1,9-Diphenylnonane-1,3,7,9-tetraone was prepared by the method of Martin, Shamma, and Fernelius[5] for azelyldiacetophenone, m.p. 56–59°; reported, not over 72°.

Anal. Calcd. for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99. Found: C, 75.03; H, 5.98.

1,10-Diphenyldecane-1,3,8,10-tetraone was prepared by the method of Martin, Shamma, and Fernelius,[5] m.p. 117–118°; reported, 117–118°.

1,11-Diphenylundecane-1,3,9,11-tetraone was prepared by the method of Martin, Shamma, and Fernelius,[5] m.p. 55–57°, reported 64.5–65.5°.

Anal. Calcd. for $C_{23}H_{24}O_4$: C, 75.80; H, 6.64. Found: C, 75.69; H, 6.52.

1,13-Diphenyltridecane-1,3,11,13-tetraone was prepared by the method of Martin, Shamma, and Fernelius,[5] m.p. 69–69.5°; reported 62.5–63.5°.

Anal. Calcd. for $C_{25}H_{28}O_4$: C, 76.50; H, 7.19. Found: C, 75.99; H, 7.18.

1,14-Diphenyltetradecane-1,3,12,14-tetraone was prepared by the method of Martin, Shamma, and Fernelius[5] for azelyldiacetophenone. The observed melting point is 113.4–114°.

Anal. Calcd. for $C_{26}H_{30}O_4$: C, 76.84; H, 7.44. Found: C, 76.61; H, 7.48.

Copper chelates. A mixture consisting of a 1:1 mole ratio of bisacetylacetonatocopper(II) and the bis(β-diketone) was ground together in a mortar and heated under vacuum at 60° for 1 day. The temperature was raised to 105–110° and the sample was allowed to come to constant weight. Completion of the reaction was also checked by a comparison of theoretical versus observed weight loss. Attempts to speed the reaction by initial heating at 110° resulted in charring. All of the mixtures were pale blue before heating; after heating the color changed to pale green.

Thermal stability by differential thermal analysis. Thermal stability of the copper chelates of the bis(β-diketones) was measured on a 0.1-g. sample of chelate diluted with 1.9 g. of aluminum oxide. A 2.0-g. sample of aluminum oxide was used as the reference standard. Samples were heated at the rate of 2° to 8° per min. in an aluminum block. The differential temperature was measured by two thermopiles of four, iron-constantan thermocouples inside a thin wall capillary. Temperature was measured by a single iron-constantan thermocouple placed in the sample. Both absolute and differential temperatures were recorded by a Brown 2 point automatic recording potentiometer. The scale for measurement of the temperature was extended by use of a "buck out" potential from a Rubicon Co. potentiometer. Differential temperatures of 0.02° could be observed. Temperatures could be determined to ±0.5°. Samples were heated in air.

Visual observation of decomposition. Visible signs of decomposition were observed with a Kofler hot stage. Samples were observed in air and in an atmosphere of carbon dioxide. No change in decomposition temperature was noted.

Melting was accompanied by evolution of a small amount of gas in both air and carbon dioxide.

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[5] D. F. Martin, M. Shamma, and W. C. Fernelius, *J. Am. Chem. Soc.*, **80**, 4891 (1958).

Salt Effects in the Solvolysis of Benzhydryl Chloride[1]

Kirk D. McMichael and Robert A. Clement

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In an extension of our studies on medium effects and relative rates,[2,3] we desired to examine the effects of salts upon the Henry's law constant for the substrate and upon the specific rate constant for a simple organic reaction in a typical organic medium. In view of the importance to theoretical organic chemistry of the solvolysis reactions of benzhydryl derivatives,[4] we undertook a study of the system, benzhydryl chloride in 90% (w./w.) aqueous bis(2-ethoxyethyl) ether at 25°. Unfortunately, our experimental technique[3] was not sufficiently sensitive to provide meaningful values of Henry's law constants for benzhydryl chloride in these solutions, so a complete study was not possible. However, we did collect some data on the kinetic salt effects observed in this system and have recorded them in Table I.

TABLE I

Initial First-order Specific Rate Constants for the Development of Acid in the Solvolysis of Benzhydryl Chloride in 90% (w./w.) Aqueous Bis(2-ethoxyethyl) Ether at 25.06° in the Presence of Salts

Salt	Salt Concn. (moles/l.)	$10^6 \times k_0$ (sec.$^{-1}$)
None	—	1.01
$(n\text{-}Bu)_4NCl$	0.100	1.12
$(n\text{-}Bu)_4NBr$	.100	1.08
$(n\text{-}Bu)_4NClO_4$	.100	1.31
$LiClO_4$	.100	2.51
$NaClO_4$	.100	2.48
NH_4ClO_4	.100	2.48
$HClO_4$	.097	1.7
$Mg(ClO_4)_2$	.0333	3.25
$Mg(ClO_4)_2$	.0500	4.05
$Mg(ClO_4)_2$	.100	6.03

EXPERIMENTAL[5]

Materials. Bis(2-ethoxyethyl) ether, b.p. 72–74° (10 mm.), was obtained by distillation of commercial material from lithium aluminum hydride and was stored under nitrogen at 8° in glass-stoppered paraffin-sealed flasks. *Benzhydryl*

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[1] Abstracted from a portion of the Ph.D. dissertation of Kirk D. McMichael, Department of Chemistry, University of Chicago, 1960.

[2] R. A. Clement and M. R. Rice, *J. Am. Chem. Soc.*, **81**, 326 (1959).

[3] R. A. Clement, J. N. Naghizadeh, and M. R. Rice, *J. Am. Chem. Soc.*, **82**, 2449 (1960).

[4] *e.g.*, (a) G. Kohnstam and B. Schillaker, *J. Chem. Soc.*, 1915 (1959). (b) C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, N. Y., 1953, p. 365.

[5] The temperature of the constant temperature bath was 25.06 ± 0.02° as determined by an N.B.S. calibrated thermometer.

chloride, n_D^{25} 1.5939 (lit.[6] n_D^{25} 1.5937), was obtained by two partial freezings of distilled material, b.p. 151–152.5° (10 mm.), and was stored, frozen, in small vials.

Magnesium perchlorate (Anhydrone) and *perchloric acid* were commercial reagent-grade materials, used as supplied. *Lithium perchlorate, sodium perchlorate* and *ammonium perchlorate* were derived from commercial reagent-grade hydrous salts by drying to constant weights at the appropriate temperatures.

Tetrabutylammonium bromide, m.p. 117–118° (lit.[7] m.p. 119.4°), and *tetrabutylammonium chloride*, m.p. 52–54° sealed cap., were each prepared by stirring a suspension of tetrabutylammonium iodide (25 g.) with a 10% excess of the appropriate silver halide in water (150 ml.) until a few drops of the solution no longer gave a brown precipitate (tetrabutylammonium triiodide) on addition to acidic aqueous sodium nitrite solution. The mixture was filtered from the precipitated silver halides, saturated with hydrogen sulfide, filtered again to remove traces of silver sulfide, and then evaporated to dryness under reduced pressure and finally at 1 mm. over Anhydrone. The anhydrous salts yielded good halogen analyses.

Anal. Calcd. for $C_{16}H_{36}BrN$: Br, 24.79. Found: Br, 24.72, 24.79. Calcd. for $C_{16}H_{36}ClN$: Cl, 12.76. Found: Cl, 12.81, 12.67.

Tetrabutylammonium perchlorate was prepared as described,[8] purified and isolated as with the tetrabutylammonium halides, had m.p. 205–206° (lit.[8] m.p. 207°), and contained *ca.* 1% perchloric acid by acidimetry.

Anal. Calcd. for $C_{16}H_{36}ClNO_4$: Cl, 10.37. Found: Cl, 10.43.

The anhydrous salts were stored in a desiccator over Anhydrone.

Kinetic measurements. The solvent, 10 parts of water to 90 parts of bis(2-ethoxyethyl) ether, was prepared from the components on a weight basis as required for each kinetic run. Each kinetic solution was prepared by diluting weighed amounts of benzhydryl chloride and anhydrous salt to the mark in a volumetric flask with freshly prepared solvent. The solutions were all 0.100 ± 0.001 molar in benzhydryl chloride.

The rates of development of acid were followed as described previously[3] to *ca.* 5% reaction. Large-scale plots of acid concentration *vs.* time were constructed, smooth curves were drawn through the points with the aid of a spline and first-order specific rate constants, k, were calculated according to equation 1 at regular successive intervals of $\Delta(\text{H}^+)$

$$k = \Delta(\text{H}^+)/(\text{RCl})\Delta t \qquad (1)$$

and Δt such that *ca.* 8 values of k were obtained from each curve. For each run, the initial first-order specific rate constant, k_0, was obtained by extrapolation of the k values to 0% reaction. These extrapolations involved, within experimental error, zero slope for all runs except those with tetrabutylammonium bromide as the added salt. In these runs, values of k rose steadily to a limiting value of 1.36×10^{-6} sec.$^{-1}$ which was attained after *ca.* 2% reaction and probably reflected approach to a steady-state concentration of benzhydryl bromide produced by capture of a reactive intermediate by bromide ion. The initial first-order specific rate constants, k_0, obtained are recorded in Table I, each value representing the average of at least two kinetic runs involving different solvent batches and possessing an average deviation of 1–3% with the exception of the value with perchloric acid as the added salt, for which the average deviation is 8%.

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[6] S. Winstein, A. H. Fainberg, and E. Grunwald, *J. Am. Chem. Soc.*, **79**, 4146 (1957).

[7] H. Sadek and R. M. Fuoss, *J. Am. Chem. Soc.*, **72**, 301 (1950).

[8] W. F. Luder, P. B. Kraus, C. A. Kraus, and R. M. Fuoss, *J. Am. Chem. Soc.*, **58**, 255 (1936).

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Anomalous Infrared Absorption Frequencies Produced by Steric Effects

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We wish to report a large frequency shift of a C—H absorption frequency in some fused ring systems. In these compounds, the rings are so fused as to force two or more methylene groups into close proximity (see Fig. 1). One result of this type of structure is the appearance of a sharp, strong absorption band in the region 3055–2980 cm.$^{-1}$ in the spectra of these saturated compounds.

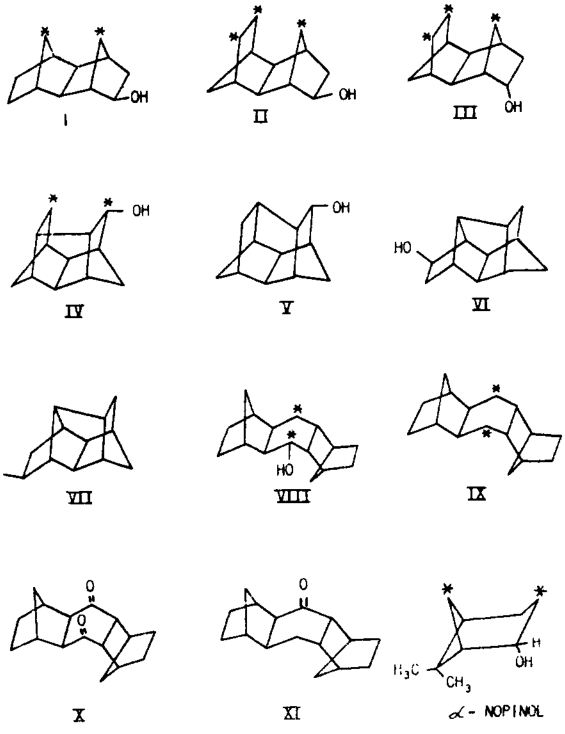

Figure 1

The frequencies and intensities of the anomalous bands are shown in Table I. The intensity data are given in terms of the integrated intensities: the observed molecular intensity in column 3, and the intensity per perturbed methylene group in column 4. No intensity data are given for compounds VIII and IX and for α-nopinol because the bands were insufficiently resolved. Compounds V, VI,