96-1; **3d** (*threo*), 17244-97-2; **3d** (*erythro*), 17244-98-3; **4** (*threo*), 17244-99-4; **4** (*erythro*), 17243-72-0; **5** (*threo*), 17243-73-1; **5** (*erythro*), 17243-74-2; **6** (*threo*), 17243-75-3; **6** (*erythro*), 17243-76-4; **7** (R = $CH_3CO$), 17243-99-1.

**Acknowledgment.**—Helpful discussion with Professor F. A. L. Anet of the University of California at Los Angeles and Professor E. W. Garbisch, Jr., of the University of Minnesota is gratefully acknowledged.

# The Acid-Catalyzed Equilibration of 1,3-Diarylallyl Alcohols

STANLEY C. BERNSTEIN

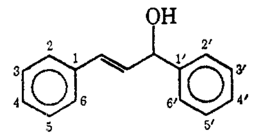
*Department of Chemistry, Wright State University, Dayton, Ohio 45431*

*Received April 15, 1968*

The equilibrium and rate constants for the acid-catalyzed (HCl in 60% aqueous dioxane) equilibrations of three 1,3-diarylallyl alcohols (chalcols) have been measured at 30°. Both ends of the allyl group are in identical environments, with the possible exception of the electronic environment which is determined by the pattern of substitution on the aromatic rings. The equilibrium constants are nearly insensitive to the *para* substituents. For the isomerizations of the 4- to the 4′-substituted chalcol, $K_{eq}$ = 0.805, 1.16, and 0.71 for nitro, bromo, and methoxy, respectively. The rate constants are quite sensitive to the substituents. The forward rate constants for the substituents (nitro and bromo, respectively) are $4.75 \times 10^{-3}$ and $2.89 \times 10^{-1}$ $(\min M)^{-1}$. The reverse rate constants are $5.87 \times 10^{-3}$ and $2.49 \times 10^{-1}$ $(\min M)^{-1}$. Both the forward and reverse rate constants for 4- and 4′-methoxychalcol are estimated to be 84 $(\min M)^{-1}$. Apparently two different kinds of resonance effects are operative. One effect, which is pronounced, involves the interaction of the substituent with the charge in the transition state. The other effect, which is minimal, is the conjugation of the substituent with the allylic double bond.

There are several studies in the literature concerned with substituent effects on the chemical properties of allylic systems.[1] Few of these studies deal with symmetric systems in which all factors (steric, etc.) except electrical effects are constant at the termini of the allylic cation under consideration.

The required symmetry can be found in the 1,3-diarylallyl (chalcol) system. There have been two previous studies of the allylic rearrangement in chalcols. Burton and Ingold[2] in 1928 isomerized 4- and 4′-methylchalcol and 4- and 4′-chlorochalcol in refluxing acetic anhydride. Because of the limited techniques available at that time, the authors were able to indicate only that the equilibrium mixtures seemed to contain more of the 4 isomer in both cases.



Braude and Waight[3] compared rate and equilibrium constants for the three reactions listed in Figure 1. The rate constants for reaction 3 were estimated rather than measured (see footnote *e*, Table I).

A comparison of the data for reactions 1 and 3 indicated that the nitro group has little effect on the equilibrium position, but a large retarding effect on the rate of equilibration. The former effect is attributed to the lack of resonance stability when a nitro group is conjugated with a double bond, and the latter effect is attributed to the destabilization of a positively charged species (presumably the transition state for the reaction) by the nitro group.

The *p*-nitrophenyl group changes the equilibrium constant from greater than 10 for reaction 2 to 0.83 for reaction 1. This illustrates the conjugative properties of an aromatic group. On the other hand, the *p*-nitrophenyl group has little effect on the rate of the reaction. This, in the opinion of Braude and Waight, is due to a balancing of the rate-retarding effect of the nitro group and the rate acceleration due to delocalization of charge into the phenyl ring.

In a later paper in the same series Braude and Gore[4] measured rate and equilibrium constants for the acid-catalyzed isomerizations of 1-naphthyl-3-phenylallyl alcohols. The equilibrium constants are close to unity reflecting the nearly identical conjugated abilities of the phenyl and (α- and β-) naphthyl groups.

The work of Braude and Waight[3] seems to establish a dichotomy of resonance effects for the nitro group. On the one hand resonance definitely retards the buildup of positive charge in the allyl group. On the other hand, resonance plays little role in determining the more favorable position for the allylic double bond in 4- and 4′-nitrochalcol. In order to test the applicability of this dichotomy of resonance effects to other groups, the rate and equilibrium constants for the acid-catalyzed isomerizations of three pairs of chalcols have been measured.

## Results

The chalcols were synthesized by a modification of the procedure of Davey and Hearne.[5] The base-catalyzed condensation of the appropriate benzaldehyde and acetophenone gave the chalcone, and borohydride reduction gave the chalcol. 4′-Methoxychalcol and 4-bromochalcol have not previously been obtained as crystalline compounds. These structures were verified by elemental and spectral analyses. It should be noted that 4- and 4′-methoxychalcol and 4- and 4′-bromochalcol were quite unstable. The methoxy compounds decomposed to oils in a few days, whereas the bromo compounds became oils in a few weeks. These

---

(1) See, for instance, R. Sneen, *J. Amer. Chem. Soc.*, **82**, 4261 (1960); R. Sneen and A. Rosenberg, *ibid.*, **83**, 895, 900 (1961).

(2) H. Burton and C. K. Ingold, *J. Chem. Soc.*, 904 (1928).

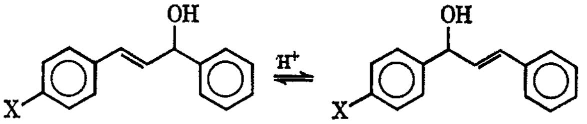
(3) E. A. Braude and E. S. Waight, *ibid.*, 419 (1953).

(4) E. A. Braude and P. H. Gore, *ibid.*, 41 (1959).

(5) W. Davey and J. A. Hearne, *ibid.*, 4978 (1964).

TABLE I

RATE AND EQUILIBRIUM CONSTANTS FOR THE ACID-CATALYZED ISOMERIZATIONS OF CHALCOLS AT 30° IN 60% AQUEOUS DIOXANE



| X | Temp, °C | $K_{eq}$ | $\Delta G°$, kcal/mol | $k_1$[a] (min $M$)$^{-1}$ | $k_{-1}$[a] (min $M$)$^{-1}$ |
|---|---|---|---|---|---|
| $NO_2$ | 29.57 ± 0.01 | 0.805 ± 0.050 | 0.13 ± 0.04 | $(4.75 \pm 0.47) \times 10^{-3}$ | $(5.87 \pm 0.21) \times 10^{-3}$ |
| $NO_2$[b] | 30 | 0.83 ± 0.01 | 0.12 ± 0.01 | $4.6 \times 10^{-3}$ | $5.6 \times 10^{-3}$ |
| Br | 29.57 ± 0.01 | 1.16 ± 0.10 | −0.09 ± 0.05 | $(2.89 \pm 0.48) \times 10^{-1}$ | $(2.49 \pm 0.17) \times 10^{-1}$ |
| $OCH_3$[c] | 29.66 ± 0.07 | 0.71 ± 0.18 | 0.21 ± 0.15 | >6 | >9 |
| $OCH_3$[d] | 29.66 ± 0.07 | | | ~84 | ~84 |
| H[b,e] | 30 | | | 0.70 | 0.70 |

[a] These are specific rate constants ($k_1$, forward; $k_{-1}$, reverse) and are obtained by dividing the pseudo-first-order rate constants by the acid concentration, 0.100. [b] From Braude and Waight.[3] [c] 4- and 4′-methoxychalcol reached equilibrium too rapidly for rate measurements. The rate constants on this line are estimated lower limits. [d] The rate constants on this line are from an estimated Hammett plot (see text below). [e] The rate constants for the symmetric unsubstituted chalcol were estimated by Braude and Waight[3] from the data of Braude and Gore[4] and Braude and Fawcett [*J. Chem. Soc.*, 800 (1950)]. Although the authors do not explicitly show how this estimation was performed, it may be assumed that the following method was used. The rates for the irreversible isomerizations of phenyl propenyl carbinols and α- (and β-) naphthyl propenyl carbinols were measured by Braude and Fawcett. If the ratio of these rates does not change when phenyl is substituted for methyl at the α position of the allyl moiety, then the rate for chalcol itself may be estimated from the results of Braude and Gore. It should be noted that the same data as given in Table I of ref 4 are too large by a factor of 10 to agree with the raw experimental data.

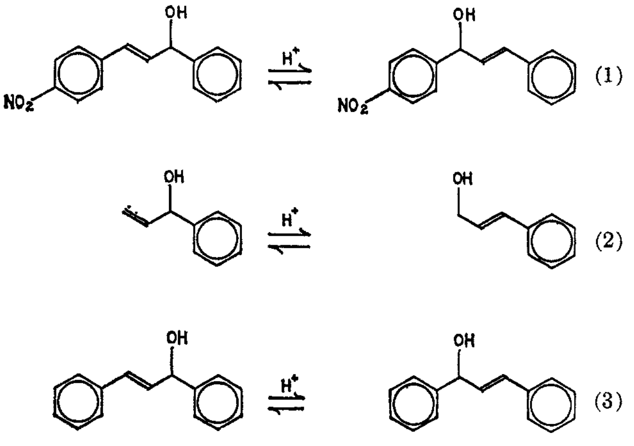


Figure 1.

chalcols were stored in their mother liquors in the cold and isolated immediately prior to the equilibration.

The chalcol was dissolved in 60% aqueous dioxane containing 0.100 $M$ HCl at 30°. Aliquots were removed periodically, diluted with sufficient ethanolic KOH to neutralize the acid, and subjected to uv analysis. The results are summarized in Table I.

## Discussion

The effect of the substituent on the rate of equilibration is not wholly unexpected. Log $k_1$ and log $k_{-1}$ may be plotted against $\sigma_p^+$,[6] as is shown in Figure 2. There are admitted difficulties with this plot. The points are scarce; the values for $H$ are estimated; and there are only small differences between log $k_1$ and log $k_{-1}$ for a given substituent. Because of these difficulties only one straight line is drawn, and this line is taken to be an approximate representation for both the forward and reverse reactions. From this line the rate constants for 4- and 4′-methoxychalcol may be estimated to be about 84 (min $M$)$^{-1}$ as shown in Table I. The slope of the line, $\rho$, for the reaction, is −2.7. This is comparable with the value of −2.97 obtained for the acid-catalyzed rearrangement of phenyl propenyl carbinols.[6,7] The substituent effect on rate is entirely consistent with a reaction in which positive charge is built up in conjugation with the substituent. The electron-donating ability of a group such as methoxy is able to meet this demand and stabilize the charge, whereas a group such as nitro resists the demand and raises the energy of the charged species.

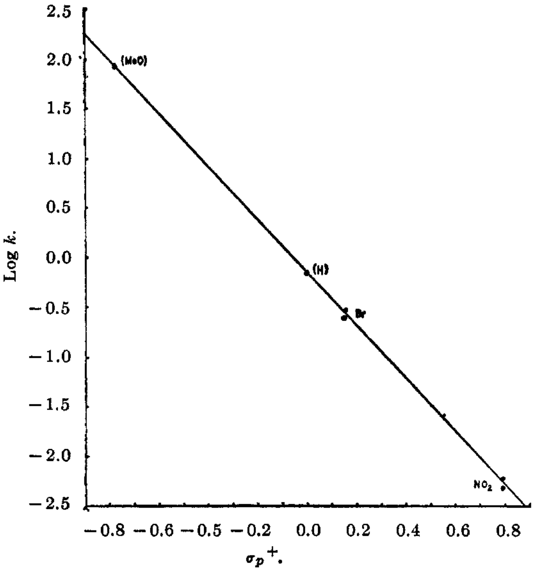


Figure 2.—Hammett plot for rates of chalcol equilibrations.

The lack of sensitivity of the equilibrium constants to the substituents is in sharp contrast to the rate data. The effects that stabilize the transition state (presumably some configuration resembling the allylic cation) do not operate in the ground state. The difference in energy between the ground states is probably due to a difference in resonance between the isomers. The 4 isomer allows for a resonance interaction between the *para* substituent and the allylic double bond,

---

(6) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

(7) E. A. Braude and E. S. Stern, *J. Chem. Soc.*, 1096 (1947).

whereas the 4′ isomer does not. As shown in Table I this difference in energy cannot be more than a few hundred calories per mole. Braude[3,4] tried to estimate quantitatively this energy difference by using MO calculations. This approach suffers from the failure that even sophisticated MO calculations are not sensitive enough to predict differences of a few hundred caloriesp er mole. It suffices to say that the three substituents measured do not interact appreciably with the allylic double bond.

The resonance effect exerts a powerful influence on a charged transition state and virtually no effect on a conjugated double bond in the ground state. It may be concluded that the electron-withdrawing or -releasing properties of a group are separate from the conjugating properties of that group.

## Experimental Section

All melting points were taken on a Thomas–Hoover capillary melting point apparatus and are uncorrected. Ultraviolet spectra were recorded on a Cary Model 14 recording spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer Model 621 infrared spectrophotometer.

**4′-Methoxychalcol.**—4′-Methoxychalcone (7.16 g, $3.00 \times 10^{-2}$ mol) in 50 ml of boiling MeOH was slowly treated with a slurry of 2.27 g ($6.00 \times 10^{-2}$ mol) of $NaBH_4$ in water. The reaction was allowed to cool to room temperature, treated with 50 ml of saturated aqueous NaCl, and extracted with ether. The combined organic layers were washed extensively, first with saturated aqueous NaCl and then with $H_2O$. The oil that remained after drying ($MgSO_4$) and concentrating the ethereal extract was taken up in benzene and treated with Norit. The product was induced to crystallize after diluting the benzene solution with Skellysolve B. After three recrystallizations from this solvent mixture, 3.59 g (50%) of the chalcol were obtained: mp 55–56°; uv max (95% $C_2H_5OH$), 256 mμ ($\epsilon$ $2.28 \times 10^4$); ir ($CCl_4$), 3597 (OH, nonbonded), 3356, broad, (OH, bonded), 1613 (C=C), and 1588 $cm^{-1}$ (aromatic).

*Anal.*[8] Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.50; H, 6.71.

**4-Bromochalcol.**—4-Bromochalcone (2.87 g, 10.0 mmol) in 50 ml of boiling MeOH was reduced with 0.76 g (20.0 mmol) of $NaBH_4$ by the same procedure given above for 4′-methoxychalcone. The crude product was taken up in Skellysolve F, charcoaled, and recrystallized from this solvent giving 1.49 g (51.5%) of the chalcol: mp 66–67°; uv max (95% $C_2H_5OH$), 260.5 mμ ($\epsilon$ $2.76 \times 10^4$); ir ($CCl_4$), 3596 (OH, nonbonded), 3323, broad (OH, bonded), 1604 (C=C), and 1590 $cm^{-1}$ (aromatic).

*Anal.*[9] Calcd for $C_{15}H_{13}BrO$: C, 62.30; H, 4.53; Br, 27.64. Found: C, 62.36; H, 4.50; Br, 27.55.

**Kinetic Experiments.**—The general procedure was the same for each compound studied. The acidic solvent was prepared by diluting 8.13 ml of concentrated HCl to 600 ml with dioxane. The volume was made up to 1 l. with water. This solution was titrated with 0.0250 *M* NaOH to the phenolphthalein end point. The acid made up in this manner was 0.100 *M*. A carefully weighed sample of chalcol was dissolved in somewhat less than 100 ml of this solvent that had been previously thermostated at 30°. The volume was then brought to exactly 100.0 ml with the same solvent. The timer was started, and the volumetric flask was replaced in the thermostat. Periodically 1.000-ml aliquots were removed and diluted to 100.0 ml with ethanolic KOH. A basic solution was prepared by dissolving 1.75 g of KOH in 250 ml of 95% EtOH. This base was titrated with 0.0250 *M* HCl to the methyl red end point. The molarity ranged from 0.107 to 0.110 *M* over the several times this solution was made up. The solution used to dilute the acid aliquots was obtained by diluting 10.00 ml of this 0.1 *M* base to 1.00 l. with 95% EtOH. In this way it was ensured that all the acid present in the aliquot was neutralized. The diluted aliquots were subjected to uv analysis. The solvent cell was filled with solution made by diluting 1.000 ml of the 60% aqueous dioxane–0.100 *M* HCl, to 100.0 ml with the 0.001 *M* ethanolic KOH.

The uv spectra of the two pure substances in question were examined to find the wavelength for which the two spectra differed most, and which were maxima or minima. These wavelengths are as follows: 4- and 4′-nitrochalcols, 256 mμ ($\epsilon_4$ $3.50 \times 10^3$, $\epsilon_{4'}$, $2.02 \times 10^4$); 4- and 4′-bromochalcols, 230 mμ ($\epsilon_4$ $5.65 \times 10^3$, $\epsilon_{4'}$ $1.26 \times 10^4$); 4- and 4′-methoxychalcols, 232 mμ ($\epsilon_4$ $3.90 \times 10^3$, $\epsilon_{4'}$ $1.18 \times 10^4$). Each reaction was followed by monitoring the appropriate wavelength during the course of the equilibration.

Equilibrium was approached from both directions. The equilibrium constant, $K_{eq}$, was obtained from the extinction coefficient after no further change was noted, $\epsilon_\infty$ (eq 4).

$$K_{eq} = \frac{\epsilon_\infty - \epsilon_4}{\epsilon_{4'} - \epsilon_\infty} \tag{4}$$

Given the extinction coefficient, $\epsilon_t$, at time, $t$, then starting with the 4 isomer, the following relationship (eq 5) is obtained.

$$\ln (\epsilon_\infty - \epsilon_t) = -k_{-1}(1 + K_{eq})t + \ln \frac{(\epsilon_{4'} - \epsilon_4)K_{eq}}{1 + K_{eq}} \tag{5}$$

Starting with the 4′ isomer, the following (eq 6) is obtained.

$$\ln (\epsilon_t - \epsilon_\infty) = -k_{-1}(1 + K_{eq})t + \ln \frac{(\epsilon_{4'} - \epsilon_4)}{1 + K_{eq}} \tag{6}$$

The first-order rate constant for the reverse reaction was calculated by a least-squares plot of ln ($\epsilon_\infty - \epsilon_t$) *vs.* $t$ in one case, and ln ($\epsilon_t - \epsilon_\infty$) *vs.* $t$ in the other. The first-order rate constant for the forward reaction was found through $k_1 = k_{-1}K_{eq}$. The rate constants obtained starting with the 4 isomer agreed, within experimental error, with those obtained starting with the 4′ isomer. At least five separate runs were made for each of the two pairs of isomers for which rate data was obtained. The poorest correlation coefficient was 0.997.

**Registry No.**—4′ methoxychalcol, 13677-45-7; 4 bromochalcol, 17245-23-7; 4 nitrochalcol, 17245-24-8; 4′ nitrochalcol, 17245-00-0; 4′ bromochalcol, 1669-60-9; 4 methoxychalcol, 3906-07-8.

---

[8] F & M CHN Analyzer (courtesy of Monsanto Research Corp., Dayton, Ohio).

[9] Analysis was by Spang Microanalytical Laboratory.