NOTES

The Rates of Condensation of Piperidine with 1-Chloro-2,4-dinitrobenzene in Various Solvents

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We record some miscellaneous measurements made in conjunction with other work. Our results are summarized in Table I.

Table I

The Reaction of Piperidine with 1-Chloro-2,4-dinitrobenzene in Various Solvents

Solvent	Rate coefficient at 30.06°, l. mole^{-1} min.$^{-1}$	ΔE, kcal./mole	$\Delta S^{\pm}$, cal./deg./mole
50% Dioxane	6.38[a]	11.2	−28.0
60% Dioxane	5.94[a]	10.5	−30.5
75% Dioxane	5.61[a]	10.2	−31.6
93% Ethanol	1.54	..	....
Methanol	0.935	11.6[b]	−30.2[b]
50% Methanol–50% benzene	0.932	..	....

[a] Extrapolated from measurements at lower temperatures. [b] These values arise from an independent study by J. F. Bunnett and E. W. Garbisch, Jr.

In view of the probability that in this reaction a zwitterionic transition state is formed from uncharged reactants, it is noteworthy that the rate, energy of activation and entropy of activation are relatively insensitive to changes in the solvent. Reactions of this charge type usually are accelerated greatly by changing to a more polar solvent,[1] owing to a lesser decrease in entropy during formation of the transition state. In the transition state of the present reaction, we believe, there is partial positive charge on the piperidine nitrogen atom and corresponding negative charge distributed between the two nitro groups. The geometry is such that the positive pole can engage in direct electrostatic interaction with a partially negatively charged oxygen of the 2-nitro group. This mutually satisfying electrostatic interaction decreases the need for solvation of these poles by external solvent molecules, and consequently the reaction rate is less sensitive to changes in the solvent. We have described this effect as "built-in solvation" and discussed it at greater length elsewhere.[2]

A plot of ΔE *vs.* $\Delta S^{\pm}$ for the three aqueous dioxane solvents is linear with slope 280°K. This slope is, as Leffler[3] has observed, the "isokinetic temperature" at which all reactions whose energies and entropies of activation are linearly related should proceed at the same rate. Our determinations at 0° were carried out just below the isokinetic temperature, and indeed our measured rates at 0° in two solvents are identical within experimental error. The rate in 50% dioxane, the "fastest" solvent, is actually somewhat lower. We thus have partially realized the inversion in relative reactivity that one should observe as the isokinetic temperature is passed. The point for methanol solvent does not fall on the above linear plot.

It is surprising that the rate, at 30.06°, is identical within experimental error in methanol and in 50% methanol—50% benzene solvents. The full significance of this observation is not apparent.

(1) R. G. Pearson, *J. Chem. Phys.*, **20**, 1478 (1952).

(2) J. F. Bunnett and R. J. Morath, This Journal, **77**, 5051 (1955).

(3) J. E. Leffler, Florida State Univ., private communication.

Experimental

Piperidine, 1-chloro-2,4-dinitrochlorobenzene and the pure solvents were prepared as previously described.[2,4] Reagent grade benzene was redistilled. Commercial "95%" ethanol was redistilled and found by density determination to contain 93% ethanol by weight. The other mixed solvents were prepared on a volume basis.

In all runs the initial concentration of 1-chloro-2,4-dinitrobenzene was approximately 0.015 M and of piperidine approximately 0.030 M. Rate coefficients were calculated from the expression: $2kt = 1/(a - x) + C$. Runs in aqueous dioxane solvents were followed by titration of chloride ion,[4] and runs in other solvents by spectrophotometric measurements[2] (at 460 mμ), as previously described. Runs in 50% dioxane at *ca.* 25.25° were followed by both techniques, and the resulting rate coefficients were identical within experimental error.

Following are the experimental rate coefficients not already listed in Table I. Each is a mean value from two or more supposedly identical runs. In all cases the average deviation was less than 1%. Units are l. mole^{-1} min.$^{-1}$. In 50% dioxane: at 25.23, 4.72; at 0.0°, 0.821. In 60% dioxane[4]: at 25.22°, 4.48; at 0.0°, 0.874. In 75% dioxane: at 25.22°, 4.26; at 0.0°, 0.870.

Arrhenius activation energies and entropies of activation were calculated from standard expressions. ΔE values are uncertain by about ±0.1 kcal., and $\Delta S^{\pm}$ by about ±0.2 cal./deg.

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(4) J. F. Bunnett and G. T. Davis, This Journal, **76**, 3011 (1954).

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Decalin-2,7-diol and Decalin-2,7-dione[1]

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In the course of a search for possible new routes to derivatives of bicyclo[5.5.0]dodecane having functional groups on both rings decalin-2,7-diol and decalin-2,7-dione were prepared. However, the synthesis *via* these intermediates was not pursued further. No previous report of either compound was found.

High pressure hydrogenation of 2,7-dihydroxynaphthalene with W-4 Raney nickel catalyst gave a 63% yield of the decalindiol. Chromic acid oxidation of the diol produced the corresponding dione (43%). The configuration at the ring juncture of the reduced compounds was not determined.

(1) From the Ph.D. Thesis of David O. Barlow.

Experimental[2]

2,7-Dihydroxynaphthalene.—This compound was prepared in 43% yield from disodium naphthalene-2,7-disulfonate by the procedure of Chakravarti and Pasupati.[3] The material so obtained was purified by the method of Johnson, Gutsche and Banerjee.[4]

Decalin-2,7-diol.—Hydrogenation of 30 g. (0.0176 mole) of purified 2,7-dihydroxynaphthalene dissolved in 100 ml. of absolute ethanol with W-4 Raney nickel catalyst[5] was carried out in the usual manner[4] at 150° and between 63 and 170 atm. with the latter the initial pressure. Hydrogen uptake ceased after 5 hours. The colorless residue remaining after removal of the catalyst and solvent was taken up in 150 ml. of dry ether and the solution cooled overnight in a refrigerator. The colorless solid which separated weighed 20.1 g. (63%), m.p. 108–110°.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.82; H, 10.31.

The dibenzoate, obtained by treatment with benzoyl chloride, was recrystallized from 50% ethanol–water and melted at 102.5–103.5°.

Anal. Calcd. for $C_{24}H_{26}O_4$: C, 76.19; H, 6.87. Found: C, 76.17; H, 6.79.

Decalin-2,7-dione.—To a stirred suspension of 10 g. (0.059 mole) of decalin-2,7-diol in 30 ml. of water cooled to 0° was added a mixture of 8.0 g. (0.08 mole) of chromic anhydride, 6.5 ml. of concentrated sulfuric acid and 40 ml. of water over a period of 2 hours. The temperature was maintained at 0° during the addition. After standing overnight at room temperature the mixture was extracted with ether in a continuous liquid–liquid extraction apparatus. The ether solution was neutralized with solid potassium carbonate and dried over magnesium sulfate. Removal of the solvent left a pale yellow oil which solidified readily. Removal of an oily fraction with a porous plate and then sublimation gave 6.5 g. (43%) of colorless crystals, m.p. 62–64°.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 72.29; H, 8.44. Found: C, 72.52; H, 8.69.

(2) Melting points were taken on a Fisher–Johns apparatus and are uncorrected.

(3) S. N. Chakravarti and V. Pasupati, *J. Chem. Soc.*, 1859 (1937).

(4) W. S. Johnson, C. D. Gutsche and D. K. Banerjee, THIS JOURNAL, **73**, 5464 (1951).

(5) H. Adkins and H. Billica, *ibid.*, **70**, 697 (1948).

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Conversion of Vitamin A Acetate to Retrovitamin A Acetate

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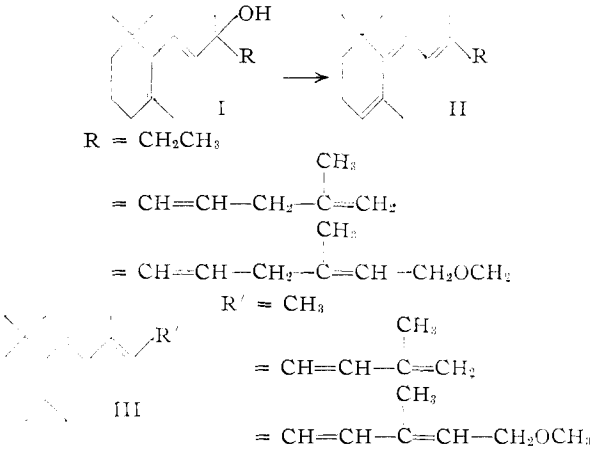
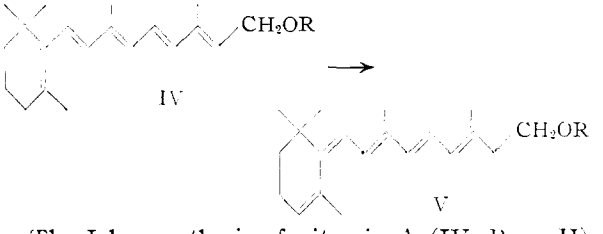
In extensive studies of the acid-catalyzed dehydration of β-ionyl alcohols I, Oroshnik and co-workers have observed the preferential formation of conjugated 2,2,6-trimethylcyclohexenylidene derivatives II rather than the formation of the isomeric 2,2,6-cyclohexenyl structures III.[2] In general, substituted cyclohexenes with an endocyclic double bond seem to be more stable than the isomeric exocyclic cyclohexylidenes.[3] It is probable that Brown's hypothesis must be modified in the particular cases studied by Oroshnik in view of the geometries of II and III. Steric interaction of the three methyl ring substituents in III with the side chain on the one hand, and the requirement of maximum coplanarity in order to minimize the energy of the conjugated π-electron system on the other might well favor the formation of II.[2,4]

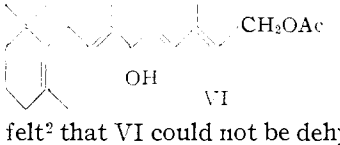


The release of strain in the transition of compounds of series III to those of series II is indicated by the shift of the respective absorption maxima to longer wave lengths, by the concomitant increase in the extinction, and by the appearance of fine structures in the ultraviolet absorption spectra.[2,4]

In the particular case of vitamin A (IV, R = H) it therefore seemed probable that conversion to *retro* vitamin A (V, R = H) should be possible. We have been able to transform vitamin A acetate (IV, R = OAc) to *retro* vitamin A acetate (V, R = OAc) in good yield by treatment with aqueous hydrobromic acid.



The Isler synthesis of vitamin A (IV, R = H) involves the dehydration of the unsaturated alcohol acetate VI.[5]



Oroshnik felt[2] that VI could not be dehydrated to *retro*-vitamin A acetate (V, R = OAc) because of the methylene group adjacent to the cyclohexene ring. We conclude from our observations, however, that the structure of the precursor VI is of secondary importance, and that only the essentially neutral dehydration conditions employed by the Swiss workers[5] permit the isolation of vitamin A acetate (IV, R = OAc). Under acidic conditions any IV formed from VI or any other precursor structure would be converted to the thermodynamically more stable *retro*-vitamin A acetate (V, R = OAc). We postulate that the prototropic isomeri-

(1) To whom inquiries should be addressed.

(2) W. Oroshnik, G. Karmas and A. D. Mebane, THIS JOURNAL, **74**, 295, 3807 (1952).

(3) H. C. Brown, J. H. Brewster and H. Shechter, *ibid.*, **76**, 467 (1954).

(4) J. Dale, *Acta Chem. Scand.*, **8**, 1249 (1954).

(5) O. Isler, W. Huber, A. Ronco and M. Kofler, *Helv. Chim. Acta*, **30**, 1911 (1947).