Tetrahedron Letters No. 31, pp 2865 - 2866.

0040-4039/79/0729-2865$02.00/0

APPROACHING A PERSISTENT FAVORSKII ZWITTERION

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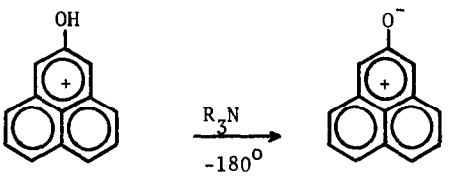
2-Phenalanone has been synthesized via a double Curtius procedure and converted to the conjugate acid of 2-phenalenylium oxide, a potential persistent Favorskii zwitterion.

The non-stereospecificity of the Favorskii reaction (α-haloketones with alkoxides) when carried out in polar, homogeneous media is conventionally ascribed[1] to the intervention of an achiral, zwitterionic intermediate (a Favorskii zwitterion) capable of tautomerization to a cyclopropanone, which subsequently undergoes cleavage by alkoxide. Independent (but also circumstantial) evidence for such zwitterions has been cited,[2,3] but none has ever been isolated or even physically detected. The synthesis of an isolable, or at least a persistent, Favorskii zwitterion must therefore be regarded as an important challenge for physical organic synthesis.

The ultimate target of this research is 2-phenalenylium oxide (1), which is envisioned as a uniquely stable but valid typewise representative of the Favorskii zwitterion class. In it,

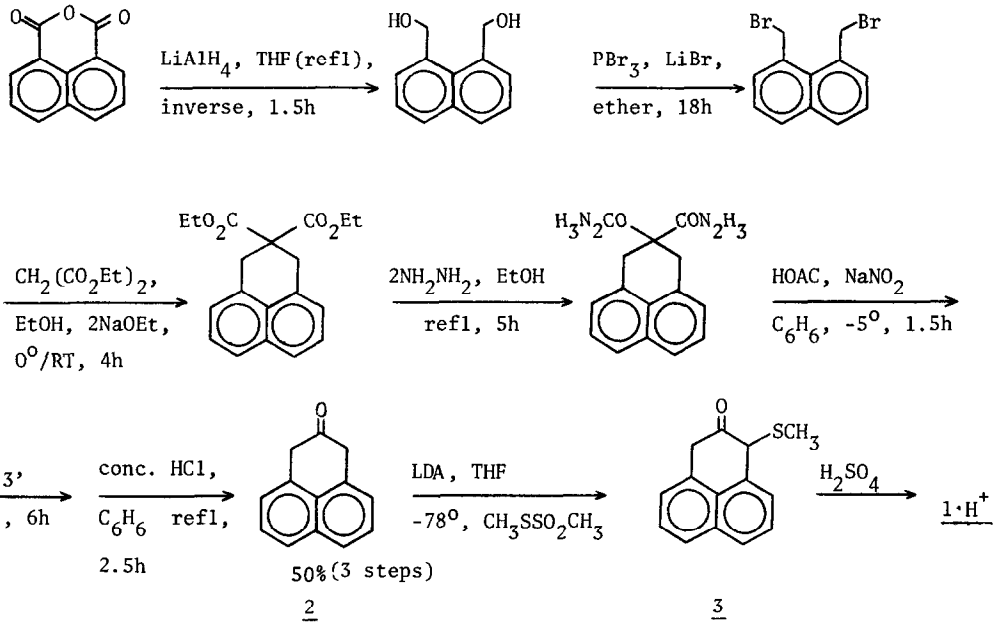


1·H⁺ 1

the allylic carbonium ion moiety characteristic of Favorskii zwitterions is part of an aromatic phenalenylium system. It will be apparent upon sufficiently close examination that no non-zwitterionic (*i.e.*, uncharged) canonical structures are available to 1 other than diradical or cyclopropane-containing ones. The phenalenylium aromatic unit is not only vital to the stabilization of 1; it also occupies a key role in the synthetic strategy. The conjugate acid of 1 (1·H⁺), which is merely 2-hydroxyphenalenylium ion, is designed to provide an isolably stable precursor to 1 which is presumably susceptible of facile de-protonation at low temperatures. The preparation of stable 1·H⁺ solutions is reported herein.

A key intermediate in the preparation of 1·H⁺ is the symmetrical ketone, 2-phenalanone (2), which previously was unknown. Although unprepossessing in terms of complexity, 2 is quite unstable and resists synthesis by most conventional means.[4] The ultimately successful route (a double Curtius procedure, Scheme 1) is rather novel and appears to warrant further investigation as a general synthetic methodology. Used in this way, diethylmalonate becomes a carbonyl dianion synthon. Ketone 2 is chromatographically unstable to alumina, silica gel, charcoal, and cellulose. Purification is accomplished by careful re-crystallization (CCl_4, N_2) and (if desired) sublimation: mp 102-105°(d); nmr ($CDCl_3$) δ3.92 (s, 4H), 7.47 (m, 6H); ir ($CHCl_3$) (cm^{-1}), 1726; mass spectrum m/e 182 (M), 154(M-CO), 153; uv ($CHCl_3$) nm 290.

Scheme 1



It was originally envisioned that bromination of 2 would yield an α-bromoketone the enol of which would ionize spontaneously to $\underline{1{\cdot}H^+}$ Br^-. However, bromination of either 2 or its enolate under a variety of conditions yields only dark blue, intractable, paramagnetic solids. The enolate of 2, generated in tetrahydrofuran at -78° using lithium di-isopropylamide, does react with methyl methanethiosulfonate to afford the α-methylthiyl ketone 3.[5] Treatment of 3 with cold concentrated sulfuric acid yields the desired $\underline{1{\cdot}H^+}$ as decisively attested by its nmr spectrum: nmr (H_2SO_4, external TMS, 100Mc) δ 8.09 (t, 2H, at C_5, C_8), 8.41 (s, 2H, at C_1, C_3), 8.74 (d, 2H, at C_4, C_9 or C_6, C_7), 8.86 (d, 2H, at C_6, C_7 or C_4, C_9). The solutions are dark green. Work is in progress to isolate crystalline $\underline{1{\cdot}H^+}$ and to study its de-protonation behavior.

Acknowledgment. The authors thank the Welch Foundation (F-149) for support of this research.[6,7]

References

1. J. G. Aston and J. D. Newkirk, J. Amer. Chem. Soc., 73, 3900 (1951).
2. A. W. Fort, ibid., 84, 4979 (1962).
3. N. J. Turro, S. S. Edelson, J. R. Williams, T. R. Darling, and W. B. Hammond, ibid., 91, 2283 (1969).
4. Including reactions of 1,8-bis (bromomethyl) naphthalene with Collman's reagent; phenalane-2,2-dicarboxylic acid with lead tetraacetate; 2-aminophenalane with phenylglyoxal; rearrangements of phenalene oxide; ring expansion of acenaphthone, and many others.
5. This derivative is even more unstable than the parent ketone, and could not be obtained in pure form; nmr ($CDCl_3$) 2.1 (s, 3H), 3.7 (s), 3.38-4.8 (several singlets), 7.25 (m, ~6H); mass spectrum m/e 228 (M).
6. This work is based in part on the dissertation of Jefferies H. Eilert, Univ. of Texas, 1971.
7. Professor Andrew S. Kende has informed us that a synthesis of 2 amazingly similar to our own has been carried out in his laboratory.

(Received in USA 26 March 1979)