219 (5.1), 181 (13.5), 169 (18.5), 131 (20.2), 119 (16.2), 108 (21.6), 70 (34.9), 69 (52.4), 58 (17.6).

 $\frac{C_{e}F_{17}CONH(CH_2)_2NH_2}{(0.8), 476(1.3), 169(1.4), 131(2.0), 119(1.7), 108(1.8), 87(2.7), 69(5.0), 58(4.6), 44(20.3), 43(17.0), 30(100).$

 $\frac{C_8F_{17}CONHCH_2CH(Me)NH_2 \text{ (VI). IR spectrum (in mineral oil, <math>v, \text{ cm}^{-1}$): 3320, 3278, 3150 (NH), 1695 (C=0), 1590 (δ , NH), 1535 (δ , NH), 1110, 1140, 1180, 1230 (CF). Mass spectrum: 519 (M-H)⁺ (3.9), 505 (12.0), 476 (2.3), 101 (6.8), 85 (9.2), 58 (42.8), 57 (16.7), 56 (12.0), 44 (100), 43 (6.2), 42 (10.2), 41 (12.2), 30 (24.4).

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CONCLUSIONS

1. Even with a large excess of ethylenediamine (20:1), ethyl trifluoroacetate gives only the symmetrical diamide, while with 1,2-propylenediamine it forms predominantly the monoamide, consisting of a mixture of the isomers $CF_3CONHCH_2CH(Me)NH_2$ and $CF_3CONHCH(Me)CH_2NH_2$ in a 1:3 ratio.

2. In the reactions of ethyl perfluoropelargonate with both diamines, the yield of the monoamide increases significantly.

LITERATURE CITED

- H. G. Brice, J. H. Simmons (editor), Fluorine Chemistry, Vol. 5, New York-London (1964), p. 370.
- 2. E. M. Rokhlin and E. G. Abduganiev, Usp. Khim., 45, 1177 (1976).
- 3. D. Singh and R. Taft, J. Am. Chem. Soc., 97, 3867 (1975).
- 4. U. S. Patent 3,963,776, April 15, 1976; Ref. Zh. Khim., 6R582 (1977).
- 5. M. Saxby, Org. Mass Spectrom., <u>2</u>, 33 (1969).
- 6. A. Prox and L. Schmidt, Org. Mass Spectrom., 2, 105 (1969).
- 7. J. W. Emsley et al., High-Resolution NMR Spectroscopy, Pergamon (1966).

PHOSPHORYLATION OF POLYFLUOROAROMATIC COMPOUNDS.

3. MICHAELIS-BECKER REACTION OF POLYFLUORINATED

BENZENE DERIVATIVES*

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In addition to the Arbuzov rearrangement, the Michaelis-Becker reaction is one of the basic methods for synthesis of alkylphosphonic acid derivatives [2]. There is little information on the synthesis of alkylphosphonic acid derivatives by such a method. Depending on the conditions, the reaction of pentachlorobenzene with Na dialkyl phosphite gives tetrachlorobenzene or a small amount of dialkyl tetrachlorophenylphosphonate [3]. Iodobenzene reacts with Na diethyl phosphite with the formation of Na monoethyl phenylphosphonate [2]. Diethyl phenylphosphonate is formed only under UV irradiation. It has been possible to carry out the Michaelis-Becker for some chloro derivatives of heteroaromatic compounds [2, 4].

Continuing the study of phosphorylation of polyfluoroaromatic compounds [1], we investigated the reaction of pentafluorobenzenes C_6F_5X [X = CN (Ia), CF_3 (Ib), F (Ic), H (Id), NO₂ (Ie), or OMe (If)] and pentafluoropyridine (II) with phosphite salts.

*For Communication 2, see [1].

Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR. Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 867-869, April, 1981. Original article submitted April 15, 1980. Compounds (Ia-f) and (II) reacted with Na dimethyl and diethyl phosphites and Na diethyl thiophosphite in THF at 60-70°C with formation of the corresponding polyfluoroarylphosphonates and polyfluoroarylthiophosphonates (III) and dimethyl (IV) and diethyl (V) 2,3,5,6-tetrafluoropyridylphosphonates in 10-65% yields. In the reaction of pentafluoronitrobenzene (Ie) with Na diethyl phosphite, a mixture of diethyl 2- and 4-nitrotetrafluorophenylphosphonates in a 3:2 ratio [compounds (VI) and (VII), respectively] (cf. [1])) was obtained. In the reaction of pentafluoroanisole (If) with Na diethyl phosphite, a mixture of 2-, 3-, and 4-methoxytetrafluorophenylphosphonic acids in 1:1 and 3:1.8 ratios [compounds (VIII), (IX), and (X), respectively] (cf. [5]). In the reaction mixtures obtained in the reaction of (Ie) and (II) with Na diethyl phosphite, diethyl fluorophosphate was observed according to the ¹⁹F and ³¹P NMR spectra: $\delta(FP) = -82.9$ ppm, $J_{F-P} = 960$ Hz; $\delta(P) = 13.3$ ppm, $J_{P-F} = 960$ Hz.



X = CN, Y = O, Z = Et (IIIa); $X = CF_3, Y = O, Z = Et$, (III b); X = E, Y = O, Z = Et (IIIc); X = H, Y = O, Z = Et (IIId); X = CN, Y = O, Z = Me (IIIe); $X = CF_3, Y = O, Z = Me$ (IIIf); X = CN, Y = S, Z = Et (IIIg); $X = CF_3, Y = S, Z = Et$ (IIIh)

From the standpoint of the concepts of the effect of solvents in reactions of type SNAr [6, 7], we could expect that the Michaelis-Becker reaction should proceed most easily in aprotic bipolar solvents. However, it was found that the use of DMFA, DMSO, sulfolane, and acetonitrile caused a decrease in the yield of phosphorylated products (IIIa-d) and (V).

We should note that in the reaction of compounds (IIIb) and (V) with Na dimethyl and diethyl phosphites at 70-80°C, polyphosphorylated products were not formed.

The structure of the obtained products was confirmed by elemental analysis and NMR spectra.

EXPERIMENTAL

The ¹⁹F and ¹H NMR spectra were recorded with a Varian A56/60A spectrometer (56.4 and 60 MHz) from the internal standards C_6F_6 and TMS, and the ³¹P NMR spectra were recorded with a Bruker HX-90 pulse spectrometer using a Fourier transformation on a B-NC 12 computer (standard of 85% H₃PO₄); the IR spectra were recorded with an MS-3301 instrument with an ionizing voltage of 70 and 13 eV. The Na dialkyl phosphites were obtained according to [2].

<u>General Procedure for Carrying Out the Reactions.</u> Into a flask with a stirring device and a reflux condenser were placed 0.1 mole of Na dimethyl (diethyl) phosphite (thiophosphite), 0.08 mole of the polyfluoroaromatic compound, and 100 ml of abs. THF. The mixture was boiled for 6-10 h, poured into water, and extracted with ether. The ether extract was dried over MgSO₄. After distillation in vacuo, the phosphorylation product was obtained. The boiling points and the ¹⁹F and ³¹P NMR and IR spectral data of the diethyl polyfluoroarylphosphonates and 2,3,5,6-tetrafluoropyridylphosphonate agree with those described in [1] and [8], and the product yields (%) were: (IIIa), 57; (IIIb), 65; (IIIc), 15; (IIId), 10; (V), 50; and mixture of (VI) and (VII), 42.

Dimethyl 4-cyanotetrafluorophenylphosphonate (IIIe), 63% yield, bp 123-125°C (2-3 mm). The ¹⁹F NMR spectrum contained two signals of equal intensity at -35 and -33 ppm. The ³¹P NMR spectrum contained a multiplet at -4.48 ppm. Found: C 38.87; H 2.15; N 4.91%. C₉H₆F₄NO₃P. Calculated: C 38.16; H 2.12; N 4.95%.

Dimethyl 4-(trifluoromethyl)tetrafluorophenylphosphonate (IIIf), 58% yield, bp 69-71°C (2-3 mm). The ¹⁹F NMR spectrum contained three signals with intensity ratios of 3:2:2 at -106.2 (CF₃), -32.6 ($F^{2,6}$), and -23.9 ppm ($F^{3,5}$), respectively. The ³¹P NMR spectrum contained a multipletat-3.62 ppm. Found: C 33.00; H 1.98; F 40.72; P 9.24%. C₉H₆F₇O₃P. Calculated: C 33.13; H 1.84; F 40.80; P 9.51%.

Diethyl 4-cyanotetrafluorophenylthiophosphonate (IIIg), 41% yield, bp 84-85°C (2 mm). ¹⁹F NMR spectrum contained two signals of equal intensity at -31.6 and -28.4 ppm. The ³P NMR spectrum contained a multiplet at 18.6 ppm. Found: C 40.18; H 3.16; F 23.16; N 4.42; S 9.54%. C₁₁H₁₀F₄O₂NPS. Calculated: C 40.37; H 3.06; F 23.24; N 4.28; S 9.79%. Diethyl 4-(trifluoromethyl)tetrafluorophenylthiophosphonate (IIIh), 37% yield, bp 46-47°C (2 mm). The ¹⁹F NMR spectrum contained three signals with intensity ratios of 3:2:2 at -108.2 (CF₃), -30.0 ($F^{2,6}$), and -22.0 ppm ($F^{3,5}$), respectively. The ³¹P NMR spectrum contained a multiplet at 21.1 ppm. The PMR spectrum contained a quartet at 3.13 ppm and a triplet at 1.33 ppm. Found: C 35.56; H 2.67; F 35.78; P 8.06; S 8.98%. C₁₁H₁₀F₇O₂PS. Calculated: C 35.68; H 2.70; F 35.95; P 8.38; S 8.65%.

Dimethyl 2,3,5,6-tetrafluoropyridylphosphonate (IV), 53% yield, bp 97-98°C (2-3 mm). The ¹⁹F NMR spectrum contained two signals of equal intensity at -73.0 and -29.4 ppm. The ³¹P NMR spectrum contained a multiplet at -3.55 ppm. Found: C 32.29; H 2.29; F 29.34; N 5.30%. $C_7H_6F_4NO_3P$. Calculated: C 32.43; H 2.32; F 29.34; N 5.41%.

Dimethyl methoxytetrafluorophenylphosphonates, 24% yield [according to GLC data: 24% (VIII), 32% (IX), and 44% (X)]. Found: C 39.68; H 3.40; F 27.73; P 11.20%; mol. wt. 272 (mass spectrometrically). C₉H₉F₄O₃P. Calculated: C 39.71; H 3.31; F 27.94; P 11.40%; mol. wt. 272. Compound (VIII): the ¹⁹F NMR spectrum contained four signals of equal intensity at -3.0 (F³), -1.2 (F⁴), -0.7 (F⁵), and -26.5 ppm (F⁶). The ³¹P NMR spectrum contained four signals of equal intensity at -3.0 (F³), -1.2 (F⁴), -0.7 (F⁵), and -26.5 ppm (F⁶). The ³¹P NMR spectrum contained four signals of equal intensity at -35.3 (F²), -3.0 (F⁴), 7.2 (F⁵), and -30.9 ppm (F⁶). The ³¹P NMR spectrum contained a multiplet at -4.63 ppm. Compound (X): the ¹⁹F NMR spectrum contained two signals of equal intensity at -8.0 (F^{3,5}) and -31.5 ppm (F^{2,6}). The ³¹P NMR spectrum contained a multiplet at -3.24 ppm.

CONCLUSIONS

Polyfluoroaromatic compounds react with Na dimethyl and diethyl phosphites and diethyl thiophosphite in the Michaelis-Becker reaction with formation of the corresponding methyl and ethyl polyfluoroarylphosphonates and thiophosphonates.

LITERATURE CITED

- 1. L. N. Markovskii, G. G. Furin, Yu. G. Shermolovich, and G. G. Yakobson, Zh. Obshch. Khim., <u>49</u>, 531 (1979).
- 2. Reactions and Methods for Investigation of Organic Compounds [in Russian], Vol. 15, Khimiya, Moscow (1966), p. 41.
- 3. M. C. Derarco, Bull. Soc. Chim. Fr., 1716 (1969).
- 4. G. M. Kosolapoff and C. H. Roy, J. Org. Chem., 26, 1895 (1961).
- 5. J. Burdon, W. B. Hollyhead, and J. C. Tatlow, J. Chem. Soc., 5152 (1965).
- 6. B. Chubar, Usp. Khim., <u>34</u>, 1227 (1965).
- 7. H. Reichardt, Solvents in Organic Chemistry [Russian translation], Khimiya, Moscow (1973).
- 8. L. N. Markovskii, G. G. Furin, Yu. G. Shermolovich, and G. G. Yakobson, Izv. Akad. Nauk SSSR, Ser. Khim., 2839 (1977).