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THE METHYLATION OF THE AMBIDENT ANIONS N,N'-DIARYLPHOSPHAMIDINES BY METHYL IODIDE

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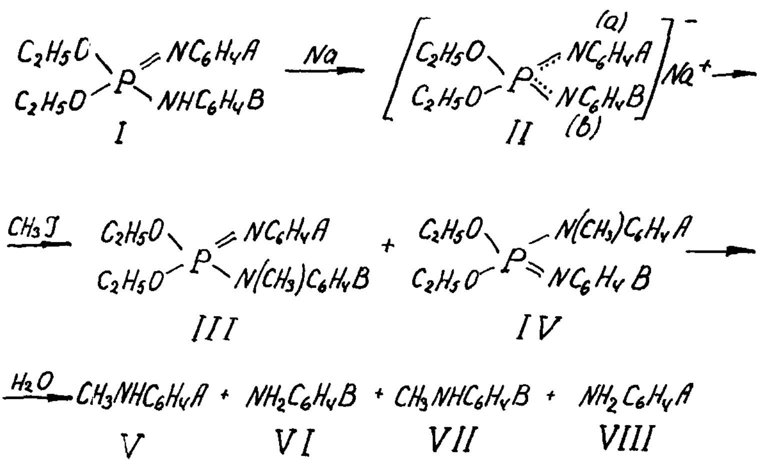
The methylation of sodium salts of N,N'- diarylphosphamidines by methyl iodide was studied to elucidate the effect produced by the polarity of the substituents in the ambident anion on the alkylation trend.

N,N'- Diarylphosphamidines /I/[1] are weak acids; their sodium salts /II/ are formed by the action of sodium or its hydride. When these salts are methylated by methyl iodide, the trend of reaction depends on the nature of A and B substituents /see diagram/.



In contrast to other known cases involving alkylation of ambident anions[2/], in phosphamidine-anions two atoms of the same element, viz. nitrogen, compete and, thus, the difference in the nature of the alkylated elements (O and C in enolate-anions, O and N in lactim--lactam anions, etc.) is eliminated. The symmetry in the structure of the salts /II/ differing only in the substituents occupying the para- and meta-positions in the phenyl rings equalizes the steric conditions of attack and thereby eliminates any effect of the steric factor on the alkylation trend[3/]. Finally, the solubility of the sodium salts of phosphamidines in tetrahydrofuran makes it possible to study methylation in a solution and thereby eliminate the effect of heterogeneity, which is so frequently observed in ambident ion reactions[4]. Thus in the instance described the influence of polar effects of A and B substituents reveals itself in a pure form.

In view of the fact that the a priory methylation mechanism is identical for both nitrogen atoms the ratio of the alkylation rate constants for both atoms is undoubtedly equal to the ratio of the yields of products /III/ and /IV/[5]:

$$K_a/K_b = Q_a/Q_b \qquad /I/$$

The effect of A and B substituents on the methylation rate constant of the "a" nitrogen atom can be described by the Hammett equation:

$$\log K_a/K_a^o = \rho_1 \sigma_A + \rho_2 \sigma_B \qquad /2a/$$

Here ρ_1 and ρ_2 is the susceptibility of the reaction centre to the effect of the substituent, transmitted, respectively, through the phenyl ring and through a longer conjugated system $-C_6H_4=N=P-$

Similarly for the effect of the substituents on the alkylation rate of the "b" nitrogen atom:

$$\log K_b/K_b^o = \rho_2 \sigma_A + \rho_1 \sigma_B \qquad /2b/$$

Naturally, here ρ_1 and ρ_2 have changed places.

Taking account of $K_a^o = K_b^o$ and equation /1/ we obtain:

$$\log\ Q_a/Q_b = (\rho_2 - \rho_1)(\sigma_B - \sigma_A) \qquad /3/$$

In the course of a preliminary investigation all the required syntheses were made, the methylation of O,O-diethyl-N,N'-diphenylphosphamidine /I, A = B = H/ and its sodium salt by methyl iodide was studied, the structure of the methylation products was elucidated, the consecutive reaction of secondary methylation, etc. was investigated and the conditions permitting a quantitative investigation were specified. In some special experiments the ratio Q_a/Q_b was found to be unaffected by the depth of transformation, i.e. that the relationship /1/ is valid.

The reaction was conducted in tetrahydrofuran; the initial component concentrations 0.07 Mol/l; temperature 20°, the experiment continued for 3 days.

The analytical method devised for the determination of Q_a/Q_b involves the hydrolysis of the reaction products by HCl treatment, the isolation of the mixture of bases /V-VIII/ by alkali treatment and a subsequent analysis of the mixture by the GPC technique on Willy Giede's apparatus /GDR/, model GCHF-18 with a katharometer. A stainless steel column, 2 m long and 6 mm in diameter was filled with diatomite firebrick 0,25-0,5 mm with 20% boiled butter; the temperature of the column was 160-190°; helium rate was about 80-85 ml/min. The composition of the mixture was determined with a relative error within 5%.

The obtained data are presented in Table 1, fig.1.

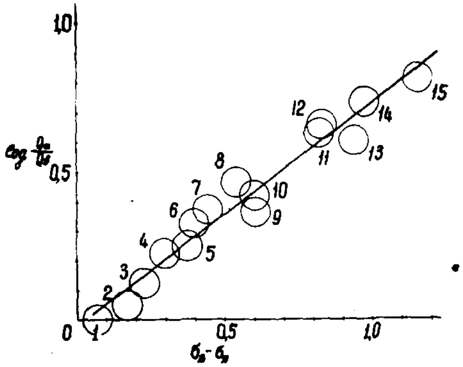


Fig.1 Dependence of Q_a/Q_b on $\sigma_B - \sigma_A$

As can be seen, they agree well with equality 3. The processing of the results by the least square method produced a linear dependence

$$\log Q_a/Q_b = 0.757\,(\sigma_B - \sigma_A) - 0.022 \quad /4/$$

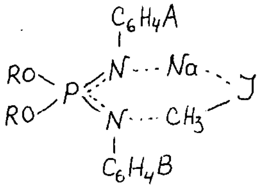
The correlation coefficient $r = 0.979$; the mean deviation $s = 0.05$. The straight line can thus be assumed to pass through the origin.

The positive value of $\rho_2 - \rho_1$ provides evidence that the methylation is primarily directed towards the nitrogen atom which is bound with the phenyl radical carrying a more electronodonor (less electronoacceptor) substituent. From our data ρ_1 and ρ_2 cannot be determined independently of one another. Since $\rho_2 - \rho_1 > 0$, one of the three possibilities must be realized:

$$1)\ \rho_2 > \rho_1 \geqslant 0; \quad 2)\ \rho_2 \geqslant 0 > \rho_1; \quad 3)\ 0 \geqslant \rho_2 > \rho_1$$

The third one is most probable; both ρ are negative and the less electrophylic is the substituent /diminishing σ / the higher is the alkylation rate. Since in absolute values $|\rho_1| > |\rho_2|$ this effect is naturally stronger in the case of a shorter conjugation chain. The analysis made supports the conclusion that the methylation is primarily directed towards a more nucleophylic nitrogen atom, i.e. towards the one in which the conjugation chain with a more electronodonor (or less electronoacceptor) substituent is shorter, a longer conjugation chain being not favourable to prevailing methylation.

The methylation of ambident anions by methyl iodide usually proceeds according to $S_{N_2}{}'$ mechanism, i.e. with the intersection of the reaction centre, the enolate-anions being methylated on the carbon, the lactim-anions, on the nitrogen, etc. Such alkylation trend is usually explained either by a higher polarization of the carbonium centre (participation of the longer conjugation chain), or by its easy desolvation or by the advantages of the benzol-like transition state with participation of metal cation[6]. In the last case the transition state in the methylation of phosphamidine anion should be represented as:



The experimental data presented in this paper do not permit, at least in the case of phosphamidine-anions, to choose any one of these interpretations.

Table 1

The Results of the Methylation of Sodium Derivatives of Substituted Diphenylphosphamidines

Experim. No.	A	B	log Q_a/Q_b	B - A
1	m-CH_3	H	0	0,069
2	p-CH_3	H	0,050	0,170
3	H	p-Cl	0,128	0,227
4	m-CH_3	p-Cl	0,226	0,296
5	H	m-Cl	0,248	0,373
6	p-CH_3	p-Cl	0,326	0,397
7	m-CH_3	m-Cl	0,373	0,442
8	p-CH_3	m-Cl	0,464	0,543
9	p-CH_3O	m-F	0,364	0,605
10	p-$(CH_3)_2N$	H	0,421	0,600
11	p-CH_3O	p-CF_3	0,630	0,819
12	p-$(CH_3)_2N$	p-Cl	0,658	0,827
13	p-$(CH_3)_2N$	m-F	0,602	0,937
14	p-$(CH_3)_2N$	m-Cl	0,739	0,973
15	p-$(CH_3)_2N$	p-CF_3	0,812	1,151

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