkoxyamine series **7** whereas this is not the case here. Furthermore, the order given by σ_p and $\sigma_{R,4-XC_6H_4}$ do not match that observed with k_d (Chart 2).

k_d	*t*-Bu < Me < MeO ≤ H < F < CF_3 < CN < NO_2
$\sigma_{U,4-XC_6H_4}$	*t*-Bu < Me < MeO < H < F < CF_3 < CN < NO_2
σ_U	*t*-Bu < Me < H < MeO < CF_3 < F < CN < NO_2
σ_p	MeO < *t*-Bu < Me < H < F < CF_3 < CN < NO_2
σ_R	MeO < F < *t*-Bu < Me < H <CN < CF_3 < NO_2
$\sigma_{R,4-XC_6H_4}$	MeO < Me < H < *t*-Bu < F < CF_3 < CN < NO_2

CHART 2

In fact, $\sigma_{U,4-XC_6H_4}$ is the best candidate because it accounts for the electrical universal effect of the *para*-substituted phenyl group, i.e. the buffering effect of the aromatic ring, the localized and delocalized electrical effect of the *para*-substituent groups. A very good correlation between $\sigma_{U,4-XC_6H_4}$ and log k_d is observed (Eqs (*5a*), (*5b*) in Table III and Fig. 2). Moreover, the order given by $\sigma_{U,4-XC_6H_4}$ matches that observed with k_d very well (Chart 2). Consequently, the more polar the aromatic ring (the higher $\sigma_{U,4-XC_6H_4}$), the higher k_d. Assuming a partial charge distribution on the C–ON bond for the transition state of the homolysis as depicted in Chart 3, the presence of an electron-withdrawing *para*-substituent on the benzene ring of alkoxyamines **2** implies a destabilization of the transition state, that is, a decrease of k_d. Hence, the increase of k_d with increasing electron-withdrawing capacities of the *para*-substituent on the benzene ring of **2** is assessed to a polar molecular state effect[25] (PMSE), i.e., larger destabilization of the ground state due to the stronger electron-withdrawing properties of the *para*-substituted aromatic group, as previously pointed out by Marque et al.[8f] for the TEMPO-alkoxyamines **7**.

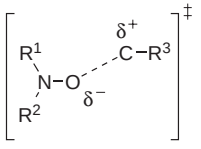
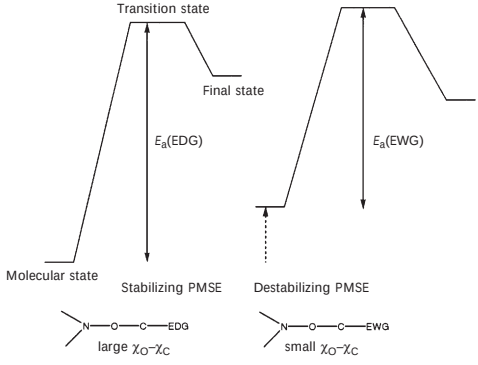


CHART 3

Although no extensive studies of the solvent effect on k_d are available, few results[8i] show that the k_d values of SG1-based alkoxyamines are not very sensitive to the solvent, which generally indicates[26] a weakly polar

transition state. Hence, the polar effect in the molecular state is larger than in the transition state. The PMSE is schematically depicted in Scheme 5, where the electronegativity (χ) difference of the cleaved O–C bond either stabilizes or destabilizes the molecular state, i.e., the larger $\chi_O - \chi_C$ (the less electron-withdrawing the carbon atom), the more stabilized the molecular state.



SCHEME 5

CONCLUSION

Our work illustrates that, like in TEMPO-alkoxyamines **7**, the polar molecular state effect occurs in alkoxyamines of type **2**, even at a long distance from the reactive center. Steric, polar and stabilizing effects will be further analyzed in forthcoming papers.

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