reduced pressure and separation by column chromatography over silica gel with 25% ethyl acetate in hexane gave the trans isomer 4 (0.063 g) and the cis isomer 3 (0.018 g).

Thermal Isomerization of *cis*-3 and *trans*-4 Esters. A solution of the cis ester 3 (0.05 g, 0.11 mmol) in benzene (2 mL) and methanol (1 mL) was refluxed under nitrogen for 4 days. Evaporation of the solvents under reduced pressure, followed by column chromatography over silica gel with 25% ethyl acetate in hexane, gave the trans ester 4 (0.012 g) and the cis ester 3 (0.020 g). After 4 days of similar treatment, the trans ester 4 was converted to the cis ester 3 to an extent of only about 1%.

Reaction of 1 with Methyl Propiolate. A solution of dehydronuciferine (1; 0.092 g, 0.314 mmol) in methanol (1 mL)–benzene (1 mL) containing excess methyl propiolate was refluxed under nitrogen for 2 days. Evaporation under reduced pressure, followed by column chromatography over silica gel with 25% ethyl acetate in hexane, gave the Michael adduct 7 in 56% yield. Crystallization from ethyl acetate gave yellow-orange crystals: mp 157.5–158.5 °C; UV max (EtOH) 240 nm (sh, log ϵ 5.15), 253 (sh, 5.13), 260 (5.17), 300 (4.70), 356 (4.35), 373 (sh, 4.30), 450 (4.11); IR (KBr) 1739, 1667, 1626 cm^{-1}; NMR (CDCl$_3$) δ 9.63–9.58 (dd, 1 H, J = 8, 2 Hz), 8.26–8.22 (dd, 1 H, J = 8, 2 Hz), 7.58–7.44 (m, 2 H), 7.08 (s, 1 H, C$_3$-H), 8.40 and 6.40 (d, 1 H each, J = 16 Hz), 4.02 (s, 3 H, OCH$_3$), 3.86 and 3.84 (s, 3 H each, OCH$_3$), 3.42 (t, 2 H), 3.16 (t, 2 H), 2.88 (s, 3 H, NCH$_3$); mass spectrum, m/e (relative intensity) 377 (100), 362 (13), 330 (17), 318 (14), 304 (100), 288 (22), 273 (63); high-resolution mass spectrum calcd for $C_{23}H_{23}NO_4$ 377.1620, found 377.1633.

Reaction of 1 with Methyl Acrylate. Excess methyl acrylate was added to a solution of dehydronuciferine (1; 0.10 g, 0.34 mmol) in methanol (1 mL) and the solution was refluxed under nitrogen for 7 days. After evaporation of the solvent, the residue was chromatographed over silica gel with 50% ethyl acetate in hexane to give recovered 1 (0.079 g) and 0.014 g of the Michael adduct 8 as a greenish yellow oil: UV max (EtOH) 230 nm (log ϵ 4.18), 256 (4.22), 275 (sh, 3.93), 312 (3.60), 354 (2.93), 373 (2.93); IR (film) 1724 cm^{-1}; NMR (CDCl$_3$) δ 9.72 (dd, 1 H, J = 8, 2 Hz), 8.02 (dd, 1 H, J = 8, 2 Hz), 7.63–7.50 (m, 2 H), 7.12 (s, 1 H, C$_3$-H), 4.03, 3.88, and 3.74 (s, 3 H each, OCH$_3$), 3.60 (t, 2 H), 3.34 (t, 2 H), 3.19 (t, 2 H), 2.79 (s, 3 H, NCH$_3$), 2.69 (t, 2 H); mass spectrum, m/e (relative intensity) 279 (5), 306 (17), 149 (19); high-resolution mass spectrum, calcd for $C_{23}H_{25}NO_4$ 379.1776, found 379.1778. Acrylonitrile failed to react under the same conditions.

Reaction of 1 with Diethyl Azodicarboxylate. To a solution of dehydronuciferine (1; 0.23 g, 0.785 mmol) in anhydrous toluene (5 mL) was added diethyl azodicarboxylate (0.15 mL, 0.952 mmol), and the mixture was refluxed for 24 h. More diethyl azodicarboxylate (0.2 mL) was added and the heating continued for 48 h. Evaporation of the solvent under reduced pressure and separation by column chromatography over silica gel with 25% ethyl acetate in hexane gave the crystalline adduct 9 (0.152 g, 41%). Crystallization from ethyl acetate gave green yellow crystals: mp 167–169 °C; UV max (EtOH) 230 nm (log ϵ 4.15), 250 (4.69), 258 (4.65), 277 (sh, 4.23), 320 (4.11), 350 (sh, 3.64), 367 (3.43); IR (KBr) 3333, 1770, 1724 cm^{-1}; NMR (CDCl$_3$) δ 9.76–9.56 (m, 1 H), 8.53–8.23 (m, 2 H), 7.66–7.53 (m, 2 H), 7.13 (s, 1 H, C$_3$-H), 4.40–4.08 (m, 4 H), 4.03 and 3.70 (s, 3 H each, OCH$_3$), 2.80 (s, 3 H, NCH$_3$), 1.33–1.10 (t, 6 H); mass spectrum, m/e (relative intensity) 467 (16), 379 (41), 335 (24), 334 (100), 319 (18), 306, (52), 305 (76); high-resolution mass spectrum calcd for $C_{25}H_{29}N_3O_6$ 467.2046, found 467.2058.

Reaction of 1 with Naphthoquinone. Excess naphthoquinone (0.19 g, 1.2 mmol) was added to a solution of dehydronuciferine (1; 0.015 g, 0.051 mmol) in methanol (2 mL) and the mixture was refluxed under nitrogen for 2 days. The unreacted dehydronuciferine was eluted first from the column with 25% ethyl acetate in hexane. A red band eluted next, which on evaporation, followed by two crystallizations from chloroform, gave red crystals of compound 10 in 27% yield: mp 295–297 °C; UV max (EtOH) 225 nm (sh, log ϵ 4.26), 239 (sh, 4.27), 260 (4.34), 271 (4.39), 282 (4.38), 316 (4.07), 341 (sh, 3.78), 355 (3.59), 490 (3.41); IR (KBr) 1653 cm^{-1}; NMR (CDCl$_3$) δ 10.12 (d, 1 H, J = 8 Hz), 9.65 (dd, 1 H, J = 8, 2 Hz), 8.34 (dd, 1 H, J = 8, 2 Hz), 8.20 (dd, 1 H, J = 8, 2 Hz), 7.80–7.64 (m, 4 H), 7.20 (s, 1 H, C$_3$-H), 5.06 (t, 2 H), 4.06 (s, 3 H, OCH$_3$), 3.96 (s, 3 H, OCH$_3$), 3.50 (t, 2 H); mass spectrum, m/e (relative intensity) 433 (100), 418 (39), 390 (14), 375 (17); high-resolution mass spectrum calcd for $C_{28}H_{19}NO_4$ 433.1308, found 433.1322.

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Registry No. 1, 7630-74-2; 3, 77027-97-5; 4, 77027-98-6; 7, 77027-99-7; 8, 77028-00-3; 9, 77028-01-4; 10, 77028-02-5; dimethyl acetylenedicarboxylate, 762-42-5; methyl propiolate, 922-67-8; methyl acrylate, 96-33-3; diethyl azodicarboxylate, 1972-28-7; naphthoquinone, 130-15-4.

Acid-Catalyzed Hydrolysis of Phenyl Acetate

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Yates and McClelland suggested that the monotonic increase in the rate of hydrolysis of phenyl acetate in 1.0–12.0 M sulfuric acid masked a changeover from an $A_{Ac}2$ to an $A_{Ac}1$ mechanism.[1] They analyzed their kinetic data using Yates' modified hydration parameter treatment (eq 1),[2] where k_ψ is the observed first-order rate coefficient,

$$\log k_\psi + mH_0 = r \log a_W + \text{constant} \tag{1}$$

m = 0.62 for acetate esters, and H_0 and a_W have their usual meanings. The value of r (1.62) at low acidity (0–70% H_2SO_4) was characteristic of an A2 reaction. At higher acidities the r plot begins to curve and its slope to fall. Unfortunately, sulfonation also begins to occur, and the hydrolysis of phenyl acetate could not be studied in >12.5 M sulfuric acid.

More recently, Rochester and Attiga have studied the hydrolysis of phenyl acetate in 0–9 M perchloric acid.[3] Analysis of the data in terms of the Bunnett w and w^* relationships[4] for a weakly basic substrate (eq 2 and 3) gave

$$\log k_\psi + H_0 = w \log a_w + \text{constant} \tag{2}$$

$$\log k_\psi - \log C_{H^+} = w^* \log a_w + \text{constant} \tag{3}$$

values of w and w^* of 2.5 (curved) and −0.3, respectively, again consistent with a bimolecular (A2) mechanism. Evidence for a possible change to an A1 mechanism was adduced from the decreasing slope of the w plot in >9.0 M perchloric acid although this could not be clearly established because kinetic data were not obtained at >9.67 M perchloric acid.

In order to confirm unequivocally the original suggestion[1] that there is a changeover of mechanism in the acid-catalyzed hydrolysis of phenyl acetate, we have extended previous data in perchloric acid to 11.5 M, followed the rate of hydrolysis in concentrated hydrochloric acid, and determined the Arrhenius parameters for hydrolysis under a variety of different acidic conditions in sulfuric and perchloric acids. Values of k_ψ for the hydrolysis of phenyl acetate in a number of mineral acids are shown in Figure 1. The data of Yates and McClelland[1] for sulfuric acid and those of Rochester and Attiga[3] for perchloric acid

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[1] K. Yates and R. A. McClelland, *J. Am. Chem. Soc.*, **89**, 2686 (1967).
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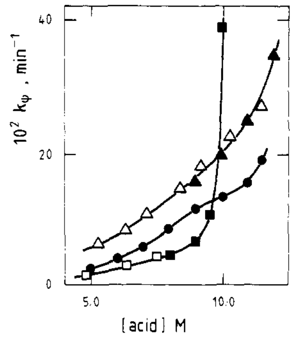


Figure 1. Hydrolysis of phenyl acetate at 25.0 °C in the following: HCl, ●; $HClO_4$, ■ (□ data from ref 3); H_2SO_4 ▲ (△ data from ref 1).

Table I. Summary of Rate Correlations

acid	C_{H^+}, M	w	w^*	r	ϕ
$HClO_4$	<8.0	2.63	−0.27	1.4	0.94
$HClO_4$	>8.0	0.18	−2.31	−1.0	0
H_2SO_4	<8.0	2.43	−0.08	1.7	0.56
H_2SO_4	>8.0	1.96	−0.85		
HCl	<8.0	2.65	−0.72	1.8	0.79

have also been included for comparison. The most striking feature of the rate profiles is the crossover of the perchloric acid data. At low acidities (1–9.5 M) the catalytic effect of acids decreases in the order $H_2SO_4 > HCl > HClO_4$, the order typically associated with an A2 mechanism.[5] At acid concentrations above 9.5 M, however, the rate of hydrolysis in perchloric acid rises sharply and exceeds first that in hydrochloric acid and then that in sulfuric acid. As a result, at acidities above 10 M the effectiveness of acids decreases in the order $HClO_4 > H_2SO_4 > HCl$. Bunton and his co-workers have suggested[5] that such an order of reactivity is characteristic of a unimolecular mechanism, transition states of carbocationic character being preferentially stabilized by anions of low charge density such as ClO_4^-, whereas the converse is the case for A2 reactions. The results of analyses of the data by various kinetic criteria are shown in Table I. Our values of w, w^*, and r for hydrolysis at low acidities in perchloric, sulfuric, and hydrochloric acids are similar to those of previous workers[1,2] and characteristic of an A2 mechanism. In concentrated perchloric acid, however, values of w and w^* change sharply to values (0.18 and −2.31, respectively) characteristic of a unimolecular mechanism. The r plot (eq 1) goes through a maximum to give a slope of approximately −1.0. Although simplistically a value of zero would be predicted for an A1 process, Yates and McClelland have suggested[1] that negative values of r can arise from a reduction in hydration accompanying conversion of the conjugate acid of the ester into a transition state leading to carbocation formation. Correlation of the data by Bunnett's linear free-energy relationship (eq 4)[6] also shows an abrupt change in slope at high concentrations of perchloric acid to a value consistent with an A1 mechanism.

$$\log k_\psi + H_0 = \phi H_0 + \log [H^+] + \log k_2^0 \qquad (4)$$

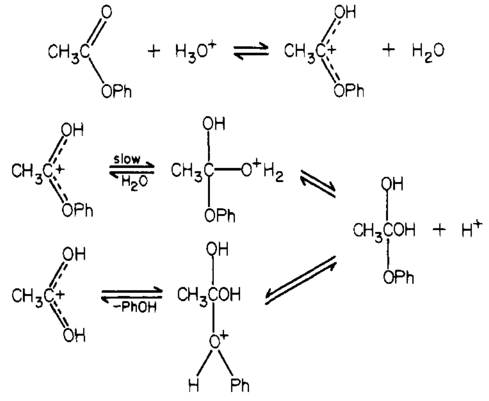
Values of the Arrhenius parameter for hydrolysis of phenyl acetate are shown in Table II. Our values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for 8.0 M $HClO_4$ are in good agreement with those of Rochester and Attiga.[3] The most striking feature of the data is the dramatic change of $\Delta S^\ddagger$ for hydrolysis in perchloric acid from fairly negative values at low acidity to much more positive values at high acidity. Such values of $\Delta S^\ddagger$ are characteristically associated with a unimolecular mechanism.[7] All the evidence therefore confirms that there is a distinct changeover in mechanism for the hydrolysis of phenyl acetate at high concentration of perchloric acid and a partial changeover for hydrolysis in sulfuric acid. Thus at low acidities hydrolysis occurs by the $A_{AC}2$ mechanism which involves rate-determining attack of water on the conjugate acid of the ester (Scheme I) and proceeds via a tetrahedral intermediate. At high acidities, however, the conjugate acid undergoes unimolecular heterolysis to form an acylium ion and phenol (Scheme II). Although NMR evidence[8] indicates that protonation occurs predominantly on the carbonyl oxygen, this does not exclude reaction occurring via small, undetectable, equilibrium concentrations of the acyl oxygen protonated species which is assumed to be the case in the $A_{AC}1$ mechanism in strong acid.

Table II. Arrhenius Parameters for Hydrolysis of Phenyl Acetate[a]

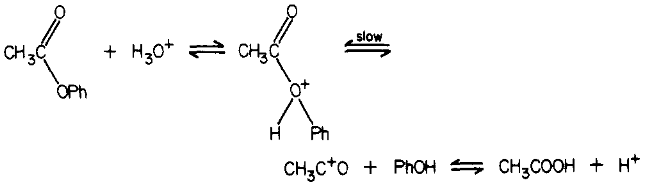
acid	C_{H^+}, M	$\Delta H^\ddagger$, kcal/mol[b]	$\Delta S^\ddagger$, eu[b]
H_2SO_4	8.00	11.3 ± 1.8	−34.2 ± 6.0
H_2SO_4	10.0	14.0 ± 0.8	−27.1 ± 2.6
H_2SO_4	12.0	15.9 ± 1.8	−20.7 ± 6.2
$HClO_4$	8.00	17.3 ± 0.5	−18.5 ± 1.5
$HClO_4$	10.0	19.5 ± 0.6	−7.8 ± 2.0
$HClO_4$	10.5	18.3 ± 0.6	−9.7 ± 1.9
$HClO_4$	11.0	21.3 ± 1.6	+2.2 ± 5.6
$HClO_4$	11.5	22.6 ± 2.1	+7.9 ± 7.2

[a] Calculated at 25 °C. [b] Standard deviations are shown.

Scheme I. $A_{AC}2$ Mechanism



Scheme II. $A_{AC}1$ Mechanism



Experimental Section

Rates of hydrolysis were determined spectrophotometrically at 267 nm by using a Unicam SP 1750 UV spectrophotometer

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[5] C. A. Bunton, J. H. Crabtree, and L. Robinson, *J. Am. Chem. Soc.*, **90**, 1258 (1968).

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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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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)	B[a]F	2	20.00
	523 (10400)	B[c]F	1	19.75
	622 (2650)			
	674 (3100)			
				ave 19.91 ± 0.1

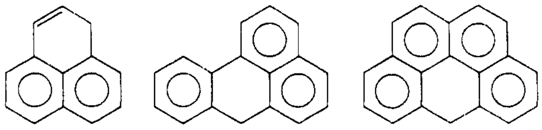
[a] Indicators and pK_{CsCHA} are as follows: In, indene, 19.93; PF, 9-phenylfluorene, 18.49; B[a]F, 11*H*-benzo[*a*]fluorene, 20.35; B[c]F, 7*H*-benzo[*c*]fluorene, 19.75. For a summary of indicator spectral properties see ref 6. [b] Statistically corrected for equivalent positions.

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 18.49 2 21.43 3 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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(2) Bowden, K.; Cockerill, A. F. *J. Chem. Soc. B* **1970**, 173.

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(9) For further details of the structures assumed, see: Wright, J. S. Dissertation, University of California, 1968.

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