Anal. Calcd for $C_{24}H_{19}N_3O_6$: C, 64.70; H, 4.29; N, 9.43. Found: C, 64.90; H, 4.66; N, 9.26.

Isomerization of 3 to 7.—A mixture of 190 mg (0.49 mmol) of **2** and 96 mg (0.50 mmol) of **3** in 10 ml of dry toluene was refluxed for 4 hr. The solvent was evaporated and the residue was extracted twice with 15-ml portions of hot petroleum ether (bp 65–75°). Evaporation of the pooled extracts gave 89 mg (92%) of **7**. The petroleum ether insoluble residue was shown to be **2**. The isomerization of **3** also occurred in high yield using 20 mg of **2** and 96 mg of **3**. Essentially the same results were obtained when triphenylphosphonium-*p*-nitro- and triphenylphosphonium-*p*-methoxyphenacylides[5] were substituted for **2**.

Registry No.—**1** (charged form), 24904-06-1; **1** (uncharged form), 20691-73-0; **2**, 859-65-4; **3**, 19614-29-0; **4** (charged form), 33406-31-4; **4** (uncharged form), 33406-30-3; **5**, 33406-32-5; **6**, 33406-33-6.

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Rearrangements, Pyrolysis, and Photolysis of Trimethylcyclopropenyl Azide[1]

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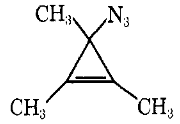
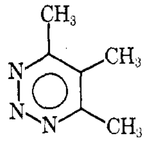
Allylic rearrangements of azides exhibit relatively few of the characteristics associated with ion-pair mechanisms. Alkyl substitution and changes in solvent polarity have minor effects on the reaction rates.[2] Concerted [3,3] sigmatropic shift would appear to be a more appropriate description of the reaction. We wish to report here the allylic rearrangement of trimethylcyclopropenyl azide (I), a system which might be expected to favor the ion-pair mechanism.

The azide I was readily prepared from the known trimethylcyclopropenyl fluoroborate and sodium azide. The nmr spectrum of I in methylene chloride showed only one transition at 1.80 ppm (TMS) at room temperature. At lower temperature the line broadened, and at −79° two sharp transitions were observed at 1.36 and 2.09 ppm with relative intensities of 1:2, respectively. The activation parameters of the apparent allylic rearrangement were extracted from a complete nmr line shape analysis[3] from spectra recorded between −61 and −9°. A least-squares analysis of the data gave activation parameters of $\Delta H^{\ddagger} = 7.5 \pm 0.6$ kcal/mol and $\Delta S^{\ddagger} = -19 \pm 4$ eu. These values should be compared with $\Delta H^{\ddagger} = 20$ kcal/mol and $\Delta S^{\ddagger} = -10$ eu obtained for α,α-dimethylallyl azide.[2] The significantly lower enthalpy of activation in the cyclopropenyl system indicated at least partial ionic character of the reaction path.



I



II

The solvent dependence of the reaction rate lends support for this hypothesis. Table I shows the activation energies estimated from the coalescence point of the methyl resonances in I in various solvents. Since no line shape analyses were made in those cases, the numbers were obtained by assuming identical preexponential factors in all solvents. This factor was determined from the data for methylene chloride. With the exception of chloroform, which shows an unusually fast rate, the general trend is as expected for an ionic pathway.

Table I

Solvent	Coalescence temp, °C	E_a
$CHCl_3$	−56	7.2
CH_3OH	−48	7.4
CH_2Cl_2	−33	7.9
CH_3COCH_3	−20	8.4
CCl_4	+35	10.2

Competing with the allylic shift, although with much slower rate, is the rearrangement of I to 4,5,6-trimethyl-*v*-triazine (II), a transformation which had been observed previously for triphenylcyclopropenyl azide.[4] Photolysis of either the azide I or the triazine II gave 2-butyne and acetonitrile in almost quantitative yield. The same products were formed on pyrolysis of I (300°) and II (*ca.* 500°). We were unable to observe any species intermediate between either I or II and the fragmentation products even at photolysis at low temperature (−50°). Trimethylcyclopropenylnitrene and trimethylazatetrahedrane are possible intermediates in these reactions.

Experimental Section

Trimethyl-3-azidocyclopropene (I).—A 1.41-g (8.4 mmol) sample of trimethylcyclopropenyl fluoroborate[5] and 0.59 g (9.2 mmol) of sodium azide were dissolved in 100 ml of water. The aqueous solution was stirred in an ice bath for 3 min and was then extracted with three 50-ml portions of methylene chloride. Vacuum fractionation (30–40° at 0.7–0.2 Torr) gave 1.10 g of material. On the basis of an nmr integral, this material was 67% I (0.74 g, 6.0 mmol, 71% yield) and 33% methylene chloride. This purity was sufficient for most of our studies.

Further purification by vacuum fractionation (−78°, 8 μ) removed most of the methylene chloride, allowing I to be prepared with greater than 99% purity (by nmr): nmr ($CDCl_3$) δ 1.82 (s), (CH_2Cl_2) δ 1.80 (s) [−79°, δ 2.09 (s, 2), 1.36 (s, 1)]; ir (neat) 2980, 2960, 2930, and 2860 (m, $-CH_3$), 2490 (w), 2090 (s, $-N_3$), 1859 and 1849 (w), 1438 (s), 1379 (m), 1279 (m), 1248 (s), 1083 (s), and 862 cm^{-1} (m); uv max (95% EtOH) 308 mμ (ϵ 71), end absorption.

4,5,6-Trimethyl-*v*-triazine (II).—A 0.50-g (3.0 mmol) sample of trimethylcyclopropenyl fluoroborate and 0.19 g (3.0 mmol) of sodium azide were treated as above. The methylene chloride extracts however, were dried over sodium sulfate and allowed to stand in the dark at room temperature for 2 days. The solvent was stripped off, and the residue was crystallized from 50:50

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[1] Supported by NSF Grant GP-18719X.

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carbon tetrachloride–methylene chloride, giving 0.11 g (0.90 mmol, 30% yield) of II: mp 146–147°; nmr ($CDCl_3$) δ 2.66 (s, 2), 2.32 (s, 1); ir (KBr) 3000 (w), 1548 (s), 1433 (w), 1399 (m), 1386 (s), 1366 (s), 1241 (w), 1137 (w), 1102 (w), 1033 (m), 991 (s), 898 (w), 769 (w), and 668 cm^{-1} (s); uv max (95% EtOH) 278 mμ (ε 610), 217 (4300), end absorption; mass spectrum (70 eV) 123.0794 (calcd for $C_6H_9N_3^+$: 123.0796). *Anal.* Calcd for $C_6H_9N_3$: C, 58.52; H, 7.37; N, 34.12. Found: C, 58.29; H, 7.49; N, 33.96.

Photolyses of I and II were carried out in benzene and methylene chloride solutions in nmr tubes in the probe of a Varian HR-60 spectrometer. At ambient temperatures and with the probe cooled to −56° (cooled only for methylene chloride solution), irradiation (1000-W mercury lamp) of I gave material with an nmr spectrum identical with that of a mixture of 2-butyne and acetonitrile. The irradiations of I and II by medium pressure mercury arc also gave 2-butyne and acetonitrile, identified by identical nmr spectra and vpc retention times.

Pyrolyses of I and II were carried out in a flow system. At 300° I gave a mixture of II, 2-butyne, and acetonitrile. At the same temperature, II did not react. At higher temperaturs (*ca.* 500°), II also gave 2-butyne and acetonitrile. Products were identified by nmr and vpc as above.

Rate measurements on I were made in a Varian A-60A spectrometer equipped with a V-6040 variable temperature controller. Temperatures were determined by measuring the separation between the methyl and hydroxyl resonances in a separate methanol sample.[6] The methanol sample was used to determine the temperature before each sample spectrum. At least 15 min were allowed for thermal equilibration each time a tube was placed in the probe and each time the probe temperature was changed. Half-widths were measured and compared with computer-calculated values.[3] A linear least squares treatment gave the indicated activation parameters.

Registry No.—I, 33209-84-6; II, 33209-85-7.

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An Investigation of the Rate of Hydrolysis of 1-Phenylethyl Phenylphosphinate as a Function of pH[1]

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During our investigation of the solvolysis of a variety of phosphinate esters, we examined the mode of reaction of 1-phenylethyl phenylphosphinate (**1**) as a function of pH. The rate of reaction of **1** was found to be very sensitive to the addition of hydroxide ion. In order to determine the molecularity of the reaction, the rate of reaction of **1** as a function of pH was studied (Table I). The rates were measured in the presence of 0.10 *M* $NaClO_4$ to minimize salt effects.

The pH–rate profile for the solvolysis of **1** is shown in Figure 1. The interesting aspects of the curve are that between pH 4 and 6 there is a plateau and above pH 9 a linear plot with a slope of 1 is observed. The entire curve is reproduced very well by eq 1 where $k_1 = 1.58 \times 10^{-4}$ sec^{-1} and $k_2 = 2.63 \times 10^2\ M^{-1}\ sec^{-1}$.

$$\text{rate} = k_1[1] + k_2[1][OH] \qquad (1)$$

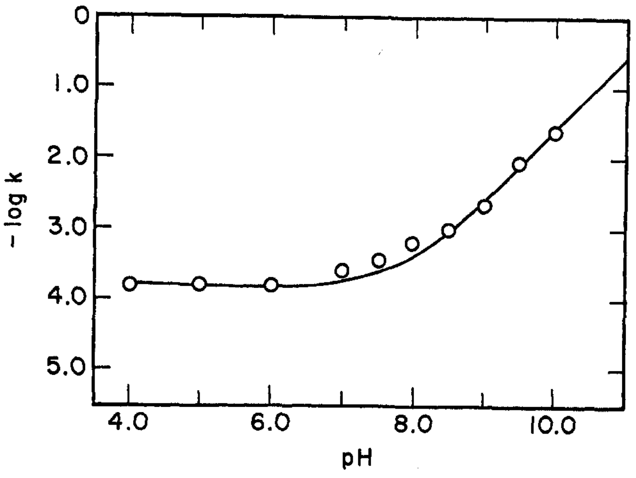

Figure 1.—pH–rate profile for the hydrolysis of 1-phenylethyl phenylphosphinate.

TABLE I

THE RATE OF REACTION OF 1 IN 30% ETHANOL–WATER (0.1 *M* $NaClO_4$) AT 45°

pH	Rate	Log *k*	Rel rate
4.0	1.60×10^{-4}	−3.796	1
5.0	1.55×10^{-4}	−3.809	1
6.0	1.58×10^{-4}	−3.801	1
7.0	2.46×10^{-4}	−3.609	1.6
7.5	3.48×10^{-4}	−3.458	2.2
8.0	6.42×10^{-4}	−3.192	4.1
8.5	8.05×10^{-4}	−3.094	5.1
9.0	2.06×10^{-3}	−2.686	13
9.5	9.06×10^{-3}	−2.043	57
10.0	2.44×10^{-2}	−1.613	154

The comparison of the rates of hydrolysis of phosphonates,[2] $(RO)_2P(O)H$, and phosphinates,[3] $(RO)C_2H_5P(O)H$, which contain a P–H bond, has led to the conclusion that the enhanced rates of highly branched esters such as R = *tert*-butyl were attributable to the incursion of an S_N1 mechanism. Since the 1-phenylethyl ester should be of the same order of reactivity and form a carbonium ion of the same stability as the *tert*-butyl group, the probable mechanism occurring in the plateau region of the curve is formation of a carbonium ion by an S_N1 mechanism. In order to substantiate the S_N1 nature of the reaction, the rates of solvolysis of 1-(*m*-chlorophenyl)ethyl phenylphosphinate ($k_1 = 9.45 \times 10^{-6}$ sec^{-1}), 1-(*p*-methylphenyl)ethyl phenylphosphinate ($k_1 = 8.28 \times 10^{-3}$ sec^{-1}), and the parent (**1**) ($k_1 = 2.95 \times 10^{-4}$ sec^{-1}) were measured in the acidic region in 30% ethanol–water (v/v) at 45.0°. The Hammett plot of the rate constants *vs.* Brown's σ^+ values gives a good correlation with a ρ of −4.25. This indicates that substantial positive charge is developed in the transition state and that the reaction in the acidic region does indeed follow a carbonium ion mechanism.

Recent investigations of alkaline hydrolysis have shown that phosphates,[4,5] phosphonates,[4] and phosphinates[6] hydrolyze by exclusive attack of the hydrox-

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[1] Supported in part by a grant from the National Science Foundation, GP-6133X.

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