and a small amount (~10%) of $(CH_3)_3PbI$, as shown by mass studies showing the expected isotope pattern. For the 208 isotope: *m/e* 380, $(CH_3)_3PbI$; *m/e* 65, $(CH_3)_2PbI$; *m/e* 350, CH_3PbI; *m/e* 253, PbI; *m/e* 223, CH_3Pb; and *m/e* 208, Pb.

Nickel slurries were prepared as described for tin slurries, except that ~1 g of Ni was codeposited with about 60 mL of solvent in about 1 h. The colors of the matrices were: toluene (red-brown), THF (yellow), and hexane (black). Generally, THF was employed as the slurry solvent, the resultant very fine black slurry was transferred by syringe to a three-necked round-bottom flask equipped with a reflux condenser, addition funnel, stirring bar, and N_2 bubbler, and about 40 mmol of alkyl halide were slowly added (15 min) followed by reflux for about 20 h. The volatile products formed (no stable organometallics were isolable) were fractionated by trap-to-trap distillation through cold traps at -77, -116, and -196 °C. The gases were analyzed by PV measurements and GLC techniques.

When less volatile products were being analyzed, no trap-to-trap distillation was carried out. The reaction mixture was simply filtered and GLC analyses carried out. For example, biphenyl and bibenzyl were analyzed on a 5 ft × 0.25 in. SE-30 column at 170 °C (bibenzyl was used as an internal standard when biphenyl was being analyzed and vice versa).

Acknowledgment. We gratefully acknowledge the National Science Foundation (CHE-7402713) for generous support and Thomas Groshens for experimental assistance.

Registry No. Aluminum, 7429-90-5; indium, 7440-74-6; zinc, 7440-66-6; cadmium, 7440-43-9; tin, 7440-31-5; lead, 7439-92-1; nickel, 7440-02-0; phenyl iodide, 591-50-4; phenyl bromide, 108-86-1; ethyl iodide, 75-03-6; diethyliodoindium, 31145-95-6; ethyldiiodoindium, 37865-57-9; methyl iodide, 74-88-4; iododimethylindium, 14799-83-8; diiodomethylindium, 37865-56-8; methyl dibromide, 74-95-3; methyl diiodide, 75-11-6; diethylcadmium, 592-02-9; ethyliodocadmium, 17068-35-8; triiodomethyltin, 3236-97-3; diiododimethyltin, 2767-49-9; iodotrimethyltin, 811-73-4; tetraiodotin, 7790-47-8; iodotrimethyllead, 17546-36-0; propyl bromide, 106-94-5; isopropyl bromide, 75-30-9; butyl bromide, 109-65-9; 2-bromobutane, 78-76-2.

Orbital Interactions. 5. Through-Space Effects of Substituents on the Reactivity of a Double Bond toward Diels-Alder and Epoxidation Reactions[1]

Michael N. Paddon-Row,*[2a] Harish K. Patney,[2a,c] and Ronald N. Warrener[2b]

Chemistry Departments, New South Wales Institute of Technology, Broadway, N.S.W. 2007, Australia, and Australian National University, Canberra, A.C.T. 2600, Australia

Received January 3, 1979

A series of 9-substituted octahydrodimethanonaphthalenes (**17a–f**) have been synthesized, and the kinetics of their Diels–Alder cycloaddition reactions with 3,6-di(2′-pyridyl)-*s*-tetrazine (**2**) have been determined. The rate of reaction of the syn alcohol **17d** is strongly solvent dependent, being some 500 times faster in Me_2SO than in $CHCl_3$ solution. This result is explained in terms of the different conformational preferences of the hydroxyl group in the two solvents, being intramolecularly H bonded (**26**) in $CHCl_3$ and intermolecularly H bonded (**27**) in Me_2SO. The remaining compounds lie in the order of decreasing reactivity **17e** > **17a** > **17f** > **17c** in both $CHCl_3$ and Me_2SO solvents. Activation parameters have been measured for the reactions of **17a**, **17c**, **17e**, **17f**, and the octahydrodimethanonaphthalen-2-one **18** with the *s*-tetrazine **2**. All these results may be explained in terms of a PMO treatment of orbital interactions through space (OITS) between the 9-substituent and the double bond of **17**. The presence of OITS in the ketone (**17c**) is further supported from UV spectral measurements of the compounds **17a**, **17c**, **18**, **29**, and **30**. The relative rates of epoxidation of the compounds **17a**, **17c**, **17e**, and **17f** by *m*-chloroperbenzoic acid were determined by using the competition method. The relative reactivities were in the same order as those for the tetrazine cycloaddition reactions, i.e., **17e** > **17a** > **17f** > **17c**, and are in agreement with the PMO predictions.

A few years ago we reported that the rates of Diels–Alder reactions of several tricyclononadienes (**1a–d**) with 3,6-di(2′-pyridyl)-*s*-tetrazine (**2**) to give **3a–d** (Scheme I) were sensitive to the nature of the substituent at the 9-position, the order of reactivity being syn methoxy (**1c**) > **1a** > ketone (**1d**).[3,4] The same sequence of reactivities was observed in the epoxidation of these compounds.[5]

Using a frontier molecular orbital (FMO) model, Paddon-Row[6] explained these observations in terms of orbital interactions through space (OITS)[7] operating between the substituents and the cyclobutene double bond. Thus the n_1–π interaction of the syn methyl ether, in the conformation depicted by **4**, is predicted to enhance the dienophilicity of the cyclobutene toward dienes having inverse electron demand[9] such as **2**. The FMO model also explained the 470-fold increase in the reactivity of the syn

---

[1] Part 4: M. N. Paddon-Row, H. K. Patney, and R. N. Warrener, *J. Chem. Soc., Chem. Commun.*, 296 (1978).

[2] (a) New South Wales Institute of Technology. (b) Australian National University. (c) ARGC Research Assistant 1976–1978.

[3] I. W. McCay, M. N. Paddon-Row, and R. N. Warrener, *Tetrahedron Lett.*, 1401 (1972).

[4] M. N. Paddon-Row and R. N. Warrener, *Tetrahedron Lett.*, 1405 (1972).

[5] M. G. Hymann, M. N. Paddon-Row, and R. N. Warrener, *Synth. Commun.*, **5**, 107 (1975).

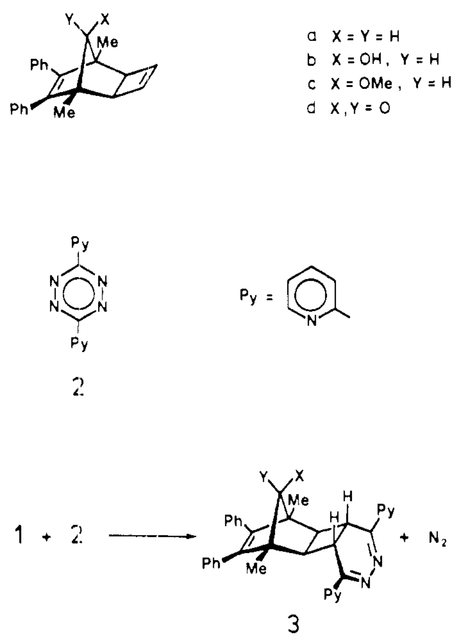
[6] M. N. Paddon-Row, *Tetrahedron Lett.*, 1409 (1972); M. N. Paddon-Row cited in I. W. McCay, Ph.D. Thesis, Australian National University, Canberra, 1971. A similar FMO model has been advanced by Sustmann to account for substituent effects on the Diels-Alder and 1,3-dipolar cycloaddition reactions.[8]

[7] Review: R. Hoffmann, *Acc. Chem. Res.*, **4**, 1 (1971).

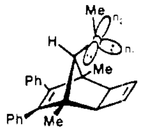
[8] R. Sustmann, *Tetrahedron Lett.*, 2717, 2721 (1971).

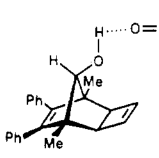
[9] J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **6**, 16 (1967).

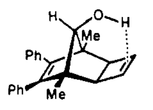
Scheme I



alcohol **1b** toward **2** upon change of solvent from $CHCl_3$ to Me_2SO. Intermolecular H bonding to Me_2SO leads to the prevalence of conformation **5** in this solvent and thence similar reactivity to **1c** (cf. **4**). In $CHCl_3$, however, intramolecular H bonding leads to **6** in which the activating $n_1-\pi$ interaction is absent.

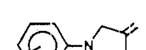

4

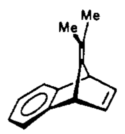

5


6

Subsequent to these findings other workers have reported on various aspects of OITS operating in Diels–Alder reactions.

The reactivities of 1-aryl-3,4-dimethylenepyrrolidines **7** toward acrolein are affected by the nitrogen lone pair–diene LUMO interaction.[10] The enhanced dienophilicity of **8** compared with **9** has been explained in terms of OITS between the double bonds of the former molecule.[11] Hyperconjugative interactions have been invoked to account for the (Diels–Alder) reactivities of **10** (compared to **11**)[12,13] and **13** (compared to **12**).[14]


7


8

The stereoselective formation of the endo, anti adduct **14** from the reaction of diazoethane with 7-chloronorbornadiene is remarkable and has been explained in terms of OITS,[15,16] as has the formation of the endo, syn adducts **15** from the reaction of 7-oxy-substituted norbornadienes with the appropriate cyclopentadiene.[17-19]

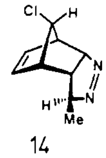

9

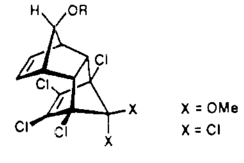

10


11


12


13


14



15

As part of a long-term objective of obtaining a quantitative relationship between the reactivity of an unsaturated center and the nature and the geometrical disposition of distal substituents[21] we have synthesized the methanonaphthalenes **17a–f** and **18** and measured their reactivities toward the tetrazine **2** and *m*-chloroperbenzoic acid. These compounds are more suitable than **1** for studying the chemical consequences of OITS because (a) substituent inductive effects will be smaller in the former series, and (b) the interacting centers in **17** are spatially closer than those in **1** (i.e., the oxygen atom–double bond separation is ca. 1.8 Å in **17e** compared with ca. 2.5 Å in **1c**.[23]

Results and Discussion

Syntheses. The anti alcohol **17b** was prepared according to a modified procedure of Battiste and his coworkers,[24] i.e., by the Gassman–Pape[25] reductive dechlorination of **16**.[26] Standard methods were used to

---

[10] P. V. Alston and R. M. Ottenbrite, *J. Org. Chem.*, **40**, 322 (1975).

[11] H. R. Pfaendler, H. Tanida, and E. Haselbach, *Helv. Chim. Acta*, **57**, 383 (1974).

[12] (a) W. L. Jorgensen and W. T. Borden, *J. Am. Chem. Soc.*, **95**, 6649 (1973); (b) W. L. Jorgensen and W. T. Borden, *Tetrahedron Lett.*, 223 (1975); (c) W. L. Jorgensen, *J. Am. Chem. Soc.*, **97**, 3082 (1975).

[13] P. T. van Duijnen, P. van der Ploeg, H. Hogeveen, and W. F. J. Huurdeman, *Tetrahedron Lett.*, 573 (1975).

[14] (a) M. Hardy, P.-A. Carrupt, and P. Vogel, *Helv. Chim. Acta*, **59**, 1685 (1976); (b) A. Chollet, C. Mahaim, C. Foetisch, M. Hardy, and P. Vogel, *Helv. Chim. Acta*, **60**, 59 (1977).

[15] M. Franck-Neumann and M. Sedrati, *Angew. Chem., Int. Ed. Engl.*, **13**, 606 (1974).

[16] For a cautionary note on this interpretation see J. W. Wilt and W. N. Roberts, *J. Org. Chem.*, **43**, 170 (1978).

[17] (a) K. Mackenzie, *Tetrahedron Lett.*, 1203 (1974); (b) K. B. Astin and K. Mackenzie, *J. Chem. Soc., Perkin Trans. 2*, 1004 (1975); (c) M. A. Battiste, J. F. Timberlake, and H. Malkus, *Tetrahedron Lett.*, 2529 (1976); (d) L. T. Byrne, A. R. Rye, and D. Wege, *Aust. J. Chem.*, **27**, 1961 (1974).

[18] Similar results were obtained in the reaction between phenyl azide and *anti*-7-*tert*-butoxynorbornadiene: G. W. Klumpp, A. H. Veefkind, J. V. der Schaaf, and F. Bickelhaupt, *Justus Liebigs Ann. Chem.*, **706**, 47 (1967).

[19] Fukui's recently developed nonequivalent orbital extension method[20] could show promise in treating the stereoselectivity of cycloaddition reactions.[17,18]

[20] S. Inagaki, H. Fujimoto, and K. Fukui, *J. Am. Chem. Soc.*, **98**, 4054 (1976).

[21] Quantitative correlations, such as that between the ionization potential of the substituent and the reaction rate, have been obtained for Diels–Alder and 1,3-dipolar cycloaddition reactions of compounds in which the substituent is *directly* bonded to the reaction zone.[22]

[22] R. Sustmann and R. Schubert, *Angew. Chem., Int. Ed. Engl.*, **11**, 840 (1972); R. Sustmann and H. Trill, *ibid.*, **11**, 838 (1972).

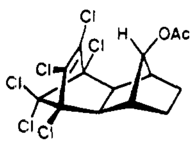
[23] These distances were estimated from Dreiding models.

[24] J. Haywood-Farmer, H. Malkus, and M. A. Battiste, *J. Am. Chem. Soc.*, **94**, 2209 (1972).

[25] P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964).

[26] Unfortunately direct addition of cyclopentadiene to the tetrahydropyranyl ether of *anti*-7-norbornenol, in accordance with the procedure of Winstein and Hansen,[27] gave an unacceptable yield (ca. 5%) of **17b**. Using the MEM ether[28] of the norbornenol in place of the tetrahydropyranyl ether likewise was unsuccessful.

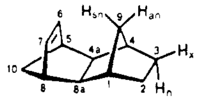
[27] S. Winstein and R. L. Hansen, *J. Am. Chem. Soc.*, **82**, 6206 (1960); S. Winstein and R. L. Hansen, *Tetrahedron Lett.*, 4 (1960).



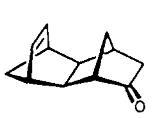
16

prepare the remaining members of **17** (Experimental Section). Isolation of the highly acid labile syn alcohol **17d** from its product of rearrangement (**19**)[29] was achieved by column chromatography under basic conditions.

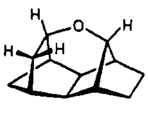
Direct addition of cyclopentadiene to norbornene or norbornen-5-one at elevated temperatures led to good yields of the parent hydrocarbon **17a**[31] and the ketone **18**, respectively. In contrast, anti-7-oxy-substituted norbornenes are essentially unreactive under these conditions.[30] The low reactivity of the 7-oxy-substituted norbornenes cannot be due to the inductive effect of the substituent for this effect is also present in norbornen-5-one. A plausible reason could be due to the decrease in the envelope angle between the methano and etheno bridges resulting from buttressing interactions between the 7-substituent and the ethano bridge. Therefore, the approach of the diene to an anti-7-substituted norbornene will be more sterically congested.



17a



18

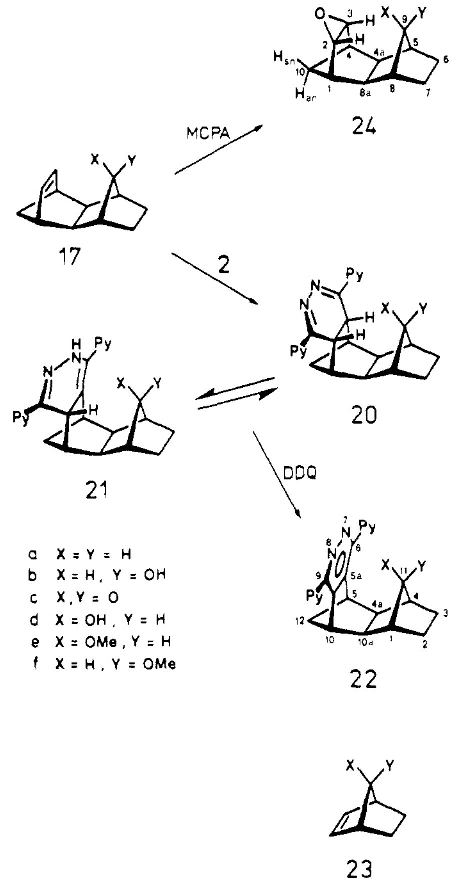


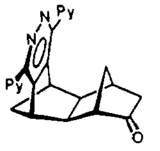
19

Reactions with the *s*-Tetrazine 2. The methanonaphthalenes **17a–f** readily reacted with the tetrazine **2** in chloroform solution to give the corresponding 4,5-dihydropyridazines **20a–f** in essentially quantitative yields (Scheme II). However, purification of these adducts was difficult because of their conversion, in varying degrees, to the corresponding isomeric 1,4-dihydropyridazines **21a–f**. Therefore, the adducts, with the exception of those of the syn alcohol **20d** and the syn methoxy compound **20e**, were oxidized to the corresponding pyridazines (**22**) with dichlorodicyano-*p*-benzoquinone (DDQ). The pyridazine **22d** could not be prepared either through DDQ oxidation of **20d** or from $LiAlH_4$ reduction of the pyridazine ketone **22c**: only intractable polymeric material was formed. DDQ oxidation of the adduct **20e** gave the corresponding pyridazine **22e** accompanied by some unidentified material. So far we have been unsuccessful in obtaining a pure sample of **22e**. The pyridazine **25** was readily obtained through DDQ oxidation of the adduct formed from the ketone **18** and the tetrazine **2**.

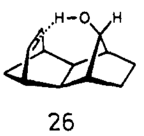
The ^1H NMR spectra of the oxidized adducts **22** nicely reveal the geometrical relationship and the proximity of the pyridazine ring to the endo methano bridge. The spectral data are reported in detail in the Experimental Section, but the following points are noteworthy. The syn (H_{sn}) and anti protons (H_{an}) of **17a** occur at δ 1.97 and 0.48, respectively.[24] However, in the corresponding pyridazine adduct **22a** the syn proton (X) resonates at δ −0.66 which corresponds to an upfield shift of 2.63 ppm. The anti proton (Y) experiences a much smaller upfield shift, resonating at 0.26 ppm. The results are in complete agreement with the expectation that the syn, and to a lesser extent the anti, protons are located within the shielding zone of the heterocyclic ring. Similarly, the syn proton X in the anti methoxy compound **22f** (ca. δ 1.7) is strongly shielded with respect to that in the precursor (**17f**, δ 4.4) by 2.7 ppm.

Scheme II

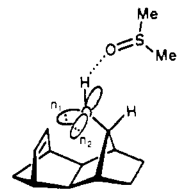




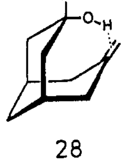
25



26



27



28

Kinetic Studies of the Reactions with *s*-Tetrazine. The kinetics of the reactions of the methanonaphthalenes **17a–f** and **18** with the *s*-tetrazine **2** were followed spectrophotometrically by monitoring the loss of absorbance at 550 nm. In each case the reaction followed clean second-order kinetics, and the results are presented in Table I together with the activation parameters. Also included are the results for norbornene (**23a**) and *anti*-7-methoxynorbornene (**23f**).

---

[28] E. J. Corey, J. Gras, and P. Ulrich, *Tetrahedron Lett.*, 809 (1976).

[29] For example, substantial rearrangement had occurred (>50%) within 10 min in untreated $CDCl_3$ solution.

[30] Under conditions that led to ca. 60% conversion of 5-norbornenone to **18** (Experimental Section), the tetrahedropyranyl ether of *anti*-7-norbornenol was recovered unchanged.

[31] A. P. Marchand and J. E. Rose, *J. Am. Chem. Soc.*, **90**, 3724 (1968).

Table I. Kinetic Data for the Reactions of Methanonaphthalenes with the Tetrazine 2

compd	solvent	temp, °C	10^2k, (L mol^{-1} s^{-1})	E_a, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	k_{rel} (28.8 °C)
17a	$CHCl_3$	28.8	12.86			1
17b, anti OH	$CHCl_3$	28.8	5.14			0.4
17c, ketone	$CHCl_3$	28.8	0.3			0.023
17d, syn OH	$CHCl_3$	28.8	0.92			0.071
17e, syn OCH_3	$CHCl_3$	28.8	77.2			6
17f, anti OCH_3	$CHCl_3$	28.8	4.82			0.38
18	$CHCl_3$	28.8	1.57			0.12
17a	Me_2SO	28.3	15.1	41.9	−129.0	0.98
		38.3	27.2			
		45.9	37.4			
		54.7	59.2			
17b, anti OH	Me_2SO	28.8	12.88			1
17c, ketone	Me_2SO	33.0	2.54	50.4	−118.5	0.14
		43.4	4.55			
		54.8	9.58			
		61.7	13.49			
17d, syn OH	Me_2SO	28.8	462.0			35.7
17e, syn OCH_3	Me_2SO	22.9	158.0	31.5	−142.3	14.0
		31.6	234.6			
		38.8	302.4			
17f, anti OCH_3	Me_2SO	30.7	6.48	37.7	−150.9	0.35
		35.3	8.50			
		40.3	10.90			
		45.7	13.04			
18	Me_2SO	34.4	4.86	43.7	−135.7	0.28
		41.6	7.12			
		49.6	10.86			
23a	Me_2SO	32.4	36.57	34.3	−148.8	2.4
		39.0	48.54			
		49.5	74.7			
23f	Me_2SO	40.4	0.537	49.4	−119.2	0.2
		49.1	0.900			
		55.3	1.267			

Table II. Solvent Effects on the Rate Constants for the Reactions of Methanonaphthalenes with Tetrazine 2

compd	k_{Me_2SO}/k_{CHCl_3} (28.8 °C)	compd	k_{Me_2SO}/k_{CHCl_3} (28.8 °C)
17a	0.98	**17e**, syn OCH_3	2.3
17b, anti OH	2.5	**17f**, anti OCH_3	0.94
17c, ketone	6.1	**18**	2.3
17d, syn OH	503		

The highly negative entropies of activation are consistent with a concerted reaction,[32] and the relative insensitivity of the reaction rates of the majority of compounds to solvent polarity (Table II) supports the assumption that little or no charge separation occurs in the transition state.[9,32]

The syn alcohol **17d** is quite exceptional, however, in that it exhibits a remarkable rate dependence upon the nature of the solvent. Thus the rate is increased by a factor of 503 upon change of solvent from $CHCl_3$ to Me_2SO, a behavior reminiscent of the syn alcohol **1b**.[3] As in the case of **1b** the exceptional behavior of syn alcohol **17d** may be explained in terms of the different conformational preferences of the hydroxyl group in the two solvents. A single OH stretching vibration for **17d** is observed at 3554 cm^{-1} (CCl_4) which is concentration independent. The free OH stretching vibration of the anti alcohol **17b** occurs at 3631 cm^{-1} (CCl_4). We conclude that the syn alcohol **17d** exists almost exclusively in the intramolecularly H-bonded form (**26**) in CCl_4 and that the OH···π bond is unusually strong as judged from the wavenumber difference, $\Delta\bar{\nu}$ (77 cm^{-1}), between the syn and anti alcohols.[33] To our knowledge the only unsaturated alcohol which has a larger $\Delta\bar{\nu}$ value is **28** ($\Delta\bar{\nu}$ = 110 cm^{-1}).[34] The ^1H NMR spectrum of syn alcohol **17d**, also run in CCl_4, is also consistent with strong H bonding between the OH and the proximate π system since both the olefinic protons and the OH proton are shifted downfield by 0.14 and 0.6 ppm, respectively, compared with the corresponding resonances in the anti alcohol **17b**. We expect that the H-bonded form (**26**) should prevail in weakly H-bonding solvents such as $CHCl_3$. The double bond is thereby deactivated in its reaction with the tetrazine **2** (vide infra). A measure of this deactivation is provided by the observation that the syn alcohol **17d** is some 6 times *less* reactive than the corresponding anti alcohol **17b** toward the tetrazine **2** in $CHCl_3$ solution.

In dipolar aprotic solvents such as Me_2SO, syn alcohol **17d** should be completely H bonded to the solvent because π bonds are known to be much weaker H acceptors than oxygen atoms.[35] Steric constraints force the alcohol–Me_2SO H-bonded complex to adopt the conformation **27** in which the oxygen sp^3-hybridized lone pair of electrons, n_1, is directed toward the double bond. OITS between n_1 and the π bond (vide infra) enhance the dienophilicity of the double bond toward dienes of inverse electron demand. Thus, in contrast to the reactions in $CHCl_3$ solution, the syn alcohol **17d** is now some 36 times *more* reactive than the anti alcohol **17b** in Me_2SO solution toward the tet-

---

[32] A. Wasserman, "Diels-Alder Reactions", American Elsevier, New York, 1965.

[33] For reviews concerning hydrogen bonding between alcohols and unsaturated linkages see M. Tichy in "Advances in Organic Chemistry: Methods and Results", Vol. 5; R. A. Raphael, E. C. Taylor, and H. Wynberg, Eds., Wiley, New York, 1965, p 115; P. von R. Schleyer, C. Wintner, D. S. Trifan, and R. Bacskai, *Tetrahedron Lett.*, 1 (1959); L. Joris, P. von R. Schleyer, and R. Gleiter, *J. Am. Chem. Soc.*, **90**, 327 (1968).

[34] C. A. Grob and H. Katayama, *Helv. Chim. Acta*, **60**, 1890 (1977).

[35] S. N. Vinogradov, "Hydrogen Bonding", Van Nostrand-Reinhold, New York, 1971; M. D. Joesten and L. J. Schaad, "Hydrogen Bonding", Marcel Dekker, New York, 1974.

razine **2**. The premise that the reactivity of the syn alcohol **17d** depends on the conformation of the hydroxyl group is further supported by the observation that the syn alcohol **17d** and the syn methyl ether **17e** exhibit comparable reactivities toward the tetrazine **2** in Me_2SO solution whereas in $CHCl_3$ solution **17d** is 85 times less reactive than **17e**. The syn ether **17e** adopts the conformation similar to that shown in **27** in *all* solvents because of steric factors.

A *lower* estimate of the ratio, K, of the intramolecularly $\pi \cdots H$ bonded form (**26**) to the free non-H-bonded conformations in $CHCl_3$ solution may be obtained by assuming that the reaction of the tetrazine **2** occurs exclusively with the non-H-bonded conformations of **17d**. Also, if the free and the H-bonded forms are in rapid equilibrium, the observed rate constant k_o is then given by the expression

$$k_o = k/K$$

where K has been defined previously and k is the rate constant for the Diels–Alder reaction step which may be taken to be equal to that for the corresponding syn ether **17e**. Therefore, K is estimated to be at least 85 (28 °C; $CHCl_3$ solution), in which case 98.8% of the alcohol exists as the intramolecularly H-bonded form (**26**). These figures would be larger if the H-bonded form (**26**) is able to react with the tetrazine.

Examination of the data in Table I reveals that the syn-methoxy compound **17e** is faster than the unsubstituted **17a** by a factor of 6 ($CHCl_3$) or 14 (Me_2SO) whereas the ketone **17c** is 44 ($CHCl_3$) or 7 (Me_2SO) times slower than **17a**. The observed rate sequence (**17e** > **17a** > **17c**) in either solvent is in complete agreement with our PMO model.[6] In $CHCl_3$ the syn-methoxy compound **17e** is 261 times more reactive than the ketone **17c** *despite the severe steric congestion* which must be present in the transition state for the reaction between the ether **17e** and tetrazine **2**.

That the substituent effects are transmitted through space and not inductively through bonds is supported by the observation that the reactivities of the methyl ethers, *syn*-**17e** and *anti*-**17f**, are comparable as are those of the ketones **17c** and **18**.

Interestingly, the E_a for the reaction of the anti ether **17f** is smaller than that for unsubstituted **17a** by some 4 kJ mol^{-1}. Clearly, the inductive (I) effect of the methoxyl group cannot be responsible for this observation since electron withdrawal from the double bond by this group should have precisely the opposite effect on the reactivity of this compound toward dienes having inverse electron demand. In support of this argument we observe that E_a for *anti*-7-methoxynorbornene (**23f**) is appreciably greater than that for norbornene (**23a**) (Table I). In **23f** the methoxy group is separated by only three σ bonds from the double bond, and inductive effects should be more apparent.

Perturbational MO (PMO) Treatment. PMO theory at the frontier orbital level of approximation has enjoyed considerable success in explaining a large number of structure–reactivity data,[36] including substituent effects on the rates of Diels–Alder reactions.[6,8,36b] In this section we describe how PMO theory provides a rationalization of the reactivity data presented in this paper in terms of OITS.

Table III. Ionization Potential Data

compd	ionization type	IP, eV	ref
norbornene	π	8.97	46
MeOEt	n	9.81	47
MeF	n	12.74	48
MeCl	n	11.28	48
i-PrBr	n	10.27	49
i-PrI	n	9.47	49
Me_2S	n	8.67	47
Me_3N	n	7.82	50

Consider the approach of *s*-tetrazine (T) to norbornene (N) in a direction leading to the Diels–Alder reaction. Extended Hückel calculated eigenvalues[37–40] of T and N reveal that HOMO(N)–LUMO(T) is the dominant stabilizing frontier interaction because the energy separation between these orbitals (1 eV) is less than that between HOMO(T)–LUMO(N) (5.8 eV). Therefore, a substituent, X, in the 9-position of the methanonaphthalene **17** which elevates the π(HOMO) energy through OITS will lead to a narrowing of the HOMO(N)–LUMO(T) energy gap. The activated complex is more stabilized than in the absence of X, and the reaction rate should be enhanced. Likewise, a substituent X of **17** which depresses the π energy of the double bond is predicted to retard the rate of reaction. These predictions hold true only for those reactions of **17** with reagents (R) having low-lying LUMO's, such as dienes having inverse electron demand, thereby ensuring the dominance of the HOMO(**17**)–LUMO(R) interaction. The effect of X on the π energy of the double bond may be analyzed by using PMO theory.

Consider the syn ether **17e** which, by dint of steric factors, exists in a conformation similar to that depicted for the syn alcohol **17d** in Me_2SO, i.e., **27** (assumed C_s symmetry). As a consequence of the structurally imposed proximity of the methoxyl oxygen and the double bond (ca. 1.8 Å) the two nonbonding atomic orbitals, n_1 and n_2 (see **27**), of the oxygen atom enter into symmetry-allowed through-space interactions with the π and π^* MO's of the double bond, respectively. The resulting second-order changes in the energies of the π and π^* MO's, δE, are given by the general expression,[42,43] eq 1, where E_i and E_j are the

$$\delta E_i = S_{ij}^2/(E_i - E_j) \qquad (1)$$

energies of the π (or π^*) and n_1 (or n_2) orbitals, respectively, and S_{ij} is the overlap integral between the appropriate interacting orbitals ($S_{\pi n_1}$ or $S_{\pi^* n_2}$). Focusing attention on the π–n_1 interaction, we deduce from expression 1 that if E_i ($i = \pi$) > E_j ($j = n_1$), then the energy of the π orbital is raised (δE_i is positive). Conversely, the inequality $E_j > E_i$ leads to a lowering of energy of the π MO. In order to

---

(36) (a) M. J. S. Dewar and R. C. Dougherty, "The PMO Theory of Organic Chemistry", Plenum Press, New York, 1975; (b) for an excellent overview of frontier orbital theory at a more simplified level consult I. Fleming, "Frontier Orbitals and Organic Chemical Reactions", Wiley-Interscience, New York, 1976; (c) K. Fukui, *Bull. Chem. Soc. Jpn.*, **39**, 498 (1966).

(37) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); *ibid.*, **40**, 2474 (1963).

(38) A modified version of QCPE Program No. 64, EXTHUC, by E. B. Moore, W. C. Cook, and A. R. M. Rom, was used to perform the EHT calculations. Standard parameters were used.[39]

(39) R. Hoffmann, S. Swaminathan, B. G. Odell, and R. Gleiter, *J. Am. Chem. Soc.*, **92**, 7091 (1970).

(40) Idealized geometries were used, that of norbornene being taken as a compromise between that of norbornadiene and norbornane[41] and that of *s*-tetrazine having D_{2h} symmetry with N–N and C–N bond lengths of 1.32 and 1.36 Å, respectively.

(41) A. Yokozeki and K. Kuchitsu, *Bull. Chem. Soc. Jpn.*, **44**, 2356 (1971); G. Dallinga and L. H. Toneman, *Recl. Trav. Chim. Pays-Bas*, **87**, 805 (1968).

(42) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, 1969; W. T. Borden, "Modern Molecular Orbital Theory for Organic Chemists", Prentice-Hall, Englewood Cliffs, NJ, 1975.

(43) N. D. Epiotis, R. L. Yates, J. R. Larson, C. R. Kirmaier, and F. Bernardi, *J. Am. Chem. Soc.*, **99**, 8379 (1977); N. D. Epiotis, W. R. Cherry, S. Shaik, R. L. Yates, and F. Bernardi, *Fortschr. Chem. Forsch.*, **70**, 1 (1977).

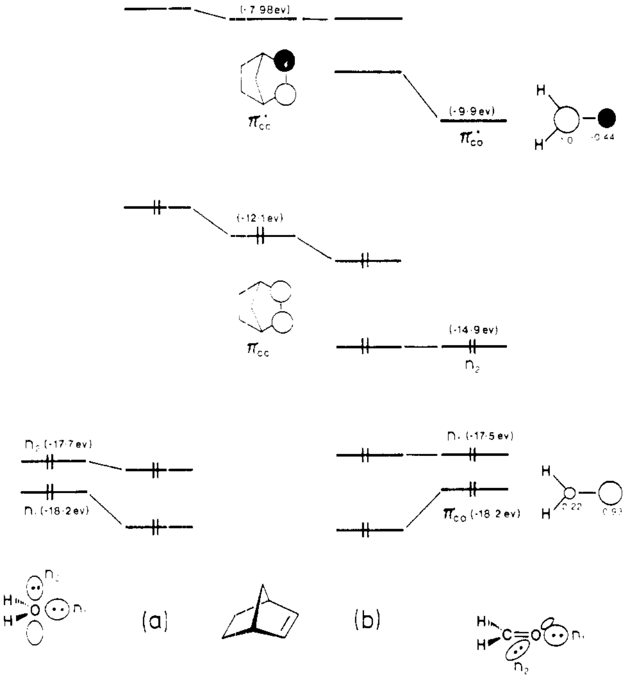


Figure 1. Extended Hückel frontier orbital coefficients and energies of H_2O, norbornene, and H_2CO and the interactions of the π and π^* MO's of norbornene with (a) n_1 and n_2 of H_2O and (b) π, n_1, n_2, and π^* of H_2CO. The "complex" of norbornene with H_2O or H_2CO has C_s symmetry, with the plane of symmetry bisecting the HOH angle of H_2O or the HCH angle of formaldehyde.

assess the energies of lone pairs for a variety of substituents, we made use of Koopmans' theorem[44] in which one-electron orbital energies are approximated by the negative of their ionization potentials (IP). These data, together with the π IP of norbornene (which is a model for **17a**), are given in Table III. Both calculation[45] and experiment (Table III) place the interacting oxygen n_1 orbital of the methoxy substituent below that of the π orbital. The energy of the latter orbital is thereby raised (Figure 1a) which explains the observed rate enhancement of the *syn*-**17e** ether compared with that of **17a**.

On the basis of the IP data given in Table III we predict that halogen substituents also should increase the Diels–Alder reactivity of **17** toward dienes having inverse electron demand.[51] We also predict that the reactivity of a series of X-substituted methanonaphthalenes (**17**) toward these dienes should follow the sequence I > OCH_3 > Br > Cl > F on the grounds that the π (HOMO) MO of **17** is perturbed more strongly by substituents having high-energy lone pairs (i.e., low IP's).

Interestingly, the dimethylamino substituent might cause a *decrease* in the rate of reaction of **17** (X = NH_2) with electron-deficient dienes since its IP is smaller than that of norbornene (Table III). However, this prediction is contingent upon the assumption that the resulting HOMO of **17** (X = NH_2), which has a higher energy than that of unsubstituted **17a**, may be neglected on the grounds that it should contain only a small admixture of the π MO. This assumption is certainly untenable in the case of the methylthio substituent because its IP is practically identical with that of norbornene. OITS in **17** (X = SCH_3) result in a HOMO whose energy is greater compared with that of **17a** but which now contains only ca. 50% π MO character; i.e., the coefficients of the double bond carbon atoms are much smaller for **17** (X = SCH_3) compared with those of **17a**. The stabilization energy of the reaction between the methanonaphthalene and *s*-tetrazine is given by expression 1. It follows, therefore, that replacement of H by SCH_3 reduces the magnitude of both numerator (which depends on the magnitudes of the orbital coefficients at the incipient bonding sites) and denominator of expression 1. Consequently, the SCH_3 group should have little effect on the reactivity of the methanonaphthalene.

The diminished reactivity of the syn alcohol **17d** in $CHCl_3$ solution may be explained in terms of the symmetry-allowed interaction between the π MO and the σ^* MO of the OH bond in the intramolecularly H-bonded form (**26**).[53] This leads to a lowering of the π (HOMO) energy with concomitant charge transfer from the double bond to the hydroxyl group.[54] Both factors deactivate the double bond toward *s*-tetrazine.

Both π and π^* MO's of the carbonyl group in the ketone **17c** have the correct symmetry for mixing with the π MO of the double bond. The overall change in the energy of the latter MO is given by expression 2, where the subscripts

$$\delta E_\pi \alpha \frac{{S_{\pi,\pi\text{CO}}}^2}{E_\pi - E_{\pi\text{CO}}} + \frac{{S_{\pi,\pi\text{CO}^*}}^2}{E_\pi - E_{\pi\text{CO}^*}} \tag{2}$$

refer to the appropriate MO's. If we assume that only the carbon atom of the carbonyl group contributes to the overlap integrals, then (2) may be approximated as eq 3,

$$\delta E_\pi \alpha \frac{C^2}{E_\pi - E_{\pi\text{CO}}} + \frac{C^{*2}}{E_\pi - E_{\pi\text{CO}^*}} \tag{3}$$

where C and C^* are the coefficients of the carbonyl carbon p atomic orbital in the π and π^* MO's, respectively.[56] Extended Hückel calculated eigenvectors and eigenvalues of the π type MO's of norbornene[40] and formaldehyde[57] are given in Figure 1b. Substitution of these data into expression 3 leads us to conclude that although the two terms of 3 have opposite signs, the second term is more important. The π (HOMO) energy of the double bond in ketone **17c** is therefore lowered (Figure 1b), and a diminished rate of reaction is predicted, in agreement with experimental findings.

Reactions of compounds such as **1** and **17** with electron-rich dienes may be analyzed similarly. For these reactions the HOMO(diene)–LUMO(dienophile) inter-

---

[44] T. Koopmans, *Physica* (*Utrecht*), 1, 104 (1933).

[45] Extended Hückel calculations on water place the energies of n_1 and n_2 at −18.2 and −17.7 eV, respectively: M. N. Paddon-Row, unpublished data.

[46] P. Bischof, J. A. Hasmall, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, **52**, 1745 (1969).

[47] D. W. Turner, *Adv. Phys. Org. Chem.*, **4** (1966).

[48] D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley-Interscience, New York, 1970.

[49] F. Brogli and E. Heilbronner, *Helv. Chim. Acta*, **54**, 1423 (1971).

[50] H. Bock, G. Wagner, and J. Kramer, *Tetrahedron Lett.*, 3713 (1971).

[51] We assume that the reactivity of all Diels–Alder reactions with dienes having inverse electron demand are governed by the HOMO(dienophile)–LUMO(diene) interaction.[52]

[52] R. N. Warrener, C. M. Anderson, I. W. McCay, and M. N. Paddon-Row, *Aust. J. Chem.*, **30**, 1481 (1977).

[53] A related PMO treatment of hydrogen bonding may be found in A. R. Gregory, M. N. Paddon-Row, L. Radom, and W.-D. Stohrer, *Aust. J. Chem.*, **30**, 473 (1977).

[54] Implicit in this analysis is the assumption that the energetics of the π–hydrogen bond are determined more by covalent than electrostatic interactions. This assumption may not be correct.[55] However, arguments based on electrostatic interactions still lead to the same conclusion.

[55] R. S. Brown and R. W. Marcinko, *J. Am. Chem. Soc.*, **99**, 6500 (1977).

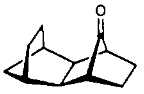
[56] Included in the constant of proportionality are the p-orbital coefficients of the C–C π bond (which are equal by symmetry) and the atomic orbital overlap integral between the carbonyl and double bond carbon atoms.

[57] M. N. Paddon-Row, unpublished data.

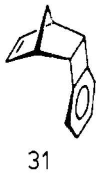
action is now the more important. As mentioned previously, methoxy and halogen substituents *raise* the π^* (LUMO) energy of the double bond through mixing with their lone-pair orbital (n_2, Figure 1a). This π^*–n_2 interaction deactivates the double bond toward electron-rich dienes. However, the π–n_1 interaction is expected to be much stronger on account of the better overlap between these orbitals (i.e., see **27**) and of the smaller energy gap separating them. Extended Hückel calculations support this expectation. Placement of a water molecule 2 Å from ethene in a configuration similar to that shown in **27** causes the π level to be raised by 1.0 eV with respect to that of isolated ethene. The π^* level of ethene is raised by only 0.1 eV. The large increase in π energy could very well determine the reactivity of these compounds with dienes having normal electron demand. If this is the case, then these substituents should enhance the reactivity of the double bond although the effect is expected to be attenuated compared to that of those reactions of **17** with dienes of inverse electron demand.

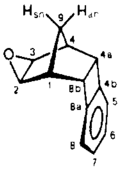
Amine and carbonyl substituents which lack an orbital of appropriate symmetry to mix with π^* will not, to a first approximation, affect this level. However, the modification to the π level (vide supra) should result in a small decrease in rate.


29

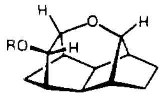


30


31



32



33

UV Spectral Data. The presence of OITS between the carbonyl group and double bond in ketone **17c** is further supported by UV data obtained for the compounds **17a**, **17c**, **18**, **29**, and **30** and are listed in Table IV. The data may be interpreted by using the interaction diagram of Figure 1b in which norbornene, formaldehyde, and the norbornene–formaldehyde "complex" serve as models for **17a**, **30**, and **17c**, respectively.

Perusal of this diagram leads to the prediction that the $n \rightarrow \pi_{CO}^*$, $\pi_{CO} \rightarrow \pi_{CO}^*$, and the $\pi_{CC} \rightarrow \pi_{CC}^*$ transitions in **17c** are hypsochromically shifted compared with those in the corresponding reference compounds **17a** and **30**. The predicted *hypsochromic* shift for the $n \rightarrow \pi_{CO}^*$ transition is unusual[58] but is due to the inability of the π_{CC}^* and π_{CO}^* orbitals to mix because of their different symmetries. In those cases where symmetry constraints are absent, extensive mixing between these orbitals causes a lowering of the π_{CO}^* energy and a corresponding *bathochromic* shift. Such is the case for 5-norbornenone for which the $n \rightarrow \pi_{CO}^*$ transition is bathochromically shifted ca. 13 nm compared with that for norbornanone.[59]

Table IV. UV Data[a]

compd	λ_{max} (ϵ_{max})	transition	solvent
17a	204.4 (4849)	$\pi_{CC} \rightarrow \pi_{CC}^*$	isooctane
	204.0 (4755)	$\pi_{CC} \rightarrow \pi_{CC}^*$	EtOH
30	295.7 (21)	$n \rightarrow \pi_{CO}^*$	isooctane
	183.8 (2486)	$\pi_{CO} \rightarrow \pi_{CO}^*$	
	292.5 (26)	$n \rightarrow \pi_{CO}^*$	EtOH
	<185	$\pi_{CO} \rightarrow \pi_{CO}^*$	
17c	287.5 (42)	$n \rightarrow \pi_{CO}^*$	isooctane
	192.5 (6268)	$\pi_{CC} \rightarrow \pi_{CC}^*$	
	282.0 (51)	$n \rightarrow \pi_{CO}^*$	EtOH
	195.0 (5100)	$\pi_{CC} \rightarrow \pi_{CC}^*$	
18	295.0 (40)		
	305.0 (38)	$n \rightarrow \pi_{CO}^*$	isooctane
	316.3 sh		
	292.5 (58)	$n \rightarrow \pi_{CO}^*$	EtOH
29	294.0 (32)		
	303.0 (30)	$n \rightarrow \pi_{CO}^*$	isooctane
	316.7 sh		
	290.5 (42)	$n \rightarrow \pi_{CO}^*$	EtOH

[a] Wavelengths are in nm.

The assignments of the transitions (Table IV) are based on solvent effects and molar absorptivity data. In perfect agreement with prediction we observe hypsochromic shifts of both $n \rightarrow \pi_{CO}^*$ and $\pi_{CC} \rightarrow \pi_{CC}^*$ transitions of **17c** compared with the same transitions of the reference compounds. For example, in isooctane solvent the $n \rightarrow \pi_{CO}^*$ transition in **17c** is hypsochromically shifted 8.2 nm with respect to the same transition in **30**. In the same solvent a hypsochromic shift of 11.9 nm in the $\pi_{CC} \rightarrow \pi_{CC}^*$ transition was observed on going from **17a** to **17c**. Unfortunately, the conditions of the experiment (N_2 atmosphere) precluded accurate measurement of the $\pi_{CO} \rightarrow \pi_{CO}^*$ transition. We were also unable to detect the presence of the charge transfer $\pi_{CC} \rightarrow \pi_{CO}^*$ transition which should occur in the range 210–260 nm.

The $n \rightarrow \pi_{CO}^*$ transitions for the ketones **18** and **29** occur at similar wavelengths. An accurate wavelength measurement of the $\pi_{CC} \rightarrow \pi_{CC}^*$ transition for **18** could not be obtained, but it appeared to be similar to that of **17a**. These results fully support our contention that the orbital interactions which occur between the double bond and the carbonyl group in **17c** are "through space" rather than "through bond".[60] This latter interaction would be present in both **17c** and **18**, since the interacting centers are separated by four σ bonds in both compounds and therefore should be detected from the UV spectrum of **18**.

Reactions with *m*-Chloroperbenzoic Acid. Despite the widespread use of the epoxidation of olefins by peracids the mechanism of the reaction is still unclear.[61] It is fairly certain, however, that the reaction is concerted and that it involves the intermediacy of a donor (olefin)–acceptor (peracid) complex.[61a] This being the case, we expect that the reaction is largely controlled by the HOMO(olefin)–LUMO(peracid) interaction. Therefore we expect that the substituted methanonaphthalenes should show the same order of reactivity toward *m*-chloroperbenzoic acid (MCPA) as toward the *s*-tetrazine **2**, i.e., **17e** > **17a** > **17f** > **17c**.[62]

---

[58] Hypsochromic shifts resulting from homoconjugative interactions have been reported for other systems: P. V. Alston and R. M. Ottenbrite, *J. Org. Chem.*, 41, 1635 (1976).

[59] P. D. Bartlett and B. E. Tate, *J. Am. Chem. Soc.*, 78, 2473 (1956).

[60] R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Am. Chem. Soc.*, 90, 1499 (1968); R. Hoffmann, *Acc. Chem. Res.*, 4, 1 (1971).

[61] (a) V. G. Dryuk, *Tetrahedron*, 32, 2855 (1976); (b) D. Swern in "Organic Peroxides", Vol. II, D. Swern Ed., Wiley-Interscience, New York, 1971, Chapter 5.

[62] Preliminary studies on the epoxidation of the syn alcohol **17d** with *m*-chloroperbenzoic acid indicated that acid-catalyzed formation of the bridged ether **19** was the exclusive reaction.

Table V. Relative Rate Data for the Reactions of Methanonaphthalenes with *m*-Chloroperbenzoic Acid in CH_2Cl_2 at 23 °C

compd	k_{rel}	compd	k_{rel}
17a	26	17f, anti OCH_3	9.5
17c, ketone	1	31	4.8
17e, syn OCH_3	342		

The methanonaphthalenes **17a**, **17c**, and **17f** reacted smoothly with MCPA in methylene chloride solution at room temperature to give respectively the epoxides **24a**, **24c**, and **24f** in excellent yields. However, the syn methyl ether **17c** gave a mixture of at least two components, neither of which corresponded to the expected epoxide. The two major components resisted separation, but ^1H NMR and IR spectroscopy indicated that they might have the overall structure **33** in which R = H for one compound and R = *m*-chlorobenzoyl for the other. In agreement with this analysis, treatment of the mixture with *KOH* led to the formation of a single alcohol whose structure we tentatively assign as **33** (R = H). The origin of the compounds **33** clearly arises from prior formation of the epoxide **24e** followed by acid-catalyzed ring opening and concomitant neighboring-group participation by the methoxyl oxygen atom. Demethylation of the bridged onium cation gives the alcohol (**33**; R = H) which may be esterified by *m*-chlorobenzoic acid. Unfortunately, current unavailability of compounds has temporarily prevented us from testing this mechanism.

Relative rate constants for the reactions of these compounds with MCPA were determined by using the competition method.[63] The *endo*-methanobiphenylene **31** was used as the competitor in the reactions of **17a**, **17c**, and **17f**, and the more reactive syn methyl ether **17e** was competed against **17a**. The relative rate constants, with respect to ketone **17c**, are listed in Table V. The rate sequence is in complete accord with prediction, the syn ether **17e** being some 342 times more reactive than the ketone **17c**.

Interestingly, our results appear to constitute only the second report demonstrating the occurrence of neighboring-group interactions in peroxidation reactions. The other report concerns the rate enhancement of the reaction of 5-*endo*-(hydroxymethyl)norborn-2-ene with perbenzoic acid.[64]

Experimental Section

All melting points are corrected and were recorded on a Gallenkamp melting point apparatus. Ultraviolet spectra were recorded with a Cary-15 spectrophotometer, employing matched silica cells of the appropriate path length. Infrared spectra were run on a Hitachi EPI-G2 instrument. 100-MHz spectra were obtained by using a Jeolco PS100 spectrometer; tetramethylsilane was used as an internal standard, and the resonances are quoted in δ units. Mass spectra were measured on an AEI MS902 mass spectrometer at 70 eV. All preparative thin-layer chromatography was carried out on plates with silica gel as adsorbent. Column chromatographic separations used neutral alumina as adsorbent. All solvents were freshly distilled before use. GLC analyses were carried out on a Bendix 1200 instrument (flame-ionization detector) with 4 m × 32 mm column containing 10% SE-30 on Chromosorb W (A/W) 60/80. Microanalyses were performed by the Australian National University Microanalytical Service under the direction of Miss B. Stevenson and Dr. J. E. Fildes.

***anti*-7-Methoxynorborn-2-ene (23f)** was prepared by the method of Brown.[65]

1,2,3,4,4a,5,8,8a-Octahydro-*endo,exo*-1,4:5,8-dimethanonaphthalene (17a) was prepared by the method of Marchand and Rose[31] and purified by silver complexation.

1,2,3,4,4a,5,8,8a-Octahydro-*endo,exo*-1,4:5,8-dimethanonaphthalene-*anti*-9-ol (17b). Sodium wire (12.9 g, 0.56 mol) was added to dry THF (300 mL), and the mixture was mechanically stirred under reflux in a nitrogen atmosphere. *tert*-Butyl alcohol (39 mL) was added to the refluxing mixture followed by the addition of the hexachloro adduct **16**[24] (8.5 g, 20 mmol) in THF (100 mL) during 45 min. The reaction mixture was stirred under reflux for 17 h after which it was cooled and filtered through glass wool onto ice. The filtrate–water mixture was extracted with ether (5 × 100 mL). The combined ether extracts were washed with saturated aqueous NaCl and then dried. Evaporation left a light yellow oil which was recrystallized from petroleum ether (bp 40–60 °C) to give tan crystals of **17b** (1.76 g, 50%). The spectral properties (^1H NMR, IR) were identical with those reported previously for **17b**.[24]

1,2,3,4,4a,5,8,8a-Octahydro-*endo,exo*-1,4:5,8-dimethanonaphthalen-9-one (17c). To a magnetically stirred suspension of pyridinium chlorochromate[66] (6.5 g, 30 mmol) in dichloromethane (30 mL) was added in one portion the anti alcohol **17b** (3.52 g, 20 mmol) in dichloromethane (10 mL). After 2 h, ether (100 mL) was added, and the supernatant was decanted from the black residue. This residue was further washed with ether (3 × 50 mL). The combined ether extracts were filtered through Celite and evaporated under reduced pressure to leave a light yellow oil. Sublimation of this oil [100 °C (5 mm)] gave a white solid (3.14 g, 90%), mp 55–56 °C (lit.[24] mp 54–56 °C), whose spectral properties (IR, ^1H NMR) were identical with those reported previously for **17c**.[24]

1,2,3,4,4a,5,8,8a-Octahydro-*endo,exo*-1,4:5,8-dimethanonaphthalen-*syn*-9-ol (17d). A solution of ketone **17c** (710 mg, 4.1 mmol) in anhydrous ether (20 mL) was added dropwise to a magnetically stirred slurry of $LiAlH_4$ (1.5 g, 39.5 mmol) in anhydrous ether (25 mL) under a nitrogen atmosphere. The mixture was stirred under reflux for 1 h after addition was complete. The excess $LiAlH_4$ was then destroyed through the cautious addition of aqueous sodium sulfate containing ca. 5% triethylamine. The ether was decanted from the solids. The residue was extracted with ether (3 × 50 mL), and the combined ether extracts were washed with 5% aqueous triethylamine (2 × 75 mL) and dried (Na_2SO_4). Evaporation of the solvent followed by distillation of the residue [160 °C (25 mm)] gave a clear distillate which was shown by ^1H NMR to consist of a mixture of the alcohol (**17d**) and the bridged ether (**19**). Column chromatography was carried out on this liquid by using neutral alumina which had been pretreated with a 0.5% solution of triethylamine in petroleum ether (bp 30–40 °C). Elution with petroleum ether (bp 30–40 °C) gave some bridged ether **19**. A pure sample of syn alcohol **17d** (445 mg, 62%) was then obtained by eluting with petroleum ether–ether (4:1) mixture followed by total distillation [130 °C (15 mm)]: IR (CCl_4) 3554 cm^{-1}; ^1H NMR (CCl_4) δ 0.92–1.88 (8 H, m, H_2, H_3, H_{4a}, H_{8a}, H_{10}), 2.04 (OH, d, J = 6.4 Hz, D_2O exchange), 2.28 (2 H, t, J = 1.5 Hz, H_1, H_4).

A solution of the alcohol in untreated $CDCl_3$ completely rearranged to the bridged ether **19** within 10 h at 20 °C. The alcohol is stable in freshly distilled (from K_2CO_3) CCl_4 solutions.

1,2,3,4,4a,5,8,8a-Octahydro-*endo,exo*-1,4:5,8-dimethano-*anti*-9-methoxynaphthalene (17f). To a stirred suspension of sodium hydride (2.5 g, 100 mmol), freed from mineral oil, in dioxane (50 mL) was added slowly a solution of the anti alcohol **17b** (1.76 g, 10 mmol) in dioxane (10 mL). The mixture was refluxed in an N_2 atmosphere for 18 h. Methyl iodide (6.0 g, 42 mmol) was added to the *cooled* solution followed by refluxing for a further 6 h. The mixture was cooled to 0 °C, hydrolyzed with ice–water, and extracted with ether (4 × 50 mL). The combined ether solution was washed with ice–water (2 × 50 mL) followed by saturated aqueous NaCl and then dried (Na_2SO_4). Evaporation of the solvent and subsequent distillation of the residue gave the anti methyl ether **17f**: 1.77 g, 93.2%; bp 116 °C (15 mm); ^1H NMR ($CDCl_3$) δ 0.84–1.44 (4 H, m, protons at positions[67] 2n, 3n, 10),

---

[63] J. F. Bunnett, *Tech. Chem. (NY)*, **5**, 158 (1974).

[64] H. B. Henbest and B. Nicholls, *J. Chem. Soc.*, 221 (1959).

[65] R. S. Brown, *Can. J. Chem.*, **54**, 3206 (1976).

[66] E. J. Corey and J. W. Suggs, *Tetrahedron Lett.*, 2647 (1975).

[67] Consult structure **17a** for the meaning of the subscripts an, sn, n, and x attached to some protons.

1.68–1.88 (2 H, m, H_{2x}, H_{3x}), 2.08 (4 H, m, H_5, H_{4a}, H_8, H_{8a}), 2.88 (2 H, irregular heptet, $J = 2.0$ Hz, H_1, H_4), 3.18 (3 H, s, OCH_3), 4.40 (1 H, brs, H_{9sn}), 6.16 (2 H, t, $J = 2.0$ Hz, H_6, H_7); MS, *m/e* (rel intensity) 190 ($M^{+}\cdot$, 18%), 150 (12), 149 (100), 129 (6), 124 (17), 123 (8), 117 (18), 115 (6), 110 (7), 109 (24), 108 (7), 97 (7), 96 (8), 93 (16), 92 (38), 91 (33), 81 (10), 80 (11), 79 (25), 78 (12), 77 (16), 73 (5), 71 (18), 67 (16), 66 (34), 65 (13), 59 (7), 55 (5), 53 (9), 51 (7), 45 (21), 44 (9), 43 (5), 41 (29), all other peaks being less than 5%. Anal. Calcd. for $C_{13}H_{18}O$: C, 82.05; H, 9.54. Found: C, 82.36; H, 9.61.

1,2,3,4,4a,5,8,8a-Octahydro-*endo,exo*-1,4:5,8-dimethano-*syn*-9-methoxynaphthalene (17e). This compound was prepared by using a procedure identical with that described above for the synthesis of the anti methyl ether **17f**. The crude reaction product was chromatographed (silica gel impregnated with $AgNO_3$, 20% w/w). The rearranged ether (**19**) was removed by eluting with petroleum ether (bp 40–60 °C). The silver nitrate complex (1 g) of **17e** was obtained by subsequent elution with methylene chloride. Treatment of the complex with saturated aqueous NaCl gave an oil which was extracted (ether), dried, and finally distilled to give **17e**: 360 mg, bp 117–118 °C (14 mm); ^{1}H NMR ($CDCl_3$) δ 0.96–1.72 (6 H, m, H_2, H_3, H_{10}), 2.03 (2 H, m, H_1, H_4), 2.23 (2 H, irregular heptet, $J = 1.8$ Hz, H_5, H_8), 2.87 (2 H, m, H_{4a}, H_{8a}), 3.05 (3 H, s, OCH_3), 3.19 (1 H, s, H_{9an}), 5.85 (2 H, t, $J = 2.0$ Hz, H_6, H_7); MS, *m/e* (rel intensity) 190 ($M^{+}\cdot$, 15), 158 (5), 149 (13), 130 (7), 129 (7), 125 (45), 124 (39), 123 (10), 117 (11), 115 (6), 110 (6), 109 (27), 94 (10), 93 (66), 92 (87), 91 (43), 86 (8), 84 (13), 81 (16), 80 (12), 79 (41), 78 (17), 77 (22), 71 (19), 67 (23), 66 (base), 65 (21), 63 (5), 57 (9), 56 (12), 55 (6), 53 (12), 51 (9), 45 (24), 44 (6), 43 (10), 42 (7), 41 (40), all other peaks being less than 5%. Anal. Calcd for $C_{13}H_{18}O$: C, 82.05; H, 9.54. Found: C, 81.73; H, 9.48.

1,2,3,4,4a,5,8,8a-Octahydro-*endo,exo*-1,4:5,8-dimethanonaphthalen-2-one (18). A mixture of 5-norbornenone[68] (5.4 g, 50 mmol) and cyclopentadiene (3.63 g, 55 mmol) was heated in a thick-walled sealed tube at 180–190 °C for 10 h. Distillation of the reaction mixture gave unreacted 5-norbornenone (2.3 g) and crude **18** [4.6 g, bp 113–115 °C (2 mm)]. A pure sample of **18** was obtained by preparative GLC (Apiezon L 10% Chromosorb W (A/W) 60/80, 2.5 m long, $^1/_4$ in. diameter): IR (CCl_4) 1744 cm^{-1} (C=O); ^{1}H NMR[67] ($CDCl_3$) δ 0.97 (1 H, d, $J = 11$ Hz, H_{9sn}), 1.20–2.60 (9 H, m, H_1, H_3, H_4, H_{4a}, H_{8a}, H_{9a}, H_{10}), 2.92 (2 H, brs, H_5, H_8), 5.96 (2 H, s, H_6, H_7). Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 83.18; H, 8.44.

Perhydro-*endo,exo*-1,4:5,8-dimethanonaphthalen-2-one (29). A solution of **18** (174 mg, 1 mmol) in ethyl acetate (20 mL) was hydrogenated at 1 atm pressure by using 10% palladium–charcoal catalyst (20 mg). After H_2 uptake had ceased the solution was filtered and distilled to yield **29** in quantitative yield: IR (CCl_4) 1742 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.17–2.60 (16 H, brm). Exact mass calcd for $C_{12}H_{16}O$, 176.1201; found, 176.1200.

Perhydro-*endo,exo*-1,4:5,8-dimethanonaphthalen-9-one (30) was prepared in a manner similar to that described above for **29**; mp 87–88 °C (lit.[24] mp 87.5–89 °C).

General Procedure for the Preparation of the Adducts Arising from the Reaction of 17 and 18 with the *s*-Tetrazine 2. Equimolar amounts of **17** or **18** and the *s*-tetrazine[69] **2** were reacted together in $CHCl_3$ solution. After nitrogen evolution had ceased the solution was evaporated to dryness, leaving a mixture of the decahydro-2,3-diazadimethanoanthracenes, i.e., **20** and **21** in the case of the olefins **17**.

The syn alcohol **17d** formed **7,8-diaza-1,2,3,4,4a,5,5a,9a,-10,10a-decahydro-*endo,exo*-1,4:5,10-dimethano-6,9-di(2′-pyridyl)anthracen-*syn*-11-ol (20d)** as yellow crystals: mp 197–199 °C (from $CHCl_3$/petroleum ether); IR (CCl_4) 3475 (OH), 3360 cm^{-1} (NH); ^{1}H NMR[67] ($CDCl_3$) δ 0.95–2.70 (12 H, m, including OH on the basis of D_2O exchange), 3.18 (1 H, s, H_{12an}), 3.32–3.68 (2 H, m, H_5, H_{10}), 3.88 (1 H, brs, H_{9a}), 7.08–8.68 (8 H, m, pyridyl H), 9.16 (1 H, brs, NH, D_2O exchange).

The syn methyl ether **17e** formed **7,8-diaza-1,2,3,4,4a,5,5a,-9a,10,10a-decahydro-*endo,exo*-1,4:5,10-dimethano-*syn*-11-methoxy-6,9-di(2′-pyridyl)anthracene (20e)** as yellow crystals: mp 222–224 °C (from $CHCl_3$/petroleum ether); ^{1}H NMR[67] ($CDCl_3$) δ 0.92–1.84 (7 H, m, H_1–H_4, H_{12an}), 2.08 (2 H, m, H_5, H_{10}), 2.54 (3 H, m, H_{4a}, H_{10a}, H_{12sn}), 3.40 (3 H, s, OCH_3), 3.52 (1 H, s, H_{11an}), 4.0 (2 H, s, H_{5a}, H_{9a}), 7.12–8.68 (8 H, m, pyridyl H). Exact mass calcd for $C_{25}H_{26}N_4O$, 398.211; found, 398.213.

The diazadecahydroanthracenes of the remaining olefins were oxidized by adding dioxan solutions of them to DDQ in dioxane containing a few drops of glacial acetic acid. The solution was stirred at room temperature for 30 min and then filtered and the residue washed with $CHCl_3$. The resulting filtrate was washed with saturated aqueous NaCl, dried (Na_2SO_4), and evaporated. The following compounds were characterized.

7,8-Diaza-1,2,3,4,4a,5,10,10a-octahydro-*endo,exo*-1,4:5,10-dimethano-6,9-di(2′-pyridyl)anthracene (22a): colorless plates, mp 187–188 °C (ether); ^{1}H NMR[67] ($CDCl_3$) δ −0.64 (1 H, brd, $J = 12$ Hz, H_{11sn}), 0.22 (1 H, d, $J = 12$ Hz, H_{11an}), 0.88–1.88 (6 H, m, H_2, H_3, H_{12}), 2.12 (2 H, brs, H_1, H_4), 2.42 (2 H, brs, H_{4a}, H_{10a}), 4.48 (2 H, brs, H_5, H_{10}), 7.16–8.76 (8 H, m, pyridyl H). Anal. Calcd for $C_{24}H_{22}N_4$: C, 78.66; H, 6.05; N, 15.29. Found: C, 79.0; H, 6.04; N, 15.0.

7,8-Diaza-1,2,3,4,4a,5,10,10a-octahydro-*endo,exo*-1,4:5,10-dimethano-6,9-di(2′-pyridyl)anthracene-*anti*-11-ol (22b): colorless plates, mp 281–282 °C (methanol); ^{1}H NMR[67] ($CDCl_3$) δ 0.98–2.26 (8 H, m, H_1–H_4, H_{12}), 1.14 (1 H, brs, OH, D_2O exchange), 2.23 (1 H, brs, H_{11sn}), 2.52 (2 H, t, $J = 2$ Hz, H_{4a}, H_{10a}), 4.49 (2 H, t, H_5, H_{10}), 7.16–8.80 (8 H, m, pyridyl H). Exact mass calcd for $C_{24}H_{22}N_4O$, 382.1793; found, 382.1800.

7,8-Diaza-1,2,3,4,4a,5,10,10a-octahydro-*endo,exo*-1,4:5,10-dimethano-6,9-di(2′-pyridyl)anthracen-11-one (22c): colorless plates, mp 247–248 °C ($CHCl_3$/petroleum ether), ^{1}H NMR[67] ($CDCl_3$) δ 1.32–2.04 (8 H, m, H_1–H_4, H_{12}), 2.71 (2 H, t, $J = 2.0$ Hz, H_{4a}, H_{10a}), 4.68 (2 H, t, $J = 2.0$ Hz, H_5, H_{10}), 7.20–8.72 (8 H, m, pyridyl H). Anal. Calcd for $C_{24}H_{20}N_4O$: C, 75.77; H, 5.30; N, 14.73. Found: C, 75.61; H, 5.21; N, 14.49.

7,8-Diaza-1,2,3,4,4a,5,10,10a-octahydro-*endo,exo*-1,4:5,10-dimethano-*anti*-10-methoxy-6,9-di(2′-pyridyl)anthracene (22f): light pink crystals, mp 237–238 °C ($CHCl_3$/petroleum ether); ^{1}H NMR[67] ($CDCl_3$) δ 0.92–1.20 (2 H, m, H_{2n}, H_{3n}), 1.52–1.96 (5 H, m, H_{12}, H_{2x}, H_{3x}, H_{11sn}), 2.22 (2 H, m, H_{4a}, H_{10a}), 2.52 (2 H, m, H_1, H_4), 2.60 (3 H, s, OCH_3), 4.56 (2 H, brs, H_5, H_{10}), 7.26–8.84 (8 H, m, pyridyl H). Anal. Calcd for $C_{25}H_{24}N_4O$: C, 75.73; H, 6.10; N, 14.13. Found: C, 75.63; H, 6.36; N, 13.90.

7,8-Diaza-1,2,3,4,4a,5,10,10a-octahydro-*endo,exo*-1,4:5,10-dimethano-6,9-di(2′-pyridyl)anthracen-2-one (25): yellow crystals, mp 196–198 °C (CH_2Cl_2/petroleum ether); IR (CCl_4) 1765 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ −0.16 (1 H, brd, $J = 12.0$ Hz, H_{11sy}), 0.74 (1 H, d, $J = 12.0$ Hz, H_{11an}), 1.84 (4 H, brs, H_3, H_{12}), 2.76 (4 H, brs, H_1, H_4, H_{4a}, H_{10a}), 4.64 (2 H, brs, H_5, H_{10}), 7.2–8.8 (8 H, m, pyridyl H). Exact mass calcd for $C_{24}H_{20}N_4O$, 380.1637; found, 380.1630.

General Procedure for the Preparation of the Epoxides. To a stirred solution of the olefin in dichloromethane was added the stoichiometric quantity of *m*-chloroperbenzoic acid (MCPA) in dichloromethane. After the reaction was complete (starch–iodide test) the mixture was shaken with several quantities of saturated $NaHCO_3$ until evolution of CO_2 had ceased. The organic layer was dried and evaporated to dryness. The residue was sublimed [120 °C (4 mm)] to give the epoxide. The following epoxides were prepared.

***anti*-2,3-Epoxyperhydro-*endo,exo*-1,4:5,8-dimethanonaphthalene (24a):** colorless plates, mp 41–43 °C; ^{1}H NMR ($CDCl_3$) δ 0.61 (1 H, d, $J = 9.5$ Hz, H_{10an}), 0.84–2.0 (9 H, m, H_5–H_9, H_{10sn}), 2.28 (2 H, brs, H_{4a}, H_{8a}), 2.60 (2 H, brs, H_1, H_4), 3.16 (2 H, s, H_2, H_3). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 82.03; H, 9.05.

2,3-Epoxyperhydro-*endo,exo*-1,4:5,8-dimethanonaphthalen-9-one (24c): colorless plates, mp 68–69 °C; ^{1}H NMR ($CDCl_3$) δ 0.72 (1 H, d, $J = 10.5$ Hz, H_{10an}), 1.24–2.20 (9 H, m, H_5–H_8, H_{4a}, H_{8a}, H_{10sn}), 2.68 (2 H, brs, H_1, H_4), 3.12 (2 H, s, H_2, H_3). Exact mass calcd for $C_{12}H_{14}O_2$, 190.0994; found, 190.0996.

2,3-Epoxyperhydro-*endo,exo*-1,4:5,8-dimethano-*anti*-9-methoxynaphthalene (24f): mp 67–69 °C; ^{1}H NMR ($CDCl_3$) δ 0.65 (1 H, brd, $J = 9.5$ Hz, H_{10an}), 0.96–1.48 (3 H, m, H_{6n}, H_{7n}, H_{10sn}), 1.22 (2 H, m, H_{4a}, H_{8a}), 2.56 (2 H, brs, H_1, H_4), 3.16 (2 H, s, H_2, H_3), 3.23 (3 H, s, OCH_3), 4.20 (1 H, brs, H_{9sn}). Exact mass calcd for $C_{13}H_{18}O_2$, 206.1306; found, 206.1293.

---

(68) P. K. Freeman, D. M. Balls, and D. J. Brown, *J. Org. Chem.*, **33**, 2211 (1968).

(69) J. F. Geldard and F. Lions, *J. Org. Chem.*, **30**, 318 (1965).

2,3-Epoxy-1,2,3,4,4a,8b-hexahydro-*endo*-1,4-methanobiphenylene (32) was obtained as colorless plates, mp 48–50 °C (from the methanobiphenylene **31**):[70] ^{1}H NMR ($CDCl_3$) δ 1.14 (1 H, d, J = 10.0 Hz, H_{9an}), 1.74 (1 H, d, J = 10.0 Hz, H_{9sn}), 2.60–2.78 (4 H, m, H_1–H_4), 3.66–3.82 (2 H, m, H_{4a}, H_{8b}), 7.0–7.26 (4 H, m, aromatic H). Exact mass calcd for $C_{13}H_{12}O$, 184.0888; found, 184.0900.

The residue from the reaction of the syn methyl ether **17e** with MCPA was treated with alcoholic KOH at reflux for 1 h. The solution was poured into water followed by extraction with ether. Evaporation of solvent led to the formation of a single solid product whose structure is tentatively assigned as **33** (R = H): IR (CCl_4) 3610 cm^{-1} (free OH); ^{1}H FT NMR ($CDCl_3$) δ 3.86 (1 H, HCO), 3.76 (2 H, HCO), 2.5–1.0 (13 H; br m). Exact mass calcd for $C_{12}H_{16}O_2$, 192.115; found, 192.115.

Kinetic Studies. All solvents were purified immediately prior to use. Dimethyl sulfoxide was distilled under reduced pressure from calcium hydride. Chloroform and dichloromethane were distilled from anhydrous potassium carbonate.

The *s*-tetrazine **2** was recrystallized from benzene. *m*-Chloroperbenzoic acid was obtained from Aldrich and used without further purification. However, the amount of peracid present in the material was determined by adding excess KI to a known weight of peracid and titrating the liberated iodine with thiosulfate solution.

Absolute rates of the reactions of compounds **17** with the *s*-tetrazine **2** in the appropriate solvent were determined spectrophotometrically by monitoring the decrease in the absorbance of **2** at 550 nm with time. Measurements were carried out on a Perkin-Elmer 124 instrument which was fitted with a constant-temperature cell compartment. The initial concentrations of the reactants were made equal, and the measurements were carried out over at least 3 half-lives. Second-order rate constants were determined by the method of integration.[71]

The general procedure for the determination of the relative rates of epoxidation by the competition method is as follows. To a magnetically stirred solution of the competing pair of olefins (0.5 mmol each) in CH_2Cl_2 (2 mL) at 22.8 °C was added rapidly *m*-chloroperbenzoic acid (0.5 mmol) in CH_2Cl_2 (2 mL) at the same temperature. The solution was stirred at 22.8 °C until a sample of it gave a negative starch–iodide test. The solution was then shaken with saturated $NaHCO_3$ (2 × 25 mL), dried (Na_2SO_4), evaporated, and analyzed by ^{1}H NMR spectroscopy ($CDCl_3$ solution).

Acknowledgment. This work was supported by the Australian Research Grants Committee (Grant C66/16344), to whom we express our gratitude. We thank H. Gotthard (NSWIT) and B. McQuillan (NSWIT) for help with the UV and GLC work, respectively, and G. Forster (NSWIT) for the NMR spectra. We are grateful to NSWIT computer center for a generous allocation of computer time. The drawings by P. Harrison (ANU) are greatly appreciated.

Registry No. 2, 1671-87-0; **16**, 28267-19-8; **17a**, 15914-93-9; **17b**, 28068-45-3; **17c**, 36204-31-6; **17d**, 36197-15-6; **17e**, 67401-91-6; **17f**, 67425-33-6; **18**, 33163-94-9; **19**, 36197-32-7; **20d**, 67401-94-9; **21e**, 71369-83-0; **22a**, 71369-84-1; **22b**, 71369-85-2; **22c**, 71369-86-3; **22f**, 71369-87-4; **23a**, 498-66-8; **23f**, 13041-10-6; **24a**, 35909-32-1; **24c**, 67401-96-1; **24f**, 67425-36-9; **25**, 71369-88-5; **29**, 40488-88-8; **30**, 36197-31-6; **31**, 27297-13-8; **32**, 40644-04-0; **33** (R = H), 71369-89-6; 5-norbornenone, 694-98-4; cyclopentadiene, 542-92-7.

---

[70] M. P. Cava and M. J. Mitchell, *J. Am. Chem. Soc.*, 81, 5409 (1959).

[71] K. J. Laidler, "Chemical Kinetics", 2nd ed., McGraw-Hill, New York, 1965, p 5.

Substituent Effects on the Rotational Barrier in Protonated 2,2'-Bithienyl and the Relation to Charge Development in Protodetritiation

David A. Forsyth* and Dennis E. Vogel

Department of Chemistry, Northeastern University, Boston, Massachusetts 02115

Received February 28, 1979

Protonation of 2,2'-bithienyl in superacid media occurs at the 5-position to give the stable arenium ion, 2-(2'-thienyl)-5-thiophenium ion (1). The energy barrier to rotation about the bond connecting the two rings was determined to be $\Delta G^{\ddagger}$ = 11.4 kcal mol^{-1} by dynamic NMR methods. Substituent effects on the rate of rotation are correlated by σ_p^+ constants with a ρ value of 4.8. The relation between substituent effects on the rotational barrier and on the rate of protodetritiation is discussed in terms of charge development in the transition state for protodetritiation.

Despite extensive NMR studies of the structure and rearrangements of stable carbocations,[1,2] relatively little attention has been paid to conformational equilibria and dynamics in these ions. The dynamic NMR (DNMR) study of conformational changes in carbocations is a potentially rich source of information about electronic interactions that may differ considerably from those in neutral systems. In this paper, we report a study of the electronic character of an arenium ion by application of DNMR methods. Specifically, we examine substituent effects on the rotational barrier in stable, protonated 2,2'-bithienyl. By comparison with substituent effects on the kinetics of protodetritiation of 2,2'-bithienyl, we gain insight into the extent of charge development in the arenium ionlike transition state for protodetritiation.

The formation of stable arenium ions by protonation of arenes in superacid media is well established.[3] The stable 2-thiophenium ion is formed by the protonation of thiophene at the 2-position.[4,5] Similarly, we find that

---

[1] G. A. Olah, "Carbocations and Electrophilic Reactions", Wiley, New York, 1974.

[2] For reviews of the methods and types of ions, see "Carbonium Ions", Vol. I-V, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York.

[3] D. M. Brouwer, E. L. Mackor, and C. MacLean in "Carbonium Ions", Vol II, G. A. Olah and P. v. R. Schleyer, Ed., New York, 1970.

[4] H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, 85, 1072 (1966).

0022-3263/79/1944-3917$01.00/0