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BORON TRIFLUORIDE ETHERATE - AN EFFECTIVE CATALYST OF 1,3-PHOSPHOROTROPIC MIGRATION IN C=N-C TRIAD

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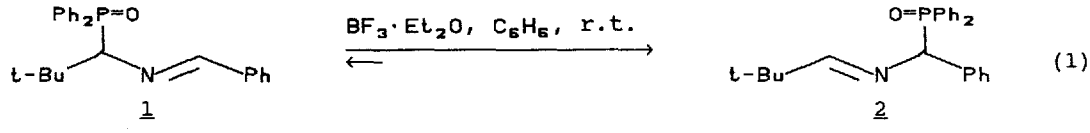
Abstract: *A facile $BF_3 \cdot Et_2O$ promoted 1,3-transfer of a diphenylphosphinoyl group in a 2-azaallylic system has been found. The isomerization was shown to proceed by an intramolecular mechanism in the complex formed with participation of a phosphorylated imine P=O group.*

Isomerizations in azaallylic systems are of general importance as an integral part of heteroallylic rearrangements. We wish to report on a novel 1,3-phosphorotropic migration in C-N=C triad. This unusual rearrangement proceeds on heating (150-200°C) and is accompanied by cleavage of the C-P bond[1,2]. Because of severe conditions, the destruction processes occur in some cases, and this restricts the synthetic possibilities of the rearrangement. Now we have found that boron trifluoride etherate essentially facilitates the rearrangement,which allows the reaction to run under much milder conditions. Thus, α-phosphorylated imine 1 in solid state or in solutions can be kept for a long time without changes. Addition of the equimolar amount of $BF_3 \cdot Et_2O$ to the benzene solution of the compound 1 resulted in spontaneous 1,3-migration of the diphenylphosphinoyl group which leads to imine 2[3] . Isomerization is completed within a day at room temperature.



1 2 (1)

The equilibrium of this reaction is essentially shifted to the right (2:1 ~ 15:1 at r.t.) and can be achieved from both sides. The rate of isomerization is not affected by the starting concentration of imine 1

(Table 1). This is indicative of the intramolecular mode of the rearrangement. The ratios 2/1 were determined from PMR spectra of the reaction mixture where the PCH-proton signals were fairly resolved. At the constant concentration of the catalyst ($[BF_3 \cdot Et_2O] = [1]_0$, C_6D_6, 25°C) the appearance of 2 or disappearance of 1 follows the first-order kinetics. From the linear relationship of $\ln\{[1]_0/([1]_0-[1])\}$ vs. time the rate constant k for isomerization of 1 was evaluated to be $2.47 \cdot 10^{-5} s^{-1}$ [4]. Hence, the half-life of 1 under these conditions is about 468 min.

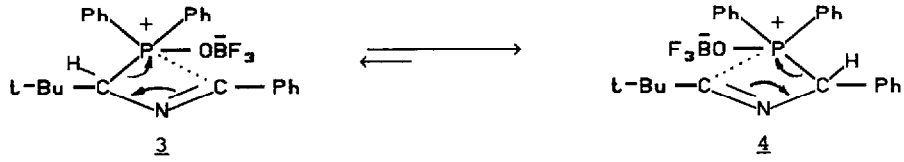
Table 1

Concentration Effects on the BF_3-catalyzed 1,3-Rearrangement of 1.

t, min	Concentration $[1]_0 = [BF_3 \cdot Et_2O]_0$, M	Conversion, %
52	0.04	12
	0.11	12
	0.40	11
138	0.04	19
	0.40	20
184	0.04	28.5
	0.40	28
340	0.04	40
	0.40	40

Boron trifluoride as a Lewis acid forms with isomers 1 and 2 complexes which are more stable than the $BF_3 \cdot Et_2O$ complex. In fact, ether is easily removed from the equimolar mixture of 1 or 2 and $BF_3 \cdot Et_2O$ by evaporation in vacuo at r.t. whereas $2 \cdot BF_3$ is stable on heating in vacuo (80°C, $5 \cdot 10^{-2}$ Torr, 5 h). To isolate the compounds 1 or 2 from the BF_3-complexes, their solutions were treated with aqueous AcONa. The resultant pure samples of 1 and 2 were characterized by elemental analysis and spectral data[5]. The comparative NMR-data for the isomers 1, 2 and their complexes with BF_3 are listed in Table 2. The largest changes in magnetic screening upon complexation are observed for C=N and CHP groups. Here, the alternation in sign of $\Delta\delta$ for 1,3-carbons in C-N=C triad takes place. Thus, the sp^3-carbon signal is shifted upfield ($\Delta\delta$ -4.1 ÷ -5 ppm), while that of sp^2-carbon is displaced to lower field ($\Delta\delta$ 3.9 ppm). Interestingly, the shielding of sp^3-carbon is accompanied by deshielding of the proton attached to it (Table 2). But the most pronounced changes are observed in the phosphorus resonance. The down-field shift in this case amounts to 15-16 ppm. As a result, the phosphorus signals of the complexes $1 \cdot BF_3$ and $2 \cdot BF_3$ are displaced to the region characteristic of quasiphosphonium salts[6]. In

addition, the P=O group band in IR spectra of 1 is shifted to low frequencies upon complexation ($\Delta\nu$ 70-80 cm^{-1}). Presumably, the complexation occurs at the donating P=O group (cf.[7]) and the resultant complexes possess the structures like 3 and 4 (scheme 2).



(2)

This supposition is substantiated by the fluorine-phosphorus spin-spin coupling ($^3J_{FP}$ 6.8 Hz) in the ^{19}F NMR spectra of the complexes.

Table 2

^1H, ^{13}C, ^{19}F, ^{31}P-NMR Data of Imines 1, 2 and Their Complexes with BF_3

Compound	δ ^{13}C, ppm (J_{CP}, Hz)				^1H	δ_P	δ_F
	C=N	CHP	$\underline{C}Me_3$	$\underline{Me}_3C$	δ_{CHP} (J_{HP})		(J_{FP})
1	164.3 (13)	83.7 (79)	36.9 (2)	29.0 (5)	3.8 (9.5)	30.9	
1·BF_3	168.2 (18)	79.6 (86)	37.4 (3)	28.7 (5.4)	4.5 (10.8)	46.4	-141.4 (6.8)
$\Delta\delta_1$	3.9	-4.1	0.5	-0.3	0.7	15.5	
2	176.0 (13)	77.3 (76)	36.9 (15)	26.8	5.2 (14)	29.8	
2·BF_3	179.9 (17)	72.3 (83)	37.1 (1.7)	26.2	5.9 (13.5)	45.7	-141.5 (6.8)
$\Delta\delta_2$	3.9	-5.0	0.2	-0.6	0.7	15.9	

Thus, the 1,3-shift of the phosphorus-containing group is effected, in fact, in the complexes: 1 $\xrightarrow{+BF_3}$ 3 $\rightleftharpoons$ 4 $\xrightarrow[-BF_3]{AcONa}$ 2. Moreover, phosphorotropic isomerization can proceed both in solution and in the solid state, the rate of isomerization being significantly lower in the latter case, probably because of less lability of a migrating group. Thus, the extent of isomerization of the solid complex 3 for 10 days at room temperature reaches only 57%. It is possible to assume that the weakening of the P-C_{sp^3} bond in the phosphonium derivatives like 3, 4 is one of the factors facilitating their isomerization. 1,3-Migration of a triphenylphosphonium group in 1,3-diarylsubstituted 2-azaallyl derivatives

was shown to be very easy[8].

One of the driving forces of the isomerization, causing thermodynamical preference of 2 to 1 or 4 to 3, is, presumably, the partial decrease in a steric strain at sp^3-carbon connected with bulky tert-butyl and diphenylphosphinoyl groups. The fact that the isomers 2 or 4 are thermodynamically more favorable in spite of the loss of stabilization produced by conjugation between the benzene ring and the C=N bond[2,9] also points out to the importance of steric factors.

It should be noted that thermal rearrangement $1 \rightleftarrows 2$ (185°C, 2 h) leads to equilibrium ratio 2/1 ~ 3.5 - 4 which is almost four times less than in the BF_3-promoted isomerization. One of the reasons of this difference may be an increase in steric hindrance in 1 during complexation which makes this structure still less favorable.

Studies on scope and applications of these findings to other systems are currently in progress.

References and Notes

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2. Onys'ko P.P., Kim T.V., Kiseleva E.I., Sinitsa A.D., *Phosphorus, Sulfur Silicon Relat. Elem.*, **1990**, 49/50, 73-76.
3. The imines 1 and 2 were synthesized independently according to the following schemes: t-BuC(Cl)=NCH_2Ph + Ph_2POEt ⟶ t-BuC[P(O)Ph_2]=NCH_2Ph ⟶ 1 ; $PhCH(NH_2)P(O)Ph_2$ + t-BuCHO ⟶ 2 . The details will be published elsewhere.
4. The calculation of the rate constant from the kinetic equation for reversible reactions, in view of the fact that $K = 2/1 = k_1/k_{-1} \sim 15$, gives practically the same value of k_1.
5. Satisfactory elemental analyses have been determined for all new compounds
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