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A REINVESTIGATION OF THE THERMAL REARRANGEMENTS OF NAPHTHVALENE

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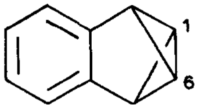
Summary. The previously reported thermal transformation of naphthvalene to benzofulvene has been shown to be a catalyzed process; naphthvalene rearranges to naphthalene under flow pyrolysis conditions.

Naphthvalene (1) has been known since 1972[1], but its thermal chemistry is yet enigmatic.[1,2] The corresponding parent molecule, benzvalene (2), cleanly undergoes thermal transformation to benzene in solution with an activation energy of 26.7 kcal/mole.[3] In dramatic contrast, 1 is reported to give no naphthalene and only benzofulvene (3) on solution thermolysis.[1] Burger and coworkers[2] have shown several other benzannelated benzvalenes to undergo similar transformations to the corresponding fulvenes, in lieu of complete aromatization. Moreover, the activation energies of rearrangement of these benzologs are significantly higher than that of benzvalene or simple substituted benzvalenes. The mechanism for rearrangement of 1 to 3 has not been previously explored to our knowledge, although others have expressed the opinion that the reaction is not catalyzed.[2b] We now wish to report results of preliminary experiments that illustrate that these rearrangements are considerably more complicated than previously indicated. Our findings suggest that rearrangement of 1 to 3 is a catalyzed process, and that naphthalene is thermally formed from 1 under certain conditions.



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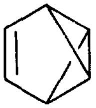

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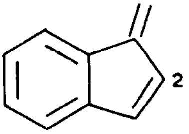

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Previous investigations of the chemistry of naphthvalene have been hampered by the difficulty of removing naphthalene formed as a synthetic byproduct.[1] We have found that purification of 1 can be conveniently effected by preparative reverse-phase HPLC.[4] Similar to previous reports,[1,2] solution thermolyses of purified 1 give only 3 in non-polar solvents. Thus, heating 1 in benzene-d_6 or CCl_4 produced benzofulvene (3) by ^1H NMR, with a half-life of approximately 2 min at 175°C. No traces of naphthalene could be detected, and varying amounts of polymeric material were observed.[5] Thermolysis results under other solution conditions were strikingly varied, however. For example, solutions of 1 in benzene over solid KOH generated 3 only slowly at 175°C ($t_{1/2}$ ca. 5 h for disappearance of 1). More interestingly, use of pyridine-d_5 as solvent shut off decomposition of 1 to 3 entirely, and gave only naphthalene along with significant amounts of intractable material (150°C, $t_{1/2}$ 130 min). Benzofulvene was stable under these conditions. Thermolyses of 1 in acetonitrile and acetone gave mixtures of 3, naphthalene, and polymer (150°C, $t_{1/2}$ ca. 4 h).

The effect of base on the rearrangement of 1 suggests the possibility of protic catalysis. Thermolyses of 1 in the presence of D_2O in benzene-d_6, acetone-d_6, or acetonitrile-d_3 gave no incorporation of deuterium in the products, however (by ^1H NMR).

Gas-phase pyrolyses of 1 proceeded somewhat differently. Heating 1 in a pyrex bulb at 165°C at less than 1 torr pressure gave a mixture of naphthalene and benzofulvene in the ratio of ca. 1:1 (ca. 10% conversion in 1 h). At 300°C, in contrast, only naphthalene was observed. Benzofulvene was independently shown to be stable to the pyrolysis conditions, and identical results were found in the presence of considerable benzene pressure. These results suggest that benzofulvene arises from a surface catalyzed process. Pyrolysis in the presence of a large amount of broken pyrex, however, gave approximately the same ratio of products at 165°C.

Somewhat different results were obtained under flow pyrolysis conditions. Sublimation of 1 through a hot tube in a flow of N_2 gave no benzofulvene, but only naphthvalene/naphthalene mixtures at lower temperatures (e.g. 17% naphthalene at 160°C, contact time 5.3 s) or naphthalene at higher temperatures (300°C). Recovery of material in the flow experiments was greater than 90%. Again, benzofulvene was found to be stable to these conditions.

No simple mechanistic scenario is readily apparent to encompass all of the above results. The capricious solution thermolyses suggest that both benzofulvene and naphthalene formation are catalyzed processes. The exact natures of the catalysts are unknown, however. The dramatic effect of base intimates protic acid catalysis for the rearrangement of **1** to **3**, yet reasonable mechanisms would incorporate deuterium into the benzofulvene in the presence of D_2O. Burger and coworkers[6] have shown that the transformations of **1** to **3** and to naphthalene can be readily catalyzed by transition metals. Moreover, the mode of rearrangement is highly specific for type of metal. Thermolysis of 1,6-dideuterionaphthvalene in CCl_4 gave benzofulvene labeled fully at the 2-position and half-labeled in the exocyclic methylene. These results are analogous to those observed for copper catalyzed rearrangements of isotopically labeled naphthvalenes.[6] We thus suggest that trace metal impurities or Lewis acids catalyze these rearrangements in solution.[7] The effect of solid KOH may be to tie up the catalysts somewhat. The formation of polymeric material is also indicative of the presence of processes more complicated than simple unimolecular transformations.[5] It is of interest to note that quartz catalysis of rearrangement of benzvalene to fulvene has been postulated previously.[8]

The flow pyrolyses suggest that the aromatization of **1** is uncatalyzed in the gas phase,[9] although the possibility of surface catalysis cannot be completely ruled out. The mechanism for static pyrolysis formation of benzofulvene is less clear, since increased surface area does not appear to affect the reaction. It is possible that other bimolecular reactions play a role in this transformation, however.[10]

In summary, the naphthvalene (**1**) to benzofulvene (**3**) rearrangement has been shown to be a catalyzed process, rather than a simple unimolecular reaction. Naphthvalene does in fact give naphthalene thermally under certain conditions, in contrast to previous assertions. Mechanistic conclusions based on transformations of benzannelated benzvalenes to the corresponding fulvenes must thus be made with qualification. The significantly lower activation energy for aromatization of benzvalene (**2**) relative to naphthvalene (**1**) is still an interesting matter for conjecture, however.[11]

REFERENCES AND NOTES

1. Katz, T. J.; Wang, E. J.; Acton, N. *J. Am. Chem. Soc.*, **1971**, *93*, 3782.
2. a) Gandillon, G.; Bianco, B.; Burger, U. *Tetrahedron Lett.* **1981**, *22*, 51.
   b) Burger, U.; Mareda, J. *Tetrahedron Lett.* **1984**, *25*, 177.

3. Turro, N. J.; Renner, C. A.; Katz, T. J.; Wiberg, K. B.; Connon, H. A. *Tetrahedron Lett.* **1976**, 17, 4133.
4. Naphthvalene was synthesized according to the procedure in Reference 1. It was purified by precipitation of naphthalene from hexane, followed by HPLC on Ultrasphere ODS (Beckman) with acetonitrile as eluting solvent.
5. Significant polymerization in thermolyses of **1** have been previously noted.[1]
6. Burger, U.; Mazenod, F. *Tetrahedron Lett.* **1976**, 17, 2885.
7. Trace metal catalysis has similarly been shown to complicate dioxetane thermolyses. See Bartlett, P. D.; Baumstark, A. L.; Landis, M. E. *J. Am. Chem. Soc.* **1974**, 96, 5557.
8. a) Kaplan, L.; Wilzbach, K. E. *J. Am. Chem. Soc.* **1968**, 90, 3291.
   b) Harman, P. J.; Kent, J. E.; O'Dwyer, M. F.; Griffith, D. W. T. *J. Phys. Chem.* **1981**, 85, 2731.
9. Scott, L. T.; Kirms, M. A. *J. Am. Chem. Soc.* **1981**, 103, 5875.
10. For example, see Scott, L. T. *Acc. Chem. Res.* **1982**, 15, 52.
11. We are grateful to the National Science Foundation (CHE 8117318) for support of this work.

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