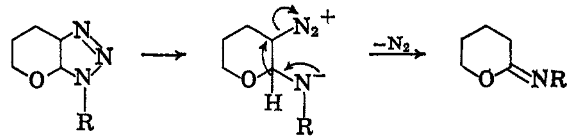
alternative path proposed by Franz and co-workers[1] and Rector and Harmon,[2] and supported by the results of other investigations,[12] is more probable.



The strikingly different reaction paths observed in the thermal and photodecompositions of IV are noteworthy. As previously pointed out,[10] the photolysis of triazolines is an excellent preparative method, well suited to the preparation of sensitively substituted aziridines.

Experimental Section[13]

9-*p*-Bromophenyl-2-oxa-7,8,9-triazabicyclo[4.3.0]non-7-ene (IV).—Dihydropyran (6.0 g, 0.072 mole) and *p*-bromophenyl azide (9.9 g, 0.050 mole) were placed in a reaction vessel and maintained at 40° ± 2° by means of a water bath. A gas buret was used to measure evolved gas. After 14 days (230 ml evolved), volatile materials were removed by evaporation at 50° (0.5 mm). The resulting deep orange oil (11.1 g) was taken up in methanol and refrigerated. A white, crystalline solid was collected and washed with cold methanol (3.4 g, 24%), mp 108–109° dec. Three recrystallizations from methanol gave material melting at 109.5–110.5° dec.

Anal. Calcd for $C_{11}H_{12}BrN_3O$: C, 46.82; H, 4.29; Br, 28.33; N, 14.89. Found: C, 46.69; H, 4.27; Br, 28.20; N, 15.02.

Thermal Decomposition of IV.—A sample of IV (322 mg) was dissolved in 4 ml of anhydrous toluene and the solution was refluxed for 1 hr. Nitrogen evolution had ceased after *ca.* 35 min. Removal of the solvent under reduced pressure gave a viscous oil that exhibited a strong absorption at 1670 cm^{-1} (C=N). The oil was treated with 1 ml of methanol and 5 ml of 25% sulfuric acid at room temperature for 16 hr, and then extracted with two 5-ml portions of methylene chloride. Evaporation of the dried extracts ($MgSO_4$) gave 104 mg (91%) of a colorless oil which showed a strong carbonyl absorption at 1730 cm^{-1}. This material was identified as δ-valerolactone by heating it for 90 min at 100° with hydrazine hydrate (150 mg). After crystallization from benzene–acetonitrile, the hydrazide (87 mg, 5-hydroxypentanoic acid hydrazide) melted at 104–105° (lit.[2,8] mp 104–106°).

The aqueous solution (above) was made basic with 30% sodium hydroxide solution and extracted with three 6-ml portions of methylene chloride. Removal of the solvent from the dried extracts ($MgSO_4$) gave 153 mg (79%) of *p*-bromoaniline, identified by comparison of the infrared spectrum and vpc retention time with those of an authentic sample.

7-*p*-Bromophenyl-7-aza-2-oxabicyclo[4.1.0]heptane (VI).—A solution containing 2.0 g (7.1 millimoles) of IV in 45 ml of anhydrous benzene was irradiated for 12 hr at room temperature. The light employed (550-w Hanovia, Type A, medium-pressure Hg arc) was filtered through two plates of Pyrex glass and a Pyrex cell (2 cm) through which cold water circulated. The colorless product solution was evaporated (aspirator, 50°) affording a crystalline, sticky solid. The infrared spectrum of this material showed a weak imine absorption at 1670 cm^{-1}. Recrystallization from ether (16 ml)–pentane (10 ml) at −78° gave 1.2 g (67%), mp 117–118°. Three additional recrystallizations from ether–pentane gave the analytical sample, mp 118.5–119.5°.

Anal. Calcd for $C_{11}H_{12}BrNO$: C, 51.98; H, 4.76; Br, 31.45; N, 5.51. Found: C, 52.20; H, 4.84; Br, 31.45; N, 5.53.

Photolysis in anhydrous tetrahydrofuran was equally successful.

A solution of 1.0 g of VI in 15 ml of dry toluene was heated at reflux for 1 hr. Removal of the solvent gave a white solid, mp 110–113°, whose infrared spectrum was essentially identical with that of VI. Recrystallization from ether–pentane (−78°) gave pure VI. The same result was obtained in an identical run in which purified, dry nitrogen was passed through the solution.

Hydrolysis of VI. 3-*p*-Bromophenylamino-2-hydroxytetrahydropyran (VII).—A sample of VI (0.40 g) was treated with 3 ml of tetrahydrofuran and 2 ml of water. The slightly cloudy mixture was shaken intermittantly during 3 hr at room temperature. Removal of the solvent (aspirator, 50°) afforded 0.44 g of a white, crystalline solid, mp 157–158.5°. Two crystallizations from acetone gave the analytical sample, mp 161–162°.

Anal. Calcd for $C_{11}H_{14}BrNO_2$: C, 48.54; H, 5.18; Br, 29.37; N, 5.15. Found: C, 48.66; H, 5.31; Br, 29.29; N, 5.29.

The infrared spectrum of the crude product, as well as the analytical sample, showed absorptions at 3610 (OH) and 3408 cm^{-1} (NH), but no absorptions in the carbonyl or imine regions.

Registry No.—Dihydropyran, 110-87-2; IV, 10409-58-2; VI, 10409-59-3; VII, 10409-57-1.

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(12) K. D. Berlin, L. A. Wilson, and L. M. Raff, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstract S97; J. E. Baldwin, G. V. Kaiser, and J. A. Romersberger, *J. Am. Chem. Soc.*, **87**, 4114 (1965).

(13) Nmr spectra were determined in deuteriochloroform with a Varian A-60 instrument, using tetramethylsilane as an internal standard. Melting points, uncorrected, were obtained with a Fisher-Johns melting point apparatus. Infrared spectra were determined for chloroform solutions with a Perkin-Elmer Model 237 instrument.

A New Synthesis of Diethyl Vinyl Phosphate

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Enol phosphate esters are easily obtained in general by use of the Perkow synthesis[2] or the alternate method recently described by Magee.[3] However, in the synthesis of the parent vinyl phosphate esters, *i.e.*, III, it is desirable to avoid Perkow's method since it involves the use of anhydrous chloroacetaldehyde.[4,5] While the procedure of Magee[3] obviates this problem, it requires the use of mercury salts which presents a definite economic barrier, particularly for large-scale preparations.

A third method reported by Upson[6] to be specifically useful for the preparation of unsubstituted vinyl phosphate esters was found to be not reproducible by Allen and co-workers.[7] We have also independently repeated the experiment as described by Upson[6] for the preparation of diethyl vinyl phosphate. Our crude reaction mixture was found to contain approximately 10% diethyl vinyl phosphate, 45% triethyl phosphate, and 45% 2-chloroethyl diethyl phosphate upon examination by glpc. The purity of our IIIb was demonstrated

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(1) To whom inquiries should be addressed at Eastman Kodak Co., Rochester, N. Y.

(2) F. W. Lichtenthaler, *Chem. Rev.*, **61**, 607 (1961).

(3) P. S. Magee, *Tetrahedron Letters*, 3995 (1965).

(4) J. F. Allen and O. H. Johnson, *J. Am. Chem. Soc.*, **77**, 2871 (1955); Food Machinery Chemical Corp., British Patent 784,985 (Oct 23, 1957); R. R. Whetstone and D. Harman (to Shell Oil Co.), U. S. Patent 2,765,331 (Oct 2, 1956).

(5) A general description of the noxious properties and notorious rapid polymerization of anhydrous chloroacetaldehyde can be found in "Chloroacetaldehyde," Dow Chemical Co. Bulletin, Code No. 164-12, June 1958. Although ref 4 described the successful use of this reagent in small-scale preparations, details of its preparation and handling were not included. See also footnote 3 in ref 3.

(6) R. W. Upson, *J. Am. Chem. Soc.*, **75**, 1763 (1953); R. W. Upson (to E. I. du Pont de Nemours and Co.), U. S. Patent 2,557,805 (June 19, 1951).

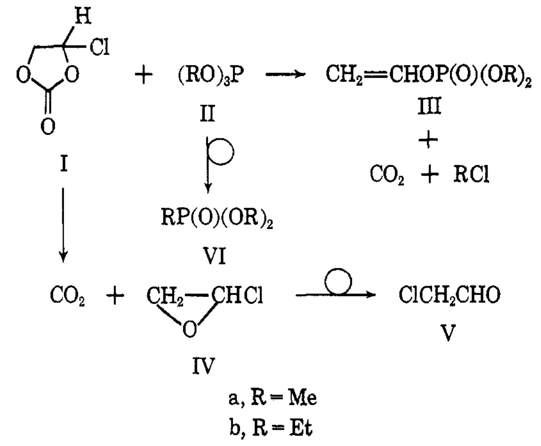
(7) J. F. Allen, S. K. Reed, O. H. Johnson, and N. J. Brunsvold, *J. Am. Chem. Soc.*, **78**, 3715 (1956).

by nmr spectroscopy and glpc and its n^{25}_{D} was 1.4109[8] (see Experimental Section). When a mixture containing 20% IIIb and 80% triethyl phosphate by volume was prepared, it was found to have an n^{25}_{D} of 1.4039. The evidence thus strongly suggests that Upson's "diethyl vinyl phosphate" was most likely a mixture containing approximately 20% IIIb and 80% triethyl phosphate. This would be consistent with his 49% yield of a product boiling at 67° (2.5 mm), n^{25}_{D} 1.4040, 16.80% phosphorous content, and which failed to polymerize on heating with a free-radical source.[6]

It is postulated that the inadequacy of Upson's method is due in part to competing ethanolysis of either or both of the starting material and product. This might be expected since both have stabilized leaving groups. Allen and co-workers[7] apparently realized this and attempted the dehydrohalogenation using nonsolvolytic conditions. However, their "improved" method utilizing 2-bromoethyl diethyl phosphate and sodium hydride similarly gave only a 10–% yield of IIIb. It would appear that more research is needed to better this method.

We now report a new, convenient method of preparation (Scheme I) of diethyl vinyl phosphate by the reaction of triethyl phosphite (IIb) with monochloroethylene carbonate (4-chloro-2-oxo-1,3-dioxolane, I). Although the method can be applied to the syntheses of other O,O-dialkyl O-vinyl phosphates, it is not generally as uncomplicated as in the preparation of the diethyl ester IIIb. For instance, in many trial experiments, the reaction of trimethyl phosphite (IIa) and I gave rise to dimethyl vinyl phosphate (IIIa) contaminated with substantial amounts of dimethyl methyl phosphonate (VIa). IIIa and VIa were very difficult to separate by distillation. The propyl esters gave similar results.

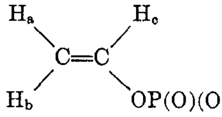
SCHEME I



The mechanism of this novel reaction was not investigated. However, it is known that I can be catalytically converted to chlorooxirane (IV) which thermally rearranges to chloroacetaldehyde (V).[10] Thus, III might have been formed by the reaction of II with V formed *in situ*. However, there is no evidence to exclude the formation of III as a result of the direct action of phosphite on I. Indeed a brief perusal of the mechanistic complexities of the Perkow synthesis[11] would indicate that extensive investigation might be required to settle this point.

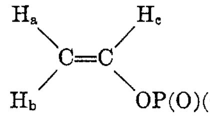
Experimental Section[12]

Diethyl Vinyl Phosphate (IIIb).[13]—A mixture of 61.2 g (0.5 mole) of monochloroethylene carbonate,[14] 200 ml of benzene, and 100 g (0.6 mole) of triethyl phosphite was heated at reflux for 2.5 days. Periodic examination by glpc indicated that the reaction was >95% complete in 10–12 hr. Fractional distillation of the product gave 48 g (50%) of pure IIIb, bp 54–56° (1 mm). *Anal.* Calcd for $C_6H_{13}O_4P$: C, 40.00; H, 7.28; P, 17.20. Found: C, 39.72; H, 7.24; P, 17.08. The infrared spectrum was identical with that of authentic IIIb.[3] The nmr spectrum is shown below.



H_a, δ 4.51	J_{ab} = 1.7 cps	J_{ac} = 6.0 cps	J_{aP} = 2.7 cps
H_b, δ 4.80	J_{ab} = 1.7 cps	J_{bc} = 13.6 cps	J_{bP} = 1.2 cps
H_c, δ 6.55	J_{ac} = 6.0 cps	J_{bc} = 13.6 cps	J_{cP} = 6.8 cps
CH_2, δ 4.10	J_{HH} = 7.2 cps	J_{PH} = 8.8 cps	
CH_3, δ 1.33	J_{HH} = 7.2 cps	J_{PH} = 0.9 cps	

Dimethyl Vinyl Phosphate (IIIa).[13]—A mixture of 24.5 g (0.2 mole) of monochloroethylene carbonate, 200 ml of benzene, and 50 g (0.4 mole) of trimethyl phosphite was heated at reflux 4 days and then distilled. The fraction boiling at 80° (10 mm) weighed 18.5 g and contained only dimethyl vinyl phosphate (IIIa) and dimethyl methyl phosphonate (VIa) in equal amounts as estimated from glpc and nmr data. The nmr spectrum of the mixture was consistent with those of the pure components in CCl_4 (TMS) and is shown below.



H_a, δ 4.59	J_{ab} = 1.9 cps	J_{ac} = 5.8 cps	J_{aP} = 2.8 cps
H_b, δ 4.89	J_{ab} = 1.9 cps	J_{bc} = 13.4 cps	J_{bP} = 0.8 cps
H_c, δ 6.62	J_{ac} = 5.8 cps	J_{bc} = 13.4 cps	J_{cP} = 6.6 cps
CH_3, δ 3.80	J_{PH} = 11.5 cps		

$CH_3P(O)(OCH_3)_2$

PCH_3, δ 1.44	J_{PH} = 17.5 cps
OCH_3, δ 3.73	J_{PH} = 11.5 cps

Registry No.—IIIa, 10429-10-4; IIIb, 4851-64-3; VIa, 756-79-6.

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[8] It should be noted that at least one current, authoritative source[9] has given only the data of Upson[6] for the properties of diethyl vinyl phosphate.

[9] "Dictionary of Organic Compounds," J. R. A. Pollock and R. Stevens, Ed., Oxford University Press, New York, N. Y., 1965, p 1025.

[10] M. Zief and C. H. Schramm, *Chem. Ind.* (London), 660 (1964).

[11] P. A. Chopard, V. M. Clark, R. F. Hudson, and A. J. Kirby, *Tetrahedron*, **21**, 1961 (1965).

[12] Boiling points were not corrected. Nmr spectra were recorded on the Varian A-60 spectrometer. Glpc columns were of 20% SE 52 on Chromosorb W or P.

[13] The ^1H portion of this ABMX system was well resolved at 60 Mc into three double sets of quartets (24 total lines) allowing a facile first-order analysis.

[14] N. D. Field and J. R. Schaefgen, *J. Polymer Sci.*, **58**, 533 (1962); M. S. Newman and R. W. Addor, *J. Am. Chem. Soc.*, **75**, 1263 (1953).