Kinetic Methods.—All runs were carried out in stoppered volumetric flasks. Stock solutions of reactants were maintained at 45.0° and used to prepare reaction mixtures for kinetic runs. For runs with *t*-butyl chloride, 5.00-ml aliquots were removed from 50 ml of reaction mixture. For runs with *t*-butyl chloride-d_9, 2.00-ml aliquots were removed from 25 ml of the reaction mixture. The extent of dehydrochlorination was determined by addition of the aliquots to 20 ml of acetone, previously rendered neutral to resorcinol blue (Lacmoid) indicator, followed by titration against a standard solution of sodium methylate in methanol. In the three illustrative runs in Table III, the first-order rate coefficients are the integrated first-order rate coefficients with respect to the *t*-butyl chloride or *t*-butyl chloride-d_9. The errors quoted along with the mean values are standard errors of the mean.

Registry No.—*t*-Butyl chloride, 507-20-0; *t*-butyl chloride-d_9, 918-20-7; NEt_4Cl, 56-34-8; NEt_4ClO_4, 2567-83-1; acetonitrile, 75-05-8.

Acknowledgment.—We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Acid-Catalyzed Reactions of α- and β-Styryl Azides[1]

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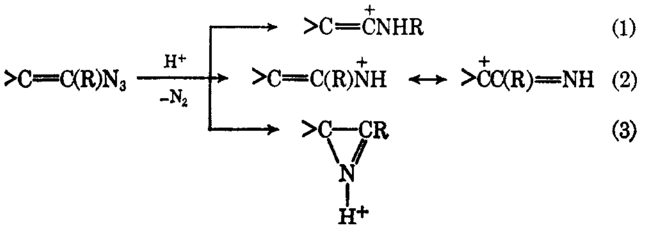
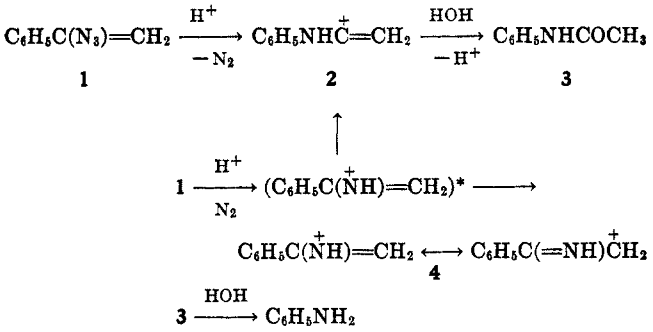
Received July 22, 1968

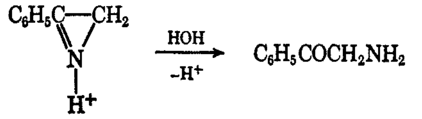
Rearrangement during acid degradation of certain alkyl azides is concerted with the evolution of nitrogen.[2] Both rearrangement[3] by path 1 and azirine ring closure by path 3 may be concerted with nitrogen evolution from a vinyl azide and an unrearranged hybrid cation may be available by path 2. If formed, it should afford certain products derived from an unrearranged carbonium ion and others from a nitrenium ion[4a] as well as rearrange to a new carbonium ion or cyclize to an azirinium ion.



Acid degradation of two vinyl azides, α- (1) and β-styryl azide (5), has been investigated. In ethanolic sulfuric acid, 1 is nearly quantitatively (94%) transformed into a mixture of acetanilide, 3, and aniline, presumably formed by hydrolysis of 3 during work-up (Scheme I).[4b] This appears to be a reaction according to path 1 and/or path 2 if in the latter event a "hot" nitrenium ion is produced and rearranged before it loses energy and becomes a resonance hybrid cation. An unrearranged hybrid cation, 4, was not detected insofar as products of rearrangement from carbon to carbon were not formed[5] and other carbonium ion reactions, *e.g.*, solvation, were not detected. Hydrolysis of the 2-phenylazirinium cation to phenacylamine,[6] without the formation of acetanilide, eliminated path 3 in the acid degradation of 1.

SCHEME I





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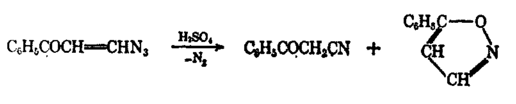
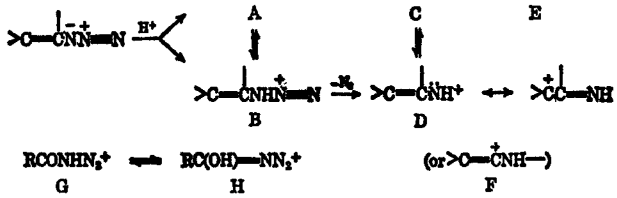
[1] Financial assistance from NASA Grant No. NGR 14-012-004.

[2] P. A. S. Smith in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, pp 468–471.

[3] A. N. Nesmeyanov and M. I. Rybinskaya, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 816 (1962); p 761 reports



[4] (a) From the assignment of a higher energy to RNH^+ (from $RNHN_2^+$) relative to RCH_2^+ (from $RCH_2N_2^+$) by R. F. Tietz and W. E. McEwen, *J. Amer. Chem. Soc.*, **77**, 4007 (1955), the hybrid cation, **4** would be expected to react as a carbonium ion excited state. (b) A referee suggested that product formation may require the intermediacy of protonation at carbon rather than at nitrogen. From the recognition that organic azides in general are protonated at nitrogen (P. A. S. Smith, "Open-Chain Nitrogen Compounds," Vol. 2, W. A. Benjamin, Inc., New York, N.Y., 1966, pp 225–226) we assumed that protonation at carbon in a vinyl azide would be relatively unimportant to account for the observed products. In failing to recognize the two pairs of tautomers, A $\rightleftharpoons$ B and C $\rightleftharpoons$ D (or the rearranged cations, E $\rightleftharpoons$ F), the referee apparently overlooked this intimate relationship of intermediates available from the two conceivable initial steps. This reaction of a vinyl azide is reminiscent of the acid-catalyzed Curtius and the Schmidt reactions where tautomers G and H must each be recognized as a possible intermediate (P. A. S. Smith, "Open-Chain Nitrogen Compounds," Vol. 2, W. A. Benjamin, Inc., New York, N. Y., 1966, p 227; P. A. S. Smith in P. de Mayo, "Molecular Rearrangements," Vol. 1, John Wiley & Sons, Inc., New York, N. Y., 1963, p 529; J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, pp 319–321).



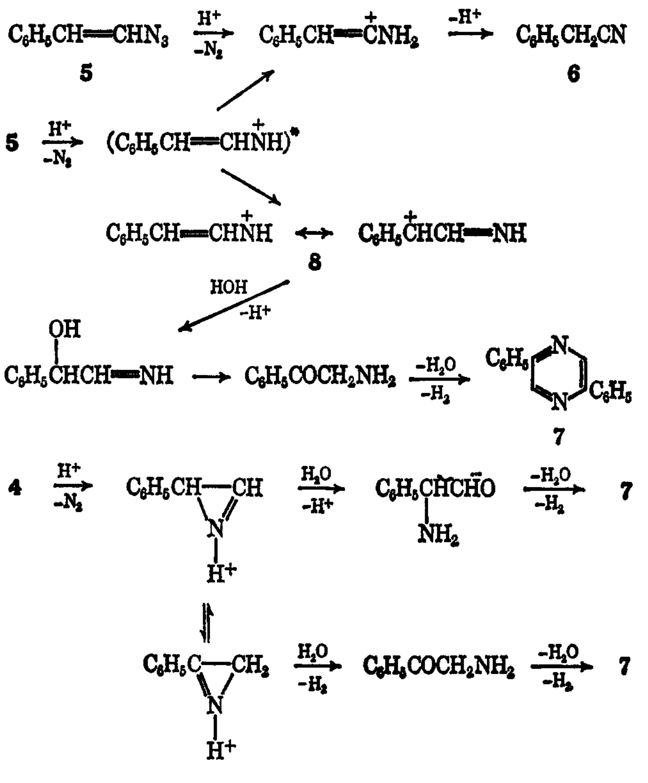
[5] This evidence also eliminates a migration from carbon to carbon concerted with nitrogen elimination.

[6] G. Smolinsky [*J. Org. Chem.*, **27**, 3557 (1962)] reports nmr (solvent unspecified) δ 5.32 (s) and 4.32 (s).

These results required a reevaluation of our earlier work on an acid-catalyzed reaction between acetophenone and an alkyl azide.[7] A resonance cation, for which a vinyl nitrenium and a carbonium ion were contributors and in equilibrium with an azirinium cation, was a proposed intermediate for the formation of benzaldehyde, formaldehyde and a primary amine. We have been unable to repeat the earlier work and it is to be considered inaccurate.

In ethanolic sulfuric acid, β-styryl azide, **5**, is transformed into phenylacetonile, **6**, 7% yield, a trace amount of 2,5-diphenylpyrazine, **7**, and intractable tar (Scheme II). Nitrile **6** appears to be a product from either a rearrangement concerted with nitrogen evolution by path 1 or from a "hot" nitrenium ion, path 2, whereas pyrazine **7** apparently results from the self-condensation of either phenacylamine (the product of an Amadori rearrangement of mandelaldimine) or α-amino-α-phenylacetaldehyde. These in turn may be hydrolysis products of isomeric phenylazirines, path 3. Phenacylamine also may be formed on combination of carbonium ion **8**, path 2, with water.

Scheme II



The sample of β-styryl azide was known to contain about 20% α-chlorostyrene which is transformed by ethanolic sulfuric acid into acetophenone, also isolated.

Experimental Section[8]

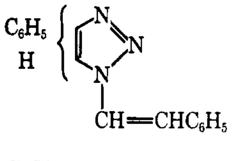
α-Styryl azide was prepared according to Smolinsky:[6] nmr (CCl_4) δ 7.3 (m, phenyl), 5.34 (d, J = 2.3 Hz) and 4.87 (d, J = 2.3 Hz).

1-Phenyl-2-azido-1-ethanol.—A solution of 100 g (0.5 mol) of phenacyl bromide in 375 ml of ethanol and 60 ml of glacial acetic acid was treated with 65 g (1.0 mol) of sodium azide.[9] Without further purification the product of this reaction was treated with 25 g (0.66 mol) of sodium borohydride.[10] Distillation gave a 52.4-g (63%) sample of 1-phenyl-2-azidoethanol: bp 111–114° (0.5 mm); $n^{25}D$ 1.5519; ir (film) 3400 (OH) and 2100 cm^{-1} (N_3); nmr (CCl_4) δ 7.17 (phenyl), 4.57 (q, CHOH), 3.93 (OH, D in DMSO-d_6) and 3.15 (m, CH_2N_3).

Anal. Calcd for $C_8H_9N_3O$: C, 58.88; H, 5.56; N, 25.75. Found: C, 58.71; H, 5.89; N, 25.77.

1-Chloro-1-phenyl-2-azidoethane.—A solution of 17.4 g (0.15 mol) of thionyl chloride in 100 ml of anhydrous ether was added to a solution of 16.5 g (0.1 mol) of 1-phenyl-2-azidoethanol in 100 ml of dry ether and 20 ml of pyridine at 0°. Stirring was continued at 0° for 8 hr and the solution was allowed to stand at room temperature overnight. The organic layer was washed with dilute hydrochloric acid, water and thoroughly with sodium bicarbonate solution to remove all acidic material. It was then dried over magnesium sulfate and evaporated under vacuum. Distillation of the residue gave a 10.1-g (55%) fraction of 1-chloro-1-phenyl-2-azidoethane: bp 78–79° (0.4 mm); $n^{25}D$ 1.5530; ir (film) 2100 cm^{-1} (N_3); nmr (CCl_4) δ 7.18 (m, 5, phenyl), 4.78 (t, 1, CH) and 3.42 (octet, 2, J = 6.8 Hz).

β-Azidostyrene.—A slurry of 8.0 g (70 mmol) of potassium *t*-butoxide in 200 ml of anhydrous ether was cooled to −25° and a solution of 9.0 g (50 mmol) of 1-chloro-1-phenyl-2-azidoethane was added dropwise. After 2 hr at −25° the solution was allowed to warm to 0° and stored in a refrigerator overnight. The ether solution was washed with water, dried over magnesium sulfate, and concentrated under vacuum to give an oil together with a solid. The solid was separated by filtration and recrystallized from benzene to give 0.2 g (3%) of a yellow solid, mp 186–187.5°, tentatively identified as 1-(β-styryl)-4- (or 5-) phenyl-1,2,3-triazole, recognized as a formal adduct between **5** and $C_6H_5C{\equiv}CH$.



Anal. Calcd for $C_{16}H_{13}N_3$: C, 77.71; H, 5.30; N, 16.99. Found: C, 77.40; H, 5.53; N, 16.92.

The remaining oil was distilled with the pot temperature below 70°, and 1.2 g (17%) of α-chlorostyrene was collected; bp 28–32° (0.6 mm); $n^{25}D$ 1.5606;[11] nmr (CCl_4) δ 7.52, 7.15 (m, 5, phenyl) and 5.59, 5.39 (2d, 2, J = 1.6 Hz, CH_2N_3). The residue was dissolved in *n*-heptane and chromatographed over alumina to give 3.2 g (44%) of β-azidostyrene: ir (film or $CHCl_3$) 2100 (N_3) and 1645 cm^{-1} (C=C); nmr (CCl_4) δ 7.14 (m, 5, phenyl) and 6.32, 6.11 (2d, 2, J = 14 Hz, probably *trans*-vinyl protons). The azide could not be distilled and decomposed below 70°.[12] It was not submitted to elemental analysis.

α-Azidostyrene with Sulfuric Acid.—Pure α-azidostyrene, 2.9 g (0.02 mol), was added dropwise to a solution of 6 ml of sulfuric acid in 16 ml of absolute ethanol. Care was taken to keep the exothermic reaction under control. When the mixture began to cool a heating mantle was attached and the reaction was heated under reflux for 1 hr. After standing overnight the solution was poured into 75 ml of ice water. Extraction with ether followed by drying over potassium carbonate and evaporation under vacuum gave 0.8 g (29.6%) of a dark solid, mp 110–112° after recrystallization from benzene. This solid was shown by mixture melting point and infrared spectrum to be acetanilide.

The water layer was made basic with excess sodium carbonate and extracted with ether. The combined organic layers were dried over potassium carbonate and evaporated to give 1.2 g (64.6%) of aniline as shown by vpc retention time and infrared spectrum identical with similar data for an authentic sample.

Reaction of β-Azidostyrene with Sulfuric Acid.—A 1.4-g (0.01 mol) sample of β-azidostyrene was added slowly to a solution of 6 ml of sulfuric acid in 16 ml of ethanol. After addition was complete the mixture was heated at 60° for 1 hr and allowed to stand overnight at room temperature. The mixture was poured into 100 ml of ice water and extracted with ether. The combined organic layers were dried over potassium carbonate and evaporated to give 0.6 g of a dark oil. This oil was shown by gas

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[7] J. H. Boyer and L. R. Morgan, *J. Amer. Chem. Soc.*, **80**, 2020(1958); **81**, 3369 (1959).

[8] Microanalyses by Microtech Laboratories, Chicago, Ill.

[9] J. H. Boyer and D. Straw, *J. Amer. Chem. Soc.*, **74**, 4506 (1952).

[10] J. H. Boyer and S. E. Ellzey, Jr., *J. Org. Chem.*, **23**, 172 (1958).

[11] K. V. Auwers [*Ber.*, **45**, 2799 (1912)] reports $n^{16.6}D$ 1.5623 and $n^{24.6}D$ 1.5590, bp 83.5–84° (23 mm).

[12] J. H. Boyer, W. E. Krueger, and G. J. Mikol, *J. Amer. Chem. Soc.*, **89**, 5504 (1967).

chromatographic analysis and nmr spectrum to be composed of α-chlorostyrene (*ca.* 16%), acetophenone (43%), and phenylacetonitrile (17%), corresponding to maximum yields of *ca.* 7, 19, and 7%, respectively. Each component was identified by its identical comparison with vpc retention time and nmr spectra for authentic samples.

The water layer was made basic with a large excess of sodium carbonate and extracted with ether to give 0.5 g of a dark oil after combining, drying over potassium carbonate, and evaporating the organic layers. Treatment of this oil with anhyrous hydrogen chloride gave a few milligrams of a yellow solid which was shown to be 2,5-diphenylpyrazine, mp 192–194°, by mixture melting point and infrared spectrum.

Reaction of α-Chlorostyrene with Sulfuric Acid.—A solution of 1.7 g (0.012 mol) of α-chlorostyrene in 6 ml of sulfuric acid and 16 ml of absolute ethanol was heated under reflux for 4 hr and allowed to stand overnight at room temperature before being poured into 200 ml of ice water. The mixture was extracted with ether and the combined extracts were dried over potassium carbonate and evaporated to give 1.1 g (73%) of acetophenone as a dark oil. This assignment was verified by infrared spectrum and vpc retention time.

Registry No.—1-Phenyl-2-azido-1-ethanol, 18756-01-9; 1-chloro-1-phenyl-2-azidoethane, 18756-02-0; **5**, 18756-03-1; 1-(β-styryl)-4-phenyl-1,2,3-triazole, 18756-04-2; α-chlorostyrene, 1018-34-8.

Chemistry of Coelenterates. XII.[1a] Hydroxyancepsenolide, a Dilactone from the Octocoral, *Pterogorgia anceps*

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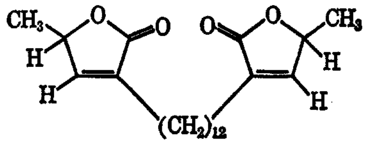
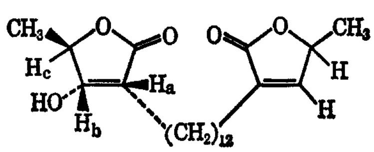
Received August 26, 1968

In an earlier paper,[2] we described the structure elucidation of ancepsenolide, I, a bisbutenolide isolated from the gorgonian, *Pterogorgia anceps* (Pallas).[3] Another dilactone has been isolated from this same organism and in this paper we wish to present evidence which confirms its structure as that shown in II. The new lactone, hydroxyancepsenolide, was isolated by hexane extraction of the dried animal and purified by column chromatography to give a white solid, mp 122.5–123.7°. Mass spectral analysis (*m/e* 380) and combustion data established the molecular formula as $C_{22}H_{36}O_5$. The significant features of the infrared spectrum were a very weak absorption at 3400 cm^{-1} (KBr, hydroxyl) and a strong, broad carbonyl absorption having a maximum at 1750 cm^{-1}. The strong carbonyl absorption at 1750 cm^{-1}, an absorption maximum in the ultraviolet spectrum at 209 mμ with approximately one-half the extinction coefficient (15,800) found for ancepsenolide (28,000), and one-proton multiplets in the nmr spectrum at δ 5.0 and 7.0 ppm identical with ones occurring in the spectrum of ancepsenolide[2] confirmed the presence in hydroxyancepsenolide of one substituted butenolide ring identical with those present in ancepsenolide. The presence of a long methylene chain in hydroxyancepsenolide is indicated by the large absorption peak at δ 1.27 ppm and a long series of peaks in the mass spectrum differing by 14 mass units.

The presence of a hydroxyl group in II was confirmed by the formation of a monoacetate and the secondary nature of this alcohol was inferred from a shift in the nmr spectrum of a one-proton signal (double doublet) centered at δ 4.24 in hydroxyancepsenolide to 5.18 ppm in the corresponding monoacetate.



I



II

Dehydration of II with phosphorus oxychloride in pyridine gave ancepsenolide in good yield. This fact, along with the evidence for the secondary character of the alcohol group, requires that the hydroxyl group of II must be attached to the β carbon of the second five-membered lactone ring. The broad carbonyl absorption in II (1730–1780 cm at one-half peak intensity) is consistent with the presence of both a saturated and an α,β-unsaturated γ-lactone. Hydrogenation of II resulted in the uptake of slightly more than 1 mol of hydrogen and gave a dihydro derivative whose infrared spectrum showed a strong absorption with a maximum at 1765 cm^{-1} (saturated γ-lactone). The nmr spectrum of dihydrohydroxyancepsenolide lacked any vinyl proton absorption and exhibited a complex absorption envelope extending from δ 4.1 to 4.9 ppm which is attributed to a combination of the absorptions due to the three protons attached to carbons bearing oxygen atoms.

The relative stereochemical assignments indicated in structure II for the substituents in the hydroxylated lactone ring are based on coupling-constant data. Proton c of the saturated γ-lactone ring in II appears as a broadened quartet in which the coupling to the methyl group is large, $J = 6$ cps, and the second splitting attributed to coupling with proton b is small, $J \cong 0.5\text{–}1$ cps. The signal assigned to proton b appears as a double doublet in which the small coupling constant, $J \sim 0.5\text{–}1$ cps, is consistent with a J_{bc} assignment and the larger J value, 6 cps, must be due to coupling with proton a of the lactone ring. A *trans* orientation of protons b and c imposes a dihedral angle of 105–115° between these protons, and this is consistent with the smaller coupling constant, $J_{bc} \sim 1$ cps.[4] A dihedral angle of close to 0° would be expected between protons a and b if they

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[1] (a) Part XI: A. J. Weinheimer, P. H. Washecheck, D. v. d. Helm, and M. B. Hossain, *Chem. Commun.*, in press. (b) To whom inquiries concerning this paper should be addressed.

[2] F. J. Schmitz, K. W. Kraus, L. S. Ciereszko, D. H. Sifford, and A. J. Weinheimer, *Tetrahedron Lett.*, 97 (1966).

[3] F. M. Bayer, "The Shallow-Water Octocorallia of the West Indian Region," Martinus Mijhoff, The Hague, Netherlands, 1961, pp 272–277.

[4] For a leading reference, see R. H. Bible, "Interpretation of NMR Spectra," Plenum Press, New York, N. Y., 1965, pp 35–37.