

Use of the Diels-Alder Reaction as a Criterion of Aromaticity in 4-Heteracyclohexa-2,5-dienones

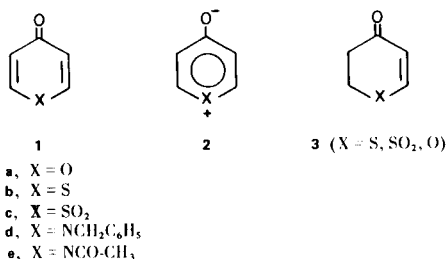
Jerry A. Hirsch,* Raymond W. Kosley, Jr. (1), Richard P. Morin,
George Schwartzkopf, and Ronald D. Brown

Department of Chemistry, Seton Hall University, South Orange, New Jersey 07079

Received March 3, 1975

A recent review (2) of the aromaticity of heterocycles prompts us to report our studies of the possible use of the Diels-Alder reaction to evaluate the heteroaromatic character of 4*H*-pyran-4-one (**1a**), 4*H*-thiopyran-4-one (**1b**) and its 1,1-dioxide (**1c**), and two 4*H*-pyrid-4-ones (**1d** and **1e**). The ability of these systems to behave as dienophiles on treatment with 2,3-dimethyl-1,3-butadiene (**3**) should be inversely related to the extent to which they possess heteroaromatic delocalization (2,4) (as in **2**). In localized form, strong resemblance to the reactivity of *p*-benzoquinone (**5**) should be encountered. Reaction of 4*H*-thiopyran-4-one-1,1-dioxide (**1c**) with 1,3-butadiene has been reported (6) to occur slowly at room temperature and more rapidly at higher temperatures, a result consistent with the expected lack of aromatic delocalization involving the sulfone group (6-8).

Only sulfone **1c** was found to behave as a dienophile toward 2,3-dimethyl-1,3-butadiene in refluxing benzene, toluene, xylene, or dioxane over periods of several weeks. This is in marked contrast to the corresponding dihydro systems **3**, which undergo Diels-Alder reactions (9) and photochemical cycloadditions (10), and to photochemical cycloadditions of substituted 4-pyrones (11). Based on the results of Fehnel and Carmack (6), the ease of Diels-Alder reactivity of sulfone **1c** was somewhat surprising (see Experimental Section).



Because of reported (12) 1-acetyl-4-pyridone (**1e**) - 4-acetoxypyridine equilibria (13) in solution and reported (14) solvent effects on 2-pyridone - 2-hydroxypyridine tau-

merizations, higher temperatures (in a bomb) and higher pressures (15,16) (up to 5 atmospheres) were utilized. However, substrates **1a** and **1e** still showed no dienophilic behavior. The ability of 2*H*-pyran-2-ones to function as dienophiles (17) and as dienes (17,18) and the absence of this behavior in 4*H*-pyran-4-one (**1a**) suggests greater electron delocalization in the latter compound. Similar conclusions apply to the 4*H*-pyrid-4-ones relative to the 2*H*-pyrid-2-ones (19).

EXPERIMENTAL

The following compounds were prepared by the indicated literature procedures with slight modification: 4*H*-pyran-4-one (20) (**1a**), 4*H*-thiopyran-4-one (21) (**1b**), 4*H*-thiopyran-4-one 1,1-dioxide (6,22) (**1c**), 1-benzyl-4-pyridone (23) (**1d**), and 1-acetyl-4-pyridone (12) (**1e**). Compounds **1a** and **1e** were quite hygroscopic, so the Diels-Alder reaction was performed separately on anhydrous and hydrated forms. Commercially available 2,3-dimethyl-1,3-butadiene (Aldrich Chemical Co.) was used without further purification. All solvents were dried prior to use.

In a typical Diels-Alder reaction, 2 mmoles of substrate (**1**) was combined with 1 mmole of diene in 5 ml. dried solvent.

Reaction of 4*H*-Thiopyran-4-one 1,1-dioxide (**1c**) with 2,3-Dimethyl-1,3-butadiene.

A solution of 1.45 g. (17.5 mmoles) of 2,3-dimethyl-1,3-butadiene in 2 ml. of dry benzene was added to 0.5 g. (3.5 mmoles) of **1c** in 5 ml. dry benzene. The resulting light yellow solution was refluxed for 6 hours (no **1c** observed by tlc analysis). Column chromatography (1:1 v/v chloroform:carbon tetrachloride, silica gel) followed by sublimation (125°, 1 mm Hg) provided 0.47 g. (60% yield) of the *cis*-fused 1:1 adduct: ir (chloroform) 1690 (conj. C=O), 1310 and 1120 cm⁻¹ (SO₂); nmr (deuteriochloroform): δ 1.65 (s, 6, CH₃), 2.37 (broad m, 4, allylic), 3.67 (broad m, 2), 6.35 (d, *J* = 11 Hz, 1, = CH-CO (9)), 7.05 (d of d, *J* = 11 and 2.5 Hz, 1, = CH-SO₂ (9)).

Anal. Calcd. for C₁₁H₁₄SO₃: C, 58.38; H, 6.24; S, 14.17. Found: C, 58.25; H, 6.36; S, 14.13.

REFERENCES

- (1) NSF Summer Undergraduate Research Participant, 1970;

Bell Laboratories Summer Research Fellow, 1971.

(2) M. J. Cook, A. R. Katritzky, and P. Linda, *Adv. Heterocyclic Chem.*, **17**, 255 (1974).

(3) A. Wasserman, "Diels-Alder Reactions," Elsevier, Amsterdam, 1965; J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961).

(4) R. Mayer, W. Broy, and R. Zahradnik, *Adv. Heterocyclic Chem.*, **8**, 219 (1967).

(5) L. W. Butz and A. W. Rylina, *Org. Reactions*, **5**, 136 (1949); R. D. Rieke, K. White, and E. McBride, *J. Org. Chem.*, **38**, 1430 (1973); K. T. Finley, "The Chemistry of the Quinonoid Compounds," Ed. S. Patai, Wiley, New York, 1974, p. 986 ff.

(6) E. A. Fehnel and M. Carmack, *J. Am. Chem. Soc.*, **70**, 1813 (1948).

(7) C. Müller and A. Schweig, *Tetrahedron*, **29**, 3973 (1973).

(8) N. Ishibe, K. Hashimoto, and M. Sunami, *J. Org. Chem.*, **39**, 103 (1974) and references therein.

(9) J. Kattenberg, E. R. de Waard, and H. O. Huisman, *Tetrahedron*, **30**, 463 (1974) and private communication.

(10) P. Margaretha, *Ann. Chem.*, 727 (1973), *Tetrahedron*, **29**, 1317 (1973), and references therein.

(11) P. Yates and D. J. MacGregor, *Can. J. Chem.*, **51**, 1267 (1973), and references therein.

(12) I. Fleming and D. Philippides, *J. Chem. Soc. (C)*, 2426 (1970).

(13) This type of equilibrium was not observed with **1d**, for which purpose an authentic sample of 4-benzyloxypyridine was prepared.

(14) P. Beak and F. S. Fry, Jr., *J. Am. Chem. Soc.*, **95**, 1700 (1973).

(15) J. R. McCabe and C. A. Eckert, *Accounts Chem. Res.*, **7**, 251 (1974), and references therein.

(16) Subsequent to these experiments, significantly higher pressures were utilized in completely different systems to promote (4+2) cycloadditions: W. G. Dauben and A. P. Kozikowski, *J. Am. Chem. Soc.*, **96**, 3664 (1974).

(17) T. Imagawa, N. Sueda, and M. Kawanisi, *Tetrahedron*, **30**, 2227 (1974); D. L. White and D. Seyferth, *J. Org. Chem.*, **37**, 3545 (1972).

(18) T. Sasaki, K. Kanematsu, Y. Yukimoto, and T. Hiramatsu, *J. Am. Chem. Soc.*, **96**, 2536 (1974); E. J. Corey and D. S. Watt, *ibid.*, **95**, 2303 (1973); A. K. Bahl and W. Kemp, *J. Chem. Soc. (C)*, 2268 (1971); N. P. Shusherina, N. D. Dmitrieva, E. A. Luk'yanets, and R. Ya. Levina, *Russ. Chem. Rev. (Engl)*, **36**, 175 (1967); and references in these papers.

(19) H. Tieckelmann, "The Chemistry of Heterocyclic Compounds," Vol. 14, Supplement, Part 3, Ed. R. A. Abramovitch, Wiley, New York, 1974, Chapter 12.

(20) E. R. Riegel and F. Zwiilmeyer, *Org. Syntheses Coll. Vol. II*, 126 (1943).

(21) F. Arndt and N. Bekir, *Ber.*, **63**, 2393 (1930) from 4-thia-cyclohexanone as prepared by P. Johnson and G. A. Berchtold, *J. Org. Chem.*, **35**, 584 (1970).

(22) G. Traverso, *Chem. Ber.*, **91**, 1224 (1958).

(23) A. R. Katritzky and R. A. Jones, *J. Chem. Soc.*, 2947 (1960); m.p. 112.5-114° (lit. 109-111°).