

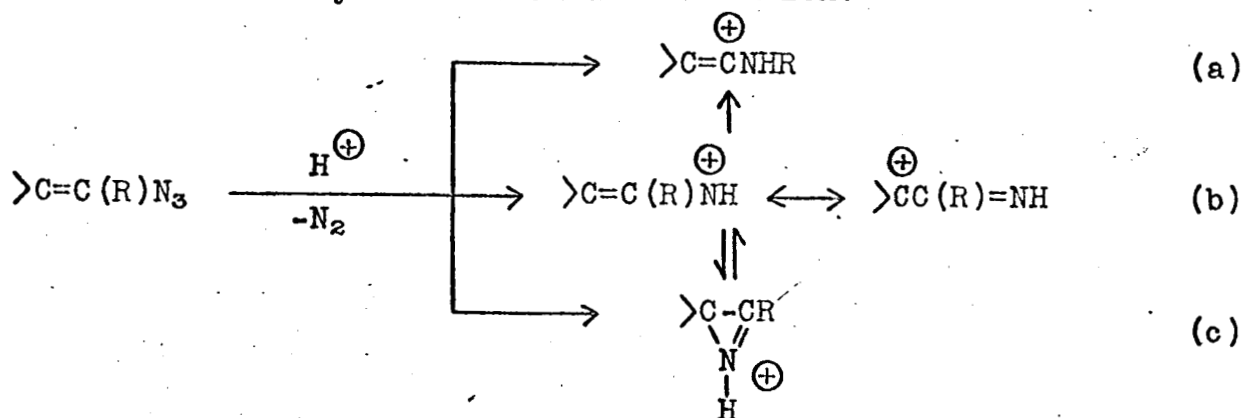
Acid Catalyzed Reactions of α - and β -Styryl Azides¹

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N 68-31349

Rearrangement during acid degradation of certain alkyl azides is concerted with the evolution of nitrogen.² Both rearrangement³ by path (a) and azirine ring-closure by path (c) may be concerted with nitrogen evolution from a vinyl azide and an unrearranged hybrid cation may be available by path (b). If formed, it should afford certain products derived from an unrearranged carbonium ion and others from a nitrenium ion⁴ 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 -, 2, styryl azide, 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 workup. This appears to be a reaction according to path (a) and/or path (b) if in the latter event a "hot" nitrenium ion is produced and rearranges before it loses energy and becomes a resonance hybrid cation.

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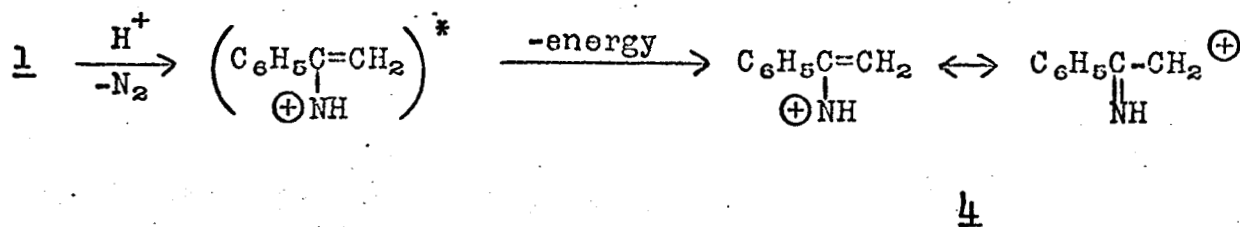
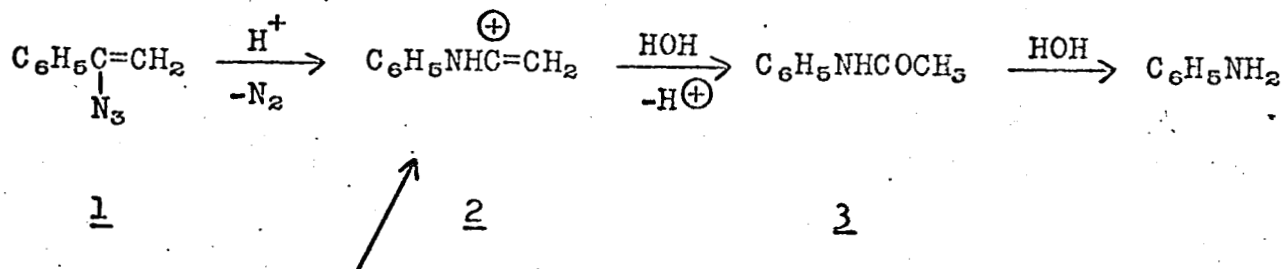
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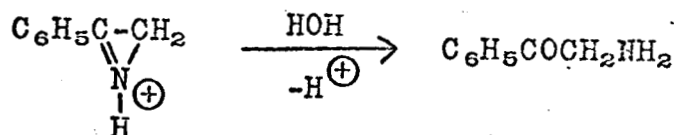
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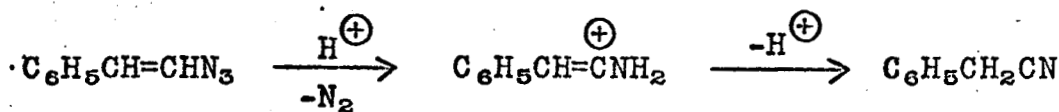
An unrearranged hybrid cation, 4, was not detected insofar as products of rearrangement from carbon to carbon were not formed⁵ and other carbonium ion reactions, e.g., solvation, were not detected. Hydrolysis of the 2-phenylazirinium cation to phenacylamine,⁶ without the formation of acetanilide, eliminates path (c) in the acid degradation of 1.



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 a 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.

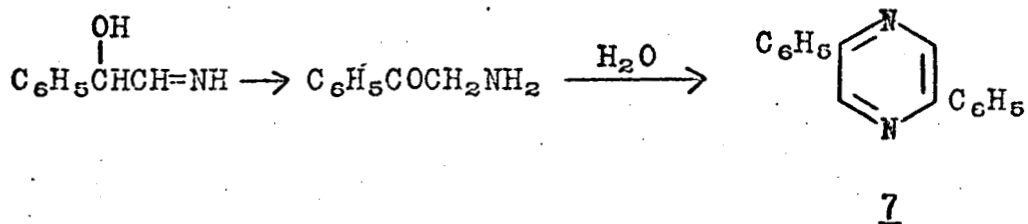
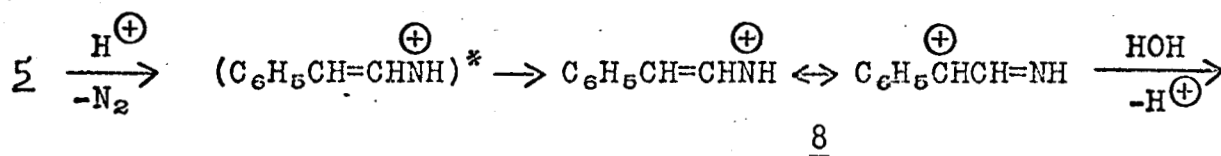
In ethanolic sulfuric acid, β -styryl azide, 5, is transformed into phenylacetone, 6, 7% yield, a trace amount of 2,5-diphenylpyrazine, 7, and intractable tar. The nitrile, 6, appears to be a

product from either a rearrangement concerted with nitrogen evolution by path (a) or from a "hot" nitrenium ion, path (b), whereas the pyrazine, 7, apparently results from the self-condensation of either phenacylamine or α -amino- α -phenylacetaldehyde. These in turn may be hydrolysis products of isomeric phenylazirines, path (c). Phenacylamine also may be formed on combination of the carbonium ion, 8, path (b), with water.

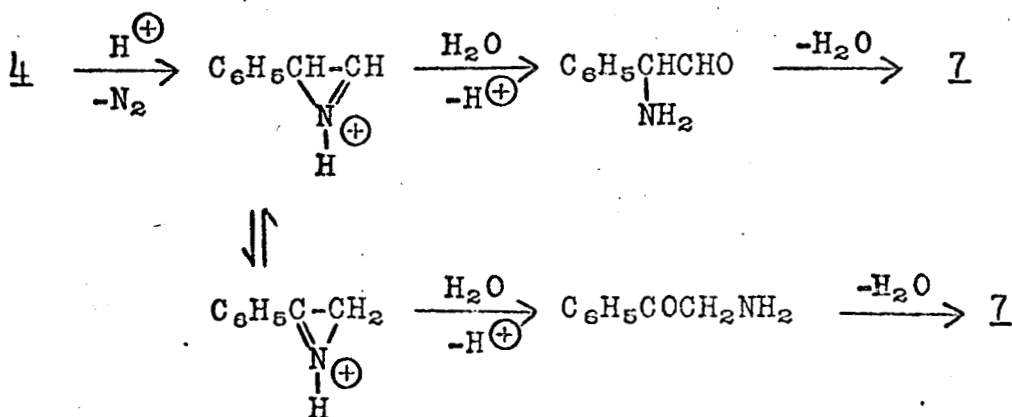


5

6



7



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

Experimental⁸

α -Styryl azide was prepared according to Smolinsky.⁶ In contrast to the earlier report⁶ of two single sharp peaks in the nmr spectrum (solvent not specified) at 4.32 and 5.32 ppm, $J = 0.0$ cps, for the nonequivalent terminal methylene protons, we have found a pair of doublets at 4.87 and 5.34 ppm, $J = 2.3$ cps, carbon tetrachloride solvent. Phenyl hydrogens showed as a multiplet at 7.3 ppm.⁶

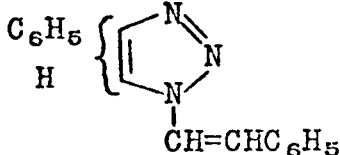
1-Phenyl-2-azido-1-ethanol. - A solution of 100 g (0.5 mole) of phenacylbromide in 375 ml of ethanol and 60 ml of glacial acetic acid was treated with 65 g (1.0 mole) of sodium azide.⁹ Without further purification the product of this reaction was treated with 25 g (0.66 mole) of sodium borohydride.¹⁰ Distillation gave a 52.4 g (63%) sample of 1-phenyl-2-azidoethanol, bp 111-114/0.5 mm. An analytical sample was prepared by redistillation, bp 112-114/0.5 mm, n_D^{25} 1.5519. The infrared spectrum (from a film) had bands at 3400 cm^{-1} (s) and 2100 cm^{-1} (vs). The nmr spectrum in carbon tetrachloride had signals at 7.17 ppm (phenyl), a quartet at 4.57 ppm (carbinol proton), at 3.93 ppm (hydroxyl proton, becomes a doublet in DMSO- D_6), and centered at 3.15 ppm (nonequivalent methylene protons).

Anal. Calc'd. 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 mole) of thionyl chloride in 100 ml of anhydrous ether was added to a solution of 16.5 g (0.1 mole) 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_D^{25} 1.5530 after redistillation. The infrared spectrum from a film showed an azide band at 2100 cm^{-1} . The nmr spectrum from a carbon tetrachloride solution exhibited the phenyl protons (5) as a multiplet centered at 7.18 ppm, the methyne proton (1) as a triplet at 4.78 ppm, and the nonequivalent methylene protons (2) as an octet centered at 3.42 ppm, $J = 6.8\text{ cps}$.

β -Azidostyrene. - A slurry of 8.0 g (70 mmole) of potassium t-butoxide in 200 ml of anhydrous ether was cooled to -25° and a solution of 9.0 g (50 mmole) 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 $186-187.5^\circ$, tentatively identified as

1-(β -styryl)-4(or 5)-phenyl-1,2,3-triazole, , and

recognized as a formal adduct between 5 and $\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$.

Anal. Calc'd. for $\text{C}_{16}\text{H}_{13}\text{N}_3$: 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 $28-32^\circ/0.6$

mm, n_D^{25} 1.5606.¹¹ The distillate gave a positive Beilstein test for halogen and the nmr spectrum (carbon tetrachloride) showed the phenyl protons (5) as a pair of multiplets centered at 7.52 ppm and 7.15 ppm and the nonequivalent terminal methylene protons (2) as a pair of doublets at 5.39 ppm and 5.59 ppm, $J = 1.6$ cps. The residue was dissolved in n-heptane and chromatographed over alumina to give 3.2 g (44%) of β -azidostyrene. The infrared spectrum from a film or in chloroform had a strong azide band at 2100 cm^{-1} with smaller absorptions at 2160, 2220, and 2280 cm^{-1} and a greatly enhanced C=C absorption at 1645 cm^{-1} . The nmr spectrum (carbon tetrachloride) exhibited the phenyl protons (5) as a multiplet centered at 7.14 ppm and the vinyl protons (2), probably trans, as a pair of doublets at 6.32 ppm and 6.11 ppm, $J = 14.0$ cps. The azide could not be distilled and decomposed below 70° .¹²

α -Azidostyrene with sulfuric acid. - Pure α -azidostyrene, 2.9 g (0.02 mole), 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 $110-112^\circ$ 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 date for an authentic sample.

Reaction of β -azidostyrene with sulfuric acid. - A 1.4 g (0.01 mole) 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 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 chromatographic analyses 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.

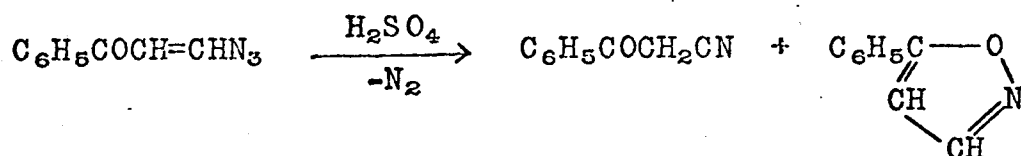
The water layer was made basic with a large excess of sodium carbonate and extracted with ether to give 0.5 g of a dark oil after combining, drying over potassium carbonate, and evaporating the organic layers. The infrared spectrum had bands at 3660, 3350, and 1700 cm^{-1} . Treatment of this oil with anhydrous hydrogen chloride gave a few milligrams of a yellow solid which was shown to be 2,5-diphenylpyrazine, mp 192.4, by mixture melting point and infrared spectrum.

Reaction of α -chlorostyrene with sulfuric acid. A solution of 1.7 g (0.012 mole) of α -chlorostyrene in 6 ml of sulfuric acid and 16 ml of absolute ethanol was heated under reflux for 4 hr and

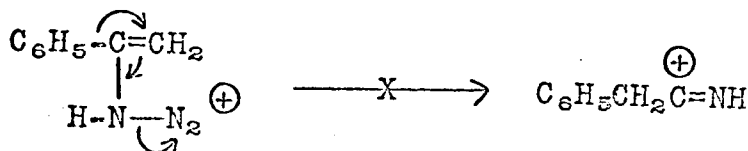
allowed to stand overnight at room temperature before being poured into 200 ml of ice water. The mixture was extracted with ether and the combined extracts were dried over potassium carbonate and evaporated to give 1.1 g (73%) of acetophenone as a dark oil. This assignment was verified by infrared spectrum and vpc retention time.

References

1. Financial assistance from NASA grant No. NGR 14-012-004.
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