1,3-Propanediamine. This is another example of an amine which has sprung to prominence in synthesis because of unique reactions brought about by a derivative, in this case its monopotassium salt.[23] Desiccation has been achieved by vacuum distillation alone,[24a] distillation from alkali metal mirrors,[24b] or distillation from KOH.[24c] Our results using the near-IR method are displayed in Table II and indicate that, not surprisingly, this amine with two coordinating centers is one of the more difficult examples to dry. It is worth noting that freshly ground KOH gives a drier sample than aged material stored in a desiccator, although as may be seen, in comparison with several other siccatives, e.g., CaC_2 or sieves, KOH is not particularly good. In addition, although seldom recommended for use in these situations, $CaSO_4$ (Drierite) was investigated in view of some of the more extravagant claims which have been made on its behalf.[25] As may be seen, the results are rather dismal.

Desiccation of Amines. General Recommendations. Perhaps not surprisingly, the results from this study lend support to the current usage of molecular sieves and CaH_2 as *serious* and widely applicable siccatives for amines. Apart from this, it is fitting to draw attention to the high efficiency of CaC_2 in these studies, which, though infrequently prescribed as a desiccant, is often seen to surpass CaH_2 in potency and is more desirable than the hydride from consideration of cost and safety in storage. On the other hand, the performance of alumina is uniformly disappointing and it cannot be advocated as a serious desiccant for amines.

Experimental Section

Details of the water assay techniques as well as the source, activation, and handling of most of the desiccants have already been described.[1-4] Determination of water content by the near-IR method[22] was carried out on a Varian Cary 17 Instrument. Calcium carbide was of industrial grade and was crushed in a mortar immediately prior to use. Appropriate venting was provided for desiccants producing gases, e.g., CaC_2, CaH_2.

Amines were of laboratory reagent grade and purified by standard methods.[11c] The pyridines and triethylamine were stood over KOH for 24 h, decanted, fractionated, and stored in dark bottles over 20% w/v 3A molecular sieves. Pyridine had bp 115–116 °C, 2-methylpyridine 128–129 °C, 2,6-dimethylpyridine 145–146 °C, and 2,4,6-trimethypyridine 176–178 °C. Et_3N had bp 89–89.5 °C. Diisopropylamine was first allowed to stand over 20% w/v 3A molecular sieves, decanted, stirred overnight with CaH_2, fractionated, and finally stored as above, bp 84 °C. 1,3-Propanediamine was mixed with 20% v/v benzene, fractionated, stirred overnight with CaH_2, and fractionated again, bp 135–136 °C.

Acknowledgment. We thank the Department of Chemistry, University of Malaya, for support of this work and Miss Lim Siew Heong for her able technical assistance.

Registry No. Pyridine, 110-86-1; 2-methylpyridine, 109-06-8; 2,6-dimethylpyridine, 108-48-5; 2,4,6-trimethylpyridine, 108-75-8; Et_3N, 121-44-8; $(Me_2CH)_2NH$, 108-18-9; $NH_2(CH_2)_3NH_2$, 109-76-2; CaH_2, 7789-78-8; CaC_2, 75-20-7; BaO, 1304-28-5; benzene, 71-43-2; KOH, 1310-58-3; Na, 7440-23-5; CaO, 1305-78-8; Al_2O_3, 1344-28-1; $CaSO_4$, 7778-18-9.

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(23) Potassium 3-aminopropylamide possesses the singular property of bringing about the conversion internal alkyne → 1-alkyne in essentially quantitative yields. See C. A. Brown and A. Yamashita, *J. Am. Chem. Soc.*, **97**, 891 (1975).

(24) (a) A. Gero, *J. Am. Chem. Soc.* **76**, 5159 (1954); (b) L. R. Dalton, J. L. Dye, E. M. Fielden, and E. J. Hart, *J. Phys. Chem.*, **70**, 3358 (1966); (c) K. C. Badri and L. Y. Goh, *Inorg. Chim. Acta*, in press.

(25) W. A. Hammond, "Drierite", the W. A. Hammond Drierite Company, Xenia, OH.

Trapping of Intermediates in the Thermolysis of α-Azidochalcone. Insight into the "Zwittazido Cleavage" Reaction

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The "zwittazido cleavage" reaction (Scheme I) has recently been the subject of considerable study[1] because this novel rearrangement possesses both interesting mechanistic and advantageous synthetic characteristics. Although a large amount of work with cyclic and acyclic ketoazides has been reported,[1,2] the mechanism of this reaction is still somewhat obscure, especially the question of whether a concerted or stepwise process (or both) occurs.

In the rearrangement of cyclic keto vinyl azides opportunity exists for an intramolecular ring closure following an initial ring cleavage (Scheme I). In acyclic systems formation of azirines, indoles, or rearranged cyano ketones can take place.[2] In transformation **1**→**2**, the reaction has been postulated to occur via intermediate **3**. An alternate pathway would involve a cleavage to ions **4** and **5**, which may recombine to **2** (Scheme II).

Our interest in the chemistry of vinyl azides[3] led us to investigate this reaction and to show that even in the acyclic case cleavage can occur and that the intermediates can be trapped with alcohols or amines.

Thermolysis of α-azidochalcone (**1**) in *o*-dichlorobenzene for 24 h produced α-cyano-α-phenylacetophenone (**2**) in 70% yield. When the reaction was carried out in the presence of 10 equiv of either ethanol or benzyl alcohol, the yield of **2** decreased while ethyl benzoate (**6**) and benzyl benzoate (**7**), respectively, were isolated. Thermolysis with 10 equiv of benzylamine yielded *N*-benzylbenzamide (**8**). In all three trapping experiments, considerable quantities of **2** were also obtained along with benzyl cyanide (**9**) and polymeric materials. The results are recorded in Table I.

The formation of compounds **6**–**9** indicates that at least part of the thermolysis of the acyclic α-azidochalcone proceeds by a cleavage mechanism as shown in Scheme II which allows for an acyclic cation intermediate **4** to react with the alcohols and amine. Protonation of **5** leads to benzyl cyanide (**9**).

We showed that the azido ketone **1** did not react with ethanol in boiling toluene to produce ethyl benzoate.[4] Furthermore, no ethyl benzoate (**6**) was detected by GC when either the cyano ketone **2** or the crude mixture resulting from heating **1** in *o*-DCB was subjected to trapping reaction conditions.[5]

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(1) H. W. Moore, *Acc. Chem. Res.*, **12**, 125 (1979), and references cited there in.

(2) D. Knittel, Hemetsberger, R. Leipert, and H. Weidman, *Tetrahedron Lett.*, 1459 (1970).

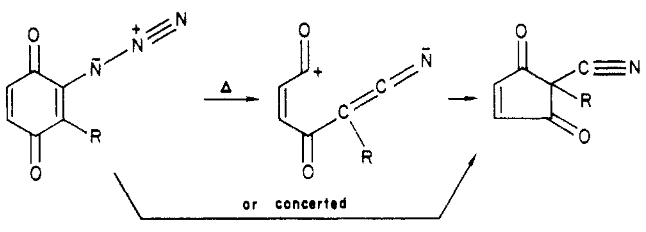
(3) For instance (a) G. L'Abbé, and A. Hassner, *Angew. Chem., Int. Ed. Engl.*, **10**, 98, (1971); (b) A. Hassner, E. S. Ferdinandi, and R. J. Isbister, *J. Am. Chem. Soc.*, **92**, 1672 (1970); (c) A. Hassner, *Acc. Chem. Res.*, **4**, 9 (1971).

(4) Azidochalcone (**1**) reacts with nucleophiles such as sodium sulfide or ylides at the azide rather than at the carbonyl function; B. A. Belinka, Jr., and A. Hassner, *J. Org. Chem.*, **44**, 4712 (1979), and unpublished results in this laboratory; G. Mathys, S. Toppet, and G. L'abbé, *Chem. Ind.* (*London*), **6**, 278 (1975).

(5) G. L'abbé and A. Hassner, *J. Org. Chem.*, **36**, 258 (1971).

0022-3263/81/1946-0631$01.00/0

Scheme I



Scheme II

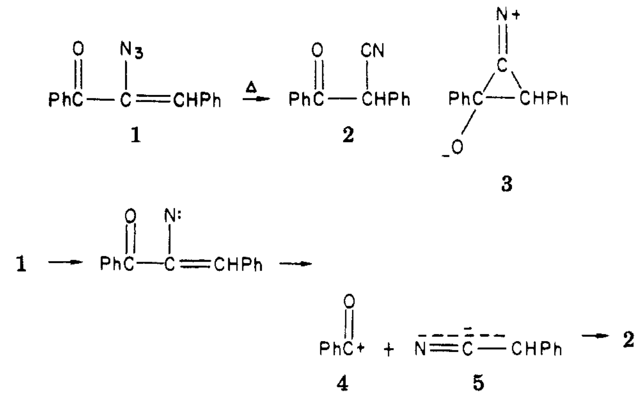


Table I. Trapping of Intermediates in the Thermolysis of 1 in *o*-Dichlorobenzene (*o*-DCB)

$$\mathbf{1} \xrightarrow{\Delta,\ o\text{-DCB}} \underset{(70\%)}{\mathbf{2}} + \text{polymer}$$

$$\mathbf{1} \xrightarrow[\text{EtOH}]{\Delta,\ o\text{-DCB}} \underset{\mathbf{6}\ (28\%)}{\mathrm{Ph}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OEt}} + \underset{\mathbf{9}\ (5\%)}{\mathrm{PhCH_2CN}} + \underset{(33\%)}{\mathbf{2}} + \text{polymer}$$

$$\mathbf{1} \xrightarrow[\mathrm{PhCH_2OH}]{\Delta,\ o\text{-DCB}} \underset{\mathbf{7}\ (32\%)}{\mathrm{Ph}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OCH_2Ph}} + \underset{(4\%)}{\mathbf{9}} + \underset{(41\%)}{\mathbf{2}} + \text{polymer}$$

$$\mathbf{1} \xrightarrow[\mathrm{PhCH_2NH_2}]{\Delta,\ o\text{-DCB}} \underset{\mathbf{8}\ (26\%)}{\mathrm{Ph}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{NHCH_2Ph}} + \underset{(6\%)}{\mathbf{9}} + \underset{(45\%)}{\mathbf{2}} + \text{polymer}$$

These results lend support to the generality of the zwittazido cleavage as a stepwise process.

Experimental Section

General. α-Azidochalcone (**1**), mp 63–64 °C, was prepared by the method of L'abbé and Hassner (lit.[5] mp 63.5–64 °C). The solvents, alcohols, and amine were distilled before use.

The esters, nitriles, and amide were identified by comparison of melting and boiling points, and nuclear magnetic resonance and infrared spectra with authentic samples.

Trapping of Intermediates in Thermolysis of α-Azidochalcone. General Procedure. To a solution of 2.49 g (10 mmol) of α-azidochalcone in 25 mL of *o*-dichlorobenzene was added 100 mmol of alcohol or amine. The magnetically stirred solution was then heated to reflux. When N_2 evolution ceased, the solvent was removed by low-pressure distillation to leave the crude product mixture.

The products were further separated and purified by distillation for liquids and crystallization for solids.

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Registry No. **1**, 26087-01-4; **2**, 5415-07-6; **6**, 93-89-0; **7**, 120-51-4; **8**, 1485-70-7; **9**, 140-29-4.

Acidities of Carbon and Nitrogen Acids: The Aromaticity of the Cyclopentadienyl Anion

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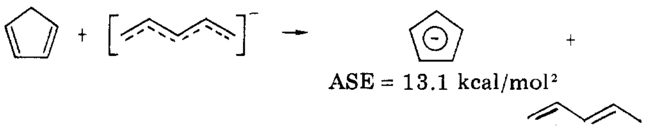
It is generally agreed that the relatively high acidity of 1,3-cyclopentadiene (CPH) is due primarily to aromatic stabilization of the cyclopentadienyl anion (CP^-), but there is little information available as to the size of this aromaticity effect. By use of the simple Hückel theory the π stabilization energy of the cyclopentadienyl anion is calculated to be 2.47β,[1] i.e., greater than that of benzene (2β); but the simple Hückel theory is known to exaggerate the aromatic stabilization energies.[1b] Adopting $\beta = 18$ kcal/mol, based on the empirical resonance energy of 36 kcal/mol, derived from the heat of hydrogenation of benzene relative to cyclohexene, places the resonance energy of CP^- at 57 kcal/mol. On the other hand, the aromatic stabilization energy (ASE) of CP^- is calculated to be only 13 kcal/mol, as compared to 25.6 kcal/mol for benzene, based on the heat of formation of benzene and that calculated by using MINDO/3 for the reaction of CP with the anion derived from (*E*)-1,3-pentadiene.[2]



To these calculated resonance energies we now add several experimentally based estimates. Our estimates, derived from equilibrium acidity data in dimethyl sulfoxide solution,[3] indicate that the aromatic stabilization energy of CP^- is about 24–27 kcal/mol.

Results and Discussion

Aromatic Stabilization Energies of 1,3-Cyclopentadiene, Indene, and Fluorene Anions Determined by Comparison with Nitrogen Analogues. The equilibrium acidities in Me_2SO of 1,3-cyclopentadiene (CPH), indene (INH), and fluorene (FLH) decrease in that order, whereas the acidities of their nitrogen acid analogues, pyrrole, indole, and carbazole, are in the reverse order (Table I). The small increases in acidity of indole and carbazole, relative to pyrrole, can be attributed to small increases in inductive and/or resonance effects resulting from the presence of the additional benzene ring(s). The successive decrease in acidities of CPH, INH, and FLH can be attributed to successive decreases in the aromaticities of the CP^-, IN^-, and FL^- anions, which overshadow the acidifying effects of the benzene ring(s). The decreasing aromaticities are analogous to those observed (per benzene ring) in the series benzene, naphthalene, and anthracene.[4]

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(1) (a) Roberts, J. D.; Streitwieser, A., Jr.; Regan, C. M. *J. Am. Chem. Soc.* **1952**, *74*, 4579–4582. (b) Ritchie, C. D. "Physical Organic Chemistry"; Marcel Dekker: New York, 1975; Chapter 5.

(2) Dewar, M. J. S. *Pure Appl. Chem.* **1975**, *44*, 767–782. The author suggests that this value may be too small since MINDO/3 tends to underestimate resonance energies of anions.

(3) Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006–7014.

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