were washed with water and saturated aqueous NaCl and dried. The total product was chromatographed on two plates. The red fraction, R_f 0.80, when recrystallized from a hexane–benzene mixture, afforded red crystals (8.7 mg, 33%) of **3,12-dihydro-3,3,5,6,9,10-hexamethyl - 12 - (2 - methylpropenyl)pyrano[3,2 - a]xanthene - 8,11-dione (18)**: mp 186.5–188°; ν_{max} 1670 s, 1658 vs, 1640 s, 1620 s, 1600 w cm^{-1}; m/e (%) at 405 (6), 404 (M$^+$, 18), 390 (28), 389 (100), 187.5 (7), 187 (27); δ 1.35, 1.45 (each s, 3, 3,3-diMe), 1.59, 2.32 (each broad s, 3, =C(Me)$_2$), 2.04 (s, 6, 5,6-diMe), 2.00, 2.12 (each s, 3, 9,10-diMe), 4.84 (broad s, 2, –CH—CH=), 5.65 and 6.39 (each d, 1, J = 10.1 Hz, 1- and 2-H of pyran); δ (C$_6$D$_6$) 1.27, 1.29 (each s, 3, 3,3-diMe), 1.49 (broad s, 3, one Me of propenyl side chain), 2.39 (d, $J_{allylic}$ = 1.0 Hz), 1.65 (s, 6, 5,6-diMe), 2.13 (s, 6, 9,10-diMe), 4.9–5.1 (m, 2, –CH—CH=), 5.38 and 6.54 (each d, 1, J = 10.2 Hz, 1- and 2-H of pyran).

Reduction of 18 to the Hydroquinone Diacetate 19b. A solution of **18** (0.011 g) in ether (10 ml) was shaken for 1 min with a solution of sodium dithionite (0.050 g) in water (10 ml). The colorless ether layer was washed with water and saturated aqueous NaCl and dried for 1 hr (the solution becomes red if left too long in the air indicating oxidation back to **18**). After removal of ether the residue was acetylated with pyridine–acetic anhydride and the product was chromatographed on one plate. There were isolated in the usual manner **18** (2 mg) and a colorless oil, R_f 0.43. The latter on recrystallization from hexane afforded white crystals (9.5 mg, 86%) of **3,12-dihydro-3,3,5,6,9,10-hexamethyl-12-(2-methylpropenyl)pyrano[3,2-a]xanthene-8,11-diol acetate (19b)**: mp 176–178°; ν_{max}^{KBr} 3000–2850 m, 1760 vs, 1625 w, 1580 w cm^{-1}; m/e (%) at 491 (19), 490 (M$^+$, 59), 476 (31), 475 (100), 433 (22), 391 (37), 389 (17), 349 (17), 189 (36); δ 1.38, 1.42 (s, 3, 3,3-diMe), 1.56 (d, $J_{allylic}$ = 0.5 Hz, 3, side-chain Me), 1.89 (d, $J_{allylic}$ = 1.0 Hz, 3, side-chain Me), 2.00, 2.22 (s, 3, two Ar-Me), 2.11 (s, 6, two ArMe), 2.39, 2.42 (s, 3, COMe), 4.88, 5.06 (each d, 1, AB quartet with J_{AB} = 11.1 Hz, –CH—CH=, broadened by long-range coupling to =C(Me)$_2$), 5.64 and 6.42. (each d, 1, J = 10.0 Hz, 1- and 2-H of pyran); δ (20% C$_6$D$_6$ in CDCl$_3$) 1.32, 1.39 (s, 3, 3,3-diMe), 1.54 (d, $J_{allylic}$ = 0.5 Hz, 3, side-chain Me), 1.87 (broad s, 3, side-chain Me), 1.95, 2.07, 2.11, 2.21 (each s, 3, 5,6,9,10-tetra-Me) 2.28, 2.32 (s, 3, COMe), 4.85, 5.04 (each d, 1, AB quartet with J_{AB} = 10 Hz, –CH—CH=, broadened by long-range coupling to =C-(Me)$_2$), 5.59 and 6.44 (each d, 1, J = 9.9 Hz, 1- and 2-H of pyran).

Anal. Calcd for C$_{30}$H$_{34}$O$_6$: C, 73.47; H, 6.94. Found: C, 73.11; H, 7.07.

Irradiation in Methanol under Nitrogen. PQ-1 (0.050 g) in methanol (30 ml) was irradiated for 3.5 hr. The light brown oily residue obtained after evaporation of the methanol was chromatographed on three plates. The fraction with R_f 0.65–0.75 contained PQ-1 (4 mg) and **2** (0.5 mg, 1%) identical (R_f and uv) with the same material isolated previously. The fraction with R_f 0.25–0.35 gave **10** (4 mg, 9%) identical (mixture melting point, R_f, uv) with **10** previously characterized. The fraction with R_f 0.05–0.20 (detected by spraying the plates with CeSO$_4$ in 2 N H$_2$SO$_4$) was eluted and obtained as a colorless oil (0.032 g, 64%) which crystallized from a hexane–chloroform mixture as white crystals of **2-(5-hydroxy-6,7-dimethyl[2,3H]benzofuran-2-yl)-2-methoxypropane (4c)**: mp 88.5–89.5°; ν_{max} 3320 s, 1626 w, 1601 w cm^{-1}; m/e (%) at 236 (M$^-$, 14), 189 (9), 164 (9), 163 (6), 73 (100); δ [(CD$_3$)$_2$SO] 1.08, 1.14 (s, 3, *gem*-diMe), 1.99 (s, 6, ArMe), 3.00 (d, J = 8.8 Hz, 2, –CH$_2$–), 3.16 (s, 3, –OMe), 4.51 (t, J = 8.8 Hz, 1, –CH–), 6.46 (s, 1, ArH), 8.42 (–OH).

Anal. Calcd for C$_{14}$H$_{20}$O$_3$: C, 71.19; H, 8.47. Found: C, 70.92; H, 8.24.

Irradiation in Aqueous Acetonitrile under Nitrogen. To a solution of PQ-1 (0.009 g) in acetonitrile (5 ml) was added water (20 ml). The mixture was irradiated for 1 hr and then extracted with ethyl acetate. The combined extracts were washed with water and saturated aqueous NaCl and dried. The material isolated by chromatography on one plate proved to be **10** (10.4 mg, 4%). From a fraction hardly moving from the starting line, a colorless oil (8.2 mg) was obtained. It was acetylated overnight at room temperature and identified as **4b** (9.4 mg). The photoproduct is thus **2-(5-hydroxy-6,7-dimethyl[2,3H]benzofuran-2-yl)propan-2-ol (4a)** (7.8 mg, 86%, based on yield of acetate).

Communications to the Editor

Brønsted Coefficients and ρ Values as Guides to Transition-State Structures in Deprotonation Reactions

Sir:

In order to apply transition-state theory to the correlation of changes in rates of reactions with changes in structures it is necessary to visualize transition-state structural models. One of the most useful guides in this respect is Leffler's approximation, which states that the transition state bears the "greater resemblance to the less stable of the species (reactants or products) of a chemical equilibrium."[1] Other guiding postulates have been proposed which lead to the same general conclusion,[2,3] and it is current practice in organic chemistry to consider that in "uphill" reactions the transition state is product-like and that in "downhill" reactions it is reactant-like.[4] In deprotonations

of carbon acids, such as nitroalkanes, ketones, etc., by bases the "crossover" point will come when the attacking base is approximately equal in strength to the anion being formed, *i.e.*, when $\Delta pK = pK_{HA} - pK_{BH^+} = 0$.[4] For "downhill" reactions ΔpK will be negative and for "uphill" reactions ΔpK will be positive. Thus, in the reaction of 1-phenylnitroethane with hydroxide ion, since $\Delta pK = -8.6$, one would expect a reactant-like transition state, and this viewpoint can be supported on several grounds.[5] As we change to progressively weaker bases the transition state should become progressively more product-like. According to the usual interpretation, the Brønsted coefficient might then be expected to increase as ΔpK approaches zero.[6] With ArCHMeNO$_2$ systems the Brønsted α is related to the Hammett ρ by the equation, $\alpha = \rho_{k_1}/\rho_{K_a}$, where ρ_{k_1} refers to the rate of deprotonation

(1) (a) J. E. Leffler, *Science*, 117, 340 (1953); (b) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 158.
(2) G. S. Hammond, *J. Amer. Chem. Soc.*, 77, 334 (1955).
(3) C. G. Swain and E. R. Thornton, *ibid.*, 84, 817 (1962).
(4) See, for example, R. P. Bell, and D. M. Goodall, *Proc. Roy. Soc., Ser. A*, 294, 273 (1966).

(5) F. G. Bordwell, W. J. Boyle, Jr., and K. C. Yee, *J. Amer. Chem. Soc.*, 92, 5926 (1970).
(6) (a) Reference 1b, pp 156–168, 238–242; (b) T. C. Bruice and S. J. Benkovic, "Bioorganic Mechanisms," Vol. 1, W. A. Benjamin, New York, N. Y., 1966, pp 37–38; (c) J. O. Edwards, "Inorganic Reaction Mechanisms," W. A. Benjamin, New York, N. Y., 1964, Chapter 3; (d) R. P. Bell and B. G. Cox, *J. Chem. Soc. B*, 194 (1970).

and ρ_{K_a} is the dissociation constant for the nitroalkane. An increase in α would then correspond to an increase in ρ_{k_1}.

The theory has been tested by determining ρ_{k_1} values for the reactions of 1-arylnitroethanes (m-CH$_3$, H, m-CH$_3$O, m-Cl, and m-NO$_2$) with hydroxide ion, piperidine, diethylamine, piperazine, and morpholine in water (Table I); ρ_{k_1} was also determined for the

Table I. Hammett ρ Values for Reactions of 1-Arylnitroethanes with Bases in Water at 25°

Base	ΔpK^a	ρ_{k_1}	r	$\sigma_{p\text{-NO}_2}$
Hydroxide	−8.6	1.18 ± 0.02	0.9990	0.823
Piperidine[b]	−4.1	1.02 ± 0.03	0.9985	0.852
Diethylamine[b]	−4.0	0.99 ± 0.01	0.9997	0.993
Piperazine[b]	−2.5	0.93 ± 0.03	0.9984	0.956
Morpholine[b]	−1.6	0.96 ± 0.02	0.9994	0.978

[a] For PhCHMeNO$_2$; ρ_{K_a} = 1.03; statistically corrected.
[b] Ionic strength, μ = 0.10.

reactions of arylnitromethanes with hydroxide ion, morpholine, and 2,4-lutidine (Table II).

Table II. Hammett ρ Values for Reactions of Arylnitromethanes with Bases in Water at 25°

Base	ΔpK^a	ρ_{k_1}	r	$\sigma_{p\text{-NO}_2}$
Hydroxide	−8.9	1.28 ± 0.02	0.9998	0.916
Morpholine[b]	−1.8	1.07 ± 0.05	0.9985	1.15
2,4-Lutidine[b]	+0.55	1.08 ± 0.04	0.9986	1.15

[a] For PhCH$_2$NO$_2$; ρ_{K_a} = 0.83; statistically corrected. [b] Ionic strength, μ = 0.10.

Interestingly enough the ρ_{k_1} (or α) values do not increase as ΔpK approaches zero. If anything the trend is in the opposite direction. The ρ values for amine bases are appreciably smaller in each system than that of hydroxide ion. These data, together with the earlier observation that Brønsted α's for deprotonation reactions can be larger than one and less than zero, negate the use of α as a guide to transition-state structures.[7] The decrease in α (or ρ) as the base type changes from hydroxide to amine bases indicates that, in the transition state, the negative charge on the benzylic carbon atom *decreases* as ΔpK becomes more positive. At the same time there is a slight increase in (calculated) $\sigma_{p\text{-NO}_2}$ as we approach ΔpK = 0 (Tables I and II). This suggests that the decreased charge is accompanied by a slight increase in delocalization of the negative charge from the benzylic carbon atom to the benzene ring. The changes in ρ and $\sigma_{p\text{-NO}_2}$ for a ΔpK change of *ca.* 7 units and a rate change of *ca.* 300-fold are surprisingly small, and the indication is that neither the charge nor geometry of the transition state has changed much over this range.

Brønsted β values calculated for the amines, piperidine, piperazine, and morpholine, reacting with Ph-CHMeNO$_2$ or its derivatives (data in Table I) are given in Table III, along with other values from the literature.

Examination of Table III shows that over a ΔpK range of almost 20 units β for deprotonation of nitro-

(7) F. G. Bordwell, W. J. Boyle, Jr., J. A. Hautala, and K. C. Yee, *J. Amer. Chem. Soc.*, **91**, 4002 (1969). See also ref 5.

Table III. Brønsted β Values for Deprotonations of Carbon Acids

Carbon acid	ΔpK range	β	Ref
1-Arylnitroethanes	−4.7 to −2.2	0.52 to 0.56	Table I
Phenylnitromethane[a]	−6 to +2	0.65	b
Nitroethane	−2.5 to +4.5	0.50 to 0.55	c
3-Nitropropene	−0.8 to 0.0	0.59	d
Nitroethane	+2.0 to +3.4	0.65	e
Menthone	−1.0 to +5.3	0.48	f
Acetone	+13.4 to +14.8	0.64 to 0.72	g

[a] A variety of base types (H$_2$O, RCO$_2^-$, HPO$_4^{2-}$, etc.) was used. [b] V. M. Belikov, Ts. B. Korchemnaya, and N. G. Faleev, *Bull. Acad. Sci. USSR, Div. Chem. Soc.*, 1383 (1969). [c] M. J. Gregory and T. C. Bruice, *J. Amer. Chem. Soc.*, **89**, 2327 (1967); J. E. Dixon and T. C. Bruice, *ibid.*, **92**, 905 (1970). [d] J. A. Hautala, unpublished results. [e] R. G. Pearson and F. V. Williams, *J. Amer. Chem. Soc.*, **76**, 258 (1954). [f] Reference 6d. [g] J. A. Feather and V. Gold, *J. Chem. Soc.*, 1752 (1965).

alkanes and ketones shows little variation, and no consistent trend. One must conclude that either β is a very poor guide to the extent of proton transfer in the transition state or that transition-state structures for these reactions vary but little over wide ΔpK ranges. It is conceivable that both parts of this statement are true.

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Kinetic Isotope Effects as Guides to Transition-State Structures in Deprotonation Reactions

Sir:

Westheimer has presented theoretical arguments to show that for a series of related proton transfers the isotope effect, k^H/k^D, will be a maximum when the transition state is symmetrical.[1] Although Westheimer's treatment ignores bending frequencies and makes other simplifying assumptions,[1] its overall conclusion has been generally accepted,[2] and the magnitude of the primary isotope effect has been frequently used as a guide to the structure of the transition state in reactions where proton transfer is rate limiting.[3]

Bell and Goodall suggested for a simple proton transfer, B$^-$ + HA → BH + A$^-$, that the most symmetrical transition state should occur when B$^-$ and A$^-$ are of approximately equal basicity, *i.e.*, when

$$\Delta pK = pK_{HA} - pK_{HB} = 0$$

(1) F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961).
(2) See (a) R. A. More O'Ferrall and J. Kouba, *J. Chem. Soc. B*, 985 (1967); (b) L. C. Gruen and F. A. Long, *J. Amer. Chem. Soc.*, **89**, 1287 (1967); (c) W. P. Jencks, "Catalysis in Chemistry and Enzymology," McGraw-Hill, New York, N. Y., 1969, Chapter 4, for discussions and literature references.
(3) (a) C. G. Swain and E. R. Thornton, *J. Amer. Chem. Soc.*, **84**, 817 (1962); (b) E. R. Thorton, *J. Org. Chem.*, 27, 1943 (1962); (c) K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1964, p 361; (d) K. C. Brown and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **92**, 4292 (1970), and earlier papers in this series; (e) R. A. More O'Ferrall, *J. Chem. Soc. B*, 785 (1970), writes: "For reactant or product-like transition states small isotope effects are normally observed, and for symmetrical transition states quite large ones."