acid. Methoxyl group: calcd. for $C_{10}H_{11}O{\cdot}OCH_3$, 17.4%; found 17.4%. Mixed melting point determination with dehydroperillic acid supplied by Dr. A. B. Anderson, m. p. 88°.

OREGON FOREST PRODUCTS LABORATORY AND
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CORVALLIS, OREGON
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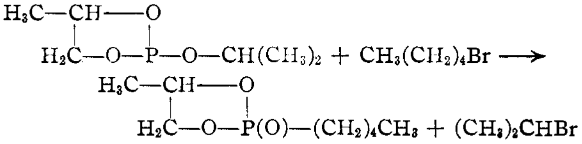
Phosphonation with a Phosphite Ester of Propanediol

BY F. W. MITCHELL, JR.,[1] AND H. J. LUCAS

The reaction of trialkyl phosphites with alkyl halides in the Arbuzov reaction[2] is essentially a phosphonation reaction, since one product is an ester of a phosphonic acid. The reaction has been studied fairly extensively with acyclic esters,[3] and has been extended recently to cyclic trialkyl phosphites derived from ethanediol and 3-methoxy-1,2-propanediol.[4] Whereas ethyl ethylene phosphite (2-ethoxy-1,3,2-dioxaphospholane)[5] underwent the isomerization reaction with ring opening, the presence of the methoxymethyl side chain in esters of 3-methoxy-1,2-propanediol led to ring stabilization. When the isomerization reagent was ethyl bromide the reaction product was the cyclic ester of ethanephosphonic acid.

In connection with work on cyclic trialkyl phosphites derived from glycols[5] it has been found that 2-isopropoxy-4-methyl-1,3,2-dioxaphospholane (isopropyl propylene phosphite) when heated with 1-bromopentane undergoes the Arbuzov reaction without ring opening. The product is propylene pentane-1-phosphonate (2-oxo-2-*n*-amyl-4-methyl-1,3,2-dioxaphospholane). The recovery of isopropyl bromide in 78% yield indicates this is essentially the sole reaction. The stability of the ring system in this case is in agreement with the conclusions of the Russian workers,[4] that a side chain in the glycol residue increases the stability of the ring system.



Experimental

In a boiler attached to a distillation column held at 60°, 0.2 mole (32.8 g.) of 2-isopropoxy-1,3,2-dioxaphospholane and 0.2 mole (30.2 g.) of 1-bromopentane, b. p., 127-127.5°, were heated at refluxing temperature for a period of 9 hours, during which time isopropyl bromide slowly distilled; weight 19 g. (78% yield); b. p. 57.5-58.5° at 745 mm.; $n^{25}\text{D}$ 1.4216 (literature value 1.4251). Distillation of the residue gave 28 g. (73% yield) of propylene pentane-1-phosphonate, a slightly viscous liquid, b. p. 131-132° at 1.5 mm., $n^{25}\text{D}$ 1.4481, d^{25}_4 1.1052.

Hydrolysis of 10 g. (0.052 mole) with 6 *N* HCl[6] for 30 minutes, followed by slow distillation with paraformaldehyde according to the procedure of Senkus[7] gave 3 ml. (63% yield) of formal. Excess formaldehyde was removed from the boiler liquid as methalal, b. p. 44-45°, and the water was evaporated at reduced pressure, leaving a dark brown oil which partly solidified overnight. Oil and solid were separated from each other by flotation with a carbon tetrachloride-ligroin mixture. Crystallization of the solid from hot ligroin gave 2.3 g. (25% yield) of thin colorless plates, m. p. 120-122°, believed to be pentane-1-phosphonic acid.[8]

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(1) National Aniline and Film Corporation, Easton, Pa.

(2) A. E. Arbuzov and A. A. Dunin, *J. Russ. Phys.-Chem. Soc.*, **46**, 295 (1914); A. E. Arbuzov, "On the Structure of Phosphorous Acid," N. Alexandria, 1905.

(3) G. M. Kosolapoff, THIS JOURNAL, **66**, 109 (1944). A number of references to earlier work are given.

(4) A. E. Arbuzov, V. M. Zoroaster and N. T. Rizpolozhenskiĭ, *Bull. acad. sci. U. R. S. S. Classe sci. chim.*, 208, 1948; *cf. C. A.*, **42**, 4932 (1948).

(5) H. J. Lucas, F. W. Mitchell, Jr., and C. N. Scully, THIS JOURNAL, **72**, 5491 (1950).

(6) Similar to the procedure of G. M. Kosolapoff, *ibid.*, **67**, 1180 (1945), who used concentrated acid, however.

(7) M. Senkus, *Ind. Eng. Chem.*, **38**, 913 (1946), recovered 2,3-butanediol from dilute aqueous solutions by conversion to the formal.

(8) Of the fourteen normal alkanephosphonic acids listed by Kosolapoff[6] none of the others melted higher than 106°.

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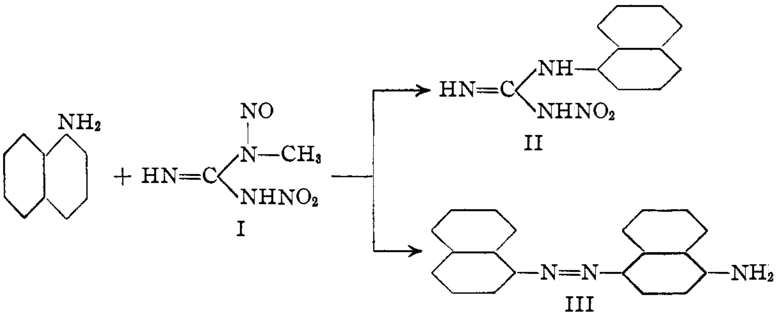
A New Method for the Preparation of Azo Dyes[1]

BY EUGENE LIEBER AND KONRAD PARKER[2]

While investigating the formation of N-Ar-N′-nitroguanidines, where Ar is a polycyclic aromatic hydrocarbon radical, by the method of McKay and Wright[3] using N-methyl-N-nitroso-N′-nitroguanidine (I), it was observed that α-naphthylamine gave rise to two products; N-(α-naphthyl)-N′-nitroguanidine (II), the expected product, in 25% yield (based on the nitroso compound used), and a large amount of dark brownish-green needles having dye properties. This was subsequently identified as 4-amino-α,α-azo-naphthalene[4] and amounted to 50% of the theoretical yield



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(1) Studies in the Guanidine Series. VIII.

(2) Abstracted from a portion of the thesis submitted by Konrad Parker to the Graduate School of Illinois Institute of Technology in partial fulfillment of the requirements for the degree, Master of Science.

(3) A. F. McKay and G. F Wright, THIS JOURNAL, **69**, 3028 (1947).

(4) Michaelis and Erdmann, *Ber.*, **28**, 2198 (1895).