phenylbutane when (S)-methylpropylphenylphosphine was the ligand.

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

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James D. Morrison,* Robert E. Burnett
Department of Chemistry, University of New Hampshire
Durham, New Hampshire 03824

Adam M. Aguiar, Cary J. Morrow, Carol Phillips
Department of Chemistry, Tulane University
New Orleans, Louisiana 70118

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3,4-Pyridyne and Its Dimer

Sir:

We report a study of gaseous 3,4-didehydro-pyridine1 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-ethylnylacrylonitrile,3 or one of its stable isomers, one bond having broken in the pyridine ring); (b) decomposition to HCN (27) and HC≡CC≡CH (50) (two bonds broken); and (c) decomposition and rearrangement to C2H2 (26) and HC≡CC≡N (51) (two bonds broken).

Kinetics were followed by TF mass spectroscopy. Initial products and intermediates appeared at about 100–150 μsec 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 50, 51, 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-ethylnylacrylonitrile, 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 μsec, 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 benzyn chemistry and 3,4-pyridyne chemistry are striking. Benzyn, under similar conditions, dimerizes to biphenylene in good yield4 (~35%) and shows no unimolecular decomposition.4 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≡N bond is about 13 kcal/mol stronger than the C≡C bond. The net difference of ~38 kcal/mol opens many bond-breaking channels in I which are energetically impossible in benzyn.

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≡CC≡N (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≡CC≡N. The ratio of C2H2:HC≡CC≡N (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-ethylnylacrylonitrile was approximately 6.5 at all pressures. The ratio of HCN:HC≡CC≡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 C2H2 with added N2. Since the C2H2:HC≡CC≡N 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 (C8H6N2 = 154.0531) with metastables at 104.8, 78.8, and 54.8 corresponding to 154+ → 127+ + 27, 127+ → 104+ + 27, and 104+ → 78+ + 27, respectively. And fragments at 127.0429 (C7H4N = 127.0422), 100.0301 (C6H4 = 100.0313), 74.0134 (C5H2 = 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≡N stretching vibrations were present. The uv spectrum (in methanol) contains maxima at 338 (log

(5) Reference 1, p 257.
The peaks are situated at (relative to TMS) 6.8.3 electron-attracting substituent on benzyne. If the range is doublet, possibly quartet), 8.0 (doublet, possibly quartet), and then on a Carbowax column. The melting point would be expected.* Four examples of substituted benzynes dimerizing to 2,6 isomers are known. If the 2,7 isomer is indeed formed, no claim is made that the 2,6 isomer is not also formed.

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 2,6 isomer is indeed formed, no claim is made that the 2,6 isomer is not also formed.

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(7) Reference 1, p 300.

Jerry M. Kramer, R. Stephen Berry*
Department of Chemistry, University of Chicago Chicago, Illinois 60637
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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. Much of the interest in these systems stems from the excited state interaction of the two groupings 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, was considered to proceed either by the formation of a charge-transfer structure such as 3 (Scheme I), or by a Norrish type I 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 methanol (λmax 253 and 305 μm (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 4a 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.

Scheme II

Irradiation of 1 in deuteriomethanol gave 4b (nmr (CDCl3)): singlet at τ 6.35 (3 H); multiplicities at τ 4.25 (2 H), 6.68 (1 H), and 7.70 (2 H) containing >98% of one deuterium at C-6, as evidenced by mass spectroscopy (i.e., m/e 187 (parent), 113 (P − CH3CO2CH3), 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-transfer structure 3.

Scheme III

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 deuteriomethanol 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.