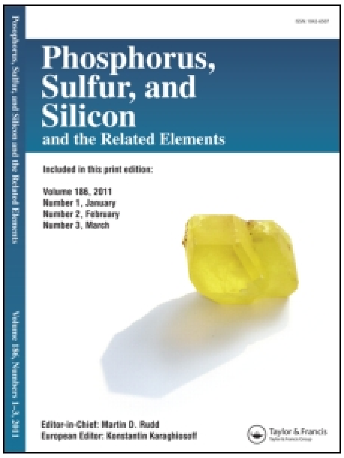

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Synthesis, Properties, and Atropisomerism of Arylcarbamates with a Phosphonium Group

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SYNTHESIS, PROPERTIES, AND ATROPISOMERISM OF ARYLCARBAMATES WITH A PHOSPHONIUM GROUP

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*The reactions of the zwitterionic species **1** with* ortho-*substituted aryl isocyanates proceed in an unusual way, resulting in the formation of the P-containing carbamates 3. In the latter (except for X=F) the CH_2P protons are anisochronous and give rise to an AB pattern at the corresponding temperatures (1H{31P}). When the temperature is increased, the AB pattern coalesces to a singlet. The $\Delta G_c^{\#}$ values, together with all pertinent data, are listed.*

Keywords: Atropisomerism; p-zwitterions; rearrangements

Intramolecular electrophilic rearrangements of the C—N type due to migration of C(:O)OAlk groups were unknown prior to our work. This event was reliably established for the interaction of P-zwitterion **1** with alkyl, aryl isocyanates, phenyl isothiocyanate,[1–5] and recently with *ortho*-substituted aryl isocyanates[6] (Figure 1).

The second step of this process involves migration of the ethoxycarbonyl group from the C atom to the N-anionic center arising from the reaction of carbanion **1** with isocyanates.

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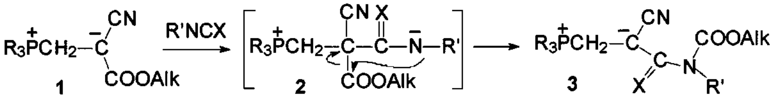
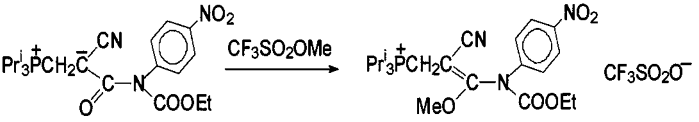


R = Pr^n, Pr^i, Bu^n, Et_2N
R'= Me, *c*-C_6H_{11} or Ar = Ph, *p*-$NO_2C_6H_4$, *o*-FC_6H_4, *o*-ClC_6H_4, *p*-ClC_6H_4, *m,p*-$Cl_2C_6H_3$, *o*-BrC_6H_4, *o*-IC_6H_4, *o*-Tol, *m*-Tol, *o*-$CF_3C_6H_4$, *o,p*-$Me_2C_6H_3$, *m,m*-$Me_2C_6H_3$, *o*-EtC_6H_4, *o*-$Pr^iC_6H_4$, 1-Naphthyl, *o*-PhC_6H_4;
Alk = Me, Et; X = O, S

FIGURE 1

This process is unusual because a carbanion rather than the ethoxy anion functions as the leaving group upon nucleophilic attack by the nitrogen atom on the carbonyl group. Apparently, this unique situation in which cleavage of a C—C bond is preferred over the cleavage of a C—O bond is due to the efficient delocalization of the negative charge in the resulting carbanions **3**. For instance, carbamate **3a** reacts with methyl trifluoromethanesulfonate with O-methylation to give **4**[7] (Figure 2).

The reaction rate of the P-zwitterions **1** with isocyanates depends strongly on their electronic and spatial characteristics. The zwitterions **1** react relatively readily with phenyl- or *meta*- and *para*-substituted aryl isocyanates; however, there are complications in the case of the bis-*ortho*-substituted aryl isocyanates and isothiocyanates in the reaction



3a **4**

FIGURE 2

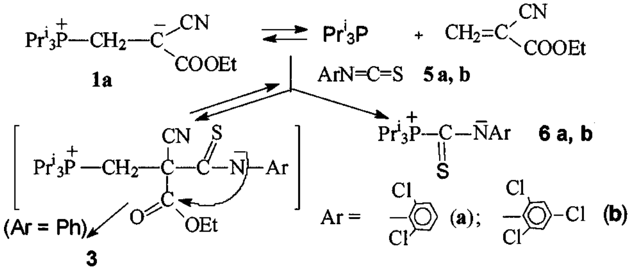


FIGURE 3

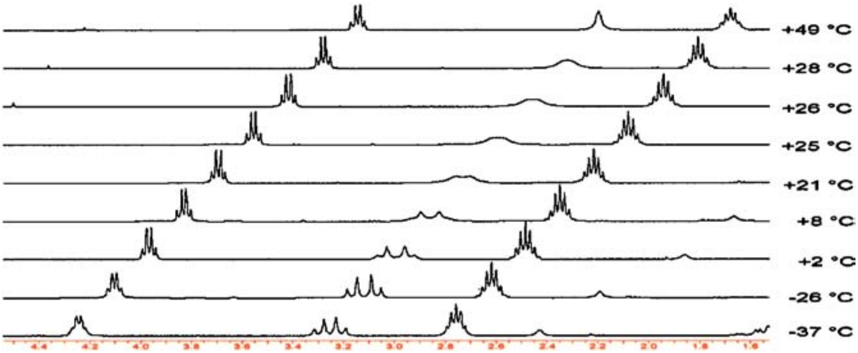


FIGURE 4 The typical change of the ^{1}H-NMR signals of the CH_2P protons ($^1H\{^{31}P\}$) with temperature for compound **3b** (X = I).

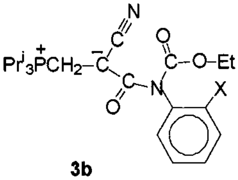
with the carbanions **1**. For instance, **1a** reacts with aryl isothiocyanates **5** to afford the zwitterions **6**, whereas phenyl isothiocyanate leads to carbamate **3**[8] (Figure 3).

The reaction rate of the zwitterion **1** with ArNCO essentially depends on the bulk of the *ortho*-substituents. The greater the latter, the lower is the rate of the reaction (Figure 1). The rotation about the Ar—N bond in the corresponding compounds **3** is slowed down, accordingly. In the *ortho*-substituted P-containing carbamates **3b** (except for X = F) the CH_2P protons are anisochronous and give rise to an AB pattern at the corresponding temperatures ($^1H\{^{31}P\}$). When the temperature is increased, the AB pattern coalesces to a singlet (Figure 4).

The $\Delta G^{\neq}$ values, together with all pertinent data, are listed in Table I. The dependence between the $\Delta G^{\neq}$ values and the bulk of the substituents

TABLE I Hindered Rotation About the N—Ar Bond in the Phosphorus-Containing Carbamates **3b**

X	r(Å)	$\Delta G_c^{\neq}$ (kJ/mol)	T_c(°C)	$\Delta\nu$ (Hz)
F	1.35	<40	<−75	(45)[a]
Cl	1.80	51.7	−19	42
Br	1.95	56.6	5	45
I	2.15	60.9	25	48
Ph	1.70	53.0	−2	153
Me[b]	2.00	56.1	0	28
Et	—	62.9	32	30



3b

[a] Value assumed.

[b] 2,4-Dimethylphenyl derivative.

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