easily reduced. β-Nitrostyrene, azoxybenzene, and azobenzene were not reduced at 90°.

Experimental Section

The data in the tables were obtained by placing 50 ml of a solution of the copper salt in the aqueous amine in a vertical, hard, glass tube (4 × 30 cm) fitted with a gas dispersion tube leading to the bottom for the introduction of carbon monoxide, an outlet near the top and stopcock at the top and bottom for adding or removing liquid samples. This vessel was placed in a hot water bath at 85° during the reaction period. Nitrobenzene (2 ml) was added and a stream of carbon monoxide passed into the reactor at atmospheric pressure at about 10 l./hr. The product was separated from the aqueous solution in a separatory funnel and analyzed by glpc.

Preparative runs with larger amounts of nitro compound were conducted in flasks fitted with good stirring or in a Parr low-pressure shaker. At these conditions all of the carbon monoxide was utilized. Essentially quantitative conversions can be obtained in less than 4 hr at 90° using 5 g each of copper carbonate, sodium hydroxide, and nitroaromatic in 50 ml of 50% ethylene-diamine in a shaking apparatus at 15 psig.

**Registry No.**—Nitrobenzene, 98-95-3.

Evidence against Aziridine Intermediates in the Reaction of Azides with Dihydropyran

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Recent reports have dealt with the thermal reaction of organic azides and 3,4-dihydro-2H-pyran. Benzenesulfonyl azides,[1,2] aryl azides,[3,4] and ethyl azidoformate[5] give imino lactones (II) with dihydropyran; analogous products are obtained with dihydrofuran.[3] Although the initially formed triazoline adduct (I)
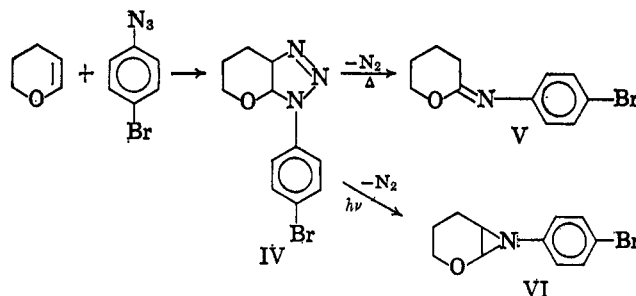

R = ArSO₂, Ar, EtO₂C
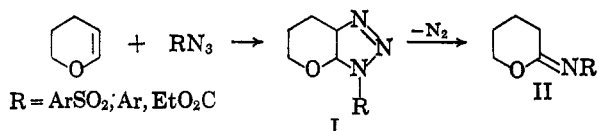
is not always isolable, kinetic evidence indicates its intermediacy.[5,6]

The pyrolytic conversion of triazolines to imines is a well-known reaction. In certain instances, however, triazolines give rise to aziridines, or mixtures of aziridines and isomeric imines.[7] Therefore, the possibility that triazolines of type I first decompose to aziridines (III) which subsequently rearrange to the observed products (II) has been suggested.[1,2] To examine this possibility, an independent preparation of III was attempted.

(1) J. E. Franz, M. W. Dietrich, A. Henshall, and C. Osuch, *J. Org. Chem.*, **31**, 2847 (1966).

(2) D. L. Rector and R. H. Harmon, *ibid.*, **31**, 2837 (1966).

(3) R. Huisgen, L. Möbius, and G. Szeimies, *Ber.*, **98**, 1138 (1965).

(4) A. S. Bailey and J. E. White, *J. Chem. Soc.*, *Sect. B*, 819 (1966); A. S. Bailey and J. J. Merer, *ibid.*, *Sect. C*, 1345 (1966).

(5) I. Brown and O. E. Edwards, *Can. J. Chem.*, **43**, 1266 (1965).

(6) A. C. Oehlschlager and L. H. Zalkow, *J. Org. Chem.*, **30**, 4205 (1965).

(7) K. Alder and G. Stein, *Ann.*, **501**, 1 (1933); A. Mustafa, S. M. A. D. Zayed, and S. Khattab, *J. Am. Chem. Soc.*, **78**, 145 (1956); F. D. Marsh and M. E. Hermes, *ibid.*, **86**, 4506 (1964); G. Szeimies and R. Huisgen, *Ber.*, **99**, 491 (1966).
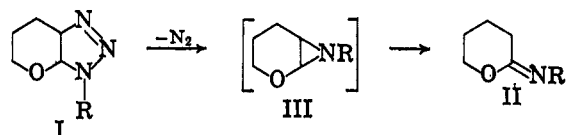
After 2 weeks at 40°, dihydropyran and p-bromophenyl azide gave adduct IV in 24% yield. The orientation of the addition accords with related azide additions to enol ethers[3] and enamines;[8] it is also in agreement with mechanistic information concerning this cycloaddition process.[9] Consistent with IV, the nmr spectrum showed a doublet at τ 4.57 (1 H, J = 6.3 cps), a multiplet at 5.90 (1 H), and a multiplet at 6.57 (2 H), as well as four aromatic and four "normal" aliphatic hydrogens. As reported for similar triazolines,[1-5] thermal decomposition of IV in toluene solution produced the imino lactone V, characterized by hydrolysis to p-bromoaniline and δ-valerolactone.

In contrast to thermolysis, the photodecomposition of triazolines has been shown to give aziridines in high yield.[10] Accordingly, the photolysis of IV was investigated. Irradiation of IV (27°, benzene, >300 mμ) resulted in a quantitative evolution of nitrogen and a crystalline solid in 67% yield. The photoproduct analyzed for C₁₁H₁₂BrNO and its infrared spectrum showed no absorption in the C=N region, 1690–1640 cm⁻¹.[11] The nmr spectrum revealed a doublet at τ 5.87 (1 H, J = 5.0 cps), a multiplet centered at 6.30 (2 H), and four aromatic and five aliphatic (7.6–8.7) hydrogens. Structure VI was therefore assigned to the photoproduct. Although the compound appears to be indefinitely stable in a dry atmosphere, it rapidly deteriorates on exposure to moist air. Hydrolysis of VI at room temperature produced the hemiacetal (VII). Similar observations have been reported by others.[5]
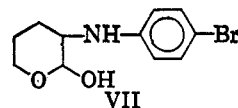
Aziridine VI was quantitatively recovered after being heated in toluene, under the conditions employed to bring about the thermal decomposition of triazoline IV. It is therefore apparent that the conversion of triazoline IV to imino lactone V does not occur *via* an aziridine intermediate. Furthermore, the result suggests that aziridines in general are not involved in the thermal reactions of azides with dihydropyran. The

(8) M. E. Munk and Y. K. Kim, *J. Am. Chem. Soc.*, **86**, 2213 (1964).

(9) P. Scheiner, J. H. Schomaker, S. Deming, W. J. Libbey, and G. P. Nowack, *ibid.*, **87**, 306 (1965).

(10) P. Scheiner, *J. Org. Chem.*, **30**, 7 (1965).

(11) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co. Ltd., London, 1958, p 268.

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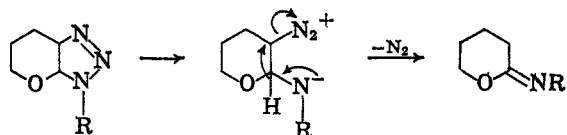
The strikingly different reaction paths observed in the thermal and photodecompositions of IV are noteworthy. As previously pointed out,[10] the photolysis of triazolines is an excellent preparative method, well suited to the preparation of sensitively substituted aziridines.

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 (MgSO₄) 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.[2,3] 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 (MgSO₄) 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.

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

(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).

(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.