(7), 1.280 (6);[14] ^{13}C NMR (360 MHz, $CDCl_3$ (intensity, 30-s delay)) δ 16.6 (92.2), 23.6 (100.0), 31.4 (78.8), 35.7 (54.1), 178.3 (38.7); IR (KBr pellet) ν (cm^{-1}) 667 (m), 716 (m), 844 (m), 927 (s), 972 (m), 1113 (s), 1233 (s), 1322 (m), 1383 (m), 1450 (s), 1666 (s), 2933 (s). Anal. (Galbraith Laboratories, Knoxville, TN) C, H. Found: 67.7, 9.7. Calcd 67.6, 9.85.

Synthesis of 2,2,3,3-Tetramethylcyclopropanecarboxylic Acid. This synthesis combined the methods of Meshcheryakov and Dolgii[9] with the separation procedures of Zimmerman and Pratt.[10] Ethyl diazoacetate and 2,3-dimethyl-2-butene (DMB) were mixed in a 2/1 molar ratio and added dropwise to a mixture containing the same amount of DMB and cupric sulfate in a 20/1 molar ratio. After 2 h of refluxing, the mixture was distilled and ethyl 2,2,3,3-tetramethylcyclopropanecarboxylate was collected at 52–53 °C and 2 torr. This was refluxed in methanol containing 15% KOH for 3 h, washed with diethyl ether, and acidified, and the ether layer was collected and dried with magnesium sulfate. After removal of the ether, the white crystals were collected and recrystallized from benzene: mass spectrum (40 eV), *m/e* (relative intensity) 142 (M^+, 8), 127 (100), 109 (36), 97 (97), 81 (67), 69 (35), 59 (50), 53 (24); ^1H NMR (60 MHz, CCl_4 (integral)) δ 1.125 (1), 1.175 (6), 1.225 (6); IR ν (cm^{-1}) (KBr pellet) 672 (m), 716 (m), 850 (m), 933 (m), 978 (m), 1117 (s), 1327 (m), 1388 (m), 1405 (m), 1450 (m), 1694 (s), 2955 (s).

Yield Measurements. For the quantitative measurements $^{14}C(CO)_2$ was prepared from $^{14}C(COOH)_2$ supplied by New England Nuclear. It has been shown previously[18] that ^{14}CO and $^{14}CO_2$ are the only products of the reaction with oxygen, and we have shown that the allene and methylacetylene products from ethylene at 100 torr account for 95% of the ^{14}CCO produced by photolysis using the oxygen reaction as a standard. Yields are based on comparison of TME products to the yield of allene and methylacetylene from ethylene. A window flow counter[19] was used for measurement of radioactivity in the flow stream from the gas chromatograph.

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Registry No. ODOD, 81359-25-3; TMCA, 15641-58-4; C_3O_2, 504-64-3; C_2O, 12071-23-7; $(CH_3)_2C{=}C(CH_3)_2$, 563-79-1; $N_2{=}CHC(O)OEt$, 623-73-4; ethyl 2,2,3,3-tetramethylcyclopropanecarboxylate, 771-10-8.

(18) Peterson, R. F.; Wolfgang, R. L. *Chem. Commun.* **1968**, 1201–1202.
(19) Wolfgang, R.; MacKay, C. *Nucleonics* **1958**, *16*, 69–73.

Thermolysis of Alkyldioxetanes: Effect of 3,3-Cyclic Substituents and Conformation on the Activation Parameters

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3,3-Tetramethylene-1,2-dioxetane (**1**), 3,3-pentamethylene-1,2-dioxetane (**2**), 3,3-hexamethylene-1,2-dioxetane (**3**), *cis*-4-*tert*-butylcyclohexanespiro-3′-(1′,2′-dioxetane) (**4**), and 4-methylcyclohexanespiro-3′-(1′,2′-dioxetanes) **5a** and **5e** were synthesized in ~10% yield by closure of the β-bromo hydroperoxides with base at low temperature. The dioxetanes were purified by low-temperature (−78 °C) column chromatography on silica gel. The configurations of **4** and **5a** were shown to have oxygen-2 in an axial position while that of **5e** was found to have oxygen-2 in an equatorial position (relative to the equatorial 4-alkyl groups). Thermal decomposition of **1–5** produced the expected cleavage products. Thermolysis of the compounds produced (directly) high yields of excited triplet carbonyl products. The activation parameters for the thermal decomposition of **1–5** in xylenes were determined by the Arrhenius method: for **1**, E_a = 23.4 kcal/mol, log A = 13.1, $k_{60°C} = 5.8 \times 10^{-3}$ s^{-1}; for **2**, E_a = 24.6 kcal/mol, log A = 13.2, $k_{60°C} = 1.2 \times 10^{-3}$ s^{-1}; for **3**, E_a = 24.7 kcal/mol, log A = 13.2, $k_{60°C} = 1.3 \times 10^{-3}$ s^{-1}; for **4**, E_a = 24.5 kcal/mol, log A = 13.1, $k_{60°C} = 1.0 \times 10^{-3}$ s^{-1}; for **5a**, E_a = 24.9 kcal/mol, log A = 13.3, $k_{60°C} = 1.1 \times 10^{-3}$ s^{-1}; and for **5e**, E_a = 24.1 kcal/mol, log A = 13.0, $k_{60°C} = 1.4 \times 10^{-3}$ s^{-1}. The data for **2–4** and **5a** are similar to those for 3,3-diethyl-1,2-dioxetane. The data for **5e** show that the "equatorial" dioxetane is less stable than the "axial" dioxetane due to lower steric interactions. An interpretation of the data for **1** suggests that the lowest steric interactions occur in **1**, resulting in the lowest E_a. The results are consistent with a diradical mechanism of dioxetane thermolysis.

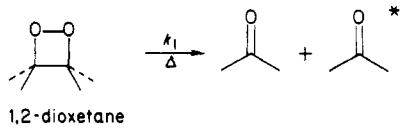
The unique, chemiluminescent thermolysis of alkyl and other simply substituted 1,2-dioxetanes to carbonyl fragments has been shown[2] to produce (directly) high yields of excited triplet carbonyls (Scheme I). For alkyldioxetanes, most experimental evidence[3] has been interpreted[2] in favor of a two-step (diradical) mechanism rather than a concerted process. Recent work has shown[4] that

(1) Fellow of the Camille and Henry Dreyfus Foundation, 1981–86.
(2) For reviews, see: (a) Wilson, T. *Int. Rev. Sci.: Phys. Chem. Ser. Two* **1976**, *9*, 265. (b) Adam, W. *Adv. Heterocycl. Chem.* **1977**, *21*, 437. (c) Horn, K. A.; Koo, J.; Schmidt, S. P.; Schuster, G. B. *Mol. Photochem.* **1978–9**, *9(1)*, 1. (d) Bartlett, P. D.; Landis, M. E. In "Singlet Oxygen"; Wasserman, H. H., Murray, R. W., Ed.; Academic Press: New York, 1979; p 243. (e) Schuster, G. B.; Schmidt, S. P. *Adv. Phys. Org. Chem.* **1982**, *18*, 187. (f) Adam, W. In "Chemical and Biological Generation of Electronically Excited States"; Cilento, G., Adam, W., Ed.; Academic Press: 1982; Chapter 4. (g) Baumstark, A. L. In "*Singlet Oxygen*"; Frimer, A., Ed.; Uniscience, CRC Press: 1984, in press; Vol. 2.

(3) (a) O'Neal, H. E.; Richardson, W. H. *J. Am. Chem. Soc.* **1970**, *92*, 6553 and correction *Ibid.* **1971**, *93*, 1828. (b) Wilson, T.; Landis, M. E.; Baumstark, A. L.; Bartlett, P. D. *J. Am. Chem. Soc.* **1973**, *95*, 4765. (c) Richardson, W. H.; Burns, J. H.; Price, M. E.; Crawford, R.; Foster, M.; Slusser, P.; Andergg, J. H. *J. Am. Chem. Soc.* **1978**, *100*, 7596 and references therein. (d) Koo, J.; Schuster, G. B. *J. Am. Chem. Soc.* **1977**, *99*, 5403. (e) Wilson, T.; Golan, D. E.; Scott, M. S.; Baumstark, A. L. *J. Am. Chem. Soc.* **1976**, *98*, 1086. (f) Kopecky, K. R.; Filby, J. E.; Mumford, C.; Lockwood, P. A.; Ding, J.-Y. *Can. J. Chem.* **1975**, *53*, 1103.
(4) Baumstark, A. L.; Wilson, C. E. *Tetrahedron Lett.* **1981**, *22*, 4363. (b) Bechara, E. J. H.; Wilson, T. *J. Org. Chem.* **1980**, *45*, 5261. (c) Lechtken, P.; Reissenweber, G.; Grubmueller, G. *Ibid.* **1977**, 2881. (d) Baumstark, A. L.; Wilson, C. E. *Tetrahedron Lett.* **1979**, 2569. (e) Kopecky, K. R.; Lockwood, P. A.; Gomez, R. R.; Ding, J.-Y. *Can. J. Chem.* **1981**, *59*, 851.

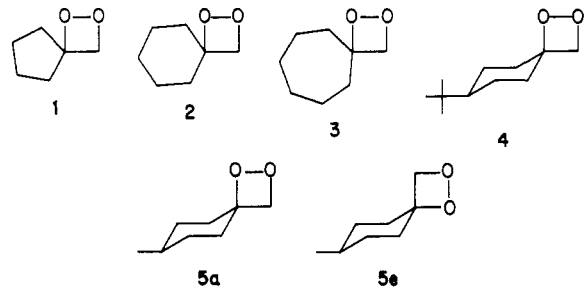
0022-3263/84/1949-4497$01.50/0

Scheme I



1,2-dioxetane

substituent effects on the thermal decomposition of alkyldioxetanes are difficult to predict. 3,4-Cyclic substituents have been found[4] to show large effects on dioxetane activation parameters. Recent results have shown[5] that increased formal substitutions in a series of 3,3-dialkyl-1,2-dioxetanes produced a systematic increase of 0.8 kcal/substitution in the activation energy (with little or no effect on $\Delta S^{\ddagger}$ terms). The results for 3,3-biphenylene-4-methoxy-1,2-dioxetane showed[6] a large decrease in the activation parameters of thermolysis compared to those of an acyclic analogue, 3,3-diphenyl-4-methoxy-1,2-dioxetane. We report the synthesis and characterization of a series of 3,3-cyclic substituted 1,2-dioxetanes **1–5**.



Results and Discussion

3,3-Tetramethylene-1,2-dioxetane (**1**), 3,3-pentamethylene-1,2-dioxetane (**2**), 3,3-hexamethylene-1,2-dioxetane (**3**), *cis*-4-*tert*-butylcyclohexanespiro-3′-(1′,2′-dioxetane) (**4**), and 4-methylcyclohexanespiro-3′-(1′,2′-dioxetanes) **5a** and **5e** were synthesized in approximately 10% yield by closure of the corresponding bromo hydroperoxides **6–11** with base at low temperature. The dioxetanes were purified to greater than 95% purity by low-temperature column chromatography. Compounds **1–5** (yellow oils) were characterized by NMR spectroscopy and by analysis of their thermolysis products. The configuration of dioxetane **4** was shown to have oxygen-2 in an axial position by conversion of both the dioxetane and the bromo hydroperoxide to the axial epoxide.[7] The configuration of **5e** was assigned on the basis of the conversion of the bromo hydroperoxide to the equatorial epoxide.[7] The configuration of **5a** was assigned (by difference) on the basis of the ^{1}H NMR chemical shifts of the dioxetane ring protons.

Thermal decomposition of dioxetanes **1–5** produced the expected carbonyl-cleavage products. The rates of thermolysis in xylenes were determined by the chemiluminescence method. The rates of dioxetane thermolysis were not effected by variations in the concentrations ($\geq 5 \times 10^{-3}$ M) of added fluorescers (DBA or DPA). The first-order rate constants (k_1) for dioxetanes **2–4** and **5a** were similar while those for dioxetane **1** were substantially larger over the 50+° temperature range employed. The activation parameter data determined by the Arrhenius method for compounds **1–5** are summarized in Table I. The activation parameter data for **2–4** and **5a** are essentially identical while the E_a for **1** is clearly lower. The activation parameter data for **5e** are intermediate. Little or no differences are observed in the log A terms. The errors in E_a shown in Table I are the 95% confidence limits.

Table I. Activation Parameters for the Thermolysis of Dioxetanes 1–5 in Xylenes

dioxetane	E_a, kcal/mol	log A	$k_{60°C}$, s^{-1}	n^a
1	23.4 ± 0.2[b]	13.1	5.8×10^{-3}	33
2	24.6 ± 0.2	13.2	1.2×10^{-3}	47
3	24.7 ± 0.2	13.2	1.3×10^{-3}	35
4	24.5 ± 0.4	13.1	1.0×10^{-3}	24
5a	24.9 ± 0.5	13.3	1.1×10^{-3}	20
5e	24.1 ± 0.4	13.0	1.4×10^{-3}	25

[a] Number of data points. [b] 95% confidence limits, correlation coefficient = 0.999 (all six cases).

As expected for alkyldioxetanes, the thermolysis of **1–5** exhibited only weak chemiluminescence without added fluorescers. Addition of 9,10-dibromoanthracene (DBA) or 9,10-diphenylanthracene (DPA) resulted in large increases in the chemiluminescence intensity without increasing the rate of dioxetane disappearance. The thermal decomposition of **1–5** directly produced high yields of triplet carbonyl products and very low yields of excited singlets (triplet/singlet > 500) as determined by the DBA/DPA method.[2] The yield of excited triplet products for **2** was found to be 10 ± 5%, similar to those for other 3,3-dialkyl-1,2-dioxetanes.[5]

The activation parameters for dioxetanes **2–4** and **5a** are very similar to those[5a] for 3,3-diethyl-1,2-dioxetane. The E_a for **1** is 1.2 ± 0.4 kcal/mol lower than that for **2**. Interestingly, the activation energies for 3,3,4,4-bis(tetramethylene)-1,2-dioxetane (E_a = 25.3 kcal/mol)[9] and 3,3,4,4-bis(pentamethylene)-1,2-dioxetane (E_a = 27.7 kcal/mol)[4b] differ by 2.4 kcal/mol. Thus, as has been noted[5a] in comparison of steric effects of acyclic dioxetanes, ΔE_a's measured for tetrasubstituted dioxetanes are roughly twice the values of those for the 3,3-disubstituted compounds.

Dioxetane **2** has two chair confirmations **2a** (oxygen-2 axial) and **2e** (oxygen-2 equatorial) that could complicate interpretation of the activation parameter data. Since conformers **2a** and **2e** are in rapid equilibrium, the rate of disappearance of dioxetane **2** is the composite[8] of k_{ax}[**2a**] + k_{eq}[**2e**]. Based on free-energy differences[8] between equatorial and axial hydroxyl and methyl groups, the population of **2** is predicted to consist mainly of conformer **2a**. The results for dioxetanes **4** and **5a**, in which the conformation is "locked" with oxygen-2 axial are within experimental error of those for **2**. Thus the results for **2** appear to reflect largely those of conformer **2a**. There should be greater steric interactions on oxygen-2 in an axial position than in an equatorial position. This suggests that conformer **2a** should be thermally more stable to cleavage than **2e**. The results of **5e** are in agreement with this interpretation. Unlike the conformation of its configurational isomer **5a**, that of **5e** is expected to be complicated and not limited to one conformation. However, the activation parameters for **5e** should reflect those largely of its conformer with oxygen-2 equatorial. The data show that

(5) (a) Baumstark, A. L.; Dunams, T. *J. Org. Chem.* **1982**, *47*, 3754. (b) Baumstark, A. L.; Dunams, T.; Catalani, L.; Bechara, E. J. H. *Ibid.* **1983**, *48*, 3713.
(6) Baumstark, A. L.; Wilson, T.; Landis, M. E.; Bartlett, P. D. *Tetrahedron Lett.* **1976**, 2397.
(7) Sevin, A.; Cense, J. *Bull. Soc. Chim. Fr.* **1974**, 963.
(8) Eliel, E. L. "Stereochemistry of Carbon Compounds"; McGraw-Hill: New York, 1962; pp 234–239.
(9) Kopecky, K. R.; Sastri, J. A. L. *Can. J. Chem.* **1980**, *58*, 2089.

5e is less stable (lower E_a) than **5a**.

Examination of models indicates the steric interactions of the 5-ring substituent with the dioxetane oxygens are lower than those of the 6-ring (or larger) substituents (for **2–5**) or those of the 3,3-diethyl group. This suggests that the low E_a for 3,3-biphenylene-4-methoxy-1,2-dioxetane[6] is due to unusually low steric interactions and not a change in mechanism. For a series of acyclic dioxetanes (3-methyl-3-alkyl) higher steric interactions were found to lead to higher E_a's. Thus the present results are consistent with substituent effects for a diradical mechanism and suggests that steric interactions between oxygen-2 and the 3,3-substituents are the major influences on the activation parameters for alkyl dioxetanes.

Experimental Section

All solvents were of reagent grade. ^{1}H NMR spectra were recorded on Varian EM 360 and JEOL GX-270 NMR spectrometers. Gas chromatographic studies were carried out on a Varian Model 920 GC with a 6 ft × 0.25 in. SE-30 on Chromosorb W column. Methylenecyclohexane was available commercially (Aldrich). Methylenecyclopentane,[10] methylenecycloheptane,[10] 4-*tert*-butylmethylenecyclohexane,[10] and 4-methylmethylenecyclohexane[11] were prepared by literature procedures. 9,10-Diphenylanthracene (Aldrich) was used without further purification. 9,10-Dibromoanthracene (Aldrich) was recrystallized from xylenes (Aldrich) before use.

Dioxetane Synthesis and Purification. The alkenes (40 mmol) were converted to the corresponding β-bromo hydroperoxides in ~60% yield by the standard procedure developed by Kopecky[3f] [NMR (CCl_4) for 1-hydroperoxy-1-(bromomethyl)-cyclopentane (**6**), δ 1.4–2.0 (br s, 8 H), 3.55 (s, 2 H), 8.0 variable (s, 1 H); for 1-hydroperoxy-1-(bromomethyl)cyclohexane (**7**), δ 1.1–2.1 (br m, 10 H), 3.47 (s, 2 H), 8.5 variable (s, 1 H); for 1-hydroperoxy-1-(bromomethyl)cycloheptane (**8**), δ 1.2–2.0 (br m, 12 H), 3.42 (s, 2 H), 8.5 variable (s, 1 H); for 1-hydroperoxy-1-(bromomethyl)-4-*tert*-butylcyclohexane (**9**), δ 0.88 (s, 9 H), 1.0–2.2 (br m, 9 H), 3.59 (s, 2 H), 7.2 variable (s, 1 H); for 1-hydroperoxy-1-(bromomethyl)-4-methylcyclohexane (**10**), δ 0.93 (d, 3 H), 1.0–2.1 (br m, 9 H), 3.67 (s, 2 H), 7.43 (s, 1 H). The signals for the hydroperoxy protons varied in chemical shift and line width from sample to sample.] The β-bromo hydroperoxides **6–8** were oils at room temperature and were used without further purification. Compounds **9** and **10** crystallized from the crude mixtures of β-bromo hydroperoxides in pentane at −70 °C. β-Bromo hydroperoxide **9**, isolated in 58% yield [mp 70.5–72 °C; Anal. C, H] was shown to be the pure axial hydroperoxide as follows: reduction of 21.8 mg of **9** with 21.6 mg of triphenylphosphine in $CDCl_3$ yielded the β-bromo alcohol, treatment of which with KOH in MeOH yielded only the axial epoxide (by comparison with an authentic sample[10]). β-Bromo hydroperoxide **10** melted below room temperature but could be isolated in pure form by collection of the crystals at low temperature. Treatment of **10** with triphenylphosphine and base as described above for **9** yielded only one epoxide, which was shown to be equatorial by comparison with an authentic sample.[10] Thus β-bromo hydroperoxide **10** was the pure "equatorial" hydroperoxide (relative to the equatorial CH_3 group). The remaining bromo hydroperoxide (after separation of pure **10**) was a mixture of **10** and the axial hydroperoxide (**11**).

The following procedure for the synthesis of dioxetane **1** was employed in the synthesis of **1–3**. The β-bromo hydroperoxide (CAUTION!) prepared from 40 mmol of methylenecyclohexane was placed in 10 mL of CCl_4 and cooled to ~0 °C (ice bath). To the rapidly stirring (magnetically) solution was added 2.0 g of KOH in 10 mL of deionized water (Na_2 EDTA added) dropwise. The mixture was stirred for 30 min (or until the color of the CCl_4 layer turned intense yellow). The resulting CCl_4 layer was separated and dried over $MgSO_4$. The dioxetane solution was concentrated at low temperature under reduced pressure. Purification was achieved by low-temperature column chromatography. A jacketed column (15 mm i.d.) was packed with 15 to 20 g of silica gel/Na_2 EDTA (100/1) with pentane as the solvent (temperature −78 °C). The dioxetane sample in CCl_4 was placed on the column and eluted with 50-mL portions of a pentane/methylene chloride step gradient (5% v/v). The temperature of the column was maintained at −78 °C and pressure from a nitrogen tank was used to speed up fraction collections. Fractions (10 mL) were collected and placed on dry ice. The fractions were analyzed for dioxetane content by placing a small aliquot into a heated solution (1 mL) of 5×10^{-3} M DBA in xylenes in the chemiluminescence monitoring apparatus. Fractions that produced the most relative light intensity were combined and the solvent was removed under reduced pressure at low temperature to yield the dioxetane as a light yellow oil. NMR spectroscopy and iodometric titration[12] showed the dioxetane to be of better than 95% purity [NMR (CCl_4) for **1**, δ 1.2–2.0 (br m, 8 H), 5.1 (s, 2 H); for **2**, 1.2–1.8 (br m, 6 H), 1.8–2.1 (br m, 4 H), 4.80 (s, 2 H), for **3**, δ 1.3–1.8 (br m, 8 H), 1.9–2.3 (br m, 4 H), 4.80 (s, 2 H)]. Combination of later fractions yielded dioxetane solutions that contained the corresponding epoxides as impurities.

Dioxetanes **4**, **5a**, **5e** proved difficult to prepare by the two phase (CCl_4/aqueous $^-$OH) method due to extreme emulsion problems. Synthesis was accomplished by addition of 0.9 equiv of KOH to a solution of the β-bromo hydroperoxide in MeOH at 0 °C, followed by addition of water and extraction with CCl_4. Dioxetanes **4** and **5e** were synthesized by closure of **9** and **10**, respectively. The configuration of **4** was confirmed by reaction of the dioxetane with triphenylphosphine to yield a phosphorane, the subsequent thermal decomposition[12] of which yielded (as expected) only the axial epoxide.[10] Dioxetane **5a** proved to be the most difficult compound of the series to prepare and purify since the pure β-bromo hydroperoxide could not be obtained. Treatment of the impure β-bromo hydroperoxide **11** yielded a mixture of **5a** and **5e**. Only partial purification could be achieved by low-temperature chromatography. **5e** was removed from the mixture by partial (thermal) decomposition at low temperature, conditions under which **5e** underwent decomposition much faster than **5a** (followed by ^{1}H NMR spectroscopy). This yielded samples of **5a** containing cleavage products. Final purification of **4**, **5a**, and **5e** was carried out as for the others by low-temperature column chromatography [NMR (CCl_4) for **4**, δ 0.85 (s, 9 H), 1.0–2.0 (br m, 9 H), 4.88 (s, 2 H); for **5a**, δ 1.0 (d, J ~7 Hz, 3 H), 1.2–2.4 (m, 9 H), 4.91 (s, 2 H); for **5e**, δ 0.88 (d, J = ~6 Hz, 3 H), 1.5–2.5 (m, 9 H), 4.99 (s, 2 H)]. The dioxetanes were stored as approximately 0.1 M solutions in CCl_4 at −70 °C. The dioxetane concentrations were determined by the iodometric method[13] used by Wilson and Schaap.

Product Studies. The following procedure was employed for compounds **1–5**. A solution of the purified dioxetane (0.1 M) in CCl_4 was heated in a capped NMR sample tube until the yellow color disappeared. The corresponding ketones were the only products detected by NMR spectroscopy. Formaldehyde, the other cleavage product, was not observed. The ketones were detected by GC analysis of the solutions.

Kinetic Studies and Yields of Excited States. The chemiluminescence monitoring system is essentially identical with that described previously.[13] The temperature (±0.3 °C) of the reaction mixture in the chemiluminescence apparatus was monitored by use of a YSI Model 425C Tele-Thermometer with a no. 423 probe before and after each run. The jacketed cell was pretreated with an aqueous Na_2EDTA solution. All experiments were carried out in xylenes (Aldrich) as the solvent. In a typical experiment, 10 to 20 μL of a dioxetane solution in CCl_4 was added to 1.0 mL of xylenes (Aldrich) containing either DBA or DPA as added fluorescer. The solution was mixed by bubbling air with a pipet. Runs carried out without added fluorescer and with varying

(10) Conia, J.; Limasset, J. *Bull. Soc. Chim. Fr.* **1967**, 1936.

(11) Modification (addition of NaH/Me_2SO after ketone and phosphonium salt) of the procedure of Klein, J.; Lichtenberg, D. *J. Org. Chem.* **1970**, *35*; 2654 improved the yield.

(12) (a) Bartlett, P. D.; Baumstark, A. L.; Landis, M. E. *J. Am. Chem. Soc.* **1973**, *95*, 6486. (b) The configuration of *trans*-3,4-diphenyl-1,2-dioxetane was proven by reduction with PPh_3. See: Koo, J.; Schuster, G. B. *J. Am. Chem. Soc.* **1977**, *99*, 5403. Bartlett, P. D.; Landis, M. E.; Shapiro, M. J. *J. Org. Chem.* **1977**, *42*, 1661.

(13) Wilson, T.; Schaap, A. P. *J. Am. Chem. Soc.* **1971**, *93*, 4126.

concentrations of DBA and DPA were of the first order for at least 3 half-lives and showed no dependence on amount or type of added fluorescer. The initial dioxetane concentrations were approximately 10^{-3} M or lower to avoid complications due to induced decomposition. First-order thermolyses with an upper limit (mixing and thermal equilibration) on k_1 of approximately 5×10^{-2} s^{-1} can be studied with this instrumentation.

The relative yields of excited states produced upon dioxetane thermolysis were determined at 50 °C by variation of the concentration of appropriate fluorescer at constant dioxetane concentration (DBA/DPA method). For the calculation of excited state yields for **2**, the value of Φ_{ET} was assumed to be 0.2. The method of calculation has been discussed in detail.[2] The instrument was calibrated by setting the yield of triplet products from the thermolysis of trimethyl-1,2-dioxetane[14] (DBA method) at 0.15.

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(14) Kopecky, K. R.; Filby, J. E. *Can. J. Chem.* **1979**, *57*, 283.

Homogeneous Catalytic Hydrogenation. 2. Selective Reduction of Polynuclear Heteroaromatic Compounds Catalyzed by Chlorotris(triphenylphosphine)rhodium(I)

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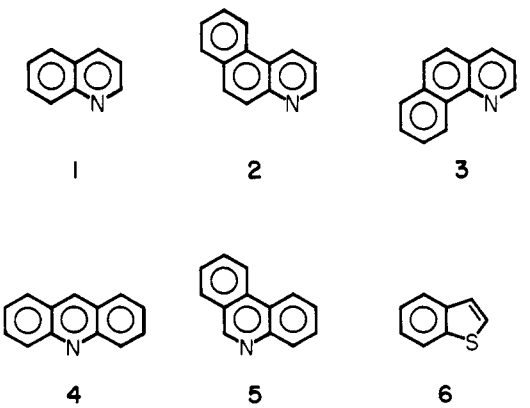
The selective reduction of polynuclear heteroaromatic nitrogen compounds such as quinoline, **1**, 5,6-benzoquinoline, **2**, 7,8-benzoquinoline, **3**, acridine, **4**, phenanthridine, and, and in one case, a sulfur heterocyclic compound, benzothiophene, **6**, with chlorotris(triphenylphosphine)rhodium(I), $(Ph_3P)_3RhCl$, provided under rather mild hydrogenation conditions the corresponding saturated nitrogen and sulfur heterocyclic analogues of the above-mentioned compounds in reasonable conversion rates and total percent yields. In addition, compounds that inhibit the initial rate of hydrogenation of **1** in the conversion to 1,2,3,4-tetrahydroquinoline, **10**, include pyridine, **7**, 3-methylpyridine, **8**, and **10** itself. These results are indicative of electronic effects in these competitive hydrogenation reactions, while 2-methylpyridine, **9**, slightly reduces the rate of hydrogenation of **1**, implicating a steric effect at the metal center. It was also observed that substrate **6**, indole, **11**, pyrrole, **12**, carbazole, **13**, thiophene, **14**, dibenzothiophene, **15**, and *p*-cresol, **16**, enhanced the initial rate of hydrogenation of **1** to **10** by an average factor of >1.5. The substitution of deuterium gas for hydrogen gas in the reduction of **1** provided information on the reversibility of the hydrogenation step, stereoselectivity in the reduction of the 3,4-double bond, and the implication of cyclometalation reactions which caused the exchange of H for D at the 8-position and possibly the 2-position. Similar deuteration data with compound **5** strengthened the concept of dehydrogenation in the hydrogenation step and in fact provided independent evidence for the facile dehydrogenation of 1,9,9,10-tetradeuterio-9,10-dihydrophenanthridine, **19**, catalyzed by $(Ph_3P)_3RhCl$. ^1H NMR and IR experiments also verify some of the postulated mechanistic aspects of these selective hydrogenation reactions.

Introduction

Recently, we discovered that the nitrogen heterocyclic ring incorporated in polynuclear heteroaromatic nitrogen compounds can be regioselectively reduced under a variety of homogeneous hydrogenation conditions.[1a,b] These results are important, since they have possible implications for the future synthetic fuel industry with regard to coal liquefaction and the upgrading of coal liquids and shale oils as well as the ultimate removal of nitrogen from these synthetic fuels.

In our quest for catalysts that could perform these reductions under rather mild conditions, we have discovered that chlorotris(triphenylphosphine)rhodium(I), $(Ph_3P)_3RhCl$, can selectively reduce the heterocyclic ring in polynuclear heteroaromatic nitrogen and sulfur model synthetic fuel compounds at reasonable initial rates and total percent yields.

Chart I. Model Synthetic Fuel Compounds Used in Hydrogenation Reactions with $(Ph_3P)_3RhCl$



Although $(Ph_3P)_3RhCl$ has been one of the most extensively studied homogeneous hydrogenation catalysts known,[2a-f] to our knowledge, this is the first reported use

(1) (a) Fish, R. H.; Thormodsen, A. D.; Cremer, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 5234. (b) Fish, R. H. *Ann. N.Y. Acad. Sci.* **1983**, *415*, 292.

0022-3263/84/1949-4500$01.50/0