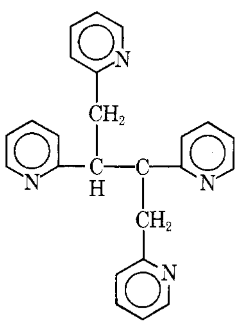
metal exchange yields 2-picolylsodium, which can couple with **1** to form **13**. A first metalation and coupling with **1** leads to **15**, where the methine group is a site of choice for further metalation, because of the inductive effect of the picolyl groups. Subsequent coupling forms **16**. The increased acidity at the methine group therefore overweighs steric hindrance, since no formation of **17** was observed.



17

The total yield of **5** and **16** is quantitative.

Experimental Section

Melting points were taken on a Kofler hot stage apparatus and are uncorrected. The ir spectra were recorded on a Perkin-Elmer 421 instrument, using KBr plates for the liquid sample and pressed KBr pellets for the solid. The nmr spectra were recorded on Varian A-60 and XL-100 spectrometers. The mass spectrum was obtained using a Du Pont 21-491 spectrometer. The uv spectra were recorded on a Cary 14 instrument.

Sodium Acetylide (2) and 2-Chloromethylpyridine (1). Ammonia was condensed into a three-neck flask fitted with a stopper, a potassium hydroxide drying tube, and a Dry Ice condenser. After 150 ml of liquid ammonia had been obtained, the condenser was disconnected from the gas cylinder and fitted with a potassium hydroxide drying tube. The contents of the flask were stirred magnetically. The stopper was replaced by a gas dispersing tube through which a stream of purified acetylene was passed. In the course of 15 min 2.3 g (0.1 mol) of sodium was added in small parts. The ammoniacal solution turned dark blue after each addition of sodium, but this color was soon discharged as a result of the reaction with acetylene. After completion of the sodium addition, the mixture was stirred for 5 min. The potassium hydroxide drying tube was replaced by a pressure-equalizing addition funnel containing 11.76 g (0.092 mol) of **1**. This reagent was added in the course of 5 min, causing the formation of a white precipitate. The mixture was stirred for 3 hr while the ammonia slowly evaporated. Water and ice were then cautiously added to the obtained dark, pasty residue. Suction filtration of the resulting mixture removed a white precipitate. This compound was recrystallized from di-*n*-butyl ether to yield 1.51 g (17.8%) of **16**, with a sharp melting point of 196°: ir 1590 (s), 1570 cm^{-1} (s); nmr ($CDCl_3$) δ 8.8–6.5 (m, 16 H, ring protons), 3.75 (d, 3 H, HCH···, J = 13 Hz), 3.45 (d, 3 H, HCH···, J = 13 Hz); cmr ($CDCl_3$) δ −34.07, −31.10, −21,14, −21.03, −8.03, −7.48, +2.65, +4.13, +6.21, +6.53, +77.95, +78.45 (shifts relative to benzene, used as an external reference).

Anal. Calcd for $C_{24}H_{22}N_4$: C, 78.66; H, 6.05; N, 15.29. Found: C, 79.03; H, 5.79; N, 15.16.

The filtrate was extracted with ether. After evaporation of the solvent, 8.0 g (86%) of a dark liquid was obtained, placed on an alumina column, and eluted with ether. A yellow liquid was collected, which decomposed when submitted to heat, thus rendering distillation or analysis by mass spectrometry impossible. A sample was analyzed by proton and ^{13}C nmr, and was identified as **5**: nmr (chloroform-*d*) δ 8.8–6.7 (m, 12 H, ring protons), 3.82 (d, 2 H, HCH···, J = 13 Hz), 3.5 (d, 2 H, HCH···, J = 13 Hz), 2.55 (s, 1 H, C≡CH); cmr (chloroform-*d*) δ −32.70, −30.07, −21.22, −20.92, −8.26, −7.62, +2.90, +4.87, +5.94, +6.32, +42.12, +50.76, +78.35, +78.74 (shifts relative to benzene, used as an external reference).

Anal. Calcd for $C_{20}H_{17}N_3 \cdot 1.3H_2O$: C, 74.4; H, 6.1; N, 13.0. Found: C, 74.65; H, 5.91; N, 11.73.

Registry No.—**1**, 4377-33-7; **2**, 1066-26-8; **5**, 51510-19-1; **16**, 51510-20-4.

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A Hammett Relationship Study for the Thermal Decomposition of Sterically Hindered Hydrogen Phthalate Esters in Solution

Raphael M. Ottenbrite* and James W. Brockington[1]

Department of Chemistry and Pharmaceutical Chemistry, Virginia Commonwealth University, Richmond, Virginia 23284

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The presently accepted mechanism for the thermal decomposition of acetate, xanthate, and related esters involves a concerted six-membered cyclic transition state. An exception to this generalization is the pyrolysis of tertiary hydrogen phthalate esters, which decompose at relatively low temperatures (less than 150°) to yield exclusively olefinic products and phthalic acid.[2]

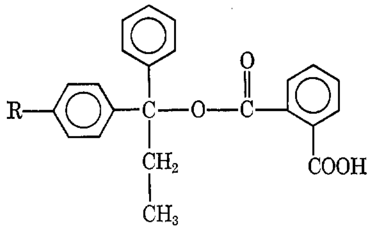
It has been found that considerable trans-elimination products are obtained from tertiary hydrogen phthalate decompositions.[2,3] To account for these products, it was suggested that carbonium ion character was apparent in the transition state. Further evidence of carbonium ion participation was obtained by partial decomposition of ^{18}O-enriched carbonyl oxygen labeled *trans*-1,2-dimethylcyclohexyl hydrogen phthalate ester which resulted in the enrichment of ^{18}O in the alkyl portion of the undecomposed ester.[4] A kinetic study of the decomposition of *cis*- and *trans*-1,2-dimethylcyclohexyl and *cis*- and *trans*-2-methyl-1-phenylcyclohexyl hydrogen phthalate esters[5] indicated that ion-pair formation was involved in the rate-determining step of the reaction.

More recently we reported that the thermal decomposition of 1,1-diphenylpropyl hydrogen phthalate ester followed first-order kinetics in DMSO solution.[6] The positive entropy of activation (7.3 eu) obtained precluded a cyclic transition state for this decomposition and gave support to the previously postulated mechanism involving heterolytic cleavage. Although homolytic decomposition of these esters has not been observed, this mode of decomposition could not be entirely ruled out. We wish to report in this paper a Hammett relationship study of the effect of substituents on the decomposition on a series of 1-aryl-1-phenylpropyl hydrogen phthalate esters which supports the concept of carbonium ion formation rather than radical pair formation in the rate-determining step.

Results and Discussion

The para 1-aryl-1-phenylpropyl alcohols were prepared by the Grignard method using the appropriate arylmagnesium halides and ketones (Table I). The hydrogen phthalate esters were prepared from the sodium salt of these alcohols and phthalic anhydride (Table I). A preparative-scale decomposition of the hydrogen phthalate esters in DMSO solution gave near-quantitative yields (>95%) of the corresponding olefin II and phthalic acid III. Kinetic decomposition studies of these esters were car-

Table I
1-Aryl-1-phenylpropyl Alcohols and Hydrogen Phthalate Esters



Substituent	Alcohol Yield, %	Alcohol Mp, °C	Alcohol Registry no.	Hydrogen phthalate esters Yield, %	Hydrogen phthalate esters Mp,[a] °C	Hydrogen phthalate esters Registry no.
H	91.5[b]	90–92[b]		46[b]	119[b]	
Cl	96[c]	Oil	51608-64-1	46.5	117	51608-68-5
Me	94[c]	Oil	51608-65-2	48	115.5	51608-69-6
Br	90[c]	Oil	51608-66-3	51	117	51608-70-9
Ph	58	102–104	51608-67-4	64.5	100	51608-71-0

[a] These decomposed on melting. [b] These data have been published [R. M. Ottenbrite, J. W. Brockington, and K. G. Rutherford, *J. Org. Chem.*, **38,** 1189 (1973)] and are included for comparison. [c] The compound did not crystallize and yields are based on purified oil. [d] The hydrogen phthalate esters all gave acceptable C, H analyses (±0.4%). Ed.

Table II
Rate Constants for the Decomposition of a Series of 1-Arylphenyl Hydrogen Phthalates in Dimethyl Sulfoxide at 65°

Compd	$k \times 10^5$, sec^{-1}	$\sigma^{+\,a}$	σ^b
Ia[c]	2.46 ± 0.01	0.00	0.00
Ib	0.679 ± 0.018	+0.11	+0.24
Ic	21.6 ± 0.7	−0.31	−0.13
Id	0.581 ± 0.033	+0.15	+0.27
Ie	7.22 ± 0.02	−0.17	+0.01

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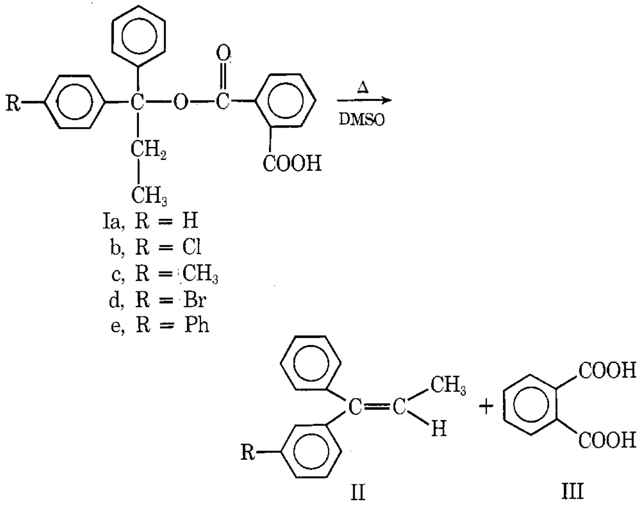

Ia, R = H
b, R = Cl
c, R = CH3
d, R = Br
e, R = Ph

II

III

ried out in DMSO solution at 65°. The rates of reaction were followed using nmr techniques previously described.[6]

Plots of log $H_a/(H_a + H_b)$ *vs.* time for the decomposition were obtained, where H_a and H_b are the height of the integrations of peaks due to the methyl group of the ester and the olefin, respectively. First-order kinetics was observed in each case. The individual rate constants for each aryl-substituted ester are listed in Table II. Hammett relationships using these rate data *vs.* σ constants and σ^+ constants were determined. The ρ value with σ was −3.74 (correlation coefficient 0.955) and with σ^+ −3.44 (correlation coefficient 0.995).

Taylor, *et al.*,[7] reported that for the pyrolysis of a series of 1-arylethyl acetates that their kinetic data correlated better with σ^+ than with σ and gave a ρ value of −0.66. From this, they concluded that the transition state was ionic in character with some charge separation. Further, free-radical reactions on the average have ρ values that are closer to zero than do ionic reactions.[8] The magnitude of the ρ values obtained for our ester decomposition study (−3.74 for σ and −3.44 for σ^+) are comparable to the ρ value (−3.97) obtained for the equilibrium between triar-

$$\mathrm{Ph_3COH} \rightleftharpoons \mathrm{Ph_3C^+} + {}^{-}\mathrm{OH}$$

ylmethanol and triarylcarbonium ion[9] in dilute sulfuric acid. Consequently, the large ρ values that we obtained for the hydrogen phthalate ester decomposition indicate that a substantial charge separation is taking place in the transitions, therefore substantiating ion-pair formation and precluding free-radical involvement in this reaction.

Experimental Section

All melting points are uncorrected and were determined in a Thomas-Hoover melting point apparatus. Infrared spectra were obtained on a Perkin-Elmer 257. Kinetic studies were performed in a mineral bath, maintained at ±0.1° by means of a Haake E-51 temperature controller. Kinetic measurements were made on a Varian A-60 nmr spectrometer in precision nmr tubes (507-PP-7 and 504-PP-7) obtained from Wilmad Glass Co. The deuterated solvents were obtained from Merck Sharp and Dohme. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill.

General Kinetic Procedure. Ester was analytically weighed and a 0.75 *M* solution was prepared in dimethyl sulfoxide-d_6. At the beginning of each run, 0.4 ml of this solution was placed into each of six nmr tubes which immediately were sealed with pressure caps. The tubes were placed simultaneously in the constant-temperature bath. Tubes were withdrawn at appropriate intervals and quenched by plunging the tube into a beaker of crushed ice and water. The tube was allowed to return to room temperature and the nmr analysis was performed. Each nmr signal was integrated six times. The averaged value for $H_a/(H_a - H_b)$ had a mean deviation of less than 1%.

Preparation of Alcohols. The alcohols were prepared by the method previously described[7] using the appropriate para-substituted phenylmagnesium halide with propiophenone. All gave similar spectral data: ir (thin film) 3560 (free O-H stretch), 3460 (broad peak, bonded O-H stretch), 1395 (O-H bend), and 1165 cm^{-1} (C-O stretch); nmr (CDCl$_3$, TMS internal standard) δ 0.80-0.82 (t, 3, J = 7 Hz, CH$_3$CH$_2$) 2.22 (q, 2, J = 7 Hz, CH$_2$CH$_3$), 2.26 (s, 1, OH), and 7.1-7.5 ppm (m, 9, aromatic). The peak at δ 2.26 disappeared upon the addition of D$_2$O.

Preparation of Hydrogen Phthalate Esters. These compounds were prepared according to the procedure previously described.[7] All gave similar spectral data: ir (KBr) 3420 (broad peak, bonded O-H stretch), 2650 and 2540 (O-H stretch characteristic of hydrogen-bonded carboxylic acids), 1734 and 1705 (C=O stretch), and 1300, 1270, 1125, and 1070 cm^{-1} (C-O stretch); nmr (dimethyl sulfoxide-d_6, TMS internal standard) δ 0.85 (t, 3, J = 7 Hz, CH_3CH_2), 2.95 (q, 2, J = 7 Hz, CH_2CH_3), and 7.0–8.0 ppm (m, 13, aromatic).

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6-Methyl-2-naphthalenesulfonate (Menasylate). A New and Useful Leaving Group for Trifluoroacetolysis

Takashi Ando,* Yoshimasa Saito, Junko Yamawaki,
Hisao Morisaki, Masami Sawada, and Yasuhide Yukawa

The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka, Japan

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Recently, trifluoroacetic acid has become an important solvolyzing solvent because of its very low nucleophilicity and relatively high ionizing power. Its strong acidity, however, restricts the method for measurement of solvolysis rates so that only the ultraviolet spectroscopic method has been the one for general use.[1] This method, developed originally by Swain and Morgan for following the reactions of arenesulfonates,[2] takes advantage of the differences in the absorptions of alkyl tosylates and tosylate anion at 261 or 272 nm; at 261 nm methyl tosylate has ϵ 671 and tosylate anion has ϵ 344 both in water. For the reactions of aralkyl arenesulfonates, whose aralkyl groups absorb in the same region as arenesulfonate groups do, extraction techniques were recommended by the original authors.[2] Although this technique has been successfully utilized by Bentley and Dewar[3] and by us[4,5] for trifluoroacetolysis of 2-arylethyl tosylates and nosylates, the experimental procedure is tedious and the accuracy of the results is limited. We report now that 6-methyl-2-naphthalenesulfonate, abbreviated as "menasylate (OMns)," is a useful leaving group for following the reactions in trifluoroacetic acid without extraction techniques.

Although menasyl chloride is commercially unavailable, it can be prepared easily from 2-methylnaphthalene.[6,7] Any indication of the presence of an isomer could not be observed for the chloride and all the menasylates prepared from it. The ultraviolet spectrum of ethyl menasylate in 95% ethanol showed maxima at 282 nm (ϵ 5650), 311 (1240), 318 (782), and 326 (936). On the other hand, the spectrum of menasylic acid in the same solvent showed maxima at 278 nm (ϵ 5470), 308 (393), and 318 (194); ϵ was only 56 at 326 nm and no maximum was observed around there. Addition of trifluoroacetic acid and sodium trifluoroacetate to the solutions did not cause any change in the spectra at all. This remarkable difference in the absorptions at 326 nm (*ca.* 20-fold) facilitated the measurement of the trifluoroacetolysis rates of several menasylates whose alkyl groups have absorptions at a longer wavelength region. Thus, the trifluoroacetolysis rates of 2-phenylethyl and 2-(p-methoxyphenyl)ethyl menasylate (**1** and **2**) were determined (Table I). In a typical run, the absorbance at 326 nm changed from 0.733 (at zero point) to 0.060 (at "infinity" after more than 10 half-lives). This large variation in the absorbance resulted in much improved accuracy and reproducibility without a great deal of skill such as necessary for extraction techniques. Correlation coefficients were better than 0.9999 in most cases. The presence of even a nitrophenyl group in the substrate (**3**) did not interfere with the measurement, although the background absorbance was relatively high in this case; the absorbance changed from 0.582 to 0.339 in one run. Application of a high temperature (>130°) caused desulfonation from the leaving group, and a small amount of 2-methylnaphthalene was detected in the products of trifluoroacetolysis of **3**.

It is apparent that menasylates can be used conveniently in any solvent other than trifluoroacetic acid; their reactions can be followed accurately and their melting points are usually high. Comparison of the present data with those reported by Nordlander and Deadman[8] revealed that the reactivity of a menasylate was almost the same as that of a tosylate.

Experimental Section

Menasylic Acid. A mixture of 71 g of 2-methylnaphthalene and 71 g of *concentrated* sulfuric acid (d 1.84) was stirred for 6 hr at 90–100°. At the end of this period the hot reaction solution was poured into 250 ml of water while stirring. The unreacted 2-methylnaphthalene and the sulfone produced as a by-product were extracted twice with 50 ml each of benzene. To the water layer was added 400 ml of aqueous solution saturated with sodium chloride. After stirring for several hours the sodium salt thus precipitated was filtered and dried at 120–150° *in vacuo*. The crystals were suspended in acetone and warmed under reflux for 2 hr. After filtration sodium menasylate recrystallized twice from water. The yield was 25–40%.

Sodium menasylate was dissolved in 3 N hydrochloric acid at 60°. Upon cooling to room temperature colorless crystals precipitated. Menasylic acid was obtained as a monohydrate after recrystallization from 3 N hydrochloric acid and then from ethyl acetate, mp 118–121°.

Anal. Calcd for $C_{11}H_{12}O_4S$: C, 54.99; H, 5.03; S, 13.34. Found: C, 55.22; H, 4.83; S, 13.23.

Menasyl Chloride. To a stirred suspension of 20 g of sodium

Table I
Trifluoroacetolysis Rates of 2-Arylethyl Arenesulfonates

Substrate	Temp, °C	$10^5 k_t$, sec^{-1}	ΔH^*, kcal/mol	ΔS^*, eu
$PhCH_2CH_2OMns$ (**1**)[a,b]	50	8.08 ± 0.01	19.9	−15.9
	60	21.1 ± 0.1		
p-$MeOPhCH_2CH_2OMns$ (**2**)[a,b]	24	6.38 ± 0.03		
p-$NO_2PhCH_2CH_2OMns$ (**3**)[b,c]	130	2.64 ± 0.00	25	−19
	150	11.9		
$PhCH_2CH_2OTs$[b,d]	50	7.75	20.8	−13.1
$PhCH_2CH_2ONs$[e]	50	26.0	19.5	−14.7

[a] 0.05 M in menasylate. [b] With 0.125 M sodium trifluoroacetate. [c] 0.025 M in menasylate. [d] Interpolated from data in ref 8. 0.05 M in tosylate. [e] Reference 5; 0.02 M in nosylate.