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-didehydropyridine[1] or 3,4-pyridyne (I), and its unimolecular decomposition and dimerization to 2,6- (or 2,7-) diazabiphenylene (II).

Solid pyridine-3-diazonium-4-carboxylate[2] 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 CO_2, N_2, 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 C_2H_2 (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 μsec after initiation. The first mass spectral sweep showing products contains masses 28 and 44, N_2 and CO_2. 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 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 benzyne chemistry and 3,4-pyridyne chemistry are striking. Benzyne, under similar conditions, dimerizes to biphenylene in good yield[4] (~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 (N_2). One expects that, with increasing pressure of N_2, 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 N_2, and 11% with two-thirds atmosphere. All absolute concentrations of gaseous products decreased with added N_2. The ratio of C_2H_2:$HC\equiv CCN$ (uncorrected for sensitivity) remained approximately constant: 1.2 with no added N_2 and 1.6 with two-thirds atmosphere—compatible with I decomposing to $C_2H_2 + HC\equiv CCN$. The ratio of C_4H_2:$HC\equiv CCN$ (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 N_2 and 5.6 at two-thirds atmosphere of N_2. This change was due to the larger decrease in the yield of C_4H_2 with added N_2. Since the C_4H_2:$HC\equiv CCN$ 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 N_2 or CH_4, excess HCN was still present and there was no increase in II with 10 atmospheres of N_2. 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 ($C_{10}H_6N_2$ = 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 (C_9H_5N = 127.0422), 100.0301 (C_8H_4 = 100.0313), and 74.0134 (C_6H_2 = 74.0156) correspond to the loss of two molecules of HCN and one of C_2H_2. 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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(1) R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967, Chapter 6.

(2) T. Kauffmann and F. P. Boettcher, *Chem. Ber.*, **95**, 949 (1962).

(3) M. P. Cava, M. J. Mitchell, D. C. DeJongh, and R. Y. Van Fossen, *Tetrahedron Lett.*, **26**, 2947 (1966).

(4) R. S. Berry, G. N. Spokes, and R. M. Stiles, *J. Amer. Chem. Soc.*, **82**, 5240 (1960).

(5) Reference 1, p 257.

(6) W. Baker, J. W. Barton, and J. F. W. McOmie, *J. Chem. Soc.*, 2666 (1958).

ϵ 3.08), 325 (3.15), 312 (3.17), 297 (3.18), 283 (3.16), 241 (5.10), and 234 mμ (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 mμ is shifted about 200 cm^{-1} to the red and the shoulder at 234 mμ 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 H$_1$ = δ 8.0, H$_3$ = δ 8.3, and H$_4$ = δ 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 benzynes 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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(7) Reference 1, p 300.

(8) M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967, pp 262–263.

(9) C. D. Campbell and C. W. Rees, *Chem. Commun.*, 192 (1965); C. R. Harrison, J. F. W. McOmie, J. B. Searle, J. P. Smith, J. O. Jenkins, and J. W. Smith, *J. Chem. Soc. C*, 1769 (1966); F. A. Hart and F. G. Mann, *ibid.*, 3939 (1957); G. Vargas Nunez, *Bol. Soc. Quim. Peru*, 31, 6 (1965).

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

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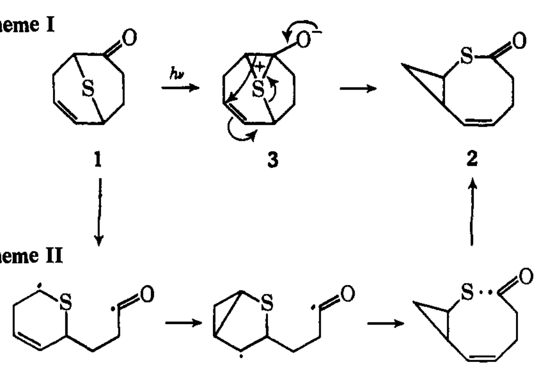
Charge-Transfer Interactions in the Photochemistry of 9-Thiabicyclo[3.3.1]non-6-en-2-one

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 groupings[6–8] and the unusual photochemistry exhibited by these systems as a result of this interaction. The photorearrangement 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 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.

Scheme I

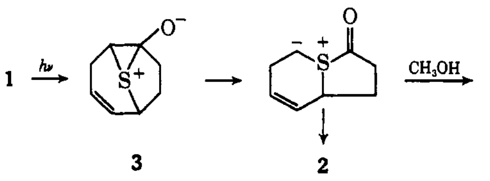


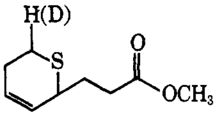
Scheme II

Irradiation of **1** in methanol[10] ($\lambda\lambda_{max}$ 253 and 305 mμ (ϵ 290 and 275)) instead of benzene gave methyl 5,6-dihydro-2*H*-thiopyran-2-propionate (**4a**) as the major product (40%) together with small amounts of **2** (5%). Identification of ester **4a**[11] 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 (P − CH$_3$CO$_2$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-transfer structure **3**.

Scheme III





4a (H)
4b (D)

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[10] and gave

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(1) P. Y. Johnson and G. A. Berchtold, *J. Amer. Chem. Soc.*, **89**, 2761 (1967).

(2) P. Y. Johnson and G. A. Berchtold, *J. Org. Chem.*, **35**, 584 (1970).

(3) W. C. Lumma and G. A. Berchtold, *J. Amer. Chem. Soc.*, **89**, 2761 (1967); *J. Org. Chem.*, **34**, 1566 (1969).

(4) C. Ganter and J. F. Moser, *Helv. Chim. Acta*, **52**, 967 (1969); **51**, 300 (1968).

(5) J. G. Pacifici and C. Diebert, *J. Amer. Chem. Soc.*, **91**, 4595 (1969).

(6) N. J. Leonard, T. L. Brown, and T. W. Milligan, *ibid.*, **81**, 504 (1959); **82**, 4075 (1960).

(7) G. Bergson, G. Claeson, and L. Schotte, *Acta Chem. Scand.*, **16**, 1159 (1962).

(8) L. A. Paquette and L. D. Wise, *J. Amer. Chem. Soc.*, **89**, 6659 (1967).

(9) A. Padwa, A. Battisti, and E. Shefter, *ibid.*, **91**, 4000 (1969).

(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.