SYNTHESIS OF ACYLPHOSPHINES AND ACYLARSINES

R. G. Kostyanovskii, Yu. I. El'natanov, and L. M. Zagurskaya

UDC 542.91:547.1'118:547.1'119

What happens to amides when the nitrogen is replaced by phosphorus or arsenic: is the most characteristic criterion, conjugation of the amide type [1], retained or does it disappear? For unequivocal proof of the latter it was necessary to synthesize a series of acylphosphines and acylarsines with various substituents on the heteroatom and the CO group [2, 3]. The present communication is devoted to the synthesis of these compounds.

The simplest method for the acylation of secondary phosphines and arsines is with ketenes [1, 2, 4, 5]. However, subsequent O-acylation of the acylphosphine [2] (see "Experimental Method," Table 1, and Fig. 1) and the addition of phosphine with the cleavage of water [5] are observed here. In addition, this method is limited by a small selection of available ketenes.

Exhaustive acylation of the unsubstituted phosphine could be achieved by treatment with carboxylic acid chlorides [6]. The similar acylation of primary phosphines gave negative results when Et_3N was used as the base [7], and proved successful in the presence of anhydrous K_2CO_3 [8]. This method was not recommended for the acylation of secondary phosphines due to the low yields when compared with synthesis via the alkali metal phosphides [7]. It was shown by us that this simple method makes it possible to obtain various acylphosphines and acylarsines in satisfactory yields.

The starting phosphines were obtained by the reduction of tetramethyldiphosphine disulfide [1] and the corresponding chlorophosphines using $LiAlH_4$, while di-tert-butylchlorophosphine was obtained using the Grignard reagent [9]. The symmetrical chlorophosphines were synthesized by the Grignard reaction from PCl_3 [10], while the unsymmetrical derivatives were synthesized from the alkyldichlorophosphines. The general procedure for this reaction and the reduction with $LiAlH_4$ is given in the "Experimental Method" on the example of an unsymmetrical phosphine. Dibenzylphosphine was obtained by the disproportionation of benzyldichlorophosphine [11], while diisopropylarsine was obtained by the reduction of diisopropylchloroarsine [12] with $LiAlH_4$. All the starting products (see Table 1) were characterized by the mass

TABLE 1. Constants of Phosphines, Arsines, and Corresponding Chlorides

Compound	Yield, %	Bp, °C (p, mm of Hg)	Literature reference
Me_2PH	73	21	[1]
Me_2CHPCl_2	56	130(745)	
Me_2CHPH_2	20	41(756)	[13]
$(Me_2CH)_2PCl$	52	155—158	[10]
$(Me_2CH)_2PH$	45	117,5—118	[14]
$(Me_3C)_2PCl$	40	65—67(9,5)	[9]
$(Me_3C)_2PH$	52	40—41(14)	[9]
$PhCH_2PH_2$	36	83(26)	
$(PhCH_2)_2PCl$	65	157—163(1,5) Mp. 81—82	[11]
$(PhCH_2)_2PH$	39	129(1)	[15]
$Me_2CHP(Cl)CH_2Ph$	50	87—90(6)	
$Me_2CHPHCH_2Ph$	32	67(3)	
$Me_2CP(Cl)CH_2Ph$	71	90(10)	
Me_2CPHCH_2Ph	41	66,5—67,5(1,5)	
$(Me_2CH)_2AsCl$	35	30,5—31(3)	[12]
$(Me_2CH)_2AsH$	40	37(28)	

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 901-908, April, 1975. Original article submitted June 14, 1974.

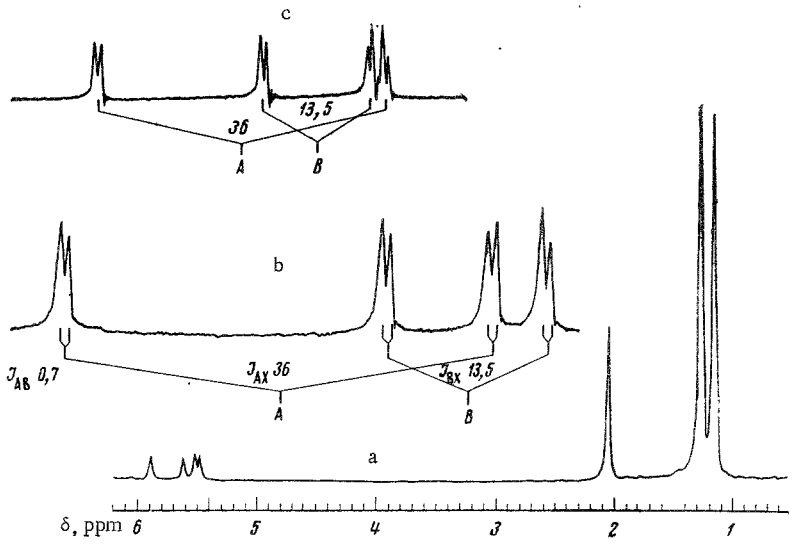
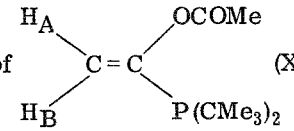


Fig. 1. NMR spectra of  (XIV) in Freon-113, chemical shifts from TMS, and J values, Hz: a) general spectrum at 100 MHz; b) H_A and H_B protons at 100 MHz; c) the same, at 60 MHz.

spectra [3] and NMR spectra (Table 2).

The phosphines and diisopropylarsine were acylated with ketenes in ether (A) and with carboxylic acid chlorides in the presence of pyridine in ether (B). The results are given in Table 3, while the general procedures are given in the "Experimental Method." When benzylphosphine was acylated with AcCl and pivaloyl chloride the yields of products (XVI) and (XVII) were, respectively, 15 and 50%. This difference can be explained by the steric hindrance of the bulky pivaloyl substituent for the formation of secondary products.

The synthesized acylphosphines and acylarsines were characterized by the IR (see Table 3), mass [3], and NMR spectra (Table 4). The pyramidal configuration of the phosphorus atom in the acylphosphines was recorded on the basis of the geminal nonequivalence of the diastereotopic CH_3 groups of the isopropyl substituent (for example, Fig. 2) and the CH_2 protons of the benzyl substituent (for example, Fig. 3). In the case of (XI) the CH_3 groups of the Me_2N substituent become equivalent at 130° (the observed doublet corresponds to J_{MeNCOP}), since the geminal nonequivalence of the CH_3 groups of the isopropyl substituent is retained here (Fig. 4). As a result, the inversion of the phosphorus atom is more hindered than the rotation around the CO–N bond. The energy parameters of the phosphorus inversion in acylphosphines are given in [2]. The NMR spectrum of acylarsine (XXI) (Fig. 5) remains unchanged when a sample is heated in diphenyl ether up to 200°. Consequently, the inversion of the arsenic atom in acylarsines is much more hindered than the inversion of the phosphorus atom in similar acylphosphines.

EXPERIMENTAL METHOD

The syntheses and study of the acylphosphines and acylarsines were run in an argon atmosphere, in absolute solvents. To remove the air and moisture all of the glass apparatus prior to experiment was evacuated (1 mm) while heated with an open flame, and then filled with dry argon. The finely disperse precipitate was filtered through dense layers of glass wool in an argon stream. The IR spectra were obtained on UR-10 and UR-20 spectrophotometers in cells with glasses made from KBr or KRS. The cells were filled in an argon chamber. The NMR spectra were obtained on JEOL JNM-C-60-HL (60 MHz) and Varian-HA-100 (100 MHz) spectrometers. The internal standards were either TMS or HMDS. The ampuls were filled in an argon stream.

Isopropylbenzylchlorophosphine. With vigorous stirring, the Grignard reagent, obtained from 4.8 g (0.2 mole) of magnesium turnings and 15.6 g (0.2 mole) of isopropyl chloride in 100 ml of ether, was added in drops to a cooled (–40°) solution of 38.6 g (0.2 mole) of benzyldichlorophosphine in 500 ml of ether. The

TABLE 2. Parameters of NMR Spectra of Phosphines, Arsines, and Corresponding Chlorides

Compound	Solvent	δ, ppm						J, Hz						
		Me_A	Me_B	HCP (HCAs)	HP (HAs)	CH_2	other groups	Me_ACH	Me_BCH	Me_AP	Me_BP	HP	CH_2P	other groups
Me_2CHPH_2	Ph_2O	0,62	0,62	1,33	2,22	—	—	7,0	7,0	14,1	14,1	228,5	—	HPCH 6,0
$(Me_2CH)_2PCl$	Freon-113	0,63	0,63	1,36	—	—	—	6,5	6,5	13,5	13,5	—	—	—
$(Me_2CH)_2PH$	Ph_2O	1,35	1,13	2,82	4,64	—	—	6,2	6,2	10,8	15,5	200,0	—	—
$(Me_3C)_2PCl$ *	CCl_4	—	—	—	—	—	Me_3C 1,15	—	—	—	—	—	—	Me_3CP 12,0
$(Me_3C)_2PH$ *	Freon-113	—	—	—	4,05	—	Me_3C 1,16	—	—	—	—	644,0	—	Me_3CP 11,2
$PhCH_2PH_2$	"	—	—	—	2,66	2,65	Ph 7,05	—	—	—	—	192,0	4,0	CH_2PH 7,0
$(PhCH_2)_2PCl$	CCl_4	—	—	—	—	3,05	Ph 7,05	—	—	—	—	—	8,0	—
$(PhCH_2)_2PH$	"	—	—	—	—	2,63	Ph 7,0	—	—	—	—	—	1,6	—
$Me_2CHP(Cl)CH_2Ph$	Pure	1,13	1,13	1,95	—	4,30	Ph 6,98	7,7	7,7	17,0	17,0	—	8,3	—
$Me_2CHPHCH_2Ph$	C_6H_6	0,94	0,90	1,46	2,64	—	H_A 2,85	6,4	6,4	13,2	15,6	252,0	—	$H_AP=H_BP$ 2,2
							H_B 2,54		$HPCH_2$ 7,3		H_AH_B 21,0			HPCH 4,3
Me_3CPHCH_2Ph	Pure	H_A 3,0	—	—	3,1	—	Me_3C 1,0	H_AP 3,6	H_APH 6,0		—	197,0	—	Me_3CP 11,6
		H_B 2,5					Ph 7,05	H_BP 5,8	H_BPH 10,5					H_AH_B 13,0
$(Me_2CH)_2AsCl$	Freon-113	1,18	1,18	(1,88)	—	—	—	6,7	6,7	—	—	—	—	—
$(Me_2CH)_2AsH$	"	1,20	1,07	(1,97)	(2,48)	—	—	7,0	7,0	—	—	—	—	—

* $(Me_3C)_2P(O)Cl$, δ 1,15 ppm (Me_3C); $J_{Me_3CP} = 16.5$ Hz (CCl_4); $(Me_3C)_2P(O)H$, δ 1,33 ppm (Me_3C); $J_{Me_3CP} = 17,0$ Hz; δ 5,13 ppm (PH); J_{HP} 652 Hz (CCl_4).

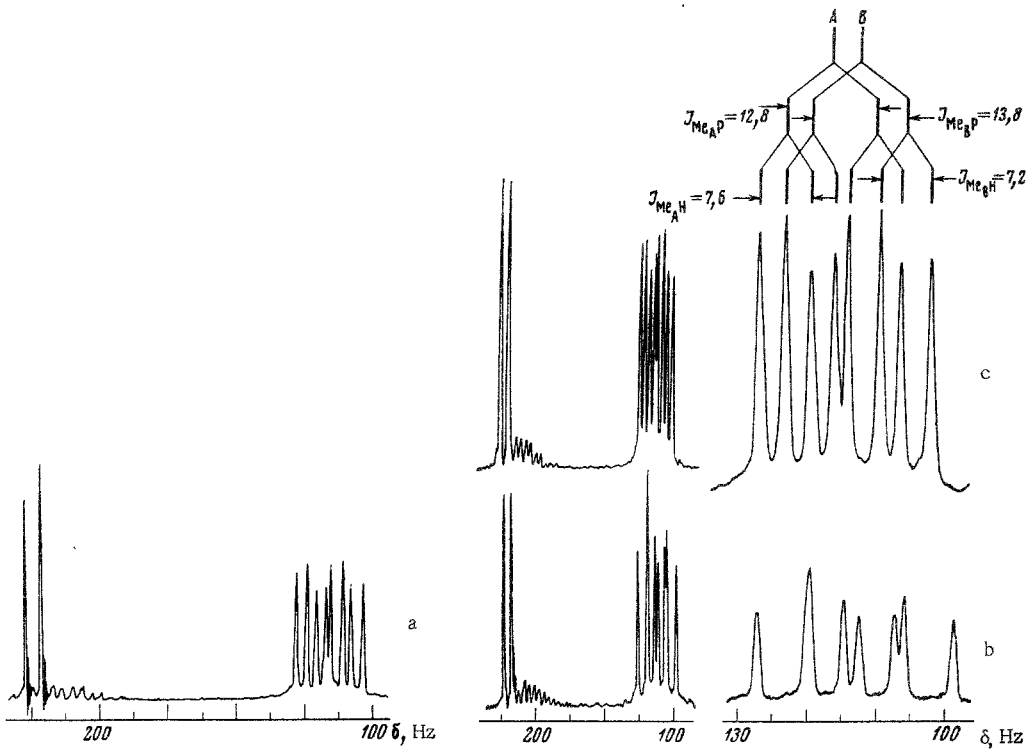


Fig. 2. NMR spectra of MeCOP(CH(Me$_A$)(Me$_B$))$_2$ (IV) at 20° (60 MHz, from TMS): a) in Freon-113; b) in C_6F_6; c) C_2Cl_4.

TABLE 3. Constants of Acylphosphines and Acylarsines

Compound	Formula	Synthesis method	Yield, %	Bp, °C (p, mm of Hg)	n_D^{20}	ν CO, cm^{-1} (mol. layer)
(I)	$MeCOPMe_2$	A	27	38—39(20)	—	1665 *
(II)	CD_3COPMe_2	B	21	38(20)	—	—
(III)	$(CF_3)_2CHCOPMe_2$	A	58	60(60)	1,3910	1685
(IV)	$MeCOP(CHMe_2)_2$	A	46	38,5—39(1)	1,4753	1663
(V)	$CD_3COP(CHMe_2)_2$	B	58	32(1)	1,4175	—
(VI)	$Me_3CCOP(CHMe_2)_2$	B	75	61—62(3)	1,4719	1674
(VII)	$PhCOP(CHMe_2)_2$	B	60	87—88(12)	1,5530	1644
(VIII)	$CF_3COP(CHMe_2)_2$	B	26	24(2)	1,4276	1693
(IX)	$(CF_3)_2CHCOP(CHMe_2)_2$	A	65	33—33,5(1)	1,4007	1678
(X)	$MeOCOP(CHMe_2)_2$	B	18	43—44(4)	1,4702	1693
(XI)	$Me_2NCOP(CHMe_2)_2$	B	21	80—81(44)	1,4928	1618
(XII)	$PhNHCOP(CHMe_2)_2$	A	68	Mp., 74—75 (from MeOH)	—	1635 (KBr pellet)
(XIII)	$MeCOP(CMe_3)_2$	A	39	39—39,5 (1)	1,4748	1668 †
(XIV)	$MeCOOC(=CH_2)P(CMe_3)_2$	A	63	64(2)	1,8438	1765 1630 (C=C)
(XV)	$CF_3COP(CMe_3)_2$	B	66	50(5)	1,4372	—
(XVI)	$MeCOPHCH_2Ph$	B	15	68—68,5(1,5)	1,5780(21°)	—
(XVII)	$Me_3CCOPHCH_2Ph$	B	50	85—86(2)	1,5458	1666
(XVIII)	$MeCOP(CH_2Ph)_2$	A	32	130(1)	1,6028	1660
(XIX)	$CF_3COP(CH_2Ph)_2$	B	42	124(1)	1,5409(20,5°)	1687
(XX)	$MeCOP(CHMe_2)CH_2Ph$	B	61	103(3)	—	1668
(XXI)	$CF_3COAs(CHMe_2)_2$	B	69	—	1,4378(21°)	
(XXII)	$(CF_3)_2CHCOAs(CHMe_2)_2$	A	60	46(1)	1,4125(19°)	

*Raman: 1661 cm^{-1}.

†IR: 1685 (gas), 1668 (liquid), 1665 (CCl_4); Raman: 1665 cm^{-1}.

mixture was brought up to ~20°, filtered, and the precipitate was washed with ether (30 ml × 2). The ether was distilled off, and the residue was vacuum-distilled. We obtained 20 g (50%) of product, bp 87-90° (6 mm). Found: C 59.92; H 7.18; Cl 17.63%. $C_{10}H_{14}PCl$. Calculated: C 59.85; H 6.98; Cl 17.70%.

TABLE 4. Parameters of NMR Spectra of Acylphosphines and Acylarsines

Compound	Solvent	δ, ppm					J, Hz					
		RCO	R′(Me_A)	R″(Me_B)	H_A	H_B(HCE)	RP	R′P*(Me_ACH)	H_AH_B	(Me_BCH)	H_AP(Me_AP)	H_BP(Me_BP)
(I) †	CCl_4	2,22	1,22	—	—	—	5,2	1,7	—	—	—	—
(III) ‡	C_6H_6	4,25	0,91	—	—	—	—	2,2	—	—	—	HCCF 7,8
(IV)	Freon-113	2,24	(1,18)	(1,13)	—	(2,17)	5,8	3,3(7,3)	—	(7,0)	(12,2)	(13,2)
(V)	"	—	(1,10)	(1,06)	—	(2,05)	—	(7,1)	—	(6,8)	(12,2)	(13,1)
(VI)	Ph_2O	1,08	(1,05)	(0,93)	—	(1,97)	—	3,0(7,0)	—	(7,0)	(10,2)	(11,7)
(VII)	"	—	(0,88)	(0,82)	—	(2,20)	—	(7,2)	—	(7,9)	(15,0)	(14,5)
(VIII)	Freon-113	—	(1,33)	(1,22)	—	(2,31)	—		—	(7,3)	(15,0)	(14,7)
(IX) **	"	3,87	(1,19)	(1,22)	—	(2,30)	3,7	2,6(7,5)	HCCF 7,0	(7,1)	(16,0)	(11,5)
(X)	Ph_2O	3,38	(1,05)	(1,02)	—	(1,95)	—	(7,1)	—	(6,8)	(12,2)	(14,1)
(XI)	"	2,68 2,93	(0,97)	(0,96)	—	(2,03)	0 2,9	(6,5) 2,3(6,7)	—	(6,7)	(13,0)	(14,3)
(XII)	CD_3OD	7,30	(1,17)	(1,12)	—	(2,13)	—	(6,6)	—	(6,6)	(14,0)	(12,3)
(XIII)	C_6H_6	2,18	1,20	—	—	—	7,3	11,0	—	—	—	—
(XV)	$CHFCl_2$	—	1,21	—	—	—	—	12,8	—	—	—	—
(XVI)	Ph_2O	1,72	—	4,10	2,94	2,64	5,8	—	15,2	—	HP 198	$HPCH_2$ 6,6
(XVII)	α-$BrC_{10}H_7$	0,68	Ph 7,96	4,07	2,99	2,77	1,8	—	14,0	$HPCH_A$ 6,7	HP 220	$HPCH_B$ 5,8
(XVIII)	Freon-113	1,90	6,40	6,40	3,05	2,77	5,5	—	15,0	—	0,5	1,7
(XIX)	α-$BrC_{10}H_7$	—	—	—	3,00	2,65	—	—	13,5	—	2,5	1,5
(XX)	Ph_2O	1,91	(0,88)	(0,85)	3,15	2,64	5,5	(7,0)	15,0	(6,8)	2,8 (14,2)	2,8 (12,4)
(XXI)	C_6H_6	—	(0,91)	(0,78)	—	(1,96)	—	(7,5)	—	(7,5)	—	—
(XXII)	α-$BrC_{10}H_7$	4,25	(0,83)	(0,73)	—	(1,78)	—	(7,0)	HCCF 8,0	(7,0)	—	—

*It is difficult to determine the J_{HCP} constants for the acyldiisopropylphosphine series; in some cases the J_{HCP} was determined by replacing the solvents: (IX) = 3.0 Hz in benzene; (XII) = 2.6 Hz in Ph_2O.

†^{31}P (in CCl_4 from H_3PO_4), δP 19.7 ppm; for comparison δP: Me_3P 5.88; Et_3P 20.4; Ph_3P 5.88 ppm.

‡^{19}F (in C_6H_6 from CF_3COOH), δ_F −14.8 ppm; $J_{FCCCP} = J_{FCCH} = 8$ Hz.

**^{19}F (in C_6H_6 from CF_3COOH), δ_F −15.4 ppm; $J_{HCCF} = 7.0$, $J_{FCC(O)P} = 10.4$ Hz.

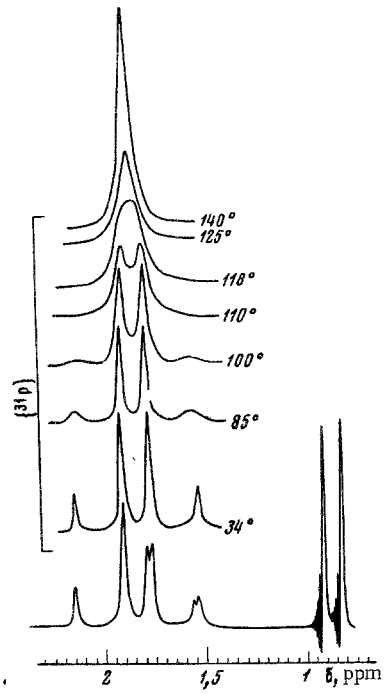


Fig. 3

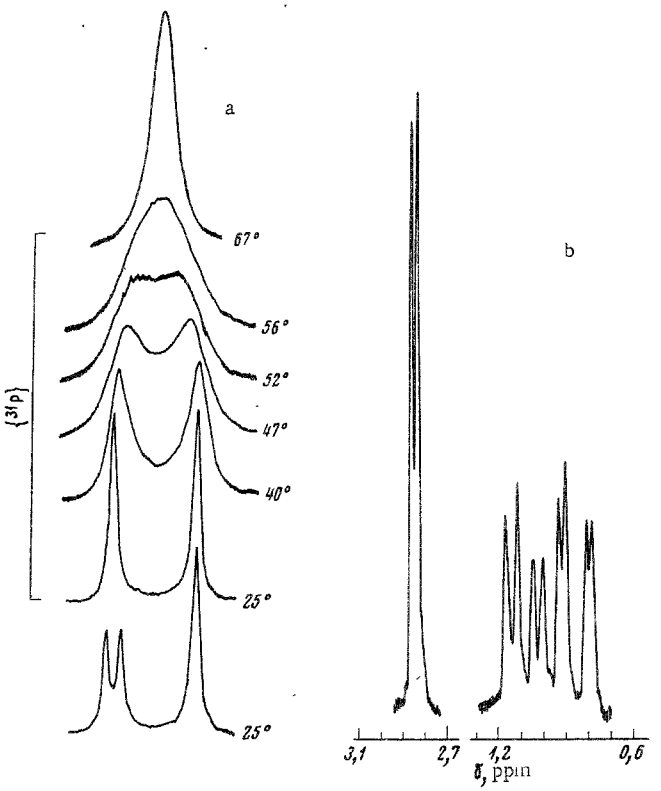


Fig. 4

Fig. 3. NMR spectrum of $MeCOP(CH_AH_BPh)_2$ (XVIII) and temperature dependence of AB portion of spectrum under conditions of decoupling from ^{31}P at 60 MHz in α-bromonaphthalene.

Fig 4. NMR spectra of $Me_AMe_BNCOP(CHMe_AMe_B)_2$ (XI) at 60 MHz in diphenyl ether: a) Me_AMe_BN portion at 25° and temperature dependence of spectrum under conditions of decoupling from ^{31}P; b) Me_A, Me_B, and Me_2N portions at 130°. A nonequivalence of Me_A and Me_B is observed here, i.e., the inversion of the phosphorus atom is hindered. The Me_2N protons are equivalent due to the rapid rotation around the amide linkage, and an a averaged constant $J_{MeNCOP} = 1.6$ is observed.

tert-Butylbenzylchlorophosphine was obtained in a similar manner (see Tables 1 and 2).

Isopropylbenzylphosphine. To a solution of 7 g (0.184 mole) of $LiAlH_4$ in 120 ml of ether at −25° was slowly added a solution of 17.8 g (0.089 mole) of isopropylbenzylchlorophosphine in 70 ml of ether. After adding half of the solution the cooling was removed. The mixture was refluxed for 30 min, cooled again (−10 to −15°), and the excess $LiAlH_4$ was carefully decomposed with saturated NH_4Cl solution, in which connection a coarsely granular precipitate is formed. The organic layer was separated by decantation and dried over $MgSO_4$. The ether was distilled off, and the residue was vacuum-distilled. We obtained 4.8 g (32%) of product, bp 67° (3 mm). Found: C 72.45; H 9.12%. $C_{10}H_{15}P$. Calculated: C 72.29; H 9.04%.

Acetyldi-tert-butylphosphine (XIII). Into a solution of 2.76 g (0.019 mole) of di-tert-butylphosphine in 125 ml of ether at −20° was passed 0.75 g (0.018 mole) of ketone (obtained by the pyrolysis of diketene). Here the mixture turned light yellow. At the end of reaction the temperature of the mixture was brought up to ~20°, the solvent was removed under reduced pressure, and the residue was vacuum-distilled twice. We obtained 1.37 g (39%) of a lemon yellow liquid, bp 39-39.5° (1 mm); from [1]: bp 45-47° (0.5 mm).

1-Di-tert-butylphosphino-1-acetoxyethylene (XIV). Under the conditions of the preceding experiment, from 2.45 g (0.016 mole) of di-tert-butylphosphine and 3.4 g (0.08 mole) of ketene in 100 ml of ether we obtained 2.42 g (63%) of a pale yellow liquid, bp 64° (2 mm) (see Fig. 1 and Table 3). Found: C 62.95; H 10.12%. $C_{12}H_{23}O_3P$. Calculated: C 62.60; H 10.0%.

Pivaloyldiisopropylphosphine (VI). To a solution of 1.45 g (0.012 mole) of diisopropylphosphine and 0.95 g (0.012 mole) of pyridine in 35 ml of ether at ~20° was added a solution of 1.44 g (0.012 mole) of

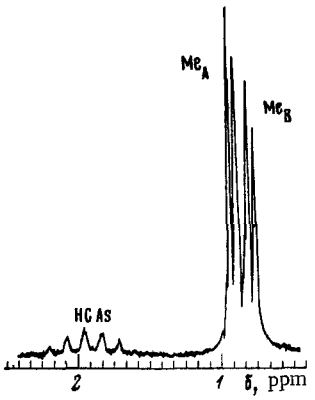


Fig. 5. NMR spectrum of $CF_3COAs(CHMe_AMe_B)_2$ at 60 MHz in benzene. The nonequivalence of the methyl groups of the isopropyl substituent is caused by the hindered inversion of the arsenic atom.

pivaloyl chloride in 10 ml of ether. The formation of a precipitate was observed and the mixture turned light yellow. The precipitate was filtered and washed withe ether (10 ml × 2). After removal of the ether the re idue was vacuum-distilled. We obtained 1.8 g (75%) of a pale yellow liquid, bp 61-62° (3 mm). Found: C 65.51; H 11.37%. $C_{11}H_{23}OP$. Calculated: C 65.35; H 11.38%.

CONCLUSIONS

1. The unsymmetrical secondary phosphines were synthesized: isopropylbenzylphosphine and tert-butylbenzylphosphine.

2. Treatment with ketenes or carboxylic acid chlorides gave a number of acyl derivatives of primary phosphines, of symmetrical and unsymmetrical secondary phosphines, and also of diisopropylarsine.

3. The parameters of the NMR spectra were measured for a number of simple phosphines, diisopropylarsine, and also the chloro and acyl derivatives.

LITERATURE CITED

1. R. G. Kostyanovskii, V. V. Yakshin, S. L. Zimont, and I. I. Chervin, Izv. Akad. Nauk SSSR, Ser. Khim., 1398 (1967); 188, 391, 677 (1968); Tetrahedron, 24, 2995 (1968); Dokl. Akad. Nauk SSSR, 188, 366 (1969).
2. R. G. Kostyanovskii and Yu. I. Él'natanov, Effect of Higher Atomic Orbitals on Physicochemical Properties of Compounds of Nontransition Elements [in Russian], Zinatne, Riga (1971), p. 138; Izv. Akad. Nauk SSSR, Ser. Khim. 1891 (1972); 1915 (1973); Dokl. Akad. Nauk SSSR, 219, 137 (1974).
3. R. G. Kostyanovsky and V. G. Plekhanov, Org. Mass Spectrometry, 6, 1183, 1199 (1972); 7, 1113 (1973).
4. H. Albers, W. Künzel, and W. Schuller, Chem. Ber., 85, 239 (1952).
5. I. L. Knunyants, É. G. Bykhovskaya, and Yu. A. Sizov, USSR Patent No. 197583; Byull. Izobr., No. 13 (1967); Zh. Vses. Khim. Obshchestva D. I. Mendeleeva, 17, 346 (1972).
6. R. Tyka and E. Plaźek, Roczn. Chem., 35, 1831 (1961); Bull. Polon. Acad. Sci., Ser. Chim., 9, 577 (1961).
7. K. Issleib and O. Löw, Z. Anorg. Allgem. Chem., 346, 241 (1966).
8. K. Issleib and R. Kümmel, Z. Naturforsch., 22b, 784 (1967).
9. H. Hoffmann and P. Schellenbeck, Chem. Ber., 100, 692 (1967).
10. P. Yates (editor), Organic Syntheses, Vol. 48, John Wiley and Sons, Inc., New York – London – Sydney – Toronto (1968), p. 47.
11. Yu. I. Baranov and S. V. Gorelenko, Zh. Obshch. Khim., 39, 836 (1969).
12. N. K. Bliznyuk, G. S. Levskaya, and E. N. Matyukhina, Zh. Obshch. Khim., 35, 1249 (1965).
13. É. E. Nifant'ev, Chemistry of Organophosphorus Compounds [in Russian], Izd. Moskov. Gos. Univ. (1971), p. 277.
14. A. W. Hofmann, Chem. Ber., 6, 294 (1873).
15. K. Isslieb and A. Tzchatsch, Ber., 92, 704 (1959).