(200 min) by gas chromatography. The ratio did not vary more than could be attributed to experimental error, and the final composition was 40% cis, 60% trans. There was also no change in the isomer ratio during reaction of excess isobutyl bromide (2.43 *M*) with **6** (0.112 *M*; 45% cis, 55% trans), which was followed to 47% completion (230 min).

Registry No.—**3**, 16327-48-3; **4a**, 16327-50-7; **4b**, 16327-49-4; **5**, 33834-95-6; *cis*-**6**, 33835-61-9; *trans*-**6**, 33835-62-0.

Acknowledgment.—We are grateful to Mr. Sidney Featherman for assistance in developing gas chromatographic conditions for **6**, and to Mr. Joseph J. Breen for obtaining ^{31}P nmr data.

Synthesis of Some Benzeneazo Derivatives of Phosphonic Acid Monoesters

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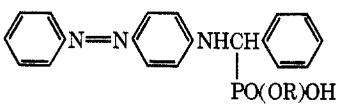
Neutral esters of α-anilinobenzylphosphonic acid were prepared by addition of dialkyl phosphites to Schiff's base. Their hydrolysis with alcoholic sodium hydroxide solution, followed by the acidification of the sodium salts obtained, afforded the corresponding monoesters.

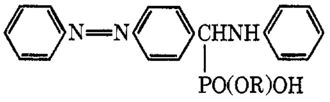
Since the first benzeneazophosphonic acid was reported,[1] a number of various benzeneazo or naphthylazo derivatives of phosphonic acid and its neutral esters have been prepared.[2-4] However, no attempt has been made to synthesize arylazo derivatives of phosphonic acid monoesters. As the syntheses of some monoesters of α-anilinobenzylphosphonic acid were described earlier[5,6] we have undertaken the present investigation to prepare several arylazo derivatives of α-anilinobenzylphosphonic acid.

Results and Discussion

Monoesters of [α-(4-benzeneazoanilino)-*N*-benzyl]-phosphonic acid (type A) and of [4-benzeneazo-α-(anilino)benzyl]phosphonic acid (type B) have been synthesized. In addition to the monoesters the corresponding diesters, *i.e.*, diethyl and dibutyl [α-(4-benzeneazoanilino)-*N*-benzyl]phosphonate (I and IV) and diethyl and dibutyl [4-benzeneazo-α-(anilino)benzyl]-phosphonate (VII and IX), were prepared. Only sodium salts of monoethyl and monobutyl esters [α-(benzeneazoanilino)-*N*-benzyl]phosphonic acid (II and V, respectively), obtained by hydrolysis of I and IV, were isolated in pure form. Neutral esters were obtained by reaction of dialkyl phosphites to Schiff's bases. They were subjected to alkaline hydrolysis to give sodium salts of the monoesters. The latter were converted to the free monoesters by acidification with a diluted mineral acid. Essentially the same reaction was applied to prepare both types of compounds. An illustration (Scheme I) is given for the preparation of the type A only. All phosphonic acid diesters are stable compounds. However, when subjected to alkaline hydrolysis they exhibit various degrees of stability. The compounds of the A type appear to be more stable than that of the B type. Thus the monoesters III and VI were obtained from the corresponding diesters I and IV in over 60% yield. Hydrolysis of diesters VII and IX yielded only about 25% of the monoesters VIII and X, together with an unidentified product (25–30%), which was insoluble in water and did not contain phosphorus, and a product (about 17%) which was identified as benzeneazocarboxylic acid-(4) (XIII) (Table I). The acid was obtained from its sodium salt by acidification with diluted hydrochloric acid and separated from a monoester due to better solubility in ethanol.



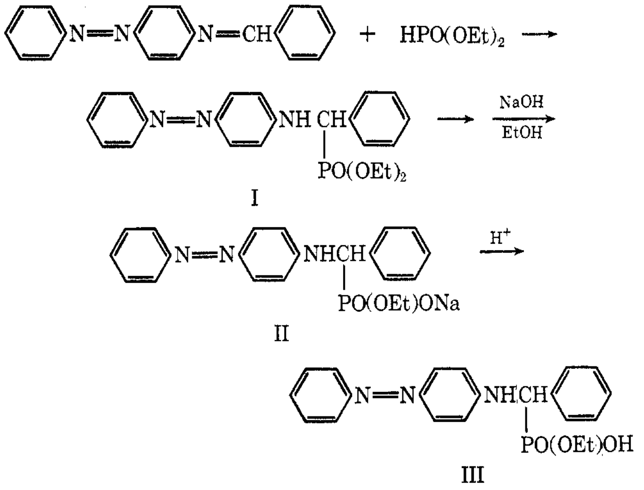
A



B

R = C_2H_5, compound III
R = C_4H_9, compound VI
R = C_2H_5, compound VIII
R = C_4H_9, compound X

SCHEME I



Attempts have been made to prepare the monoester of the following formula.

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[1] G. M. Kosolapoff and G. G. Priest, *J. Amer. Chem. Soc.*, **75**, 4847 (1953).

[2] T. M. Moshkina and A. N. Pudovik, *Zh. Obshch. Khim.*, **35**, 2042 (1965).

[3] A. M. Lukin, N. A. Bolotino, and G. B. Zavarkhina, *Inst. Khim. Reaktov Osobo Chist. Khim. Veshchestv.*, No. 30, 5 (1967); *Chem. Abstr.*, **68**, 88177a (1968).

[4] Houben-Weyl, "Methoden der Organischen Chemie," Vol. XII/2, Georg Thieme Verlag, Stuttgart, 1964, pp 545–547.

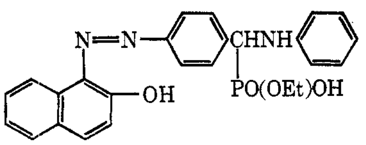
[5] V. Jagodić, *Chem. Ber.*, **93**, 2308 (1960).

[6] V. Jagodić and M. J. Herak, *J. Inorg. Nucl. Chem.*, **32**, 1323 (1970).

TABLE I

Compd	Formula	Mp, °C	Yield, %	Calcd, % C	H	N	P	H_2O	Found, % C	H	N	P	H_2O
I	$C_{23}H_{26}N_3O_3P$	134.5–135	90	65.23	6.19	9.92	7.32		65.02	6.44	10.15	7.21	
II	$C_{21}H_{21}N_3O_3PNa \cdot 1.5H_2O$	232	66	56.75	5.45	9.46	6.97	6.08	56.83	5.61	9.62	6.79	5.92
III	$C_{21}H_{22}N_3O_3P$	182	82	63.79	5.61	10.63	7.83		64.04	5.80	10.87	7.70	
IV	$C_{27}H_{34}N_3O_3P$	122.5–123	92	67.63	7.14	8.76	6.64		67.79	7.15	8.68	6.29	
V	$C_{23}H_{25}N_3O_3PNa \cdot H_2O$	243	60	59.61	5.87	9.07	6.68	3.88	59.57	5.96	8.93	6.66	3.09
VI	$C_{23}H_{26}N_3O_3P$	167	59	65.23	6.19	9.92	7.32		65.42	6.11	10.14	7.27	
VII	$C_{23}H_{26}N_3O_3P$	157–158	86	65.23	6.19	9.92	7.32		64.99	6.12	10.17	7.17	
VIII	$C_{21}H_{22}N_3O_3P$	177.5–178	25	63.79	5.61	10.63	7.83		63.97	5.58	10.84	7.74	
IX	$C_{27}H_{34}N_3O_3P$	112.5–113	82	67.63	7.14	8.76	6.46		67.81	7.35	8.82	6.33	
X	$C_{23}H_{26}N_3O_3P$	178–178.5	26.6	65.23	6.19	9.92	7.32		65.15	6.34	9.81	7.22	
XI	$C_{23}H_{17}N_3O_2$	160.5–161	68.8	78.61	4.88	11.96			78.54	4.83	12.04		
XII	$C_{27}H_{28}N_3O_4P$	149–150	82	66.25	5.77	8.58	6.33		66.11	5.96	8.60	6.08	
XIII	$C_{13}H_{10}N_2O_2$	246–247[a]	17	69.02	4.45	12.38			68.85	4.71	12.53		

[a] Mp 248.5–249.5°: H. D. Anspon, *Org. Syn.*, **25**, 86 (1945).



Although the corresponding diethyl [4-(2-naphtholazo)-α-anilinobenzyl]phosphonate (XII) was prepared in over 80% yield and was quite stable, we were not able to prepare the above monoester. Regardless of the temperature on which the hydrolysis was carried out, kind of the solvent applied (ethanol or water), or duration of hydrolysis, only a mixture consisting of various proportions of decomposition products and unchanged XII resulted. When the product of hydrolysis was dissolved in water and acidified with a mineral acid a compound was obtained which showed in the ir spectrum a strong band at 1680 cm^{-1}, characteristic for the carboxylic acids. This indicates that here, similarly to the hydrolysis of diesters VII and IX, the rupture of the C–P bond and the formation of a carboxylic acid took place. Such a great instability of diester XII in alkaline medium is probably due to the presence of the naphthyl OH group.

The color of the products varies from orange to red. Monoesters of the A type are more readily soluble in common organic solvents than those of the B type.

Experimental Section

The yields and physical properties of the compounds prepared are listed in Table I. The analyses were obtained from the Microanalytical Laboratory, Rudjer Bošković Institute. Melting points are uncorrected.

Preparation of Diesters I, IV, VII, IX, and XII.—Neutral esters of phosphonic acids were prepared by heating an equimolar mixture of Schiff's base and dialkyl phosphite in a water bath for 8 hr. Contrary to the original method[7] this addition was carried out without any catalyst. The reaction products solidified upon cooling and were recrystallized from ethanol.

Hydrolysis of Diesters.—Approximately 5% solution of neutral esters in ethanol was refluxed with an excess of sodium hydroxide (2–2.5 mol/mol of diester) for 20 hr. To precipitate the excess of the base, carbon dioxide was introduced into the solution. Sodium carbonate formed was filtered off and the resulting solution was evaporated to dryness *in vacuo*. Sodium salts II and V, obtained from the corresponding diesters I and IV, were recrystallized from absolute ethanol. Sodium salts obtained from diesters VII and IX were used in a crude form to prepare the free monoesters.

Preparation of Monesters III, VI, VIII, and X.—Sodium salts were dissolved in water and the solution was filtered to remove any insoluble impurities. The resultant solution was stirred and a small excess of 5% hydrochloric or sulfuric acid was added dropwise causing the monoesters to separate as a precipitate. They were collected by filtration, dried, and recrystallized as follows: monoesters I and VI from a benzene–ether (1:50) mixture; VIII from ethanol; and X from a ethanol–ether mixture.

Preparation of Schiff's Bases.—4-Benzeneazo-*N*-benzalaniline[8] and 4-(benzeneazobenzal)aniline[9] were prepared as described. 4-(2-Naphtholazo)benzalaniline (XI) was obtained by heating a mixture of 0.4 g (0.00143 mol) of 4-(2-naphtholazo)benzaldehyde[10] and 0.15 g (0.0015 mol) of aniline on a steam bath for 0.5 hr. After standing overnight at room temperature a solid product formed. It was recrystallized from ethanol giving 0.35 g (68.8%) of XI, mp ~150°. Repeated recrystallization from ether yielded a red product melting at 160.5–161°.

Registry No.—I, 33521-43-6; II, 33521-44-7; III, 33521-45-8; IV, 33521-46-9; V, 33521-47-0; VI, 33521-48-1; VII, 33521-49-2; VIII, 33521-50-5; IX, 33521-51-6; X, 33521-52-7; XI, 33521-53-8; XII, 33521-54-9.

Acknowledgments.—The authors are indebted to Dr. Š. Mesarić and Associates for the microanalyses and to Mr. Z. Despotović for the thermogravimetric analyses of water.

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[7] A. N. Pudovik and M. V. Korchemkina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 940 (1952).

[8] F. G. Pope and W. I. Willett, *J. Chem. Soc.*, **103**, 1258 (1913).

[9] F. J. Alwey, *Amer. Chem. J.*, **28**, 47 (1902).

[10] P. Friendländer and E. Lenk, *Chem. Ber.*, **45**, 2084 (1912).