CATALYTIC PHOSPHORYLATION OF POLYFLUOROALKANOLS.

12. SYNTHESIS AND STEREOCHEMISTRY OF (1,1-DIHYDROPOLYFLUORO-

ALKYL)(α-POLYFLUOROALKYLBENZYL) CHLOROPHOSPHATES

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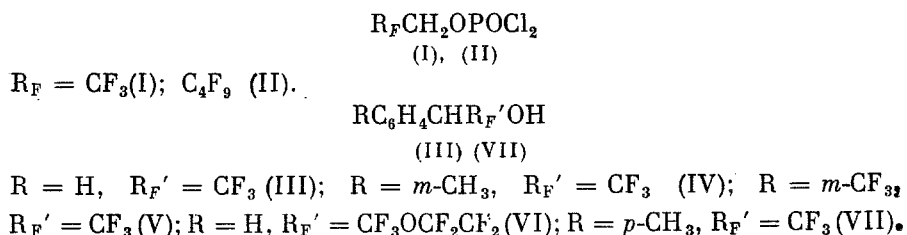T. M. Shcherbina, L. S. Zakharov,
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Catalytic phosphorylation of α-polyfluoroalkylbenzyl alcohols with excess 1,1-dihydropolyfluoroalkyl dichlorophosphates afforded (1,1-dihydropolyfluoroalkyl) (α-polyfluoroalkylbenzyl) chlorophosphates in a high yield. According to NMR (^1H, ^{19}F, ^{31}P) spectral data, these compounds are a mixture of two diastereomers with a ratio close to the statistical.

Earlier we showed that catalytic phosphorylation of sterically hindered tertiary α,α-dihydropolyfluoroalkyl dichlorophosphate leads to the formation of unsubstituted monochloro-phosphates [1] in which disproportionation of nonidentical polyfluoroalkyl radicals does not take place under the reaction conditions

$$R_FCH_2OPOCl_2 + R_F'C(CH_3)_2OH \xrightarrow{\text{Cat, } t°} R_FCH_2OP(O)(Cl)OC(CH_3)_2R_F'$$
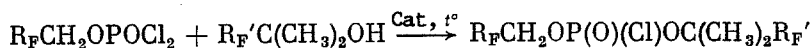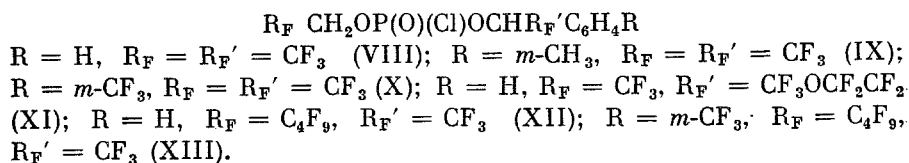
This led us to conclude that catalytic phosphorylation would also be suitable for synthesizing asymmetric chlorophosphates containing, in addition to primary 1,1-dihydropoly-fluoroalkyl groups, sterically hindered secondary groups such as α-polyfluoroalkylbenzyl.

To test this hypothesis, we studied the reactions of 2,2,2-trifluoroethyl dichlorophosphate (I) and 2,2,3,3,4,4,5,5,5-nonafluoropentyl dichlorophosphate (II) with α-polyfluoro-alkylbenzyl alcohols (III)-(VII) in the presence of catalytic amounts of anhydrous $CaCl_2$ or metallic Mg·

$$R_FCH_2OPOCl_2$$
$$\text{(I), (II)}$$

$$R_F = CF_3(I); \; C_4F_9 \; (II).$$

$$RC_6H_4CHR_F'OH$$
$$\text{(III) (VII)}$$

R = H, R_F' = CF_3 (III); R = m-CH_3, R_F' = CF_3 (IV); R = m-CF_3,

R_F' = CF_3(V); R = H, R_F' = $CF_3OCF_2CF_2$(VI); R = p-CH_3, R_F' = CF_3(VII).

In order to impede the formation of absolute ethers as side products, a twofold excess of the phosphorylating agent was used in all cases, and the reaction was carried out at the lowest possible temperature.

Catalytic phosphorylation of alcohls (III)-(VI) with dichlorophosphate (I) and of alcohols (III) and (V) with dichlorophosphate (II) afforded (2,2,2-trifluoroethyl)(α-poly-fluoroalkylbenzyl) chlorophosphates (VIII)-(XI) and (2,2,3,3,4,4,5,5,5-nonafluoropentyl) (α-polyfluoroalkylbenzyl) chlorophosphates (XII) and (XIII), respectively:

$$R_F \; CH_2OP(O)(Cl)OCHR_F'C_6H_4R$$

R = H, R_F = R_F' = CF_3 (VIII); R = m-CH_3, R_F = R_F' = CF_3 (IX);
R = m-CF_3, R_F = R_F' = CF_3 (X); R = H, R_F = CF_3, R_F' = $CF_3OCF_2CF_2$
(XI); R = H, R_F = C_4F_9, R_F' = CF_3 (XII); R = m-CF_3, R_F = C_4F_9,
R_F' = CF_3 (XIII).

TABLE 1. Catalytic Phosphorylation of α-Polyfluoroalkylbenzyl
Alcohols with 1,1-Dihydropolyfluoroalkyl Dichlorophosphates

$$2R_FCH_2OPOCl_2 + RC_6H_4CHR'_FOH \xrightarrow[-HCl]{Cat., 140°} R_FCH_2O\overset{*}{P}(O)(Cl)O\overset{*}{C}HR'_FC_6H_4R$$
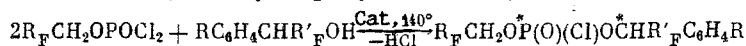
R_F	$R_{F'}$	R	Catalyst*	Reaction time, h	Yield, %	Diastereomer ratio a/b in reaction mixture (from ^{31}P NMR spectra)
CF₃	CF₃	H	CaCl₂	5,0	66	52 : 48
CF₃	CF₃	H	Mg	1,5	70	48 : 52
CF₃	CF₃	m-CH₃	Mg	1,5	70	52 : 48
CF₃	CF₃	m-CF₃	CaCl₂	11,0	71	52 : 48
CF₃	CF₃OCF₂CF₂	H	Mg	9,5	76	48 : 52
C₄F₉	CF₃	H	CaCl₂	6,0	68	51 : 49
C₄F₉	CF₃	H	Mg	2,5	74	48 : 52
C₄F₉	CF₃	m-CF₃	CaCl₂	13,0	76	48 : 52
C₄F₉	CF₃	m-CF₃	Mg	5,0	75	48 : 52

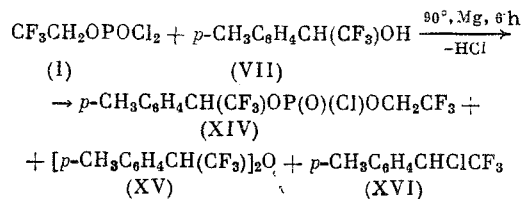*0.025 mole catalyst per mole $RC_6H_4CHR'_FOH$.

The catalytic phosphorylation conditions and yields of monochlorophosphates are shown in Table 1; constants for the synthesized compounds are presented in Table 2.

The phosphorylation rate for secondary α-polyfluoroalkylbenzyl alcohols, as seen from the data in Table 1, depends on the structure of the alcohol and the dichlorophosphate. It decreases with an increase in the acceptor character of the R substituent in the alcohol bezene ring and with an increase in the chain length of the polyfluoroalkyl radical of the dichlorophosphate or the alcohol. However, a change in the R_F' radical of the phosphorylating alcohol has a significantly greater effect on the reaction rate than an analogous change in the R_F radical of 1,1-dihydropolyfluoroalkyl dichlorophosphate.

A comparison of the catalytic activity of Mg and CaCl₂ showed that Mg is much more effective than CaCl₂, though both catalysts are fully soluble in the reaction mixture.

The monochlorophosphates that are formed are readily separated from the phosphorylating agent by distillation. The latter is regenerated nearly quantitatively (88-98%) and is sufficiently pure for repeated use.

The phosphorylation of unsubstituted α-polyfluoroalkylbenzyl alcohols (III) and (VI) and of alcohols (V) and (IV), which contain either an acceptor substituent (m-trifluoromethyl group) in the benzene ring or a weak donor (m-methyl group), by dichlorophosphates (I) and (II) at 140°C affords almost no side products. However, p-methyl-α-trifluoromethylbenzyl alcohol (VII), which contains a stronger donor substituent, reacts in a more complex manner with a twofold excess of dichlorophosphate (I) in the presence of Mg even at a lower temperature (90°C): in addition to the anticipated (2,2,2-trifluoroethyl)(p-methyl-α-trifluoromethylbenzyl) chlorophosphate (XIV), di-p-methyl-α-trifluoromethylbenzyl ether (XV) and p-methyl-α-trifluoromethylbenzyl chloride (XVI) were also detected in the reaction mixture by means of TLC

$$CF_3CH_2OPOCl_2 + p\text{-}CH_3C_6H_4CH(CF_3)OH \xrightarrow[-HCl]{90°, Mg, 6 h}$$
$$(I) \qquad\qquad (VII)$$
$$\rightarrow p\text{-}CH_3C_6H_4CH(CF_3)OP(O)(Cl)OCH_2CF_3 +$$
$$(XIV)$$
$$+ [p\text{-}CH_3C_6H_4CH(CF_3)]_2O + p\text{-}CH_3C_6H_4CHClCF_3$$
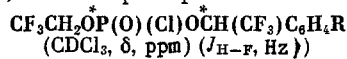$$(XV) \qquad\qquad (XVI)$$

Benzoyl chloride (XVI) can be easily isolated by fractional distillation together with the phosphorylating agent. However, monochlorophosphate (XIV) and ether (XV), with very close boiling points, cannot be separated; the isolated product, as determined from its PMR and ^{19}F NMR spectra, is a mixture of compounds (XIV) and (XV) with a ratio of about 4:1.

TABLE 2. (1,1-Dihydropolyfluoroalkyl)(α-Polyfluoroalkylbenzyl) Chlorophosphates $R_FCH_2OP(O)(Cl)(OCHR_{F'}\text{-}C_6H_4R)$

Compound	R_F	$R_{F'}$	R	Bp, °C (p, mm Hg)	n_D^{20}	d_4^{20}	Found/Calculated, %					Empirical formula
							C	H	Cl	F	P	
(VIII)	CF_3	CF_3	H	64–66 (0,1)	1,4242	1,4854	33,7 / 33,7	2,3 / 2,3	9,7 / 9,9	32,4 / 32,0	8,5 / 8,7	$C_{10}H_8ClF_6O_3P$
(IX)	CF_3	CF_3	m-CH_3	86–87 (0,5)	1,4297	1,4437	35,5 / 35,6	2,7 / 2,7	9,6 / 9,6	34,0 / 30,8	—	$C_{11}H_{10}ClF_6O_3P$
(X)	CF_3	CF_3	m-CF_3	81–82 (0,5)	1,4028	1,5632	31,1 / 31,1	1,6 / 1,7	8,2 / 8,3	40,3 / 40,3	7,4 / 7,3	$C_{11}H_7ClF_9O_3P$
(XI)	CF_3	$CF_3OCF_2CF_2$	H	97–98 (0,5)	1,3960	1,5588	30,5 / 30,5	1,7 / 1,7	7,0 / 7,5	39,4 / 40,2	6,6 / 6,6	$C_{12}H_8ClF_{10}O_4P$
(XII)	C_4F_9	CF_3	H	102–103 (0,5)	1,3934	1,5870	30,8 / 30,8	1,6 / 1,6	7,1 / 7,0	44,9 / 45,0	6,0 / 6,1	$C_{13}H_8ClF_{12}O_3P$
(XIII)	C_4F_9	CF_3	m-CF_3	107–108 (0,5)	1,3800	1,6407	29,1 / 29,3	1,0 / 1,2	5,9 / 6,2	49,6 / 49,6	5,4 / 5,4	$C_{14}H_7ClF_{15}O_3P$

TABLE 3. $^{31}P-\{^1H\}$ NMR Spectral Data for (1,1-Dihydropoly-fluoroalkyl)(α-Polyfluoroalkylbenzyl) Chlorophosphates $R_FCH_2\overset{*}{O}P(O)(Cl)\overset{*}{O}CHR'_FC_6H_4R$

Compound	R_F	R'_F	R	Solvent	δa (s)	δb (s)	$\Delta\delta$
					ppm		
(VIII)	CF₃	CF₃	H	—	4,46	4,32	0,14
				C₆H₆	4,56	4,32	0,24
				CCl₄	5,44	5,14	0,30
				CHCl₃	5,55	5,44	0,11
(IX)	CF₃	CF₃	m-CH₃	—	4,46	4,31	0,15
				C₆H₆	4,66	4,47	0,19
				CCl₄	5,68	5,36	0,32
				CHCl₃	5,43	5,43	0,00
(X)	CF₃	CF₃	m-CF₃	—	4,76	4,44	0,32
				C₆H₆	4,86	4,36	0,50
				CCl₄	6,20	5,73	0,47
				CHCl₃	5,71	5,47	0,24
(XI)	CF₃	CF₃OCF₂CF₂	H	—	4,58	3,97	0,61
				C₆H₆	4,59	3,99	0,60
				CCl₄	5,46	4,66	0,80
				CHCl₃	5,31	4,82	0,49
(XII)	C₄F₉	CF₃	H	—	4,99	4,62	0,37
				C₆H₆	5,01	4,61	0,40
				CCl₄	5,95	5,54	0,41
				CHCl₃	5,66	5,47	0,19
(XIII)	C₄F₉	CF₃	m-CF₃	—	5,39	4,69	0,70
				C₆H₆	5,29	4,39	0,90
				CCl₄	6,40	5,66	0,74
				CHCl₃	6,03	5,46	0,57
(XIV)	CF₃	CF₃	p-CH₃	—	—	—	—
				C₆H₆	4,44	4,36	0,08
				CCl₄	—	—	—
				CHCl₃	—	—	—

Ether (XV) could also have been formed under catalytic phosphorylation conditions as a result of the alkylation of alcohol (VII) by monochlorophosphate (XIV). In fact, these compounds react vigorously even at 120°C; the major reaction product, as determined by GLC, is ether (XV)

$$p\text{-}CH_3C_6H_4CH(CF_3)OH + p\text{-}CH_3C_6H_4CH(CF_3)OP(O)(Cl)OCH_2CF_3 \xrightarrow[-HCl]{120°, 2 h} (XV)$$
$$\text{(VII)} \qquad\qquad\qquad \text{(XIV)}$$

$$-[PO_2Cl]$$

We also studied some stereochemical aspects of the catalytic phosphorylation reaction of α-polyfluoroalkylbenzyl alcohols with excess 1,1-dihydropolyfluoroalkyl dichlorophosphate, in which the phosphorus atom is converted from prochiral (in the original dichlorophosphate) to chiral. Since, in addition to the asymmetric phosphorus atom, the (1,1-dihydropolyfluoro-alkyl)(α-polyfluoroalkylbenzyl) chlorophosphates that are formed contain a second chiral center in the benzyl moiety, we might expect that these compounds would be a mixture of two diastereomers,* as in the O-(α-polyfluoroalkylbenzyl)methylchlorophosphonates studied by us earlier [2]. Indeed, in addition to the signal at $\sim$8.5 ppm belonging to the excess phosphory-lating agent, the $^{31}P-\{^1H\}$ NMR spectra of the reaction mixtures contain two signals in close proximity at about 5 ppm, which belong to diastereomers a** and b of the monochlorophosphate. The diastereomer ratio (see Table 1) is practically independent of the structure of the original reagents (alcohols and dichlorophosphates) and of the catalyst used and, in all cases, falls (within the limits of experimental error) within the statistical range (1:1). This result differs from the case of O-(α-polyfluoroalkylbenzyl)methylchlorophosphonates, in which marked stereoselectivity was observed in the catalytic phosphorylation process [2].

When the reaction mixture obtained in the phosphorylation of benzyl alcohol (V) with excess dichlorophosphate (II) in the presence of anhydrous CaCl₂ at 140°C (and containing monochlorophosphate (XIII) and excess phosphorylating agent) was heated to 200°C for 7 h,

*Each diastereomer is a racemic mixture of two enantiomers.
**a is an arbitrary designation for the diastereomer whose signal in the $^{31}P-\{^1H\}$ NMR spec-trum is shifted downfield.

TABLE 4. ^{19}F NMR Spectra for (2,2,2-Trifluoroethyl)(α-Tri-
fluoromethylbenzyl) Chlorophosphates

$$CF_3CH_2\overset{*}{O}P(O)(Cl)O\overset{*}{C}H(CF_3)C_6H_4R$$
(CDCl$_3$, δ, ppm) (J_{H-F}, Hz)

Compound	R	Diastereomer a			Diastereomer b		
		δCF₃CH₂	δCF₃CH	δR	δCF₃CH₂	δCF₃CH	δR
(VIII)	H	2,266 t (7,8)	0,558 d (6,0)	—	2,266 t (7,8)	0,288 d (6,0)	—
(IX)	m-CH₃	2,369 t (7,9)	0,708 d (6,1)	—	2,366 t (7,8)	0,457 d (6,1)	—
(X)	m-CF₃	2,213 t (7,7)	0,476 d (5,9)	14,364 s	2,190 t (7,7)	0,217 d (5,8)	14,389 s
(XIV)	p-CH₃	2,318 t (7,8)	0,546 d (6,1)	—	2,305 t (7,8)	0,280 d (6,1)	—

the $^{31}P-\{^1H\}$ NMR spectra did not show signs of significant thermal decomposition.* The dis-
astereomer ratio in compound (XIII) remained practically unchanged, i.e., was close to the
statistical value. Thus the diastereomer composition of (1,1-dihydropolyfluoroalkyl)(α-
polyfluoroalkylbenzyl) chlorophosphate is also independent of the temperature, at least up
to 200°C. Generally, the diastereomer ratio remains close to the statistical value also in
monochlorophosphates (VIII)-(XIII) isolated from the reaction mixtures by fractional dis-
tillation.

It should be noted that the $^{31}P-\{^1H\}$ NMR spectra of these compounds, which are similar
qualitatively (two singlet signals are observed in all cases), differ in their diastereo-
meric anisochrony (DA) values (see Table 3). The DA value depends on the nature of the R
substituent in the benzyl moiety of the molecule, the chain length of polyfluoroalkyl
radicals R$_F$ and R$_F$' and the type of solvent. When the solvent is changed from benzene to
CHCl₃, the DA value decreases in all cases, usually quite significantly. Similar changes
in the DA were observed, for example, for (EtO)MeP(S)SCH₂CONHCH(Alk)COOH [3].

In the ^{19}F NMR spectra of (2,2,2-trifluoroethyl)(α-trifluoromethylbenzyl) chlorophos-
phates (VIII)-(X), (XIV) (Table 4) the signals of the CF₃ groups are doubled, which also is
an indication of the presence of two diastereomers in the reaction mixture. It should be
noted that the DA of CF₃CH groups for all compounds in CHCl₃ (in the case of chlorophos-
phate (VIII), also in CCl₄ and benzene) is about equal (0.25-0.28 ppm), and is significantly
higher than the DA of CF₃CH₂ groups (0.000-0.023 ppm). In contrast, in the PMR spectra of
chlorophosphates (VIII)-(XIII), which also exhibit the DA phenomenon (Table 5), Δδ for
methylene protons of OCH₂R$_F$ radicals always significantly exceeds Δδ for methine protons
of OCHR$_F$' groups.

In the case of chlorophosphates (X) and (XIII), which contain a strong electron acceptor
group (m-trifluoromethyl) in the benzene ring, the methylene proton signals of 1,1-dihydro-
polyfluoroalkylbenzyl radicals in each diastereomer appear as quadruplet doublets (for (X))
and triplet doublets** (for (XIII)) and represent the A part of type A₂M₃X or A₂M₂X spin
systems, respectively, where M = ^{19}F and X = ^{31}P. For the remaining chlorophosphates, the
proton signals of these radicals (for both diastereomers) no longer are first-order spectra;
they represent AB quadruplets, each component of which, in turn, is split into a quadruplet
(for R$_F$ = CF₃) or a triplet** (for R$_F$ = C₄F₉), due to spin—spin interaction with ^{19}F
nuclei linked to the carbon atom adjacent to the polyfluoroalkyl chain, and simultaneous
doublet splitting due to spin—spin interaction with the ^{31}P nucleus. Similar types of
spectra for OCH₂R$_F$ groups of chlorophosphates (VIII), (IX), (XI), and (XII) indicate that,
in addition to the phenomenon of diastereomeric anisochrony, there is magnetic nonequivalence
of diastereotopic geminal protons attached to the prochiral α-carbon atom of these groups.

The PMR and ^{19}F NMR spectral data also show that the diastereomer ratio in monochloro-
phosphates (VIII)-(XIV) almost coincides with the statistical value. We may assume that

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*Compounds (II) and (XIII) behave in the same manner when heated alone under similar condi-
tions.
**Each component of this multiplet is additionally split into a triplet (J_{H-F} ∿ 1.4 Hz),
due to remote spin—spin interaction with ^{19}F nuclei of the nonafluoropentyl radical's γ-
or δ-difluoromethyl groups.

TABLE 5. PMR Spectral Data for (1,1-Dihydropolyfluoroalkyl)(α-Polyfluoroalkylbenzyl) Chlorophosphates $RC_6H_4CHR'_FOP(O)(Cl)OCH_AH_BR_F$ (CDCl₃, δ, ppm, J and Δν, Hz)

Compound	R	R'_F	R_F	Diastereomer	CHR'_F δ	³J_H-F	³J_H-P	δH_A	δH_B	Δν H_AH_B	J_H_A-H_B	³J_H_A-F	³J_H_B-F	³J_H_A-P	³J_H_B-P	δR	δ for aromatic protons
(VIII)	II	CF₃	CF₃	a	5,789 d.q	6,0	11,8	4,361	4,308	10,6	12,0	7,8	7,8	9,3	9,5	—	7,34—7,53 m
				b	5,808 d.q	6,0	11,7	4,467	4,406	12,2	12,0	7,8	7,8	9,4	9,4		
(IX)	m-CH₃	CF₃	CF₃	a	5,704 d.q	6,1	11,8	4,345	4,287	11,6	12,0	7,7	7,8	9,2	9,4	2,335 s	7,16—7,36 m
				b	5,719 d.q	6,1	11,7	4,447	4,383	12,7	12,0	7,7	7,8	9,3	9,3		
(X)	m-CF₃	CF₃	CF₃	a	5,880 d.q	5,9	12,0	4,416	4,446	—	—	7,7	7,7	9,6	9,6	—	7,53—7,83 m
				b	5,897 d.q	5,9	11,8	4,497	4,497	—	—	7,9	7,9	9,5	9,5		
(XI)	II	CF₃OCF₂CF₂	CF₃	a	5,856 d.d.d	14,4* / 8,0*	11,0*	4,288	4,191	19,4	12,0	7,7	7,7	9,0	9,4	—	7,33—7,54 m
				b	5,877 d.d.d	14,3* / 7,8*	10,8*	4,442	4,370	14,3	12,0	7,7	7,7	9,0	9,0		
(XII)	II	CF₃	C₄F₉	a	5,817 d.q	6,0	11,8	4,543	4,480	12,7	12,4	12,6**	12,7**	8,7	8,7	—	7,39—7,59 m
				b	5,836 d.q	6,0	11,8	4,662	4,602	12,0	12,3	12,5**	12,6**	8,8	8,8		
(XIII)	m-CF₃	CF₃	C₄F₉	a	5,911 d.q	6,0	11,9	4,552	4,552	—	—	12,6**	12,6**	8,9	8,9	—	7,52—7,83 m
				b	5,911 d.q	6,0	11,9	4,639	4,639	—	—	12,5**	12,5**	8,8	8,8		

*Spin-spin interaction constants ³J_H-F and ³J_H-P were identified by comparison with ¹⁹F and ³¹P NMR spectral data.

**4 (or 5) J_H-F ∿ 1.4 Hz.

this ratio, as in the case of the structurally similar O-(α-polyfluoroalkylbenzyl)methyl-chlorophosphonates [2], is thermodynamically controlling. However, unlike chlorophosphon-ates, diastereomers a and b in (1,1-dihydropolyfluoroalkyl)(α'-polyfluoroalkylbenzyl) chlorophosphate are thermodynamically equivalent and thus exist in the mixture in almost equal amounts.

EXPERIMENTAL

PMR and ^{19}F NMR spectra were recorded on a Bruker WP-200SY instrument (with TMS as internal standard in PMR spectra, and CF_3COOH in ^{19}F NMR spectra). ^{31}P NMR spectra were recorded on a Bruker HX-90 instrument (85% H_3PO_4 as internal standard).

GLC analysis was carried out using a glass column (2.5 m) with 2% Dexil 200 on Chromosorb W, 80/100 mesh (flame-ionizing detector; gel rate, 30 ml/min). The sample was loaded directly onto the column; column temperature varied from 90 to 260°C at a rate of 6°C/min.

TLC analysis was carried out using Silufol UV-254 plates (eluent, hexane).

The synthesis of benzyl alcohols (III)-(VII) was described by us earlier [4, 5]; di-chlorophosphate (I) was obtained by the modified method of Zakharov et al. [6].

2,2,3,3,4,4,5,5,5-Nonafluoropentyl Dichlorophosphate (II). A mixture containing 100.0 g (0.4 mole) 2,2,3,3,4,4,5,5,5-nonafluoropentanol, 367.2 g (2.4 moles) $POCl_3$, and 1.11 g (0.01 mole) anhydrous $CaCl_2$ was boiled for 2.5 h with a reflux condenser; excess $POCl_3$ was dis-tilled in a Vigreaux column, and the residue was fractionated in a vacuum. A 105.5-g yield (72%) of compound (II) was obtained; bp 81-82°C (20 mm), n_D^{20} 1.3513, d_4^{20} 1.7301. Found: C 16.4; H 0.5; Cl 19.3; F 46.7; P 8.5%; MR 45.79. $C_5H_2Cl_2F_9O_2P$. Calculated: C 16.4; H 0.6; Cl 19.3; F 46.6; P 8.4%; MR 45.73. ^{31}P NMR spectrum (δ, ppm): 8.18 t, $^3J_{H-P} = 10.4$ Hz.

(1,1-Dihydropolyfluoroalkyl)(α-Polyfluoroalkylbenzyl) Chlorophosphates (VIII)-(XIII). A mixture containing 0.01 mole α-polyfluoroalkylbenzyl alcohol, 0.02 mole 1,1-dihydropoly-fluoroalkyl dichlorophosphate, and 0.25 mmole catalyst was heated for several hours at 140°C until the end of HCl evolution. The excess phosphorylating agent was evaporated. Vacuum distillation of the residue afforded (1,1-dihydropolyfluoroalkyl)(α-polyfluoroalkylbenzyl) chlorophosphates, whose constants are shown in Table 2.

Catalytic Phosphorylation of p-Methyl-α-trifluoromethylbenzyl Alcohol (VII) with Excess 2,2,2-Trifluoroethyl Dichlorophosphate (I). A mixture containing 1.9 g (0.01 mole) of com-pound (VII), 4.3 g (0.02 mole) of compound (I), and 6 mg (0.25 mg-atom) Mg was heated for 6 h at 90°C until the end of HCl evolution. The excess compound (I) and the benzyl chloride (XVI) that was formed were evaporated, and the residue was fractionated in a vacuum. A mixture containing 1.2 g of compounds (XIV) and (XV) was obtained; bp 96-105°C (1 mm); n_D^{20} 1.4292. PMR spectrum of compound (XIV) ($CDCl_3$, δ, ppm): 2.339 s (CH_3), 4.172-4.580 m (CH_2), 5.736 d.q (CH, diastereomer a, $^3J_{H-F} = 6.1$ Hz, $^3J_{H-P} = 11.7$ Hz), 5.765 d.q (CH, diastereomer b, $^3J_{H-F} = 6.1$ Hz, $^3J_{H-P} = 11.6$ Hz), 7.16-7.43 m (C_6H_4). PMR spectrum of com-pound (XV) ($CDCl_3$, δ, ppm): 2.292 s (CH_3), 4.857 q (CH, $^3J_{H-F} = 6.5$ Hz), 7.05-7.33 m (C_6H_4).

Alkylation of p-Methyl-α-trifluoromethylbenzyl Alcohol (VII) with (2,2,2-Trifluoroethyl) (p-Methyl-α-trifluoromethylbenzyl) Chlorophosphate (XIV). A mixture containing 0.15 g (0.79 mmole) of compound (VII) and 0.3 g (0.81 mmole) of compound (XIV) was heated for 2 h at 120°C until the end of HCl evolution; 10 ml of ether was extracted. The extract was chro-matographed on 2 g Al_2O_3 (eluent, ether), the eluate was evaporated in a vacuum, and 0.16 g (55%) of ether (XV) was isolated from the residue by PTLC on silica gel (eluent, hexane); mp 24-29°C (cf. [7]).

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REACTIONS OF DIAZOALKANES WITH UNSATURATED COMPOUNDS.

6. CATALYTIC CYCLOPROPANATION OF UNSATURATED HYDROCARBONS

AND THEIR DERIVATIVES WITH DIAZOMETHANE*

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A systematic study has been conducted of the catalytic reaction of diazomethane with cyclic and polycyclic unsaturated hydrocarbons, conjugated dienes, as well as with a series of functionalized unsaturated compounds. The feasibility of using transition metal, nontransition metal, and rare earth metal compounds of, for example, Co, Ni, Zr, Cr, Rh, and Dy, has been demonstrated for the first time. It has also been established that $Pd(acac)_2$ has very high activity as a catalyst for the cyclopropanation of terminal and endocyclic double bonds by diazomethane, and that its activity is reduced upon the introduction of n-donor ligands or in the presence of strong polar solvents.

The catalytic cyclopropanation of unsaturated compounds with diazomethane (DAM) makes it possible, due to the effect of complex formation, not only to direct the reaction process, but also to suppress almost entirely side reactions of the olefin starting materials and the cyclopropane products [2-4]. In most cases copper and palladium compounds have been used as the cyclopropanation catalysts. Little attention has been paid however to the side reactions of DAM which compete with cyclopropanation.

In the present paper we have examined the catalytic reactions of DAM with linear, cyclic, and polycyclic unsaturated hydrocarbons, conjugated dienes, as well as with a series of functionalized allyl type derivatives; the effects of the nature of the double bond, reaction conditions, nature of the catalyst, and to some extent of the ligand environment around Pd complexes on the degree of cyclopropanation product formation have been elucidated, and the feasibility of using a series of transition metal and rare earth metal compounds as cyclopropanation catalysts has been demonstrated for the first time.

Using the cyclopropanation of norbornene (I) as a model reaction, the effect of the nature of metal and its ligand environment on the yield of product, namely, exo-tricyclo-[$3.2.1.0^{2,4}$]octane (II), was studied
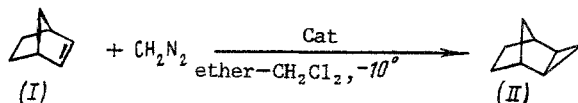
The experiments were carried out by mixing equimolar amounts of DAM and (I) in the presence of 0.7-0.8 mole % catalyst in ether—CH_2Cl_2 medium (4:1 by volume) at —10°C. The yield

*For previous communication, see [1].