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phenylbutane when (S)-methylpropylphenylphosphine was the ligand.²

Experiments with other readily prepared ligands having multiple chiral centers are in progress.

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3,4-Pyridyne and Its Dimer

Sir:

We report a study of gaseous 3,4-didehydropyridine¹ or 3,4-pyridyne (I), and its unimolecular decomposition and dimerization to 2,6- (or 2,7-) diazabiphenylene (II).

Solid pyridine-3-diazonium-4-carboxylate² was photolyzed neat. The reaction was monitored by time-of-flight (TF) mass spectroscopy and kinetic ultraviolet spectroscopy. Gaseous products were separated by low-temperature sublimation and analyzed by mass spectroscopy. Solids were separated by glc.

Pyridine-3-diazonium-4-carboxylate upon photolysis decomposes to CO₂, N₂, and I (by inference from the formation of II). We observe that I may undergo any of three related unimolecular reactions as well as dimerization to II. These are: (a) rearrangement to a stable product of mass 77 with a prominent fragment at 50 (77 is presumably β -ethynylacrylonitrile,³ or one of its stable isomers, one bond having broken in the pyridine ring); (b) decomposition to HCN (27) and HC \equiv CC \equiv CH (50) (two bonds broken); and (c) decomposition and rearrangement to C₂H₂ (26) and HC \equiv CCN (51) (two bonds broken).

Kinetics were followed by TF mass spectroscopy. Initial products and intermediates appeared at about 100–150 μ sec after initiation. The first mass spectral sweep showing products contains masses 28 and 44, N₂ and CO₂. Mass 77 appears, as a parent peak, together with 51, 50, 27, 26, and others in the first or second product spectrum. At ionizing energies of 25 and 50 eV, masses 51, 50, 27, and 26 all appear prominently. Thus mass 77 at early times may correspond to I, β -ethynylacrylonitrile, or a combination of the two. Likewise, 51, 50, 27, and 26 may be parents, fragments, or both. Mass 154 (II) appears at the same time as mass 77, increases in intensity for approximately 100 μ sec, and then levels off. In the same time interval, 77 is approximately constant. Quantitative measurements of the dimerization rate constant are now in progress.

The differences between gaseous benzyne chemistry and 3,4-pyridyne chemistry are striking. Benzyne, under similar conditions, dimerizes to biphenylene in good yield⁴ (~35%) and shows no unimolecular decomposition.⁵ I dimerizes in poor yield (~5%) and shows three channels of unimolecular decay. Energetics seem to explain the differences: the resonance energy of pyridine is about 15 kcal/mol less than that of benzene; the C–N bond is about 10 kcal/mol weaker than the C–C bond; and the C \equiv N bond is about 13 kcal/mol stronger than the C \equiv C bond. The net difference of ~38 kcal/mol opens many bond-breaking channels in I which are energetically impossible in benzyne.

To test the unimolecular reaction hypothesis, products were studied as a function of pressure of inert gas (N₂). One expects that, with increasing pressure of N₂, I would be stabilized, unimolecular reactions would be quenched, and the yield of II would increase.

II was produced in 5% yield with no added gas, 12% with one-third atmosphere of N₂, and 11% with two-thirds atmosphere. All absolute concentrations of gaseous products decreased with added N₂. The ratio of C₂H₂:HC \equiv CCN (uncorrected for sensitivity) remained approximately constant: 1.2 with no added N₂ and 1.6 with two-thirds atmosphere—compatible with I decomposing to C₂H₂ + HC \equiv CCN. The ratio of C₄H₂:HC \equiv CCN (uncorrected for sensitivity or fragmentation of 77) was approximately 2 at all pressures. Thus the two decomposition modes are about equally likely and are affected similarly by pressure. The ratio of diacetylene to β -ethynylacrylonitrile was approximately 6.5 at all pressures. The ratio of HCN:HC \equiv CC \equiv CH was 2.2 with no added N₂ and 5.6 at two-thirds atmosphere of N₂. This change was due to the larger decrease in the yield of C₄H₂ with added N₂. Since the C₄H₂:HC \equiv CCN ratio remained approximately constant it was concluded that HCN was produced in another reaction.

Two other possible sources of HCN are another primary reaction or unimolecular decay of II. No product compatible with an additional primary reaction was observed. At 10 atmospheres of N₂ or CH₄, excess HCN was still present and there was no increase in II with 10 atmospheres of N₂. II initially contains approximately 135 kcal/mol (estimated from bond energies). This suggests an immediate loss of HCN in some dimerizations.

II is a white solid, mp 169–169.5°. A high-resolution mass spectrum shows a parent (100% base peak) at 154.0544 (C₁₀H₆N₂ = 154.0531) with metastables at 104.8, 78.8, and 54.8 corresponding to 154⁺ \rightarrow 127⁺ + 27, 127⁺ \rightarrow 100⁺ + 27, and 100⁺ \rightarrow 74⁺ + 26, respectively. Fragments at 127.0429 (C₉H₅N = 127.0422), 100.0301 (C₈H₄ = 100.0313), and 74.0134 (C₆H₂ = 74.0156) correspond to the loss of two molecules of HCN and one of C₂H₂. The strongest band in the ir spectrum (KBr pellet) is at 838 cm⁻¹ characteristic of a 1:2:4 trisubstituted benzene.⁶ No C \equiv N stretching vibrations were present. The uv spectrum (in methanol) contains maxima at 338 (log

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ϵ 3.08), 325 (3.15), 312 (3.17), 297 (3.18), 283 (3.16), 241 (5.10), and 234 $m\mu$ (4.98). Addition of HCl shifts the long-wavelength bands about 500 cm^{-1} to the blue with almost no change in band contour. The peak at 241 $m\mu$ is shifted about 200 cm^{-1} to the red and the shoulder at 234 $m\mu$ disappears. The nmr (in CDCl_3) shows three groups of protons in the ratio of 1:1:1. The peaks are situated at (relative to TMS) δ 8.3 (doublet, possibly quartet), 8.0 (doublet, possibly quartet), and 6.8 (sextet, possibly octet). The protons are assigned $\text{H}_1 = \delta$ 8.0, $\text{H}_3 = \delta$ 8.3, and $\text{H}_4 = \delta$ 6.8.

A strong case can be made that II is a pure compound; a weaker case can be made that II is the 2,6 isomer. II was separated first on an SE-30 column and then on a Carbowax column. The melting point range is 0.5°. The nitrogen atom in I acts like an electron-attracting substituent on benzyne.⁷ If the dehydro bond is polarized significantly, a 2,6 isomer would be expected.⁸ Four examples of substituted benzyne dimerizing to 2,6 isomers are known.⁹ If the 2,6 isomer is indeed formed, no claim is made that the 2,7 isomer is not also formed.

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(10) National Science Foundation Trainee, 1965-1969.

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Charge-Transfer Interactions in the Photochemistry of 9-Thiabicyclo[3.3.1]non-6-en-2-one

Sir:

There have been a number of recent reports dealing with the photochemical behavior of cyclic β -keto sulfides.¹⁻⁵ Much of the interest in these systems stems from the excited state interaction of the two groupings⁶⁻⁸ and the unusual photochemistry exhibited by these systems as a result of this interaction. The photo-rearrangement of 9-thiabicyclo[3.3.1]non-6-en-2-one (1) to 2-thiabicyclo[6.1.0]non-6-en-3-one (2), recently reported from these laboratories,⁹ was considered to proceed either by the formation of a charge-transfer structure such as 3 (Scheme I), or by a Norrish type I

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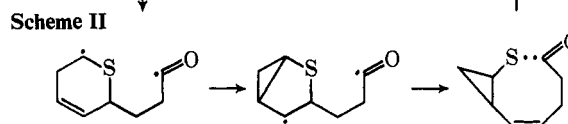
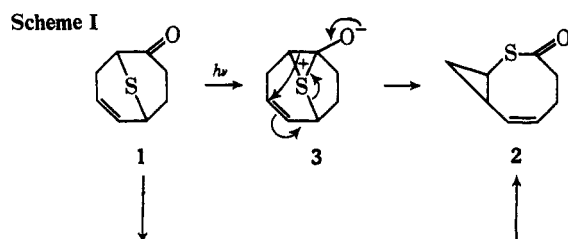
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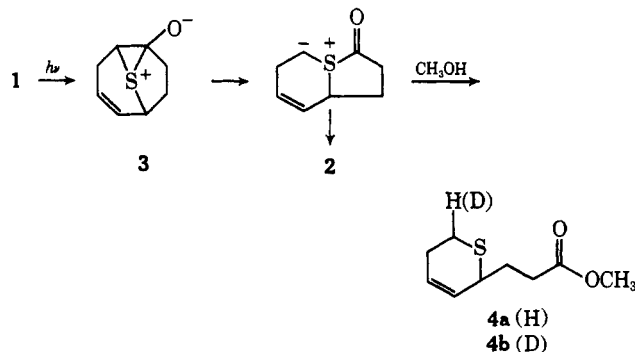


homolysis followed by diradical reorganization (Scheme II). The present work was initiated in the hope of distinguishing between these two possibilities. In this communication, we report evidence which indicates the intermediacy of a charge-transfer structure in this transformation.

Irradiation of 1 in methanol¹⁰ (λ_{max} 253 and 305 $m\mu$ (ϵ 290 and 275)) instead of benzene gave methyl 5,6-dihydro-2H-thiopyran-2-propionate (4a) as the major product (40%) together with small amounts of 2 (5%). Identification of ester 4a¹¹ is based on its hydrogenation (Raney Ni) to methyl octanoate coupled with its nmr spectrum, which shows the presence of two vinyl hydrogens. The mass spectrum of 4a shows the parent ion at m/e 186 and fragment ions at m/e 112 and 99 (base) in accord with expectation for the proposed structure.

Irradiation of 1 in deuteriomethanol gave 4b (nmr (CDCl_3): singlet at τ 6.35 (3 H); multiplets at τ 4.25 (2 H), 6.68 (1 H), and 7.70 (7 H)) containing >98% of one deuterium at C-6, as evidenced by mass spectroscopy (i.e., m/e 187 (parent), 113 ($\text{P} - \text{CH}_3\text{CO}_2\text{CH}_3$), and 100 (base)). This observation cannot be interpreted in terms of the intermediacy of a ketene formed via Norrish type I cleavage followed by internal disproportionation, since the deuterium atom should appear α to the carbonyl group if this path was followed. This result, however, may be readily accommodated by Scheme III which involves formation of charge-

Scheme III



transfer structure 3.

Efforts to firmly establish the generality of this path led us to examine the photochemistry of the related 9-thiabicyclo[3.3.1]non-2-one (5) system. β -Keto sulfide 5 (mp 155-156°) prepared by the catalytic reduction of 1 was irradiated in deuteriomethanol¹⁰ and gave

(10) All irradiations were done using a 450-W Hanovia lamp fitted with a Pyrex filter.

(11) All compounds analyzed satisfactorily. Complete spectroscopic and degradative details will be given in our full publication.