equipped with a slave recorder and a thermostated cell compartment (±0.05 °C). All kinetic runs were carried out in duplicate. Values of k_ψ were calculated numerically from the standard equation or graphically for each run.

Registry No. Phenyl acetate, 122-79-2; $HClO_4$, 7601-90-3; H_2SO_4, 7664-93-9; HCl, 7647-01-0.

Carbon Acidity. 62. Equilibrium Acidities of Some Phenalene Hydrocarbons: SCF-π MO Correlation

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Received February 4, 1981

Phenalene, 1, benzanthrene, 2, and the recently prepared 6*H*-benzo[*cd*]pyrene,[1] 3, form a related group of hydrocarbons that have special significance in the correlation of structure with carbon acidity; they are relatively acidic hydrocarbons but are not derived from cyclopentadiene, and they have planar π-electron systems. The pK_a of phenalene has been reported as 19.45 by the H_- method in aqueous Me_2SO.[2] We now report the p*K*'s of 1 and 3 in the cesium cyclohexylamide (CsCHA)–cyclohexylamine system to compare with the pK_{CsCHA} value reported previously for 2.[3]

Phenalene was prepared by the method of Bondjouk and Johnson.[4] One sample of 3 was the kind gift of Professor Murata; additional quantities were prepared by his procedure.[1] The acidity measurements were carried out as described previously.[3,5] Results are summarized in Table I.

The results provide the acidity values shown in Chart I on the CsCHA ion pair scale.[6] The results are poorly correlated by resonance considerations or by HMO calculations.[7,8] A better correlation is obtained by a standard SCF-π approach with explicit incorporation of electron repulsion. Table II gives the results for a number of hydrocarbons with emphasis on those whose carbanions are expected to be coplanar. Standard structures were assumed with regular hexagons and pentagons, where possible, with bond distances of 1.40 Å.[9]

The SCF-π MO approach gives the correct ordering of the acidities of 1, 2, and 3. Moreover, they give an excellent correlation with pK_{CsCHA} values of other conjugated hydrocarbons both with and without five-membered rings (Figure 1).

Table I. Determination of Equilibrium Acidities

RH	R^-Cs^+ (CHA), λ_{max} (ϵ)	indicator[a]	no. of determinations	pK_{CsCHA}[b]
1	442 (39460)	In	2	18.55
		PF	4	18.47
				ave 18.49 ± 0.02
3	456 (44200) 523 (10400) 622 (2650) 674 (3100)	B[a]F B[c]F	2 1	20.00 19.75
				ave 19.91 ± 0.1

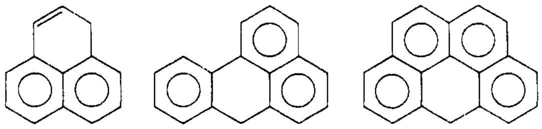
[a] Indicators and pK_{CsCHA} are as follows: In, indene, 19.93; PF, 9-phenylfluorene, 18.49; B[a]F, 11*H*-benzo[*a*]fluorene, 20.35; B[c]F, 7*H*-benzo[*c*]fluorene, 19.75. For a summary of indicator spectral properties see ref 6. [b] Statistically corrected for equivalent positions.

Table II. SCF-π Calculations

RH	$-E_\pi$[a] RH	$-E_\pi$[a] R^-	ΔE_π	pK_{CsCHA}[b]
toluene	9.666	1.600	8.066	41.2
2-methylnaphthalene	16.756	8.952	7.804	38.2[c]
1-methylnaphthalene	16.756	9.209	7.547	37.9[c]
diphenylmethane[d]	19.332	12.934	6.398	28.6[d]
9*H*-benzo[*def*]fluorene	24.108	18.312	5.796	22.9
10*H*-benzo[*b*]fluorene	27.207	21.415	5.788	23.7[e]
fluorene	20.109	14.334	5.775	23.0
2	27.235	21.536	5.699	21.43
3	31.349	25.724	5.625	19.91
7*H*-benzo[*c*]fluorene	27.243	21.738	5.505	19.75
11*H*-benzo[*a*]fluorene	27.215	21.794	5.421	20.35
indene	12.290	6.872	5.419	19.9
1	19.405	14.129	5.277	18.49
cyclopentadiene	4.522	−0.610	5.132	16.25

[a] π bond energies; $\beta^\circ = -1.75$ eV; Mataga–Nishimoto repulsion integrals (ref 10) used with $\gamma_{11} = 10.98$ eV. [b] Reference 6 and this work. [c] Derived from: Streitwieser, A., Jr.; Granger, M. R.; Mares, F.; Wolf, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 4257. [d] The pK_{CsCHA} for a planar diphenylmethyl anion was estimated from 9,9-dimethyl-9,10-dihydroanthracene with correction for two *o*-alkyl substituents. [e] Revised value.

Chart I



1 2 3

18.49 21.43 19.91

pK_{CsCHA}

Experimental Section

Melting points are uncorrected. NMR spectra were determined on a Varian EM-390 spectrometer and expressed as δ values, parts per million downfield from Me_4Si as an internal standard. Mass spectra were obtained at 70 and 9.2 eV on a CEC-103 spectrometer. Visible spectra were determined on a Carey 118 visible–UV spectrophotometer using a thermostated cell block held at 25 °C. Elemental analyses were performed by the Analytical Services Laboratory of the University of California, Berkeley.

Phenalene (1). This preparation was derived from that of Bondjouk and Johnson[4] except that the final isolation stage was carried out under red light because of the sensitivity of 1 to light. To a solution of perinaphthenone (4 g, 22 mmol) in 80 mL of benzene under nitrogen was added 44 mL of DIBAL (20% in hexane) dropwise over 1 h. The solution was refluxed overnight, then cooled to room temperature, and quenched with 8 mL of

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(10) Nishimoto, K.; Mataga, N. *Z. Phys. Chem.* **1957**, *12*, 335. Nishimoto, K. *Ibid.* **1957**, *13*, 140.

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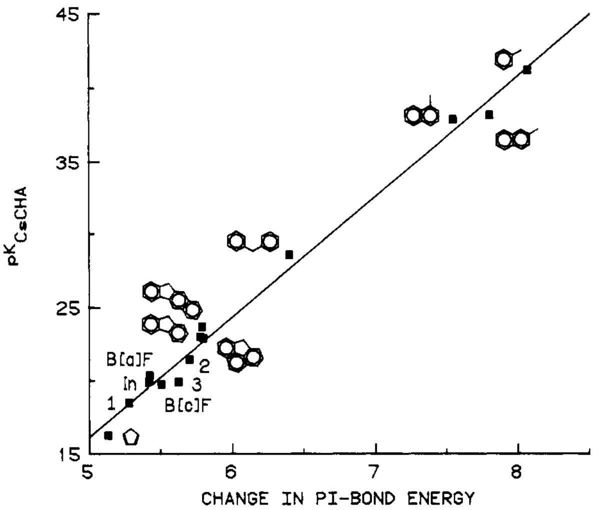

Figure 1. Correlation of pK_{CsCHA} with SCF-π ΔE_π values. The regression line is $pK = -23.153 + 7.887\Delta E_\pi$, $r = 0.993$.

saturated NH_4Cl. Under a red bulb the mixture was extracted with 50 mL of hexane and washed with 20 mL of NH_4Cl solution. The organic layer was dried over $MgSO_4$ and evaporated with 1 g of Florisil to dryness. This product was placed on a column (5 × 20 cm) packed with dry, deoxygenated Florisil under N_2 and eluted with degassed hexane. The solvent was evaporated to give a white solid. The solid was recrystallized from pentane at dry ice temperatures: yield 1.12 g (62%); mp 82.5–83.5 °C (lit.[4] mp 83–84 °C); ^1H NMR (CCl_4) δ 3.96 (m, 2 H), 5.88 (dt, J = 10, 4.5 Hz, 1 H), 6.42 (dt, J = 10, 2.5 Hz, 1 H), 6.75 (d, J = 7.5 Hz, 1 H), 7.15 (m, 5 H); mass spectrum, m/e 82 (7), 165 (100), 166 (44); low-voltage mass spectrum, m/e 165 (8), 166 (100), 167 (14). Note that even at low voltage some formation of M − 1 cannot be avoided.

6*H*-Benzo[*cd*]pyrene (3). This compound as donated by Professor I. Murata (Osaka University) and also prepared by his method[1] was purified by chromatography twice on alumina (Woelm, activity grade 1) under argon with degassed 1:3 benzene–hexane and was stored under argon in the dark.

Acidity Measurements. The spectra and extinction coefficients of the cesium salts and their equilibria with indicator hydrocarbons were determined as described previously.[5] Statistical corrections were applied to give results on a per-hydrogen basis.[6]

Acknowledgment. This work was supported in part by USPH Grant GM-12855 and NSF Grant CHE 79-10814.

Registry No. 1, 203-80-5; 2, 199-94-0; 3, 191-33-3; toluene, 108-88-3; 2-methylnaphthalene, 91-57-6; 1-methylnaphthalene, 90-12-0; diphenylmethane, 101-81-5; 9*H*-benzo[*def*]fluorene, 203-64-5; 10*H*-benzo[*b*]fluorene, 243-16-3; fluorene, 86-73-7; 7*H*-benzo[*c*]fluorene, 205-12-9; 11*H*-benzo[*a*]fluorene, 238-84-6; indene, 95-13-6; cyclopentadiene, 542-92-7; perinaphthenone, 548-39-0.

An Unexpected Product from the Peracid Oxidation of Furan Derivatives and a New ε-Lactone Synthesis

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Received January 22, 1981

Previous work in our laboratory has shown that certain furanosesquiterpenes are hepatotoxins.[1] The toxicity of these compounds is enhanced by the cytochrome oxidase enzyme system.[2] Efforts to elucidate the structures of in vitro metabolites are running concurrently with model studies involving the chemical oxidations of furans. This paper describes the results of the latter, using *m*-chloroperbenzoic acid (*m*CPBA), which is occasionally used as a mimic for cytochrome oxidase.[3]

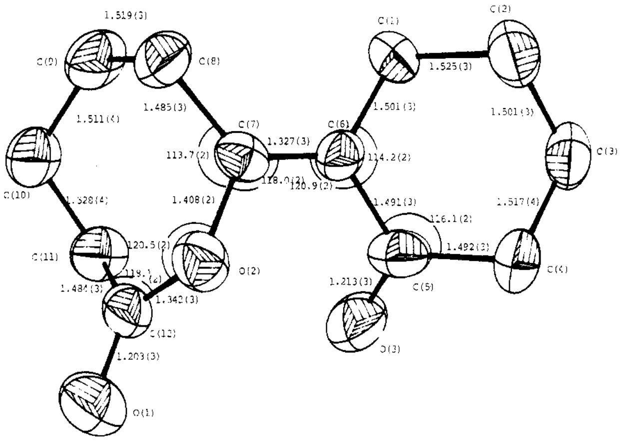
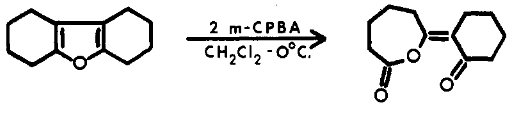


Figure 1. Perspective view of the molecular structure of lactone 2.

In the only other example of peracid oxidation of a furanosesquiterpene, lindestrene, was shown to consume 1 mol of perbenzoic acid to form the γ-lactone via the NIH shift reaction.[4] In contrast, the reaction reported herein (eq 1) produces a stereospecific ε-lactone in nearly quantitative yield from the consumption of 2 mol of perbenzoic acid. The transformation is complete in 5 min at 0 °C. In an experiment where only 1 mol of peracid is used, only one-half of the furan substrate reacted to form the ε-lactone. Since no intermediate is observed during this procedure, the addition of both peracid molecules must be facile.



1 2 (1)

The basic structure for the new ε-lactone, **2**, followed directly from ^1H and ^{13}C NMR and IR spectroscopy. However, the stereochemistry about the double bond was not evident from these data and necessitated a single-crystal X-ray analysis. The results presented in Figure 1 clearly establish the detailed structure including the *Z* character of the olefinic moiety.

A second furan substrate, which is a better model for naturally occurring furan compounds, was also studied (eq 2). The major difference in the ^{13}C NMR data between structures 2 and 4 was the presence of a doublet at 190 ppm in the gated decoupled spectrum of 4. Also, when 4 was derivatized with 2,4-DNP reagent, this resonance

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