CATALYTIC PHOSPHORYLATION OF POLYFLUOROALKYL ALCOHOLS.

COMMUNICATION 8. SYNTHESIS AND STEREOCHEMISTRY OF BIS(α-TRIFLUOROMETHYL-m-TRIFLUOROMETHYLBENZYL) CHLOROPHOSPHATE

E. I. Goryunov, L. S. Zakharov,
P. V. Petrovskii, and M. I. Kabachnik

UDC 541.128:542.91:541.63:
547.1'118

In catalytic phosphorylation of primary polyfluoroalkyl alcohols by phosphorus oxychloride in the ratio of 2 : 1.25 in the presence of anhydrous $CaCl_2$ as the catalyst, bispolyfluoroalkyl chlorophosphates are the primary products of the reaction [1].

However, in phosphorylation of secondary α-trifluoromethylbenzyl alcohol by $POCl_3$ in similar conditions, di-α-trifluoromethylbenzyl ether was isolated instead of the expected monochlorophosphate [2]. As found later, a simple ether is obtained as a result of alkylation of the starting benzyl alcohol by the intermediate product formed, α-trifluoromethylbenzyl dichlorophosphate [3]. It was also shown that when a donor substituent, a p-methyl group, was present in the α-trifluoromethylbenzyl alcohol molecule, formation of a simple ether is facilitated, and the reaction takes place in much softer conditions in comparison to an unsubstituted alcohol [3].

It could be hypothesized that introduction of a strong enough electron-acceptor substitutent, for example, a m-trifluoromethyl group, into the α-trifluoromethylbenzyl alcohol molecule would favor formation of the products of phosphorylation, and this would permit extending the reaction of catalytic phosphorylation to synthesis of bis(α-polyfluoroalkylbenzyl) chlorophosphates.

Actually, when a mixture of α-trifluoromethyl-m-trifluoromethylbenzyl alcohol (I) is heated to 140°C with $POCl_3$ in the ratio of 2 : 1 in the presence of catalytic quantities of anhydrous $CaCl_2$, bis(α-trifluoromethyl-m-trifluoromethylbenzyl)chlorophosphate (II) is formed as the basic product of the reaction (see Table 1), but phosphorylation is extremely slow at this temperature: According to the data from the ^{31}P NMR spectra, the reaction mixture contains 25% $POCl_3$, 50% α-trifluoromethyl-m-trifluoromethylbenzyl dichlorophosphate (III), and a total of 25% of (II) after 13 h; even after 73 h, when there is no more $POCl_3$ in the mixture, the ratio of (II) : (III) is only 77 : 23; on further heating, this ratio remains almost unchanged. The TLC analysis of the reaction mixture showed the absence of products of the simple benzyl ether type. In phosphorylation of alcohol (I) by $POCl_3$ in the presence of $CaCl_2$, formation of the simple ether is not observed even at 200°C, in contrast to unsubstituted α-trifluoromethylbenzyl alcohol, and the basic product of the reaction in these conditions is monochlorophosphate (II). Use of anhydrous $MgSO_4$ as the catalyst results in a slight decrease in the time of the reaction in comparison to $CaCl_2$, but the process is accompanied by significant resinification, and the ^{31}P NMR spectrum of a solution of the reaction mixture in CCl_4 contains a group of unidentified signals in the region of −14 to −16 ppm in addition to the signals assigned to chlorophosphates (II) and (III) (ratio of 96 : 4); the overall intensity of the unidentified signals is commensurate with the intensity of the signals of chlorophosphate (II). When metallic Mg, which is dissolved and apparently transformed into $MgCl_2$ during the reaction, is used instead of $MgSO_4$, the reaction time at 200°C is only 6 h, and judging by the data from the ^{31}P NMR spectra, only insignificant amounts of byproducts are formed, in contrast to $MgSO_4$, and the yield of chlorophosphate (II) attains 66%. An increase in the catalytic activity in going from anhydrous $CaCl_2$ to Mg has also been observed in catalytic phosphorylation of phenols [4].

Catalytic phosphorylation of benzyl alcohol (I) containing a strong electron-acceptor substituent in the benzene ring by $POCl_3$ in the ratio of 1 : 2 thus primarily yields monochlorophosphate (II), regardless of the type

---

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1593-1597, July, 1984. Original article submitted May 13, 1983.

0568-5230/84/3307-1463$08.50

TABLE 1. Catalytic Phosphorylation of α-Trifluoromethyl-m-trifluoromethylbenzyl Alcohol by $POCl_3$

$$\underset{(I)}{2m\text{-}CF_3C_6H_4CH(OH)CF_3} + POCl_3 \longrightarrow$$

$$\xrightarrow[-HCl]{\text{Catalyst}\ ,\ ^\circ C} \underset{(II)}{[m\text{-}CF_3C_6H_4CH(CF_3)O]_2POCl}$$

Catalyst*	T., °C	Reaction time, h	Yield of (II) %
$CaCl_2$	140	80	46
$CaCl_2$	200	18	53
$MgSO_4$	200	12	44
Mg	200	6	66

---

*0.025 mole of catalyst per 1 mole of $POCl_3$.

TABLE 2. Dependence of the Diasteromeric Composition of Bis-(α-trifluoromethyl-m-trifluoromethylbenzyl)chlorophosphate (II) on the Conditions of the Catalytic Phosphorylation Reaction

Catalyst	T., °C	Time from the beginning of the reaction, h	Concentration of diastereomers in the mixture according to data from the ^{31}P-{^1H}NMR spectra, %			Ratio of diastereomers
			A (or B)	C + D	B (or A)	
$CaCl_2$	140	13	25	49	26	1 : 2 : 1
		73	24	50	26	1 : 2,1 : 1,1
	200	18	23	52	25	1 : 2,3 : 1,1
$MgSO_4$	200	12	23	53	25	1 : 2,3 : 1,1
Mg	200	6	23	54	23	1 : 2,3 : 1

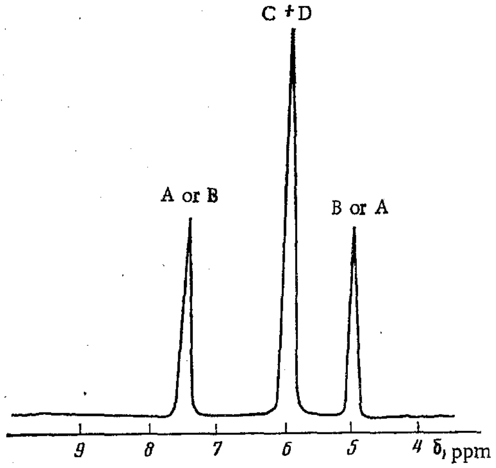
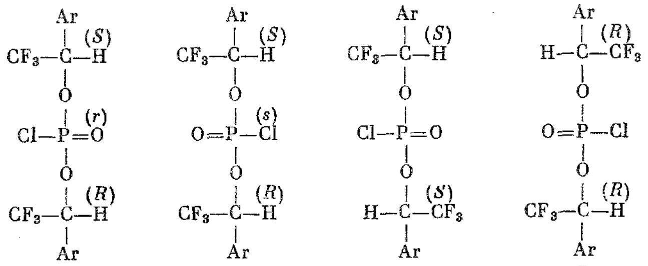


Fig. 1. ^{31}P-{^1H} NMR spectra of bis(α-trifluoromethyl-m-trifluoromethylbenzyl)chlorophosphate (II) in a solution of CCl_4 (c 0.4 mole/liter).

of catalyst used and the temperature of the reaction, and in contrast to unsubstituted α-trifluoromethylbenzyl alcohol, formation of simple benzyl ether was not observed in any of the cases examined.

Compound (II) is of limited interest with respect to the stereochemistry. There are two asymmetric carbon atoms and a pseudoasymmetric pentavalent tetracoordinated phosphorus atom in the molecule of its chlorophosphate. For structures containing a pseudoasymmetric site, the existence of four stereoisomers is possible in principle, i.e., two mesoforms A and B, which only differ with respect to the configuration at the pseudoasymmetric site, and two optically active stereoisomers C and D, which are enantiomers with respect to each other, in which the phosphorus atom is nonasymmetric



A B C D

Mesoforms

Racemate

Ar=*m*-$CF_3C_6H_4$

Since stereoisomers C and D are indistinguishable in the NMR spectra, three signals could be expected for each of the indicator nuclei in the NMR spectra. Actually, three singlet signals are observed in the ^{31}P-$\{^1H\}$ NMR spectrum of chlorophosphate (II) (Fig. 1). We note that a qualitatively similar picture was previously observed in the study of the ^{31}P-$\{^1H\}$ NMR spectra of phosphonites $[C_2H_5CH(CH_3)O]_2PR$ (where R = Me, Ph) with a pseudoasymmetric trivalent phosphorus atom [5].

The ratio of stereoisomers in chlorophosphate (II) (Table 2) is almost independent of the type of catalyst used, the temperature, and the time after the onset of the reaction, and actually coincides with the statistical ratio of diastereomers: 1 : 2 : 1. Judging by the relative integral intensity of the signals in the ^{31}P-$\{^1H\}$ NMR spectrum, the central signal can be assigned to a racemic mixture of stereoisomers C and D, and the other two signals can be assigned to mesoforms A and B.

Regardless of the conditions of catalytic phosphorylation, formation of chlorophosphate (II) is thus nonstereoselective, in contrast to O,O-bis(α-polyfluoroalkylbenzyl)methylphosphonates, for which important stereoselectivity is observed [6]. It is necessary to remember that the ratio between the total amount of mesoforms A and B and the concentration of a racemic mixture of stereoisomers C and D should in all probability be a kinetically controllable value which applies to the ratios of the mesoforms; in view of the important possibility of the mutual transformation of these forms, for example, by a mechanism of epimerization of the pseudoasymmetric phosphorus atom due to the rotation of the configuration of the nucleophilic exchange of the chlorine atom as for O-(α-polyfluoroalkylbenzyl)methylchlorophosphonates [7], the possibility of thermodynamic control of this aspect of the stereochemistry of the reaction cannot be excluded.

EXPERIMENTAL

The ^{31}P NMR spectra were made on a Bruker HX-90 spectrometer (36.43 MHz) in the pulsed mode with suppression of spin–spin interactions with protons (85% H_3PO_4 external standard); the chemical shifts in the weak field had positive values. The TLC analysis was conducted on Silufol UV-254 plates.

Bis(α-trifluoromethyl-m-trifluoromethylbenzyl)chlorophosphate (II). a) A mixture of 12.2 g (0.05 mole) of α-trifluoromethyl-m-trifluoromethylbenzyl alcohol (I), 3.8 g (0.025 mole) of $POCl_3$, and 70 mg (0.625 mmole) of anhydrous $CaCl_2$ were heated for 80 h at 140°C and fractionated in a vacuum. Yield of 6.6 g (46%) of (II), bp 126-127°C (0.1 mm), n_D^{20} 1.4313, d_4^{20} 1.5445. Found: C 38.0, H 1.8, Cl 5.8, F 40.4, P 5.6%. $C_{18}H_{10}ClF_{12}O_3P$. Calculated: C 38.0, H 1.8, Cl 6.2, F 40.1, P 5.4%. Yield of 0.9 g (10%) of α-trifluoromethyl-m-trifluoromethylbenzyl dichlorophosphate (III), bp 67-69°C (0.1 mm), n_D^{20} 1.4361 (compare [8]).

b) A mixture of 12.2 g (0.05 mole) of (I), 3.8 g (0.025 mole) of $POCl_3$, and 70 mg (0.625 mmole) of anhydrous $CaCl_2$ were heated for 18 h at 200°C and fractionated in a vacuum. Yield of 7.5 g (53%) of (II) and 1.3 g (14%) of (III).

c) A mixture of 12.2 g (0.05 mole) of (I), 3.8 g (0.025 mole) of $POCl_3$, and 75 mg (0.625 mmole) of anhydrous $MgSO_4$ was heated for 12 h at 200°C, 10 ml of CCl_4 were added, the mixture was filtered, the filtrate was evaporated, and the residue was distilled in a vacuum. Yield of 6.3 g (44%) of (II) and 0.6 g (7%) of (III).

d) A mixture of 12.2 g (0.05 mole) of (I), 3.8 g (0.025 mole) of $POCl_3$, and 15 mg (0.625 g-atom) of metallic Mg were heated for 6 h at 200°C and distilled in a vacuum. Yield of 9.4 g (66%) of (II).

CONCLUSIONS

1. Catalytic phosphorylation of α-trifluoromethyl-m-trifluoromethylbenzyl alcohol by $POCl_3$ in the ratio of 2 : 1 primarily yielded bis(α-trifluoromethyl)m-trifluoromethylbenzyl)chlorophosphate regardless of the conditions of the reaction, and in contrast to unsubstituted α-trifluoromethylbenzyl alcohol, absolutely no simple benzyl ether was formed.

2. The bis(α-trifluoromethyl-m-trifluoromethylbenzyl) chlorophosphate obtained is a mixture of three diastereomers in a ratio close to the statistical ratio.

LITERATURE CITED

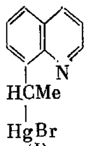
1. L. S. Zakharov, V. V. Pisarenko, N. N. Godovikov, and M. I. Kabachnik, Izv. Akad. Nauk SSSR, Ser. Khim., 2671 (1971).
2. L. S. Zakharov, E. I. Goryunov, L. L. Morozov, T. M. Shcherbina, S. T. Ioffe, and M. I. Kabachnik, Izv. Akad. Nauk SSSR, Ser. Khim., 2391 (1974).
3. L. S. Zakharov, E. I. Goryunov, L. L. Morozov, V. A. Svoren', É. P. Lur'e, T. M. Shcherbina, and M. I. Kabachnik, Izv. Akad. Nauk SSSR, Ser. Khim., 2090 (1978).
4. S. Percec, A. Natansohn, D. Galea, and M. Dima, Phosphorus Sulfur, 8, 109 (1980).
5. R. Marty, D. Houalla, R. Wolf, and J. Riess, J. Org. Magn. Reson., 2, 141 (1970).
6. M. I. Kabachnik, L. S. Zakharov, E. I. Goryunov, P. V. Petrovskii, V. A. Svoren', and T. M. Shcherbina, Izv. Akad. Nauk SSSR, Ser. Khim., 1182 (1981).
7. L. S. Zakharov, E. I. Goryunov, V. A. Svoren', and M. I. Kabachnik, Izv. Akad. Nauk SSSR, Ser. Khim., 1935 (1977).
8. L. S. Zakharov, E. I. Goryunov, S. T. Ioffe, L. L. Morozov, T. M. Shcherbina, and M. I. Kabachnik, Izv. Akad. Nauk SSSR, Ser. Khim., 1834 (1976).

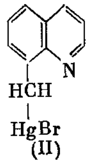
REDOX REACTIONS OF MERCURY DERIVATIVES OF 8-ALKYLQUINOLINES WITH Pd(0) AND Pt(0) COMPLEXES

V. V. Bashilov, É. V. Maskaeva,
A. A. Musaev, V. I. Sokolov,
and O. A. Reutov

UDC 542.91:547.254.9:
547.567:541.49:546.9

Our knowledge of redox demercuration by Pt(0) and Pd(0) complexes, despite the numerous examples studied [1], is incomplete. Specifically, with a single exception [2], no instances are known of the formation in this way of chelatemetallocycles in which the transition metal is bonded with an aliphatic sp^3-hybridized carbon atom. We encountered the problem of the reactivity of alkylmercury compounds containing a donor nitrogen atom in the γ-position when choosing a model reaction for a study of the stereochemistry of redox demercuration. The chiral 8-(α-bromomercuriethyl)quinoline (I) [3] and its homolog (II) [3] and its homolog (II) have recently been proposed as model compounds


(I)


(II)

It was expected that the reaction of (I) or (II) with the d^{10}-complexes $(Ph_3P)_3Pt$ (III), $(Ph_3P)_4Pd$ (IV), $(DBA)_3Pd_2 \cdot CHCl_3$ (V)* or $(DBA)_2Pd$ (VI) would afford, following replacement of the mercury, the chelate metal-

---

*DBA is dibenzylideneacetone.

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1597-1601, July, 1984. Original article submitted May 31, 1983.

0568-5230/84/3307-1466$08.50